NITRATION OF HYDROCARBONS

AND OTHER ORGANIC COMPOUNDS

by

A. V. TOPCHIEV
U.S.S.R. ACADEMY OF SCIENCES

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CATHERINE MATTHEWS, M.Sc.

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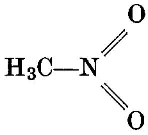
INTRODUCTION

NITRATION of organic substances, a reaction discovered in 1834 (MITCHERLICH, synthesis of nitrobenzene), is one of the most common and important reactions in organic chemistry.

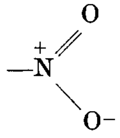
The aim of nitration is to substitute one or several hydrogen atoms in the aromatic or heterocyclic nucleus, or in saturated hydrocarbon, by one or several nitro groups.

Nitro compounds contain one or more monovalent nitro group NO_2; the nitrogen atom is linked directly with a carbon atom of the organic radical. Nitro compounds are isomeric with the esters of nitrous acid RONO in which the nitrogen atom is linked with carbon indirectly, through oxygen

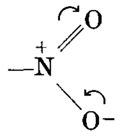


$$H_3C—O—N{=}O$$

The following structure is ascribed at present to the nitro group:



This structure assumes the existence of one semipolar linkage in the group. It should be mentioned that such a structural formula does not reflect the experimentally proved symmetry of the nitro group. The equivalence of the two oxygen atoms in nitro compounds is better represented in the following structural formula:



The names of nitro compounds are derived from those of the corresponding hydrocarbons by the addition of the prefix "nitro". For example: nitromethane, nitropropane, nitrobenzene, nitrotoluene, etc. (according to the Geneva nomenclature the position of the nitro group is indicated by a number and not a letter). Nitro compounds are designated as primary, secondary and tertiary depending on the character of the hydrocarbon radical with which the nitro group is linked.

Nitro compounds play a most important part in industry as final and intermediate products, as explosives (e.g. di- and trinitrobenzene, trinitrotoluene, tetranitrotoluene, picric acid, etc.) as aromatic substances (e.g. nitrobenzene, trinitro-tertiarybutyltoluene). Nitro derivatives form essential intermediates in the manufacture of aniline dyes and various synthetic products.

Nitro compounds are strongly active against micro-organisms (nitrophenols [1], chloropicrin). Chloropicrin was used as a poison in World War I. It is a valuable insecticide and fungicide and is used in treating grain silos and seed grain.

A large number of nitro compounds, including the nitro dye-stuffs, have been investigated from the chemotherapeutic point of view in a series of trypanosome infections (recurrent fever and others). They have also been used as disinfectants against staphylococci and intestinal bacteria [2]. Some of the aromatic oxynitro compounds can be used effectively against agricultural pests. A solution of dinitro-*o*-*cyclo*hexylphenol in kerosene is strongly active against the eggs of some insects which are agricultural pests [3].

The lower nitroparaffins, especially when mixed with alcohols, are good solvents for cellulose esters and vinyl resins.

Polynitroparaffins are used as additions to various liquid fuels [4]. Some of the nitroolefines are active fungicides.

The wide application of nitro compounds in the preparation of various organic substances only became possible after the remarkable discovery made in 1842 by the eminent Russian chemist N. N. Zinin who found that aniline could be obtained from nitrobenzene by reduction with ammonium sulphide. The importance of this discovery in the history of organic chemistry can hardly be overestimated, enabling as it did the chemists to use the transition from nitro compounds to primary amines in the synthesis of the most varied organic compounds. Aromatic amines are at present the most important intermediates in the aniline dye-stuffs, pharmaceutical and many other branches of organic chemical industry. Moreover, phenols, ethers, halogen derivatives, nitriles, etc. can be prepared from primary amines using diazotization as an intermediate step. These in their turn are used in various aspects of organic chemical industry.

Nitric acid is usually employed for the introduction of the nitro group into organic compounds.

Nitration can be represented schematically as follows:

$$RH+HONO_2 \rightarrow RNO_2+H_2O$$

where RH is a saturated or aromatic hydrocarbon, a heterocyclic compound or a derivative of these, exchanging the hydrogen atom for a nitro group.

It is essential to point out that the schematic representation given above does not show the course of the reaction; it merely gives a general view of its result. In reality the reaction goes through a series of intermediate stages, and not infrequently it is not the nitric acid itself but its transformation products which enter into reaction with the organic molecule.

The number of nitro groups entering the organic molecule depends on the concentration of the acid used, on temperature and the duration of the process, on the nature of the substance being nitrated and on other factors. In the course of nitration the main reaction is accompanied by side reactions which diminish the yield of the main product—the nitro compound. The oxidizing effect of nitric acid is responsible for one of these undesirable side reactions. This oxidizing effect is enhanced by rises in temperature, in water content of the reaction mixture and in the amount of nitrogen oxides in the nitric acid. Under very drastic conditions of nitration a breakdown of the organic molecule may occur, as, for example, in the preparation of trinitrobenzene when tetranitromethane is formed as a by-product.

The reaction scheme given above shows that the introduction of a nitro group into an organic molecule is accompanied by the formation of a molecule of water. The accumulation of water in the reaction mixture lowers the concentration of nitric acid. If nitric acid alone is used as a nitrating agent, the lowering of its concentration below a certain limit leads to practical cessation of the reaction, and complete utilization of the nitric acid becomes impossible. Hence in practice a mixture of nitric and sulphuric acids is used for nitration. This is the so-called "nitration mixture". However, as shown below, nitration takes place most rapidly when approximately 90 per cent and not 100 per cent sulphuric acid is used. This suggests that in the process of nitration sulphuric acid does not act merely as a dehydrating agent.

There is great technical advantage in using the "nitration mixture" instead of nitric acid alone. The mixture does not corrode iron and can therefore be stored for a long time in iron vessels and distributed along iron pipes. It must be noted that the presence of water also has considerable effect on the character of the action of nitric acid. As a rule the more concentrated the nitric acid used, the higher its nitrating power and the weaker its oxidizing action. In some cases, however, the opposite effect is seen, viz. the weakening of its oxidizing properties in the presence of water; for example, the action of nitric acid, dissolved in acetic acid, on anthracene gives 2 : 7-dinitroanthracene and anthraquinone. The presence of water favours the formation of dinitroanthracene with a simultaneous diminution in the amount of anthraquinone. Elimination of water from the reaction mixture (by using a mixture of nitric acid with glacial acetic acid and acetic anhydride) leads to complete suppression of the nitrating reaction and a quantitative yield of anthraquinone results [5].

The formation of by-products in the course of nitration reactions has long been known. Usually as the result of side reactions hydroxynitro compounds are obtained during nitration, indicating simultaneous introduction of hydroxy- and nitro- groups into the organic molecule. Thus, for example, in the nitration of nitrobenzene the side product is 2 : 4 : 6-trinitroresorcinol [6], whilst the nitration of naphthalene is accompanied by the formation of 2 : 4-dinitro-α-naphthol [7].

Dinitrophenol and picric acid are formed as by-products during nitration of benzene [8]. BENNET [6] suggests that in the nitration of nitrobenzene there is an interaction between the organic molecule and not the nitrogen but the positively charged oxygen of the nitrating agent, leading to the formation of nitrophenol in the first place. As the result of subsequent nitration of the nitrophenol 2 : 3 : 4 : 6-tetranitrophenol is obtained, in which the nitro group in position 3 is known to be very mobile, and whose substitution by a hydroxy group gives 2 : 4 : 6-trinitroresorcinol. The above suggestion does not, however, explain either the formation of *m*-chlorophenol during the nitration of chlorobenzene or a number of other reactions.

The formation of hydroxy compounds (e.g. during nitration of benzene) is explained according to A. I. TITOV [9] by the initial interaction of benzene with nitrosyl sulphuric acid giving nitrosobenzene. The nitrosobenzene so obtained takes on a proton, then takes on a hydroxyl ion in the para position to the nitrogen-containing group giving *p*-hydroxyarylhydroxylamine. The latter is oxidized to *p*-nitrosophenol and then to *p*-nitrophenol which, in the process of nitration, becomes dinitro- and trinitrophenol. This mechanism fails, however, to explain the formation of trinitroresorcinol from nitrobenzene. The mechanism of the formation of side products in the process of nitration cannot be regarded as finally established and further research into the problem is necessary.

Other reagents besides nitric and sulphuric acids are at times used for nitration. Thus it is convenient to use a mixture of nitric and acetic acids if a mononitro derivative is desired in those cases where the use of concentrated HNO_3 and H_2SO_4 mixture leads to a greater degree of nitration, giving di- or polynitro derivatives.

The mixture of nitric and acetic anhydrides gives the ester CH_3COONO_2 which can also be used as a nitrating agent [10]. There are numerous references in the literature describing the use of ethyl and benzoyl nitrates as nitrating agents: for example, the action of ethyl nitrate on *cyclo*pentadiene in the presence of sodium ethoxide gives nitro*cyclo*pentadiene [11].

Benzene reacts vigorously with ethyl nitrate in the presence of $AlCl_3$. Nitration of toluene under similar conditions gives predominantly *o*-nitrotoluene (the ratio of the *o*- and *p*- isomers in the mixture is 5 : 1) [12]. Phenylnitromethane can be synthesized from benzyl cyanide by using ethyl nitrate in the presence of sodium ethoxide [13]. Benzoyl nitrate is used as a laboratory nitrating agent. It gives *o*-nitro derivatives in those cases where other reagents give predominantly the corresponding *p*-derivatives. Thus its action on anisole and phenetole gives a theoretical yield of the corresponding *o*-nitro compounds [14].

It is interesting to note that polyalkylsubstituted benzenes give on interaction with benzoyl nitrate good yields of the corresponding nitro compounds in which the nitro group enters the side chain and not the nucleus [15] e.g. durene gives 1′-nitrodurene.

References [15a] have recently appeared to the nitration of some organic substances with acetocyanhydrin nitrate in an alkaline medium.

It is possible to use a mixture of sulphuric acid and a salt of nitric acid instead of the usual nitrating mixture of nitric and sulphuric acids. The salt usually used is sodium nitrate. The reaction takes place at an elevated temperature; sulphuric acid liberates free nitric acid from the salt. The drawback in this method is the formation of a considerable amount of bisulphate which has only limited uses. The substitution of ammonium nitrate for the sodium salt gives ammonium sulphate as by-product which may be utilized as a fertilizer. However, the high cost of ammonium nitrate makes its use as a nitrating agent very limited.

The author of this book investigated the use of boron fluoride as a catalyst in the nitration of organic compounds with salts of nitric acid. These investigations form the basis for a theory of the mechanism of aromatic nitration with inorganic nitrates in the presence of $AlCl_3$ and BF_3 which is advanced.

The catalytic action of mercury or its salts in the sulphonation of aromatic compounds has long been known. The first experimental investigation into the influence of mercury salts on nitration, however, gave no positive results. But as early as 1913, WOLFENSTEIN and BÖTERS [16] obtained nitrophenol and nitrobenzene by nitration of benzene with dilute nitric acid in the presence of mercury salts. Simultaneous processes of nitration and oxidation occur during this reaction; its course depends on the concentration of nitric acid.

Other catalytic agents in the nitration reaction are compounds of chromium, tungsten, molybdenum, tantalum, niobium, vanadium, gallium and indium [17]. The use of boron fluoride as a catalyst in nitration of aromatic substances should be particularly stressed [18].

In some cases of nitration nitrous acid can also show catalytic properties, as for instance in the nitration of phenol [19], aliphatic ketones [20], and naphthalene [21] where it accelerates the reaction.

At times it is necessary to carry out nitration in a solvent medium. *o*-Dichlorobenzene and chlorobenzene in particular are used as solvents in industrial nitration. 3-Nitroalizarin may be cited as an example; it is obtained by nitration of alizarin with nitric acid in *o*-dichlorobenzene. Chloro derivatives of ethane can similarly be used as solvents. The nitration of phenol to picric acid can be carried out in ethyl alcohol [22], or, better still, in methyl alcohol [23] which is considerably more stable to nitric acid.

The effects of solvents on the course of nitration was studied by nitrating phenol in various solvent media [24].

The temperature at which nitration is carried out is another very important factor affecting the course of the process. Nitration is an exothermic reaction, and when a mixture of nitric and sulphuric acids is used in the nitration of aromatic compounds a large amount of additional heat is given off by the dilution of sulphuric acid with water formed in the reaction. Hence, it is usually necessary to use external cooling and to mix the reagents gradually. Variation in temperature not only affects the number of nitro groups entering a molecule but also the position which the nitro group enters. It is self-evident, therefore, that for each particular nitration there is an optimal temperature.

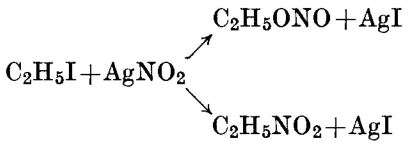
Whilst the chemistry of aromatic nitration was developed and found extensive industrial application many years ago, suitable methods for the preparation of nitro compounds of the aliphatic series have only been developed in the last decades.

The absence, until recently, of convenient and cheap methods of preparation of aliphatic nitro compounds has been the chief obstacle to their introduction into practical spheres. The reason for these difficulties is the great inertness of paraffin hydrocarbons to nitric acid as compared with aromatic hydrocarbons. For many years attempts to introduce the nitro group into acyclic hydrocarbons by the direct action of nitric acid met with no success. Similarly, no positive results were obtained with attempts to nitrate the side chains in aromatic hydrocarbons. But the ready availability of paraffin hydrocarbons (the U.S.S.R. being particularly rich in natural gases which are the source of the lower paraffin hydrocarbons) caused many chemists to study the problem of converting the saturated hydrocarbons into nitroparaffins. This class of compounds finds application in various branches of chemical industry. Moreover, nitroparaffins are very reactive substances and can serve as the basis for the synthesis of many new and valuable chemical products, some of which have already found practical application.

Nitroalcohols—condensation products of nitroparaffins and aldehydes—are of great practical value. Their derivatives and products resulting from their interaction with various reagents are used as plasticizers for cellulose esters and may be used as explosives [25], etc.

Halogen derivatives of nitroparaffins are used as insecticides and as solvents for purification of lubricating oils.

Indirect and often quite complicated methods had to be resorted to in order to synthesize nitroparaffins. In 1872 V. Meyer first synthesized nitroparaffins by the action of nitrous salts on alkyl halides :



$$\begin{tikzcd}[column sep=small, row sep=small] & C_2H_5ONO+AgI \\ C_2H_5I+AgNO_2 \arrow[ur] \arrow[dr] & \\ & C_2H_5NO_2+AgI \end{tikzcd}$$

An ester of nitrous acid is formed simultaneously with the nitroparaffin.

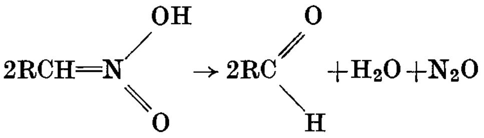
Towards the end of the last century the prominent Russian chemist M. I. Konovalov [26] first succeeded in showing the possibility of introducing nitro groups into aliphatic hydrocarbons and into aliphatic side chains of aromatic hydrocarbons by direct nitration with nitric acid. Modern industrial methods of nitrating aliphatic hydrocarbons arose on the basis of these studies. These methods initiated a new branch of industrial organic chemistry, the manufacture of nitroparaffins and their many derivatives.

Konovalov established a series of significant factors concerned in the process of nitration of paraffins. He demonstrated the importance of the concentration of nitric acid, of temperature, and of pressure. Konovalov's work showed that *iso*paraffins were easier to nitrate than the normal ones; that an increase in pressure enhanced the yield of nitro products, whilst a rise in temperature increased the yield of primary, in relation to secondary, nitro compounds. On nitration of propane, the butanes and pentanes, mixtures of isomeric nitro compounds were seen to be formed, secondary nitro compounds forming a considerable proportion (sometimes over 50 per cent).

Konovalov's work served as a stimulus for the study of paraffins, olefines and naphthenes. The Konovalov reaction is often used to characterize the individual constituents of petroleum in the course of its processing.

Konovalov's method was subsequently studied in detail by another Russian scientist, V. V. Markovnikov [27], who established the dependence of the nitration reaction on the concentration of nitric acid and other conditions. Markovnikov used the nitration of saturated hydrocarbons for the determination of the composition of petroleum based on the character of the nitro derivatives obtained.

Nametkin and co-workers [28] showed that the first stage of the action of nitric acid on saturated hydrocarbons resulted in the formation of an *iso*-nitro compound which, depending on the reaction conditions, could either assume the stable nitro form or break down with the formation of aldehyde, ketone or carboxylic acids:



$$2RCH{=}N\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown O\end{matrix} \rightarrow 2RC\begin{matrix}/\!\!/ O\\ \diagdown H\end{matrix} + H_2O + N_2O$$

Nametkin and co-workers investigated the action of nitric acid on octadecane $C_{18}H_{38}$ and hexatriacontane $C_{36}H_{74}$ and confirmed the conclusions reached by Konovalov. The only product obtained on nitration of octadecane was the secondary nitrooctadecane $CH_3(CH_2)_{15}CH(NO_2)CH_3$ whilst the nitration of hexatriacontane gave a mixture of the secondary mononitro derivative with the secondary $\beta : \beta'$-dinitro derivative [29].

Nitration of bicyclic saturated hydrocarbons with nitric acid gives structurally isomeric nitro compounds with the nitro group entering different rings of the system; in the case of fenchane nitration gives 2-nitrofenchane and 6-nitrofenchane [30].

The question of the reaction mechanism of nitration has long been a subject for investigation. The interest shown by various workers in this problem is doubtless linked with the great importance of nitration in various branches of industry and with the possibility of solving practical problems by elucidating the theory of the process. In the case of aromatic hydrocarbons the theory explaining the process of their nitration is closely connected with the structure of the benzene ring and the mechanism of its reactivity.

Numerous and at times contradictory references to reaction mechanism in nitration are scattered throughout Soviet and foreign journals, making familiarity with them very difficult. We have therefore listed systematically the main works on the subject of aromatic nitration in a subsequent chapter.

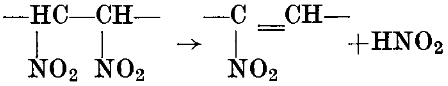
Although the reaction of nitric acid with olefines has not been as extensively studied as its reaction with saturated hydrocarbons there is a series of communications dealing with it. Unsaturated aliphatic compounds undergo nitration more readily than saturated hydrocarbons. *iso*butylene is relatively easily nitrated [31]. Unsaturated side chains of aromatic compounds are easier to nitrate than the aromatic rings. Likewise, acetylene hydrocarbons are easily nitrated. The reaction between concentrated nitric acid and acetylene gives, among other products, trinitromethane [32]. Nitration of isomeric octenes with concentrated HNO_3 gives unsaturated primary nitro derivatives [33]. The introduction of a nitro group into the olefine molecule results in the shift of the double bond to the β-position.

The method of nitrating hydrocarbons and their derivatives in the vapour phase has acquired much importance. It especially concerns aliphatic hydrocarbons. Some paraffins undergo nitration more readily in the vapour phase than the liquid.

Nitration in the vapour phase was carried out by Hass, Hodge and Vanderbilt [34], Hass and Alexander [35], Danzig and Hass [36], Bullock and Mitchell [37] and others. The method found wide industrial application, as it eliminated the need for using pressure. During nitration at raised temperatures (up to 400–500°C) destructive decomposition of the parent hydrocarbons into free radicals can be observed. Nitro groups become attached to these with the formation of nitroparaffins with fewer carbon atoms than the parent hydrocarbons. This observation does not extend to the naphthene series. No polynitro derivatives are formed in this process.

The work done in the last two decades on nitration with nitrogen oxides is of particular interest. It has been studied by many chemists, among them Wieland, Demianov, Shorygin, Topchiev, Titov and others.

Investigation of the reaction mechanism in nitration of unsaturated compounds with nitrogen oxides showed that nitrogen dioxide added on, like the halogens, across the double bond giving dinitro derivatives. These latter, on treatment with alkali split off nitrous acid as a salt and give mononitrosubstituted ethylene hydrocarbons:



$$\underset{NO_2}{\text{—HC}}\text{—}\underset{NO_2}{\text{CH}}\text{—} \rightarrow \underset{NO_2}{\text{—C}}{=}\text{CH—} \quad + HNO_2$$

Nitro derivatives are also obtained by the action of nitrogen dioxide on aromatic compounds, such as benzene, toluene, naphthalene, phenanthrene, naphthol, chlorobenzene, phenol and cresol. Good results are obtained with the aid of such reagents as concentrated sulphuric acid, aluminium chloride, ferrous chloride. The lower normal paraffins, from methane to pentane, can be nitrated in the gaseous phase with nitrogen dioxide giving mono- and dinitro derivatives. The primary nitro compounds are formed exclusively. However, nitration of paraffins is accompanied by their decomposition; thus propane gives nitromethane, nitroethane, 1-nitropropane and 2-nitropropanol [38].

Nitration with nitrogen oxides has been carried out by Shorygin and Topchiev [39], Topchiev and Alania [40], McKee and Wilhelm [41], Valiashko, Blizniukov and Lutski [42] and others.

The work of SHORYGIN and TOPCHIEV (1935) on nitration of hydrocarbons with nitrogen oxides at low temperatures found great practical application. This work subsequently led the author of this book to the elaboration of an original method for the nitration of saturated hydrocarbons in the gaseous phase by the simultaneous action of chlorine and nitrogen oxides [40].

Nitrogen pentoxide can likewise be used for the nitration of organic compounds [43]. When nitration of paraffins with this reagent is carried out at temperatures below 0°C the reaction products consist chiefly of alkyl nitrates, with some nitroalkanes and carboxylic acids [44].

The use of nitrogen oxides as nitrating agents is of great industrial importance, since this method makes possible the utilization of the gaseous mixture obtained by the oxidation of atmospheric nitrogen or ammonia. A number of patents deal with this process [45, 46].

Further development and technological application of methods for the nitration of saturated hydrocarbons, as well as nitration in the vapour phase, belong to the problems of modern applied chemistry.

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CHAPTER I

NITRATION OF AROMATIC AND HETEROCYCLIC COMPOUNDS WITH NITRIC ACID AND NITRATING MIXTURE

THE introduction of the nitro group into aromatic or heterocyclic compounds exhibiting aromatic properties is usually effected by means of nitric acid or of nitrating mixtures.

It has been possible to obtain nitro compounds by the action of nitric acid alone, although better results are commonly obtained by using the nitrating mixture and other nitrating agents. Even when anhydrous nitric acid is used for nitrating aromatic and heterocyclic compounds its dilution by the water formed during the reaction raises its oxidizing properties at the expense of its nitrating properties. Nonetheless, in some cases, the use of nitric acid alone has certain advantages over other nitrating agents. When used alone, nitric acid must be present in great excess of the theoretical amount (the excess is usually 50 per cent). After the separation of the nitro product the used acid is fortified with concentrated HNO_3 and used for further nitration. In isolated cases of readily nitrated compounds such as phenols, phenolic esters, alizarin, etc., dilute nitric acid can be used, and nitration is at times carried out in the presence of solvents such as chlorobenzene, polychlorobenzenes, etc.

A survey of the most important experimental data found in the literature in connexion with the nitration of aromatic and heterocyclic compounds with nitric acid, both in the presence and absence of activating agents, is given below.

1. NITRATION WITH NITRIC ACID

SPINDLER [1] investigated the nitration of benzene, chlorobenzene, bromobenzene and toluene with nitric acid of different concentrations. Nitration was carried out by slow addition of the substance to be nitrated to an excess of nitric acid (the ratios of gramme molecules of nitric acid to 1 gramme molecule of the substances to be nitrated were as follows: for benzene 3 . 8, toluene 4 . 6, chlorobenzene 4 . 4, bromobenzene 4 . 6). Experiments on the effect of varying the concentration of nitric acid used in nitrating hydrocarbons (the same amount of acid being diluted with various amounts of water) showed that the yield of nitro compounds fell rapidly at first, slowly later; starting with the concentration corresponding to the ratio of nitric acid (sp. gr. 1·5) to water 10 : 6 v/v, the yield again dropped rapidly with further dilution, and at the ratio of 2 : 1 nitration ceased altogether.

No formation of nitro compounds has been observed on attempts to carry out nitration with dilute nitric acid (5–10 vols. of H_2O to 1 vol. of HNO_3) by heating the reaction mixture on a water bath for 120 hr. Analysis of the products showed that under these conditions the reaction tended towards oxidation. SPINDLER, in his comparative studies of experimental data on nitration of benzene, toluene, chlorobenzene and bromobenzene with acid of the same concentration, concludes that the presence of a halogen or a methyl group in the aromatic ring enhances the yield of nitro derivatives on nitration with concentrated and slightly diluted nitric acid. The influence of substituent groups in the ring on nitration when moderately dilute nitric acid is used is not so noticeable, as it is partially compensated for by the influence of dilution. (With increasing dilution of nitric acid the yield of nitro derivatives of toluene, chlorobenzene and bromobenzene is lowered to a greater extent than that of benzene itself).

The main product obtained when benzene is nitrated with concentrated nitric acid at room temperature is mononitrobenzene; prolonged heating with boiling nitric acid gives *m*-dinitrobenzene [2].

The introduction of alkyl groups into the aromatic ring facilitates the entry of the nitro group. Thus, toluene can be nitrated with nitric acid even at room temperature; *o*- and *p*-nitrotoluenes are the main products (*m*-nitrotoluene is formed in small amounts only) [2–4]. If the nitration is effected with fuming nitric acid at high temperature the main reaction product is 2 : 4-dinitrotoluene [2].

HOLLEMAN [5] studied the effect of varying temperatures on the nitration of toluene with nitric acid sp. gr. 1·475. The experiments showed that in spite of the variation in temperature over a wide range (from −30 to 60°C) there was no significant change in the relative amounts of the isomers of nitro compounds obtained (Table 1). As can be seen from the data given in this table raising the temperature increases the yield of *o*- and *m*-nitrotoluenes, whilst decreasing that of *p*-nitrotoluene.

Nitration of *p*-chlorotoluene at 0°C with nitric acid sp. gr. 1·48, the ratio of acid to hydrocarbon being 4 : 1, gives a mixture of nitro compounds which contains 58 per cent 4-chloro-3-nitrotoluene and 42 per cent 4-chloro-2-nitrotoluene. Nitration at higher temperatures (30 and 60°C) leads to the formation of polynitro-4-chlorotoluenes in addition to the above-mentioned nitro derivatives.

Xylenes are also easily nitrated with concentrated nitric acid even at room temperature. Nitration of *m*-xylene with fuming nitric acid gives rise to 4-nitro-*m*-xylene and 4 : 6-dinitro-*m*-xylene [6, 7]; if, however, the nitration is effected with an excess of concentrated nitric acid with heating on a water bath the reaction products are 4 : 6-dinitro-*m*-xylene and 2 : 4-dinitro-*m*-xylene [8]. *p*-Xylene gives 2-nitro-*p*-xylene when treated with fuming nitric acid, and the reaction mixture is cooled by ice [9]; if the reaction is carried out at raised temperatures, however, the products are 2 : 3-dinitro-*p*-xylene and 2 : 6-dinitro-*p*-xylene [10].

Nitration of *o*-xylene with fuming nitric acid at room temperature gives 4-nitro-*o*-xylene and 3-nitro-*o*-xylene [11]. *o*-Xylene (50 g) was nitrated [12] with nitric acid (300 g) cooled to −15°C, the hydrocarbon being added dropwise to the acid and the reaction temperature being maintained at −4°C. The reaction products obtained were: 4-nitro-*o*-xylene, 3-nitro-*o*-xylene, 3 : 4-dinitro-*o*-xylene, 4 : 6-dinitro-*o*-xylene and 4:5-dinitro-*o*-xylene. Nitration of *o*-xylene (25 g) with a greater excess of fuming nitric acid

(250 g) at 20–25°C gives a mixture of 3 : 4-dinitro-*o*-xylene, 4 : 6-dinitro-*o*-xylene and 4 : 5-dinitro-*o*-xylene with the total yield of the dinitroxylols close to the theoretical.

Table 1. *Content of nitrotoluene isomers in the reaction products of nitration of toluene with* HNO_3 *depending on the reaction temperature*

Temperature (°C)	Content in reaction products (% of total amount of nitro compounds)		
	o-Nitrotoluene	*p*-Nitrotoluene	*m*-Nitrotoluene
−30	55·6	41·7	2·7
0	56·0	40·9	3·1
30	56·9	39·9	3·2
60	57·5	38·5	4·0

Mesitylene gives mononitro derivatives when nitrated with HNO_3 (sp. gr. 1·38) at elevated temperatures; when nitration is carried out with an excess of HNO_3 (sp. gr. 1·5) and heating on a water bath for 2 hr a mixture of di- and trinitromesitylenes, which can be precipitated by diluting the reaction mixture with water, is obtained. To separate these nitro derivatives the mixture of polynitromesitylenes is treated with alcohol in which only the 2 : 4-dinitromesitylene is soluble (m.p. 87·5°C) [8].

Nitration of phenol with dilute nitric acid gives a mixture of *o*- and *p*-nitrophenols. Veibel [13] has studied the relative quantities of isomeric nitrophenols and nitrocresols formed in the products of nitration. The best results were obtained [14] by nitrating phenols with nitric acid of moderate concentration. The process is carried out as follows: to nitric acid (sp. gr. 1·35) cooled to 8–9°C, phenol is added dropwise with vigorous stirring (the phenol is liquefied by the addition of a small amount of water). The reaction mixture immediately changes colour and after 10–20 min precipitation of the yellow reaction product begins. The reaction mixture is stirred for another 30 min after the addition of phenol is complete. The temperature is kept at 8–9°C throughout. The mass is cooled to − 10°C. The mixture of *o*- and *p*-nitrophenol so obtained is filtered off with suction until dry (at 0°C), and *o*-nitrophenol is separated off by steam-distillation. The yield is approximately 40 per cent of the theoretical. The residue from steam distillation is extracted several times on a boiling-water bath with 2 per cent HCl, cooled slightly and filtered. On cooling the filtrate, *p*-nitrophenol precipitates out in plate-like crystals. The yield is approximately 40 per cent of the theoretical. A small amount of 2 : 4-dinitrophenol can be obtained from the filtrate.

Nitration of *p*-hydroxybenzoic acid with 8 N NHO_3 gives picric acid with a yield of 95 per cent of the theoretical [15].

Dinitro-*o*-cresol can be obtained by a continuous method according to the following scheme [16]: *o*-cresol (12·9 kg) and 70 per cent nitric acid

(34 kg) are run during 1 hr through calibrated nozzles into a water-cooled metallic pipe 1 m long and 38 mm in diameter. The yield of dinitrocresol is 80 per cent of the theoretical.

As regards phenolic esters (such as anisole, phenetole), they are more easily nitrated with concentrated nitric acid.

m-Nitroacetophenone can be obtained in good yield by the following method [17]. Acetophenone is added dropwise to cooled nitric acid, (sp. gr. 1·51). The process is conducted with cooling (0–8°C) and stirring. The reaction product is poured on to ice, filtered and recrystallized from methyl alcohol. The yield of *m*-nitrocresol is approximately 90 per cent of the theoretical.

Nitration of propiophenone with fuming nitric acid, with cooling, gives a mixture of *o*- and *m*-nitropropiophenone, which is separated by 95 per cent ethyl alcohol [18].

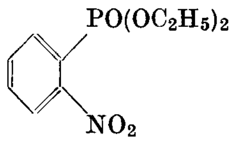
Phenylacetic acid, when treated with an excess of fuming nitric acid gives 2 : 4-dinitrophenylacetic acid [19].

Hunsberger [20] attempted to obtain nitro derivatives of diphenylacetic acid by nitric acid nitration. On addition of diphenylacetic acid to an excess of nitric acid (sp. gr. 1·5) at 30°C and pouring the reaction mixture into water, followed by recrystallization from acetic acid, the author obtained 3 : 4′-dinitrodiphenylacetic acid in negligible yield (7·4 per cent of the theoretical).

Nitration of alkylated derivatives of benzene with dilute nitric acid, carried out in a sealed tube, results in the entry of the nitro group not into the ring, but into the side chain. Thus, when ethyl benzene is heated with five to six times its amount of dilute nitric acid (sp. gr. 1·075) in a sealed tube at 105°C, α-nitroethylbenzene $C_6H_5CH(NO_2)CH_3$ is formed with a yield of 44 per cent of the theoretical. *iso*Propylbenzene under similar conditions gives phenylnitro*iso*propane $C_6H_5C(NO_2)(CH_3)_2$ [21].

Legge [22] studied the action of nitric acid on 1 : 4-di-*tert.*-butylbenzene. On gradual addition of 1 : 4-di-*tert.*-butylbenzene (100 g) at 15–30°C to 96 per cent HNO_3 (300 ml) and subsequent heating of the reaction mixture for 5 hr at 60°C the author obtained the 2 : 6-dinitro derivative with a yield of 53 per cent of the theoretical. On cooling the filtrate, it was possible to separate out a certain amount of the 2 : 5-dinitro derivative. Nitration of 1 : 4-di-*tert.*-butylbenzene with nitric acid mixed with acetic anhydride and acetic acid gave the same authors not the 2 : 6-dinitro but the 2-nitro derivative with a yield of 80 per cent.

Nitration of diethylbenzene phosphate $C_6H_5PO(OC_2H_5)_2$ with fuming nitric acid at 30–35°C as done by Kosolapov [23] gave a nitro derivative with a yield of approximately 67 per cent of the theoretical. The author presumes that the nitro derivative is a mixture:



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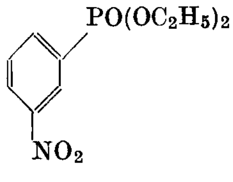
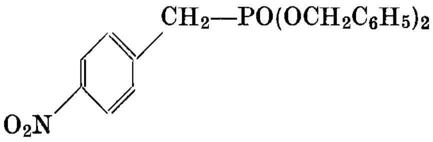
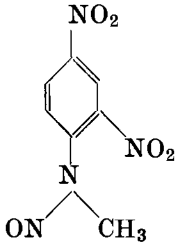


However, nitration of the corresponding benzyl derivative $C_6H_5CH_2PO(OCH_2C_6H_5)_2$ at 0°C with fuming nitric acid (or a mixture of nitric and sulphuric acids) the same author [24] obtained the *p*-nitro derivative.



The action of dilute nitric acid on aniline and other aromatic amines results not in nitration but in oxidation. There are some indications, however, that aniline treated with nitric acid of various concentrations gives a mixture of *o*-nitrophenol and 2 : 4- and 2 : 6-dinitrophenol. No *p*-nitrophenol is formed under these conditions [25].

Lang [26] obtained:



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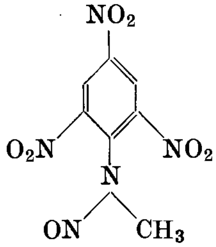
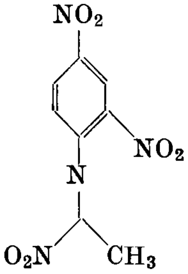


by the action of nitric acid (conc. ⩽ 70 per cent) on dimethylaniline. If nitric acid of higher concentration than 70 per cent is used, the resulting product is:

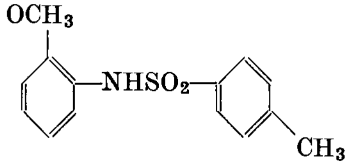


Lang further established that the same compounds were obtained by treating 2 : 4-dinitromethylaniline and 2 : 4 : 6-trinitromethylaniline with nitric acid of concentration over 70 per cent.

In the case of acylated aromatic amines, nitration of the aromatic ring occurs simultaneously with saponification of the acyl group [27].

Arylsulphonyl derivatives of aromatic amines are easily nitrated with dilute nitric acid. Thus, a mononitro derivative is obtained by treating *p*-toluenesulphanilide with dilute nitric acid [28].

Nitration [29] of 1-methoxy-2-*p*-tolylsulphamidobenzene:



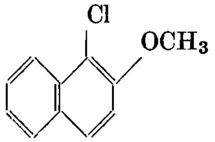
with nitric acid (sp. gr. 1·055) during 6 hr at 80–85°C gives 1-methoxy-2-*p*-tolylsulphamido-5-nitrobenzene. Corresponding ethyl and propy derivatives can be obtained analogously. Treatment of *o*-methoxy-acetanilide with concentrated nitric acid gives *p*-nitro-*o*-methoxyaniline.

Polycyclic aromatic compounds can be nitrated by nitric acid at room temperature. Naphthalene treated with concentrated nitric acid (sp. gr. 1·33) at 20°C gives α-nitronaphthalene [30]. Fuming nitric acid acting on naphthalene at the boiling point temperature of the former gives 1 : 5-dinitronaphthalene and 1 : 8-dinitronaphthalene [31]. In addition to the α-nitronaphthalene obtained on nitration of naphthalene it has been possible to isolate as side products 4·5 per cent of β-nitronaphthalene and 0·5–3·5 per cent of 2 : 4-dinitro-1-naphthol [32].

MAKAROV-ZEMLIANSKII and BIBISHEV [33] showed that the nitration of tetralin with nitric acid resulted in the formation of 1 : 2- and 1 : 3-dinitrotetralin, whereas if the nitration mixture was used it was impossible to isolate the reaction products, owing to considerable tar formation.

SERGIEVSKAIA and URETSKAIA [34] studied the nitration of the alkyl derivatives of naphthalene. 1-Propylnaphthalene treated with nitric acid at 40°C gives 4-nitro-1-propylnaphthalene with a yield of 35 per cent of the theoretical.

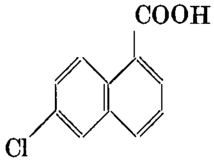
The preparation of nitro derivatives of 1-chloro-2-methoxynaphthalene:



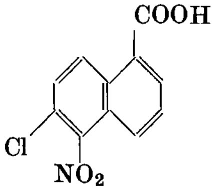
is described in a British patent [35].

1-Chloro-2-methoxynaphthalene is slowly added to an excess (two and a half times the theoretical quantity) of 62 per cent nitric acid at 40°C using chlorobenzene as solvent. A mixture of isomeric 4-, 6- and 8-nitro-1-chloro-2-methoxynaphthalene is obtained.

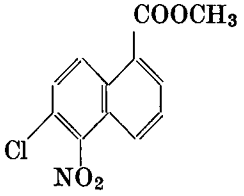
Nitration of 6-chloro-1-naphthoic acid [36]:



by an excess of HNO_3 (sp. gr. 1·49) during 5–10 min, on a water bath, gives 5-nitro-6-chloro-1-naphthoic acid:



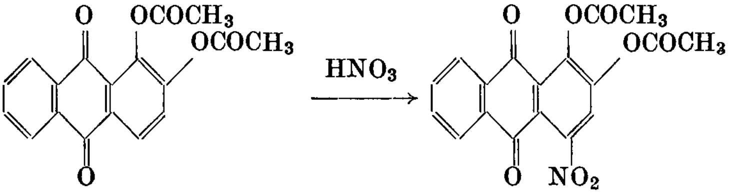
with a yield of 27·5 per cent of the theoretical (after purification). If the methyl ester of 6-chloro-1-naphthoic acid is taken as the starting material and subjected to the above treatment, the 5-nitro-6-chloro-1-methyl ester of naphthoic acid is obtained with a yield of 30 per cent of the theoretical:



Treatment of diphenyl with fuming nitric acid results in the formation of 4 : 4′-dinitrodiphenyl and 2 : 4′-dinitrodiphenyl [37, 38].

Bell and Kenyon [39] nitrated diphenyl with fuming nitric acid and obtained 4 : 4′-dinitrodiphenyl, 4 : 2′-dinitrodiphenyl (m.p. 70–80°C) and 2 : 2′-dinitrodiphenyl (m.p. 127–128°C). They also synthesized 2-nitrodiphenyl and 4-nitrodiphenyl according to the method of Hübner and Lüddens [40] (treating diphenyl with fuming nitric acid in acetic acid solution at 60°C). The action of fuming nitric acid (14 ml) diluted with water (2 ml) on 2-nitrodiphenyl (20 g) for 30 min gives 4 : 2′-dinitrodiphenyl and 2 : 2′-dinitrodiphenyl; 4-nitrodiphenyl under the same conditions gives 4 : 2′-dinitrodiphenyl.

Nitric acid acting on anthracene oxidizes it to anthraquinone. Concentrated nitric acid gives a nitro derivative of diacetyl alizarin even in the cold:



Nitration of phenanthrene has been fairly well studied. As long ago as 1879 Schmidt [41], treating phenanthrene with a large excess of fuming nitric acid, obtained a mixture of α-, β- and γ-nitrophenanthrenes. He succeeded in isolating the isomers from this mixture. Subsequently, Schmidt [42] nitrated phenanthrene at room temperature with nitric acid (sp. gr. 1·56) and obtained 3-nitrophenanthrene, m.p. 170–171°C, which was identical with γ-nitrophenanthrene described by Schmidt.

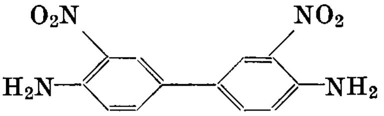
Schmidt [43] also nitrated phenanthrenequinone with nitric acid according to the following method: a mixture of purified phenanthrenequinone (30 g) and conc. HNO_3 (sp. gr. 1·4; 900 ml) was heated until the phenanthrenequinone was completely dissolved, and boiling was continued for a further 20 min. The nitro derivatives precipitated out as yellow flakes on pouring the reaction mixture into 2 l. of water. The precipitate was filtered off, washed with water and treated with boiling alcohol; 4-nitrophenanthrenequinone passed into solution, crystallizing from the alcohol no cooling. Pure 4-nitrophenanthrenequinone, m.p. 176–177°C, was obtained on recrystallization from glacial acetic acid. The alcohol-insoluble residue left after the separation of 4-nitrophenanthrenequinone was dissolved in glacial acetic acid. On cooling, yellow needles of 2-nitrophenanthrenequinone, m.p. 256–260°C, crystallized out.

Of the new nitro compounds which have found considerable application in the control of vineyard and orchard pests, 1 : 3 : 6 : 8-tetranitrocarbazole should be mentioned [44]. Nitration of fluorenone by boiling with fuming nitric acid for 3 hr gives 2 : 7-dinitrofluorenone [45].

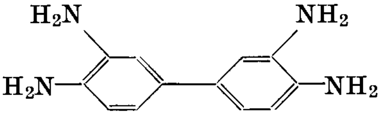
The interaction (with heating) of dibenzanthrone and 70 per cent nitric acid in the presence of *o*-nitrotoluene gives a mononitro derivative [46].

IOFFE and EFROS [47] describe the nitration of dibenzpyrene with nitric acid. The nitration is effected in nitrobenzene at 25–30°C using nitric acid sp. g. 1·52. An appreciably larger excess of nitric acid must be used in order to obtain 5 : 10-dinitrodibenzpyrene. In the course of nitrating dibenzpyrene and its monosubstituted derivatives the nitro group enters the most reactive positions (5 and 10) irrespective of the nature of the substituent already present in the molecule.

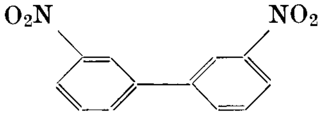
BRUNNER and WITT [48] employed nitration with nitric acid for the preparation of dinitrobenzidine, starting with diacetobenzidine: diacetobenzidine (10 g) was added to fuming nitric acid (100 g) at room temperature. The dinitro derivative obtained was precipitated by ice water, filtered off and washed with hot water. The yield of dinitrodiacetobenzidine was 12·5 g (93 per cent of the theoretical). Moderate heating of dinitrodiacetobenzidine with one and a half times its amount of concentrated KOH solution in the presence of a small amount of alcohol gave a quantitative yield of dinitrobenzidine:



Dinitrobenzidine is insoluble in water, soluble in phenol and slightly soluble in alcohol; on reduction it gives tetraaminodiphenyl:



Dinitrobenzidine dissolved in sulphuric acid and treated with nitrite gives a diazo compound; boiling the latter in absolute alcohol leads to the decomposition of the diazo groups with liberation of nitrogen and resultant formation of 3 : 3′-dinitrodiphenyl (m.p. 197–198°C):



Nitro derivatives of heterocyclic compounds exhibiting aromatic properties can be obtained by the action of nitric acid. Meyer and Stadler [49] obtained nitrothiophene by passing air saturated with thiophene vapour through fuming nitric acid, using 4 vols. of nitric acid to 1 vol. of thiophene. The reaction mixture was finally diluted with water and the oil collected over the aqueous layer was separated off and steam-distilled. The reaction products included mononitrothiophene (m.p. 44°C) and two isomeric dinitrothiophenes of which one (obtained with a higher yield) melted at 52°C, and the other at 75–76°C.

Nitration of quinoline by nitric acid at elevated temperatures gives 5- and 8-nitroquinoline in almost equal quantities, together with a small amount of 6 : 8- and 5 : 7-dinitroquinoline [50]. Pyridine is markedly more difficult to nitrate with nitric acid; according to Friedl [51] boiling pyridine with concentrated nitric acid for 24 hr gives only an insignificant amount of nitropyridine.

2. NITRATION WITH A MIXTURE OF NITRIC AND SULPHURIC ACIDS

The most widespread method for nitrating aromatic compounds uses a mixture of nitric acid with concentrated sulphuric acid ("nitration mixture"). This mixture is a more powerful nitrating agent than nitric acid alone.

The presence of sulphuric acid not only contributes its dehydrating properties (similar to those of the glacial acetic acid and acetic anhydride mixture) but also enhances the nitrating action of nitric acid, whilst diminishing its oxidizing properties. Moreover, sulphuric acid serves as a good solvent for many nitro compounds, which is another favourable factor in nitrating processes.

The nitration of benzene to give the mononitro derivative has been known for many decades and adopted industrially. In order to avoid the formation of the dinitro derivative, nitric acid is taken in rather less (5 per cent) than the theoretical amount [44]. Lewis and others [52] showed that even gentle stirring of the reagents is sufficient for a high yield. Nitration of benzene under more drastic conditions (temperature of 75–80°C, concentration of acid after use 86 per cent) gives a mixture of isomeric dinitrobenzenes. The mixture contains 90 per cent *m*-, 8–9 per cent *o*- and 1–2 per cent *p*-isomer [53].

Kobe and Mills [54] carried out detailed studies concerning the optimal conditions for the preparation of mononitrobenzene. They studied the effect of temperature, amount of nitric acid, amount of sulphuric acid and its concentration, on the yield of the product. The optimal results were obtained when the reaction was carried out as follows: benzene (250 g) and 84 per cent sulphuric acid (120 g) were placed, with cooling, in a reaction vessel of boronsilicate glass. Nitrating mixture (180 g sulphuric acid and 1·5–1·8 per cent excess nitric acid) was gradually added, with stirring. The temperature was 60°C and the duration of the process 40 min. On completion of nitration the reaction mixture was shaken in a separating funnel with 400 g of ice. The nitrobenzene obtained was steam-distilled and dried. Yield 98–99 per cent of the theoretical.

McCormack [55] synthesized *m*-dinitrobenzene directly from benzene. Benzene (69 g) is added slowly from a dropping funnel to a pre-heated (70°C) mixture of 59·9 per cent nitric acid (617 g) and fuming sulphuric acid (oleum with 20 per cent SO_3) (836 g); 2 hr after the initial addition of benzene the temperature of the reaction mixture rises spontaneously to 109°C. When the evolution of heat ceases, the mixture is heated with vigorous stirring for a further 2 hr, maintaining the temperature at 109°C. The yield of dinitrobenzene is 79 per cent of the theoretical. It is possible [56] to obtain *m*-dinitrobenzene by nitrating benzene at a lower temperature, if the reaction is started at 30–60°C and then completed at 80°C. The ratio of the reagent is:

$$H_2SO_4/HNO_3 = 3 \div 6/1; \qquad HNO_3/C_6H_6 = 2{\cdot}1/1$$

Direct nitration of benzene to trinitrobenzene is considerably more difficult to accomplish than that of its homologues, such as toluene. Nitration of dinitrobenzene even under exceptionally drastic conditions only gives very low yields of trinitrobenzene. This method has, therefore, not achieved practical application.

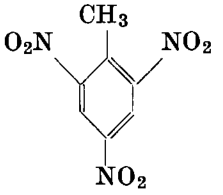
The presence of a methyl group in toluene facilitates its nitration appreciably.

Nitration of toluene to mononitrotoluene proceeds smoothly and under the same conditions as those used for the nitration of benzene. The following mixture of isomers is obtained:

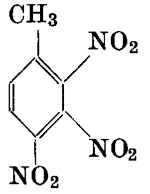
o-isomer	56 per cent
p-isomer	39 per cent
m-isomer	5 per cent

Raising the temperature of nitration increases the amount of the *m*-isomer formed [57]. Toluene can also be nitrated to the mononitro derivative by a continuous process. The mixture of nitrotoluenes is converted by further nitration to dinitrotoluene. The reaction is carried out at 75°C and the concentration of acid after use is approximately 80 per cent; a mixture of dinitrotoluenes is thus obtained containing approximately 75 per cent of the 1 : 2 : 4-isomer and approximately 21 per cent of 1 : 2 : 6-isomer, together with a small admixture of other isomers [58]. Trinitrotoluene is prepared by nitrating nitrotoluene in one or more stages depending on whether the starting material is mono- or dinitrotoluene. Of the three isomeric nitrotoluenes the *o*- and *p*-nitrotoluenes are converted only into 2 : 4 : 6-trinitrotoluene. The conversion of dinitrotoluene to trinitrotoluene is effected by an anhydrous mixture of nitric and sulphuric acids containing 20–25 per cent of nitric acid with a ratio of nitric acid to dinitrotoluene of 1 : 4 or 1 : 5. The reaction begins at ordinary temperature, which rises at first slowly and then rapidly [59]. The nitration of xylene proceeds more easily than that of toluene, owing to the facilitating effect of the concentration of alkyl groups in the ring.

Will [60] studied the nitration of isomeric dinitrotoluenes. 2 : 5-dinitrotoluene treated with a mixture of concentrated nitric acid (1 part) and oleum containing 20 per cent free SO_3 (2 parts) over a long period of time and with heating to 95°C gives γ-trinitrotoluene:



3 : 4-dinitrotoluene gives a mixture of γ-trinitrotoluene (75 per cent) and β-trinitrotoluene:



β-Trinitrotoluene is obtained exclusively by the action of a nitrating mixture, consisting of 5 parts of nitric acid (sp. gr. 1·52) and 12 parts of oleum, at 95°C and continued over 3 days.

Schultz and **Flaschländer** [61] treated ethyl benzene with a nitrating mixture. The mixture, containing 82·5 g nitric acid (sp. gr. 1·456) and 107·6 g sulphuric acid (sp. gr. 1·842), was added to 100 g. ethyl benzene at 30°C. When all the acid had been added the reaction mixture was first heated on a water bath for 2 hr and then on a sand bath to 135°C. The yield of nitroethyl benzene was 94·6 per cent of the theoretical.

2 : 4-dinitroethylbenzene was obtained by **Weisweiller** [62] by slow addition of ethyl benzene (30 g) to a mixture of 2 parts of concentrated sulphuric acid (sp. gr. 1·88) and 1 part of concentrated nitric acid (sp. gr. 1·43), with subsequent heating of the reaction mixture to 125–130°C for 10 min. The structure of 2 : 4-dinitroethyl benzene was proved by its oxidation with nitric acid to 2 : 4-dinitrobenzoic acid.

Weisweiller obtained a symmetrical trinitroethyl benzene with a 70 per cent yield by the following method: ethyl benzene (10 g) was added to a mixture of nitric acid (sp. gr. 1·525; 40 g) and four times its volume of fuming sulphuric acid ($SO_3 \cdot 2H_2SO_4$) cooled with ice; the reaction mixture was then heated to 100°C. The reaction product is almost exclusively trinitroethyl benzene with traces of dinitro derivative [62].

Dolgov and **Kuchumova** [63] studied the nitration of ethyl benzene with nitrating mixture. They obtained chiefly 2-nitroethyl benzene by adding ethyl benzene (25 g) to a mixture of nitric acid (20·5 gr; sp. gr. 1·5 and sulphuric acid (27 g; sp. gr. 1·86) with cooling and subsequent heating to 135°C. In a similar way *m*-diethylbenzene gives the 2 : 4 : 6-nitro derivative.

Nitration of *iso*propylbenzene has been studied in detail by Haun and Kobe [64]. On treating cumene (250 g), emulsified in 97 per cent sulphuric acid (300 g) and water (34·2 g), with a nitrating mixture of 97 per cent sulphuric acid (215·5 g) and 70 per cent nitric acid (225 g) 323·7 g of nitrocumene was obtained; the yield was 94·5 per cent of the theoretical. The authors established that nitrocumene obtained during nitration at temperatures from 0 to 45°C consisted of 24 per cent *o*- and 76 per cent *p*-isomers.

Hansh and Helmkamp [65] prepared 2 : 4-dinitro*iso*propylbenzene with a 96 per cent yield by nitrating *p*-nitrocumene (253 g) with a mixture containing concentrated nitric acid (542 g) and concentrated sulphuric acid (800 g) at a temperature of 45–60°C.

Nitration of *tert.*-butylbenzene with a nitrating mixture (22·3 per cent HNO_3, 65·6 per cent H_2SO_4 and 12·1 per cent H_2O) gives a 96 per cent yield of a mixture of *o*-, *m*-, and *p*-nitro-*tert.*-butylbenzenes [66].

Brown and Bonner [67] studied the proportion of isomers in the mixtures of mononitro derivatives obtained on nitration of ethyl and *iso*propylbenzene. The hydrocarbons were treated with a nitrating mixture composed of 22·3 per cent HNO_3, 65·6 per cent H_2SO_4 and 12·1 per cent H_2O. The reaction products were fractionally distilled through a highly effective fractionating column. The composition of the mononitro derivatives of ethyl and *iso*propylbenzene, as well as of toluene and *tert.*-butylbenzene [66] is given in Table 2.

Table 2. Isomer content (per cent) in mononitro products obtained on nitration of a series of aromatic hydrocarbons

Hydrocarbon	Isomer		
	o-	*m*-	*p*-
Toluene	58·45	4·1	37·15
Ethylbenzene	45·4	6·5	48·2
*iso*Propylbenzene	30·0	7·7	62·3
tert.-Butylbenzene	15·8	11·5	72·7

It can be seen from the table that the amount of *o*-isomer is noticeably lowered as the hydrocarbon radical increases, with a corresponding rise in the amount of *p*-isomer. The amount of *m*-isomer rises appreciably with an increase in the side chain. This change in the content of *o*-isomer is evidently associated with the strong steric effects of the alkyl group on substitution in the *o*-position.

Crossley and Renouff [68] studied the nitration of *o*-xylene with nitrating mixture. The mixture, consisting of nitric acid (25 g) and concentrated sulphuric acid (100 g) is slowly added to *o*-xylene cooled to 0°C. The main products are 3-nitro-*o*-xylene and 4-nitro-*o*-xylene together with a small amount of dinitro-*o*-xylenes. If *o*-xylene (30 g) is nitrated with an excess of nitric acid, adding the hydrocarbon to the mixture consisting of nitric acid (50 g) and sulphuric acid (100 g), i.e. in the reverse order to that in the previously mentioned synthesis; a theoretical yield of dinitro-*o*-xylenes is obtained.

Marqueroll and Loriette [69] nitrated *o*-xylene (35 g) in sulphuric acid solution (65 g 70 per cent H_2SO_4) with gradual addition of the nitrating mixture (85 g) containing 56 per cent sulphuric acid, 28 per cent nitric acid and 16 per cent water. The reaction mixture was stirred and the temperature maintained below 30°C. The yield of mononitroxylene was 45·2 g. *m*-Xylene nitrated with a mixture of nitric and sulphuric acids at a temperature below 0°C gives 4-nitro-*m*-xylene and 2-nitro-*m*-xylene [70].

Nitration of *p*-xylene is described by Bowen [71]. A mixture of concentrated nitric acid (133 g) and concentrated sulphuric acid (212 g) is added dropwise to 1 mole of *p*-xylene at 25–30°C. After separating the organic layer and its neutralization, the reaction product is steam-distilled and extracted with benzene which is then driven off by distillation. The yield of nitro-*p*-xylene is 78–87 per cent of the theoretical. The maximal yield (90 per cent) of mononitro-*p*-xylene was obtained by Kobe and Levin [72] by using an excess of nitric acid of 11 per cent (dehydrating value of sulphuric acid—3·0), at a temperature of 30°C; duration of the reaction was 30 min. 2 : 3- and 2 : 6-Dinitro-*p*-xylene and *p*-toluic acid were found as admixtures.

Of the three isomers of xylene the most easily nitrated one is *m*-xylene [73]. Maximal yield of mononitro-*m*-xylene (98 per cent) is obtained when nitration is carried out under the following conditions: 1·08 moles H_2SO_4 (81 per cent) and 10 per cent excess of HNO_3 are added to 1 mole *m*-xylene at 30°C. The reaction continues for 1 hr.

For the nitration of *m*-xylene half the amount of sulphuric acid used in the nitration of *o*- and *p*-isomers is taken. The data for mononitration of isomeric xylenes are given in Table 3.

Table 3

Molar ratio H_2SO_4 : xylene	Temperature (°C)		Excess HNO_3 (%)	Concentration H_2SO_4 (%)		Reaction time (min.)	Max. yield (%)
	Allowable	Optimal		Optimal	Allowable		
o-xylene, 2·22	6–35	25	15·8	80	78–82	60	90
p-xylene, 2·2	20–40	30	5·0	85	77–85	30	92
m-xylene, 1·08	5–55	30	10·0	81	77–85	60	98

Polynitroxylenes are formed on treating xylenes with nitrating mixture. Noelting and Geisman [74] obtained a mixture of two dinitro-*p*-xylenes, 2 : 3-dinitro-*p*-xylene (m.p. 24°C) and 2 : 6-dinitro-*p*-xylene (m.p. 124°C) by nitrating *p*-xylene with a mixture containing fuming nitric acid (80 g) and sulphuric acid (40 g) and heating on a water bath for 24 hr. The mixture can be separated by fractional crystallization from toluene. The authors prepared 2 : 3 : 5-trinitro-*p*-xylene (m.p. 139–140°C) by heating *p*-xylene (20 g) on a water bath for 16 hr with fuming nitric acid (80 g) and sulphuric acid (120 g).

On nitration of *p*-xylene at 80°C with an excess (10 per cent) of nitric acid (dehydrating value of sulphuric acid—8·0) and reaction time of 15 min, KOBE and LEVIN [72] obtained a 95 per cent yield of a mixture of dinitro-*p*-xylenes consisting of 60–80 per cent of 2 : 3-dinitro-*p*-xylene and 40–20 per cent of 2 : 6-dinitro-*p*-xylene.

LECORCHE and AUBERTEIN [75] describe the preparation of trinitro-*m*-xylene. *m*-Xylene (53 g) is slowly added to 365 g of a mixture of sulphuric and nitric acids (62·5 per cent H_2SO_4, 14·5 per cent HNO_3, 23·0 per cent H_2O) at 50°C. The reaction continues for 1½–2 hr. The product is 85 g of a mixture of equal parts of mono- and dinitroxylene. The mixture obtained, in a solution of 92 per cent sulphuric acid (320 g) is added to 65 g of a mixture of nitric and sulphuric acids (86·7 per cent HNO_3, 8·4 per cent H_2SO_4, 4·9 per cent H_2O) at 70°C. The temperature is then gradually raised to 100°C, and then quickly to 120°C. From 100 to 108 g of trinitroxylene of good quality is obtained.

Nitro derivatives of chlorobenzene are of great practical interest. Nitration of chlorobenzene gives a mixture of *p*- and *o*-nitrochlorobenzene. MCCORMACK [55] studied the nitration of chlorobenzene with a mixture of nitric and sulphuric acids of various concentrations. Chlorobenzene, previously cooled to −50°C, is gradually added to the nitrating mixture with rapid cooling. Optimal results are observed when the reaction mixture is maintained at 10°C. The duration of nitration is about 4 hr. With a view to raising the efficiency of the reaction MCCORMACK also nitrated chlorobenzene with heating to 80–95°C and general duration of nitration being 2½ hr. In this case he used a nitrating mixture composed of 106·5 parts of nitric acid (65·5 per cent) and 107·9 parts of sulphuric acid (93·6 per cent) to 100 parts of chlorobenzene. In both cases the yield of nitrochlorobenzene was 98 per cent of the theoretical, leaving 7 per cent of nitric acid unchanged. The reaction product was a mixture of 66 per cent *p*-nitrochlorobenzene and 34 per cent *o*-nitrochlorobenzene. On further nitration of the mixture of nitrochlorobenzene isomers a mixture of dinitrochlorobenzenes is obtained in which 2 : 4-dinitrochlorobenzene predominates, together with an appreciable quantity of 2 : 6-dinitrochlorobenzene. Other isomers are present as small admixtures.

Nitration of *p*-dichlorobenzene gives mainly 2 : 6-dinitro-1 : 4-dichlorobenzene together with two other possible isomers [76].

Nitration of *o*-dichlorobenzene gives 3 : 5-dinitro-1 : 2-dichlorobenzene 77], whilst that of *m*-dichlorobenzene results mainly in the formation of 4 : 6-dinitro-1 : 3-dichlorobenzene together with some 2 : 4-dinitro-1 : 3-dichlorobenzene [78]. The interaction of 1 : 2 : 4-trichlorobenzene with 100 ml of a mixture of sulphuric acid (sp. gr. 1·82) and nitric acid (sp. gr. 1·52) in the ratio 3 : 1, during 24 hr at room temperature and 8 hr at 50–60°C gives 11 g of 1 : 2 : 4-trichloro-3 : 5-dinitrobenzene, m.p. 101–103°C [79].

Preparation of dinitrofluorobenzene is described by ZAHN and WÜRZ [80]. Fluorobenzene (40 g) is added dropwise to a mixture of nitric acid (sp. gr. 1·52; 120 g) and sulphuric acid (sp. gr. 1·84; 280 g) at 0–20°C. When the addition is complete the mixture is heated for 2 hr on a water bath, cooled, and poured onto ice. The crystalline product contains a certain amount of acid. It is removed by repeated treatment with warm water and filtration until the washings are quite neutral. The product is finally purified by high vacuum distillation (during which a certain amount of polymerization occurs). The yield is 65·8 g, m.p. 25·8°C.

FINGER *et al.* [81] recommend the following conditions for the nitration of benzotrifluoride: 10 per cent excess of the theoretical amount of concentrated nitric acid; initial reaction temperature of 30–35°C, rising finally to 60°C. Yield 90 per cent of the theoretical.

HODGSON and BEARD [82] employed the nitrating mixture for the preparation of nitro derivatives from aromatic aldehydes. Nitrobenzaldehyde was prepared by them in the following manner: benzaldehyde (180 g) was added over a period of 2½ hr to a mixture of nitric acid (160 ml; sp. gr. 1·4) and concentrated sulphuric acid (700 ml). The temperature was not allowed to rise above 10°C. After the introduction of benzaldehyde the stirring was continued for a further 45 min. The reaction product, *m*-nitrobenzaldehyde, was filtered off from the liquid (oil). The precipitate was freed from remaining oily product by successive washing with water, then with sodium carbonate solution, then water again. It was then dried. The yield of crude *m*-nitrobenzaldehyde was 152 g. The oil filtrate was extracted with ether, the extract filtered, dried over calcium chloride and the ether then distilled off. The residue contained a mixture of *o*- and *p*-nitrobenzaldehydes. The total yield of nitrobenzaldehydes was 215 g. The sodium carbonate extract gave 10 g of a mixture of benzoic acid and *o*- and *p*-nitrobenzoic acids.

USHAKOV and FREIDBERG [83] obtained a mixture of nitrobenzaldehydes from toluene. The reaction was carried out as follows: toluene (106 g) was added over a period of 4–5 hr to a solution of potassium nitrate (110 g) in concentrated sulphuric acid (325 ml) at 5°C. The yield of *m*-nitrobenzaldehyde was 46–61 per cent of the theoretical. The mother-liquor yielded 25 per cent of the *o*-isomer. If the reaction occurs at 25–35°C the yield of the *m*-isomer is raised to 75–78 per cent.

The interaction of toluene (25 ml) and a mixture of fuming nitric acid (18 ml) and sulphuric acid (63 ml) during 3 hr at 40°C, then at 90°C (at temperatures above 100°C the reaction proceeds explosively) gave NISHI and TOKI [84] 18 g of purified *m*-nitrobenzoic acid.

Cinnamic acid gives high yields of nitrobenzaldehydes [85]. Cinnamic acid (30 g) in concentrated sulphuric acid (250 ml) is treated at temperatures below 20°C with nitric acid (11 ml; sp. gr. 1·52). After suitable treatment *o*-nitrobenzaldehyde (yield 50 per cent of the theoretical) and *p*-nitrobenzaldehyde (yield 39 per cent) are obtained.

Nitration of phthalic anhydride by PONOMARENKO [86] gave 3-nitrophthalic acid with a yield of 25 per cent of the theoretical.

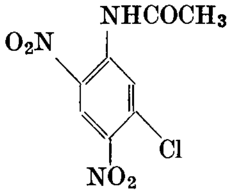
Nitrating mixture is used for the preparation of dinitrophenylacetic acid [87] with a high yield. To phenylacetic acid (163 g) at 0°C a mixture of fuming nitric acid (260 ml) and concentrated sulphuric acid (600 ml) is added at such a rate that the temperature of the reaction mixture remains at 60°C. 2 : 4-Dinitrophenylacetic acid is obtained with a yield of 95 per cent of the theoretical.

Nitro derivatives of diarylsulphate [88] are obtained when it (16 g) is treated with a mixture of nitric acid (sp. gr. 1·48; 11 g) and sulphuric acid (sp. gr. 1·84; 14·3 g). Pure *p*-nitrophenylsulphate (7 g) is obtained after recrystallization of the crude product (21 g). When this substance is treated with a mixture of nitric acid and oleum (20 per cent SO_3) 2 : 4-dinitrophenylsulphate is formed. On hydrolysis it gives 2 : 4-dinitrophenol.

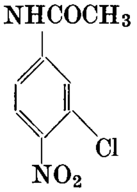
Gradual addition of *p*-bromotoluene (1 ml) to a mixture of 98 per cent sulphuric acid (4 ml) and 70 per cent nitric acid (2 ml) at 90°C gives 2 : 3-dinitro-4-bromotoluene [89]. Nitration of 2 : 3 : 5-tribromotoluene with a mixture of fuming nitric and concentrated sulphuric acids gives 3 : 5 : 6-tribromo-2 : 4-dinitrotoluene [90].

In preparation of nitro amines the amino group is usually protected by replacing a hydrogen atom in the amino group by an acyl group. McCormack [55] obtained *p*-nitroacetanilide with a yield of 83·5 per cent of the theoretical by gradual addition of 100 parts of acetanilide in 400 parts of sulphuric acid to a mixture of 76 parts of H_2SO_4 (91 per cent) and 73 parts of HNO_3 (61·3 per cent).

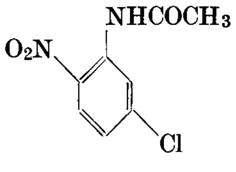
The interaction of *m*-chloroacetanilide with a mixture of nitric acid (sp. gr. 1·52) and sulphuric acid (sp. gr. 1·8) at 0°C gives [91] 3-chloro-4-nitroacetanilide (yield 10 per cent of the theoretical) and 3-chloro-4 : 6-dinitroacetanilide (yield 10 per cent of the theoretical):



If oleum (12 per cent SO_3) is used instead of sulphuric acid the only product is 3-chloro-4 : 6-dinitroacetanilide with a yield of 20 per cent of the theoretical. *m*-Chloroacetanilide treated with a mixture of potassium nitrate and concentrated sulphuric acid gives 3-chloro-4-nitroacetanilide with a yield of 54 per cent of the theoretical [92]:



If, however, the nitration is effected with concentrated nitric acid, the product is 3-chloro-6-nitroacetanilide:



Nitration of *ortho* substituted aromatic amines is described in an American patent [93]. The nitration is carried out in a sulphuric acid solution of the amine at 0–5°C. The nitration of *o*-anisidine is cited as an example and the product is 5-nitro-*o*-anisidine.

Nitration of acyl derivatives of diphenylamine with nitrating mixture proceeds very smoothly, giving a theoretical yield of 2 : 4-dinitrodiphenylamine [94]. If the nitration is carried out with a mixture of fuming nitric acid and concentrated sulphuric acid the resulting product is 2 : 4 : 6-trinitrodiphenylamine.

Kogan and Kutepov [95] studied the preparation of nitro derivatives of diphenyl urea. Nitration of diphenyl urea with a mixture of 68·3 per cent nitric acid and concentrated sulphuric acid at 0°C gives 4 : 4′-dinitrodiphenyl urea:

No tetranitro derivative could be detected. Investigation of the effect of nitric acid concentration showed that the best yields were obtained using 48–67 per cent nitric acid. The optimal temperature for the reaction is approximately 15°C. It is interesting to note that in a number of cases the concentration of sulphuric acid has considerable effect on the position in the ring taken up by the incoming nitro group. Thus, for example, in the nitration of acetanilide with a nitrating mixture, the substitution of the monohydrate by 78·8 per cent sulphuric acid enhances the yield of the *o*-isomer at the expense of the *p*-isomer [96].

Nitro derivatives of the naphthalene series are of great practical interest. Nitration of naphthalene at 25°C with a mixture of 83 parts HNO_3 (61·3 per cent) and 233 parts of H_2SO_4 (91 per cent) gives α-nitronaphthalene with a yield of 85 per cent of the theoretical.

Lenhold (laboratory of the Kineshemskii factory) demonstrated the formation under these conditions of a very small admixture of β-nitronaphthalene.

The action of the nitrating mixture on naphthalene under more drastic conditions gives a mixture of 1 : 5- and 1 : 8-dinitronaphthalene. The preparation of dinitronaphthalene is usually carried out in two stages: first, naphthalene is treated with nitric acid (approximately 62 per cent) only, with cooling, giving α-mononitronaphthalene. To the reaction mixture so obtained a mixture of 3 parts of sulphuric acid (92 per cent), 1 part oleum (60 per cent SO_3) and 1½ parts nitric acid (approximately 62 per cent) is added slowly, with stirring and cooling. After appropriate treatment 1 : 5-dinitronaphthalene and 1 : 8-dinitronaphthalene are obtained with a yield of 27 per cent of the theoretical for the former and 67 per cent for the latter [97]. Subsequent nitration of the dinitronaphthalene mixture gives tri- and tetranitronaphthalenes [98] which are used as explosives.

Nitration of 2-methylnaphthalene [99] gives a mixture of isomers, the chief product being 1-nitro-2-methylnaphthalene. The highest yield (57 per cent) is obtained when 70 per cent nitric acid (70 per cent excess) is used at a temperature of 0–30°C. If a 15 per cent excess of a mixture consisting of 25 per cent nitric acid, 55 per cent sulphuric acid and 20 per cent water is used the main product is also 1-nitro-2-methylnaphthalene. If, however, acetic anhydride is used in the nitration, 2-methylnaphthalene gives a dinitro derivative.

Nitration of α-naphthol proceeds smoothly and gives 2 : 4-dinitro-α-naphthol. PONOMARENKO and MATSIEVICH [100] obtained 1 : 2 : 3 : 4-tetrahydro-6 : 8-dinitronaphthalene with a yield of 33 per cent of the theoretical by nitrating 1 mole of tetrahydronaphthalene with a mixture of 170 g nitric acid (sp. gr. 1·48) and sulphuric acid (sp. gr. 1·83).

4 : 5-Dinitro-1-naphthoic acid can be obtained with 52 per cent of theoretical yield by nitration of 5-nitro-1-naphthoic acid with nitrating mixture at 0°C [101]. It is noted that if glacial acetic acid is substituted for sulphuric acid nitration does not occur, even on heating.

Of the other nitro products of polycyclic compounds dinitroanthraquinone should be mentioned. It can be prepared by heating anthraquinone dissolved in strong sulphuric acid with a nitrating mixture at 70–80°C. This gives a mixture containing chiefly 1 : 5- and 1 : 8-dinitroanthraquinone, together with other isomers [102]. Nitration of phenanthrene results in a mixture of 9-, 2-, 4-, and 3-mononitrophenanthrene and a small amount (1 per cent) of 1-nitrophenanthrene [103].

The mixture of nitric and sulphuric acids is also used in the case of compounds difficult to nitrate, such as pyridine. In the opinion of several investigators it is the tertiary nitrogen atom contained in pyridine which exerts an unfavourable influence on nitration; the introduction of an amino or hydroxyl group neutralizes this effect and leads to satisfactory nitration of pyridine.

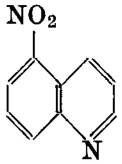
FRIEDL [104] nitrated pyridine by treating it with a mixture of sulphuric and nitric acids (the latter being nascent, resulting from the interaction of potassium nitrate with sulphuric acid). To a solution of pyridine (20 g) in oleum (18 per cent SO_3; 120 g) heated on a sand bath, potassium nitrate (110 g) was added gradually and simultaneously, a strong current of air was circulated through the reaction vessel and receiver. The nitration was carried out in 1 hr at 330°C. The distillate consisting of nitric acid, pyridine and nitropyridine was evaporated on a water bath to drive off most of the HNO_3 and after neutralization with soda it was treated with ether. (The ether took up nitro-pyridine and excess pyridine.) After distilling off the ether and pyridine, the residue was dissolved in nitric acid. From this solution crystals of nitropyridine nitrate separated out on standing; they were then dissolved in dilute nitric acid and on treatment with soda nitropyridine was obtained. The crude product was purified by solution in benzene or alcohol and precipitation by ligroin or water. Using this method, FRIEDL obtained nitropyridine (m.p. 41°C) with a yield of 15 per cent of the theoretical. By reducing the product to aminopyridine which was identified as β-aminopyridine FRIEDL proved that the nitration product was β-nitropyridine. This case served to confirm the rule that the presence of a tertiary nitrogen atom orientates negative substituents first of all to the β-position.

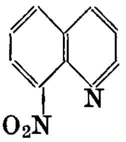
Nitration of 1-hydroxypyridine with a mixture of concentrated sulphuric and concentrated nitric acids at 100°C gives 4-nitro-1-hydroxypyridine

[105]. The yield increases if fuming sulphuric acid is used at 130°C. Further raising the temperature to 140°C decreases the yield. Nitration of 1-hydroxypyridine with a mixture of fuming sulphuric acid and potassium nitrate gives 4-nitro-1-hydroxypyridine with a yield of 52·4 per cent of the theoretical [106].

The addition of 3 : 5-diethoxypyridine (4·5 g) in 10 ml concentrated sulphuric acid to a mixture of 11 ml of strong nitric acid and 2 ml of fuming nitric acid over a period of 30 min at 70°C gives 3 : 5-diethoxy-2-nitropyridine with a yield of 45 per cent of the theoretical [107]. If the nitration is carried out at a higher temperature (80°C) and with a larger excess of fuming nitric acid 3 : 5-diethoxy-2 : 6-dinitropyridine is formed with a yield of 40 per cent of the theoretical. 4-Nitropyridine-N-oxide [108] is obtained with a yield of 85–90 per cent of the theoretical on adding, dropwise, pyridine-N-oxide (1·5 g) in 3 ml concentrated sulphuric acid to a mixture of fuming nitric acid (sp. gr. 1·52; 5 ml) and concentrated sulphuric acid (3 ml). When the addition is complete the reaction mixture is heated for 1½ hr at 90°C, then poured on ice, made alkaline and extracted with ether. After removing the ether the final product is obtained.

The action of nitrating mixture on quinoline [109] gives two isomeric mononitro derivatives which are formed in equal amounts as main products. These isomers are 5-nitroquinoline and 8-nitroquinoline:





The introduction of a second nitro group into the quinoline nucleus by means of nitrating mixture presents considerable difficulty and is not always possible. Kaufmann and Decker [110] developed a method for the preparation of dinitro derivatives of quinoline from the corresponding mononitro derivatives. It is impossible to nitrate 6-nitroquinoline with a mixture of nitric and sulphuric acids even by boiling for several days. However, nitration of 6-nitroquinoline with a calculated amount of potassium nitrate and sulphuric acid in a sealed tube during 10 hr at 130–140°C gives two dinitro derivatives: 6 : 8-dinitroquinoline (m.p. 154°C; identical with the product synthesized from 2 : 4-dinitroaniline) and 5 : 6-dinitroquinoline (m.p. 185°C). It is appreciably easier to nitrate 7-nitroquinoline. Refluxing 5 g of the latter with a mixture of nitric acid (sp. gr. 1·5; 100 ml) and concentrated sulphuric acid (150 ml) for 6 hr, Kaufmann and Decker obtained two nitro derivatives, one melting at 225°C, the other at 175°C (judging by the character of the crystals and other physical properties, the latter compound was evidently 5 : 7-dinitroquinoline).

8-Nitroquinoline treated with nitrating mixture over a period of 20 hr gave 6 : 8-dinitroquinoline with an almost quantitative yield. This derivative had a m.p. 154°C and was identical with the products obtained by nitration of 6-nitroquinoline (see above) and also by synthesis from 2 : 4-dinitroaniline. 6 : 8-Dinitroquinoline can be obtained without admixture of 5 : 6-dinitroquinoline by treating 6-nitroquinoline (1 part) with a mixture of SO_3 (1 part) and concentrated nitric acid (2 parts) with stirring and gradual raising of the temperature to 100°C over a period of 2 hr (6-nitroquinoline is introduced into the nitrating mixture). Using the same method for nitration of 5-nitroquinoline gives 5 : 8-dinitroquinoline [111]. 1-Hydroxyquinoline gives 1-hydroxy-4-nitroquinoline with a good yield when treated with potassium nitrate and sulphuric acid at 70°C [105].

ADAMS [112] added a solution of 4-hydroxyquinoline (10 g) in 45 ml concentrated sulphuric acid at 0–5°C to a mixture of nitric acid (10 ml; sp. gr. 1·5) and concentrated sulphuric acid (10 ml) and obtained 9·9 g of 6-nitro-4-hydroxyquinoline.

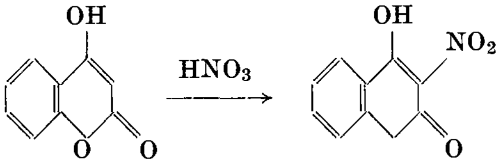
Nitration of 2 : 4-dimethylquinoline gives 6-nitro-2 : 4-dimethylquinoline together with 8-nitro-2 : 4-dimethylquinoline [113] which are separated by means of hot dilute sulphuric acid. 4 : 6-Dimethylquinoline treated with nitrating mixture at temperatures below 0°C gives a very good yield of 5-nitro-4 : 6-dimethylquinoline [114]. The original communications should be consulted for details of the nitration of 4-aminoquinoline [106, 115, 116].

4-Chloro-6-methoxyquinaldine gives a very good yield of 4-chloro-6-methoxy-8-nitroquinaldine (the only reaction product) when treated with a mixture of sulphuric acid and potassium nitrate [117].

Nitration of benzothiazole with a mixture of HNO_3 (sp. gr. 1·5) and conc. H_2SO_4 at 0°C gives a mixture of 6-nitrobenzothiazole and a mononitro derivative of benzothiazole in which the position of the nitro group has not been established [118]. It is presumed that this nitro derivative is a molecular compound of 6-nitro and 7-nitro derivatives of benzothiazole.

Nitration of 5-methyl-2-thiophenecarboxylic acid with nitrating mixture at −5°C gives 4-nitro-5-methyl-2-thiophenecarboxylic acid [119] with a good yield, as well as a small amount of dinitro-2-methylthiophene. If the reaction is carried out at a higher temperature the yield of the mononitro derivative of thiophenecarboxylic acid decreases whilst that of the dinitro derivative of thiophene increases.

KLOSA [120] nitrated 4-hydroxycoumarin with a mixture of sulphuric and nitric acids obtaining a poor yield of the nitro derivative. A better yield is obtained by nitrating 4-hydroxycoumarin in chloroform:



Nitrogen containing derivatives of coumarin are physiologically interesting in connexion with antibiotics.

3. NITRATION WITH NITRIC ACID AND GLACIAL ACETIC ACID OR ACETIC ANHYDRIDE

A fairly common method of nitrating aromatic compounds uses a mixture of nitric acid with acetic acid and also with acetic anhydride. A systematic investigation of this method was carried out by **Konovalov** and **Gurevich** [121]. The authors studied the nitration of toluene, xylenes (*o*-, *m*- and *p*-isomers), ethyl benzene, diethyl benzene and other substances using nitric acid (sp. gr. 1·495) and glacial acetic acid. In all cases except ethyl benzene and diethyl benzene the reaction was carried out by refluxing over a period of 1½–2 hr. In the case of the ethyl benzenes, gentle heating was used. The reaction mixture was then poured into water, washed with soda and treated with a solution of alkali in aqueous alcohol to remove the products in which the side chain had been nitrated. These products were isolated by treating with CO_2 and extraction with ether. The products in which the ring was nitrated were extracted with ether and then fractionated. The authors' investigations led them to the following conclusions:

(1) Acetic acid, when used with nitric acid, plays the same part as water; it weakens the effect of nitric acid on the aromatic nucleus and favours its action (at elevated temperatures) on the side chain.

(2) The various hydrocarbons in general show the same tendency to react with nitric acid mixed with acetic acid as they do with dilute nitric acid.

(3) The side chain undergoes oxidation simultaneously with the nitration with the resultant formation of the corresponding carboxylic acids. This occurs especially if the reaction is carried out under drastic conditions.

Since glacial acetic acid is a solvent, it is possible to avoid using an excess of nitric acid. Moreover, glacial acetic acid and, to a still larger extent, acetic anhydride serve to bind the water which is produced in the course of nitration. Nitration with a mixture of nitric and glacial acetic acids shows the same properties as nitration with aqueous nitric acid [122]. The substitution of concentrated sulphuric acid by acetic anhydride in the process of nitration is of interest because of the disappearance of the orientating effect of sulphuric acid which directs the nitro group to a particular position.

The main conditions which determine the course of the reaction when aromatic hydrocarbons are nitrated with a mixture of nitric acid and acetic anhydride are the relative amounts of nitric acid, water, and the substance to be nitrated.

When toluene is nitrated with nitric acid taken in excess in relation to the hydrocarbon (3–4 moles of nitric acid to 1 mole of toluene) in the absence of acetic anhydride, only a small yield (17–18 per cent) of nitro derivatives is obtained. (The ratio of nitric acid to water contained in the solution and formed during the nitration is 2·66 : 1.) If, however, the reaction is carried out in the presence of acetic anhydride a quantitative yield of nitro derivatives (mixtures of *o*- and *p*-nitrotoluene) is obtained [123].

A mixture of nitric acid and acetic acid can be used successfully for the nitration of mesitylene. Nitro-mesitylene is obtained in 50 per cent yield by heating to boiling over 1½ hr 1 part of mesitylene dissolved in 4 parts of glacial acetic acid, with 1 part of fuming nitric acid. The reaction product is precipitated with water and after separating the latter, it is made alkaline with NaOH and steam-distilled. Mesitylene is distilled off from the aqueous distillate and the nitro-mesitylene is recrystallized from alcohol; it separates out on cooling in the form of prisms [124].

BAMBERGER and RISING [125] used the following method of nitration to prepare mononitromesitylene: concentrated nitric acid (sp. gr. 1·51; 100 g) is introduced into a mixture of mesitylene (100 g) and glacial acetic acid (400 ml). A vigorous reaction, accompanied by evolution of heat, takes place and the liquid begins to boil; boiling is maintained for 50 min. On completion of nitration the cooled reaction mixture is poured into 1 l. of water and ice. The heavy oil which then separates out is filtered off from the suspended crystals of mesitylenic acid and treated with ether; the ethereal extract is shaken several times with 20 per cent solution of potassium carbonate and then with 15 per cent solution of potassium hydroxide in order to remove mesitylenic acid and xylyl-nitromethane (the latter is isolated from the alkaline solution by saturating with CO_2). Ether is distilled off from the ethereal extract and the residue is fractionally steam-distilled; mesitylene comes off first and then nitromesitylene. The latter crystallizes on cooling (m.p. 125°C). This method of nitration gives nitromesitylene as the main product, whereas nitration according to KONOVALOV's method [126] gives predominantly xylyl nitromethane where substitution by the nitro group occurs chiefly in the side chain.

Mesitylene can also be nitrated by a mixture of nitric and glacial acetic acids and acetic anhydride [127]. A mixture of fuming nitric acid (sp. gr. 1·51; 31·5 g) glacial acetic acid (20 g) and acetic anhydride (20 g) is added gradually to a mixture (cooled to 10°C) of mesitylene (40 g) and acetic anhydride (60 g). The rate of addition and the cooling are so adjusted that the temperature does not rise above 20°C. When the addition is complete, the reaction mixture is left at room temperature for 2 hr, then heated to 50°C and, on cooling, poured with stirring into 800 ml ice water. NaCl (40 g) is then added, the product separated, and the aqueous layer extracted with ether. This extract is added to the main bulk of the product. It is then washed with 10 per cent NaOH (until the reaction is frankly alkaline), the ether is distilled off, 150 ml of 10 per cent NaOH is added to the residue and nitromesitylene is steam-distilled. The oily layer of the distillate so obtained is separated and dissolved in ether. After distilling off the ether on a water bath the residue is distilled at 243–250°C. The crude product so obtained is purified by recrystallization from methyl alcohol. The yield of nitromesitylene is 75–76 per cent of the theoretical.

Nitration of *o*-xylene gives 4-nitro-*o*-xylene [128]; it is added gradually to a mixture of fuming nitric acid with half its volume of glacial acetic acid at 20–25°C. The product is obtained after suitable treatment in the form of yellow prisms (m.p. 30°C). 3-Nitro-*o*-xylene can be obtained from the filtrate.

o-Diethyl benzene is nitrated by a mixture of nitric and acetic acids at 10–20°C with the formation of 1 : 2-diethyl-4-nitrobenzene. The yield is 41 per cent of the theoretical [129].

Nitrophenols can also be synthesized by treating phenols with a mixture of nitric and acetic acids. *m*-Cresol, for instance, can be nitrated as follows: a mixture of *m*-cresol (140 g) and glacial acetic acid (140 g) is cooled to 5°C and added slowly to a cold mixture (– 15°C) of nitric acid (sp. gr. 1·5; 200 g) and glacial acetic acid (400 g). When all the *m*-cresol has been added, the mixture is left for 1½ hr during which the temperature must not be allowed to fall below – 1°C. To isolate the products, the reaction mixture is poured into ice and water; a viscous liquid separates out which later crystallizes and on steam-distillation 4-nitro-*m*-cresol (m.p. 56°C) and 6-nitro-*m*-cresol (m.p. 129°C) are obtained [130].

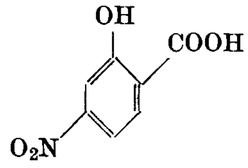
When *o*-propyl phenol (20·4 g) in acetic acid (20·4 g) is added to a mixture of nitric acid (sp. gr. 1·42; 40·8 g) and acetic acid (61·2 g) at – 4°C to – 6°C, 2-nitro-6-propyl phenol is formed with a yield of 39 per cent of the theoretical [131].

2 : 6-Di-*tert.*-butyl phenol is nitrated with a mixture of concentrated nitric and acetic acids (1 : 1) with the formation of 4 : 6-dinitro-2-*tert.*-butyl phenol [132].

Benzyl chloride is nitrated with a mixture of nitric acid and acetic anhydride at 25°C giving 32 per cent *o*-, 15·5 per cent *m*- and 52·5 per cent *p*-nitrobenzyl chloride [133].

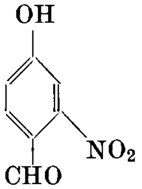
The 5-nitro derivative of *o*-methoxyphenol (guaiacol) is prepared [134] by the addition of a solution of the acetyl derivative of guaiacol (135 g) in acetic acid (120 ml) to a solution of nitric acid (sp. gr. 1·5; 115 ml) in acetic acid (180 ml). During this addition the temperature rises to boiling. The resultant product is hydrolysed by 50 ml 10 per cent NaOH. The yield of the 5-nitro derivative calculated from the initial acetyl derivative is 42 per cent.

Bazany and Pianka [135] suggest an improved method for nitrating of aromatic orthohydroxycarboxylic acids and their esters. It is as follows: 1 mole of the appropriate compound in a small amount of acetic acid is treated briskly with a mixture of 1 mole of nitric acid and 9 vols. of acetic acid at room temperature with subsequent heating until the solution becomes brown. The nitro derivative formed is precipitated by the addition of water. Salicylic acid gives a 5-nitro derivative under these conditions with a yield of 41 per cent of the theoretical.



The ethyl and methyl esters of salicylic acid give 5-nitro derivatives with yields of 51 per cent and 64 per cent of the theoretical.

Nitration of *p*-hydroxybenzaldehyde [136] with a mixture of nitric and glacial acetic acids leads to the formation of 2-nitro-4-hydroxybenzaldehyde:



Nitration of a solution of *p*-hydroxybenzaldehyde in glacial acetic acid is carried out by gentle heating with nitric acid (sp. gr. 1·4).

Nitration of benzoic acid with a mixture of nitric acid and acetic anhydride gives a good yield of *m*-nitrobenzoic acid.

Aniline and its derivatives can be successfully converted to their nitro derivatives by a mixture of nitric and acetic acids. In point of fact, it is acetanilide and not aniline itself which is usually nitrated with nitric acid, with the predominant formation of *p*-nitroacetanilide and only insignificant amounts of *o*-nitroacetanilide. WITT and UTTERMANN [137] showed that using a mixture of nitric and acetic acids substantially altered the ratio of the resulting isomers.

WITT and UTTERMANN's method consists of pouring a solution of nitric acid (sp. gr. 1·5; 23 g) and urea (1 g) in 23 g of glacial acetic acid into a solution of acetanilide (45 g) in glacial acetic acid (22 g). The addition is carried out with cooling. The reaction mixture is left for 24 hr. The precipitation of the crude product and the separation of the isomers are effected as follows: 350 g ice is added to the reaction mixture and the precipitate which separates out and which consists of a mixture of *o*- and *p*-nitroacetanilides is treated with alcoholic KOH; this saponifies only the *o*-nitroacetanilide, the *p*-isomer remaining unchanged. The main reaction product (as distinct from nitration with nitric acid in the absence of acetic acid) is *o*-nitroacetanilide. The ratio of the isomers is 3 : 1. The total yield of the nitro derivatives (crude) is 87 per cent of the theoretical.

Nitration of aniline derivatives giving nitroamino compounds can also be successfully achieved by using a mixture of nitric acid and acetic anhydride; thus tribromoaniline can be converted quantitatively to tribromonitroaminobenzene (2:4:6-tribromophenylnitroamine $C_6H_2Br_3NHNO_2$) [123]. The method consists of dissolving the aniline derivative to be nitrated in 98–99 per cent glacial acetic acid and adding to this solution, with cooling, nitric acid in the ratio of 2–3 moles to 1 mole of the aniline derivative. Acetic anhydride is slowly added to this mixture, also with cooling, and taking care to keep the temperature below 25°C. It is essential to use nitric acid free of HNO_2 in order to obtain a good yield of nitroamines, since nitrous acid may diazotize the nitroamine:

$$C_6H_2Br_3NHNO_2 + HNO_2 = C_6H_2Br_3N = NNO_3 + H_2O$$

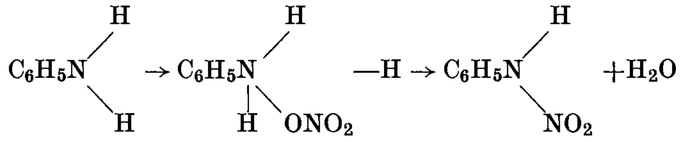
Nitric acid can be freed from nitrous acid by vacuum distillation at 20–30 mm, but better results are obtained by treating nitric acid with urea nitrate.

Nitration of amino compounds which contain few substituents and can thus be more easily acetylated (e.g. 2 : 4-dichloroaniline), can be effected by dissolving the amine in glacial acetic acid and slowly adding the solution to a mixture consisting of nitric and acetic acids and acetic anhydride. Nitration occurs in this case at low temperatures (the reaction vessel being cooled with water and ice). This method gives excellent yields of nitro compounds from aniline derivatives in which one or both of the positions ortho to the amino group is not substituted. Isomeric nitroanilines are formed as side products in small quantities.

When dialkyl anilines are nitrated by this method it is evident that nitrous acid activates the process; in other words it has the opposite effect to that which it shows during the nitration of other aniline derivatives. The mixture of acetic anhydride with nitric acid free of nitrous acid does not react with dialkyl anilines. If the latter are nitrated with a mixture of acetic anhydride and ordinary nitric acid which contains some nitrous acid, the reaction proceeds with evolution of heat and formation of dinitro derivatives. Thus N-dimethyl aniline gives 2 : 4-dinitro-N-dimethyl aniline.

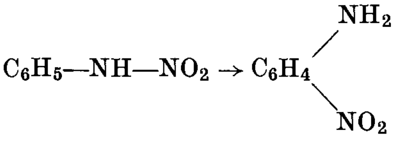
Acetanilide and *p*-chloroacetanilide are nitrated with a mixture of nitric acid and acetic anhydride. A quantitative yield of the corresponding nitro derivatives is obtained. The optimal ratio of the reagents is 4 moles nitric acid free of nitrous acid to 1 mole of the compound to be nitrated. On the other hand, 2 : 4-dichloroacetanilide does not undergo nitration when similarly treated.

Bamberger [138] who studied the nitration reactions of anilines using a mixture of nitric acid and acetic anhydride suggested a mechanism for this reaction. He submits that aniline reacts with nitric acid to give aniline nitrate which then changes to phenylnitroamine with the loss of one molecule of water:



$$C_6H_5N\begin{array}{l}\diagup H\\ \diagdown H\end{array} \rightarrow C_6H_5N\begin{array}{l}\diagup H\\ |\diagdown ONO_2\\ H\end{array} —H \rightarrow C_6H_5N\begin{array}{l}\diagup H\\ \diagdown NO_2\end{array} + H_2O \qquad (1)$$

Acetic anhydride acts as a dehydrating agent. Further studies showed that in the aromatic nitroamines the nitro group linked with the nitrogen atoms migrates to the nucleus in the presence of mineral acids which act as catalysts for this rearrangement. For example, phenylnitroamine gives *o*- and *p*-nitroanilines under the catalytic action of mineral acids.

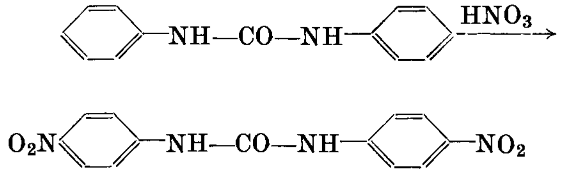


$$C_6H_5—NH—NO_2 \rightarrow C_6H_4\begin{array}{l}\diagup NH_2\\ \diagdown NO_2\end{array} \qquad (2)$$

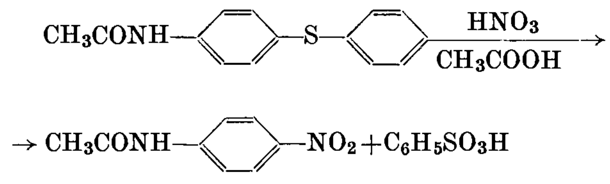
Therefore, using the two reactions mentioned above, (1) and (2), it is possible to nitrate aromatic bases in two stages, the first one being the introduction of the nitro group into the side chain (formation of aromatic nitroamines) and the second the migration of the nitro group to the ring (formation of nitroanilines).

Nitration of a solution of triphenylamine in glacial acetic acid with a mixture of nitric acid (sp. gr. 1·49) and acetic acid gives 4-nitrotriphenylamine with a yield of 20·25 per cent, 4 : 4′-dinitrotriphenylamine with a yield of 30 per cent and 4 : 4′ : 4″-trinitrotriphenylamine with a yield of 40 per cent of the theoretical. This was carried out by **Bugai** [139].

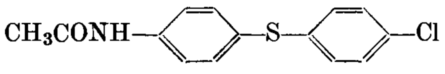
Diphenylurea [140] is nitrated by a mixture of nitric acid (sp. gr. 1·50) and glacial acetic acid at 40°C with the formation of *p* : *p*′-dinitrodiphenylurea:



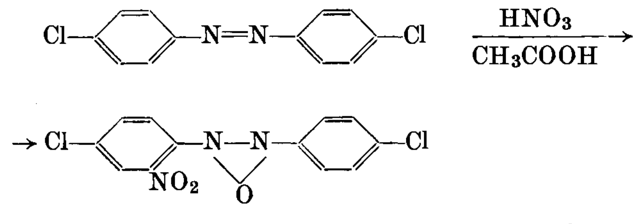
4-Acetamidodiphenyl sulphide shows an interesting reaction with a mixture of nitric acid (sp. gr. 1·4) and glacial acetic acid, giving *p*-nitroacetanilide and benzenesulphonic acid [141]:



A similar cleavage of the molecule takes place if the starting molecule is:



Nitration of *p* : *p*′-dichloroazobenzene with a mixture of fuming nitric and acetic acids at – 10°C gives 4 : 4′-dichloro-2-nitroazoxybenzene [142]:



The same compound can be prepared by nitration of *p* : *p*′-dichloroazoxybenzene.

Nitrodiphenyls are also synthesized in the presence of acetic acid. Thus, 1 mole of diphenyl is nitrated by 2 moles nitric acid (sp. gr. 1·50) in the presence of acetic acid, with heating. The reaction products consist of *p*-nitrodiphenyl (colourless needles, m.p. 113°C), *o*-nitrodiphenyl (m.p. 200–201°C) and 3 : 5 : 4′-trinitro-4-hydroxydiphenyl (m.p. 202°C) [143].

Nitration of diphenylene oxide with a mixture of nitric and acetic acids gives 2-nitrodiphenylene oxide with a yield of 56 per cent of the theoretical [144].

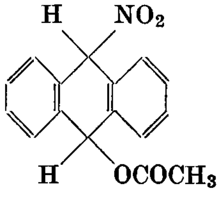
THOMSON *et al.* [145] describe the preparation of mono and dinitro derivatives of 1 : 5-dimethoxynaphthalene with high yields. 1 : 5-dimethoxynaphthalene (10 g) in acetic acid (400 ml) is slowly heated with a mixture of nitric acid (sp. gr. 1·42; 4 ml) and acetic acid (4 ml). The reaction mixture is maintained at 80°C for 30 min. 4-Nitro-1 : 5-dimethoxynapththalene is so obtained in the form of yellow crystals, m.p. 167°C, yield 89 per cent of the theoretical. If a larger excess of nitric acid is taken (8 ml instead of 4 ml) and the reaction mixture is boiled, the resulting product is the 4 : 8-dinitro derivative of 1 : 5-dimethoxynaphthalene with a yield of 84 per cent of the theoretical. This compound (2 g) in acetic acid (150 ml) refluxed for 1 hr with nitric acid (15 ml) gives 2 : 4 : 8-trinitro-1 : 5-dimethoxynaphthalene with a yield of 43 per cent of the theoretical. This product in turn gives 2 : 4 : 6 : 8-tetranitro derivative with a 23 per cent yield of the theoretical when it is added in small portions to nitric acid (sp. gr. 1·5) at 0°C.

Nitration of 1-hydroxy-2-naphthoic acid and of its methyl ester gives a good yield (70–77 per cent of the theoretical) of 4-nitro-1-hydroxy-2-naphthoic acid when treated with a mixture of nitric and acetic acids [135].

Halogen derivatives of naphthalene can also be nitrated with nitric acid mixed with glacial acetic acid. For example, 1 : 5-difluoronaphthalene (2 g) in glacial acetic acid (8 ml) treated with nitric acid (sp. gr. 1·52; 8 g) with heating on a water bath for 4 hr gives 1 : 5-difluoro-4-nitronaphthalene with a yield of 82 per cent. More energetic nitration results in a mixture of isomers which are difficult to separate [146]. IZMAILSKII and KOZIN [147] obtained 8-nitro-1-chloromethyl naphthalene by nitrating 1′-chloro-1-methyl naphthalene.

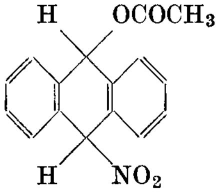
Nitration of acetyl-β-naphthylamine leads to the formation of 1-nitro-2-acetylnaphthylamine [148]. Nitric acid (sp. gr. 1·4; 200 g) is added slowly and with constant stirring to a mixture of acetyl-β-naphthylamine (300 g) and glacial acetic acid (500 ml). The reaction mixture is maintained at a temperature of not higher than 40°C by means of a cooling mixture. Stirring is continued for a further 10 min after the addition of nitric acid is complete and the reaction mixture is then left in ice-water for 3 hr. The crystals obtained are filtered off, washed with 50 per cent acetic acid and ether and recrystallized first from benzene and then from 95 per cent alcohol. The resultant nitro product melts at 123–124°C. The yield is approximately 50 per cent of the theoretical.

A mixture of nitric and acetic acids can also be used for the nitration of anthracene. The action of 63 per cent nitric acid on anthracene, suspended in glacial acetic acid, at a temperature not above 30–35°C gives anthracene-nitroacetate:



When water is added to this compound a viscous mass separates out. It is gradually transformed into nitroanthracene on heating with dilute NaOH. Nitroanthracene can also be obtained by treating the reaction mixture containing anthracene-nitroacetate with concentrated sulphuric acid at room temperature [149].

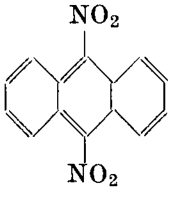
MEISENHEIMER and CONNERADE [150] investigated the action of nitric acid on anthracene in the presence of acetic acid and acetic anhydride. Nitric acid (sp. gr. 1·4; 20 ml) was added slowly to anthracene (50 g) suspended in glacial acetic acid (200 ml); the reaction was carried out with cooling and the temperature maintained within the range 30–35°C. After 15 min a clear solution was formed in the reaction flask which was poured out in a thin stream into cold water; the yellow mass which then separated out was washed with water and, after drying in vacuum, dissolved in ether. On prolonged standing, crystals of anthracene-nitroacetate precipitated out:



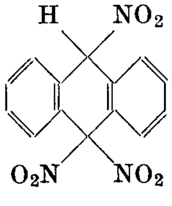
The yield was 45 per cent of the theoretical.

Using an excess of nitric acid MEISENHEIMER and CONNERADE obtained other reaction products. Concentrated nitric acid (sp. gr. 1·4; 20 ml) diluted with acetic acid (40 ml) was slowly added to a mixture of anthracene (20 g) and glacial acetic acid (80 ml). The reaction mixture was cooled and the temperature maintained within the range of 30–35°C. After 2 hr crystals began to separate out from the reaction mixture. After standing for 2 days the crystals were filtered, washed with acetic acid and dried. The authors isolated the following products from these crystals:

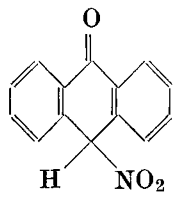
Dinitroanthracene (m.p. 294°C)



Trinitrodihydroanthracene (m.p. 139–140°C)



Nitroanthrone (m.p. 148°C)



Nitro and dinitroanthracenes can also be prepared by direct nitration of anthracene using a mixture of nitric acid with acetic anhydride and acetic acid. The method is as follows: finely powdered anthracene (10 g) is introduced into glacial acetic acid (40 ml) and to this mixture nitric acid (sp. gr. 1·5; 10 ml) which is free from nitrogen oxides, acetic anhydride (6 ml) and glacial acetic acid (15 ml) are slowly added from dropping funnels, with strong cooling. The temperature of the reaction is maintained within the range 15–20°C. After a time crystals begin to separate out in the reaction mixture; these are filtered off 24 hr later, washed with alcohol and treated with boiling alcohol which dissolves nitroanthracene. This crystallizes out on cooling (m.p. 145–146°C). The crystals which do not dissolve in alcohol consist of dinitroanthracene which is purified by recrystallization from xylene.

SCHMIDT and HEINLE [151] studied the nitration of phenanthrene with a mixture of nitric acid and acetic anhydride. Pure phenanthrene (80 g) was dissolved in hot acetic acid (160 ml) and to this solution was slowly added a mixture of acetic anhydride (120 ml) and concentrated nitric acid (sp. gr. 1·45; 60 ml). The reaction mixture was heated on a water-bath. The heating was continued until no more gases were evolved. The reaction product was poured into cold water nitrophenanthrenes being precipitated out. These were filtered off and washed with water until free from nitric acid and acetic anhydride. The crude product was purified from tarry admixtures by dissolving in alcohol. Four mononitrophenanthrenes were isolated from this solution by fractional crystallization: 2-nitrophenanthrene (m.p. 99°C), 3-nitrophenanthrene (m.p. 170–171°C), 4-nitrophenanthrene (m.p. 80–82°C) and 9-nitrophenanthrene (m.p. 116–117°C). The main product of the reaction was 9-nitrophenanthrene (60 per cent of the total amount of mononitrophenanthrenes contained in the crude product). The total yield of mononitrophenanthrenes was 60–61 per cent of the theoretical.

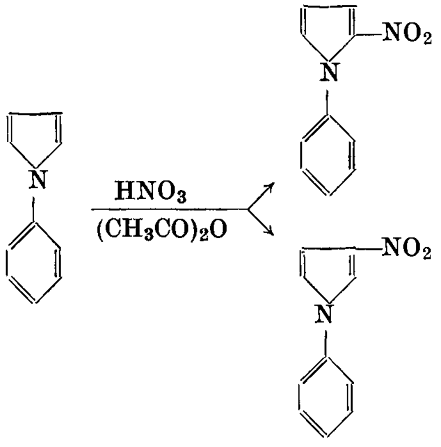
The conversion of the halogen derivatives of phenanthrenes into the corresponding nitrohalogen derivatives can also be achieved by using a mixture of nitric acid with acetic anhydride. Thus, nitric acid (sp. gr. 1·45; 5 ml) is slowly added to a mixture of 9-bromophenanthrene (20 g), acetic acid (20 ml) and acetic anhydride (8 ml) with heating on a water-bath for 20 min. On cooling the reaction mixture, a solid product separates out; it is recrystallized from toluene and then from acetone. The yield of the nitro derivative is 8 g. It melts at 175–190°C [152].

Fluorene is nitrated with a higher yield (79 per cent of the theoretical) [153] when nitric acid (sp. gr. 1·42) in glacial acetic acid is used. The reaction is carried out with stirring and at an initial temperature of 50°C, which then rises to 65°C and finally to 80°C. 2-Nitrofluorene is obtained in yellow needles which melt at 156°C.

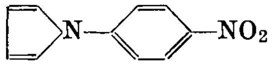
When 4-hydroxypyridine-N-oxide, in glacial acetic acid, is heated with nitric acid (sp. gr. 1·36) on a water-bath for a short time a 3 : 5-dinitro derivative is formed with a yield of 83 per cent of the theoretical.

Carbazole is nitrated with nitric acid mixed with glacial acetic acid to give dinitrocarbazole [154]. A mixture of 5 parts of glacial acetic acid and 1 part carbazole is heated to 80°C and to this 1·3 parts of nitric acid (sp. gr. 1·38) is slowly added with stirring. The reaction mixture is then heated for 30 min at 100°C, with subsequent cooling and separating of 3 : 6-dinitrocarbazole.

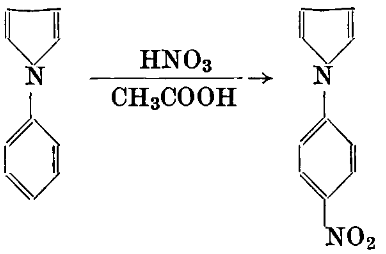
Nitration of N-phenylpyrrole with nitric acid in acetic anhydride gives 1-phenyl-2-nitropyrrole and 1-phenyl-3-nitropyrrole [155]:



If, however, N-phenylpyrrole is nitrated with a mixture of nitric and sulphuric acids the nitro group enters the benzene ring giving 1-(4-nitrophenyl)-pyrrole



Iuriev *et al.* [156] nitrated N-phenylpyrrolidine with nitric acid mixed with glacial acetic acid, obtaining N-(*p*-nitrophenyl)-pyrrolidine with a yield of 52 per cent of the theoretical. Since N-phenylpyrrolidine is less stable than, e.g. dimethylaniline, the nitration is carried out under gentler conditions (at a temperature of −20°C). To N-phenylpyrrolidine (10 g) in glacial acetic acid (70 ml) at −20°C nitric acid (sp. gr. 1·35; 13 ml) is added dropwise. The reaction mixture is stirred by shaking the flask. After standing for 24 hr a precipitate of N-(*p*-nitrophenyl)-pyrrolidine separates out. The yield is 6·9 g (52 per cent of the theoretical). If the nitration is carried out at temperatures above −20°C the yield drops to 12–20 per cent:

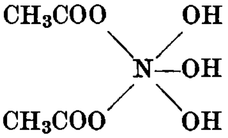


2-Nitrothiophene is formed in good yield by the nitration of thiophene [157]. A solution of thiophene (42 g) in acetic anhydride (170 ml) is added slowly, with stirring and energetic cooling (temperature not over 10°C) to a mixture of fuming nitric acid (sp. gr. 1·51; 40 g) and glacial acetic acid (300 ml). On completion of the reaction the mixture is allowed to stand at room temperature for 2 hr and then poured onto ice. Nitrothiophene separates out as pale yellow crystals which are filtered off with suction, washed with ice-water, pressed dry and finally dried in a desiccator. On recrystallization from petroleum ether 2-nitrothiophene is obtained (m.p. 44–45°C; yield 85 per cent of the theoretical).

Coumarin derivatives are nitrated with a mixture of nitric and acetic acids with the formation of dinitro derivatives of coumarin. Thus, when 7-hydroxy-3 : 4-dimethyl coumarin, suspended in acetic acid, is treated with nitric acid with heating on a water-bath 7-hydroxy-3 : 4-dimethyl-6 : 8-dinitrocoumarin is formed [158].

The reaction mechanism of nitration with nitric acid mixed with acetic anhydride or acetic acid has been relatively little studied. It is suggested that the nitrating agent in these mixtures is a compound resulting from the interaction of acetic anhydride (or acetic acid) and nitric acid (diacetylorthonitric acid or acetylnitrate).

Pɪᴄᴛᴇᴛ and Gᴇɴᴇǫᴜᴀɴᴅ [159] found that when nitric acid was mixed with acetic acid or acetic anhydride a mixed anhydride of acetic and *o*-nitric acids was formed—diacetyl-*o*-nitric acid which has the structure:



When nitric acid (sp. gr. 1·4) is added to an equal volume of acetic anhydride a vigorous reaction takes place with evolution of heat which causes the liquid to boil. On fractional distillation of the reaction product it is possible to isolate the main fraction which distils over at 127·7°C (at 730 mm). The same product is formed on mixing glacial acetic acid with fuming nitric acid (sp. gr. 1·52) but in this case the reaction proceeds less vigorously. If to 1 mole of nitric acid 2 moles of acetic acid are taken, the reaction product distils over almost completely at 127–128°C. Analysis has shown that the product obtained corresponds to the formula $C_4H_9NO_3$ i.e. contains elements of 1 mole HNO_3 and 2 moles acetic acid. The evolution of heat during the reaction, as well as the fact that the boiling point of the resultant product is higher than the boiling points of the original substances indicates in this case the formation of a new compound and not merely a mixture of components. Diacetyl-*o*-nitric acid is a colourless liquid which fumes in air and has the following constants: sp. gr. 1·197 (at 15°C), $n_D^{23} = 1{\cdot}38432$, b.p. 127·7°C (at 730 mm) and 45°C (at 17 mm). It dissociates completely in aqueous solutions to give 2 moles of acetic acid and 1 mole of nitric acid. It acts very vigorously on organic compounds as an acetylating, oxidizing or nitrating agent depending on the conditions of the reaction and the nature of the substance subjected to its action.

PICTET and GENEQUAND consider that in mixtures of nitric acid with acetic acid or acetic anhydride it is diacetyl-*o*-nitric acid which is the nitrating agent. It was used by PICTET [160] for nitrating a series of aromatic compounds. This showed that as a nitrating agent the diacetyl-*o*-nitric acid approximates dilute nitric acid, since it exhibits a weak nitrating and fairly pronounced oxidizing action. Aniline, phenol and nitrobenzene are not nitrated by this substance.

COHEN and WIBAUT [161] studied the kinetics of aromatic nitration in the presence of acetic anhydride. They first studied the interaction of nitric acid and acetic anhydride in the absence of the compound to be nitrated. The rate of this reaction was measured by the change in the HNO_3 titre (in moles per 1000 ml solution). It was found that with initially low concentrations of nitric acid the reaction rate was disproportionately slow as compared with experiments with higher initial concentrations of nitric acid. The results of kinetic measurements also showed that in the first 75–100 min the reaction mixture still contained free HNO_3 which later entered into reaction with acetic anhydride forming acetyl nitrate:

$$HNO_3+(CH_3CO)_2O \rightleftarrows CH_3CONO_3+CH_3COOH$$

150 min after the beginning of the reaction the acetyl nitrate begins to diminish noticeably as it reacts with acetic anhydride forming nitro derivatives of the latter (nitro acetates).

Experiments designed to study the kinetics of the interaction of benzene with nitric acid in the presence of acetic anhydride differed from one another in the various initial concentrations of nitric acid, as well as the quantitative ratios of the components. Practically no nitration takes place with low concentrations of nitric acid and benzene. The reaction only proceeds at an appreciable rate when the initial quantities of the reagents are as follows: nitric acid 0·8 moles and benzene 1·2 moles. In order to obtain a clearer picture of the course of the reaction simultaneous measurements are made of the concentration of nitric acid and of nitrobenzene. It is evident that the nitration of benzene occurs at first rapidly but with time slows down and the total amount of nitric acid and acetyl nitrate used up exceeds the amount of the reagents necessary to form nitrobenzene. The results obtained indicate that the process of aromatic nitration is accompanied by a side reaction which consists of the interaction between acetyl nitrate and acetic anhydride (see above).

Comparison of both the reactions studied gives the following conception of the nitration of benzene with nitric acid in the presence of acetic anhydride: at the beginning of the process nitric acid is the only nitrating agent and only subsequently another nitrating agent, acetyl nitrate, is formed. The latter, besides nitrating the aromatic compound, also enters into reaction with acetic anhydride giving nitroacetates.

The influence of nitrous acid on nitration has also been studied; experiments with the addition of urea, which destroys nitrous acid, demonstrated considerable lowering of the reaction rate compared with experiments in the presence of nitrous acid. Therefore these experiments showed the catalytic effect of nitrous acid. It was found in the experiments in which no urea was added that the concentration of nitrous acid grows at a marked rate as the reaction proceeds; this is evidently connected with the oxidizing action of nitric acid on benzene, which leads to the formation of further quantities of nitrous acid. The catalytic action of nitrous acid is enhanced as its concentration increases. However, this holds only up to a certain limit beyond which further formation of nitrous acid has no appreciable effect on the rate of the reaction.

The kinetics of the nitration of aromatic hydrocarbons and their halogen derivatives with nitric acid in acetic anhydride have also been studied by TRONOV, KAMAI and KOVALENKO [162]. A mixture of equimolecular amounts of nitric acid, acetic anhydride and the substance under investigation was heated at 0–20°C. After certain intervals of time the mixture was titrated with NaOH. The relative rate of nitration of various compounds was calculated by the time in which an equal diminution of acidity took place, i.e. in which the same quantity of nitric acid had reacted (the amount of alkali used up in the neutralization of acetic anhydride was also taken into account). The experiments showed that the rate of nitration of hydrocarbons increases in the following order (rate of nitration of benzene was taken as unity): benzene (1) $<$*m*-xylene (7) $<$mesitylene (25) $<$pseudocumene (28). The halogen derivatives can be arranged in the following ascending series corresponding to their rates of nitration:

$$\mathrm{C_6H_5Cl}\ (0{\cdot}15) < \mathrm{C_6H_5Br}\ (0{\cdot}25) < \mathrm{C_6H_5CH_2Cl}\ (0{\cdot}4) <$$

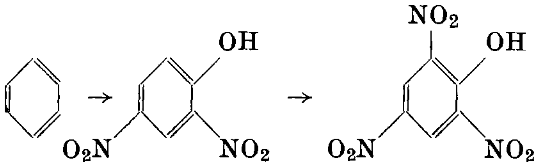
$$< m\text{-}\mathrm{CH_3C_6H_4Cl}\ (0{\cdot}5) < p\text{-}\mathrm{CH_3C_6H_4Cl}\ (1{\cdot}15) <$$

$$< o\text{-}\mathrm{CH_3C_6H_4Cl}\ (1{\cdot}2)$$

4. NITRATION IN THE PRESENCE OF CATALYSTS

The catalytic action of mercurous nitrate in the nitration of anthraquinone and methylanthraquinone was discovered in 1906 [163]. Somewhat later the peculiar catalytic action of mercury salts was found in the nitration of benzene. It has been established that the nitration of benzene in the presence of Hg $(NO_3)_2$ at a certain concentration of HNO_3 is directed towards the formation of nitrophenols. The action of concentrated nitric acid or a mixture of nitric and sulphuric acids on benzene in the presence of mercury gives only nitrobenzene; it is necessary for the formation of nitrophenols that the nitric acid be dilute, when it can exert its oxidizing effect. The formation of nitrophenols during nitration of aromatic hydrocarbons by dilute nitric acid in the presence of mercury nitrate depends to a marked degree on the temperature of the reaction and the concentration of the acid; the presence in the reaction mixture of sulphuric acid in amounts which do not affect the concentration of nitric acid has no effect on the yield of nitrophenols.

Nitrophenols are prepared by heating on a water-bath a mixture of benzene (100 g), nitric acid (sp. gr. 1·31; 800 g) and mercury nitrate (15 g). The reaction is carried out with vigorous stirring. The products obtained are 2 : 4-dinitrophenol and picric acid, together with a small amount of nitrobenzene:



According to CARMACK's data [164] the optimal conditions for oxidizing nitration aimed at giving dinitrophenol consist of using 50–55 per cent nitric acid containing 0·2–0·5 mole/l. of mercury nitrate, at a temperature of 50°C. The yield of dinitrophenol reaches 85 per cent of the theoretical. (Other investigators [105] indicate a lower yield.) The side-products are nitrobenzene and picric acid. If the reaction is conducted at a higher temperature the formation of picric acid is enhanced at the expense of dinitrophenol.

BACHMAN *et al.* [165] who also studied the composition of the products obtained on oxidative nitration of phenol carried out the reaction as follows: benzene (50 g) at 50°C was added over a period of 3·3 hr to a mixture of 10·65 M nitric acid (750 ml), 0·37 M $Hg(NO_3)_2$* and $NaNO_2$ (0·1 g) at 50°C. The reaction mixture was stirred for approximately 2½ hr and then cooled, when dinitrophenol separated out. Side-products were isolated from the filtrate. The yield of dinitrophenol was 68·4 per cent. In addition to dinitrophenol the following substances were isolated: picric acid, 4·0 per cent; nitrobenzene, 7·8 per cent; CO_2, 9·7 per cent; oxalic acid, 2·5 per cent. Nitrophenols are formed as the result of two processes: oxidation and nitration, with oxidation apparently preceding the nitration. The latter supposition is confirmed by the fact that when nitric acid acts on nitrobenzene it either remains unaltered or is transformed into dinitrobenzene but not into nitrophenol. The reaction giving picric acid

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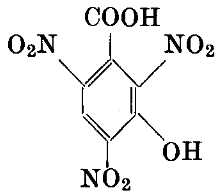
* HgO (60 g) added to 70 per cent HNO_3 (541 ml) and diluted to 750 ml.

from benzene proceeds according to the following equation which expresses the final result of the nitration:

$$C_6H_6+4HNO_3=C_6H_2(OH)(NO_2)_3+3H_2O+HNO_2$$

It is supposed that at first a complex of benzene and mercury is formed as an intermediate product which subsequently breaks down under the action of excess nitric acid [166].

It is also known that mercury nitrate exerts a catalytic action on the nitration of benzoic acid with nitric acid, directing the reaction towards the formation of trinitrohydroxybenzoic acid (under ordinary conditions of nitration, i.e. without catalysts, benzoic acid gives nitrobenzoic acids). The trinitrohydroxybenzoic acid, which on heating splits out CO_2 to become picric acid, has the following formula:



In this case too, the presence of mercury facilitates the entry of the hydroxyl group into the aromatic ring [167].

The action of nitric acid in the presence of mercury on aromatic compounds and their derivatives has also been studied by BLECHTA and PATEK [168]. When toluene is nitrated with 50 per cent nitric acid in which 2 per cent mercury is dissolved, nitrotoluenes and *p*-nitrobenzoic acid are formed with a yield of 10 per cent of the theoretical; *p*-nitrobenzoic acid melts at 237–238°C. Trinitro-*m*-cresol is also found among the products of the reaction. These authors do not confirm the formation of nitrosalicylic acid which was observed by other investigators [167].

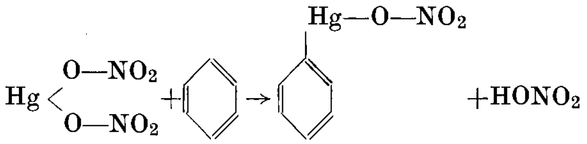
Nitration of benzene with a mixture of nitric and sulphuric acids in the presence of 2 per cent mercury gives nitrobenzene and trinitrophenol. When toluene is nitrated with the same mixture it gives nitrotoluenes, nitrocresol and *p*-nitrobenzoic acid. In other words, the same products are obtained as those formed during nitration with nitric acid. These results indicate that the addition of sulphuric acid has no influence on the nitration of aromatic compounds with nitric acid in the presence of mercury. It is also shown that the nitration of nitrobenzene with 80–85 per cent nitric acid in the presence of mercury gives higher yields of dinitrobenzene than those obtained without catalyst.

The mechanism of the nitration of aromatic compounds in the presence of mercury is explained by BLECHTA and PATEK in the following way. The mercury salt forms an intermediate mercury-organic complex with benzene, $C_6H_5HgNO_3$, which breaks down under the action of nitric acid with liberation of nascent hydrocarbon. The hydrocarbon thus activated is easily nitrated by the nitric acid. The authors represent the course of the reaction schematically as follows:

$$2C_6H_5—Hg—NO_3+4HNO_3 \rightarrow 2C_6H_5OH+2Hg(NO_3)_2+N_2O_3+H_2O$$

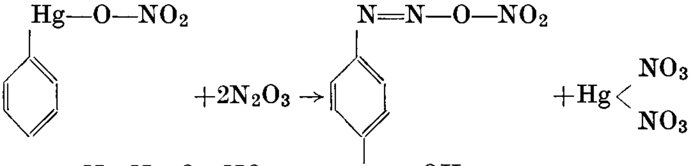
the phenol thus formed reacts immediately with nitric acid giving nitrophenol.

The following reaction mechanism [169] is offered for the explanation of the formation of picric acid from benzene when the latter is nitrated in the presence of mercury salts. In the first stage of the process it is supposed that a mercury compound of benzene, in which the mercury is directly linked with the benzene ring, is formed:



(1)

Then it is suggested that the nitrous acid in the form of the anhydride reacts with the mercury-benzene compound giving diazobenzene nitrate (2) which on hydrolysis decomposes to give phenol, nitrogen and nitric acid:



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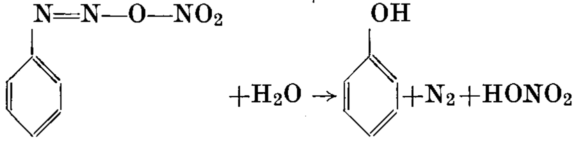
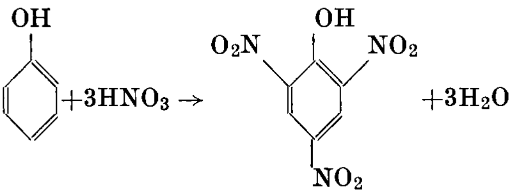


(3)

The last stage of the process consists of the nitration of phenol by nitric acid giving the final reaction product—picric acid:



(4)

The nitration of benzene in the presence of mercury salts has also been studied by VIGNON [170]. By heating a mixture of benzene (100 g), nitric acid (36° Baumé) (800 g) and mercury nitrate (20 g) at 70°C for 5 hr, VIGNON obtained picric acid (138 g) and nitrobenzene (32 g). On further investigation he found that nitration of benzene in the presence of mercury salts showed the following distinctive features:

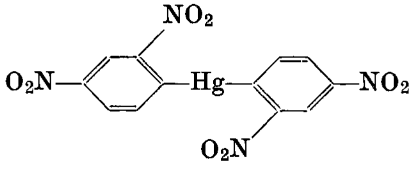
(1) At concentrations in excess of a certain limit picric acid is oxidized completely, as it is formed, by nitric acid to CO_2.

(2) Excess of benzene in relation to nitric acid increases the total yield of hydroxynitroderivatives since it favours the formation of dinitrophenols at the expense of a partial decrease in the yield of picric acid. Thus, for example, using 5 parts of benzene to 10 parts of nitric acid it is possible to get a yield of nitrophenols of approximately 85 per cent of the theoretical, whereas if 1 part of benzene is taken to 10 parts of nitric acid the yield only amounts to 34 per cent.

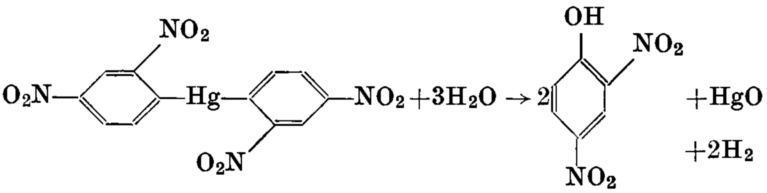
By varying the conditions of nitrating benzene in the presence of $Hg(NO_3)_2$ VIGNON obtained the optimal results using the following method: a mixture of nitric acid (36° Baumé; 100 g), benzene (50 g) and $Hg(NO_3)_2$ (2·5 g) is heated under a reflux condenser for 6 hr at 75–80°C. The excess benzene helps to maintain the temperature of the mixture and dissolves the nitrophenols which are thereby made less susceptible to the oxidizing action of nitric acid. When nitration is complete, the benzene containing nitrophenols in solution is separated from the aqueous layer, the latter is washed with benzene after which both the benzene solutions are combined and the benzene is distilled off first, then the nitrobenzene is steam-distilled. The residue consists of a mixture of nitrophenols (52 per cent dinitrophenol and 48 per cent picric acid).

If it is desired to convert the dinitrophenol into picric acid, the mixture of nitrophenols may be treated with nitric acid or sodium nitrate in sulphuric acid.

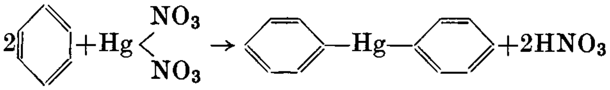
BRODERS [171] carried out a detailed study of all the gaseous products formed during the nitration of benzene with nitric acid in the presence of $Hg(NO_3)_2$. He failed to detect the presence of N_2 amongst them, but found nitrogen oxides, NO_2 and N_2O_4. He further showed that a certain amount of *o*- and *p*-dinitrobenzenes was formed during the nitration of benzene. Their formation could be explained by the oxidation by nitric acid of the corresponding intermediate products—nitronitrosobenzenes. BRODERS also nitrated benzene with dilute nitric acid in the presence of mercury at low temperatures and succeeded in isolating as intermediate products nitrobenzene and a compound to which he ascribed the following structure:



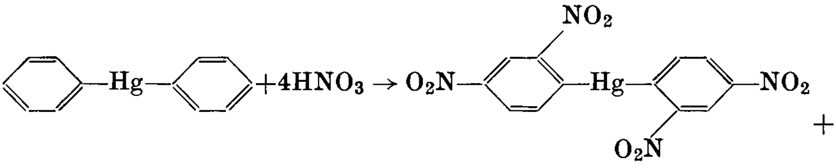
This compound (tetranitrodiphenylmercury) decomposes on hydrolysis to give dinitrophenol:



Desvergens [173], taking into account the data obtained by Broders, as well as the work of Bamberger [172] who showed that the compound of benzene with mercury (diphenylmercury) reacted with N_2O_4 to form nitrobenzene and phenyl nitrate of mercury, suggests the following mechanism for the nitration of benzene in the presence of mercury nitrate: $Hg(NO_3)_2$, interacting with benzene, gives diphenylmercury (1); the latter reacts with nitric acid to give tetranitrodiphenylmercury (2), which enters completely into the aqueous phase; tetranitrodiphenylmercury is an unstable compound which is quickly decomposed by nitric acid into dinitrophenol and N_2O_4 with regeneration of $Hg(NO_3)_2$ (3):

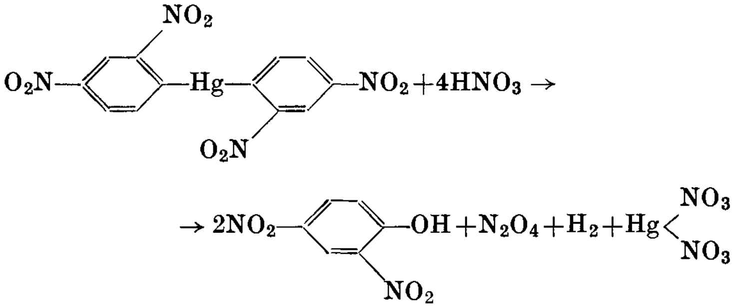


(1)



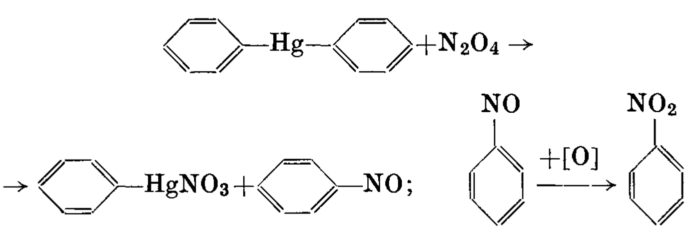
(2)

$+4H_2O$



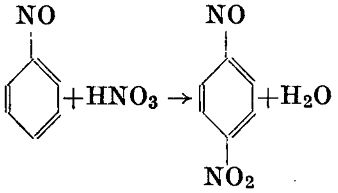
(3)

Desvergens explains the appearance of nitrobenzene among the reaction products by the action of N_2O_4, formed according to equation (3) above, on diphenylmercury, with subsequent oxidation of nitrosobenzene by nitric acid to nitrobenzene (4)



(4)

Desvergens also suggests that nitric acid can act as a nitrating agent on nitrosobenzene, converting it to nitronitrosobenzene (5). The latter, on further oxidation gives *p*-dinitrobenzene (6), which is also found among the reaction products: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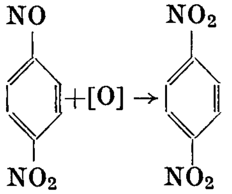
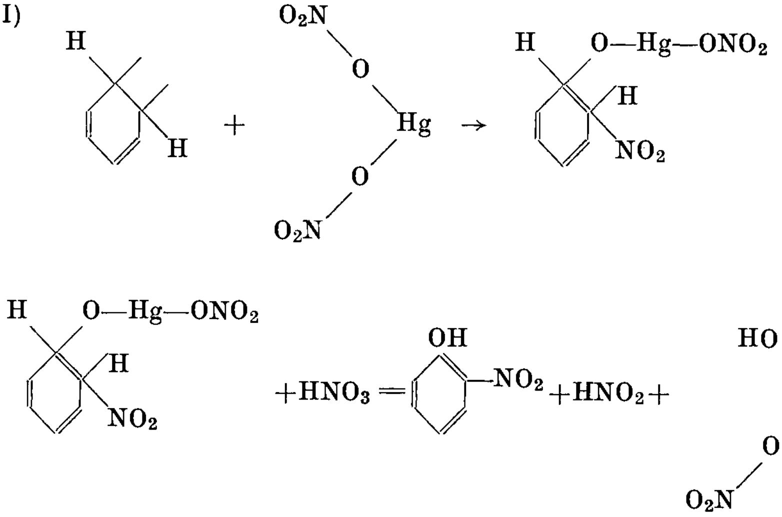

(6)

In order to study the optimal conditions for the nitration of benzene in the presence of $Hg(NO_3)_2$, Desvergens carried out a series of experiments in which he varied the concentration of nitric acid, the ratios of the reactants, the temperature and the duration of nitration. In some of the experiments the nitration was done by passing benzene vapour through a reaction vessel containing nitric acid and the catalyst. These experiments gave less favourable results than those in which liquid benzene was used. The optimal results (yield of nitrophenols approximately 70 per cent of the theoretical) were obtained under the following conditions: ratio of reagents—1·4 parts benzene, 3 parts nitric acid (61 per cent), 0·06 parts $Hg(NO_3)_2$; reaction temperature 75–80°C; duration of nitration 6 hr. Desvergens also showed that nitration of benzene in the presence of nitrates of manganese, aluminium, copper and zinc gives a small yield of nitro compounds.

Zakharov [174] brings the following arguments against the mechanism suggested by Desvergens concerning the formation of dinitrophenol and nitrobenzene: (1) The conversion of benzene to dinitrophenol according to Desvergens is accompanied by the evolution of hydrogen. However, Zakharov did not succeed in detecting the formation of hydrogen even when nitrating large quantities of benzene. (2) Formation of nitrobenzene by the interaction of diphenylmercury and N_2O_4 with subsequent oxidation of nitrosobenzene (see above) is unlikely. The amount of nitrogen oxides should gradually rise as the reaction proceeds, reaching their greatest accumulation towards the end of the process. If Desvergens' suggestion is accepted then a predominant formation of nitrobenzene at the expense of nitrophenols should be expected towards the end of the nitration. This is not observed in reality; even on additional saturation of the reaction mixture with N_2O_4 there is no appreciable rise in the yield of nitrobenzene.

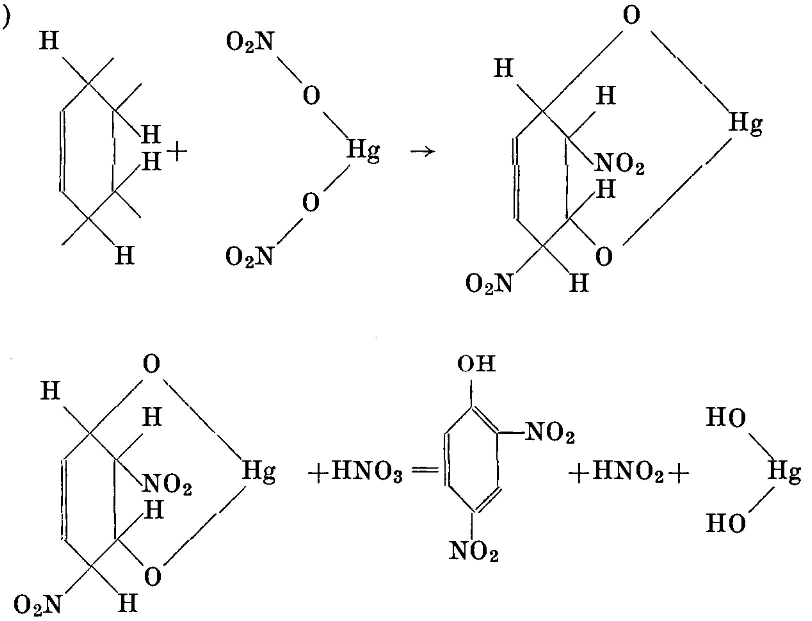
Zakharov suggests another scheme based on the assumption that the main role of the catalyst is concerned with the weakening of the general stability of the benzene ring, through the breaking of the double bonds. This weakening of the ring can occur in two different places (I and II):

(I)

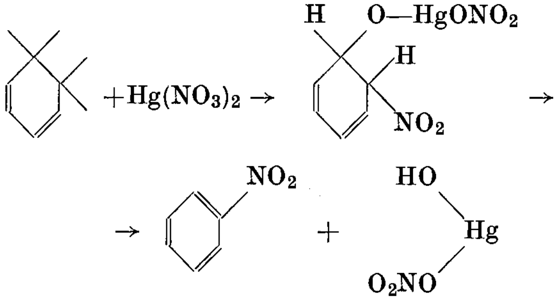


or

(II)



Zakharov's experiments show that the formation of nitrophenols takes place only when the concentration of nitric acid is low (below 60 per cent), when its oxidizing properties are most in evidence. If nitric acid of relatively high concentration (65–70 per cent) is used, at a temperature of 60–65°C which does not favour its oxidizing action, only nitrobenzene is obtained, at the beginning of the reaction; nitrophenols appear only some time after the beginning of the process following the lowering of nitric acid concentration in the reaction mixture. Thus Zakharov comes to the conclusion that the introduction of the hydroxyl group in this reaction depends not on the presence of catalyst but only on the concentration of nitric acid used and the temperature of the reaction. Zakharov further considers that the formation of nitrobenzene takes place in accordance with the following scheme:



When the acid is used repeatedly, both the rate of reaction and the yield of dinitrophenol are increased as shown by Zakharov. For example, when nitration is carried out with freshly prepared solution containing 59–60 per cent nitric acid and with a 30 per cent content of catalyst, at 35–40°C the yield of dinitrophenol is about 40 per cent. On re-using the acid (keeping the other conditions constant) the yield of dinitrophenol increases to 50–55 per cent. On re-using the acid again, for the third, fourth and fifth time, the yield of dinitrophenol rises to 65 per cent, 75 per cent and 80 per cent respectively. The author explains this by a more active state of the catalyst in the re-used acid.

Zakharov also studied the catalytic nitration of benzene derivatives in the presence of $Hg(NO_3)_2$. These compounds apparently only give nitro derivatives, i.e. they do not have the ability to undergo simultaneous oxidation such as is observed in the case of benzene itself. Phenol, for instance, on being nitrated in the presence of $Hg(NO_3)_2$ with dilute nitric acid (3–4 per cent) at low temperature (down to −5°C) gives almost pure *p*-isomer of nitrophenol with a yield of 60 per cent. The optimal conditions for the nitration of phenol are the addition of phenol (50 g) in small portions to dilute nitric acid (calculated on 36 g of the monohydrate) containing catalyst (5 g). Nitration of salicylic acid with 10–12 per cent nitric acid in the presence of $Hg(NO_3)_2$ gives a mixture of isomeric mononitro derivatives with a total yield of 92–93 per cent. The predominant product is *p*-nitrosalicylic acid. It is essential to carry out the reaction with strong cooling (the optimal temperature 44–47°C).

The accelerating action of $Hg(NO_3)_2$ on the nitration of naphthalene was noted by Enz and Pfister [175]. According to these authors the yield of 2 : 4-dinitro-α-naphthol is also increased.

Contrary to this Zakharov maintains that the polycyclic aromatic hydrocarbons (naphthalene, anthracene) and their derivatives give only mononitro derivatives (and not hydroxynitro derivatives) when they are nitrated with nitric acid and $Hg(NO_3)_2$. Nitration of β-naphthol gives exclusively α-nitro-β-naphthol. Zakharov recommends the following method for the nitration of β-naphthol: β-naphthol (50 g) is added to 2–4 per cent nitric acid (calculated on 44 g monohydrate) containing catalyst; the reaction is carried out at 30–35°C, with stirring. The yield of α-nitro-β-naphthol under these conditions reaches 84–85 per cent of the theoretical.

E. I. Orlov [176] studied the nitration of *m*-xylene with dilute nitric acid in the presence of mercury. A mixture of *m*-xylene with 45–50 per cent nitric acid was refluxed for 6 hr in the presence of 2 per cent mercury. The reaction product was steam-distilled. A small amount of oil with the odour of nitrobenzene distilled over. The residue consisted of a mixture of two substances, one of which was in the form of yellow crystals soluble, on heating, in water, ether, alcohol, benzene and xylene, whilst the second one was in orange-coloured lumps. Investigation showed that the second substance was a tautomeric form of the first. In order to determine the nitro group content of the yellow crystals, they were reduced with $SnCl_2$ and HCl. After removal of HCl the resultant amine was destroyed with sulphuric acid and the nitrogen was estimated by the Kjeldhal method. The results of the analysis, giving the carboxyl group and nitrogen content, showed that the nitration product was a hydroxynitrobenzene dicarboxylic acid.

Nitration of xylene with nitric acid in the presence of mercury was also studied by Kholevo and Eitington [177]. Nitric acid (50·2 per cent; 800 g) and metallic mercury (16 g) (or a corresponding amount of $Hg(NO_3)_2$) were placed in a round-bottomed flask fitted with a reflux condenser and a stirrer; the contents of the flask were heated with stirring to 75°C and to this *m*-xylene (100 g) was added dropwise. When all the xylene had been added, heating (75–80°C) was continued for 5 hr, with stirring. In all the experiments the reaction products were 4-nitro-*m*-xylene and 4-nitro-3-methylbenzoic acid. No hydroxynitro compounds were obtained. By carrying out the nitration of *m*-xylene under these conditions but without catalyst these authors obtained the same compounds with the same yields. The yield of mononitroxylene from 100 g *m*-xylene was 35 g irrespective of whether the reaction took place with catalyst or without. The authors also nitrated *m*-xylene under the conditions indicated by Orlov [176]. Their results, however, did not confirm his data concerning the formation of hydroxynitrobenzene dicarboxylic acid as the main reaction product. They isolated mononitroxylene and, as the main product, 4-nitro-3-methyl benzoic acid. These authors came to the conclusion, based on experimental findings, that mercury showed no catalytic action on the nitration of *m*-xylene, as distinct from benzene. In their opinion, this is due to the tendency of xylene to give mononitrocarboxylic acids easily. These prevent the mercury from exercising its catalytic action. In this case the carboxyl group counteracts, as it were, the introduction of the hydroxy group into the ring. Such an effect is similar to that seen when other groups, e.g. the nitro group, are present in the ring.

The nitration of aromatic compounds with nitric acid has also been studied by Davis and collaborators [178, 179]. This work has clarified the mechanism of the reaction and the part played by the addition of $Hg(NO_3)_2$. These workers carried out their experiments on benzene in a round-bottomed pyrex flask fitted with a ground-glass condenser. Nitric acid was first placed in the flask and mercury oxide or $Hg(NO_3)_2$ was dissolved in it. Benzene was then added and the mixture heated on a sand-bath, with gentle boiling and slight evolution of nitrogen oxides. On completion of the reaction an equal volume of water was added and the mixture steam-distilled. The first part of the distillate contained benzene which had not reacted and nitrobenzene; the latter contained a considerable amount of dinitrophenol from which it was separated by shaking with sodium carbonate solution. The next portion of the distillate contained two dinitrobenzenes and 2 : 4-dinitrophenol. The two dinitrobenzenes were separated from each other by fractional crystallization. The residue remaining after steam-distillation, containing the mercury salt, was subjected to hot filtration. Crystals of picric acid separated out from the filtrates on cooling. It was found that in order to obtain good results it was necessary to use a relatively larger quantity of nitric acid than indicated in the communication of WOLFFENSTEIN and BÖETERS [166].

When benzene (200 g) was nitrated during 7 hr with nitric acid (sp. gr. 1·42; 600 ml) in which mercury oxide (10 g) was dissolved, the following products were obtained: 41 g unreacted benzene, 61·3 g nitrobenzene, 105 g picric acid and 4 g of a mixture consisting of equal parts of *m*-dinitrobenzene and 2 : 4-dinitrophenol, and a certain amount of *p*-dinitrobenzene.

It is further shown that depending on the concentration of nitric acid (from 100 to 20·6 per cent) there is variation in the quantitative relations and the character of the reaction products. At concentrations of nitric acid of 70 per cent and higher satisfactory yields are obtained of mono and dinitrobenzenes, but picric acid is only formed in small amounts. Nitration of toluene with nitric acid in the presence of mercury proceeds much more energetically than that of benzene. The reaction was carried out over a prolonged period with a gradual raising of the temperature (12½ hr at 65–85°C, 2 hr at 85–95°C, 1 hr at 95°C and finally 7 hr on a sand-bath). During the nitration of toluene (200 g) with nitric acid (sp. gr. 1·4; 600 ml) containing HgO (10 g) dissolved in it, the following products were obtained: 48 g unreacted toluene, 15 g *o*-nitrotoluene, 12 g *p*-nitrotoluene, 8·8 g *p*-nitrobenzoic acid and 6 g trinitro-*m*-cresol. The formation of larger quantities of *p*-nitrobenzoic acid is apparently explained by the oxidation of *p*-nitrotoluene by the nitric acid.

TSUTSUMI *et al.* [180] studied the influence of various metallic oxides and nitrates on the ratios of isomeric nitrotoluenes obtained by nitrating toluene. Nitration of toluene (60 g) with nitric acid (65 per cent; 66 g) (without additions) during 8 hr at 30°C gives *o*-, *m*- and *p*-nitrotoluenes in the ratio of 63·1 : 3·7 : 33·2. If the nitration is carried out under the same conditions but with the addition of one of the oxides (AgO, PbO, CuO, WO_3 and PtO_2) or the nitrates (Pd, Cu, Ba, Cd, Co, Mg, Zn, Cr, Fe, Mn, Al or Bi) the ratio of isomers is practically unaffected. If, however, the nitration is effected with the addition of HgO (2 g), $Hg(NO_3)_2$ or $Ni(NO_3)_2$ (in amounts equivalent to 2 g of the corresponding metal oxide) the following ratio of the isomers is obtained:

Isomer	HgO	$Hg(NO_3)_2$	$Ni(NO_3)_2$
o-nitrotoluene	50·5	40·5	58·1
m-nitrotoluene	3·7	3·4	3·9
p-nitrotoluene	45·8	56·1	38·0

Thus the use of these additions only affects the ratio of *o*- and *p*-isomers. The proportion of *m*-nitrotoluene is virtually unaltered.

The same authors [181] studied the effect of added nitrates of various metals on the ratio of isomers obtained during the nitration of benzyl chloride. They used nitric acid (82–94 per cent) in acetic anhydride. In the absence of any additions the ratio of *o*- and *p*-isomers was 0·55–0·6 (the content of *m*-isomer being 3·9–4·1 per cent). In the presence of the nitrates of Hg, Ag, Cu, Ba, or Pb the ratio of *o*- to *p*-isomer reaches approximately 0·92 whilst the content of the *m*-isomer remains unchanged.

Chlorobenzene, as distinct from toluene, reacts with nitric acid in the presence of mercury considerably more slowly than benzene. Nitration of chlorobenzene (100 g) with nitric acid (sp. gr. 1·4; 300 ml) with 5 g HgO dissolved in it, over a period of 10 hr, gives the following products: 57·6 g unreacted chlorobenzene, 7·6 g *p*-nitrochlorobenzene and 1·5 g trinitro-*m*-chlorophenol.

DAVIS [178, 179] also carried out the nitration of naphthalene under conditions close to those which proved to be optimal for benzene. HgO (5 g) was dissolved in nitric acid (sp. gr. 1·42; 300 ml) and the solution was added in small portions to naphthalene (100 g). On completion of the initially violent reaction, the mixture was heated on a boiling water-bath with constant stirring. The oily reaction product was separated from nitric acid, washed with hot water and treated with a hot solution of sodium carbonate. The alkaline solution was acidified with HCl and shaken with ether. Nitronapththol was isolated from the ethereal solution. It amounted to 1·5 per cent of the total weight of nitro derivatives. Fractional crystallization of the residue from the ethereal extraction using alcohol, ethyl acetate and acetone gave α-nitronaphthalene (20 per cent), 1 : 3-dinitronaphthalene (35 per cent; m.p. 144°C) and 1 : 5-dinitronaphthalene (40 per cent; m.p. 213–213·5°C). Another crystalline product was found in the used nitric acid which proved to be nitronaphthoic acid (m.p. 207–208°C).

DAVIS also nitrated naphthalene under milder conditions, using dilute nitric acid at low temperatures. The experiments show that under these conditions nitronaphthols are predominantly formed, i.e. the reaction is directed to the formation of hydroxylated compounds. For example, a mixture of 1 mole naphthalene with 1 l. of a solution containing 600 ml nitric acid (sp. gr. 1·35) and 1 mole $Hg(NO_3)_2$ was heated to 35°C with stirring for 37 hr. The main reaction product was 2 : 4-dinitro-α-naphthol (m.p. 138°C); besides this a small amount of 2-nitro-α-naphthol (m.p. 128°C) was also obtained. The total yield of nitronaphthols was 55 g.

In order to elucidate the role of $Hg(NO_3)_2$, Davis and co-workers boiled nitrobenzene with nitric acid in the presence of $Hg(NO_3)_2$ for 4 hr. No picric acid was formed. The only reaction product was a small amount of dinitrobenzene. When *m*-dinitrobenzene was boiled with nitric acid and $Hg(NO_3)_2$, 82 per cent of it remained unaltered, whilst the rest was oxidized to oxalic acid; no picric acid was found on boiling 1 : 3 : 5-trinitrobenzene with nitric acid, although it gives picric acid when treated with other oxidizing agents. It is inferred from these experiments that mercury does not play the part of a catalyst which facilitates the oxidation of hydrogen atoms in the aromatic ring containing NO_2 groups, i.e. formation of picric acid from benzene does not go through the preceding stage of benzene nitration. Davis supposes that the role of the mercury salt consists of the formation of an intermediate complex with benzene which is evidently further oxidized to a mercury salt of dinitrophenol. The latter, under the action of nitric acid, is converted into picric acid with regeneration of $Hg(NO_3)_2$. The linking of $Hg(NO_3)_2$ with the aromatic ring in the first stage of the reaction apparently takes place in such a way that the NO_2 group joins one of the carbon atoms whilst the residue $—O—Hg—ONO_2$ joins another.

Nitration of toluene and chlorobenzene in the presence of $Hg(NO_3)_2$ gives phenols in which the hydroxyl group is in the *m*-position relative to the methyl group or the chlorine atom, both of which are usually *o*- and *p*-orientating. This unexpected result can be satisfactorily explained if it is assumed that the nitro group of $Hg(NO_3)_2$ enters the *o*- or *p*-position relative to the methyl group or the chlorine atom, whilst the residue, $—O—Hg—ONO_2$, enters the neighbouring, i.e. the *m*-position relative to the methyl group or the chlorine atom. Thus, thanks to the formation of a complex with $Hg(NO_3)_2$, simultaneous nitration and hydroxylation of the aromatic ring can occur.

McKee [182] studied the action of $Hg(NO_3)_2$ on the nitration of a series of aromatic compounds with nitric acid or nitrating mixture; xylene, naphthalene, bromobenzene, phenanthrene, phenol, chlorophenol, α-naphthol, benzaldehyde, etc. McKee's experiments show that in the majority of cases $Hg(NO_3)_2$ has a favourable effect on nitration, raising the total yield of nitro derivatives, including hydroxynitro compounds. Nitration of phenanthrene with nitric acid (sp. gr. 1·5) in the presence of $Hg(NO_3)_2$ gives a 13 per cent higher yield of nitrophenanthrene than that obtained by nitration without catalyst. The yield of nitrophenol on nitrating phenol with dilute nitric acid rises by 22–25 per cent on addition of the mercury salt. α-Naphthol, nitrated with a mixture of nitric acid and sulphuric acid in the presence of mercury gives a yield of α-nitronaphthol which is 10 per cent higher than that obtained by nitration without catalyst.

The main objections to the use of mercury salts as catalysts for nitration are:

(1) The necessity for considerable expenditure of mercury.

(2) The difficulty of regenerating mercury.

(3) The undesirability of contaminating the nitro products with mercury salts.

Nitration of phenol in the presence of $Pb(NO_3)_2$ at 20°C gives an increased amount of *p*-nitrophenol at the expense of the *o*-isomer. If the nitration is carried out at a higher temperature the proportion of the two isomers becomes the usual one [183].

VOLODARSKI and KALININA [184] showed that in the presence of $CuSO_4$ the nitration of α-naphthalene sulphonic acid to 1 : 8-nitronaphthalene sulphonic acid results in a higher yield than that obtained without the addition of catalyst.

According to a French patent [185] compounds of the following elements can be used as catalysts in nitration: chromium, tungsten, molybdenum, tantalum, niobium, vanadium, gallium and indium. The patent asserts that if one of these catalysts is used it is easy to obtain tetranitronaphthalene and other polynitro derivatives with small expenditure of strong acids.

Boron trifluoride can also be used as catalyst [186]. The nitration of aromatic compounds in the presence of boron trifluoride can be represented schematically as follows:

$$RH+HNO_3+BF_3 \rightarrow RNO_2+BF_3 . H_2O$$

Nitrobenzene was nitrated in the presence of BF_3 by adding to nitrobenzene (31 g; 0·25 M) fuming nitric acid (sp. gr. 1·5; 19 g) (0·3 M); BF_3 (17 g) was passed through the mixture with stirring. The temperature of the reaction was not allowed to rise over 80°C. The mixture was then heated at 100°C for 30 min. The reaction product was poured into 500 ml of hot water and stirred until cool. The dinitrobenzene was filtered off and recrystallized from alcohol. The yield was 36·5 g (87 per cent of the theoretical). Benzoic acid, phthalic anhydride and other compounds (Table 4) can be similarly nitrated.

BF_3 can be regenerated on completion of the reaction by adding a sufficient amount of water to convert $BF_3 . H_2O$ to $BF_3 . 2H_2O$. The latter is isolated by vacuum distillation as a clear heavy liquid. Treatment with CaF_2 regenerates BF_3 according to the equation:

$$2BF_3 . 2H_2O+CaF_2 \rightarrow Ca(BF_4)_2+4H_2O$$

$$Ca(BF_4)_2 \rightarrow 2BF_3+CaF_2$$

The work of TITOV should be particularly noted in connexion with the mechanism of catalytic nitration of aromatic compounds in the presence of mercury salts.

In his work with BARYSHNIKOVA [187] and somewhat later with LAPTEV [188], TITOV showed that during the interaction of an aromatic compound with $Hg(NO_3)_2$ in nitric acid there was first a combination of the aromatic molecule with mercury, forming a metallo-organic compound, the reaction being reversible:

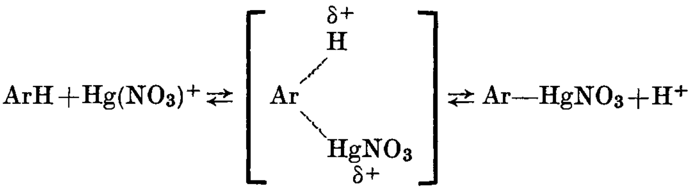
$$Ar—H+Hg(NO_3)_2 \rightleftarrows Ar—HgNO_3+HNO_3$$

In the absence of nitrogen oxides the reaction is represented completely by this equation. Thus benzene gives phenyl mercury nitrate, which has been isolated from the reaction mixture.

Table 4. *Nitration of aromatic compounds in the presence of* BF_3

Parent substance (moles)	HNO_3 (moles)	BF_3 (moles)	Reaction time (hr)	Temperature (°C)	Product obtained	Yield (%)
Nitrobenzene (0·25)	0·30	0·25	0·5	80–100	*m*-Dinitrobenzene	87
Benzoic acid (0·25)	0·30	0·37	0·5	80	*m*-Nitrobenzoic acid	82
p-Toluene-sulphonic acid (0·10)	0·15	0·12	0·5	100	2-Nitro-4-toluene-sulphonic acid	92
Methyl benzoate (0·10)	0·15	0·12	1·0	0–10	Methyl ester of *m*-nitrobenzoic acid	77
Phthalic anhydride (0·10)	0·15	0·28	13·0	100	3-Nitrophthalic acid	81

In the linkage C—$HgNO_3$ the carbon is polarized somewhat more negatively than in the ordinary C—H bond, and from the point of view of the general theory of activity of aromatic compounds in reactions of electrophilic substitution, it can be, to a certain extent, likened to the *o*- and *p*-atoms of carbon in such highly reactive compounds as phenols and amines, whilst the $HgNO_3$ radical corresponds to the so-called mobile hydrogen. There is no doubt, however, that the specific chemical properties of mercury must become apparent to some extent in the transformations of the C—$HgNO_3$ group. It has been established that the extent of mercury bonding decreases with increased concentration of nitric acid. Nitric acid, up to a certain degree of concentration, in the absence of nitrogen oxides, has an exclusively splitting action on the aryl mercury compound, leading to regeneration of the original hydrocarbon. The authors represent the mechanism of the reversible reaction as follows:



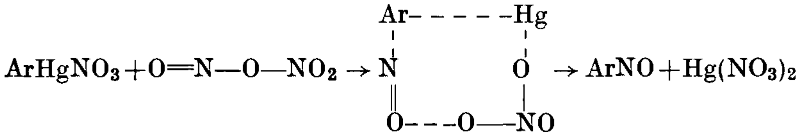
$$ArH + Hg(NO_3)^+ \rightleftarrows \left[Ar \begin{matrix} \overset{\delta+}{H} \\ \underset{\delta+}{HgNO_3} \end{matrix} \right] \rightleftarrows Ar\text{—}HgNO_3 + H^+ \qquad (1)$$

A concentration of 40–50 per cent nitric acid has a slow splitting action at ordinary temperature, which becomes more rapid at 100°C.

The reaction of the mercury-aromatic compound to nitric acid containing nitrogen oxides or to nitrogen dioxide by itself is completely different.

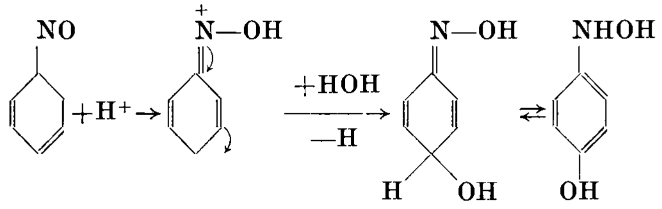
Phenyl mercury nitrate or acetate interacts with 50–60 per cent nitric acid containing nitrogen oxides very rapidly, with evolution of heat, even at low temperatures. On slow addition of the aryl-mercury compound, and mechanical stirring, the reaction proceeds fairly smoothly and leads to the formation of the same mixture of products which is obtained by nitrating benzene in the presence of mercury salts, namely, nitrophenols, nitrobenzene and *p*-dinitrobenzene. On the basis of their experimental findings, the authors conclude that the catalytic action of the salts on the oxidative nitration of aromatic hydrocarbons only takes place in the presence of nitrogen oxides. Aryl-mercury nitrate treated with HNO_3 containing nitrogen oxides reacts quickly with the formation of a nitroso compound. This was proved by its isolation from the reaction mixture.

Titov and Laptev suggest the following scheme for the formation of nitroso compounds from mercury derivatives under the action of N_2O_4 in its nitrosyl nitrate form:

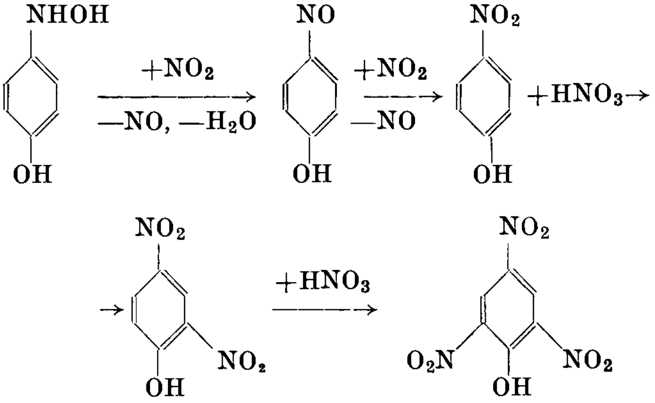


$$ArHgNO_3 + O{=}N{-}O{-}NO_2 \rightarrow \begin{array}{ccc} Ar & \text{- - - - -} & Hg \\ \vdots & & \vdots \\ N & & O \\ \| & & | \\ O & \text{- - -}O\text{——} & NO \end{array} \rightarrow ArNO + Hg(NO_3)_2 \qquad (2)$$

The further transformation of the nitrosobenzene so formed into di- and trinitrophenol is represented by these authors as follows: as the result of the addition of a proton with subsequent addition of the hydroxyl ion in the *p*-position to the nitrogen-containing group, a tautomer of *p*-hydroxyphenylhydroxylamine is formed:



It is oxidized first to *p*-nitrosophenol and then to *p*-nitrophenol, which subsequently undergoes nitration to di- and trinitrophenol:



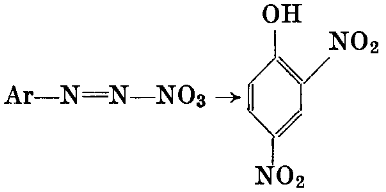
(3)

The hydroxyl group finds itself in the *p*-position to the position formerly occupied by the nitroso group.

It should be noted that the formation of benzene mercury nitrate is the slowest reaction which determines the rate of the whole process of the conversion of benzene to di- and trinitrophenol and depends on the concentration of nitric acid, since lowering the nitric acid concentration leads to a sharp drop in the rate of combination with mercury. Besides the main direction of the reaction mentioned above, there is another possible reaction which consists of an initial interaction between nitrosobenzene and nitrogen oxide with the formation of diazonium nitrate [189]:

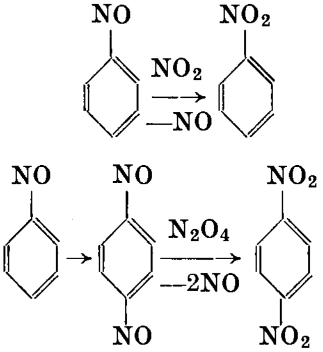
$$C_6H_5NO + 2NO \rightarrow ArN{=}N{-}NO_3$$

The diazo compound obtained breaks down with the formation of phenol which is easily nitrated with dilute nitric acid to give di- and trinitrophenol, with the hydroxyl group in the same position which had been occupied by the nitroso group:



(4)

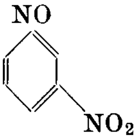
The formation of nitrobenzene and *p*-dinitrobenzene as side products during oxidative nitration of benzene in the presence of $Hg(NO_3)_2$ is also explained by a corresponding transformation of nitrosobenzene:



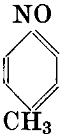
(5)

In the case of substituted derivatives of nitrosobenzene which do not contain strongly electrophilic substituents similar to the nitro group, but have a free *p*-position, such as for example *o*-nitrosotoluene, the same reactions are observed as those seen in the case of benzene. As a rule, under ordinary conditions, nitration in the presence of mercury salts leads to the formation of corresponding nitrophenols [equation (3)] and nitrohydrocarbon [equation (5)].

Nitroso compounds containing a strongly electrophilic substituent, e.g.



or in which the position *para* to the nitroso group is occupied, e.g.

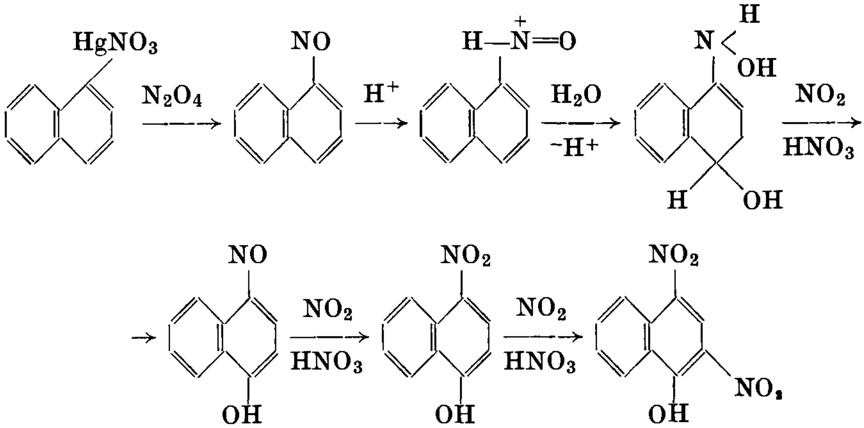


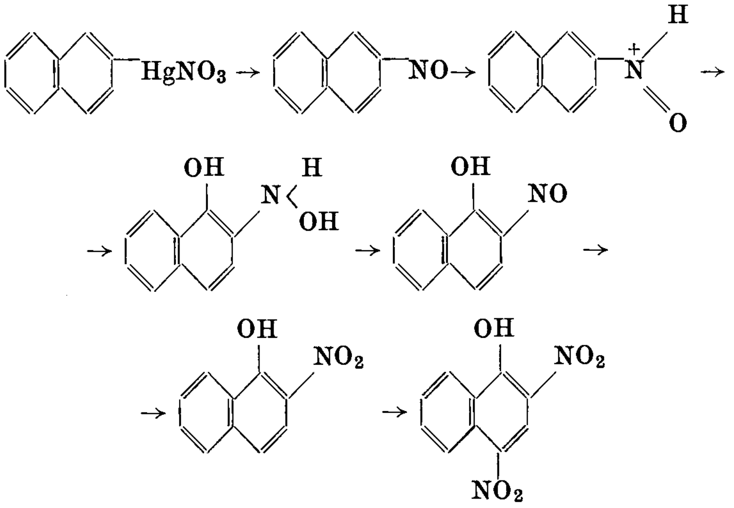
are most stable under the usual conditions of nitration and can only undergo reactions according to equations (4) and (5).

Titov and Laptev explain the absence of appreciably accelerating effect of added mercury salts and lack of increase in the amount of nitronaphthols formed on nitration of naphthalene by the fact that the nitration of this hydrocarbon occurs very rapidly in the presence of nitrogen oxides, the rate of its nitration being incomparably greater than that of its combination with mercury. The same phenomenon is observed with other substances which react quickly with nitrogen oxides (e.g. amines and phenols). The authors conclude that the addition of mercury salts can only lead to acceleration of the reaction and augmentation of the yield of nitrophenols when substances undergoing nitration show if not a higher, at least a comparable rate of combination with mercury to that of their direct interaction with NO_2.

The catalytic effect of added mercury salts can be brought out by selecting suitable conditions such as increasing the concentration of the mercury salts and decreasing the amount of NO_2.

In their other work, Titov and Laptev [190] showed that α- and β-naphthyl mercury nitrates are converted by the action of concentrated nitric acid in the presence of nitrogen oxides into 2 : 4-dinitro-α-naphthol with a yield of over 50 per cent of the theoretical:





5. THE CATALYTIC ACTION OF NITROUS ACID IN NITRATION

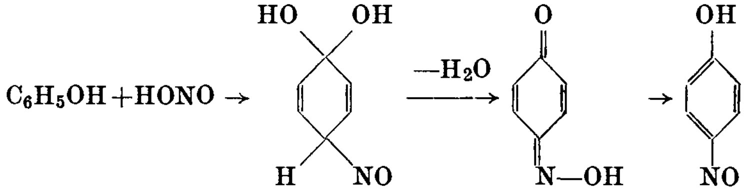
Phenol is one of the most easily nitrated substances; it gives mononitro derivatives when treated with very dilute nitric acid. It has been established by a number of workers that the nitration of phenol is a complex autocatalytic reaction.

Martinsen [8] studied the nitration of phenol with nitric acid of various concentrations and found that the presence of nitrous acid has a catalytic effect on the reaction. Further studies revealed that the concentration of nitrous acid in the solution increased in the course of the reaction, owing to the partial reduction of nitric acid concurrent with oxidative side-reactions. The rate of transformation of nitric acid into nitrous acid is markedly diminished by the presence of mercury, silver or their salts. Their use serves to regulate the process of nitration [191]. Thus the nitration of phenol is an autocatalytic process which takes place without the introduction of extraneous catalysts. Martinsen established that the rate of nitration rose with an increase in the concentration of nitric acid and fell with an increase in the concentration of phenol.

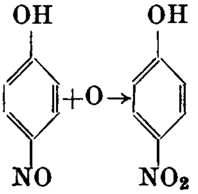
Kartashev [192] found on studying the nitration of phenol with dilute nitric acid (sp. gr 1·010–1·060) that the reaction proceeded with satisfactory results only in the presence of excess nitric acid. By varying the concentration of nitric acid, its excess, and the temperature of the reaction, he established that the influence of these factors on nitration was as follows: (1) excess of nitric acid lowered the initial temperature of the reaction much more sharply than an increase in its concentration; (2) lowering of the reaction temperature diminished oxidative processes; (3) nitric acid reacted with phenol at concentrations not lower than 2·8 per cent (sp. gr. 1·015); (4) high temperature evoked vigorous oxidative processes even at concentration of nitric acid of approximately 2 per cent.

According to Kartashev's observations, the initial action of nitric acid on phenol in dilute aqueous solutions (sp. gr. 1·015–1·045) is an oxidative one, accompanied by the formation of nitrous acid, which plays a definite role in the process of nitration. When phenol is treated with pure nitric acid, free of nitrogen dioxide and nitrous acid, in ethereal solution, nitration of the phenol does not take place [193]. The author proposes the following reaction mechanism: phenol reacts with nitrous acid forming nitrosophenols (quinoximes) which, under the action of nitric acid, are easily oxidized to nitrophenols:

$$HNO_3 \rightarrow HNO_2 + O \qquad (1)$$



(2)



(3)

In order to verify the above mechanism experimentally, **Kartashev** conducted experiments in which nitrous acid and *p*-nitrosophenol were added to the reaction mixture. The experiments showed that the nitration of phenol with nitric acid (sp. gr. 1·015 and 1·030) in the presence of nitrous acid can be achieved at a lower initial temperature. The addition of *p*-nitrosophenol has the same effect. The oxidative action of weak nitric acid on nitrosophenol is confirmed by experiments in which *p*-nitrosophenol treated with nitric acid (sp. gr. 1·030–1·015) gives *p*-nitrophenol, and on more prolonged heating (up to 1 hr) α-dinitrophenol.

Kartashev also studied the nitration of phenol in ethyl acetate. His observations showed that two stages can be distinguished in the process: the initial stage which is unaccompanied by any change in the temperature of the reaction mixture, and a second stage which is exothermic, the rise in temperature being slow at first but accelerating later. Such a course of the reaction indicates that the interaction of phenol and nitric acid is an autocatalytic process whose development and course proceed at the expense of some intermediate reaction which serves as a source of the catalyst.

The addition of urea shows the effect of HONO on the nitration of phenol, viz. in spite of its poor solubility in ethyl acetate urea causes marked slowing of the reaction.

Nitration carried out in an atmosphere of CO_2, i.e. in the absence of the oxidative effect of atmospheric oxygen on nitrous acid which usually exists under ordinary conditions of nitration, proceeds at a faster rate.

Other investigators [194] support **Kartashev**'s views on the mechanism of the catalytic action of nitrous acid on the nitration of phenol. Nevertheless, this explanation cannot be considered sufficiently well-founded. The relative importance of the formation of nitrosophenol (at the usually low concentration of nitrous acid in the reaction mixture) can hardly be great. Besides, it must be noted that the nitration of phenol with nitric acid gives a mixture of almost equal amounts of *o*- and *p*-nitrophenols. If the reaction mechanism of nitration were confined to the oxidation of nitrosophenol by nitrous acid to give nitrophenol the formation of the *p*-isomer only, and not of a mixture of nitrophenols, would be expected, as it is known that the interaction of nitrous acid and phenol gives only *p*-nitrosophenol. The formation of nitrophenols during the nitration of phenol in the presence of large concentrations of nitrous acid can proceed via nitrosophenol. But, as was shown in this case (e.g. nitration of phenol in the presence of 2 moles HNO_2 to 1 mole of HNO_3) instead of the usual ratio of *o*-nitrophenol : *p*-nitrophenol = 1 : 1, the ratio obtained is 1 : 9. As expected, the amount of the *p*-isomer shows a sharp increase [195].

ARNALL [196] studied the kinetics of the nitration of phenol in absolute alcohol. He carried out the nitration using an equivalent amount of nitric acid at 25·5°C. The rate of the reaction was measured by the amount of free acid found in the solution after given intervals of time; these observations indicated that the reaction accelerated autocatalytically, which is explained according to ARNALL by the influence of nitrous acid formed in the course of side reactions. In order to verify this ARNALL added small amounts of nitrous acid (0·02 per cent) to the nitrating mixture; experiments indicated a considerable increase in the rate of reaction compared with control experiments. This increase was particularly evident in those cases where nitrous acid was added at the very beginning of the reaction. In another series of experiments ARNALL used excess nitric acid both in the absence and in the presence of nitrous acid; it became apparent that a 100 per cent excess of nitric acid increased the rate of reaction although in the initial period the reaction proceeded relatively slowly, with subsequent acceleration; during nitration with a 50 per cent excess of nitric acid, but in the presence of nitrous acid, the rate of reaction accelerates rapidly right from the beginning and the rate of acceleration is more uniform than in the former case. The results thus confirm the hypothesis that the formation of nitrophenols is accelerated autocatalytically, as the reaction proceeds, under the influence of nitrous acid; the catalytic action of the latter is also proved by experiments in which urea (0·5 per cent), hydrazine sulphate and phenyl hydrazine hydrochloride were added; in these experiments considerable slowing of nitration was observed in the presence of urea and complete cessation of reaction in the presence of the last two reagents.

ARNALL found further that the addition of *p*-nitrosophenol had no effect on the nitration of phenol. He concludes that the reaction does not go through the nitrosophenol stage but follows another route. He considers the following a possible mechanism for the nitration of phenol:

$$HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O$$

$$C_6H_5OH + N_2O_4 \rightarrow O_2NC_6H_4OH + HNO_2$$

ARNALL's experiments on the nitration of phenol in acetic acid solution showed that the use of this solvent leads to almost quantitative yields of nitrophenol. The reaction proceeds smoothly and quickly, and without tar formation; at 45°C nitration with 20 per cent nitric acid gives a 98·7 per cent yield of mononitrophenols. The reaction can also be carried out at room temperature.

The following method was used by ARNALL for the analysis of the reaction products: first the total amount of *m*-, *o*- and *p*-nitrophenols was determined by titration with titanium chloride, then *o*-nitrophenol was steam-distilled and the *m*- and *p*-nitrophenol content of the residue was estimated by titanium chloride; the latter were converted by treating with benzyl chloride to the corresponding *m*- and *p*-nitrophenylbenzyl esters; the composition of the ester mixture was determined by the lowering of the freezing point observed when a weighed quantity of this mixture was added to a definite amount of the pure *p*-derivative.

During the nitration of phenol in acetic acid solution, ARNALL discovered certain variations in the ratios of the nitrophenols obtained, depending on the temperature and the concentration of nitric acid as shown in Table 5. The best yields of nitrophenols result when the nitration is effected with 10 per cent nitric acid at 25°C; ARNALL used the following ratios, by weight, of the reagents: 23·5 g (0·25 mole) phenol, 15·75 g (0·26 mole) nitric acid, sp. gr. 1·42, and 157·5 g, acetic acid.

The effect of other solvents on the nitration of phenol has also been studied.

Table 5. Nitrophenol isomer content of the reaction products formed during nitration of phenol in relation to temperature and concentration of nitric acid

Nitric acid concentration (%)	10°C			25°C			45°C		
	o-	*p*-	*m*-	*o*-	*p*-	*m*-	*o*-	*p*-	*m*-
5	57·6	40·0	3·4	58·1	39·0	2·9	54·9	38·2	2·4
10	57·8	39·0	3·1	59·2	38·1	2·7	60·6	37·2	2·2
20	58·9	38·3	2·8	60·3	37·3	2·4	61·5	36·4	2·1

Using 10 per cent nitric acid throughout and varying the solvents the following results were obtained: in acetic anhydride the reaction proceeds almost instantaneously; in acetone nitration during 3 hr gives an 80 per cent yield of nitrophenols; in ether, after 12 hr the yield is 68 per cent; in a mixture of alcohol (2 parts) and acetic acid (1 part) the yield is 75 per cent after 48 hr, whilst in absolute alcohol the yield is 55 per cent after 48 hr. The quantitative ratios of the isomeric nitrophenols vary depending on the solvent used as can be seen from Table 6 (concentration of nitric acid = 10 per cent, reaction temperature = 10°C except in the first two experiments in which the nitration was carried out at 25°C).

Nitration in acetic acid in the presence of $Cu(NO_3)_2$ and iodine did not alter the usual results, but in the presence of $Hg(NO_3)_2$ the following ratios of the isomers resulted: 53·5 per cent *o*-nitrophenol, 42·7 per cent *p*-nitrophenol and 3·8 per cent *m*-nitrophenol.

VEIBEL [13, 197], in order to elucidate the mechanism of the nitration of phenol in the presence of nitrous acid, investigated the effect of the concentration of nitric acid on the direction of the reaction, i.e. the ratio of *o*- and *p*-nitrophenols. Nitration was carried out at 25°C with dilute solutions of nitric acid (1, 1·5, 2 and 3 N) using a considerable excess of the acid in relation to phenol (20 : 1) in all experiments. The quantity of nitric acid was thus practically constant during the experiment. A definite amount (corresponding in some experiments to 0·001 N in others to 0·003 N HNO_2) of $NaNO_2$ was introduced into the acid; phenol solution was then added dropwise in the proportion of $\frac{1}{20}$ mole to 1 mole nitric acid. When all the phenol had been added the reaction mixture was allowed to stand for some time until the reaction was complete. The reaction products were separated as follows: excess nitric acid was neutralized with sodium hydroxide, the solution was made faintly acid with acetic acid and the *o*-nitrophenol was then steam-distilled. The *o*-nitrophenol in the distillate was estimated by titration with titanium chloride. *p*-Nitrophenol and side-products of the nitration were determined in the residue left after the steam-distillation. *p*-Nitrophenol was dissolved out with water; the water-insoluble side-product was separated from it by filtration. On analysis this side-product was seen to be an oxidation product of indophenol. As VEIBEL supposes the indophenol could have been formed by the condensation of one molecule of phenol with one molecule of nitrophenol or with an intermediate product of the reaction.

Table 6. Content of nitrophenol isomers in the reaction products formed by nitration of phenol with nitric acid in relation to the solvent used

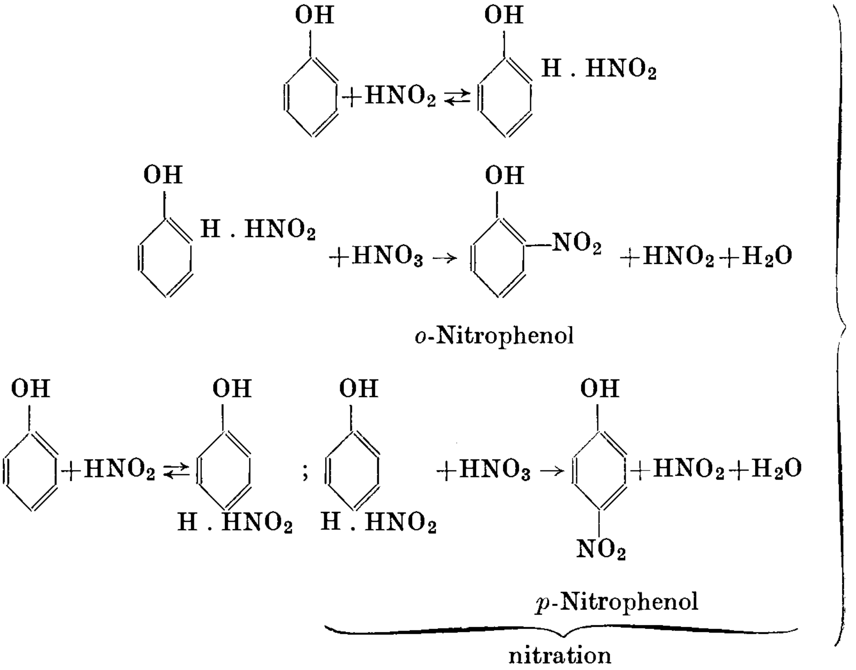
Solvent	Nitrophenol (%)		
	o-	*p*-	*m*-
Acetic anhydride	59·6	37·8	2·6
Acetic acid	59·2	38·1	2·7
Acetic acid	57·8	39·1	3·1
Acetone	57·4	39·6	3·0
Ether	57·8	39·2	3·0
Alcohol (2 parts) and acetic anhydride (1 part)	57·6	39·3	3·1
Alcohol	57·7	39·2	3·1

VEIBEL's experiments show that the nitration of phenol with nitric acid of concentrations varying from 1 to 3 N gives almost equal quantities of *o*- and *p*-nitrophenol. The ratio *o*-nitrophenol : *p*-nitrophenol rises to a small extent with increased concentration of nitric acid. The yield of the condensation product drops from 12 to 3 per cent as the nitric acid concentration rises from 1 to 3 N.

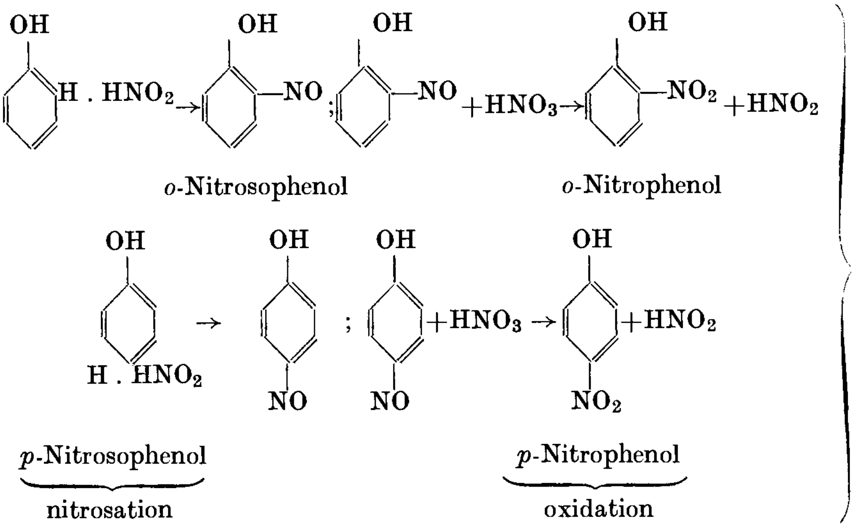
Nitration of *o*- and *m*-cresols was also studied by Veibel. *m*-Cresol undergoes nitration more slowly than phenol and *o*-cresol. The rate of formation of the condensation product is the same as in the case of phenol and *o*-cresol; the nitration of *m*-cresol is thus accompanied by a higher proportion of condensation products than that seen in the case of other phenols. Nitration of *m*-cresol gives 6-nitro- and 4-nitro-*m*-cresols in the ratio, by weight, of 2 : 3; this ratio is independent of the concentration of nitrous and nitric acid. Nitration of *o*-cresol gives 6-nitro- and 4-nitro-*o*-cresols in the ratio of 1 : 1. This ratio remains constant independently of the initial concentration of nitrous acid; on the other hand it rises to a small extent with increased concentration of nitric acid. On further nitration 6-nitro- and 4-nitro-*o*-cresols give dinitro derivatives in equal proportion; nitration of 6-nitro- and 4-nitro-*m*-cresols gives dinitro derivatives with the 6-nitro-*m*-cresol derivative predominating.

Veibel also studied the formation of nitrosophenol from phenol. He established that the ratio *o*-nitrosophenol : *p*-nitrosophenol does not correspond to the ratio *o*-nitrophenol : *p*-nitrophenol which is obtained on nitrating phenol.

On the basis of experimental findings, Veibel proposes the following mechanism for the nitration of phenol: phenol forms a complex with nitrous acid which, under the influence of nitric acid, gives nitrophenol [scheme (1)]. This main reaction is accompanied by a side-reaction in which the complex is converted to *o*-nitrosophenol which is further oxidized by nitric acid to nitrophenol [scheme (2)]. Another side-reaction is the formation of a condensation product of the complex with phenol, which is oxidized by nitric acid [scheme (3)].



(1)



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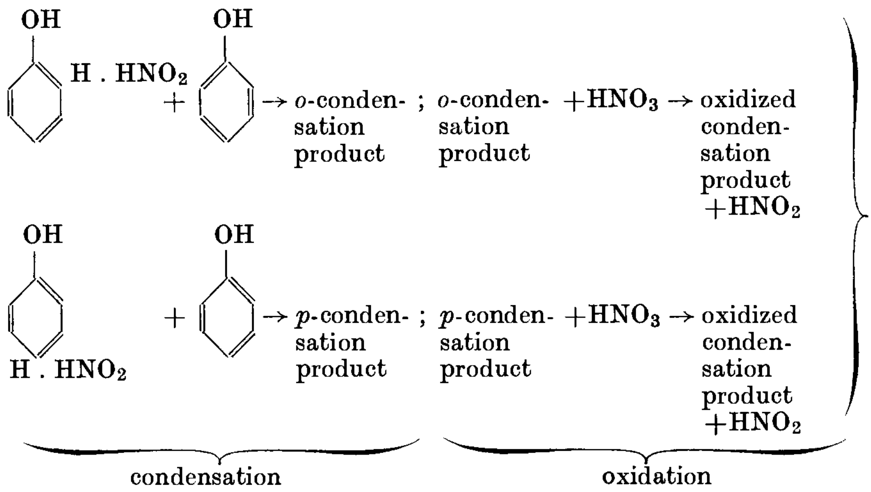

(3)

This mechanism provides satisfactory explanations for: (1) the catalytic action of nitrous acid in the nitration of phenol, as established by a number of workers; (2) the discrepancy in the ratios *o*-nitrosophenol : *p*-nitrosophenol and *o*-nitrophenol : *p*-nitrophenol. The formation of nitrophenols occurs only partially according to scheme (2) (nitrosation and oxidation); the main part of *o*- and *p*-nitrophenols is formed according to scheme (1), i.e. in the course of a nitration reaction. A comparison of schemes (1), (2) and (3) reveals that only the rate of the nitration reaction (1) is in direct relation to the concentration of nitric acid, which is confirmed experimentally. This dependence is not the same for *o*- and *p*-nitrophenols, and so the ratio of *ortho* : *para* isomer varies with changes in the concentration of nitric acid. The reaction giving nitrophenols from nitrosophenols (2) is not in direct relationship with the concentration of nitric acid; however, quantitatively the yield of nitrophenols in this reaction is considerably less than in reaction (1). Consequently, the dependence of the *ortho* : *para* ratio on the concentration of nitric acid is not subjected to appreciable variations. The rate of formation of oxidized condensation products according to scheme (3) is also independent of the concentration of nitric acid, which agrees with experimental findings. (At HNO_3 concentration of 3 N less of the condensation product is formed than at concentration of HNO_3 of 1 N, whereas the rate constants of other reactions increase with rising concentrations of acid.)

VEIBEL's subsequent work aimed at studying separately the mechanism of the main reaction of nitration and the formation of nitrophenols from nitrosophenols. His kinetic measurements of the rate of reaction of the nitrosating of phenol showed that the variation of concentration of phenol and nitric acid in one direction leads to dissimilar variation in the rate constants. VEIBEL explains this by the formation of dinitroso as well as nitroso compounds if an excess of nitric acid is present, and this leads to higher rate constants. Excess phenol favours the formation of condensation products and hence a diminution of rate constant is observed.

VEIBEL also studied the kinetics of the reaction in which *p*-nitrosophenol is oxidized to *p*-nitrophenol, and found that the rate of reaction rose markedly with increased concentration of nitric acid but, on the other hand, did not depend on the concentration of nitrosophenol and nitrous acid. Experiments showed that oxidation occurs normally only when there is a minimal concentration of nitrous acid. Oxidation of *o*-nitrosophenol proceeds considerably more rapidly than that of *p*-nitrosophenol (twenty-five times more rapidly).

Measurements of the rate of nitration of phenol using nitric acid in concentrations of 1, 1·5 and 2 N showed that at concentration of 1 N the rate constant remained unchanged throughout the experiment, whilst at concentrations of 1·5 and 2 N the value of the constant rose at the beginning of the experiment and only became stable after a certain time. This phenomenon is explained by an insufficiency of nitrous acid; by increasing twofold the initial concentration of the latter nitration proceeds normally from the very beginning of the reaction, i.e. the value of the rate constant remains unchanged throughout the experiment.

The rate of nitration of phenol also depends on the concentration of the latter; doubling its concentration (from 0·2 to 0·4 N) at constant concentrations of nitric and nitrous acids leads to a sharp drop in the rate of the reaction. This is explained by the peculiarity of the nitration reaction which consists of two stages: (1) formation of a complex with nitrous acid and (2) nitration itself. At an initial concentration of nitrous acid double that of phenol a relatively greater amount of phenol enters into the complex-forming reaction with nitrous acid; this complex then participates in the subsequent process.

Naphthalene does not react with nitric acid (sp. gr. 1·17 and 1·36) at room temperature in the absence of nitrogen oxides. It reacts very slowly with concentrated nitric acid. Introduction of a small amount of potassium nitrate into the reaction mixture leads to a violent reaction and the formation of α-nitronaphthalene [198].

Studies of the nitration of phenol and other aromatic substances with nitric acid thus show that this reaction is undoubtedly catalyzed by nitrous acid. At a given concentration of nitric acid the rate of the reaction is directly proportional to the concentration of nitrous acid.

The suggestion put forward by VOROZHTSOV Jr. that the catalytic effect of nitrosophenol on the nitration of phenol consists in the formation of NO_2 from nitric acid (at the expense of the oxidation of nitrosophenol to nitrophenol) appears to be quite feasible, since NO_2 catalyzes the nitration of phenol much more effectively than nitrous acid [199].

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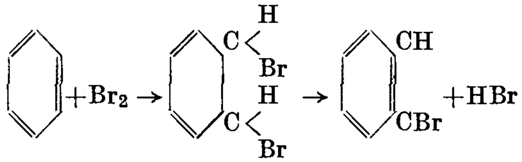
CHAPTER II

THE MECHANISM OF THE NITRATION OF AROMATIC COMPOUNDS WITH NITRIC ACID AND NITRATING MIXTURE

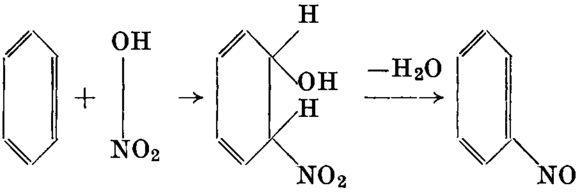
THE present chapter deals with the theoretical studies concerned with the kinetics and the reaction mechanism of nitration with nitric acid and nitrating mixture (HNO_3 and H_2SO_4).

It should be noted that there are a great many works on this subject, both Russian and foreign, and only the most important ones will be considered here.

In the 1920's, WIELAND [1, 2] proposed a theory which regarded nitration as an addition of the nitrating agent (in this case nitric acid) across the double bond of the compound undergoing nitration. WIELAND based this on the view held by TIEHLE [3] and HOLLEMANN [4] that every aromatic substitution is a result of initial addition. For example, aromatic bromination leading to the substitution of a hydrogen atom in the aromatic compound by bromine, according to this view, takes place through an initial addition:



During nitration, according to WIELAND, nitric acid adds on across a double bond in the aromatic ring with subsequent splitting out of water:



The study of nitration of unsaturated compounds led WIELAND to suggest that the initial product of nitration was a nitrohydrin (nitro-alcohol) formed as the result of the addition of nitric acid across the double bond in the unsaturated compound:

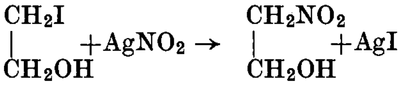
$$CH_2 : CH_2 + HONO_2 \rightarrow HOCH_2CH_2NO_2$$

Nitration of the first member of the olefine series, ethylene, was accomplished in 1869 by KEKULÉ [5]. By treating ethylene with a mixture of nitric and sulphuric acids he obtained an oil which, in his opinion, was a nitrite-nitrate of ethylene glycol:

$$CH_2(ONO)CH_2(ONO_2)$$

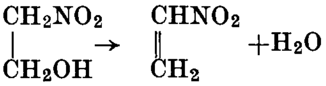
WIELAND, repeating this synthesis, used an improved method of purification (steam-distillation followed by repeated vacuum distillations). He found that the oil obtained on nitration of ethylene consisted of a mixture of two compounds, one of which (with a lower b.p.) was identical with the dinitrate of glycol $CH_2(ONO_2)CH_2(ONO_2)$, whilst the other, formed in smaller quantity, was an ester of nitric acid and β-nitroethyl alcohol $CH_2(ONO_2)CH_2(NO_2)$. WIELAND considered the latter to be formed as the result of the esterification by nitric acid of the primary reaction product of β-nitroethyl alcohol (β-nitrohydrin) $CH_2(NO_2)CH_2(OH)$. To verify this, WIELAND subjected pure nitroethyl alcohol to the action of the nitrating mixture; the product of this reaction proved to be identical with nitroethyl nitrate obtained by nitration of ethylene.

The structure of β-nitroethyl alcohol was proved by WIELAND by synthesizing it according to V. MEYER's method from ethyleneiodohydrin and silver nitrite:



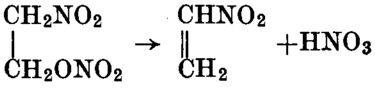
$$\begin{array}{l} CH_2I \\ | \\ CH_2OH \end{array} + AgNO_2 \rightarrow \begin{array}{l} CH_2NO_2 \\ | \\ CH_2OH \end{array} + AgI$$

Distillation of nitroethyl alcohol over phosphorus pentoxide or anhydrous bisulphate gave a good yield of nitroethylene:



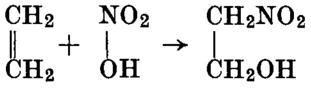
$$\begin{array}{l} CH_2NO_2 \\ | \\ CH_2OH \end{array} \rightarrow \begin{array}{l} CHNO_2 \\ \| \\ CH_2 \end{array} + H_2O$$

This product can also be obtained from nitro ethyl nitrate:



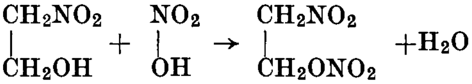
$$\begin{array}{l} CH_2NO_2 \\ | \\ CH_2ONO_2 \end{array} \rightarrow \begin{array}{l} CHNO_2 \\ \| \\ CH_2 \end{array} + HNO_3$$

On the basis of the experimental findings given above WIELAND proposes the following reaction mechanism for the nitration of ethylene with nitric acid:



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{l} NO_2 \\ | \\ OH \end{array} \rightarrow \begin{array}{l} CH_2NO_2 \\ | \\ CH_2OH \end{array}$$

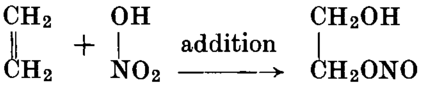
Ethylenenitrohydrin
(β-nitroethyl alcohol)



$$\begin{array}{l} CH_2NO_2 \\ | \\ CH_2OH \end{array} + \begin{array}{l} NO_2 \\ | \\ OH \end{array} \rightarrow \begin{array}{l} CH_2NO_2 \\ | \\ CH_2ONO_2 \end{array} + H_2O$$

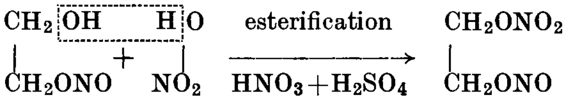
Nitroethyl nitrate

WIELAND explains the formation of the second reaction product, glycol dinitrate, in the following way: nitric acid adds as $—NO_2$ and —OH across the double bond of the olefine undergoing nitration, the $—NO_2$ group linking with the olefine through an oxygen atom and not the nitrogen atom; the glycol mononitrite so formed is converted to the dinitrate by the further action of nitrating mixture.



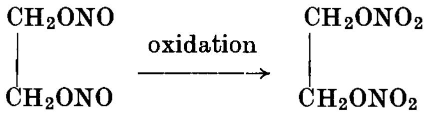
$$\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix} + \begin{matrix}OH\\ | \\ NO_2\end{matrix} \xrightarrow{\text{addition}} \begin{matrix}CH_2OH\\ | \\ CH_2ONO\end{matrix}$$

Ethylene glycol mononitrite



$$\begin{matrix}CH_2\boxed{OH \quad H}O\\ | \quad + \quad | \\ CH_2ONO \quad NO_2\end{matrix} \xrightarrow[HNO_3+H_2SO_4]{\text{esterification}} \begin{matrix}CH_2ONO_2\\ | \\ CH_2ONO\end{matrix}$$

Nitrite-nitrate
of ethylene glycol



$$\begin{matrix}CH_2ONO\\ | \\ CH_2ONO\end{matrix} \xrightarrow{\text{oxidation}} \begin{matrix}CH_2ONO_2\\ | \\ CH_2ONO_2\end{matrix}$$

Glycol dinitrate

Nitration of α : α-diphenylethylene with nitric acid in carbon tetrachloride solution gives α : α-diphenyl-β-nitroethyl alcohol [6] (m.p. 106°C):

$$\underset{\alpha;\ \alpha\text{-Diphenylethylene}}{(C_6H_5)_2C{=}CH_2} \xrightarrow{HNO_3} (C_6H_5)_2C(OH)CH_2NO_2$$

Only the first stage of the reaction, viz. addition, takes place in this case. **Wieland** obtained among other products nitro*iso*amylene by treating *iso*amylene with a solution of anhydrous nitric acid in carbon tetrachloride. This is a product of a substitution reaction:

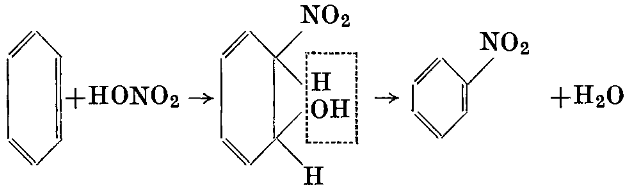
$$(CH_3)_2C{=}CH{-}CH_3 \xrightarrow{HNO_3} [(CH_3)_2C(OH){-}CH(NO_2){-}CH_3] \rightarrow$$

$$\rightarrow (CH_3)_2C{=}C(NO_2){-}CH_3 + H_2O$$

Nitro*iso*amylene

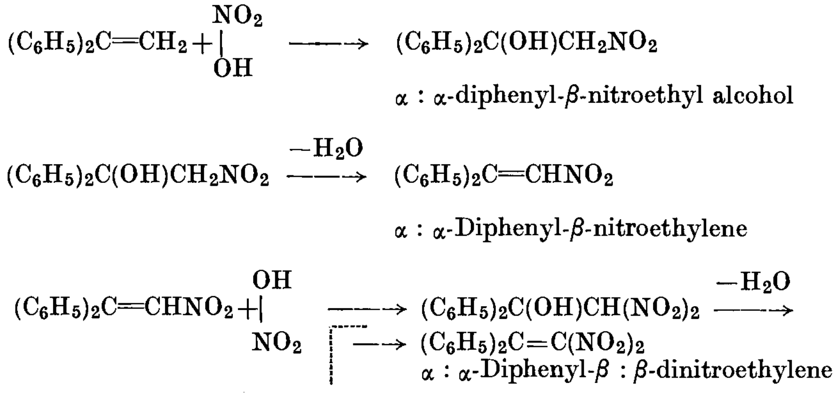
Kohler and **Drake** [7] showed that the nitration of α : α-diphenylethylene occurs with good yields if nitric acid is added gradually and with efficient stirring to the hydrocarbon at low temperature. The reaction products in this case are α : α-diphenylnitroethylene and α : α-diphenylnitroethyl alcohol.

Wieland studied the nitration of phenanthrene which adds on nitric acid readily with simultaneous splitting out of water from the nitro alcohol giving the corresponding ether. He performed the nitration as follows: to a solution of phenanthrene (20 g) in CCl_4 (100 ml), cooled to −15°C, concentrated HNO_3 (10 ml) was added slowly dropwise, with stirring. The reaction product, which was in the form of a tarry precipitate, was recrystallized from benzene. After a second recrystallization from acetone, according to the author, an ether was obtained which was formed from two molecules of 8-hydroxy-9-nitrophenanthrene (m.p. 167°C). WIELAND supposes that in the nitration of aromatic compounds, as in the interaction between ethylene compounds and concentrated nitric acid, there is initial addition of the nitric acid molecule across the double bond of the aromatic ring, forming an unstable nitro-hydroxy derivative, which decomposes to give the corresponding aromatic nitro derivative and water.



For example, nitration of benzene gives a primary product, nitrohydroxy-*cyclo*hexadiene, an extremely unstable compound which readily decomposes to give nitrobenzene and water. WIELAND takes the transient brown coloration observed on mixing nitric acid and benzene as a sign of the existence of an intermediate product. However, he does not furnish any direct proof of the existence of such an intermediate product.

The work of ANSSHÜTZ and GILBERT [8] must also be mentioned in connexion with WIELAND's studies of the nitration of unsaturated compounds, on the basis of which he proposed his theory of aromatic nitration: These authors nitrated α : α-diphenylethylene in acetic acid solution with an equimolecular amount of nitric acid first at ordinary temperature and then at 100°C until on diluting a sample of the solution with water a crystalline and not an oily product was obtained; on the completion of nitration water was added and a precipitate separated out. The authors obtained three products on fractional crystallization of this precipitate from alcohol: α : α-diphenyl-β-nitroethyl alcohol (m.p. 106–107°C), α : α-diphenyl-β-nitroethylene (m.p. 87–88°C) and α : α-diphenyl-β : β-dinitroethylene (m.p. 146–147°C). The formation of these three reaction products is explained as follows:



$$(C_6H_5)_2C{=}CH_2 + \overset{NO_2}{\underset{OH}{|}} \longrightarrow (C_6H_5)_2C(OH)CH_2NO_2$$

α : α-diphenyl-β-nitroethyl alcohol

$$(C_6H_5)_2C(OH)CH_2NO_2 \xrightarrow{-H_2O} (C_6H_5)_2C{=}CHNO_2$$

α : α-Diphenyl-β-nitroethylene

$$(C_6H_5)_2C{=}CHNO_2 + \overset{OH}{\underset{NO_2}{|}} \longrightarrow (C_6H_5)_2C(OH)CH(NO_2)_2 \xrightarrow{-H_2O}$$

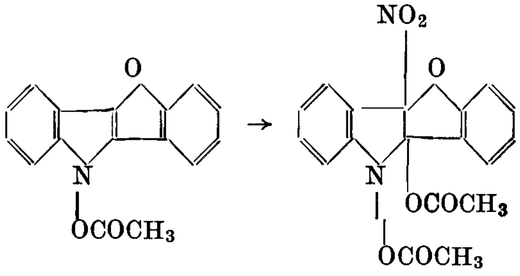
$$\longrightarrow (C_6H_5)_2C{=}C(NO_2)_2$$

α : α-Diphenyl-β : β-dinitroethylene

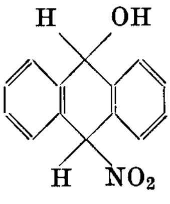
The formation of nitro alcohol was also observed as the result of the action of nitric acid on α : α-di-*p*-tolyl ethylene.

References to addition compounds formed during the nitration of aromatic compounds occur in the literature. ODDO [9] obtained an oily product on nitrating naphthalene with nitric acid which, in the author's opinion, represented a molecular complex of naphthalene with nitric acid. This complex proved to be very unstable and rapidly split out water giving α-mononitronaphthalene. ODDO explains the mechanism of the nitration and the formation of the addition product by assuming that the benzene rings of the naphthalene molecule show dissimilar reactivity; one has an aromatic and the other an aliphatic character (alicyclic nucleus). The latter is more reactive, contains two conjugated double bonds, and shows the greatest reactivity in the α : α′-position. It is in this position that nitric acid adds on when naphthalene is mixed with nitric acid, forming a complex which splits out water and gives α-mononitronaphthalene. On further nitration of naphthalene, i.e. on introducing a second nitro group, ODDO assumes a preliminary regrouping of the rings with a transfer of aliphatic properties to the other ring when nitric acid adds on in positions 5 and 8. The complexes formed then split out water and give dinitro compounds (1 : 5- and 1 : 8-dinitronaphthalenes).

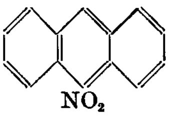
Apart from ODDO's work, there are references to the addition of nitric acid to benzalphthalimidine and benzaldiphenylmaleide [10]. Moreover, it has been shown that the action of a mixture of nitric and glacial acetic acids on N-acyl derivatives of coumarono-(2 : 3 : 2′ : 3′)-indole is accompanied by the addition of the $—NO_2$ and $—OCOCH_3$ groups across the double bond to give the corresponding nitroacetates [11]:



MEISENHEIMER [12] obtained an addition product of nitric acid and anthracene-dihydronitroanthranol $C_{14}H_{10}NO_3H$:



On treating this product with alkali the corresponding nitro compound—mesonitroanthracene was obtained:



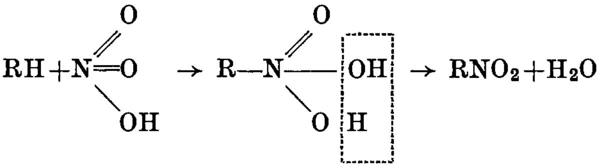
whose structure was proved by reduction with zinc and HCl to give mesoanthramine $C_{14}H_9NH_2$. This latter was identical with the compound prepared by treating anthranol with ammonia solution.

A number of objections have been raised to WIELAND's hypothesis concerning the formation of aromatic nitro compounds by the elimination of water from a primary product given by the addition of a molecule of nitric acid across a double bond of the aromatic ring. The following objections merit a note:

(1) The derivatives of *cyclo*hexadiene formed by the addition of nitric acid should be extremely unstable and their subsequent transformation exclusively in the direction of splitting out water is most unlikely.

(2) Against the addition of a molecule of nitric acid across aromatic double bonds is the discrepancy in the rates of various substitution reactions, e.g. the extreme difficulty of brominating benzene (without catalysts) and the ease of its nitration.

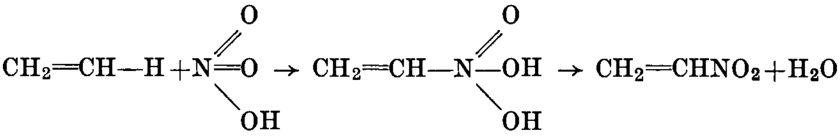
Considering WIELAND's hypothesis unsatisfactory, TRONOV [13, 14] as well as NAMETKIN and ZABRODINA [15] put forward a different concept of aromatic nitration, according to which the aromatic ring is linked with the nitrogen atom of nitric acid by forming a C—N bond with simultaneous migration of the hydrogen atom, previously linked with the carbon atom, to one of the oxygen atoms of the nitric acid molecule:



$$\mathrm{RH}+\mathrm{N}\overset{\displaystyle\nearrow \mathrm{O}}{=}\mathrm{O}\ \searrow\mathrm{OH} \rightarrow \mathrm{R{-}N(=O)}\boxed{\mathrm{{-}OH}}\ \mathrm{(O}\boxed{\mathrm{H}}\mathrm{)} \rightarrow \mathrm{RNO_2+H_2O} \qquad (1)$$

This hypothesis provides for the preservation of the aromatic properties of the intermediate reaction product, which explains the absence of any tendency on its part to undergo the various transformations associated with derivatives of *cyclo*hexadiene.

The formation of nitric acid esters of nitroalcohols by the action of nitric acid on unsaturated aliphatic compounds is explained by these authors by preliminary nitration:

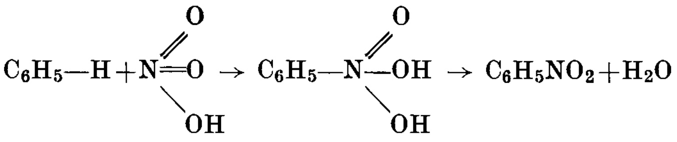


$$\mathrm{CH_2{=}CH{-}H}+\mathrm{O{=}N(=O)(OH)} \rightarrow \mathrm{CH_2{=}CH{-}N(=O)(OH){-}OH} \rightarrow \mathrm{CH_2{=}CHNO_2+H_2O}$$

The second molecule of nitric acid adds on across the double bond giving the nitric acid ester of the nitroalcohol:

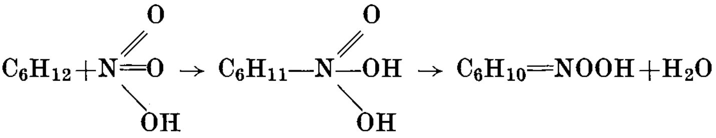
$$CH_2{=}CHNO_2+HNO_3 \rightarrow O_2N{-}O{-}CH_2{-}CH_2{-}NO_2$$

Contrary to **Wieland**'s view that nitric acid can only enter addition reactions by cleavage across the HO—NO_2 bond, **Michael** and **Carlson** [16] suggest that when nitric acid reacts with unsaturated compounds at low temperatures it can add on in accordance with **Tronov**'s and **Nametkin**'s scheme with cleavage of the H—ONO_2 bond. The formation of nitro compounds occurs as the result of a secondary reaction. The process of aromatic nitration should thus proceed as follows:



$$C_6H_5{-}H+\overset{\displaystyle O\diagup\!\!\!\!\diagup}{\underset{\displaystyle \diagdown OH}{N}}{=}O \rightarrow C_6H_5{-}\overset{\displaystyle O\diagup\!\!\!\!\diagup}{\underset{\displaystyle \diagdown OH}{N}}{-}OH \rightarrow C_6H_5NO_2+H_2O$$

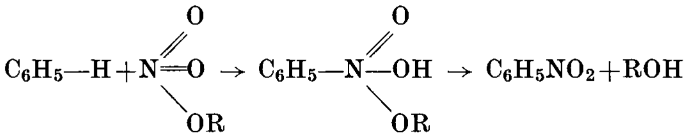
whilst the nitration of *cyclo*hexane should follow the reaction:



$$C_6H_{12}+\overset{\displaystyle O\diagup\!\!\!\!\diagup}{\underset{\displaystyle \diagdown OH}{N}}{=}O \rightarrow C_6H_{11}{-}\overset{\displaystyle O\diagup\!\!\!\!\diagup}{\underset{\displaystyle \diagdown OH}{N}}{-}OH \rightarrow C_6H_{10}{=}NOOH+H_2O$$

*iso*Nitro*cyclo*hexane

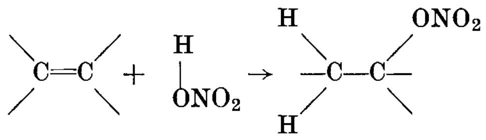
It might be supposed from the above that the nitration of aromatic hydrocarbons would proceed similarly were nitric acid replaced by its esters. In such a case the following reaction would be expected:



$$C_6H_5{-}H+\overset{\displaystyle O\diagup\!\!\!\!\diagup}{\underset{\displaystyle \diagdown OR}{N}}{=}O \rightarrow C_6H_5{-}\overset{\displaystyle O\diagup\!\!\!\!\diagup}{\underset{\displaystyle \diagdown OR}{N}}{-}OH \rightarrow C_6H_5NO_2+ROH$$

but in reality no nitro compound is formed.

As regards the nitration of unsaturated compounds, the same authors consider that addition across the double bond occurs in the following manner:

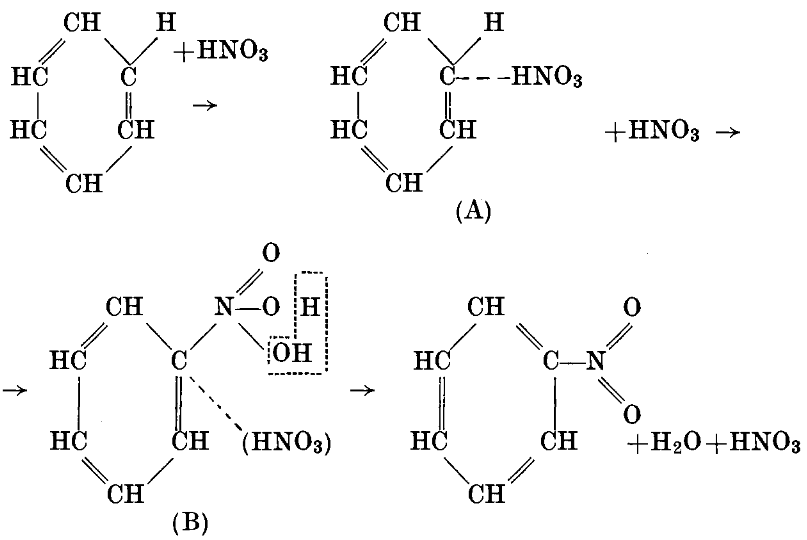


$$\diagdown\!\!\!\underset{\diagup}{C}{=}\underset{\diagdown}{C}\!\!\!\diagup + \overset{\displaystyle H}{\underset{\displaystyle ONO_2}{|}} \rightarrow {-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle ONO_2}{C}{-}$$

Thus **Tronov**'s, **Nametkin**'s and **Zabrodina**'s scheme could not account for the absence of nitrating properties of nitric acid esters in the case of aromatic compounds. No change was observed on mixing benzene and its homologues (xylene and pseudocumene), as well as the easily nitrated anisole, with ethyl nitrate and *iso*amyl nitrate, even after the mixtures had been standing for as long as 4–5 years. It is difficult to allow that the substitution of a hydrogen atom in nitric acid by a hydrocarbon radical could in itself affect the breakdown of the HNO_3 molecule into

—NO_2 and —OH or the cleavage of the double bond between nitrogen and oxygen. It could be more readily concluded that the hydrogen atom of nitric acid participated in nitration.

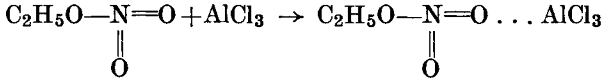
Taking the facts mentioned above, as well as the findings of Gierschbach and Kessler [17] which showed that the reaction between nitric acid and benzene in nitrobenzene solution is bimolecular in respect of nitric acid, Tronov considers that two molecules of nitric acid participate in aromatic nitration, one of the molecules acting as catalyst, evidently through its mobile hydrogen atom. The reaction mechanism consists of nitric acid attaching itself to a ring carbon atom to form a complex (A). This weakens the carbon–hydrogen bond; the hydrogen atom consequently becomes mobile and is easily split off, thus facilitating the formation of complex (B) by interaction of complex (A) with another molecule of nitric acid. This is followed by the breakdown of complex (B) with splitting out of a molecule of nitric acid and a molecule of water, which results in the formation of nitrobenzene:



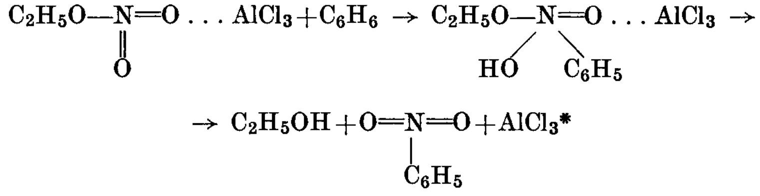
Tronov explains the absence of nitrating properties observed in nitric acid esters (with respect to aromatic compounds) by the need for a catalyst in this reaction, which in the case of nitric acid nitration is supplied by the acid itself.

Bearing in mind the findings of Boedtker [18], who showed that ethyl nitrate reacted vigorously with benzene in the presence of $AlCl_3$, Tronov investigated the effect of a series of chlorides (BCl_3, $SnCl_4$, PCl_3, $FeCl_3$, $AlCl_3$, $SiCl_4$, $SbCl_5$) on the nitration of benzene by ethyl nitrate. A concentration of 0·5 mole of the substance under investigation for catalytic properties was added to equimolecular amounts of the reactants. (In the case of $AlCl_3$ the amounts of catalyst were varied.) The mixtures were kept at room temperature for 48 hr, then diluted with water and ether. The ethereal solution was dried over calcium chloride and evaporated for 1 hr at 105–110°C to remove ethyl nitrate and benzene (nitrobenzene was determined in the residue). The experiments showed that of the substances studied only $AlCl_3$, $SnCl_4$, $SbCl_5$ and $FeCl_3$ exhibited catalytic activity, of different degrees as can be seen in Table 7.

Werner's [19] and Pfeifer's [20] findings which showed that these four chlorides possessed the ability to form various complexes led Tronov to explain their catalytic action on nitration with ethyl nitrate by their complex-forming properties (as distinct from BCl_3, $SiCl_4$, PCl_3). Since it is known that $AlCl_3$ and $SnCl_4$, which proved to be the most effective catalysts (see Table 7), react vigorously with ethyl nitrate, Tronov suggests that they form a complex with ethyl nitrate which then enters into reaction with benzene.*



$$C_2H_5O-\underset{\underset{O}{\|}}{N}=O+AlCl_3 \rightarrow C_2H_5O-\underset{\underset{O}{\|}}{N}=O\ldots AlCl_3 \qquad (1)$$



$$C_2H_5O-\underset{\underset{O}{\|}}{N}=O\ldots AlCl_3+C_6H_6 \rightarrow C_2H_5O-\underset{HO\quad C_6H_5}{N}=O\ldots AlCl_3 \rightarrow C_2H_5OH+O=\underset{\underset{C_6H_5}{|}}{N}=O+AlCl_3{}^* \qquad (2)$$

Table 7. Comparison of the catalytic activity of $AlCl_3$, $SnCl_4$, $SbCl_5$ *and* $FeCl_3$

Catalyst	Amount of catalyst (moles)	Yield of nitrobenzene (% of theoretical)
$AlCl_3$	0·1	12·0
$AlCl_3$	0·3	39·5
$AlCl_3$	0·5	50·8
$SnCl_4$	0·5	35·0
$SbCl_5$	0·5	7·1
$FeCl_3$	0·5	9·8

By analogy with the scheme given above for nitration with ethyl nitrate in the presence of $AlCl_3$, Tronov supposes that the nitration of aromatic

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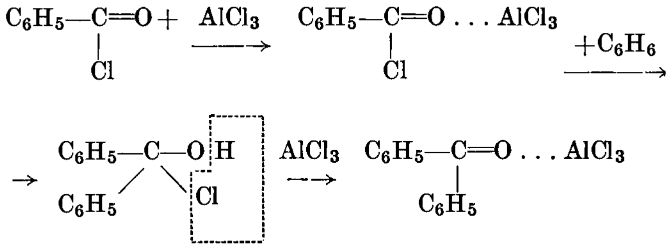
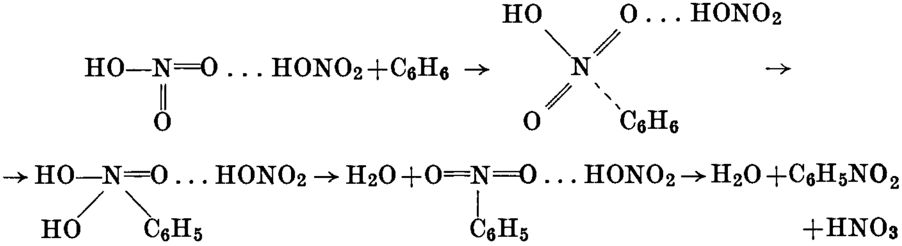
* This scheme is devised by Tronov along the lines of the reaction in which ketones are formed by the interaction of acid chloroanhydrides with aromatic hydrocarbons in the presence of $AlCl_3$; it is usually taken that in this reaction there is a primary formation of a complex of 1 mole of acid chloroanhydride and 1 mole $AlCl_3$:



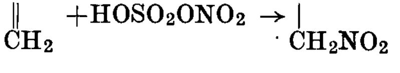
$$C_6H_5-\underset{\underset{Cl}{|}}{C}=O+AlCl_3 \longrightarrow C_6H_5-\underset{\underset{Cl}{|}}{C}=O\ldots AlCl_3 \xrightarrow{+C_6H_6} \boxed{\begin{matrix}C_6H_5-C-OH\\ C_6H_5\quad Cl\end{matrix}}\; AlCl_3 \longrightarrow C_6H_5-\underset{\underset{C_6H_5}{|}}{C}=O\ldots AlCl_3$$

compounds with nitric acid occurs not according to scheme (1) as he thought previously (see above) but according to scheme (3) (the nitration of an aromatic compound being effected by a complex of two molecules of nitric acid of which one is the nitrating agent whilst the other acts as a complex-maker):

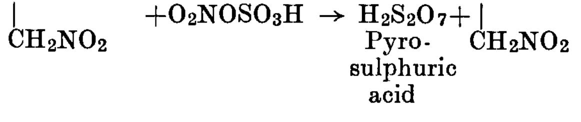


(3)

As indicated above, nitration according to Wieland goes through a primary stage of nitric acid addition as the result of which saturated nitrohydrins are formed. In the case of aliphatic compounds the nitrohydrins break down into nitroolefines and water or, through esterification, give the corresponding esters of nitric acid (these two processes may also occur simultaneously). The nitration of the aromatic ring Wieland pictures as the addition of the HO and NO_2 radicals across the double bond in the ring followed by the decomposition of the complex so obtained to give the nitro derivative and water. Michael and Carlson [21] do not consider this hypothesis proved experimentally; under the conditions used by Wieland for the nitration of unsaturated compounds with nitric acid and nitrating mixture the process of nitration is markedly complicated by side reactions which lead to the formation of compounds which may play the part of nitrating agents. During the nitration of ethylene with nitrating mixture Wieland, in addition to oxidation products, obtained a nitric ester of nitroalcohol (nitro-nitrate) $CH_2(ONO_2)CH_2NO_2$ whose formation he explains by the esterification by nitric acid of the nitroalcohol—the primary product of the direct addition of a molecule of nitric acid to ethylene. In Michael and Carlson's opinion another mechanism is much more probable in this case, since in the mixture of nitric and sulphuric acids the nitrating agent is not HNO_3 but a mixed anhydride $HOSO_2ONO_2$ which has, as all mixed anhydrides, a great tendency to undergo addition reactions. When this anhydride adds on to ethylene an intermediate product is formed $CH_2(OSO_3H)CH_2NO_2$ in which the $—SO_3H$ group can be readily replaced by the more negative $—NO_2$ radical, giving the nitro-nitrate:



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + HOSO_2ONO_2 \rightarrow \begin{matrix}CH_2OSO_3H\\ |\\ CH_2NO_2\end{matrix} \qquad (1)$$



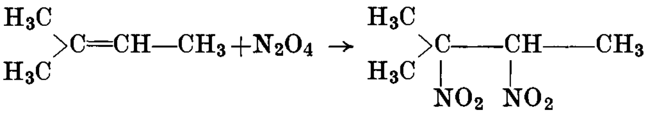
$$\begin{matrix}CH_2OSO_3H\\ |\\ CH_2NO_2\end{matrix} + O_2NOSO_3H \rightarrow \underset{\text{Pyro-sulphuric acid}}{H_2S_2O_7} + \begin{matrix}CH_2ONO_2\\ |\\ CH_2NO_2\end{matrix} \qquad (2)$$

Moreover, with the appearance in the reaction mixture of nitrogen oxides resulting from oxidative processes, the possibility arises of N_2O_3 and N_2O_4 entering the reaction. The interaction of these oxides with ethylene (addition) also leads to the formation of nitro-nitrate.

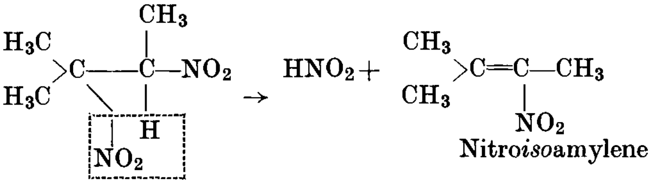
As indicated above, when WIELAND nitrated *iso*amylene in CCl_4 solution the main reaction product was α-nitro*iso*amylene with a certain amount of nitro-nitrate:

$$(CH_3)_2C(ONO_2)CH(NO_2)CH_3$$

Taking the rule of positive–negative addition into account, MICHAEL and CARLSON consider that if the reaction followed WIELAND's scheme, the primary product would be mainly $(CH_3)_2C(NO_2)CH(OH)CH_3$ and only a small amount of $(CH_3)_2C(OH)CH(NO_2)CH_3$ would be formed. Esterification of the first product by nitric acid should lead to the final product $(CH_3)_2C(NO_2)CH(ONO_2)CH_3$ and not to the isomer which WIELAND actually obtained. If, however, it is assumed that the reaction proceeds by way of addition of N_2O_4 the formation of the products obtained by WIELAND can be explained:

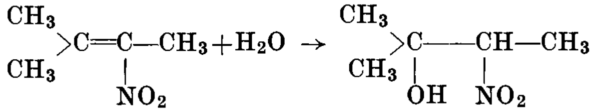


$$(H_3C)_2C{=}CH{-}CH_3 + N_2O_4 \rightarrow (H_3C)_2\underset{NO_2}{C}{-}\underset{NO_2}{CH}{-}CH_3 \qquad (1)$$

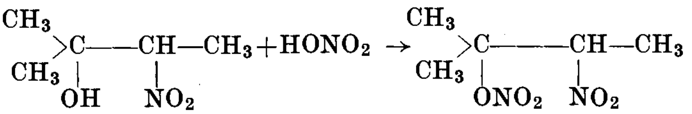


$$(H_3C)_2\underset{\boxed{NO_2}}{C}{-}\overset{CH_3}{\underset{\boxed{H}}{C}}{-}NO_2 \rightarrow HNO_2 + (CH_3)_2C{=}\underset{NO_2}{C}{-}CH_3 \qquad (2)$$

Nitro*iso*amylene



$$(CH_3)_2C{=}\underset{NO_2}{C}{-}CH_3 + H_2O \rightarrow (CH_3)_2\underset{OH}{C}{-}\underset{NO_2}{CH}{-}CH_3 \qquad (3)$$



$$(CH_3)_2\underset{OH}{C}{-}\underset{NO_2}{CH}{-}CH_3 + HONO_2 \rightarrow (CH_3)_2\underset{ONO_2}{C}{-}\underset{NO_2}{CH}{-}CH_3 \qquad (4)$$

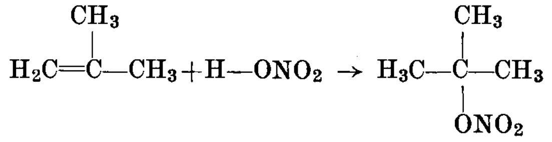
MICHAEL and CARLSON analysed WIELAND's experimental data on the nitration of α : α-diphenylethylene with nitric acid and concluded that in this case nitrogen oxides (formed as a result of oxidative side reactions) participated in the process of nitration (it is known that α : α-diphenylethylene gives with N_2O_3 an oily product which easily decomposes into nitrohydrin and derivatives of nitroethylene; with N_2O_4 in the presence of water diphenylethylene gives α : β-nitrohydrin).

In order to verify experimentally their views on the action of nitric acid and nitrating mixture on unsaturated hydrocarbons, MICHAEL and CARLSON conducted the nitration of olefines under conditions excluding oxidative processes which lead to the formation of nitrogen oxides, viz. using solvents (chloroform, carbon tetrachloride and methylene chloride) low temperatures and efficient stirring. They nitrated ethylene with nitric acid (98·6 per cent) either by means of bubbling ethylene through nitric acid in methylene chloride solution at −25°C, or by adding nitric acid to the solvent through which ethylene was passed at −28°C with vigorous stirring; in both cases an oily reaction product was obtained which decomposed even on moderate heating. The gases evolved consisted of nitrogen oxides.

Nitration of butylene, which adds on HBr and water more readily than ethylene, led only to the formation of oxidation products. Methylethylketone was isolated from the latter; this compound could have been formed by the oxidation of the nitric ester of secondary butyl alcohol.

Nitration of *iso*amylene and *iso*butylene gave more satisfactory results, owing to the greater ability of these hydrocarbons to add on acids as compared to ethylene and butylene, and also owing to the greater stability of esters with tertiary radicals to oxidation as compared to the corresponding secondary derivatives.

Contrary to Wieland's and Rahn's [2] indications, Michael and Carlson obtained the nitric ester of tertiary amyl alcohol as the main product on nitrating *iso*amylene. The nitration was carried out by adding 98·6 per cent nitric acid to a solution of *iso*amylene at −20°C. Under similar conditions the authors nitrated isobutylene with the formation of the nitric ester of tertiary butyl alcohol. The authors explain the formation of nitrates by the addition of a molecule of nitric acid to a molecule of olefine according to the scheme:



$$H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3 + H{-}ONO_2 \rightarrow H_3C{-}\underset{\underset{\displaystyle ONO_2}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_3$$

During the nitration of $\alpha:\alpha$-diphenylethylene which Michael and Carlson carried out in chloroform or CCl_4 solution at 0°C, it was discovered that the hydrocarbon did not react with nitric acid to give a nitro derivative, but was partially converted to a polymer. In glacial acetic acid no reaction occurred between the polymer and nitric acid at room temperature; when the reaction was carried out with heating it was possible to isolate from the reaction mixture $\alpha:\alpha$-diphenyl-β-nitroethyl alcohol. These findings confirm that the compounds obtained by Wieland could have been formed by the interaction of the hydrocarbon with nitrogen oxides and not by the direct addition of nitric acid.

Going on to the nitration of aromatic hydrocarbons, Michael and Carlson point out the incorrectness of the scheme suggested by Wieland for the process of nitration of benzene. Their criticism is based on the following reasons: under ordinary conditions benzene has little tendency to undergo addition reactions (in respect of halogen for example) but, owing to intramolecular energy changes, addition to one pair of carbon atoms entails a transfer of capacity for addition to the two remaining pairs of carbon atoms. Analogous phenomena should be observed during nitration with nitric acid. It can be concluded from this that if the nitration of benzene proceeded along the lines put forward by WIELAND it should lead to the formation of trinitrobenzene exclusively.

On nitration of phenanthrene with nitric acid WIELAND obtained the ester of 8-hydroxy-9-nitrophenanthrene, formed, in his opinion, by the condensation of two molecules of 8-hydroxy-9-nitro derivative with splitting out of one particle of water. The 8-hydroxy-9-nitro derivative of phenanthrene is a primary addition product of the —OH and —NO_2 groups to the carbon atoms in positions 8 and 9 (according to WIELAND, only these carbon atoms show the capacity to undergo addition reactions analogous to the ethylene hydrocarbons). Findings reported in earlier literature [22] do not confirm these views of WIELAND, since on nitration of phenanthrene in acetic acid solution not only the 9-nitro but also the 3-, 2- and 4-nitrophenanthrenes were obtained. The ester isolated by WIELAND was, evidently, formed by the action of nitrous fumes on phenanthrene (according to SCHMIDT's findings [23] nitration of phenanthrene by nitrous fumes leads to the formation of the same ester as that obtained by WIELAND). When MICHAEL and CARLSON treated phenanthrene with 98·6 per cent nitric acid in chloroform solution at −20°C they obtained a 25 per cent yield of a mixture of nitrophenanthrenes.

MICHAEL and CARLSON propose a theory of "aldolization" based on their experimental findings obtained in the course of studying the nitration of olefines and aromatic compounds. It is derived from the following principles: the oxygen atom of nitric acid linked by two bonds with nitrogen must possess considerably greater chemical energy than the partially "hydrogenated" oxygen in the —OH group and hence be more able to "attract" the benzene ring hydrogen, thus separating it from the carbon atom linked with it. The fundamental factors which determine the nitrating properties of nitric acid are the chemical potentials of oxygen and of nitrogen as regards the hydrogen of aromatic ring and the phenyl radical (aryl) respectively. From this point of view the nitration of benzene can be represented by the following scheme:

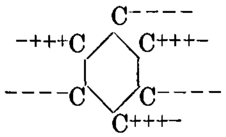
$$C_6H_6 + HONO_2 \rightarrow C_6H_5NO(OH)_2 \rightarrow C_6H_5NO_2 + H_2O$$

This hypothesis, as well as the others mentioned previously, evolve from the assumption that it is the molecule of nitric acid which is the nitrating agent, giving a primary complex with the aromatic compound which subsequently breaks down into the nitro compound and water. It is taken that the addition of nitric acid can either occur across the double bond of the aromatic ring (WIELAND) or, conversely, that the aromatic nucleus combines with a molecule of nitric acid (TRONOV, NAMETKIN and ZABRODINA; MICHAEL and CARLSON).

BERKENHEIM [24] puts forward an original conception of the mechanism of aromatic nitration and the nature of nitro compounds. According to this author, in the case of the nitration of benzene for example, there is weak dissociation of the benzene molecule into the H^+ and $C_6H^-_5$ ions and an amphoteric dissociation of the nitric acid molecule, on the one hand into

H^+ and NO_3^- (I) and, on the other hand, into NO_2^+ and OH^- (II). The dissociation of nitric acid in the first direction occurs to a markedly greater extent. However, the greater concentration of H^+, by hindering the weak dissociation of the benzene molecule, results in the dissociation of nitric acid according to (I) being unable to bring about the formation of nitro derivatives. The dissociation of nitric acid in the direction of (II) enhances the dissociation of the benzene molecule owing to the formation of H_2O at the expense of H^+ and OH^- ions, and leads to the formation of the poorly ionized nitro compound.

Berkenheim's views on the nature of nitro compounds are based on the assumption that the benzene molecule consists of carbon atoms alternately charged, with four negative and three positive and one negative charges, according to the following scheme:



During the nitration of benzene the nitrogen atom of nitric acid, which has five positive charges, links up with the carbon atom which carries four negative charges, thus leading to the formation of a normal nitro compound.

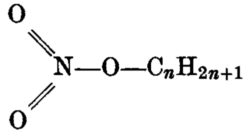
Below are given those theories of nitration in which it is taken that in the system aromatic compound–nitric acid several forms of nitric acid in its ionized and unionized state act as nitrating agents.

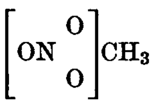
Hantzsch [25, 26] studied the physical and chemical properties of nitric acid solutions in water, sulphuric acid and organic solvents. He concluded that different forms of nitric acid existed in solution, their quantitative inter-relations varying with the concentration of the solvent.

Before the appearance of Werner's work, all oxygen containing acids were regarded as hydroxylic compounds, and the salts and esters of these acids as hydroxyl compound derivatives:

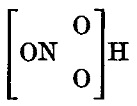
$$O_2N\,.\,OH; \qquad O_2N\,.\,OMe; \qquad O_2N\,.\,OC_nH_{2n+1}$$

These structural formulae could not explain the fundamental differences between electrolytes and non-electrolytes, and between salts and esters of acids. Werner, proceeding from his teachings about coordinate bonds and the structure of complexes, reached a different concept, according to which only the esters have the structure of hydroxylic compound derivatives; the salts and the acids, however, being electrolytes, are complexes made up of a complex anion and an ionically linked cation, metal or hydrogen, present in the second sphere of attraction of the central atom, viz. nitrogen:





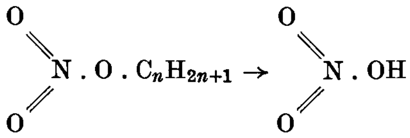
$$\left[ON\begin{matrix}O\\ \\O\end{matrix}\right]CH_3$$



$$\left[ON\begin{matrix}O\\ \\O\end{matrix}\right]H$$

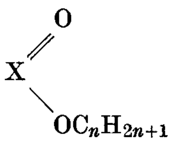
Schaeffer's [27] investigations, in which he studied the absorption spectra of homogeneous nitric acid and its solutions in non-ionizing media, as well as of the corresponding salts and esters, showed, however, that the absorption spectra of nitric acid and its esters had definite similarity; only in greatly diluted aqueous solutions are the absorption spectra of nitric acid analogous to the spectra of its salts.

Hantzsch studied the absorption spectra of various acids, their salts and esters and discovered that the salts and esters of one and the same acid differed from each other in their optical properties, whilst the acids occupied an intermediate position and, depending on their nature and the solvent, were optically identical either with the salts or with the esters. Hantzsch also established that ionization did not alter optical properties. In fact, acids which show the same absorption spectrum as their salts are identical with the latter not only in the undissociated state, but also in the form of ions. To explain the results obtained, Hantzsch assumes that the optical properties of the compounds investigated depend on their structure. For instance, those acids which are optically identical with esters have structures analogous to the latter, i.e. contain a hydroxyl group corresponding to the alkoxyl group of the esters:



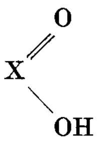
These acids are not electrolytes and are, according to Hantzsch, "pseudo-acids". The true acids are those which are identical with salts, i.e. contain hydrogen corresponding to the metals of the salts; true acids, as distinct from pseudo-acids, possess electrolyte properties, since the atoms of hydrogen forming cations are linked ionically (in the second sphere of attraction of the central N atom) with several (at least two) atoms of oxygen. The relationships mentioned above may be generally represented in the following way (HXO_2—acids):

(I) Esters



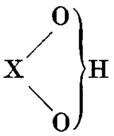
Non-electrolytes

Pseudo-acids



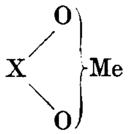
Hydroxylic forms

(II) True acids



Electrolytes

Salts



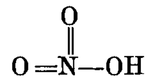
Complex forms

Compounds within each group have similar structures.

In his investigation of the structure of acids, Hantzsch also employed a chemical method based on the different nature of the interaction of true acids and pseudo-acids with diazoacetic ester. Diazoacetic ester reacts with acids with evolution of nitrogen according to the following equation:

$$(COOC_2H_5)CHN_2 + HX \rightarrow (COOC_2H_5)CH_2X + N_2$$

Oxygen containing acids in which there is only one atom of oxygen are either inert with respect to diazoacetic ester or only react with it very slowly. However, acids which contain more than one atom of oxygen (XO_2H, XO_3H, etc.) enter into reaction with diazoacetic ester with evolution of nitrogen even in their undissociated state, but in that case only if they contain ionically linked hydrogen, i.e. behave in solution as true acids. If, on the other hand, they are pseudo-acids, i.e. are hydroxylic compounds ($OX.OH$), either no reaction occurs with diazoacetic ester, or a very feeble one similar to that observed in the case of other hydroxylic compounds. Making use of the diazoacetic ester reaction Hantzsch established that nitric acid in ethereal solution readily underwent transformation from a true acid $(NO_3)^-H^+$ to a "pseudo-acid":



$$O{=}\overset{\overset{\displaystyle O}{\|}}{N}{-}OH$$

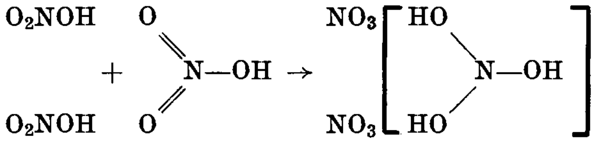
These results correspond to Schaeffer's findings [27] which showed that in ethereal solution nitric acid was optically identical with its esters.

Hantzsch's investigation of aqueous solutions of nitric acid by means of optical methods confirmed Schaeffer's findings indicating the presence in these solutions of the true acid form of nitric acid $H(NO_3)$. He also showed that with increasing concentrations of nitirc acid the spectra of its aqueous solutions approached more and more closely the spectra of esters, which proved the gradual transition from the true form $H(NO_3)$ to the hydroxylic form of the pseudo-acid $O_2N.OH$. Further studies led Hantzsch to the view that in aqueous solutions nitric acid is found not in the free state but as a hydroxonium salt. Water acts as a very weak base and forms a salt with nitric acid. The transition of the "pseudo" form of nitric acid to a hydroxonium salt on dilution with water can be represented by the following equation:

$$O_2NOH + H_2O \rightarrow (H_3O)^+(NO_3)^-$$

Hydroxonium nitrate or $O_2NOH + nH_2O = (NO_3)^-(H^+)(H_2O)_n$

Comparative studies of the ultraviolet absorption of homogeneous (absolute) nitric acid and of its esters showed that nitric acid absorption was considerably weaker than that shown by the esters (this phenomenon cannot be ascribed to so insignificant a difference in structure as that arising from the substitution of the pseudo-acid hydroxyl group by an alkoxy group). In order to explain this optical anomaly, which gave rise to sharp criticism of Hantzsch's theory by Halban [28], Hantzsch proposes the existence in homogeneous nitric acid, along with the pseudo-form, O_2NOH, of yet another form of nitric acid which shows less ultraviolet absorption than the pseudo-acid and is an electrolyte (this latter assumption explains the relatively high electrical conductivity of homogeneous nitric acid in spite of the fact that the pseudo-acid is not an electrolyte). Hantzsch considers that this form of nitric acid is formed by the association of three molecules of the pseudo-acid with an intramolecular re-arrangement of the hydrogen atoms:



The complex so obtained has salt-like characteristics; Hantzsch called it nitronium dinitrate. It dissociates into negative nitrate ions and the positive nitronium ion:*

$$(NO_3)_2[N(OH)_3] \rightleftarrows 2NO_3^- + H_3NO_3^{++}$$

If Hantzsch's later work is considered, his theories on the structure of homogeneous nitric acid and of its aqueous solutions can be reduced to the following:

Absolute (homogeneous) nitric acid consists of a solution of electrically conducting, nitracidium dinitrate $(NO_3)_2[(HO)_3N]$ in the pseudo-acid which is non-conducting. These two forms of nitric acid exist in equilibrium:

$$3O_2N\,.\,OH \rightleftarrows (NO_3)_2[(HO)_3N].$$

In 98·6 per cent nitric acid the concentration of pseudo acid is 80 per cent the rest being in the form of nitracidium dinitrate. On diluting nitric acid with water a rearrangement occurs of the pseudo-acid into a salt of hydroxonium and the true acid, i.e. a new equilibrium is set up:

$$O_2NOH + nH_2O \rightleftarrows (NO_3)^-[H^+\,.\,(OH_2)n]$$

Nitracidium dinitrate disappears in the process. Beginning with concentration of nitric acid 77 per cent solution contains pseudo-acid and true acid (in the undissociated state as hydroxonium salt and as ions). On further dilution the pseudo-acid content diminishes whilst that of true acid rises; at HNO_3 concentration of 31·6 per cent, i.e. after the addition of 8 moles of water, the rearrangement of pseudo-acid to true acid is complete, about 40 per cent of the true acid being in the dissociated state, whilst the remainder is in the form of undissociated hydroxonium salt.

Hantzsch gives a table for the aqueous solutions of nitric acid which shows the interrelations of the pseudo and true acid forms depending on the water content (Table 8).

Hantzsch also investigated the system nitric acid–sulphuric acid, and established that this system was distinguished by a considerably higher

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[*] Hantzsch calls the $H_2NO_3^+$ and $H_3NO_3^{++}$ ions "nitronium ions". Later these ions became known as nitracidium ions, whilst the NO_2^+ ion was called nitronium ion. We shall in future adhere to this more recent nomenclature.

electro-conductivity than that of nitric acid, and also by an anomalously large depression of the freezing-point. **Hantzsch** postulates the following explanation of these phenomena. He assumes the presence of electrolytes in the sulphuric acid–nitric acid mixture which are formed as the result of the interaction of a molecule of nitric acid with one or two molecules of sulphuric acid (since pseudo nitric acid has two unsaturated oxygen atoms the possibility exists for the formation of two salt-like complexes):

$$O_2NOH + HSO_4H \rightarrow [NO(OH)_2][SO_4H] \quad \text{Nitracidium sulphate} \qquad (1)$$

$$[NO(OH)_2][SO_4H] \rightleftarrows H_2NO_3^{+} + HSO_4^{-}$$

$$O_2NOH + 2HSO_4H \rightleftarrows [N(OH)_3][SO_4H]_2; \quad \text{Nitracidium disulphate} \qquad (2)$$

$$[N(OH)_3][SO_4H]_2 \rightleftarrows H_3NO_3^{++} + 2HSO_4^{-}$$

Hantzsch showed that there was similar interaction between nitric acid and perchloric acid, gave nitracidium perchlorates:

$$O_2NOH + HClO_4 \rightarrow [NO(OH)_2]ClO_4$$

$$O_2NOH + 2HClO_4 \rightarrow [N(OH)_3](ClO_4)_2$$

These compounds, which are very stable, were isolated by **Hantzsch** as colourless solids on mixing nitric acid with anhydrous perchloric acid. The reaction was carried out with strong cooling and stirring. After recrystallization of the monoperchlorate (from nitric acid) and the diperchlorate (from perchloric acid) **Hantzsch** obtained pure products in the form of needle-like crystals.

Table 8. *Ratios of pseudo-acid and true acid in aqueous solutions of* HNO_3 *depending on its water content*

Concentration HNO_3 %	Moles H_2O per 1 mole HNO_3	Pseudo-acid (%)	Undissociated true acid (%)	Ionized true acid ($NO_3' + H^{\cdot}$) (%)
77·3	1·0	70	25	5
48·3	3·75	50	32	18
31·6	7·5	2	60	38

Farmer [29] taking into account **Hantzsch**'s and **Schaeffer**'s findings concerning the structure of nitric acid ascribes its esterifying and nitrating properties to its pseudo acid form. This distinguishes it sharply from other strong acids, e.g. sulphuric acid, since, according to **Hantzsch**, the ability of strong acids to undergo transformation to the pseudo form is less marked than that of weak acids. Of all the states of nitric acid it is only the pseudo form which possesses nitrating properties.

Farmer explains the maximal value of the nitration rate constant at a certain water content level of sulphuric acid thus: as the relative sulphuric acid content of the nitrating mixture ($H_2SO_4+HNO_3$) rises, the pseudo form content initially shows a rise, but begins to decrease when a considerable excess of sulphuric acid is reached, owing to the formation of a certain amount of nitracidium sulphate at the expense of this pseudo form. Therefore the nitrating activity of the mixture is at first enhanced by the rise in its sulphuric acid content, but, beyond a certain limit, it begins to decline.

A number of investigators studied the kinetics of nitration. MARTINSEN considers that the nitration of aromatic compounds with an equimolecular quantity of nitric acid in an excess of sulphuric acid is a bimolecular reaction and that its rate is directly proportional to the concentration of both the nitric acid and the compound undergoing nitration [30].

LAUER and ODDA [31], whilst studying the kinetics of nitration of anthraquinone with nitric acid in aqueous solutions of sulphuric acid within the range of concentration of the latter of 87 to 95·6 per cent, found that the maximal rate of reaction corresponded to the concentration of 89 per cent. This is related to the presence in the nitrating mixture of various forms of nitric acid depending on the concentration of sulphuric acid. As will be seen later, the concentration of sulphuric acid and water is not the only determining factor in the rate of nitration. LAUER and ODDA infer from the results obtained that the nitrating agent in mixtures of nitric acid with sulphuric acid in the presence of water is a form of nitric acid different from that in mixtures of nitric acid with anhydrous sulphuric acid. An analysis of their results leads the authors to the following conclusions:

(1) At concentration of sulphuric acid below 89 per cent nitric acid consists of two modifications: true ($H—NO_3$) and pseudo ($HO—NO_2$) nitric acids, only the pseudo-acid, whose content is lowered by the addition of water, acting as a nitrating agent.

(2) At concentrations of sulphuric acid from 89 to 98 per cent nitric acid consists mainly of pseudo acid together with a certain amount of nitracidium sulphate $[NO(OH)_2](SO_4H)$, whose content rise with increased sulphuric acid concentrations.

(3) On raising the concentration of sulphuric acid from 98 to 100 per cent the nitracidium sulphate content of the mixture is greatly increased.

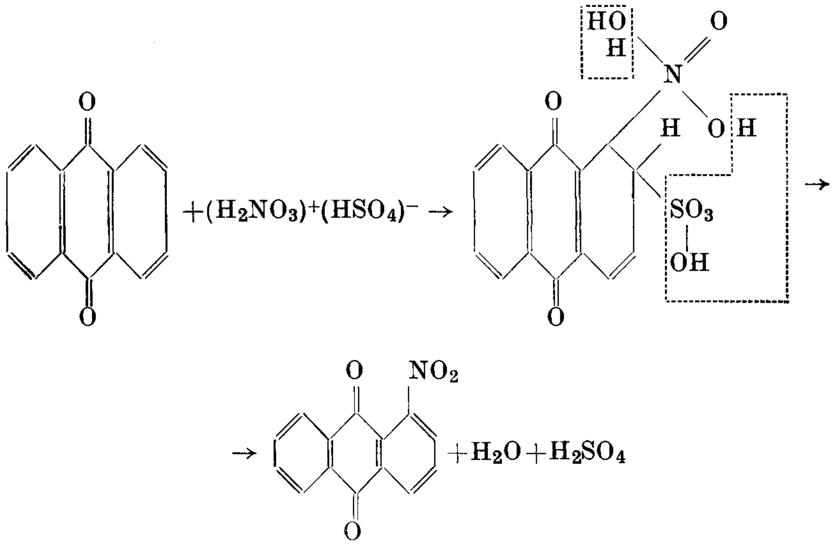
(4) In the mixture of nitric and fuming sulphuric acids the nitrating agent is exclusively the nitracidium sulphate.

The fact that the nitration reaction in anhydrous sulphuric acid proceeds at a lower rate than in aqueous solutions of this acid is explained by the authors by the greater "protection" offered the nitrogen atom in the nitracidium ion by the three hydroxyl groups as compared to the pseudo acid, and it is this ion which is the nitrating agent in this case. In aqueous solutions with concentrations of sulphuric acid below 89 per cent the lowering of the rate of nitration on further dilution of the acid with water is explained by the diminution in the pseudo-nitric acid content, in other words diminution in the amount of the nitrating agent. The lowering of the rate of nitration at higher concentrations of sulphuric acid is explained by the diminution of pseudo nitric acid content as the result of its partial replacement by nitracidium sulphate. Thus the intensity of nitration in aqueous solutions of sulphuric acid is determined by the pseudo nitric acid content, which is maximal at H_2SO_4 concentration of 89 per cent.

Lauer and Odda also studied the nitration of nitrobenzene with nitric acid in 90 and 100 per cent sulphuric acid. Experiments showed that the main reaction product was *m*-dinitrobenzene; on increasing the concentration of sulphuric acid the yield of *o*-dinitrobenzene increased while that of the *m*- and *p*-isomers decreases.

The reaction mechanism of aromatic nitration with nitric acid in aqueous solutions of sulphuric acid consists, in the authors' view, of the addition across the double bond of the aromatic ring of the molecule of pseudo nitric acid, which initially breaks down into $—NO_2$ and —OH groups (the $—NO_2$ group goes to the anionic C atom). The nitro derivative is formed in the second stage of nitration through the splitting out of water from the HNO_3— aromatic compound complex.

During nitration in anhydrous solution of sulphuric acid the reaction mechanism consists of the addition of nitracidium sulphate across the double bond with subsequent elimination of water and sulphuric acid:



Lantz [32] puts forward an original hypothesis concerning the reaction mechanism of aromatic nitration. He considers nitration as a process connected with the acid-base equilibrium in the system; he uses the concepts formulated by Brönsted, who defines "acid" [33] as a substance able to donate protons to another substance which he calls "base". The reversible reaction which thus occurs gives rise to a new "base" and a new "acid":

$$\text{acid (1)} + \text{base (1)} \rightleftarrows \text{base (2)} + \text{acid (2)}$$

According to Brönsted, the properties of "acid" and "base" become apparent only if the acid and the base are found together. Some substances in the presence of certain acids display basic properties whilst in the presence of certain bases they display acidic properties. For example, organic carboxylic acids, phosphoric and nitric acids which are acids in relation to ordinary bases become in turn "bases" in the presence of stronger acids—sulphuric, pyrosulphuric and perchloric.

When sulphuric acid acts on nitric acid an equilibrium is set up which, adopting Hantzsch's concept, can be represented as follows:

$$2H_2SO_4+HNO_3 \rightleftarrows 2HSO_4^-+(OH)_3N^{++}$$

Some substances can give an acid-base equilibrium without the participation of other compounds, i.e. in a homogeneous state or in an indifferent solvent: the substance can be simultaneously both an acceptor and a donor of protons. A well-known example of such substances is water which can give an equilibrium system with two of its molecules:

$$H_2O+H_2O \rightleftarrows OH^-+H_3O^+$$

Ammonia possesses similar properties:

$$NH_3+NH_3 \rightleftarrows NH_2^-+NH_4^+$$

The equilibria established by Hantzsch in homogeneous sulphuric acid determining its chemical properties can also be considered from the point of view of Brönsted and Lantz, assuming that they resulted from the interaction of two molecules ("acid" and "base"); the negative ion HSO_4^- and the positive ion $H_3SO_4^+$ are thus formed:

$$\underbrace{H_2SO_4+H_2SO_4}_{HSO_4H} \rightleftarrows HSO_4^-+H_3SO_4^+$$

The interaction of the molecules can also occur according to a different equation:

$$\underbrace{H_2SO_4+2H_2SO_4}_{2HSO_4H} \rightleftarrows 2HSO_4^-+H_4SO_4^{++}$$

The influence of added water on the reactions occurring in the sulphuric acid medium is explained by Lantz by the formation of hydrated ions such as the ion $(SO_4H_3 . H_2O)^+$ or $S(OH)_5^+$. By losing a proton this ion becomes the acid $H_2SO_4 . H_2O$ whose existence is proved by the melting point curves for the system H_2SO_4—H_2O. Formation of hydrated ions causes a decrease of $H_3SO_4^+$ ions.

Going on to nitration with nitric acid in sulphuric acid medium Lantz proposes the following mechanism for the reaction, dependent on the variation of the concentrations of water and sulphuric acid. In the monohydrate nitric acid is present wholly in the form of nitracidium salt, which can be expressed by the equation given above:

$$2H_2SO_4+HNO_3 \rightleftarrows 2(HSO_4)^-+(OH)_3N^{++} \qquad (1)$$

On the addition of water, hydrated sulphuric acid $H_2SO_4 . nH_2O$ (probably

$n = 1$) is formed; the latter, being a base in relation to H_2SO_4, leads to a new acid-base equilibrium which can be expressed by the equation:

$$H_2SO_4+nH_2SO_4 . H_2O \rightleftarrows HSO_4^-+nH_2SO_4 . H_3O^+ \qquad (2)$$

As the result of the latter reaction more HSO_4^- ions are formed, shifting the equilibrium in equation (1) from left to right and correspondingly there is an increase of $(OH)_3N^{++}$ ions and diminution in the amount of free (undissociated) acid. On introducing a further quantity of water there may come a point when strongly hydrated H_2SO_4 or even free water, substances which are relatively strongly basic, will be present. A new equilibrium will be set up in which free (undissociated) nitric acid acts as an acid forming NO_3^- ions. For example, in the presence of free water the following process takes place:

$$HNO_3+H_2O \rightleftarrows NO_3^-+H_3O^+ \qquad (3)$$

which leads to a decrease in the amount of unionized free acid. As can be seen from equations (1) to (3), undissociated acid cannot exist in either too "acid" a medium (i.e. containing little water), as in equation (1) or in too "basic" a medium (i.e. containing a large amount of water), equation (3).

Studying the nitration of naphthalene sulphonic acids with nitrating mixture at varying concentrations of sulphuric acid, LANTZ established that two nitro groups enter the nucleus when naphthalene disulphonic acids are nitrated at concentration $H_2SO_4 = 90$ per cent and a sufficient excess of nitric acid. In the case of naphthalene trisulphonic acids only one nitro group enters the ring, whilst naphthalene tetrasulphonic acids do not undergo nitration under these conditions. The rate of nitration during the entry of the last nitro group is maximal at concentration of sulphuric acid of from 85 to 90 per cent depending on the nature of the compound to be nitrated and the conditions of nitration. On increasing the sulphuric acid content the rate of reaction drops very rapidly and at concentration 100 per cent it is practically zero at normal temperatures).

An analysis of the results ofhis experimentsin the light of BRÖNSTED's concepts led LANTZ to the following conclusions:

(1) The compounds to be nitrated are not passive but participate in the acid–base equilibrium by adding on a proton or positive ion. For this reason the rate of nitration depends not only on the activity of the nitrating agent but also on the structure of the compound to be nitrated: the more groups it contains which give it a basic character the more reactive it is with respect to the "acid" (in this case the nitrating agent).

(2) When nitration with nitric acid is carried out in an aqueous solution of sulphuric acid the undissociated molecule HNO_3 is the nitrating agent; during nitration in anhydrous H_2SO_4 the nitracidium ion is the nitrating agent.

HETHERINGTON and MASSON [34] also conclude, on the basis of kinetic data, that in the nitrating mixture it is the undissociated molecule of HNO_3 which is the nitrating agent. However, as distinct from LANTZ, they think that HNO_3 enters into reaction not with the ionized aromatic compound, but with a complex cation formed by the aromatic compound and nitric acid. Studying the nitration of nitrobenzene with a mixture of nitric and sulphuric acids at various concentrations of the components of this mixture (sulphuric acid, nitric acid and water) HETHERINGTON and MASSON established that the reaction ceased before the nitrobenzene and nitric acid were completely used up if the amount of sulphuric acid present in the reaction mixture was insufficient for the formation of a hydrate $H_2SO_4 \cdot H_2O$ with the water present at the beginning of the reaction and formed in the course of it. The critical point in the nitrating mixture is reached when the sulphuric acid content in relation to the mixture of acids (in moles) equals 0·5. If it is less than this nitric acid participates in nitration only partially. If it is higher, nitric acid nitrates nitrobenzene completely. The nitration of nitrotoluene, which on the whole proceeds much more rapidly than the nitration of nitrobenzene, is characterized by an analogous dependence of the rate of reaction on the concentration of sulphuric acid.

The results obtained by HETHERINGTON and MASSON led them to conclude that the first condition necessary for the reaction to have a perceptible rate was a shift to the right of the equilibrium between the components of the nitrating mixture as expressed in equation (1):

$$H_2SO_4+(H_3O)^++NO_3^- \rightleftarrows (H_3O)^++(HSO_4)^-+HNO_3 \qquad (1)$$

Considering further the work published earlier by one of the authors [35] HETHERINGTON and MASSON maintain that nitrobenzene can form complexes with sulphuric and nitric acids [see equations (2) and (3)]; the reaction mechanism consists of the entry of the cation of these complexes $(C_6H_5NO_2H)^+$ into reaction with nitric acid to give dinitrobenzene [equation (5)].

$$H_2SO_4+C_6H_5NO_2 \rightleftharpoons (C_6H_5NO_2 \cdot H)^+(HSO_4)^- \qquad (2)$$

$$HNO_3+C_6H_5NO_2 \rightleftharpoons (C_6H_5NO_2 \cdot H)^+(NO_3)^- \qquad (3)$$

$$(C_6H_5NO_2 \cdot H)^++H_2O \rightleftharpoons C_6H_5NO_2+(H_3O)^+ \qquad (4)$$

$$(C_6H_5NO_2 \cdot H)^++HNO_3 \rightleftharpoons C_6H_4(NO_2)_2+(H_3O)^+ \qquad (5)$$

As the sulphuric acid is used up the equilibrium expressed by equation (1) is shifted to the left and this lowers the concentration of anhydrous nitric acid. The marked slowing effect of water discovered experimentally is explained by water not only hydrating acids, but also reacting with the organic cation of the complexes of nitrobenzene with anhydrous acids $(C_6H_5NO_2H)^+$ [equation (4)], removing this ion from the sphere of reaction and thus hindering the formation of dinitrobenzene according to equation (5).

Thus, in the opinion of HETHERINGTON and MASSON the nitrating agent is the undissociated molecule of nitric acid, which not only enters the reaction with the formation of a complex with nitrobenzene, but also reacts with the active ion of this complex $(C_6H_5NO_2H)^+$ giving the corresponding dinitro compound. The role of sulphuric acid consists of hindering the dissociation of nitric acid, and it participates on an equal basis with nitric acid in the formation of the active ion $(C_6H_5NO_2H)^+$.

USANOVICH *et al.* [36] studied the electro-conductivity of binary systems one of whose components was nitric acid, and found that the activity of these mixtures was determined by the amphoteric nature of nitric acid and the acidic–basic functions of the components. Thus, for example in relation to water, nitric acid displays its properties of a strong acid; in relation to sulphuric acid, however, it behaves as a substance with marked basic properties. Experiments showed that nitric acid forms a double compound with CH_3COOH and CCl_3COOH, acting apparently as an acid in relation to CH_3COOH and as a base in relation to CCl_3COOH. Nitric acid does not react at all with $CH_2ClCOOH$ and $CHCl_2COOH$ indicating the absence in these mono- and dichloro substituted acetic acids of any acidic-basic functions with respect to nitric acid.

An interesting fact emerges from consideration of the action of nitrating mixtures on aromatic hydrocarbons. It is seen that nitration of these compounds is facilitated by the addition to nitric acid of substances such as H_2SO_4 or H_3PO_4, i.e. substances in relation to which HNO_3 is a base; conversely the addition to nitric acid of substances in relation to which it is an acid, such as water, nitrobenzene and others, hinders the nitration of aromatic compounds. Since nitric acid forms nitracidium cations $[NO(OH)_2]^+$ and $[N(OH)_3]^{++}$ by interaction with acids, and the nitrate anion by interaction with bases, the fact mentioned above bears out that these cations are in fact the nitrating agents in aromatic nitration, whilst the nitrate anion is inert. Converse effects are observed in the nitration of aliphatic compounds, viz. dilution with water or acetic acid (substances in relation to which HNO_3 is an acid) facilitates the nitration of these hydrocarbons. It indicates that the nitrating agent in the case of aliphatic compounds is NO_3^-.

In order to verify his views on the action of nitrating mixtures USANOVICH investigated, in three series of experiments, the nitration of aromatic hydrocarbons (using toluene) in the presence of three sorts of solvents—bases, acids and indifferent substances in relation to HNO_3.

In the first series of experiments the nitration of toluene was carried out in the presence of acetic acid and nitrobenzene with variations in the ratios of the components of the nitrating mixture. The nitration was performed with heating on a water bath at 90–92°C for 3½ hr; under these conditions nitric acid nitrated not only the aromatic ring but also the side chain (compare with the findings of KONOVALOV and SHORYGIN, Chapter III, Section 2). The formation of phenylnitromethane increases (with a corresponding decrease in the yield of ring-substituted nitro products) with increased concentration of solvents. In acetic acid solution the highest yields of phenylnitromethane is obtained when a nitrating mixture of 20 per cent HNO_3 and 80 per cent CH_3COOH is used. In nitrobenzene solution the maximum yield of phenylnitromethane is given by a mixture of 30 per cent HNO_3 and 70 per cent $C_6H_5NO_2$. Di- and poly-nitro compounds are formed simultaneously with phenylnitromethane. When toluene is nitrated with mixtures containing 80–90 per cent CH_3COOH and

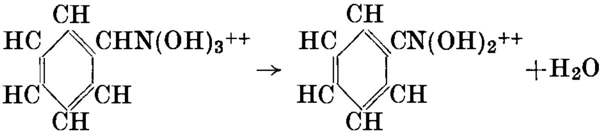
5–10 per cent HNO_3 ring-substituted nitro compounds are formed almost exclusively. This is explained by the fact that in the first case the nitration of the ring by the concentrated nitric acid proceeds much more rapidly than that of the side chain; in the second case, with 5–10 per cent nitric acid, its relative amount is insufficient for the nitration of the side chain. The action of HNO_3 on toluene in the presence of acetic acid or nitrobenzene leads to the formation of benzoic acid as well as the nitro products. This indicates that HNO_3 under these conditions acts as an oxidizing agent as well, especially with large excess of solvent.

In the second series of experiments the nitration of toluene was carried out in the presence of sulphuric and trichloracetic acids (with heating on a water bath to 90–95°C for $3\frac{1}{2}$ hr). These experiments revealed that in the presence of these solvents, which act as acids in relation to HNO_3, nitration occurs principally in the ring. The yields of nitrotoluene and dinitrotoluene (the latter is only formed during nitration with a mixture of HNO_3 and H_2SO_4) rise as the relative amount of solvent increases. The maximal yield of nitrotoluene, when nitration is effected with a mixture HNO_3–H_2SO_4, is obtained when the mixture contains from 60 to 40 per cent HNO_3. If the concentration of nitric acid is lowered further the yield of nitrotoluene drops sharply. At concentration of 15 per cent and lower dinitrotoluene is the only reaction product. Dinitrotoluene is not formed when nitration is carried out with a mixture HNO_3–CCl_3COOH; the yield of nitrotoluene in this case is higher than when a mixture of nitric and sulphuric acids is used.

The influence of the solvent on the process of nitration is very marked, and the comparison of the experiments in the first and second series leads to the conclusion that solvents which act as acids in relation to HNO_3 direct the reaction to the benzene ring (nitration by nitracidium cations) whilst solvents which act as bases in relation to HNO_3 facilitate the nitration of the side chain (nitration by NO_3^- anion).

The third series of experiments on the nitration of toluene in the presence of indifferent solvents, monochloroacetic acid and ethyl nitrate, showed that under these conditions both the ring and the side chain undergo nitration. When the relative amount of the solvent is increased the nitrating ability of nitric acid diminishes, and to a greater extent than would have corresponded to the decreased concentration of HNO_3 in the solution. This indicates that nitration occurs at the expense of the NO_3^-, $H_2NO_3^+$ and $H_3NO_3^{++}$ ions, whose concentration rapidly decreases with dilution, and not at the expense of the undissociated nitric acid molecule. (In the latter case the absolute yields of nitro products would have been directly proportional to the concentration of nitric acid.)

Usanovich's explanation of the reaction mechanism of nitration is as follows: aromatic compounds can add on HNO_3 owing to the coordinate unsaturation of their carbon atoms; the coordinate link is formed by the pair of electrons of the coordinately unsaturated carbon atoms. The NO_3^- ion will not add on to benzene because of its negative charge. Nitric acid molecules and nitracidium cations, however, can add on to the benzene ring; this ability should increase with the increase in positive charge associated with the transition from HNO_3 to $N(OH)_3^{++}$. The addition of HNO_3, $NO(OH)_2^+$ and $N(OH)_3^{++}$ to one of benzene ring carbon atoms should increase the mobility of the hydrogen atom associated with that carbon atom. This hydrogen atom then forms a molecule of water with one of the hydroxyl groups from the nitracidum ion.



(1)

The second product of this reaction [equation (1)]—the complex cation $C_6H_5N(OH)_2^{++}$ gives nitro benzene on dilution of the reaction mixture with water [equation (2)]:

$$C_6H_5N(OH)_2^{++} + 2H_2O \rightarrow C_6H_5NO_2 + 2(H_3O)^+ \qquad (2)$$

In the case of aliphatic hydrocarbons, however, where there are no coordinately unsaturated carbon atoms, the NO_3^- ion can add on to RCH_3, but it must first dislodge a hydrogen atom and occupy its place:

$$RCH_3 + NO_3^- \rightleftarrows RCH_2NO_2(OH)^-$$

Owing to the large expenditure of energy involved in this re-grouping, the resultant compound is unstable and breaks down in the reverse direction. In an acid medium, however, the reaction can become irreversible, since the complex anions which are formed can split out the hydroxy group which is then bound by the hydroxonium ion:

$$RCH_2NO_2(OH)^- + H_3O^+ \rightarrow RCH_2NO_2 + 2H_2O$$

The explanation of nitration reaction put forward by Usanovich clarifies the well-known fact that aqueous solutions of nitrates cannot enter into Konovalov's reaction with hydrocarbons in spite of their containing NO_3^- ions.

The work of Halban and Eisenbrand [28] should be mentioned in connexion with the views on the role of the nitrate ion in nitration. These authors studied the absorption spectra of nitrates and of solutions of nitric acid of various concentrations in water and other solvents (sulphuric, perchloric, phosphoric and acetic acids). According to their findings the spectra of greatly diluted aqueous solutions of HNO_3 reveal close similarity to the spectra of nitrates, i.e. the light absorption of these dilute solutions depends on the presence of the NO_3^- ions. The spectra preserve their similarity to those of nitrates up to the concentration of nitric acid of 10 N (60 per cent HNO_3); at this concentration a substantial change occurs in the character of the spectrum, indicating a transition from the nitrate (ionic) form to a different form of nitric acid. Studies of the partial pressures of nitric acid vapour over aqueous solutions of the acid disclose that at concentrations of about 10 N, the content of undissociated molecules of nitric acid is still very small. Halban and Eisenbrand therefore suppose that the change in the spectrum at concentration 10 N is caused by the formation of associated or complex ions. If the former suggestion, which is the more likely one, is accepted, aqueous solutions of HNO_3 of medium concentration should exist in equilibrium as expressed by the equation:

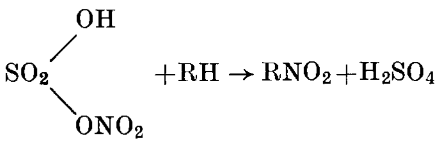
$$H_3O^+ + NO_3^- \rightleftharpoons \underset{\substack{\text{Associated}\\ \text{ionic pair}}}{H_3O^+NO_3^-} \rightleftharpoons HNO_3 + H_2O$$

Studies of spectra of HNO_3 solutions in ether and in acetic acid lead the authors to the conclusion that in these solutions nitric acid consists mainly (60 per cent) of optically similar associated ions ($H_3O^+NO_3^-$) or complex ions ($H_2NO_3^+$); the remainder of the nitric acid is in the undissociated form (pseudo acid).

The study of the spectra of HNO_3 in solutions in sulphuric acid reveal that starting with aqueous solutions of sulphuric acid and gradually raising the concentration of the acid the same effects are observed as in the case of aqueous solutions of HNO_3. As higher concentrations of sulphuric acid are approached, the spectra become analogous to the spectra of esters. At the point of transition to anhydrous H_2SO_4 (if, for example, the concentration of sulphuric acid is raised by the gradual addition of SO_3) there is a sudden lowering of absorption. In this case, Halban and Eisenbrand consider that the spectrum corresponds not to the nitracidium sulphate, but to a mixed anhydride of H_2SO_4 and HNO_3. It should be noted that Markovnikov [37] expressed his views much earlier on the role in nitration of the mixed anhydride of sulphuric and nitric acids (nitrosulphuric acid solution in excess sulphuric acid) formed during nitration in the nitrating mixture.

$$H_2SO_4 + HNO_3 \rightarrow HOSO_2ONO_2 + H_2O$$

Owing to the high reactivity of the nitric acid particle contained in nitrosulphuric acid, the nitrating mixture is a powerful nitrating agent. The formation of the mixed anhydride is proved by the evolution of heat on mixing the acids and by the action of the nitrating mixture on organic compounds. Whereas HNO_3 reacts with tertiary carbon atoms of the aliphatic series at 0°C, the nitrating mixture only acts on the latter when heat is applied. On the other hand, aromatic compounds are much more readily nitrated by a mixture of acids than by HNO_3. Markovnikov explains this by the greater readiness of the nitro group in the mixed anhydride to enter double decomposition reactions as compared with HNO_3. Nitration by nitrosulphuric acid according to this author proceeds as follows:



$$SO_2\begin{cases} OH \\ ONO_2 \end{cases} + RH \rightarrow RNO_2 + H_2SO_4$$

However, the formation of an intermediate product has not been proved by him.

Klemenz and Scholler [38] approach the question of the mechanism of aromatic nitration with HNO_3 from a completely original point of view. They consider nitration as an oxidation-reduction process (Fergusson [39] shares this point of view). They compare the following processes:

$$HNO_3 + 2H \rightarrow HNO_2 + H_2O$$

$$HNO_3 + RH \rightarrow RNO_2 + H_2O$$

Studying the kinetics of the nitration of phenol with nitric acid in aqueous solution as well as in ether, they found that the reaction was catalytically accelerated not only by nitrous acid as shown by Martinsen [30] and other investigators, but also by nitrogen oxides, and to a considerably greater extent. On the basis of their conductivity studies on nitrating solutions, Klemenz and Scholler concluded that the catalytic action of nitrogen oxides is explained by their participation in the formation of an intermediate compound (ϵ-acid) which is the nitrating agent. The reaction proceeds with regeneration of NO_2:

$$2HNO_3 + NO_2 \rightleftarrows \underset{(\epsilon\text{-acid})}{H_2N_3O_8} \qquad (1)$$

$$2RH + H_2N_3O_8 \rightarrow 2RNO_2 + NO_2 + 2H_2O. \qquad (2)$$

The authors consider that this intermediate product, which acts as the active agent, is also formed in the presence of nitrous acid which serves as a source of NO_2. Thus in their opinion the nitration of phenol in aqueous and ethereal solutions is an autocatalytic process*: oxidation reactions occur together with nitration and lead to the formation of nitrogen oxides and nitrous acid. These are involved in the formation of the nitrating agent—ϵ-acid. This autocatalytic process is analogous to the oxidation of organic compounds by permanganate in the presence of sulphuric acid. Klemenz and Scholler decided to verify experimentally the assumption made by some investigators who ascribe to nitrous acid the role of forming nitrosophenol which is then oxidized to nitrophenol with simultaneous regeneration of nitrous acid:

$$C_6H_5OH + HNO_2 \rightarrow \underset{\text{Nitrosophenol}}{C_6H_4(NO)OH} + H_2O$$

$$C_6H_4(NO)OH + HNO_3 \rightarrow C_6H_4(NO_2)OH + HNO_2$$

Klemenz and Scholler's experiments on the oxidation of nitrosophenol by HNO_3 showed, however, that this reaction had an autocatalytic character, viz. the process was at first slow, then the rate of reaction rapidly increased to be followed by a later decrease. On the other hand during the nitration of phenol in the presence of nitrosophenol they could not discover any positive influence of the latter on the process. These results led Klemenz and Scholler to conclude that the nitration of phenol did not go through the stage of nitrosophenol formation.

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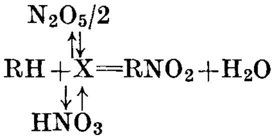
* See above, Chapter I concerning nitration of phenols.

On investigation of the nitration of phenol with nitric acid in concentrated sulphuric acid solution these authors found that the reaction was not accelerated catalytically by the addition of nitrous acid and nitrogen oxides to the nitrating mixture. This indicated that in this case nitration was effected not by ϵ-acid but by some other nitrating agent.

Klemenz and Scholler established that the reaction rate constants were the same for nitration both with nitric acid and nitric anhydride in sulphuric acid if the calculation in the latter case was based on $N_2O_5/2$. In both cases the reaction is bimolecular. Further investigations caused them to conclude that nitration in concentrated sulphuric acid was effected by a nitrating agent X, which was in equilibrium with HNO_3 and N_2O_5:



$$RH+\underset{\underset{HNO_3}{\downarrow\uparrow}}{\overset{\overset{N_2O_5/2}{\uparrow\downarrow}}{X}}=RNO_2+H_2O$$

Taking Wibaut's [40] findings, Klemenz and Scholler adopt the same reaction mechanism for nitration in the presence of acetic acid or of acetic anhydride.*

The earlier works of Sapozhnikov [41] should be mentioned in connexion with the reaction mechanism postulated by Klemenz and Scholler for nitration with nitric acid in sulphuric acid solution. This author explains the nitrating action of the HNO_3–H_2SO_4 mixture (H_2SO_4 content from 70 to 90 per cent) by the presence of nitric anhydride in the reaction mixture, formed as the result of dehydration of HNO_3. On investigating the vapour pressure of mixtures of H_2SO_4 and HNO_3 with varying concentrations of the components (H_2SO_4, HNO_3 and H_2O) he found that the vapour pressure of HNO_3 gradually increased as the concentration of H_2SO_4 in the nitrating mixture was raised, reaching its maximum value at H_2SO_4 concentration of about 60 per cent. He explains this rise in vapour tension of HNO_3 by an increase in the number of particles of free HNO_3 formed as the result of the dehydrating action of sulphuric acid on the hydrates of nitric acid:

$$HNO_3 \,.\, mH_2O+H_2SO_4 \rightarrow HNO_3 \,.\, (m-n)H_2O+H_2SO_4 \,.\, nH_2O$$

On further increasing the concentration of sulphuric acid, a lowering of nitric acid vapour pressure occurs, particularly noticeable at concentration H_2SO_4 around 90 per cent. In Sapozhnikov's opinion this is caused by the more powerful dehydrating action of sulphuric acid leading to the conversion of nitric acid into nitric anhydride. He found that the nitrating mixture corresponding to the maximal vapour pressure of HNO_3 possessed maximal nitrating properties, using the nitration of cellulose as an index.

According to Schaarschmidt [42] the mechanism of nitration with a mixture of HNO_3 and H_2SO_4 consists of the dehydration of nitric acid to

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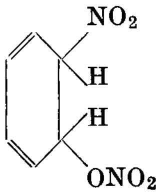
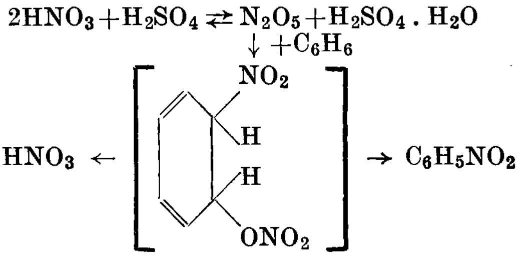
* See above, Chapter I, Section 3.

nitric anhydride followed by its addition to the benzene ring. The dihydro derivative of benzene thus formed:



is an unstable compound and decomposes into nitrobenzene and nitric acid. The latter again undergoes dehydration by sulphuric acid with the formation of the anhydride. Schaarschmidt submits the following scheme for the nitration of aromatic compounds with HNO_3 in sulphuric acid solution



The assumption that HNO_3 and not N_2O_5 adds on to the benzene ring is unlikely according to Schaarschmidt, since it does not explain the part played in this process by H_2SO_4; in his opinion sulphuric acid does not participate in the formation of the complex with benzene. As proof of the influence of nitrogen oxides on nitration, Schaarschmidt takes as an example the nitration of phenol which is accelerated by nitrogen oxides and hindered by mercury nitrate. This action of $Hg(NO_3)_2$ he considers to be due to its hindering the formation of nitrogen oxides. If nitration is carried out in aqueous solutions and in ether it is necessary to add extraneous nitrogen oxides or nitrous acid because in the absence of a dehydrating agent under these conditions they cannot be formed from nitric acid in the way that is possible when nitration is performed in concentrated sulphuric acid.*

A. I. Titov [43] has elaborated an interesting hypothesis based on numerous experiments on the nitration of aromatic compounds with nitric acid. According to this hypothesis the nitration of aromatic hydrocarbons proceeds through a stage of primary interaction of the aromatic ring with various oxygen-containing compounds of nitrogen present in the reaction

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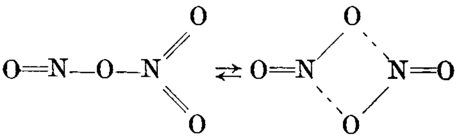
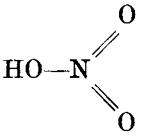
* The latest investigations by Bennet, Brand and Williams [44] have not confirmed the findings of Klemenz and Scholler concerning the existence in nitrating mixture of N_2O_5 as an undissociated molecule (which corresponds also to the views of Sapozhnikov and Schaarschmidt, as mentioned above). By studying the electrolysis of N_2O_5 solution in oleum, Bennet and Brand established that N_2O_5 exists in this solution in an ionized state. The results of Klemenz and Scholler's experiments may be explained by the fact that in H_2SO_4 medium the dissociation of nitric anhydride leads to the formation of the same ions, possessing nitrating properties, as the dissociation of HNO_3.

medium and with the resultant cations. The following electrophilic radicals are in his opinion present in ordinary nitric acid:

$\mathrm{HO{-}N{=}O} \qquad \mathrm{O{=}N{=}O} \qquad \mathrm{O{=}N{-}O{-}N{=}O}$



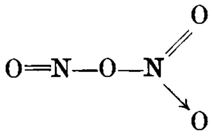


$\mathrm{HO{-}N}\begin{smallmatrix}/\!\!/\,\mathrm{O}\\ \backslash\!\!\backslash\,\mathrm{O}\end{smallmatrix}$

$[\mathrm{N{=}O}] \qquad [\mathrm{O{=}N{-}OH}]$

TITOV considers that the force responsible for the reactions which give nitroso and nitro compounds, favouring the formation of intermediate complexes, is a gain in energy associated with the transfer of electrons from the aromatic compound to the nitrogen atoms of the active agents through the corresponding carbon atoms of the ring.

The difference in electron affinity, which is necessary for the formation of an intermediate complex, depends on the spatial accessibility and coordinate unsaturation of the nitrating and nitrosating agents. Since according to experimental data the coordination number of nitrogen in its oxygen-containing compounds does not exceed 3, the nitrogen atom in the nitric acid molecule is coordinately saturated, showing only a weak electrophilic tendency. In TITOV's opinion this makes the formation of complexes between nitric acid and aromatic compounds difficult. On the other hand, nitrogen atoms in the compounds mentioned above have coordination numbers of 1 and 2, and can display their electrophilic character actively and enter into reaction with the nucleophilic carbon atoms of the aromatic ring. On this basis the highest activity should be shown by the nitrosyl cation $[\mathrm{N{=}O}]^+$ and the nitrosyl nitrate form of the nitrogen dioxide dimer:

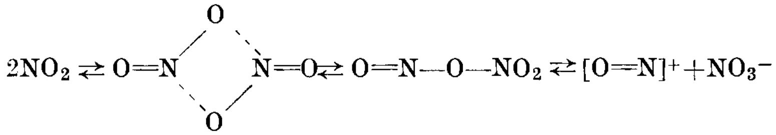


$\mathrm{O{=}N{-}O{-}N}\begin{smallmatrix}/\!\!/\,\mathrm{O}\\ \searrow\mathrm{O}\end{smallmatrix}$

Likewise, the monomer of nitrogen dioxide $\mathrm{O{=}N{\rightarrow}O}$ should show high reactivity (when the primary complexes of this monomer with aromatic compounds are formed there is an additional gain in energy through the exchange interaction of the $—\mathrm{NO_2}$ electron with the mobile electrons of the ring π-bonds).

This theoretical analysis caused TITOV to conclude that nitration with nitric acid goes through a stage of interaction between the aromatic compound and nitrosyl nitrate or the monomeric form of nitrogen dioxide or with the cations formed by them. Nitric acid merely serves as a source of nitrogen dioxide, and also regenerates it from the lower oxides of nitrogen formed during the reaction. Titov considers that such a course of the reaction is only followed up to a certain concentration of nitric acid. On raising it beyond this level the process of nitration occurs with the participation of other agents arising from nitric acid and possessing greater reactivity than NO_2. The author regards the "anhydrous" nitronium cation $[O{=}N{=}O]^+$ as one of such energetic nitrating agents. It contains a highly electrophilic and coordinately unsaturated nitrogen atom. Compounds which contain a $—NO_2$ group which can be easily split off (e.g. $O_2N—OSO_3H$, $O_2N—ONO_2$, etc.) also belong to the group of such agents.

The most energetic nitrating agents (NO_2, $ON—ONO_2$, $[O{=}N]^+$) would be in equilibrium:

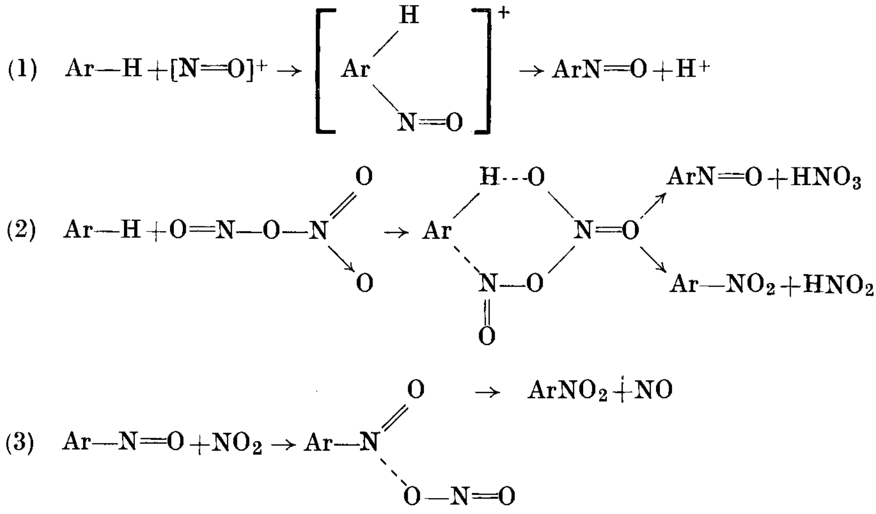


(A) (B) (C) (D)

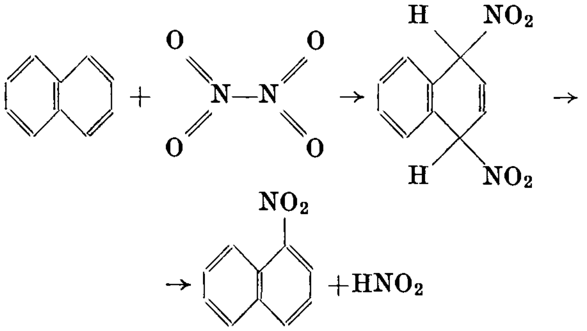
raising the temperature and increasing the dilution will in every case shift the equilibrium in favour of the monomer (A). Increasing the polarity of the medium will also favour the dissociation of the dimer (B), its transition to the polar nitrosyl nitrate form (C), and formation of nitrosyl cation (D).

Taking into account that nitric acid is considerably less reactive than the oxygen containing compounds of nitrogen listed above, Titov suggests that the direct interaction of nitric acid with aromatic compounds can only occur at high temperatures.

He puts forward the following scheme based on the usual conceptions of substitution reaction mechanisms in aromatic compounds:

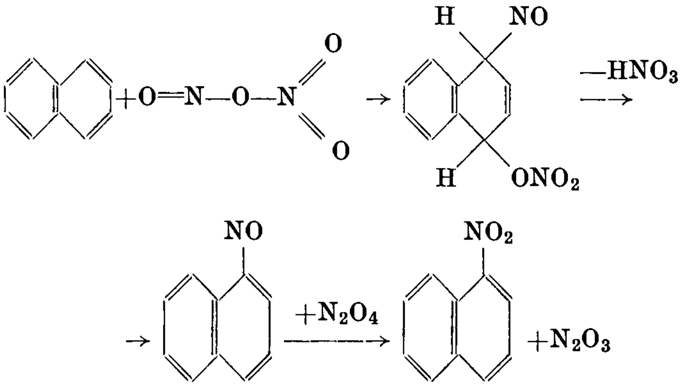


Nitration of compounds of the naphthalene type goes through an intermediate interaction with nitrogen oxides at a relatively high concentration of the nitrating agents even when greatly diluted nitric acid is used. The reaction proceeds according to the equation



$$HNO_2+HNO_3=N_2O_4+H_2O, \text{ etc.}$$

or, if the nitrosyl nitrate formula for the structure of N_2O_4 is taken:



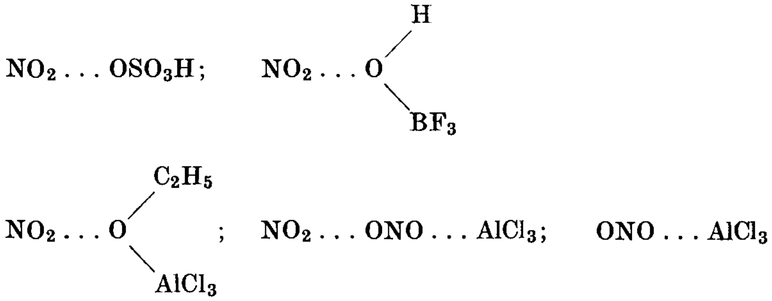
$$N_2O_3+2HNO_3 \rightarrow 2N_2O_4+H_2O$$

TITOV verified his theoretical assumptions experimentally by comparing the action of nitric acid containing a known amount of nitrogen oxides with the action of acid in which nitrogen oxides had been preliminarily destroyed by means of various additions, such as ammonium salts and urea nitrate. In the case of highly reactive aromatic compounds such as, for instance, methyl naphthalenes and anthrocene, salts of hydrazine were used to ensure a more complete removal of nitrogen oxides.

Experiments with α- and β-methylnaphthalene showed that on adding nitric acid (sp. gr. 1·357) the reaction began very quickly, whereas in the presence of hydrazine sulphate even after 4 hr no indication of reaction could be seen. This confirmed that nitration with nitric acid (sp. gr. 1·4 and lower) only occurs in the presence of nitrous acid. Experiments on phenol, cresol, anisole, methyl ester of *m*-cresol, naphthols and their esters, resorcinol, dimethylaniline, phenanthrene, anthracene and their homologues were carried out using nitric acid (sp. gr. 1·357) with and without added hydrazine sulphate. It was confirmed experimentally that in the former case no reaction occurred even after a prolonged period.

TITOV and LAPTEV [45] studied oxidative nitration of aromatic nitroso compounds and arylhydroxylamines (see Chapter I).

Titov [46] established a series of rules concerning the process of nitration of aromatic compounds with nitric acid and nitrating mixture, which comprise the following: benzene and its homologues react slowly with NO_2 and with weak nitric acid, but are easily nitrated by concentrated nitric acid or nitrating mixture, the presence of NO_2 in the latter being immaterial. In the process of reaction with nitric acid, nitration of aromatic compounds takes place not in the organic layer, but in the nitrating mixture. Aromatic nitration is markedly accelerated by the addition of strongly protonic and aprotonic acids ($AlCl_3$, $TiCl_4$, BF_3, H_2SO_4) to the nitric acid. Their positive activating role is due to their enhancing the coordinate unsaturation and electrophilic properties of the nitrogen atom in the nitrating agents. These compounds readily split out the nitronium cation during the chemical interaction:



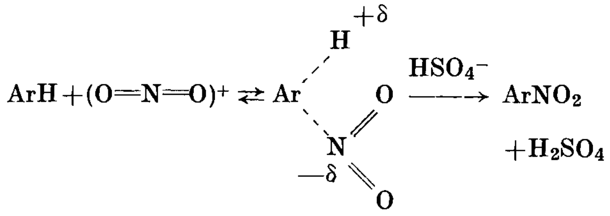
$NO_2 \ldots OSO_3H$; $NO_2 \ldots O(H)(BF_3)$

$NO_2 \ldots O(C_2H_5)(AlCl_3)$; $NO_2 \ldots ONO \ldots AlCl_3$; $ONO \ldots AlCl_3$

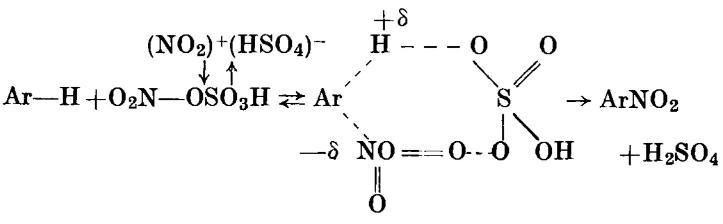
Titov's observations show that the rate of nitration in the vapour phase is much slower that in the liquid phase. Aromatic nitration with moderately concentrated nitric acid is acclerated by the addition of mercury salts. Titov regards nitration of aromatic compounds as an ionic–complex reaction. He suggests the following scheme for the aromatic nitration reaction:

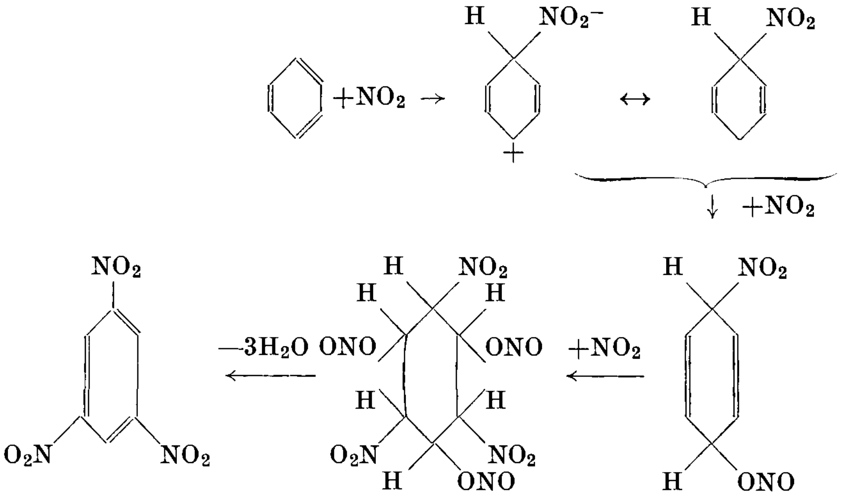
$$HONO_2 + 2H_2SO_4 \rightleftarrows (O{=}N{=}O)^+ + H_3O^+ + 2HSO_4^-$$

$$NO_2^+ + HSO_4^- \rightleftarrows O_2N{-}OSO_3H$$

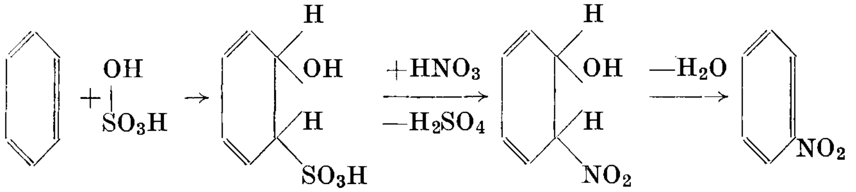


or

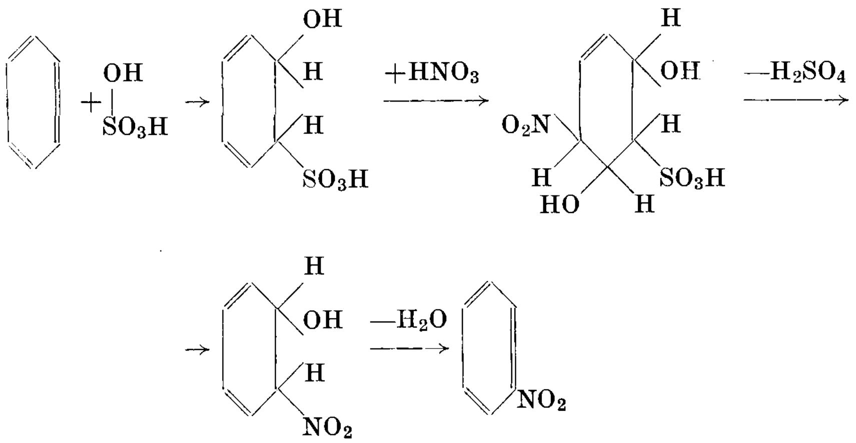




Vorozhtsov [47] considers nitration with nitric acid in the presence of sulphuric acid as an initially additive process. However, unlike the majority of authors, he supposes that the sulphuric acid, as well as the nitric, is capable of entering into the addition reaction. He thinks that in the first stage of nitration an addition product of sulphuric acid and the aromatic ring is formed; this addition product subsequently either exchanges its sulpho group for a nitro group [scheme (A)] or adds on a molecule of nitric acid [scheme (B)]; the double complex obtained in the latter case then undergoes stabilization with loss of water and sulphuric acid:



(A)



(B)

As an example of the ability of the sulpho group to be replaced by a nitro group especially in the presence of a ring-activating —OH group, VOROZHTSOV cites the formation of picric acid during the nitration of phenolsulphuric and disulphonic acids.

Of the works concerned with the kinetics of nitration with nitric acid, those of MARTINSEN and the later ones of TRONOV and G. I. BER merit consideration.

MARTINSEN [30] studied the kinetics of nitration with HNO_3, in the presence of sulphuric acid, of aromatic compounds more or less resistant to the action of HNO_3 (among them nitro compounds). Using nitrobenzene, MARTINSEN showed that the rate of nitration in concentrated H_2SO_4 depended on the concentration of the latter. The rate reaches its maximum at concentration H_2SO_4 around 90 per cent and then drops rapidly at the transition to anhydrous H_2SO_4. (The rate of reaction in 95 per cent H_2SO_4 is three times faster than in 100 per cent.) The rate of nitration rises when hydrogen in the nitrobenzene molecule is replaced by a methyl group and drops if it is substituted by a carboxyl group. This slowing effect of the carboxyl group is diminished by esterification. The nitro group lowers the rate of reaction even more than the carboxyl group.

p-Nitroaniline is nitrated with a mixture of HNO_3 and H_2SO_4 with a simultaneous entry of two nitro groups and formation of picramide. α-Nitronaphthalene undergoes nitration more readily than nitrobenzene. The nitration of phenol in aqueous nitric acid is a complicated autocatalytic reaction; the rate of reaction rises with increased concentration of nitric acid and drops with increased concentration of phenol. The addition of substances containing the NO_3^- ion (nitrates) increases the rate of nitration. Nitrous acid is a positive catalyst in the nitration of phenol. MARTINSEN succeeded in proving the formation of nitrous acid during the nitration of phenol by using a colorimetric method. In his opinion, this explains the autocatalytic nature of this reaction. The nitration of *p*-cresol is also an autocatalytic reaction accompanied by the formation of nitrite.

Further studies of the nitration of various benzene derivatives in the presence of H_2SO_4 disclose that the observed increase in the rate of reaction at the transition from the monohydrate to H_2SO_4 (sp. gr. 1·839) depends on the nature of the substance undergoing nitration.

MARTINSEN obtained the following data (Table 9) in the course of his investigation of the influence of the concentration of sulphuric acid on the rate of nitration of various compounds at 25°C. The substances listed in the table can be divided into two groups. The first comprises compounds for which the rate of reaction increases approximately three times at the transition from the monohydrate (100 per cent H_2SO_4) to sulphuric acid of the composition $H_2SO_4 \cdot 0{\cdot}3H_2O$ (95 per cent H_2SO_4). The second group of compounds is characterized by a considerably greater rate of reaction under these conditions than that seen in the first group. Nitro derivatives and chloronitro derivatives of aromatic hydrocarbons belong to the first group, whilst the carboxyl and sulpho derivatives of aromatic hydrocarbons belong to the second.

The data in Table 9 confirm the view that within certain limits of H_2SO_4

concentration the rate of nitration decreases sharply with a rise in this concentration. The value of the reaction rate constant for the nitration of nitrobenzene decreases during the transition from $H_2SO_4 . 0{\cdot}3H_2O$ to $H_2SO_4 . 0{\cdot}4SO_3$ proportionally to the decrease in the amount of water.

Table 9. The relation of the rate constant for nitration to the concentration of sulphuric acid

Substance	K_1 (for $H_2SO_4 . 0{\cdot}3\,H_2O$)	K_2 (for H_2SO_4)	K_1/K_2
4:6-Dinitro-*m*-xylene	0·0040	0·0014	2·86
p-Chloronitrobenzene	0·18	0·050	3·60
m-Chloronitrobenzene	0·39	0·14	2·78
o-Chloronitrobenzene	7·15	2·18	3·28
Nitrobenzene	1·50	0·37	4·05
2:4-Dinitroanisole	0·17	0·053	3·21
2:4-Dinitrophenol	0·85	0·39	2·18
Benzenesulphonic acid	~26	2·3	~11·30
Benzoic acid	~100	~5·4	~18·50

The various substituents can be arranged in a series according to the character and degree of their influence on the rate of nitration:

$$NO_2 > SO_3H > COOH > Cl < CH_3 < OCH_3 < OC_2H_5 < OH$$

Chlorine occupies the middle position since it sometimes has a slowing and sometimes an accelerating effect. To the right of chlorine are the substituents which raise the rate of nitration, to the left those which lower it. This arrangement discloses that the substituents which slow down the reaction orientate the nitro group to the *m*-position, while those that accelerate the reaction, and also Cl, orientate the nitro group to the *o*- or *p*-position.

It has been established on the basis of kinetic findings that the nitration of nitrobenzene and 2 : 4-dinitrotoluene with nitric acid in sulphuric acid is a reaction of the second order.

MARTINSEN carried out a series of experiments in the presence of phosphorus anhydride in order to verify the views held by some authors (SCHAARSCHMIDT, SAPOZHNIKOV and others) concerning the part played by H_2SO_4 as a dehydrating agent in the process of nitration with nitrating mixture. The experiments showed that phosphorus anhydride had no effect on the rate of reaction, from which it could be inferred that the dehydrating action of sulphuric acid was not a factor determining the rate of nitration.

BONNER *et al.* [48] studied the nitration of nitrobenzene and *p*-chloronitrobenzene and found that the relative rates of nitration of these compounds changed little with variation in the concentration of sulphuric acid. The optimal concentration was 90·4 per cent.

OGATA [49] studied the reactivity of various aromatic compounds. He found that during the nitration of 2-phenylanthraquinone, 1-anthraquinone carboxylic acid and naphthanthraquinone the nitro group enters the benzene or naphthalene ring. Some of the compounds investigated can be arranged in the following series according to their reactivity:

$$C_6H_5CH_2COOH > C_6H_5SO_3H > C_6H_5NO_2 > 2,4\text{-}(NO_2)_2C_6H_3CH_3$$

Tronov and Ber [50] studied the kinetics of the nitration of aromatic compounds in nitrobenzene solution with molar ratios $HNO_3 : C_6H_5NO_2 = 1 : 2$. The experiment was performed as follows: the substance was dissolved at 0°C in a mixture of 2 moles nitrobenzene and 1 mole HNO_3 after which the solution was allowed to stand for some time at 16–18°C. Samples of the liquid were taken at definite intervals of time and the amount of unreacted nitric acid was determined by titration. The relative rate of nitration of the different compounds was calculated by the interval of time in the course of which the same percentage of nitric acid was used up. The rate of reaction was measured three times, viz. after 5, 15 and 25 per cent of nitric acid had entered the reaction. Their experiments showed that the substituents have an accelerating or decelerating effect on the rate of the reaction, and that this action is not uniform over the various stages of nitration. The authors obtained three series of substituents arranged according to their effect on nitration. These three series correspond to the moments at which 5, 15 and 25 per cent of nitric acid had entered the reaction. To the right of hydrogen, which corresponds to unsubstituted benzene, are the substituents which slow down the reaction, to the left those which accelerate it.

(1) For the moment of entry into reaction of 5 per cent HNO_3:

$$CH_3CO > Cl > CH_2Cl > Br > C_2H_5 > H <$$

$$< CH_3 < C_6H_5CH_2 < CH_2CN < CN < C_6H_5CO < NO_2$$

(2) For the moment of entry into reaction of 15 per cent HNO_3:

$$CH_3CO > CH_2Cl > Br > H < C_2H_5 < CH_3 < C_6H_5CH_2$$

(3) For the moment of entry into reaction of 25 per cent HNO_3:

$$CH_3CO > \ldots > C_2H_5 > H < CH_3 < Br < Cl$$

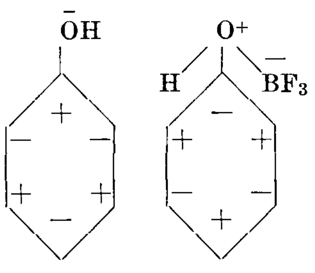
The authors' experiments showed the absence of simple interdependence between the rate of reaction and the orientating effect of the substituents, which had been previously assumed. For example, the methyl group, which orientates *ortho* and *para*, shows a decelerating effect on nitration; the replacement of H in the methyl group by Cl, which increases the yield of the *m*-derivative, accelerates the reaction. Diphenylmethane gives almost exclusively *o*- and *p*-nitro compounds and reacts more slowly than toluene; halogens at first accelerate nitration but with time their effect becomes reversed. Only those groups which orientate strongly to the *m*-position adhere completely to the rule and slow down the reaction very markedly (NO_2, CN, CH_2CN, C_6H_5CO). The acetyl group which orientates less definitely, has a powerful accelerating effect. The second and particularly the third methyl groups have an opposite effect to that of the first methyl group, markedly accelerating nitration: *o*-, *m*- and *p*-xylenes undergo nitration 1·6–1·9, 4·5–4·9, 5·7–10·5 times more rapidly than toluene. Mesitylene and pseudocumene are nitrated even more rapidly.

During the nitration of bromo and nitro derivatives of biphenyl oxide [51] the introduction of the nitro group into position 4 is easier than into position 1.

Nitration of phenylthiazoles with HNO_3 and H_2SO_4 at 0°C gave exclusively the *p*-nitro derivative, whilst the nitration of benzyl alcohol gives only the *m*-nitro derivative [52].

TERENTIEV's and KEDROV's investigation [53] shows that the concentration of sulphuric acid used in nitration plays a significant part in the direction of the entry of the nitro group into the ring. They found that when acetanilide is nitrated with nitrating mixture with 78·8 per cent instead of 100 per cent H_2SO_4 the yield of *p*-nitroacetanilide diminishes with a simultaneous increase in the yield of the *o*-isomer.

TOPCHIEV, ALANIA and SCHNEIDER [54] studied the influence of boron fluoride as a catalyst on the nitration of phenol and aniline. The investigation was carried out as follows. Phenol was saturated with BF_3 to constant weight, after which the complex of phenol with BF_3 was placed in a round-bottomed flask and nitric acid was added at a temperature of 5–20°C with constant stirring. On the completion of the reaction the resultant mixture of nitrophenols was treated with a 20 per cent solution of alkali to destroy the complex. The nitration of phenol in the presence of BF_3 was effected with anhydrous, 20, 10 and 5 per cent HNO_3, with and without solvent. The results showed that in the presence of BF_3 up to 9·4 per cent *m*-nitrophenol is formed, whereas nitration of phenol with dilute nitric acid without BF_3 gives only the *o*- and *p*-isomers. The presence of BF_3 thus not only affects the position at which the nitro group enters the ring, but also increases the yield of the nitro products. This divergence from the rule of orientation is explained by the authors as follows: the hydroxyl group in the benzene ring increases the density of the electron cloud around the *ortho* and *para* C atoms of the benzene ring. When monosubstituted benzene is treated with an electrophilic reagent the electrophilic group of that reagent (in the case of the nitration of phenol the —NO_2 group) goes to that atom of the benzene ring which has an increased electron density. The formation of the complex of BF_3 and phenol affects the distribution of electron density in the benzene ring; it will be diminished at the *ortho* and *para* carbon atoms and hence these positions will be made passive, since a trivalent positively charged oxygen atom is formed in the complex with BF_3:



Because the position occupied by the incoming substituent is determined by the relative rates of three simultaneously competing reactions and the *o*- and *p*-positions are made passive, the likelihood of the new substituent entering the *m*-position should be increased. This has been confirmed experimentally with both phenol and aniline. Nitration of aniline with nitrating mixture in the presence of BF_3 gave a yield of 98 per cent of the theoretical of mononitroanilines, consisting of 67·2 per cent *m*-isomer, 12·8 per cent and 20 per cent *o*- and *p*-isomers respectively.

Modic [55] studied the question of the relation of isomers obtained on nitration of 2 : 5-dichloronitrobenzene and 2 : 5-dibromonitrobenzene in sulphuric acid of various concentrations at different temperatures. The results of these experiments, based on the determination of the infrared spectra of the reaction mixtures, are given in Table 10.

Table 10. *Ratios of the different isomers obtained during nitration of dichloronitrobenzene and dibromonitrobenzene*

Concentration H_2SO_4 (%)	Temperature (°C)	Dichloronitrobenzene		Dibromonitrobenzene	
		m-/*o*-	*o*-/*p*-	*m*-/*o*-	*o*-/*p*-
Fuming	100	3·7	0·45	18·6	0·07
96·2	100	2·4	0·77	—	—
95·0	100	2·0	0·95	—	—
89·0	100	1·6	1·2	—	—
96·2	140	1·7	0·91	—	—
Fuming	140	4·7	0·33	—	—
96·8	100	—	—	3·6	0·38
90·0	100	—	—	1·7	1·4
96·8	120	—	—	2·6	0·67
96·2 (+$KHSO_4$)	100	2·0	0·89	—	—
96·2 (+$KClO_4$)	100	1·9	0·98	—	—
Fuming HNO_3 +20% $HClO_4$	100	1·4	1·6	1·6	1·4

Westheimer and Kharasch [56] studied the kinetics of aromatic nitration in sulphuric acid, and found that the main factor influencing the rate of reaction was the acidity of the reaction medium. The acidity was optimal in their experiments at concentration $H_2SO_4 = 90$ per cent, which agrees with the earlier findings of Martinsen. While determining the rate constants for the nitration of nitrobenzene in sulphuric acid of moderate concentration at 25°C, Westheimer and Karasch found that these constants increased with a drop in sulphuric acid concentration from 95·6 to 90 per cent. On further decrease of H_2SO_4 concentration there is a sharp fall in the rate constant, which at 80 per cent H_2SO_4 is diminished 3000 times as compared with 90 per cent H_2SO_4.

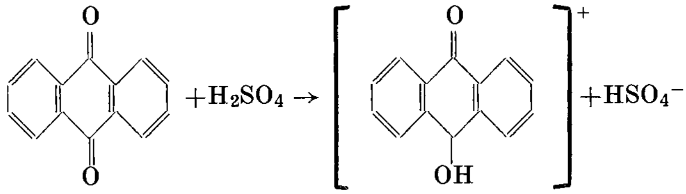
Westheimer and Kharasch then studied the effect of various additions on the rate of nitration and found that substances which did not alter the acidity of the medium, e.g. dinitrobenzene and phosphoric anhydride, did not affect the rate of reaction. The addition of potassium bisulphate, which is basic in relation to H_2SO_4 (it increases the concentration of HSO_4^- ions) affects the rate of nitration differently depending on the acidity of the medium. In solutions whose acidity is above the optimal level (at concentration H_2SO_4 above 90 per cent) the added bisulphate lowers the acidity approximating it to the optimum and thus has a favourable effect on the rate of nitration; in less acid solutions (below optimal level) the bisulphate lowers the acidity still further and so diminishes the rate of reaction. The addition of nitric acid has an analogous effect, since it too is basic in relation to sulphuric acid. If the solvent is 90 per cent sulphuric acid, i.e. the acidity is optimal, the added nitric acid lowers the rate of reaction; in solutions above optimal acidity nitric acid brings it down nearer the optimal level and so accelerates the reaction. The optimal concentration of sulphuric acid rises to 91 per cent on raising the reaction temperature from 25 to 40°C; conversely, lowering the temperature shifts the optimum towards lower concentrations of sulphuric acid. Nitration of dinitromesitylene and dinitroxylene has also been studied and it was found that the curves for the change in the rate of reaction in relation to the concentration of sulphuric acid for these compounds show maxima at the same concentrations as the maximum observed in the case of nitrobenzene (the experiments being carried out at the same temperature).

Two possible mechanisms were considered in connexion with the question of ionization mechanism determining the nitrating action of nitric acid in sulphuric acid solution:

$$HNO_3 + H_2SO_4 \rightleftarrows H_2NO_3^+ + HSO_4^- \qquad (1)$$

$$HNO_3 + 2H_2SO_4 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (2)$$

To discover whether the ionization of nitric acid occurs according to scheme (1) or (2), the ionization of two indicators in sulphuric acid solution was studied; one of these indicators ionizes according to equation (1), the other according to equation (2). Half the first indicator—anthraquinone—changes to the coloured ionic form in 89·7 per cent sulphuric acid:



The second indicator, ionizing as in equation (2)—trinitrotriphenylcarbinol—changes to the coloured ionic form in 90 per cent sulphuric acid:

$$(O_2NC_6H_4)_3COH + 2H_2SO_4 \rightarrow (O_2NC_6H_4)_3C^+ + H_3O^+ + 2HSO_4^-$$

The study of the ionization of these two indicators was carried out at various concentrations of sulphuric acid; the degree of transformation to the coloured form was determined colorimetrically. The curves representing the ionization of anthraquinone and of trinitrotriphenylcarbinol against the range of sulphuric acid concentration of from 80 to 90 per cent, and the curve showing the dependence of the rate constant for the nitration of nitrobenzene in sulphuric acid on the concentration of the latter were superimposed and the curves for trinitrotriphenylcarbinol and for nitrobenzene were found to coincide. The authors deduce* that ionization during the nitration of nitrobenzene occurs according to equation (2), i.e. NO_2^+ being the nitrating agent.

BENNET [57] and a number of other investigators consider the role of sulphuric acid to be as follows:

(1) It is essential for the formation of the nitrating agent (NO_2^+) from nitric acid, and it is surmised that its formation occurs in two stages:

$$2HNO_3 \rightleftarrows H_2NO_3^+ + NO_3^-$$

$$H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O$$

(2) It is a most powerful proton donor.

(3) It serves as a solvent for the hydrocarbon.

GOLD *et al.* [58] studied the kinetics of nitration with nitric anhydride in aprotonic solvents (CCl_4); the authors consider that on the one hand the nitration of the aromatic molecule is effected by nitric anhydride, and on the other, by ionization of N_2O_5 according to the scheme:

$$2HNO_3 \rightarrow N_2O_5 + H_2O;\ N_2O_5 \rightarrow NO_2^+ + NO_3^-$$

the nitronium ion acting as a nitrating agent.

WILLIAMS and LOWEN [59] investigated the nitration of compounds containing an active aromatic ring; in particular they measured the rate of nitration of the trimethyl-*p*-tolylammonium ion in sulphuric acid (at concentrations of 75–82 per cent) over the range of temperature of 17·5–45°C. They found that at 25°C the rate of nitration rose rapidly if the concentration of sulphuric acid was over 80 per cent and approached zero at concentration of sulphuric acid equal to 75 per cent. The nitronium ion is formed under these conditions in amounts sufficient to act as a nitrating agent, but insufficient to enable it to be detected by Raman spectra. BENNET *et al.* [44] found that during electrolysis of nitric acid solution in fuming sulphuric acid the nitric acid was in solution in the form of a cation (as shown by its movement to the cathode). Nitric acid dissociates in fuming sulphuric acid giving NO_2^+ which is an active nitrating agent. The absence of free nitric acid in nitrating mixture is confirmed by the low vapour pressure of nitric acid, which diminishes with decreasing water content. On the addition of water to the mixture the new active form is transformed to the ordinary one with reduction of nitrating capacity. The dissociation of nitric acid in sulphuric acid can be represented by the following equation:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

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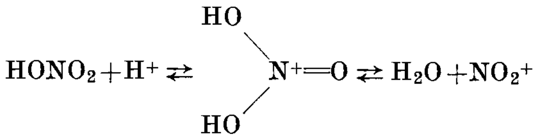
* The author's findings do not provide a basis for their conclusion.

The formation of the nitronium ion [60] evidently occurs through the addition of a proton to HNO_3:



$$HONO_2 + H^+ \rightleftarrows (HO)_2N^+{=}O \rightleftarrows H_2O + NO_2^+$$

Solutions of nitric acid in sulphuric acid have also been subjected to spectrum analysis [61].

Williams and Simkins [62] studied the kinetics of the reversible conversion of guanidine nitrate to nitroguanidine in 71·5–83 per cent sulphuric acid at temperatures of 14·8–35°C. The general kinetic equation for the reaction is:

$$\frac{d[HNO_3]}{dt} = K_2[CH^+] \times [HNO_3] - K_1[PH^+]$$

where CH^+ and PH^+ are the guanidonium and nitroguanidonium ions. The first term of the equation corresponds to the forward and the second to the reverse reaction. The constants K_2 and K_1 increase with higher acidity, and K_2 is considerably more dependent on acidity that K_1. The following relationships have been observed as regards the rate of nitration: with 78·3 per cent H_2SO_4, $K_2 = 1{\cdot}6 \times 10^7 \exp(-13{,}230/RT)$, for 74·5 per cent H_2SO_4, $K_2 = 7{\cdot}71 \times 10^7 \exp(-13{,}790/RT)$, for 81·1 per cent H_2SO_4, $K_2 = 8{\cdot}15 \times 10^5 \exp(-8940/RT)$. Variations in the concentration of nitric acid are almost without effect on the value of K_2. It does show some diminution when the concentration of guanidine is raised. This effect is similar to that of added inorganic salts and both are apparently connected with alteration in the acidity of the medium.

Bennet, *et al.* [63] investigated the kinetics of the nitration of 2 : 4-dinitrotoluene with nitric acid in sulphuric acid of various concentrations, starting from aqueous solutions containing 87·4 per cent sulphuric acid and up to oleum containing 29·1 per cent free SO_3. The reaction temperature was varied from 60 to 120°C. Nitration was carried out in homogeneous media. When the reaction was performed in aqueous solutions of sulphuric acid different amounts of sulphuric acid and water were taken in which small quantities of dinitrotoluene and nitric acid were dissolved. Of the components of nitrating mixture sulphuric acid and water were taken in large excess to ensure a constant medium for the nitration reaction. For example, in the experiments where nitration was carried out in 95·7 per cent sulphuric acid the initial composition of the system was: 0·04 mole dinitrotoluene, 1·8 mole H_2SO_4, 0·02 mole HNO_3 (0·7 per cent of the total nitrating mixture), 0·44 mole water. Thus the amounts of water and nitrous acid formed during the reaction (the latter as the result of an oxidation side-reaction) were so insignificant that they could not appreciably affect the composition of the system and the rate of reaction. Studies were made of the dependence of the rate of reaction on the following factors: (1) composition of the reaction medium; (2) concentrations of the reagents (nitric acid and dinitrotoluene); (3) addition of various amounts of potassium bisulphate and nitrosyl bisulphate.

At constant initial concentrations of dinitrotoluene (0·4 mole) and nitric acid (0·2 mole) and variable composition of the reaction medium—from 87 per cent H_2SO_4 to oleum containing 29 per cent SO_3 the authors found the maximal rate of reaction to be in the medium containing 92 per cent sulphuric acid and 8 per cent water (optimal medium). Studies of the kinetics of the reaction in a heterogeneous medium reveal that in practice the reaction only occurs in the acid layer, since the rate of reaction in the organic layer is very low. The experiments showed that the effect of the concentration of the substance undergoing nitration and of nitric acid, and of the addition of bisulphate, on the rate of reaction was different, depending on whether the sulphuric acid content of the reaction medium was greater or less than the optimal concentration. The bimolecular rate constant rose in media containing more than the optimal concentration of sulphuric acid when: (1) the initial concentration of nitric acid was increased (with constant initial concentration of dinitrotoluene); (2) the initial concentration of dinitrotoluene was increased (at constant initial concentration of nitric acid); (3) the concentration of bisulphate, added as potassium bisulphate or as nitrosyl bisulphate, was increased (at constant initial concentrations of nitric acid and dinitrotoluene). The relations listed under (1) and (2) were also observed in the medium of oleum.

When the reaction media contained less than the optimal concentration of sulphuric acid the bimolecular rate constant decreased (1) with increased initial concentration of nitric acid; (2) with increased initial concentration of dinitrotoluene; (3) with increased concentration of the added bisulphate. In order to explain these results it is assumed that the nitrating agent in all the sulphuric acid media, from oleum to equimolecular mixtures of sulphuric acid and water, is the NO_2^+ ion. In the medium sulphuric acid–water the concentration of the NO_2^+ ion depends on the equilibria (1) and (2)*:

$$HONO_2+2H_2SO_4 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^- \tag{1}$$

$$H_2O+H_2SO_4 \rightleftarrows H_3O^+ + HSO_4^- \tag{2}$$

It was further assumed that the nitration was complete when there was not only the addition of the NO_2^+ ion to the aromatic ring but a proton was given off from the ring to a special acceptor as well, i.e. the reaction medium displays both acidic and basic properties. Thus the rate of nitration was determined by the frequency of collisions between the dinitrotoluene molecule, the NO_2^+ ion and the proton-acceptor molecule. The bisulphate ion can be the most active acceptor in sulphuric acid–water medium. However, it is not the only acceptor, since the rate constant for nitration in 100 per cent sulphuric acid is only three times smaller than its maximal value in 92 per cent sulphuric acid. The sulphuric acid molecule is considered to be the most probable proton acceptor; it is able to

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* In mixtures where the molar ratio $H_2O/H_2SO_4 = 1$ the concentration of NO_2^+ ions reaches zero and nitration ceases (nitration can only occur with molar ratios $H_2O/H_2SO_4 < 1$).

undergo autoionization as shown by HANTZSCH. The following is a possible mechanism of participation of sulphuric acid in nitration:

$$H^+ + H_2SO_4 \rightarrow H_3SO_4^+$$

$$H_3SO_4^+ + HSO_4^- \rightleftharpoons 2H_2SO_4$$

Taking the above as a basis, the nitration of dinitrotoluene can be represented by the following equations:

$$CH_3C_6H_3(NO_2)_2 + NO_2^+ + HSO_4^- \rightarrow CH_3C_6H_2(NO_2)_3 + H_2SO_4 \quad (3)$$

$$CH_3C_6H_3(NO_2)_2 + NO_2^+ + H_2SO_4 \rightarrow CH_3C_6H_2(NO_2)_3 + H_3SO_4^+ \quad (4)$$

The reason for the decrease of the rate constant at a level of acidity above the optimal can be explained from this point of view by the lowering in bisulphate ion concentration as the sulphuric acid concentration is increased. Hence the addition of bisulphate ion to the reaction mixture when the acidity of the medium is above the optimal level has a positive effect; it restores the concentration of active proton acceptor (bisulphate ion) necessary for the reaction. According to these concepts the lowering of the rate of reaction at acidity levels below the optimal is caused by a decrease in the NO_2^+ ion concentration [formed as in equation (1) above]. The addition of bisulphate ion under these conditions should slow the rate of reaction, since it assists in shifting the equilibrium in equation (1) from right to left, i.e. further lowering the concentration of NO_2^+ ions. The influence of the initial concentration of nitric acid on the rate of reaction is determined by the concentration of bisulphate ion in the system, its increase leads, as can be seen from equation (1) to a rise in the concentration of the bisulphate ion. Therefore in those cases where the increase of bisulphate ions has a favourable effect on the rate of reaction the same is true for increased initial concentration of nitric acid, whilst in cases where the bisulphate ion effect is negative, the rate of reaction drops if the initial concentration of nitric acid is increased. When nitric acid acts on an aromatic compound in the presence of oleum the main proton acceptors are the sulphuric acid molecule and the pyrosulphate ion, as represented by the following equations:

$$CH_3C_6H_3(NO_2)_2 + NO_2^+ + H_2SO_4 \rightarrow CH_3C_6H_2(NO_2)_3 + H_3SO_4^+$$

$$CH_3C_6H_3(NO_2)_2 + NO_2^+ + HS_2O_7^- \rightleftharpoons CH_3C_6H_2(NO_2)_3 + H_2S_2O_7$$

In the absence of sulphuric acid the NO_2^+ ion can be formed according to the equation:

$$3HNO_3 \rightleftharpoons NO_2^+ + H_3O^+ + 2NO_3^-$$

TITOV [46] gives a different explanation for the maximal rate of reaction at a definite concentration of sulphuric acid. He points out that the cations formed by the combination of aromatic substances with a proton, e.g. $C_6H_5NO_2H^+$, should enter into substitution reactions with much more difficulty than the corresponding neutral molecules.

VOROZHTSOV [64] gives an equation for the rate of reaction. The overall rate of reaction corresponds to the equation:

$$\frac{d[\mathrm{TNT}]}{dt} = K[\mathrm{DNT}]\times[\mathrm{NO_2^+}]\times[\mathrm{HSO_4^-}]+K'[\mathrm{DNT}]\times[\mathrm{NO_2^+}]\times[\mathrm{H_2SO_4}]$$

where [TNT] and [DNT] are the concentrations of trinitrotoluene and dinitrotoluene, and K and K' are the rate constants whose values are independent of the medium (concentration of sulphuric acid). Since the concentration of NO_2^+ can be found from the expression for the equilibrium constant:

$$\mathrm{HNO_3+2H_2SO_4 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^-}$$

$$K_c = \frac{[\mathrm{NO_2^+}][\mathrm{H_3O^+}][\mathrm{HSO_4^-}]^2}{[\mathrm{HONO_2}][\mathrm{H_2SO_4}]^2}$$

with $[\mathrm{HNO_3}] = [\mathrm{NO_2^+}]+[\mathrm{HONO_2}]$ (concentration of nitric acid equal to the sum of the concentrations of nitronium cation and remaining undissociated $HONO_2$) the part Q of nitric acid transformed to NO_2^+ equals:

$$Q = \frac{[\mathrm{NO_2^+}]}{[\mathrm{HNO_3}]} = \frac{1}{1+\dfrac{[\mathrm{H_3O^+}][\mathrm{HSO_4^-}]^2}{K_c[\mathrm{H_2SO_4}]^2}}$$

Whence

$$[\mathrm{NO_2^+}] = Q[\mathrm{HNO_3}]$$

and the equation for the rate of nitration can be written as

$$\frac{d[\mathrm{TNT}]}{dt} = K[\mathrm{HSO_4^-}]+K'[\mathrm{H_2SO_4}][\mathrm{DNT}][\mathrm{HNO_3}]Q$$

The equation for the bimolecular reaction corresponds to the rate of reaction at constant concentration of sulphuric acid:

$$\frac{d[\mathrm{TNT}]}{dt} = K_2[\mathrm{HNO_3}][\mathrm{DNT}]$$

Therefore the rate constant of the bimolecular reaction equals

$$K_2 = K[\mathrm{HSO_4^-}]+K'[\mathrm{HS_2O_4}]/Q$$

Since during nitration in sulphuric acid and in oleum H_2SO_4 and the $HS_2O_7^-$ ion can act as proton acceptors, the equation of the rate of nitration can be generally (both for dilute sulphuric acid and for oleum) expressed as:

$$\frac{d[\mathrm{TNT}]}{dt} = (K[\mathrm{HSO_4^-}]+K'[\mathrm{H_2SO_4}]+K''[\mathrm{HS_2O_7^-}])[\mathrm{DNT}][\mathrm{HNO_3}]Q$$

The concentration of $HS_2O_7^-$ is calculated on the assumption that the equilibrium constant for the reaction:

$$\mathrm{H_2SO_4+H_2S_2O_7 \rightleftarrows H_3SO_4^+ + HS_2O_7^-}$$

equals 1.

As already mentioned, the solvent plays an important part in the process of nitration. In this connexion the work of HOLSTED and LAMBERTON [65] is among those which merit attention. These authors studied nitration in various solvents without sulphuric acid. They showed that the nitration of urethane, methylurethane and urea was irreversible in acetic acid–acetic anhydride medium. Nitration of urethane, methylurethane and urea in $(CH_3CO)_2O : CH_3COOH = 24 : 1$ medium at 25°C over 1 hr gives yields of nitro derivatives of up to 60–80 per cent. Nitration of urethane at 25°C over 20 hr in media with ratios of $(CH_3CO)_2O : CH_3COOH = 1 : 1$ and $1 : 19$ gives yields of the nitro derivatives of 80 and 40 per cent respectively. Nitration fails to take place in a system acetic acid–water with the ratio $CH_3COOH : H_2O = 199 : 1$. When the corresponding nitro amides are dissolved in the solvents indicated above no free nitric acid is detected. Nitration of urethane in 60 per cent $HClO_4$ is reversible. Equilibrium for urethane at 70°C is reached after 20 min. The yield of nitrourethane is 53 per cent.

In the works of BENNET *et al.* [63] cited above it is suggested that nitration occurs as a trimolecular process:

$$NO_2^+ + ArH + HSO_4^- \rightarrow ArNO_2 + H_2SO_4$$

In such a process the removal of a proton from the aromatic ring must be of substantial importance for the kinetics of the reaction, inasmuch as it requires the presence of a base. MELANDER [66], in order to verify this suggestion studied the nitration of toluenes containing tritium in various positions and concluded, on the basis of his results, that the main suggestion put forward by BENNET *et al.* was untenable. MELANDER obtained 2 : 6-dinitrotoluene by the nitration of 2-T-toluene, the active and inactive derivatives being formed in equal quantities. This fact can only be explained by a very rapid splitting off of the proton in the general process of nitration, so that this stage of the process does not determine the general rate of reaction. Were the course of the reaction that of a one-stage trimolecular process the quantities of the active and inactive dinitrotoluenes would have been unequal because of the presence of an isotopic effect. MELLANDER confirmed by these experiments that nitration did not take place as a trimolecular reaction.

INGOLD and co-workers have made extensive studies of the kinetics and mechanism of aromatic nitration. These authors [67, 68] studied nitration with nitrating mixture $(HNO_3+H_2SO_4)$, nitric acid alone and nitric acid in organic solvents (nitromethane and acetic acid). The chief experimental facts so found are listed below.

When aromatic compounds are nitrated with nitrating mixture the reaction is of the second order:

$$\text{Rate in } H_2SO_4 = K[HAr][HNO_3] \qquad (1)$$

This is established on nitration of nitro-substituted benzenes, benzoic acid, benzenesulphonic acids and anthraquinones.

Nitration with nitric acid alone is a reaction of the first order:

$$\text{Rate in } HNO_3 = K_1[HAr] \qquad ([HNO_3] = \text{const}) \qquad (2)$$

This is established on nitration of nitrobenzene, *p*-chloronitrobenzene and 1-nitroanthraquinone.

When nitromethane or acetic acid is used as solvent the nitration of aromatic compounds sufficiently reactive to electrophilic substitutions takes place as a reaction of zero order, whilst that of weakly reactive ones occurs as a first-order reaction:

$$\text{Rate in } CH_3NO_2 = K_0 \qquad ([HNO_3] = \text{const}) \tag{3}$$

(established on nitration of benzene, toluene and ethylbenzene).

$$\text{Rate in } CH_3NO_2 = K_1[HAr] \qquad ([HNO_3] = \text{const}) \tag{4}$$

(established on nitration of *p*-dichlorobenzene and 1 : 2 : 4-trichlorobenzene).

When aromatic compounds of intermediate reactivity are nitrated in organic solvents the reaction is of fractional order (from 0 to 1):

$$\text{Rate in } CH_3NO_2\text{: intermediate between rates given in equations (3) and (4)} \tag{5}$$

(established for halogen substituted benzene).

It was further shown that the nitration of aromatic compounds with nitric acid and especially in organic solvents was accelerated by the addition of sulphuric acid and slowed down by the addition of dissociating metallic nitrates. A linear relationship is observed between the addition of sulphuric acid and the rate of nitration, as well as between the addition of nitrate and the reciprocal value of the rate of reaction. It should be emphasized that both these additions only influence the rate of reaction without altering its order (first in the case of nitration with nitric acid, and zero or first in CH_3NO_2 or CH_3COOH solvents).

The influence of water was also investigated. The addition of a small amount of water also decreases the rate of nitration in solvents without altering the order of the reaction. As in the case of added nitrate the reciprocal value of the rate of reaction changes linearly with the concentration of water. In general, the effect of adding relatively small quantities of water is very small as compared to the effects of sulphuric acid and nitrate. It must be stressed that the preservation of the order of reaction is only observed when the additions of water are small. The addition of large quantities of water changes the reaction of zero order (e.g. nitration of benzene with nitric acid in organic solvent) to a reaction of the first order.

On investigation of the effect of varying the composition of the reaction medium on the rate of nitration in organic solvents it was found that an increase in the nitric acid content caused a sharp rise in the rate constant of both the zero and first order. It was also found that the rate constants for nitration of both these orders were considerably higher when nitromethane, and not acetic acid, was used as solvent. As regards the effect on the order of reaction it was found that lowering the concentration of nitric acid led to a change in the kinetics of the reaction from that of zero to first order. The order of the reaction changes from zero to first when the concentration of nitric acid is kept constant whilst nitromethane is replaced by acetic acid as solvent.

INGOLD *et al.* arrived at a number of conclusions, based on their experimental findings, concerning the mechanism of aromatic nitration with nitric acid both in the presence of organic solvents and in their absence: their first conclusion concerns the zero order of nitration in organic solvents of aromatic compounds which are sufficiently reactive to electrophilic substitutions. Such kinetics of nitration, in this case, indicate that the rate of reaction depends on some preliminary process occurring without the participation of the substance undergoing nitration and able, because of the solvent present, to take place sufficiently slowly to be the rate determining stage for the overall reaction. This preliminary process does not include the solvent itself, since chemically different solvents produce the same effect. Therefore this preliminary process must involve only nitric acid itself. The change that it undergoes occurs at a measurable rate which determines the rate of nitration of zero order. Such a change cannot consist merely of the migration of a proton, since in oxygen-containing acids this occurs instantaneously. The authors therefore conclude that this preliminary process occurring with certain activation energy must involve the cleavage of a bond. The laws of orientation and the effect of substituents on reactivity established during the nitration of aromatic compounds obviously confirm the electrophilic character of this reaction; the authors therefore consider that the cleavage of a bond in the nitric acid molecule must be of a heterolytic nature. Only this can lead to the formation of an electrophilic nitrating agent, viz. a group of atoms with a nitrogen atom deficient in electrons. The simplest realization of this can be seen in the following equation:

$$O_2N{-}\vdots{-}OH \rightarrow O_2N^+ + HO^- \qquad (1)$$

However, the fact that the addition of acids stronger than nitric markedly increases the rate of nitration led the authors to suppose that the heterolytic fission was preceded by the acceptance of one proton by the nitric acid molecule, transforming it into the $H_2NO_3^+$ ion. Subsequent fission of this ion would occur according to the equation:

$$O_2N \vdots OH_2^+ \rightarrow O_2N^+ + OH_2 \qquad (2)$$

and lead to the formation of the nitronium ion NO_2^+. Thus the proton taken up by the nitric acid molecule is evidently supplied by the stronger acid present in the system, and the whole mechanism of the first stage of nitration—formation of the nitronium ion—may be expressed by the equation (3):

$$\left.\begin{array}{ll} (a) & HNO_3 + H_2SO_4 \rightleftarrows H_2NO_3^+ + HSO_4^- \\ (b) & H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O \\ (c) & H_2O + H_2SO_4 \rightleftarrows H_3O^+ + HSO_4^- \end{array}\right\} \qquad (3)$$

In the absence of acids stronger than nitric, the latter acts itself as a proton donor, forming the nitrate ion:

$$\left.\begin{array}{ll} (a) & HNO_3+HNO_3 \rightleftarrows H_2NO_3^+ + NO_3^- \\ (b) & H_2NO_3^+ \rightleftarrows NO_2^+ + H_2O \\ (c) & H_2O+HNO_3 \rightleftarrows HNO_3 \, . \, H_2O \end{array}\right\} \quad (4)$$

Such a scheme for the formation of the nitronium ion makes it possible to explain the kinetics of aromatic nitration established by INGOLD *et al.* The second order of nitration in sulphuric acid is due to the rapid formation of the nitronium ion in its presence, since the equilibrium of stage (*b*) process (3) is shifted strongly from left to right. When nitration is effected with nitric acid alone (i.e. without a strong acid) the nitronium ion is also formed rapidly, but only in small equilibrium concentration. This concentration remains constant during the process of nitration, which leads to a reaction of the first order with respect to the substance undergoing nitration. For the same reason nitration in organic solvents of weakly reactive aromatic compounds is a reaction of the first order with respect to these compounds. Actually, even if under these conditions the small equilibrium concentration of nitronium ions is formed slowly it is still conceivable that the rate of this process is much greater than that of their entry into reaction with the aromatic substances undergoing nitration. As a result the concentration of the nitronium ion will be stationary and approach the equilibrium concentration, which signifies kinetics of the first order with respect to the compound to be nitrated. Of particular interest is the possibility of finding, on the basis of the scheme proposed, the reason for the nitration of sufficiently reactive aromatic compounds in organic solvents following the kinetics of zero order. This is determined by the fact that the relatively slowly formed (in organic solvent) nitronium ion reacts immediately with the highly reactive aromatic compound. Hence the rate of nitration will be equal to the rate of formation of the nitronium ion. This latter, however, is constant if nitric acid is present in constant excess. Therefore the nitration will be a reaction of zero order.

Further sound experimental confirmation of the proposed scheme for the formation of the nitronium ion is, in the authors' opinion, the diminution of the rate of nitration, both of zero and first order, on the addition of metallic nitrates. This indicates that the formation of the nitronium ion involves also the formation of the nitrate ion and that this reaction can be shifted in the reverse direction by the addition of extraneous nitrate ions. Actually the proposed scheme satisfies this requirement completely, since the reversible stage (*a*) of process (4) includes the appearance of the nitrate ion.

The authors consider the diminution of the rate of nitration of zero order by the addition of metallic nitrates without alteration of the order itself to be particularly significant. The zero order of nitration indicates that all the nitronium ion formed is used up for the nitration of the aromatic compound. This can only be reconciled with the fact that the addition of metallic nitrates diminishes the rate of nitration by assuming that the process of formation of the nitronium ion, which is the stage that determines the rate of the whole nitration reaction of zero order, itself consists of two stages. Moreover, that stage during which the formation of the nitrate ions occurs must be, as indicated above, reversible; the second and final stage in the formation of nitronium ion must be irreversible. Only in this case could the addition of nitrate ions reduce the rate of nitration of zero order without changing the order itself. Thus it is only necessary, in the particular case of nitrations of zero order, to alter schemes (3) and (4) with respect to stages (*b*) which occur irreversibly. The formation of the nitronium ion will now be expressed by equations (3_0) and (4_0):

$$\left.\begin{aligned} &(a)\quad HNO_3^+ + H_2SO_4 \rightleftarrows H_2NO_3^+ + HSO_4^- \\ &(b)\quad H_2NO_3^+ \rightarrow NO_2^+ + H_2O \\ &(c)\quad H_2O + H_2SO_4 \rightleftarrows H_3O^+ + HSO^- \end{aligned}\right\} \qquad (3^0)$$

$$\left.\begin{aligned} &(a)\quad HNO_3 + HNO_3 \rightleftarrows H_2NO_3^+ + NO_3^- \\ &(b)\quad H_2NO_3^+ \rightarrow NO_2^+ + H_2O \\ &(c)\quad H_2O + HNO_3 \rightleftarrows HNO_3 \,.\, H_2O \end{aligned}\right\} \qquad (4^0)$$

These equations lead directly to the proportionality between the concentration of nitronium ions and the equilibrium concentration of the $H_2NO_3^+$ ion. Thus the scheme postulated by the authors explains the experimentally observed linear growth of the rate of nitration on addition of sulphuric acid and the linear growth of the reciprocal of the rate of reaction on addition of metallic nitrates in the case of nitration of zero order. It should be noted that a linear, and not a quadratic, effect indicates that in stage (*a*) of process (3_0) the nitric acid molecule acquires only one proton, whilst in stage (*a*) of process (4_0) only one nitrate ion is formed. In other words during nitration the ion $H_2NO_3^+$ is formed, and not $H_3NO_3^{++}$.

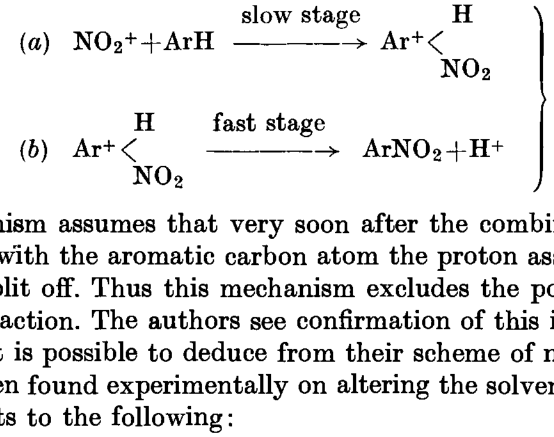
According to schemes (3_0) and (4_0) water only appears in the irreversible stages and if only for this reason its action in nitration of zero order cannot be significant. In order to explain the observed slight inhibitory effect of added water, the authors formulate yet another process for the decomposition of the $H_2NO_3^+$ ion in the reversible reaction:

$$\left.\begin{aligned} &(a)\quad HNO_3 + H_3O^+ \rightleftarrows H_2NO_3^+ + H_2O \\ &(b)\quad H_2NO_3^+ \rightarrow H_2O + NO_2^+ \end{aligned}\right\} \qquad (5^0)$$

It is assumed that the equilibrium for stage (*a*) in process (5_0) is shifted so strongly from left to right that relatively small additions of water can shift it only slightly to the left and consequently only decrease slightly the fixed concentration of the $H_2NO_3^+$ ion. This results in only a small diminution of the rate of formation of the nitronium ion; hence the weak inhibitory action of added water. The linear effect of added water fully corresponds with equations (5^{0}).

Transition to nitration of the first order is associated, in the authors' opinion, with the fact that the reverse interaction of the nitronium ion with water [i.e. the reverse reaction of stage (*b*) in processes (3^{0}) and (4^{0})] proceeds much more rapidly than the interaction of this ion with the aromatic compound undergoing nitration. In this case, therefore, both stages (*a*) and (*b*) of the process of formation of the nitronium ion must be regarded as reversible [equations (3) and (4)]. Nitration of the first order is determined by the fixed concentration of the nitronium ion which is maintained throughout and to which the rate constant of the first order is proportional. As shown by equations (3) and (4) this fixed nitronium ion concentration is proportional to the additions of sulphuric acid and inversely proportional to the additions of metallic nitrates. From this springs the observed linear relation of the rate of nitration of the first order to these additions.

The second stage of nitration, both with nitric acid alone and in the presence of organic solvents, is, according to the authors, the interaction of the nitronium ion with the aromatic compound undergoing nitration. They give the following scheme:



$$\left.\begin{array}{ll}(a) & NO_2^+ + ArH \xrightarrow{\text{slow stage}} Ar^+\langle^{H}_{NO_2} \\ (b) & Ar^+\langle^{H}_{NO_2} \xrightarrow{\text{fast stage}} ArNO_2 + H^+\end{array}\right\} \qquad (6)$$

Such a mechanism assumes that very soon after the combination of the nitronium ion with the aromatic carbon atom the proton associated with this atom is split off. Thus this mechanism excludes the possibility of a trimolecular reaction. The authors see confirmation of this in the kinetic effects which it is possible to deduce from their scheme of nitration, and which have been found experimentally on altering the solvents. This conclusion amounts to the following:

The first stage of nitration—formation of nitronium ion as, for example, in scheme (4)—consists of forward and reverse processes. As the result of the forward process three neutral molecules become one neutral molecule and two ions. The reverse reaction gives the opposite result. Consequently such a process of nitronium ion formation must be considerably enhanced during nitration in a more polar medium, since increased solvating properties of the medium should enhance the forward and inhibit the reverse processes.

The second stage of nitration, proceeding as in scheme (6) does not include either the formation or disappearance of ionic charges. Therefore its rate will not depend on the polarity of the medium. It is now possible to predict how alteration of solvent will affect the rate and order of nitration.

It was shown above that the rate of nitration of zero order depends only on the forward processes of nitronium ion formation, and these in turn depend to a great extent on the polarity of the medium. Therefore increasing the nitric acid content or replacing acetic acid by nitromethane (which increases the polarity of the medium) should accelerate nitration, and this has found experimental confirmation.

The rate of nitration of the first order depends on two factors: fixed nitronium ion concentration and the rate constant of the interaction between the nitronium ion and the compound undergoing nitration. The first factor corresponds to the equilibrium concentration which, in its turn, is determined by the reversible conversion of three neutral molecules into two ions and one molecule. It follows that the fixed nitronium ion concentration will grow with increased polarity of the medium. The second factor is insensible to changes in polarity of the medium since the interaction of NO_2^+ with the compound being nitrated is not accompanied by the appearance or disappearance of ionic charges. The sum-total effect of increasing the polarity of the medium should be marked acceleration of nitration of the first order. This, too, has been confirmed experimentally.

As regards the order of the reaction, it is clear that it will be determined by the way in which the overwhelming majority of the nitronium ions will be used up—in the reversible stages of the process of NO_2^+ formation or in the interaction of NO_2^+ with the compound being nitrated. In the former case the reaction will be of the first order, in the latter of zero order. As shown above, the rate of the processes occurring in the first case can be decreased by increasing the polarity of the medium; no such effect will be observed in the second case. Hence the result of increasing the polarity of the medium must be the experimentally observed change of the order of the reaction from first to zero.

Blackall and Hughes [69] extended the mechanism proposed by Ingold *et al.* for the C-nitration of reactive aromatic compounds in organic solvents to N- and O-nitration. The main suggestion made by these authors is that if N- and O-nitration also occurs with the help of the nitronium ion, then nitration of zero order should proceed at the same rate, independently of the nature of the compound being nitrated. The rate of nitration would be determined solely by the rate of formation of the nitronium ion. The latter, other conditions being equal, will be independent of whether N-, C- or O-nitration is taking place.

The experimental results of Blackall and Hughes, testing this hypothesis, are given in Table 11.

Table 11. *Rates of nitration of zero order*
(4 M HNO_3 *in nitromethane at* 24·9°C)

Compound being nitrated	Initial concentration (mole/l.)	Rate (mole/l. × sec.)
Toluene	0·099	$10{\cdot}3 \times 10^{-5}$
Methylpicramide	0·119	$10{\cdot}4 \times 10^{-5}$
Methyl alcohol	0·491	$10{\cdot}2 \times 10^{-5}$

The table shows that the rates of C-, N- and O-nitrations of zero order are in fact similar and therefore the authors' hypothesis of the same reaction mechanism for C-, N- and O-nitration with the nitronium ion has some experimental support.

Further development in the work of INGOLD *et al.* was the study of aromatic nitration with aqueous nitric acid with the addition of stronger acid (sulphuric or perchloric) [70]. 2-Phenylethylsulphonic and benzylsulphonic acids were subjected to nitration under these conditions. The authors consider it most likely that it is the anions of these sulphonic acids that undergo nitration in aqueous solutions; moreover their reactivity (with respect to nitration) is comparable to the reactivity of aromatic compounds whose nitration in organic solvents follows kinetics of zero order. It was found that nitration of the sulphonic acids mentioned, with aqueous nitric acid (with an admixture of perchloric acid) is a reaction of the first order with respect to the aromatic compound. Besides, it was found that alteration of the composition of the reaction medium had a very marked effect on the rate of reaction. Actually, even a small change within definite and narrow limits of the concentration of either the nitric or perchloric acids or of water alters the rate of reaction from very low to very high. There are, therefore, thresholds in the concentrations of the components of the medium beyond which a slow reaction becomes very rapid. In the vicinity of such thresholds the addition of $NaClO_4$ accelerates, whilst the addition of $NaNO_3$ slows down the nitration.

In considering the mechanism of nitration with aqueous solutions of nitric acid the authors first of all discuss the possible changes in nitronium ion formation (as in scheme (40) relative to kinetics of zero order) during the transition from nitration in organic solvents to nitration in aqueous solutions. According to this scheme, water is formed simultaneously with the nitronium ion. This means that on adding sufficient quantities of water this stage must become reversible with a strong shift of the equilibrium to the left. In such a case, therefore, an overwhelming part of the nitronium ion formed will revert to the $H_2NO_3^+$ ion, and only a small part will be available for nitrating the aromatic compound. Thus the transition to aqueous solutions must be associated with a change of the reaction rate from zero to the first order, which is confirmed experimentally. This phenomenon can, however, be explained in a different way. It is possible to assume that the presence of large quantities of water completely suppresses the formation of nitronium ion. As the result of this the nitration will be effected by the less active $H_2NO_3^+$ ion. In order for such nitration to follow kinetics of the first order it is sufficient that, of the two possible reactions involving $H_2NO_3^+$ (splitting off a proton and interaction with the aromatic compound) the first one occurs considerably more rapidly than the second.

Additional data necessary for establishing the mechanism of nitration with aqueous nitric acid were obtained by examining the Raman spectra of the nitrating mixture used by the authors in these experiments. The composition of the mixture was as follows: H_2O 72 mole %, HNO_3 17 mole %, ClO_4^- 11 mole %. Examination of the Raman spectra showed that practically all the perchloric acid was present as H^+ and ClO_4^- ions, whilst most of the nitric acid (up to 96 per cent) was unionized, only 4 per cent (i.e. 0·68 per cent of the whole mixture) being present as nitrate ions. It should be taken into account, however, that examination of the Raman spectra cannot answer the questions concerning the extent to which the nitric acid molecules, functioning as bases, accept protons (split off from $HClO_4$) and exist as $H_2NO_3^+$ ions, nor concerning the extent to which the molecules of water combine with protons to form hydroxonium ions.* Nonetheless, the fact that only 4 per cent of the nitric acid under consideration is present in the ionized state leads to the conclusion that a considerable part of the acid is present as HNO_3 molecules. Actually, even if it is accepted that all the 11 per cent of protons, formed during the ionization of perchloric acid, combine with the nitric acid molecules giving $H_2NO_3^+$ ions, over 5 per cent (of the whole mixture) of molecular nitric acid still remains. This is an important factor, since even small changes in the composition of nitrating mixture, which cannot materially affect the concentration of molecular nitric acid, do cause marked changes in the rate of nitration. This doubtless leads to the inference that in the experiments with aqueous nitric acid nitration by HNO_3 molecules does not take place.

The second conclusion which can be arrived at from the spectral data is that if the $H_2NO_3^+$ ion acts as the nitrating agent then it must be present only in relatively small concentrations; in other words there can be no preferential combination of protons, obtained from perchloric acid, with nitric acid molecules and not with water molecules. In fact, if this occurred, then the concentration of $H_2NO_3^+$ ion could not have been such a sensitive function of the nitrating mixture composition: e.g. it would have to change proportionally to the amount of perchloric acid added, whereas in reality even small increases in the concentration of this acid above a certain value cause a very abrupt rise in the rate of nitration.

The authors explain the thresholds of concentration mentioned above (beyond which the rate of reaction increases abruptly) as follows, accepting the $H_2NO_3^+$ ion as the nitrating agent. They consider three cases:

(1) Concentrations of nitric acid and water remain constant, whereas the concentration of perchloric acid is increased. The protons formed during the dissociation of perchloric acid react chiefly with water, giving hydroxonium ions H_3O^+. In the presence of water the protons combine with nitric acid molecules to a small extent only, since water exhibits more basic properties compared to nitric acid. It should be borne in mind that water also hydrates nitric acid molecules, combining with the positively charged nucleus of the latter. The authors express this by the following formula for the hydrate of nitric acid: $H_2O \ldots HONO_2$. It is not unreasonable to suppose that both the proton and the molecule of nitric acid can give not only mono- but also higher hydrates. As the result of a gradually increasing concentration of perchloric acid, a moment must come when all the water present in the system will be bound in the form

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* This is usually explained by the fact that such ions ($H_2NO_3^+$, H_3O^+) exchange their protons with such great frequency that it prevents the formation of a precisely defined vibrational energy level.

of hydrate. Beginning with this moment all the additional protons (from $HClO_4$) will react with nitric acid forming the $H_2NO_3^+$ ion. Since this ion is the nitrating agent, the rate of nitration will start increasing rapidly from this moment onwards.

(2) Concentrations of water and perchloric acid remain constant, whilst the nitric acid content is increased. As in the preceding case water binds the protons and hydrates nitric acid molecules. Gradual increase of nitric acid content will at a certain moment result in binding of most of the water. Beginning with this moment added nitric acid will interact with protons, forming $H_2NO_3^+$ ions, i.e. abruptly increasing the rate of nitration.

(3) Concentrations of perchloric and nitric acids are constant, the amount of water is increased. In this case at the very beginning of the reaction (in the absence of water) the rate of nitration is maximal, since all the protons formed react with nitric acid, giving $H_2NO_3^+$ ions. Gradual addition of water causes an ever increasing take up of protons to form H_3O^+ ions and reaction rate decreases gradually. When a certain level of water content is reached the number of protons reacting with nitric acid falls steeply and, beginning with this moment, the rate of nitration drops sharply.

On further studies of the nitration of various aromatic compounds with nitric acid in organic solvents INGOLD *et al.* [71, 72] showed that the nitration of phenols, aromatic amines and their alkylated derivatives differs from the nitration of other aromatic compounds. This difference is apparent in the different effect of nitrous acid on the rate of nitration. As we have seen, nitration (in organic solvents) of aromatic compounds which are reasonably reactive to electrophilic substitutions (benzene, toluene, etc.) follows the kinetics of zero order, and the addition of nitrous acid slows the reaction down to some extent. The expression for the rate of reaction in this case is as follows:

$$\frac{d[\mathrm{RNO_2}]}{dt} = K[\mathrm{ArH}]^0\{a+b[\mathrm{HNO_2}]^{\frac{1}{2}}\}^{-1}$$

Nitrous acid acts differently on the nitration of phenols, aromatic amines and their alkylated derivatives. Its addition increases the rate of reaction, and the reaction becomes of second instead of zero order:

$$\frac{d[\mathrm{RNO_2}]}{dt} = K[\mathrm{ArH}][\mathrm{HNO_2}]$$

If nitrous acid is formed as the result of oxidative processes during the nitration of these aromatic compounds the reaction becomes autocatalytic.

Thus a different reaction mechanism, called "special" by INGOLD, is met with in the case of the nitration of phenols, aromatic amines and their alkylated derivatives. It also became apparent that a transition was possible, in the case of these highly reactive substances, from the usual nitration by the nitronium ion to this special mechanism. This transition can be effected by varying the concentration of nitric and nitrous acids. At low concentrations of nitric acid the reaction is strongly catalysed by nitrous acid and follows the kinetics of the second order (see expressions for rate). Gradual increase of nitric acid concentration leads first to a diminution of the catalytic action of nitrous acid, then to its complete cessation when the order of the reaction becomes zero and finally to a slight inhibiting action.

In determining the mechanism of the action of nitrous acid Ingold *et al.* start from the fact that the nitration of phenols and aromatic amines, following the usual laws of orientation, is an electrophilic substitution. Consequently its mechanism must include an electrophilic reagent. Taking into account that the rate of reaction during nitration in the presence of nitrous acid depends on the concentration of the latter (and does not depend on the concentration of nitric acid) the authors reach the natural conclusion that the substance supplying this electrophilic reagent must be nitrous acid itself.

In the work of Ingold referred to, nitrous acid for most of the experiments was prepared by dissolving pure N_2O_4 in nitric acid; it was shown that N_2O_4 dissolved in nitric acid is a strong electrolyte. The nature of the ions formed was established by Goulden and Millen [73] who studied the Raman spectra of the solutions and found that N_2O_4 dissociated not only homolytically but also heterolytically according to the equation:

$$N_2O_4 \rightleftarrows NO^+ + NO_3^-$$

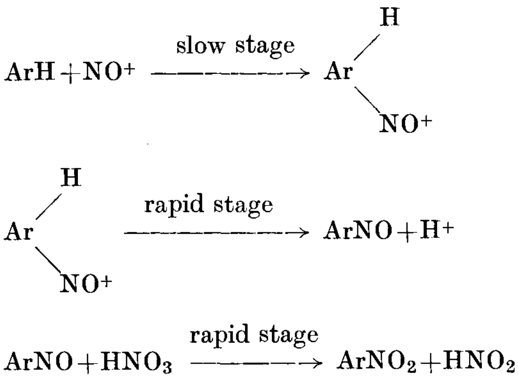
As the result the authors concluded that the electrophilic agent in nitration in the presence of nitrous acid was the nitrosonium ion NO^+. This immediately allowed Ingold to formulate a mechanism for nitration accelerated by nitrous acid by analogy with the mechanism postulated earlier for nitration by the nitronium ion. The first stage of nitration accelerated by nitrous acid is the formation of nitrosonium ion NO^+:

$$HNO_2 + HNO_3 \rightleftarrows H_2NO_2^+ + NO_3^-$$

$$H_2NO_2^+ \rightleftarrows NO^+ + H_2O$$

$$NO^+ + NO_3^- \rightleftarrows N_2O_4$$

The second stage of this reaction is the addition of nitrosonium ion to the compound being nitrated (the slow stage of the reaction) followed by very rapid extrusion of a proton giving a nitroso compound which is then also rapidly oxidized to the nitro compound:



$$ArH + NO^+ \xrightarrow{\text{slow stage}} Ar\begin{matrix} H \\ NO^+ \end{matrix}$$

$$Ar\begin{matrix} H \\ NO^+ \end{matrix} \xrightarrow{\text{rapid stage}} ArNO + H^+$$

$$ArNO + HNO_3 \xrightarrow{\text{rapid stage}} ArNO_2 + HNO_2$$

The school of INGOLD has also considered the long known experimental fact concerning the influence of the concentration of sulphuric acid present in the medium on the rate of nitration.

As already mentioned above, various investigators have stated that the rate of nitration is maximal at sulphuric acid concentration around 90 per cent. The reduction of the rate of nitration on lowering the concentration of sulphuric acid below 90 per cent is at present explained by the associated diminution in the concentration of the nitronium ion. The reason for the reduction of the rate of nitration observed when the concentration of sulphuric acid exceeds 90 per cent remains unclear. The explanation put forward by BENNET *et al.* [63], based on the acceptance of a trimolecular reaction as the determining stage of the process of nitration, has proved to be, according to MELANDER [66], untenable. It has been shown above that INGOLD also denies the existence of a trimolecular reaction in the nitration of aromatic compounds. However, there is another hypothesis in the literature concerning the deceleration of the rate of nitration at sulphuric acid concentrations above 90 per cent which associates this fact with the basic character of the compound being nitrated.

In order to verify this hypothesis and to determine the true reason for the phenomenon observed, GILLESPIE and NORTON [74] studied the influence of the composition of nitrating mixture on the rate of nitration at 25°C of trimethylphenylammonium ion and *p*-chlorophenyltrimethylammonium ion (both as nitrates) and *p*-chloronitrobenzene, which has a basic character. Nitration was carried out in sulphuric acid medium, both aqueous (to 12 per cent H_2O) and containing free sulphur trioxide (to 13 per cent SO_3). It was found that the rate of nitration of all three substances was reduced on increasing the concentration of sulphuric acid from 90 to 100 per cent. It follows from this that the basicity of the compound being nitrated cannot be regarded as the main cause of the reduction in the rate of reaction.

On transition to oleum it became apparent that as the sulphur trioxide content rose, the rate of nitration of the ions increased whilst that of *p*-chloronitrobenzene continued to fall. The latter, in the authors' opinion, is caused by the basic character of *p*-chloronitrobenzene, i.e. the ability of its nitro group to add on a proton. Such a nitro group exerts a more pronounced deactivating influence than an ordinary nitro group.

The authors explain the main fact of the drop in the rate of nitration of all three substances when the concentration of sulphuric acid is changed from 90 per cent up to 100 per cent and the subsequent rise in the rate on transition to oleum by the change in the dielectric constant of the solvent and the change in its solvating properties associated with this. The authors consider that during nitration there is a dispersion of charge, at the moment of transitional state, which is concentrated in the nitronium ion to the aromatic ring. Therefore a diminution of the dielectric constant of the solvent which, as the authors suppose, occurs as the result of the formation of ions when water or sulphur trioxide is added to 100 per cent sulphuric acid, should in fact increase the rate of nitration both on transition from 100 to 90 per cent sulphuric acid and on raising the sulphur trioxide content of oleum. The reaction of nitration and hydroxylation with pernitrous acid discovered by ROBINSON [75, 76] is an example of homolytic as against heterolytic mechanism of nitration. ROBINSON and co-workers showed that the interaction of nitrous acid and hydrogen peroxide produced pernitrous acid, which can nitrate and hydroxylate aromatic compounds. The authors consider that pernitrous acid decomposes homolytically into two free radicals:

$$HO\cdot + NO_2\cdot$$

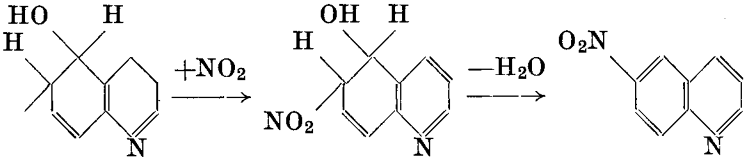
The presence of free radicals is demonstrated by the ability of pernitrous acid to initiate the process of polymerization of methylacrylate. Moreover when pernitrous acid acts on benzene phenol is formed.

Nitration with pernitrous acid is carried out under the following conditions: the aromatic compound (100 g) is mixed with 5 per cent H_2O_2 (100 ml), 3 N HCl (5 ml) and H_2O (250 ml); 5 per cent $NaNO_2$ (150 ml) is added over a period of 30 min, at room temperature and with constant stirring.

ROBINSON and co-workers studied the nitration with pernitrous acid of a series of aromatic compounds: benzene, toluene, chlorobenzene, nitrobenzene, phenol, dimethylaniline, phenetole, phenylpropyl ether and acetophenone. The yield of nitro and hydroxylated derivatives is not large (of the order of 10 per cent).

In their discussion of the possible mechanism of nitration with pernitrous acid the authors reach the conclusion that a heterolytic mechanism in this case is to be rejected. Formation of nitronium ion NO_2^+ is, in fact, unlikely in such weakly acid solutions as those used in this type of nitration. Moreover, the products obtained differ from those formed during nitration of the same compounds with nitrating mixture. Thus, during electrophilic substitution the NO_2 group usually enters the *o*- or *p*- position when suitable orientating groups are present in the molecule (e.g. Cl, OH, CH_3, etc.). During nitration with pernitrous acid, however, the nitro group enters the *m*-position in the presence of the same substituents (e.g. chlorobenzene becomes *m*-nitrochlorobenzene, etc.).

WATERS and collaborators [77] reached identical conclusions; they showed that nitration of quinoline with pernitrous acid gave 6- and 7-nitroquinolines. Heterolytic nitration (with $HNO_3 + H_2SO_4$ mixture) usually gives 5- and 8-nitroquinolines. The authors explain this difference by a homolytic mechanism of nitration with pernitrous acid: the —OH radical enters the α-position, thus allowing the β-position to interact with the —NO_2 group:

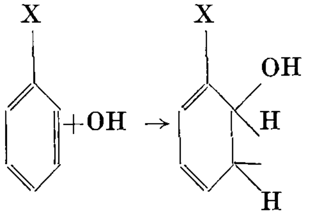


It should be noted that 6- and 7-nitroquinolines had been obtained earlier by Topchiev and Shorygin [78] by the action of NO_2 on quinoline at 100°C. It would seem that in this case also nitration follows a homolytic mechanism.

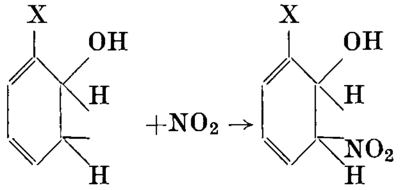
Robinson and collaborators have postulated the following detailed mechanism for nitration with pernitrous acid, based on the results obtained by them. The first stage consists of the decomposition of pernitrous acid to give the —OH and —NO_2 radicals. The former adds on to the aromatic compound, forming an aryl radical [stage (2)], which reacts with NO_2 to give an unstable molecular compound [stage (3)] which decomposes splitting out water, or HNO_2, or H_2 [stage (4)]:

(1) $HOONO \rightarrow OH + NO_2$

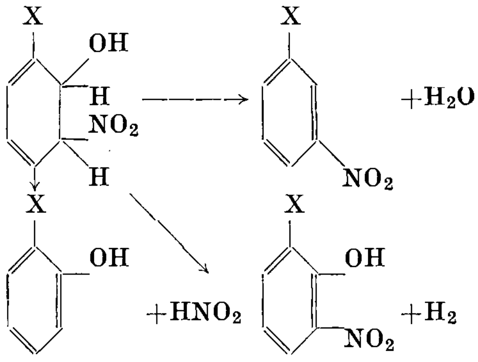
(2)



(3)



(4)



Lauer and co-authors [79] studied the nitration of monodeuterium substituted benzene in order to clarify the question as to whether the loss of a proton during nitration was the rate determining stage of the reaction.

Nitration of monodeuterobenzene, containing 91·5±1·7 mole %, C_6H_5D gives nitrobenzene which contains 74·9±0·7 mole % monodeuteronitrobenzene, and *m*-dinitrobenzene which contains 60·9±2·0 mole % monodeutero-*m*-dinitrobenzene. The decrease in deuterium content is not, as shown experimentally, the result of deuterium exchange reaction, since treatment of ordinary C_6H_6, $C_6H_5NO_2$ and *m*-dinitrobenzene with deuterosulphuric acid leads to only an insignificant introduction of D into these molecules. When C_6H_5D is treated with concentrated H_2SO_4 at 50–60°C the C_6H_5D content drops to 76·7 mole % in less than 1 hr. If the isotope exchange were to reach equilibrium the C_6H_5D content should decrease to 41 mole %. Consequently, the reaction of deuterium exchange proceeds at a slower rate than the reaction of nitration. The authors infer from the results of the experiments that the splitting off of a proton complex formed during the reaction is not a rate determining stage of nitration.

The work of Jones, Thorn, Lyne and Taylor [80] should be mentioned among those dealing with the mechanism of aromatic nitration. These authors studied the absorption spectra of nitric acid, beginning with 80 per cent aqueous solution and up to a solution containing 24 per cent excess N_2O_5. They found that the maximum absorption was in the vicinity 2650 Å and that the intensity of this maximum varied depending on the composition of the solution.

Spectroscopic measurements show that the intensity of absorption rises with increasing concentration of the acid, reaching a maximum value when the water content is 7 per cent (for aqueous solutions); further increase in the concentration of nitric acid is accompanied by a steep fall (minimum at water content of 5 per cent). On still further diminution of water content the intensity of absorption again rises, but on transition to anhydrous nitric acid the absorption maximum becomes diffuse.

The addition of nitric anhydride leads to increasing intensity of absorption, but the maximum becomes progressively less noticeable (at N_2O_5 content of 12 per cent the maximum disappears). These results have been explained by the presence of the following equilibria in the system:

$$NO_3^- + NO_2^+ \underset{-H_2O}{\overset{+H_2O}{\rightleftarrows}} N_2O_5 + H_2O \rightleftarrows 2HNO_3 \underset{-2H_2O}{\overset{+2H_2O}{\rightleftarrows}} 2H_3O^+ + 2NO_3^-$$

Solutions containing 7 per cent water, which give the greatest intensity of absorption, correspond to the greatest concentration of undissociated nitric acid, in the opinion of these investigators. On further reduction of the water content, which leads to the diffusion of the maximum, transition from nitric acid to N_2O_5 occurs with the formation of the equilibrium:

$$2HNO_3 \rightleftarrows N_2O_5 + H_2O$$

(nitric anhydride ionizes partially according to the scheme $N_2O_5 \rightleftarrows NO_3^- + NO_2^+$).

Spasokukotskii [81] interprets the results referred to above in a different way. He proceeds from the supposition that, in aqueous solution, there is in addition to the usual ionization:

$$HNO_3 + H_2O \rightleftarrows H_3O^+ + NO_3^-$$

some degree of simultaneous auto-ionization according to the scheme:

$$3HNO_3 \rightleftarrows NO_2^+ + H_3O^+ + 2NO_3^-$$

The absorption maximum at 2650 Å can be ascribed to the presence of the NO_2^+ ion, in Spasokukotskii's opinion. The process of auto-ionization becomes more and more apparent as the concentration of the acid is increased further. The enhancement of auto-ionization is, however, slower than the decrease of normal ionization with water, and the amount of undissociated nitric acid therefore increases.

As the concentration corresponding to a 7 per cent content of water is reached the formation of nitric anhydride begins according to the scheme:

$$2HNO_3 \rightleftarrows N_2O_5+H_2O$$

Since water is formed in the course of this process the increase in the amount of undissociated acid occurs with disturbance of the auto-ionization equilibrium, which is accompanied by the disappearance from the system of a certain amount of NO_2^+ ions.

As a consequence of this a decrease in the intensity of absorption is observed. When the water content reaches 5 per cent ionization of nitric anhydride begins, associated with increased absorption at wavelengths around 2650 Å. Thus, according to Spasokukotskii, the overall scheme for the processes taking place is expressed by the following system of equations:

$$\begin{tikzcd} N_2O_5+H_3O^++NO_3^- \arrow[r, shift left] \arrow[d, shift left] & 3HNO_3 \arrow[l, shift left] \arrow[r, shift left, "+3H_2O"] \arrow[d, shift left] & 3H_3O^++3NO_3^- \arrow[l, shift left, "-3H_2O"] \text{ (normal ionization)} \\ NO_3^-+NO_2^+ \arrow[u, shift left] & 2NO_3^-+H_3O^++NO_2^+ \arrow[u, shift left] \\ & \text{(auto-ionization)} \end{tikzcd}$$

The present chapter gives a survey of mechanisms postulated in the last three decades for the nitration of aromatic compounds with nitric acid or nitrating mixture. The survey reveals that the initial concept of this reaction being a series of additions and eliminations has been replaced by the recognition that the true process involved in nitration is one of substitution.

Nitration as a process of addition-elimination in Wieland's interpretation (1920–1921) consisted of the addition of nitric acid across the aromatic double bond followed by elimination of water and restoration of the double bond, whilst in the interpretation of Tronov (1924–1929), Nametkin and Zabrodina (1925), as well as of Michael and Carlson (1935) it consisted of the addition of the nitric acid molecule as a whole to one of the aromatic carbon atoms with simultaneous migration of a hydrogen atom from this carbon atom to one of the oxygen atoms of the nitric acid molecule with subsequent elimination of water. The concept of nitration as an addition–elimination process persisted until the end of the 1940's and was generally accepted; only the views regarding the nature of the nitrating agent underwent some modifications, but the elimination of a multi-atom compound continued to be always postulated (water, sulphuric acid, etc.) as against that of only a hydrogen atom in whose place the nitro group should come in as the result of nitration.

The beginning of speculations concerning the nature of the nitrating agent as distinct from the molecule of undissociated nitric acid dates from for work of Hantzsch (1906–1909 and 1917–1926). As already mentioned, HANTZSCH concluded, as the result of cryoscopic and conductivity measurements, that in strong acids in the absence of water there was migration of a proton from one acid molecule to another. As the result of this the molecule acting as a proton donor became a negative ion, whilst the acceptor molecule became a positive ion. In the case of nitric acid this would lead to the formation of the positive ions $H_2NO_3^+$, $H_3NO_3^{++}$ and the negative nitrate ion NO_3^-. In the case of a mixture of two acids, such as nitric and sulphuric for example, the stronger acid will act as proton donor and, consequently, the $H_2NO_3^+$ (or $H_3NO_3^{++}$) and HSO_4^- ions will be formed. These views received considerable confirmation when HANTZSCH obtained the crystalline perchlorates $[H_2NO_3]^+[ClO_4]^-$ and $[H_3NO_3]^{++}[ClO_4]_2^{--}$.

HANTZSCH himself did not study the nitration of aromatic compounds, but his theory of the structure of homogeneous nitric acid and its mixtures with sulphuric acid exerted marked influence on all the subsequent developments in the studies of this process. It became impossible to ignore the presence of ionic formations in nitrating mixture and to confine the process of nitration to the interaction of neutral nitric acid molecules and the compound being nitrated. The highly reactive nature of ionic formations made their participation in the reaction undoubted and it became impossible not to take them into account.

One of the first reflections of this was the view of HETHERINGTON and MASSON who were studying the nitration of nitrobenzene and concluded (1933) that in this reaction there was a preliminary formation of the complex $[C_6H_5NO_2 . H]^+[NO_3]^-$, whose cation interacted with an undissociated molecule of nitric acid to give $C_6H_4(NO_2)_2$ and $[H_3O]^+$. Thus, although these authors consider nitration as an ionic-complex reaction, they do nonetheless accept that the ionic formation is the compound being nitrated which becomes a cation as the result of the addition of a proton, whilst the nitrating agent is the undissociated molecule of nitric acid.

LANTZ subscribed to a similar point of view (1939). He likewise concluded that during nitration in an aqueous solution of sulphuric acid the aromatic compound being nitrated became a cation by adding on a proton and subsequently interacted with an undissociated molecule of nitric acid.

LAUER and ODDA took up a dual position; in their work (1936) devoted to the study of nitration of nitrobenzene and anthraquinone, they made a sharp distinction between the reaction mechanisms depending on whether the reaction took place in aqueous or anhydrous medium. In the first case the nitrating agent in their opinion is the undissociated molecule of nitric acid, whose elements add on across the double bond with subsequent elimination of water. Thus in this instance they adopt completely the mechanism postulated by WIELAND. In the second case, i.e. during nitration in anhydrous solutions of sulphuric acid, the authors maintain that the nitrating agent is the nitracidium sulphate $[H_2NO_3]^+HSO_4]^-$, which adds on across the aromatic double bond to give an intermediate compound. This latter becomes the nitro compound after splitting out water and sulphuric acid. Such a mechanism is in full accord with HANTZSCH's concept of the structure of nitric acid.

USANOVICH (1940) also promulgated the ionic mechanism of aromatic nitration. Accepting HANTZSCH's view about the presence of nitracidium ion in nitrating mixture, USANOVICH considers that the first event in nitration is the combination of this ion with one of the aromatic carbon atoms. The intermediate compound so formed splits out water and a proton, which give H_3O^+, and becomes the nitro compound.

In the early 1940's other authors besides LAUER and ODDA, and USANOVICH also subscribed to the view that the nitrating agent in aromatic nitration was the nitracidium ion. It should be remarked that such a "replacement" of the nitrating agent (nitracidium ion instead of undissociated molecule of nitric acid) was completely consistent with the concept of nitration as an addition–elimination process.

Towards the middle 1940's, however, it could no longer be considered that the nitracidium ion was universally accepted as the nitrating agent. Moreover, various works of the second half of the 1940's gave objective evidence proving that the nitrating agent in aromatic nitration was the nitronium ion NO_2^+, and not the nitracidium ion $H_2NO_3^+$ or $H_3NO_3^{++}$.

EULER [82] was the first to postulate the existence of the NO_2^+ ion as far back as 1903. He again returned to it in 1922 [83]. This ion was also mentioned in the literature in subsequent years [84–86], but up to the work of INGOLD and collaborators [87] in 1946 in which studies were made of the effect of nitric acid on the freezing point of sulphuric acid and of spectra of combination scattering of mixtures of nitric acid with other acids, no objective proof of the existence of the nitronium ion was available.

This work of INGOLD, and of other authors, has not, for the sake of consistency, been considered in this survey of the mechanisms of aromatic nitration even though it provided reliable confirmation of the existence of the nitronium ion, but not through studies of the process of nitration. The basis for these contributions has been the cryoscopic and spectroscopic measurements on mixtures of nitric acid with other acids. It is, however, expedient at the end of this survey to present these proofs of the existence of the nitronium ion in nitrating mixtures as well.

In 1946 INGOLD and co-workers [87], using improved cryoscopic techniques developed since HANTZSCH's time, were able to show that the depression of freezing point of sulphuric acid caused by nitric acid dissolved in it was four times greater than the depression expected for an ideal solution. HANTZSCH, who in 1908 observed a threefold increase in the depression of the freezing point of sulphuric acid when nitric acid was dissolved in it, explained the phenomenon by the conversion of nitric acid into the nitracidium ion:

$$HNO_3 + 2H_2SO_4 \rightarrow H_3NO_3^{++} + 2HSO_4^-$$

INGOLD fully subscribes to the addition of protons to nitric acid proposed by HANZSCH. INGOLD's explanation for the fourfold instead of threefold increase in the depression of freezing point lies in the further decomposition of the nitracidium ion to give nitronium and hydroxonium ions—NO_2^+ and H_3O^+. The overall equation therefore becomes:

$$HNO_3+2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

INGOLD considers that no other explanation can be found for the fourfold depression of the freezing point of the system HNO_3–H_2SO_4. And it is indeed difficult not to agree with this conclusion.

The second objective proof of the existence of the nitronium ion came from the studies of spectra of combination scattering of mixtures of nitric acid with other acids, chiefly sulphuric. The spectra of these mixtures always show two lines (1400 and 1050 cm^{-1}) and their nature excludes the possibility that their source might be the unchanged nitric acid molecule. CHEDIN [88], however, succeeded in demonstrating the presence of these frequencies in the spectrum of combination scattering of homogeneous nitric acid. Consequently their source must be some product formed from nitric acid. CHEDIN succeeded further in discovering that such a product was formed as the result of dehydrating nitric acid and that it was destroyed by the addition of water which led to the regeneration of molecular nitric acid. At the same time SUSZ and BRINER [89] found the frequencies 1400 and 1050 cm^{-1} in the spectrum of combination scattering of nitric anhydride N_2O_5 dissolved in nitric acid, after which it became certain that their source must be a special form of nitric anhydride. In the work cited above BENNET, BRAND and WILLIAMS [44] suggested that such a form was produced on ionization of nitric anhydride; the frequency 1400 cm^{-1} corresponds to nitronium ion, and 1050 cm^{-1} to nitrate ion. Decisive confirmation of this view was obtained by INGOLD and co-workers [87] in 1946. In this work a study was made of the spectra of combination scattering of mixtures of nitric and perchloric and also of nitric and selenic acids. In both cases the frequency 1400 cm^{-1} was observed, whilst the frequency 1050 cm^{-1} was absent and in its place were found the frequencies corresponding to the anions of perchloric and selenic acids. Further investigation by these authors established that the appearance of the 1400 cm^{-1} line was evoked by a source which produced no others. It is known that a single main line in the spectrum of combination scattering can only be given by di-atomic and linearttri-atomic particles with identical end atoms. In the case under consideration only the nitronium ion can be such a particle.

Finally yet another proof of the existence of the nitronium ion can be cited. INGOLD and co-workers [90], using improved technique, repeated HANTZSCH's experiment on the preparation of solid products of interaction of nitric and perchloric acids. As already mentioned above, HANTZSCH ascribed the composition and structure of nitracidium perchlorates to these products. INGOLD, however, demonstrated that in fact these compounds were a mixture of nitronium and hydroxonium perchlorates —$(NO_2)^+(ClO_4)^-$ and $(H_3O)^+(ClO_4)^-$.

Summing up the results of cryoscopic and spectroscopic measurements on nitric acid itself and chiefly on its mixtures with other acids, it can be said that toward the end of the 1940's the existence of the nitronium ion in these media could no longer be doubted. This was, naturally, reflected in the mechanisms subsequently postulated for aromatic nitration. Actually all the mechanisms proposed for this process since the end of the 1940's accept the nitronium ion as the nitrating agent.

The distinguishing and positive feature of the work carried out in this period (TITOV, WESTHEIMER and KHARASCH, WILLIAMS AND LOWEN, BENNET, BRAND and WILLIAMS, TOMLINSON and GROGGINS and more especially INGOLD *et al.*) is the ever growing role of the elucidation of the kinetics of the reaction as well as of its chemical aspects. The majority of the kinetic data on aromatic nitration, as can be seen from the above survey could be satisfactorily explained when the nitronium ion was accepted as the nitrating agent. This applies primarily to so important a kinetic characteristic as the change of the order of the reaction depending on the composition of the nitrating mixture and the solvent. It must be acknowledged that INGOLD and his school elucidated brilliantly these seemingly obscure kinetic peculiarities of the reaction.

It can thus be stated that at the end of the 1940's and beginning of the 1950's not only was the existence of the nitronium ion in nitrating media proved, but it was also used to effect the nitration of aromatic compounds*. Such a replacement of the nitracidium ion by the nitronium ion in the scheme of the reaction mechanism signifies the transition to a concept of nitration as a process of substitution. In fact nitration is now regarded as the combination of the nitronium ion with an aromatic carbon atom with subsequent or simultaneous detachment from this carbon atom of a hydrogen atom linked with it in the form of a proton. It follows that in this case no new substance is formed by the combination of the proton with some part of the combined nitrating agent.

The establishment of such a mechanism as a process of substitution does not determine whether it is effected in a single stage or in a sequential series of two stages. BENNET *et al.* assumed the former, INGOLD and collaborators, the latter. As already mentioned the question was decided by MELANDER's experiments using labelled atoms which demonstrated that nitration occurred in two stages, of which the first one consisted of the combination of the nitronium ion with the aromatic molecule and took place relatively slowly, whilst the second stage consisted of the splitting out of a proton and occurred very rapidly. As the result the rate of the first stage determines the rate of the whole process of nitration.

The material of this chapter shows that the main inference drawn from a long series of studies of the mechanism of aromatic nitration has been that its mechanism is ionic. Such nitration is therefore a heterolytic reaction. As will be shown in the next chapter there are grounds for postulating an entirely different, free radical, mechanism for the nitration of

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* It should be recalled that according to INGOLD, under certain conditions, the nitronium ion is not invariably the nitrating agent. Thus during nitration with dilute nitric acid the nitrating agent is the nitracidium whilst during the nitration of phenols, amines and alkylated derivatives in the presence of nitrous acid it is possible to pass from the usual nitration by the nitronium ion to nitration by the nitrosonium ion.

aliphatic compounds, which is thus a homolytic reaction. Until recently it could be considered that this was the principal difference between aromatic and aliphatic nitration. In recent years, however, the first works have appeared which suggest that such a sharp distinction between the processes of nitration of the two classes of compounds may well need revision. These works of ROBINSON *et al.* and of WATERS *et al.* show that under certain conditions the nitration of aromatic compounds can be effected by the free radical mechanism. The authors succeeded in demonstrating that when a series of aromatic compounds was nitrated with nitrous acid in the presence of hydrogen peroxide the process was homolytic. No mechanism was proposed for such a nitration of aromatic compounds apart from the suggestion that the pernitrous acid formed decomposed into the $—OH$ and $—NO_2$ radicals which "lead" the process:

$$HOONO \rightarrow OH + NO_2$$

It can be assumed, however, that in this case the formation of free radicals occurs in the same way as in reactions involving hydrogen peroxide and ions of variable valency. SEMENOV [91], taking URI's [92] data on free energy changes in the following processes:

$$Fe^{3+} + H_2O_2 \rightleftarrows Fe^{2+} + H^+ + HO_2$$

and

$$Cu^{2+} + H_2O_2 \rightleftarrows Cu^+ + H^+ + HO_2$$

calculated the equilibrium concentrations of the HO_2 radical formed in the systems. These reactions proved to be entirely adequate for the initiation of a chain reaction.

Analogous formation of the free radicals $—OH$ and $—NO_2$ in a system nitrous acid–hydrogen peroxide can be represented as follows:

(1) $HONO \rightleftarrows OH^- + NO^+$
(2) $NO^+ + H_2O_2 \rightleftarrows NO_2 + H^+ + OH$
(3) $OH + HONO \rightleftarrows H_2O + NO_2$
(4) $NO_2 + H_2O_2 \rightleftarrows NO_3^- + H^+ + OH$
(5) $OH + NO_2 \rightleftarrows HNO_3$

The possibility of the dissociation of nitrous acid into the ions OH^- and NO^+ (equation 1) is at the basis of such a scheme. The nitrosonium ion NO^+ becomes a free radical $—NO_2$ by reacting with hydrogen peroxide according to the type of reaction given above for the ions Fe^{3+} and Cu^{2+}; there is also simultaneous formation of the radical $—OH$ (equation 2). In the absence of an aromatic compound reactions 3, 4 and 5 will occur in such a system, and the overall equation for the process will be:

$$2HNO_2 + 2H_2O_2 \rightarrow 2HNO_3 + 2H_2O$$

If, however, an aromatic compound is added to such a system the free radicals $—OH$ and $—NO_2$ will, in addition to interacting according to reactions 3, 4 and 5, enter partially into the reactions:

(6) $ArH + OH \rightarrow Ar + H_2O$
(7) $Ar + NO_2 \rightarrow ArNO_2$

which lead to the formation of nitro derivatives.

Therefore, in those cases where the formation of free radicals in a system becomes possible nitration of aromatic compounds can also follow the radical mechanism.

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CHAPTER III

NITRATION OF SATURATED, AROMATIC-ALIPHATIC AND UNSATURATED HYDROCARBONS WITH NITRIC ACID

As a result of the successful synthesis of nitroparaffins a series of works on their properties has appeared seeking various ways of using them in organic syntheses. Since the material concerning the properties of nitroparaffins is scattered through Soviet and foreign journals we consider it useful to give a brief survey of the subject in this chapter.*

1. PROPERTIES OF NITROPARAFFINS

Almost all the mononitroparaffins are colourless liquids with boiling points 101·7°C and higher. Nitromethane is soluble in water 1 : 10 by volume at 20°C; the solubility of other nitroparaffins decreases with increasing molecular weight (Table 12).

Table 12. *Physical properties of nitroparaffins*

Nitro compound	M.W.	d_{20}^{20}	M.p. (°C)	B.p. (°C)	Vapour pressure at 20°C (mm)	n_D^{20}	Solubility (ml/ 100 ml H_2O)
Nitromethane	61·04	1·139	−29	101·2	27·8	1·3818	9·5
Nitroethane	75·07	1·052	−90	114·0	15·6	1·3916	4·5
1-Nitropropane	89·09	1·003	−108	131·6	7·5	1·4015	1·4
2-Nitropropane	89·09	0·992	−93	120·3	12·9	1·3941	1·7

The majority of organic solvents (aromatic hydrocarbons, alcohols, esters, ketones, ethers, carboxylic acids) are miscible with nitroparaffins.

Nitromethane is an excellent solvent for cellulose esters; so is 2-methyl-2-nitropropane. Mixtures of nitroparaffins and alcohols are good solvents not only for cellulose esters but also for vinyl resins, cellulose ethers and mixed cellulose esters, such as cellulose acetate–butyrate and acetate–propionate.

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* For references to nitroparaffins see:

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For references to nitroolefines see:

V. V. Perekalin and A. S. Sopova. *Usp. khim.* **24**, 5 (1955).

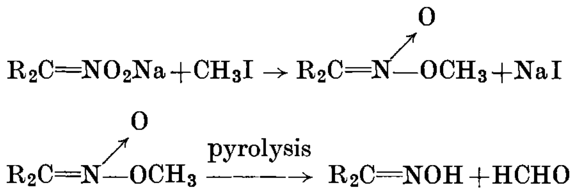
From the chemical point of view nitroparaffins are rather curious substances. They are capable of various transformations and condensation reactions owing to their change to a tautomeric form of "nitronic acid". On condensation with aldehydes they give nitro alcohols which, in turn, can be used in the preparation of esters, ethers, aminoalcohols, etc. Nitroolefines can also be obtained from nitroparaffins; by virtue of their reactive double bond nitroolefines can give various condensation products.

Reduction of Nitroparaffins

The reduction of nitroparaffins to amines can be effected by means of various reagents: zinc, lead and iron in acid medium [1–5], aluminium amalgam [6], etc.; nitroparaffins are hydrogenated in the vapour phase in the presence of Adams' catalyst [7], as well as of nickel, copper and platinum [8]; hydrogenation with Raney nickel also gives good results.

Nitroparaffins are reduced to alkyl hydroxylamines by the action of metals, e.g. Sn and Zn, in the presence of acids [9, 10], or in neutral conditions [11] by the action of $SnCl_2$ [12], and also by catalytic hydrogenation. Nitroparaffins can be hydrogenated to alkyl hydroxylamines [13, 14] in the presence of palladized $BaSO_4$. Electrochemical reduction of nitroparaffins can also give alkyl hydroxylamines [15]. This conversion can also be achieved by the action of metallic alkyl derivatives and halogenated metallic alkyl compounds [16].

Oximes can be obtained from nitroparaffins, for instance, by treating nitroparaffins with zinc dust in the presence of glacial acetic acid [17]. Primary and secondary nitroparaffins can be converted to oximes by pyrolysis of the products of their alkylation to the "nitronic" ester stage:

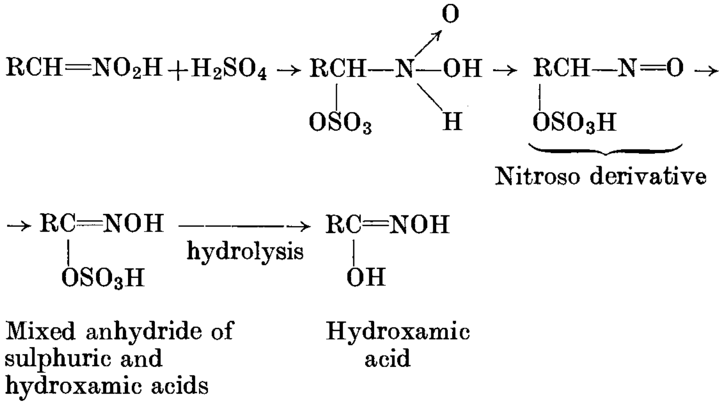


$$R_2C{=}NO_2Na + CH_3I \rightarrow R_2C{=}\overset{\overset{O}{\nearrow}}{N}{-}OCH_3 + NaI$$

$$R_2C{=}\overset{\overset{O}{\nearrow}}{N}{-}OCH_3 \xrightarrow{\text{pyrolysis}} R_2C{=}NOH + HCHO$$

The Action of Mineral Acids on Nitroparaffins

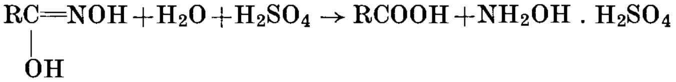
Good yields of carboxylic acids and hydroxylamine salts are obtained when nitroparaffins are treated with concentrated strong mineral acids. For example, acetic acid is synthesized in this way from nitroethane [18] with a 90 per cent yield, propionic acid from 1-nitropropane with a 96 per cent yield, and *iso*butyric acid from 1-nitro*iso*butane with a 90 per cent yield. The reaction gives hydroxylamine salts at the same time, with 86–90 per cent yield. This process is carried out as follows: a mixture of 1 mole nitroparaffin and 1 mole 85 per cent sulphuric acid is refluxed with stirring until an exothermic reaction occurs; heating is continued for 8 hr after the cessation of this reaction. It is supposed that the mechanism of the reaction consists of a preliminary tautomerization of the nitroparaffins to the aci-form (nitronic acid) with the mineral acid adding on across its double bond; the compound formed is converted, by loss of water, to a nitroso derivative; the latter undergoes rearrangement to a mixed anhydride of sulphuric and hydroxamic acids which on hydrolysis gives hydroxamic (alkylhydroxamic) acid:



$$RCH{=}NO_2H+H_2SO_4 \rightarrow \underset{OSO_3}{\underset{|}{RCH}}{-}\underset{\searrow H}{\overset{O \nearrow}{N}}{-}OH \rightarrow \underbrace{\underset{OSO_3H}{\underset{|}{RCH}}{-}N{=}O}_{\text{Nitroso derivative}} \rightarrow$$

$$\rightarrow \underset{\text{Mixed anhydride of sulphuric and hydroxamic acids}}{\underset{OSO_3H}{\underset{|}{RC}}{=}NOH} \xrightarrow[\text{hydrolysis}]{} \underset{\text{Hydroxamic acid}}{\underset{OH}{\underset{|}{RC}}{=}NOH}$$

Hydroxamic acid, in turn, undergoes hydrolysis with the formation of the end-products of the reaction—carboxylic acid and hydroxylamine salt:



$$\underset{OH}{\underset{|}{RC}}{=}NOH+H_2O+H_2SO_4 \rightarrow RCOOH+NH_2OH\,.\,H_2SO_4$$

Some authors have succeeded in isolating alkylhydroxamic acid when treating nitroparaffins with mineral acids; as mentioned above this is an intermediate reaction product.*

Bamberger and Rüst [18] obtained a 2 per cent yield of the corresponding alkyl hydroxamic acid from phenylnitromethane. Lippincot and Hass [19] synthesized propane hydroxamic acid from 1-nitropropane and obtained a 44 per cent yield.

Dilute strong mineral acids acting on nitroparaffins lead to a synthesis of aldehydes and ketones [20]:

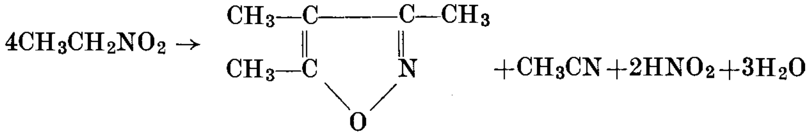
$$2RCH{=}NO_2Na+2H_2SO_4 \rightarrow 2RCHO+2NaHSO_4+N_2O+H_2O$$

$$2R_2C{=}NO_2Na+2H_2SO_4 \rightarrow 2R_2CO+2NaHSO_4+N_2O+H_2O$$

Calcium salts of aci-nitroparaffins react with dilute acids giving better yields than do the sodium salts. Johnson and Degering [21], using calcium salts, converted nitroparaffins to aldehydes and ketones with 80–85 per cent yields.

The Action of Bases on Nitroparaffins

Nitroparaffins react with bases to give trialkyl*iso*xazoles [22]; for example, nitroethane treated with alkali gives trimethyl*iso*xazole:



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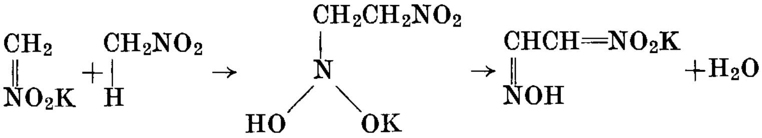
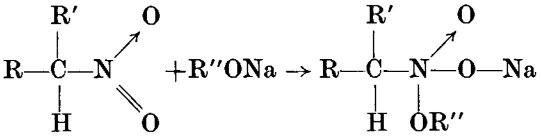
* Hydroxamic acids are used as flotation agents for some copper ores.

As distinct from other nitro paraffins, nitromethane gives methazonic acid. The following scheme is suggested for the reaction:



Nitroparaffins react with sodium alkoxides to give an addition product with the base:



Formation of Halogen Derivatives of Nitroparaffins

Halogenated nitro compounds contain the halogen atom at the same carbon atom as the nitro group. They can be used as oxidizing agents in various reactions. Some of these compounds can be used as fumigating substances against harmful insects.

A variety of methods is available for the preparation of chloro derivatives of nitroparaffins. Monochloronitromethane can be obtained by treating the sodium salt of nitromethane with chlorine water [23]. Chloropicrin [24] is obtained in quantitative yield by chlorination of nitromethane in the presence of an aqueous suspension of $CaCO_3$ which is added in order to maintain a weakly acid reaction. This product can also be prepared by treating nitromethane with the hypochlorites of alkali and alkali-earth metals [25].

Monochloro derivatives of nitroethane, 1-nitropropane, 2-nitropropane and 1-nitro-2-methylpropane can be prepared by passing gaseous chlorine through an aqueous solution of the sodium salts of the aci-nitroparaffins [26, 27]. Chloronitroparaffins are given by the action of nitrosyl chloride NO_2Cl on unsaturated hydrocarbons [28]. Chloronitroparaffins can also be obtained by a variety of other methods, e.g. nitration of chloroparaffins with nitric acid [29, 30], chlorination of nitro olefines [31, 32], action of nitrosyl chloride or hypochlorites on oximes [33], action of PCl_5 on nitro alcohols [26], etc. A method has been developed for the preparation of dichloronitroparaffins by chlorination of nitroparaffins or their monochloro derivatives [34].

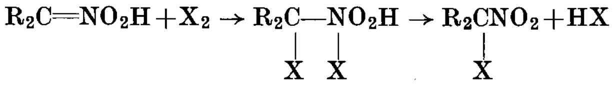
When nitroalkanes are chlorinated photochemically in anhydrous media the chlorine replaces a hydrogen atom attached to a carbon atom other than the one carrying the nitro group. Thus nitroethane gives 2-chloro-1-nitroethane almost exclusively [35].

Of the chloronitro derivatives, 1 : 1-dichloro-1-nitroethane is an insecticide; other chloronitroparaffins are used as selective solvents in the purification of lubricating oils [36].

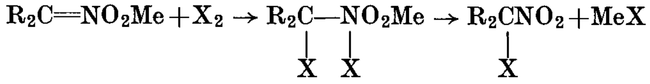
Bromination of nitroparaffins has been thoroughly studied; this reaction occurs so rapidly that it is used as a means of determining the conversion of nitroparaffins into their tautomeric form (nitronic acid).

Iodine derivatives are also easily obtained by direct iodination of nitroparaffins, but the compounds are unstable [37].

The mechanism of halogenation in the presence of a base is thought to consist of an addition of the halogen X to the nitronic acid or its salt, with subsequent loss of HX or MeX:



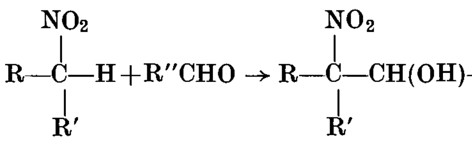
$$R_2C{=}NO_2H + X_2 \rightarrow R_2\underset{\underset{X}{|}}{C}{-}\underset{\underset{X}{|}}{N}O_2H \rightarrow R_2\underset{\underset{X}{|}}{C}NO_2 + HX$$



$$R_2C{=}NO_2Me + X_2 \rightarrow R_2\underset{\underset{X}{|}}{C}{-}\underset{\underset{X}{|}}{N}O_2Me \rightarrow R_2\underset{\underset{X}{|}}{C}NO_2 + MeX$$

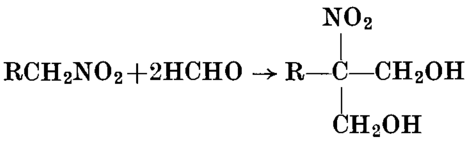
Condensation of Nitroparaffins with Aldehydes (formation of Nitroalcohols)

The condensation reaction between nitroparaffins and aldehydes, first discovered by Henry [38], leads to the formation of very interesting compounds—nitroalcohols, which are of great practical importance. The reaction can be represented generally thus:



$$R{-}\underset{\underset{R'}{|}}{\overset{\overset{NO_2}{|}}{C}}{-}H + R''CHO \rightarrow R{-}\underset{\underset{R'}{|}}{\overset{\overset{NO_2}{|}}{C}}{-}CH(OH){-}R''$$

or for the condensation of nitroparaffins with formaldehyde:



$$RCH_2NO_2 + 2HCHO \rightarrow R{-}\underset{\underset{CH_2OH}{|}}{\overset{\overset{NO_2}{|}}{C}}{-}CH_2OH$$

The condensation of nitroparaffins with aldehydes is of the aldol type and consists of one, two or three hydrogen atoms linked with the carbon atom carrying the nitro group combining with the oxygen atom of the aldehyde to form hydroxyalkyl substituted nitroparaffins. Preliminary tautomerization of the nitroparaffin to the nitronic acid is an essential prerequisite for this reaction. The significance of bases used in very low concentrations as catalysts in this reaction lies in their raising the concentration of nitronic acid, shifting the equilibrium between nitroparaffin and its aci-form towards the formation of the latter as it is used up in the reaction with the aldehyde. This reaction can be carried out most effectively [39] if the aldehyde is replaced by its bisulphite compound and the nitroparaffin by a corresponding sodium salt: the bisulphite compound sets free the nitronic acid without increased hydrogen ion concentration which has a negative effect since it converts the aci-form of the nitroparaffin to its neutral form.

According to VANDERBILT and HASS [40] the following substances can be used as catalysts in the above-mentioned synthesis of nitroalcohols: bases, carbonates, sodium methoxide and sodium ethoxide, sodium sulphite, sodium acetate and borax. These authors found that the activity of an alkaline catalyst was more closely related to its pH than to its concentration in the reaction mixture, e.g. 0·9 per cent NaOH was more active than Na_2CO_3 of higher concentration.

When nitroparaffins are condensed with aldehydes the main process of nitroalcohol formation is accompanied by the following side reactions: (1) aldol condensation; (2) polymerization of the reacting aldehyde; (3) conversion of the nitroparaffin to the *iso*xazole or, in the case of nitromethane to methazonic acid (see above); (4) formation of the corresponding nitroolefine and the product of its polymerization. In order to prevent the first three side reactions it is necessary to use a minimal quantity of the alkaline catalyst. The last side reaction is reduced to a minimum by using low temperatures which do not favour the formation of nitroolefines (VANDERBILT and HASS consider 30–35°C to be the optimal temperature). In addition, the concentration of aldehyde is kept low, adding it gradually to the nitroparaffin, in order to diminish polymerization. This also prevents the formation of hydroxyaldehydes.

On condensation of formaldehyde with nitroparaffins the reactivity of the homologous series of the latter decreases with increasing molecular weight. Nitromethane condenses readily with three molecules of formaldehyde to form $(HOCH_2)_3CNO_2$. The reaction occurs less readily when nitromethane is condensed with other aldehydes, especially if the number of carbon atoms in the aldehyde exceeds five; in the latter case the reaction often stops after combination with one or two molecules of aldehyde.

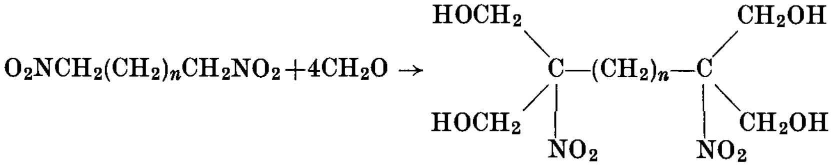
When homologues of nitromethane undergo condensation with acetaldehyde and its homologues only one molecule of the aldehyde combines relatively easily; the others do so with considerably more difficulty. Secondary nitroparaffins react much more slowly, whilst tertiary nitroparaffins, lacking hydrogen atoms in the α-position, do not react with aldehydes at all. The purification of nitroalcohols from the usual admixture of nitroolefines presents no difficulties since the nitroolefines polymerize easily and can be removed as tars [40].

Another interesting method for the preparation of nitroalcohols is the condensation of olefine oxides with nitrites [41–43].

Aliphatic polynitro compounds also condense readily with aldehydes to form polynitro alcohols. Thus, the addition of the potassium salt of dinitromethane to a solution of formalin gives the potassium salt of 2 : 2-dinitropropandiol-1 : 3, from which a 66 per cent yield of 2 : 2-dinitro-propandiol-1 : 3 can be obtained by acidifying with acetic acid [44].

1 : 4-Dinitrobutane, condensed with formaldehyde in the presence of $Ca(OH)_2$ gives 2 : 5-bis-(hydroxymethyl)-2 : 5-dinitrohexandiol-1 : 6 (I) with a 40 per cent yield. The same method of condensation using

1 : 5-dinitropentane and formaldehyde gives 2 : 6-bis-(hydroxymethyl)-2 : 6-dinitroheptandiol-1 : 7 (II) with a 50 per cent yield. Finally, the interaction of 1 : 6-dinitrohexane and formaldehyde gives 2 : 7-bis-(hydroxymethyl)-2 : 7-dinitrooctandiol (III) [45]. The reaction occurs according to the equation:

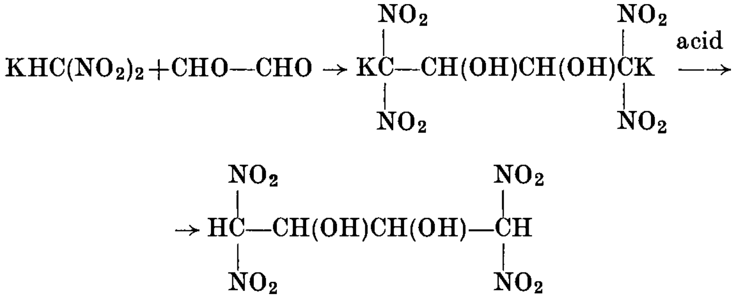


$$O_2NCH_2(CH_2)_nCH_2NO_2+4CH_2O \rightarrow (HOCH_2)_2C(NO_2)\text{—}(CH_2)_n\text{—}C(NO_2)(CH_2OH)_2$$

(I) $n=2$; (II) $n=3$; (III) $n=4$

Trinitroalcohols can be obtained by the interaction of trinitromethane $CH(NO_2)_3$ with aldehydes and ketones. $(NO_2)_3CCH_2OH$ is formed by the interaction of trinitromethane with formaldehyde [46] or with paraformaldehyde [47]. Condensation of trinitromethane with acetaldehyde gives secondary trinitropropyl alcohol $CH_3CH(OH)C(NO_2)_3$ [46].

Tetranitroglycols are formed by the interaction of the potassium salt of dinitromethane with dialdehydes [48]; e.g. condensation of the potassium salt of dinitromethane with glyoxal gives the di-potassium salt of 1 : 1 : 4 : 4-tetranitrobutandiol-2 : 3 which on treatment with dilute sulphuric acid gives 1 : 1 : 4 : 4-tetranitrobutandiol-2 : 3:



$$KHC(NO_2)_2+CHO\text{—}CHO \rightarrow KC(NO_2)_2\text{—}CH(OH)CH(OH)C(NO_2)_2K \xrightarrow{\text{acid}}$$

$$\rightarrow HC(NO_2)_2\text{—}CH(OH)CH(OH)\text{—}C(NO_2)_2H$$

Similarly 1 : 1 : 6 : 6-tetranitrohexandiol-2 : 5 can be obtained from the dinitromethane salt and the dialdehyde of succinic acid.

The following nitro alcohols have received industrial application: $(HOCH_2)_3CNO_2$; $(HOCH_2)_2C(CH_3)NO_2$; $(HOCH_2)C(CH_3)_2NO_2$; $(HOCH_2)_2C(C_2H_5)NO_2$ and $(HOCH_2)CH(C_2H_5)NO_2$.

Of the compounds obtained from nitroalcohols the most important are their esters and aminoalcohols. Esters of nitric acid can be prepared by the action of cold (from 0 to $-20°C$) concentrated nitric acid on nitroparaffins in the presence of sulphuric acid, e.g.

$$(HOCH_2)_3CNO_2+3HNO_3 \xrightarrow{H_2SO_4} (O_2NOCH_2)_3CNO_2+3H_2O$$

The ester of nitric acid and nitroalcohol $(HOCH_2)_3CNO_2$ is highly explosive (7 per cent more than nitroglycerine) [49].

Nitroalcohols react with phosphorus oxychloride giving corresponding esters of phosphoric acid [50]. Esters of phosphoric acid and nitro alcohols are used as plasticizing agents for cellulose esters. Esters of organic acids and nitro alcohols are formed by the action on the latter of acids, acid anhydrides and chloroanhydrides in the presence of sulphuric acid. These esters are used as plasticizing agents.

Aminoalcohols can be prepared from nitroalcohols by reduction with nascent hydrogen from tin and HCl or iron and acetic acid, and also by hydrogenation. Hydrogenations have been carried out with palladium in oxalic acid solution [51] or Raney nickel [52] as catalysts. The following aminoalcohols are in use: $(HOCH_2)_3CNH_2$; $(HOCH_2)_2C(CH_3)NH_2$; $(HOCH_2)C(CH_3)_2NH_2$; $(HOCH_2)_2C(C_2H_5)NH_2$ and $(OHCH_2)CH(C_2H_5)NH_2$. These compounds give highly emulsifying soaps with the higher fatty acids and are thus particularly valuable. It would seem probable then that aliphatic nitroalcohols, as well as their esters and ethers, will be of great technological importance in the future.

As indicated above, aromatic aldehydes in the presence of inorganic bases condense with nitroparaffins to form nitroalcohols. If, however, the condensation is carried out with amines as catalysts [53] the products obtained are nitroolefines:

$$ArCHO + RNH_2 \rightarrow ArCH{=}NR + H_2O$$

$$ArCH{=}NR + RCH_2NO_2 \rightarrow RNH_2 + ArCH{=}C(NO_2)R$$

ω-Nitrostyrene can be prepared in this way from benzaldehyde and nitromethane [54]:

$$C_6H_5CHO + CH_3NH_2 \rightarrow C_6H_5CH{=}NCH_3 + H_2O$$

$$C_6H_5CH{=}NCH_3 + HCH_2NO_2 \rightarrow C_6H_5CH{=}CHNO_2 + CH_3NH_2$$

If the condensation is performed in the presence of alcoholate, an alkali salt of the aci-form of nitroalcohol is formed in the first stage of the reaction which gives the nitroalcohol on being acidified with a weak acid:

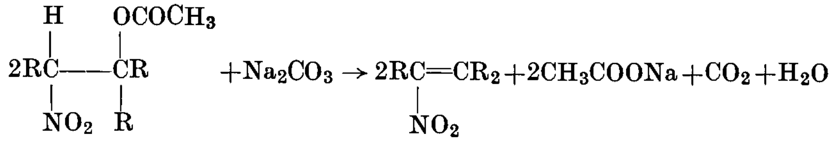
$$ArCHO + CH_3NO_2 + KOH \rightarrow ArCH(OH)CH{=}NO_2K + H_2O$$

The action of mineral acid on the salt of nitroalcohol gives an unsaturated nitro compound [55, 56]:

$$ArCH(OH)CH{=}NO_2K + HCl \rightarrow ArCH{=}CHNO_2 + H_2O$$

$$ArCH(OH)CH{=}NO_2K + CH_3COOH \rightarrow ArCH(OH)CH_2NO_2 + CH_3COOK$$

Nitroolefines can also be prepared from the acetates of nitroalcohols by heating these with carbonates [57]:



$$2R\underset{\displaystyle NO_2}{\overset{\displaystyle H}{C}}-\underset{\displaystyle R}{\overset{\displaystyle OCOCH_3}{C}}R + Na_2CO_3 \rightarrow 2R\underset{\displaystyle NO_2}{C}{=}CR_2 + 2CH_3COONa + CO_2 + H_2O$$

Nitroolefines are also formed by the action of dehydrating agents on nitroalcohols [58]:

$$(HOCH_2)CH_2NO_2 \xrightarrow{NaHSO_4} CH_2{=}CHNO_2+H_2O$$

Phthalic anhydride and a complex catalyst consisting of the orthophosphates of Ca and Mg (10 per cent) are recommended as dehydrating agents [59]. Alkali acting on nitronitrates containing the NO_2 and ONO_2 groups on adjacent carbon atoms also gives nitroolefines from nitroalcohols [60].

Nitroolefines in turn can undergo various conversions: for example, they can be reduced to the corresponding amines. 1-Phenyl-2-nitropropene-1 gives a 40 per cent yield of the corresponding amine when hydrogenated in the presence of Raney nickel [61]. Hydrogenation of ω-nitrostyrene in the presence of platinum oxide gives β-phenetylamine with a 93 per cent yield; 3 : 4-methylene-dioxy-ω-nitrostyrene and 3-nitro-ω-nitrostyrene also give their corresponding amines when similarly hydrogenated [7].

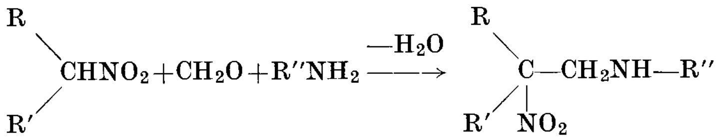
It is also possible to obtain saturated nitro compounds by catalytic hydrogenation (with platinum oxide) of nitroolefines [62].

Nitroolefines treated with iron shavings and hydrochloric acid [31] give ketones (when excess HCl is used) and ketoximes (with minimal amounts of HCl). Oximes have also been obtained by reduction of nitroolefines with zinc dust and acetic acid [63].

Further details of the properties of nitroolefines are given in Section 4 of the present chapter.

Condensation of Nitroparaffins with Aldehydes and Amines (Formation of Nitroamines)

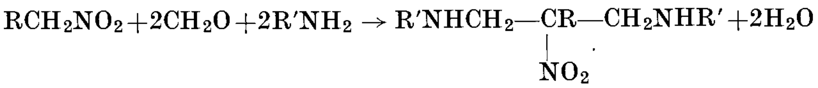
The condensation of nitroparaffins with aldehydes and amines, which is a particular case of the Mannich reaction, leads to the formation of nitroamines, a most interesting group of organic compounds containing both an amino and a nitro group. The reaction can be represented in a general way as follows:



$$\begin{matrix}R\\ \diagdown\\ \end{matrix}\!\!\begin{matrix}\\CHNO_2\\ \end{matrix}\!\!\begin{matrix}\\ \diagup\\R'\end{matrix} + CH_2O + R''NH_2 \xrightarrow{-H_2O} \begin{matrix}R\\ \diagdown\\ \end{matrix}\!\!\begin{matrix}\\ \underset{\substack{|\\NO_2}}{C}\\ \end{matrix}\!\!\begin{matrix}\\ \diagup\\R'\end{matrix}-CH_2NH-R''$$

When a primary nitroparaffin containing two mobile hydrogen atoms is condensed the reaction gives either nitroamine or a nitrodiamine:

$$RCH_2NO_2+CH_2O+R'NH_2 \rightarrow RCH(NO_2)CH_2NHR'+H_2O$$

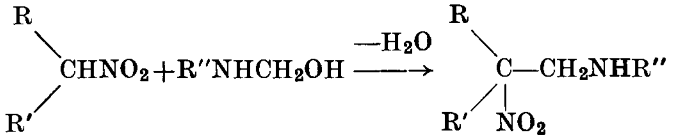


$$RCH_2NO_2+2CH_2O+2R'NH_2 \rightarrow R'NHCH_2-\underset{\substack{|\\NO_2}}{CR}-CH_2NHR'+2H_2O$$

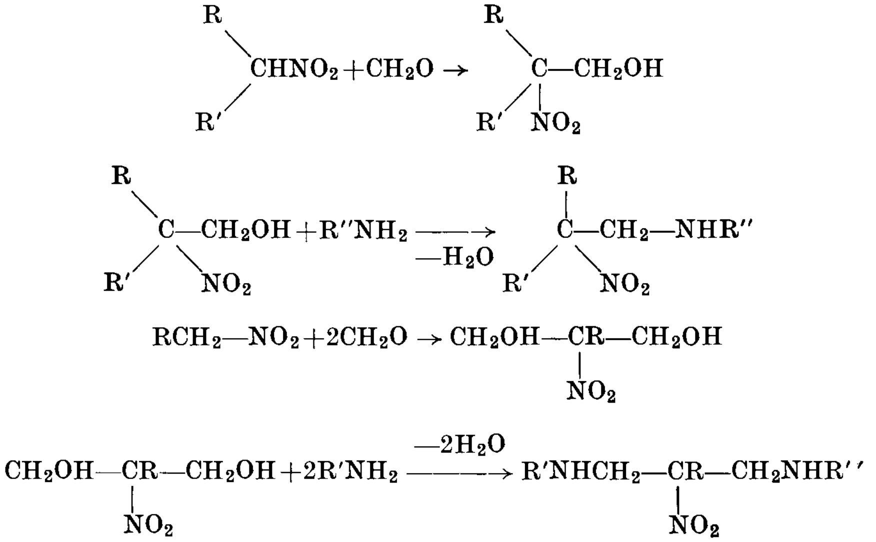
Tertiary nitroparaffins or tertiary amines which do not possess a mobile hydrogen atom do not undergo the Mannich reaction. Two methods are available for the condensation of primary or secondary nitroparaffins with formaldehyde and primary or secondary amines [64, 65].

(1) Formaldehyde is first mixed with the amine and the nitroparaffin is then added to the N-derivative of the amine so formed:

$$CH_2O + RNH_2 \rightarrow RNH{-}CH_2OH$$



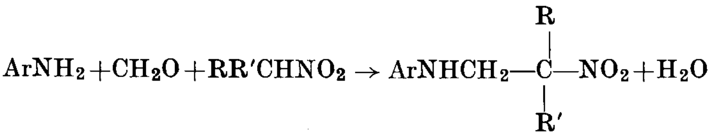
(2) When a nitroparaffin is condensed with formaldehyde a nitroalcohol is formed in the case of a secondary nitroparaffin or a nitroglycol in the case of a primary nitroparaffin. These initially obtained products are then subjected to condensation with the amine:



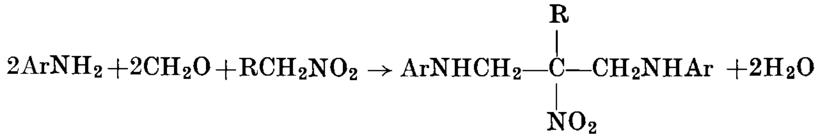
$$RCH_2{-}NO_2 + 2CH_2O \rightarrow CH_2OH{-}\underset{NO_2}{\underset{|}{CR}}{-}CH_2OH$$

$$CH_2OH{-}\underset{NO_2}{\underset{|}{CR}}{-}CH_2OH + 2R'NH_2 \xrightarrow{-2H_2O} R'NHCH_2{-}\underset{NO_2}{\underset{|}{CR}}{-}CH_2NHR''$$

Aromatic amines also enter into condensation reactions with formaldehyde and primary or secondary nitroparaffins. The reaction is carried out in the presence of a strongly basic catalyst [66]. In the case of a secondary nitroparaffin, with one mobile hydrogen atom, the reaction gives an aromatic nitroamine, whilst in the case of a primary nitroparaffin, with two mobile hydrogen atoms, two molecules each of the aromatic amine and of formaldehyde enter the reaction giving an aromatic nitrodiamine:



$$ArNH_2 + CH_2O + RR'CHNO_2 \rightarrow ArNHCH_2{-}\overset{R}{\underset{R'}{C}}{-}NO_2 + H_2O$$



$$2ArNH_2 + 2CH_2O + RCH_2NO_2 \rightarrow ArNHCH_2{-}\overset{R}{\underset{NO_2}{C}}{-}CH_2NHAr + 2H_2O$$

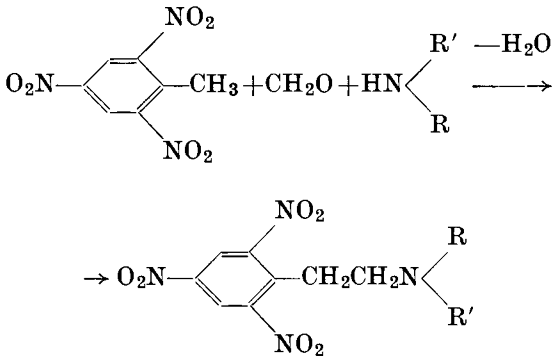
Both the amino groups of aromatic diamines condense with formaldehyde and nitroparaffins:

$$NH_2ArNH_2 + 2CH_2O + 2RR'CHNO_2 \rightarrow$$

$$\rightarrow NO_2-\underset{R'}{\overset{R}{C}}-CH_2NHArNHCH_2-\underset{R'}{\overset{R}{C}}-NO_2 + 2H_2O$$

Nitroamines obtained from aromatic amines, formaldehyde and nitroparaffins are solid substances, usually insoluble in water and slightly soluble in saturated hydrocarbons. They are soluble in alcohol, benzene and ketones.

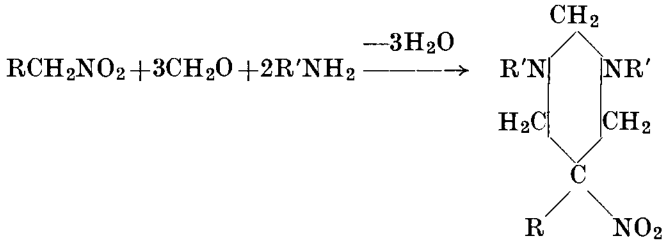
2 : 4 : 6-Trinitrotoluene, like the nitroparaffins, can undergo the Mannich reaction with the formation of trinitrophenylethylamines [67]:



Yields of the condensation products are usually close to the theoretical.

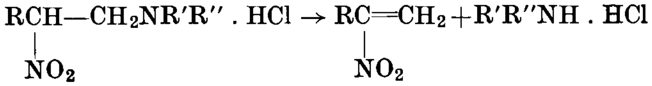
Like 2 : 4 : 6-trinitrotoluene, 2 : 4-dinitrotoluene also undergoes the Mannich reaction [68].

Nitro derivatives of heterocyclic bases (nitrohexahydropyrimidines) can also be prepared by condensation of a primary nitroparaffin, formaldehyde and a primary amine taken in the ratio 1 : 3 : 2 [69–71]:



The condensation reaction of nitroparaffins with amines and formaldehyde has opened up the possibility of synthesizing a series of nitroamines whose preparation by other methods is complicated by great experimental difficulties, and in some cases is probably altogether impossible.

Reduction of the nitroamines obtained by the Mannich reaction gives polyamines. Pyrolysis of the nitroamine hydrochlorides obtained by condensation of primary nitroparaffins with formaldehyde and amines gives the corresponding nitroolefines [72]:

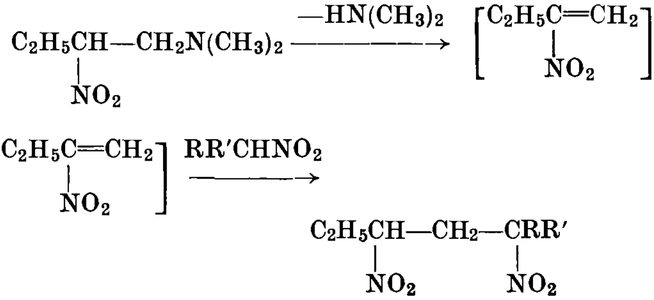


$$\underset{\substack{|\\ NO_2}}{RCH}—CH_2NR'R''\,.\,HCl \rightarrow \underset{\substack{|\\ NO_2}}{RC}=CH_2+R'R''NH\,.\,HCl$$

The yield of nitroolefines given by this reaction can be increased to 80–90 per cent by substituting molecular compounds of the nitroamines with BF_3 for the hydrochlorides [73].

When 1- and 2-nitropropanes are heated with 1-(dimethylamino)-2-nitrobutane (I) 3 : 4-dinitroheptane (II) and 2 : 4-dinitro-2-methylhexane (III) respectively are formed with a 34 per cent and a 22 per cent yield. Snider and Hamlin [74] explain the formation of these dinitroparaffins by deamination of the nitroamine with subsequent addition of 1- or 2-nitropropane to the 2-nitroolefine which is formed:

(I)



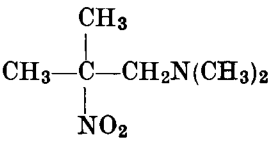
$$C_2H_5\underset{\substack{|\\ NO_2}}{CH}—CH_2N(CH_3)_2 \xrightarrow{-HN(CH_3)_2} \left[C_2H_5\underset{\substack{|\\ NO_2}}{C}=CH_2\right]$$

$$\left[C_2H_5\underset{\substack{|\\ NO_2}}{C}=CH_2\right] \xrightarrow{RR'CHNO_2} C_2H_5\underset{\substack{|\\ NO_2}}{CH}—CH_2—\underset{\substack{|\\ NO_2}}{CRR'}$$

(II) $R=C_2H_5$; $R'=H$

(III) $R=R'=CH_3$

The mechanism proposed by Snider and Hamlin is confirmed by the fact that 1-(dimethylamino)-2-nitro-2-methyl propane:



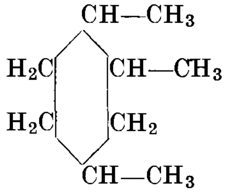
$$CH_3—\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ NO_2}}{C}}—CH_2N(CH_3)_2$$

which is unable to undergo deamination since it contains no hydrogen atom on the β-carbon atom is not alkylated by nitroparaffins.

2. PREPARATION OF MONONITROPARAFFINS AND NITRO COMPOUNDS OF THE ALIPHATIC–AROMATIC SERIES

Nitration of paraffins and other aliphatic compounds is usually done not with concentrated but with dilute nitric acid. This is explained by the largely oxidative effect of concentrated nitric acid on paraffin hydrocarbons. Mixture of nitric and sulphuric acids used for the nitration of aromatic compounds is unsuitable for the nitration of paraffins, since primary nitroparaffins are rapidly hydrolyzed by hot sulphuric acid and secondary and tertiary isomers become tars.

In 1888 the well-known Russian chemist M. I. Konovalov first succeeded in nitrating saturated hydrocarbons, nonaphthene in particular, with dilute nitric acid. The structural formula of this cyclic hydrocarbon found in Caucasian petroleum is:



Prior to Konovalov a number of workers studied the nitration of saturated cyclic hydrocarbons (Bayer, Vreden, Markovnikov, Beilstein, Kurbatov and others). These investigators used concentrated nitric acid (sp. gr. not less than 1·38) as the nitrating agent and obtained chiefly the oxidation products of the hydrocarbons with small yields of nitro compounds. Konovalov, on the other hand, nitrated nonaphthene using dilute nitric acid (sp. gr. 1·155, 1·075 and 1·036) in sealed tubes at 120–130°C. The optimal yield of nitro derivatives (51 per cent) was obtained by Konovalov [75] by heating nonaphthene at 120–130°C with nitric acid sp. gr. 1·075 taken in the ratio, by volume, to the hydrocarbon 4 : 1. The main products of this reaction proved to be tertiary nitro derivatives formed by the substitution of the nitro group for the hydrogen atoms in the $\rangle$CH groups; small amounts of secondary nitro compounds were also formed. These experiments, showing the possibility of introducing nitro groups into saturated cyclic hydrocarbons led Konovalov to the study of dilute nitric acid action on saturated aliphatic hydrocarbons (synthesis of nitroparaffins by direct nitration of hydrocarbons with nitric acid was at that time considered to be impossible). In 1893 Konovalov communicated the results of his experiments on the nitration of aliphatic hydrocarbons with dilute nitric acid which gave quite satisfactory yields of nitroparaffins. Thus, nitration of *n*-hexane with nitric acid sp. gr. 1·075 at 140°C and prolonged heating (4–6 hr) gave nitrohexane with a yield of around 40 per cent, and *n*-heptane and *n*-octane treated with nitric acid of the same concentration for 5–9 hr at 125–130°C gave the corresponding nitro compounds with yields of 47 per cent and 49–52 per cent respectively [76].

Heating di*iso*butyl with nitric acid sp. gr. 1·075 in a sealed tube at 105–110°C [77] gave, in addition to other products, mononitrodi*iso*butyl:

$$(CH_3)_2C(NO_2)CH_2CH_2CH(CH_3)_2$$

The same reaction conducted at a higher temperature (120–125°C) gave a crystalline dinitrodi*iso*butyl:

$$(CH_3)_2C(NO_2)CH_2CH_2C(NO_2)(CH_3)_2$$

Di*iso*propyl and di*iso*amyl undergo analogous nitration, but in the case of di*iso*amyl the reaction occurs at a higher temperature. There are indications that the nitro derivatives of *n*-hexane, *n*-heptane and more readily of *n*-octane are also obtained by nitration with more concentrated nitric acid (sp. gr. 1·42). The yield of mono- and dinitrooctane is 60–70 per cent of the theoretical [78].

2-Nitro derivatives of the higher paraffin hydrocarbons are easily prepared by passing nitric acid vapour through the heated hydrocarbon [79].

KONOVALOV showed further that the method developed by him could also serve for the introduction of the nitro group into the aliphatic chain of aromatic hydrocarbons contrary to the established view that dilute nitric acid, with heating, acts too vigorously on aliphatic aromatic compounds, oxidizing the side chain without nitrating it. KONOVALOV [80] not only proved brilliantly the possibility of nitrating the aliphatic side chain with dilute nitric acid, but also, by varying the main factors affecting the course of nitration (concentration of nitric acid, temperature and duration of the process) determined the optimal conditions for a series of aliphatic–aromatic hydrocarbons. He established that when alkylated derivatives of benzene were heated with dilute nitric acid in a sealed tube the nitro group entered the side chain and not the ring. For example, ethylbenzene on nitration with 12·5 per cent nitric acid (sp. gr. 1·075) for 9–11 hr at 105–108°C gives a 44 per cent yield of phenyl-nitroethane. Lowering the concentration of nitric acid to 6·5 per cent (sp. gr. 1·036) leads to decrease of the yield to 26 per cent. KONOVALOV's experiments also demonstrated that nitric acid of very low concentrations (0·25–0·14 per cent) could still nitrate ethylbenzene whilst concentrated nitric acid only succeeds in doing so if the mixture of the acid and ethylbenzene is allowed to stand in a sealed tube for 45 hr at room temperature. The nitration of propylbenzene is more effective than that of ethylbenzene: treated with nitric acid (sp. gr. 1·075) at 105°C for 4–5 hr this hydrocarbon gives a 74 per cent yield of phenylnitropropane. It can even be nitrated with 1 per cent nitric acid at 100–105°C for 90 hr. A mixture of xylylnitromethanes (total yield of nitro derivatives = 33 per cent) is obtained when pseudocumene is nitrated with nitric acid sp. gr. 1·075 at 110°C for 5 hr.

KONOVALOV's experiments [80] on the nitration of alkylbenzenes (toluene, *m*- and *p*-xylenes, mesitylene and *tert.*-butyltoluene) with dilute nitric acid sp. gr. 1·075 (ratio by volume acid to hydrocarbon 4 : 1) gave interesting results. The nitration was carried out at temperatures around 100°C to diminish the oxidizing action of nitric acid.

Of the hydrocarbons listed above *tert.*-butyltoluene gave the highest yield of nitro derivatives (approximately 74 per cent), when nitrated at 105°C for 4–5 hr. *m*-Xylene gave a 51 per cent yield of nitro derivative (average duration of reaction 16 hr). *p*-Xylene, mesitylene and toluene give lower yields of nitro derivatives (approximately 30 per cent) under these conditions. Nitration of toluene with nitric acid (sp. gr. 1·2) for 40 hr raises the yield of phenylnitromethane to 43 per cent. A somewhat higher yield is obtained by using a large excess of dilute nitric acid. The reaction is carried out as follows: toluene is heated with dilute nitric acid sp. gr. 1·075 (ratio 1 : 6) in a sealed tube at 105°C for 5 hr. The reaction mixture is treated with potassium hydroxide solution and extracted with ether. Phenylnitromethane comes out as a yellow oil when carbon dioxide is passed through the alkaline solution of its salt. The product is separated and vacuum-distilled after removal of solvent.

KONOVALOV also studied the rate of nitration of alkylbenzenes with nitric acid sp. gr. 1·075 by refluxing the reagents in open vessels (ratio of acid to hydrocarbon 4 : 1). Under these conditions mesitylene was the quickest to react followed by *p*-xylene; butytoluene and *m*-xylene reacted relatively slowly and toluene very slowly.

Nitration of the aliphatic side-chain of aromatic hydrocarbons in all the cases cited led predominantly to the formation of mononitro derivatives. Concentrated nitric acid and cooling are needed for the formation of polynitro derivatives. KONOVALOV recommends the following method for the preparation of, for example, dinitromesitylene with a good yield: mononitromesitylene (1 part) is added gradually to nitric acid sp. gr. 1·48 (5 parts) cooled to −10°C; on completion of the reaction the mixture is poured into ice-water. Trinitromesitylene can be synthesized by treating di or mononitromesitylene with a large excess of concentrated nitric acid sp. gr. 1·51.

Parallel experiments also showed that nitration of aliphatic–aromatic and aliphatic hydrocarbons in open vessels gave lower yields of nitro derivatives than nitration under pressure (in sealed tubes), the difference being more marked in the case of aliphatic hydrocarbons. Nitration of paraffins with nitric acid sp. gr. 1·2 in open vessels proceeds very feebly; it is more energetic with nitric acid sp. gr. 1·42 but the yields of nitro derivatives (mixture of mono- and dinitro compounds) are small.*

The main conclusions from KONOVALOV's classical work on the nitration of saturated hydrocarbons and aliphatic side-chains of aromatic compounds may be summarized as follows:

(1) The nitro group can be introduced into saturated aliphatic and cyclic hydrocarbons, as well as into the aliphatic side-chains of aromatic compounds by means of dilute nitric acid.

(2) The main factors affecting the rate of nitration and the yield of the nitro derivatives are the concentration of nitric acid, temperature of the reaction mixture and the duration of the reaction, the degree of effect produced by these factors depending on the nature and structure of the hydrocarbon undergoing nitration. Experiments on the nitration of saturated hydrocarbons and the aliphatic side-chains of aromatic compounds showed, in general, that the weaker the acid the greater the difficulty with which the reaction would occur and the higher the temperature and the longer the duration needed for the reaction to take place.

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* These results do not correspond to those published earlier by WORSTALL [81] who obtained relatively high yields of nitroparaffins using the open vessel method: up to 70 per cent from nonane, 55 per cent from octane and 40 per cent from heptane. WORSTALL himself subsequently acknowledged the inaccuracy of these results.

(3) Nitration of saturated and aliphatic–aromatic hydrocarbons proceeds most favourably under pressure. Nitration in open vessels gives relatively lower yields of nitro compounds (aliphatic–aromatic compounds) or else the reaction proceeds very feebly (aliphatic hydrocarbons). On the other hand when the reaction is carried out in sealed tubes nitro compounds are formed even in those cases where the process is conducted at room temperature, provided the duration is sufficiently long.

(4) The following data concerning the relation between nitration of hydrocarbons with dilute nitric acid and their structure emerge:

(a) Nitration of the ring in aromatic hydrocarbons is considerably more difficult than nitration of saturated hydrocarbons; e.g. benzene cannot be nitrated with nitric acid sp. gr. 1·075 at 130°C, that is under conditions suitable for the nitration of paraffins.

(b) Cyclic saturated hydrocarbons containing tertiary carbon atoms are relatively easily nitrated with dilute nitric acid. For example nonaphthene is nitrated with nitric acid sp. gr. 1·075 at 120–130°C with a 51 per cent yield; unsubstituted polymethylenes, in which there is no $\rangle$CH group, are more difficult to nitrate according to the latest findings of Markovnikov.

(c) The aliphatic side-chain of aromatic hydrocarbons is nitrated more easily than saturated hydrocarbons, both in open vessels and under pressure in sealed tubes, owing evidently to the activating effect of the adjacent aromatic ring.

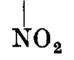
(5) The optimal results as regards yields and purity of products are obtained when the nitration of hydrocarbons is carried out with nitric acid sp. gr. 1·075 in sealed tubes at temperatures 110–140°C.

(6) The ease of substituting the nitro group increases from primary hydrogen (in the CH_3 group) to secondary hydrogen (in the $\rangle CH_2$ group); it is still easier to replace tertiary hydrogen (in the —$\rangle$CH group). An increase in the formation of secondary and primary nitro derivatives is observed when the concentration of nitric acid is raised.

(7) When straight-chain (normal) aliphatic hydrocarbons are nitrated with nitric acid the nitro group substitutes at the second carbon atom.

(8) Nitration with dilute nitric acid is accompanied by oxidative side reactions. Konovalov regards these reactions as secondary (action of nitric acid on the nitro compounds formed in the first place). He mentions the following facts in support of his view:

(a) It is observed that α-phenylnitroethane



$$C_6H_5\underset{\displaystyle NO_2}{\underset{|}{C}}HCH_3$$

undergoes conversion to benzoic acid during distillation;

(b) if the yield of nitro compounds is reduced by raising the reaction temperature, increasing the duration of nitration or the concentration of nitric acid there is a corresponding rise in the yield of those acids which can arise from the nitro compounds formed. Thus, for example, when mesitylene is nitrated with nitric acid sp. gr.

1·155 at 100°C xylylnitromethane $(CH_3)_2C_6H_3CH_2NO_2$ is formed; on prolonged boiling of mesitylene with nitric acid mesitylenic acid is chiefly formed. The latter can also be obtained from xylylnitromethane by prolonged heating of this compound with nitric acid sp. gr. 1·155. Another example is provided by the formation of *tert.*-butyltoluic acid during the nitration of *tert.*-butylxylene [82]; the same acid is obtained by the direct action of oxidizing agents on the potassium salt of the primary nitro derivative of *tert.*-butylxylene.

KONOVALOV [83] also studied the nitration of aliphatic–aromatic compounds with nitric acid in acetic acid solution with refluxing for 1½–2 hr. In the case of ethylbenzene the reaction is very vigorous and therefore the reaction mixture is only gently heated until there is slight evolution of nitrogen oxides. KONOVALOV's experiments showed that the alkylbenzenes studied by him exhibited different reactivities similar to those shown by them during nitration with aqueous nitric acid. *tert.*-Butylbenzene was the least reactive followed by, in order of increasing ease of nitration, *o*-xylene, *p*-xylene, pseudocumene, ethylbenzene and diethylbenzene. In KONOVALOV's opinion acetic acid weakens the action of nitric acid on the aromatic ring and directs it towards the side-chain. Nitration of *m*-xylene and mesitylene demonstrated that the more nitric acid was diluted with acetic acid the more of the primary and other nitro compounds NO_2-substituted in the side-chain were formed. With little dilution nitration occurs chiefly in the ring. It was also established that in the presence of acetic acid (as in aqueous soultion) nitration was accompanied by oxidation reactions. For example, when *p*-xylene and *p*-diethylbenzene were nitrated terephthalic acid was found among the reaction products.

The fact that *iso*butane contains several primary hydrogen atoms and only one tertiary hydrogen atom which is markedly more readily substituted by the NO_2 group as found by KONOVALOV led one to expect a good yield of mononitro*iso*butane. This expectation was justified by experiment, when nitro*iso*butane was obtained for the first time by nitrating *iso*butane with nitric acid in a sealed tube at 150°C by KONOVALOV's method [84].

Nitration of saturated cyclic and aliphatic hydrocarbons was also studied by MARKOVNIKOV [85]. On the basis of his many investigations he showed that normal paraffin hydrocarbons and especially paraffins containing quaternary carbon atoms underwent nitration with difficulty when treated with dilute nitric acid. For example [86], in order to convert *iso*hexane $(CH_3)_3CCH_2CH_3$ into nitro*iso*hexane $(CH_3)_3CCH(NO_2)CH_3$ and *iso*heptane $(CH_3)_3CCH_2CH_2CH_3$ into nitro*iso*heptane $(CH_3)_3CCH(NO_2)CH_2CH_3$ the hydrocarbon has to be heated for a prolonged period (27 hr) with nitric acid sp. gr. 1·235 at 110–115°C.

In 1926 a patent was published [87] which described the preparation of mono- or dinitro derivatives of aliphatic hydrocarbons by heating the latter with nitric acid at approximately 115°C in the presence of aluminium nitrate. However, it was subsequently established [88] that aluminium nitrate did not, in this reaction, act as a catalyst, but merely served to raise the boiling point of nitric acid.

As regards the nitration of saturated cyclic hydrocarbons, MARKOVNIKOV showed that dilute nitric acid nitrated not only those compounds which contain alkyl substituted methylene groups but also unsubstituted polymethylenes. In the latter case, however, nitration occurs less readily and therefore more concentrated nitric acid has to be used. Hexanaphthene treated with nitric acid sp. gr. 1·235 for 9½ hr at 100°C (KONOVALOV's method) gives approximately an 18 per cent yield of nitrohexanaphthene $C_6H_{11}NO_2$ calculated on the hydrocarbon. Oxidation occurs concurrently with nitration as indicated by the large amount of adipic acid found among the reaction products.

Studying the action of fuming nitric acid sp. gr. 1·52 on paraffins and naphthenes MARKOVNIKOV [85] established that nitric acid of this concentration acted slowly on normal paraffins and very vigorously on paraffins containing the $\text{—}\rangle CH$ group. It reacts relatively quickly with penta- and hexamethylene and very quickly with substituted cyclic hydrocarbons, e.g. homologues of *cyclo*pentane. Saturated cyclic and aliphatic hydrocarbons give only insignificant amounts of polynitro derivatives when treated with this concentration of nitric acid; the main reaction products are those of oxidation: CO_2, volatile fatty acids (on nitration of paraffins) dibasic acids (on nitration of paraffins and polymethylenes, in the latter case in large quantities).

MARKOVNIKOV also showed that nitrating mixture (nitric and sulphuric acids) did not react with saturated hydrocarbons (paraffins and naphthenes) at ordinary temperatures and only very slowly on heating.

MARKOVNIKOV [89] made an extensive study of the hydrocarbons found in petroleum using KONOVALOV's reaction as an investigating technique, the identification of individual hydrocarbons being based on the relation referred to above between the ease of nitro group substitution and structure.

Relatively recently TITOV [90] made a study of the nitration of *n*-heptane and 2 : 7-dimethyloctane. The author showed that even nitric acid sp. gr. 1·42 did not, by itself, react with the paraffins. Nitration only occurred in the presence of nitrogen oxides. Parallel experiments were set up in which *n*-heptane was nitrated in sealed tubes, with and without nitrogen oxides, the heating being continued for 3 hr. In the former case 2·52 g crude 2-nitroheptane (1·37 g after purification) was obtained from 5·8 g heptane, 10 ml nitric acid sp. gr. 1·2 and 1 g N_2O_4. In the latter case, using the same amounts of reactants but without the addition of N_2O_4, no excessive pressure was observed and only traces of nitro compound were obtained. Taking the nitration of 2 : 7-dimethyloctane as an example, the author showed that nitric acid sp. gr. 1·42 had no accelerating action on the interaction of N_2O_4 with that hydrocarbon.

NAMETKIN's extensive experiments have revealed new aspects of KONOVALOV's reaction. Whilst investigating the nitration of saturated hydrocarbons with dilute nitric acid NAMETKIN [91] noted the significance of the relative amount of nitric acid in this process. This factor, as distinct from the concentration of the acid and the temperature which affect the rate of reaction, is chiefly concerned with determining the direction of the reaction, i.e. the nature of the products formed. The author demonstrated that by selecting a suitable amount of nitric acid it was possible to reduce appreciably the effect of side reactions (oxidation) and raise the yield of the nitro compounds. By nitrating hexahydropseudocumene with nitric acid sp. gr. 1·3 in open vessels and using different ratios of acid to hydrocarbon, NAMETKIN found the optimal conditions giving a good yield of the nitro derivatives. The nitration was carried out in an Erlenmeyer flask fitted with a condenser. The flask was heated on a sand-bath to gentle boiling (an aluminium wire was introduced into the liquid to prevent bumping and overheating). On completion of the reaction, which usually took 6 hr, the upper layer, containing a mixture of the hydrocarbon and the nitro products, was separated from the acid layer, washed successively with water, soda and water again, then dried over calcium chloride and fractionally distilled. These experiments gave the following results: with a ratio of hydrocarbon to nitric acid 1 : 0·75 the yield of nitro product was 65 per cent; on doubling the relative quantity of nitric acid the yield dropped to 58–59 per cent; further increase of the relative amount of nitric acid (ratio hydrocarbon to acid = 1 : 2·5) lowered the yield to 45–46 per cent. In order to determine the relative amounts of mono- and polynitro compounds formed during the nitration NAMETKIN subjected the reaction product to fractional distillation at reduced pressure (40 mm) after distilling off the unchanged hydrocarbon; the mononitro derivatives distilled over at 140–145°C at this pressure, whilst the polynitro derivatives were determined in the residue. Comparison between experiments using different relative amounts of nitric acid revealed that increasing the ratio of nitric acid to the hydrocarbon increased the amount of polynitro derivatives and correspondingly lowered the yield of the mononitro compounds.

Consideration of his results in the light of published findings led NAMETKIN to the following conclusions:

(1) The action of nitric acid is a mixed one, i.e. there is concurrent formation of nitration and oxidation products.

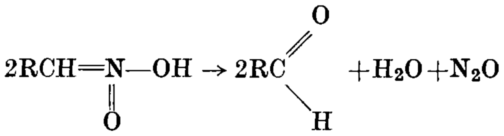
(2) For a given reactive mass of nitric acid the effectiveness of nitration is independent of its concentration (given a suitable choice of temperature and pressure). Thus, for example, using nitric acid sp. gr. 1·3 (47·5 per cent) NAMETKIN obtained the same yield of mononitro compounds as KONOVALOV did using sealed tubes and nitric acid sp. gr. 1·075 (13·5 per cent).

(3) The rate of nitration depends on three factors: temperature, pressure and concentration of acid, which do not, within certain limits, influence the direction of the reaction. A rise in temperature and pressure causes acceleration of the reaction, the more marked the higher the concentration of the acid. With nitric acid sp. gr. 1·3 the reaction proceeds at atmospheric pressure at a practically acceptable rate; with a lower concentration (sp. gr. 1·075–1·055) the reaction is slow and hence the use of pressure becomes necessary.

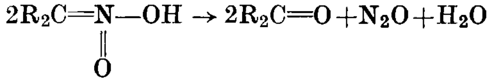
(4) The relative quantity of nitric acid and the duration of the process affect chiefly the direction of the reaction, i.e. the nature of the products obtained. Prolonged boiling with a large excess of nitric acid gives predominantly oxidation products. Decreasing the time of heating and the relative amount of nitric acid increases the yield of nitro products.

Proceeding on the basis of the relation between the course of nitration of saturated hydrocarbons and the factors listed above, Nametkin successfully nitrated hexamethylene (hexanaphthene).* By boiling equal volumes of hydrocarbon and nitric acid sp. gr. 1·3 in a sealed flask Nametkin obtained nitrohexamethylene with a yield of 58·6 per cent of the theoretical. The author also nitrated synthetic hexamethylene, prepared by hydrogenation of benzene, by heating it with nitric acid sp. gr. 1·2 at 105–110°C under pressure (in sealed tubes). The experiments showed that a fourfold increase in the relative amount of nitric acid (in the first series of experiments the ratio of nitric acid to hydrocarbon was 1·5 : 1, in the second, 6 : 1) lowered the yield of nitro derivatives from 49 per cent to 36 per cent with a corresponding rise in the amount of oxidation products (organic acids).

In order to verify Konovalov's suggestion that oxidation is a secondary process, Nametkin studied the action of oxidizing agents, nitric acid in particular, on the product described above—nitrohexamethylene. The action of nitric acid sp. gr. 1·3 on nitrohexamethylene proved to be fairly slow and the yield of adipic acid half that obtained during the direct action of nitric acid on hexamethylene. On the other hand the reaction occurs very quickly and gives an 83·3 per cent yield of adipic acid if nitrohexamethylene in a weakly alkaline solution, in which it is present as a salt of the corresponding aci-form (*iso*nitro compound), is introduced into boiling nitric acid. Nametkin concludes that it is not nitrohexamethylene that undergoes oxidation, but a product of its transformation—*iso*nitrohexamethylene, which is a very unstable compound. The oxidation of the *iso*nitro compound to the organic acid occurs, evidently, through the intermediate formation of an aldehyde (if the labile form corresponds to a primary nitro compound) or a ketone (in the case of a secondary nitro compound):



$$2\mathrm{RCH{=}\underset{\underset{O}{\|}}{N}{-}OH} \rightarrow 2\mathrm{RC}\begin{smallmatrix}\diagup\!\!\diagup \mathrm{O}\\ \diagdown \mathrm{H}\end{smallmatrix} + \mathrm{H_2O} + \mathrm{N_2O} \qquad (1)$$



$$2\mathrm{R_2C{=}\underset{\underset{O}{\|}}{N}{-}OH} \rightarrow 2\mathrm{R_2C{=}O} + \mathrm{N_2O} + \mathrm{H_2O} \qquad (2)$$

According to Nametkin's concepts the action of nitric acid on saturated hydrocarbons gives, in the first place, *iso*nitro compounds which are unstable in acid medium at high temperatures. These compounds either

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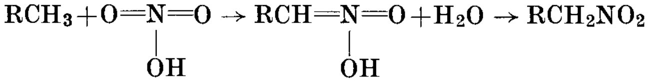
* Hexanaphthene constitutes the main part of the fraction of Caucasian petroleum boiling at 80–82°C.

undergo transformation to the stable form of nitro compounds or, through aldehydes and ketones formed as in the equations given above, are oxidized to the corresponding carboxylic acids.

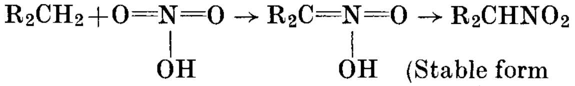
Formation of intermediate oxidation products was observed by Konovalov [92], who isolated the aldehyde of 1 : 6 : 6-trimethylheptilic acid on nitration of di*iso*amyl with concentrated nitric acid, and also by Nametkin during nitration of Caucasian petroleum (fraction boiling at 142–144°C).

Intermediate *iso*nitro compounds are formed only during the nitration of hydrocarbons containing hydrogen atoms linked with a primary or secondary carbon atom:



$$RCH_3+O{=}\underset{\substack{|\\ OH}}{N}{=}O \rightarrow RCH{=}\underset{\substack{|\\ OH}}{N}{=}O+H_2O \rightarrow RCH_2NO_2 \tag{1}$$

(Labile *iso*nitro
compound, or
aci-form)



$$R_2CH_2+O{=}\underset{\substack{|\\ OH}}{N}{=}O \rightarrow R_2C{=}\underset{\substack{|\\ OH}}{N}{=}O \rightarrow R_2CHNO_2 \tag{2}$$

(Stable form
of nitro
compound)

Hydrocarbons containing hydrogen linked with a tertiary carbon atom form the stable nitro compound directly:

$$R_3CH+HONO_2 \rightarrow R_3CNO_2+H_2O$$

Nametkin and Zabrodina [93] studied the nitration of *iso*octane (2 : 2 : 4-trimethylpentane $(CH_3)_3CCH_2CH(CH_3)_2$) by the Konovalov method in sealed tubes. Into each tube was placed hydrocarbon (5 g) and nitric acid sp. gr. 1·075 (35 ml). Heating at 143—147°C was continued for 20 hr with interruptions every 5 hr to reduce pressure. The upper oily layer was washed with bicarbonate solution. From 315 g of 2 : 2 : 4-trimethylpentane the following were obtained: nitromethane and *iso*octane (unreacted): 138 g; 2 : 2-dimethylpentanone-4 $(CH_3)_3CCH_2COCH_3$: 1·7 g; 2 : 2 : 4-trimethylpentanone-3 $(CH_3)_3CCOCH(CH_3)_2$: 5·0 g; (the formation of this ketone is regarded as the result of the breakdown of the secondary *iso*nitrooctane formed as an intermediate product); acetone: a small amount; secondary nitro*iso*octane $(CH_3)_3CCH(NO_2)CH(CH_3)_2$; 2·4 g; tertiary nitro*iso*octane $(CH_3)_3CCH_2C(NO_2)(CH_3)_2$: 60 g; dinitro*iso*octane $(CH_3)_3CCH(NO_2)C(NO_2)(CH_3)_2$: 5·1 g.

As has already been mentioned Konovalov showed by the nitration of hexane, heptane and octane with weak nitric acid (13·15 per cent) that the only product given by normal paraffins under those conditions was secondary *β*-nitro compounds. Nametkin, Nifontova and Sushchik [94] studied the nitration of octadecane ($C_{18}H_{38}$) by the Konovalov method in sealed tubes, and found that the only reaction product was a secondary β-nitro compound $CH_3(CH_2)_{15}CH(NO_2)CH_3$, i.e. an analogous compound to that obtained by KONOVALOV from hexane. When hexatriacontane ($C_{36}H_{74}$) is treated with dilute nitric acid under analogous conditions the main reaction product is a bis-secondary β: β'-dinitro compound $CH_3CH(NO_2)(CH_2)_{32}CH(NO_2)CH_3$, i.e. nitration occurs at both ends of the molecule and both nitro groups enter the β-position. The yield of the dinitro compound is twice that of the mononitro compound. The authors suggest on the basis of their work that up to a certain limit of molecular weight the only reaction product resulting from the nitration of normal paraffin hydrocarbons is the corresponding secondary β-nitro compound. Above this limit of molecular weight the main reaction product of nitration by Konovalov's method becomes the β : β'-dinitro derivative which, evidently, results from the further nitration of the mononitro derivative.

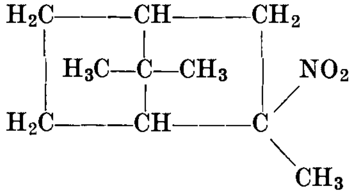
However, as shown by PONI and COSTACHESCU [95] the nitration of *iso*pentane with nitric acid sp. gr. 1·38–1·42 in a sealed tube at 140°C gives, in addition to 2-nitro-2-methylbutane, 2 : 3-dinitro-2-methylbutane $(CH_3)_2C(NO_2)CH(NO_2)CH_3$ as well at a small yield of 1 : 2 : 3-trinitro-3-methylbutane $(CH_3)_2C(NO_2)CH(NO_2)CH_2NO_2$ (m.p. 189–190°C).

On nitration of *iso*octane with dilute nitric acid sp. gr. 1·075 by the Konovalov method NAMETKIN and ZABRODINA [96] isolated from the acid layer the following substances: acetic, *iso*butyric, trimethylacetic, *tert.*-butylacetic, α : α-dimethylsuccinic acids and traces of oxalic acid. The same authors [97–98] also studied, on *iso*octane, the relationship between nitration and oxidation of saturated hydrocarbons by nitric acid. Taking into account that saturated nitro compounds are very stable to nitric acid even on boiling and are oxidized much more slowly than the corresponding saturated hydrocarbons, the authors conclude that the intermediate products during oxidation of saturated hydrocarbons with nitric acid are not nitro but *iso*nitro compounds. The latter are very unstable in acid medium. Formed early in the reaction, *iso*nitro compounds either undergo immediate isomerization to the corresponding nitro compounds or break down with the formation of N_2O and aldehydes, which in turn are oxidized to carboxylic acids. In the case of *iso*octane *iso*nitro*iso*octane is first formed, then secondary nitro*iso*octane (2 : 2 : 4-trimethyl-3-nitropentane), the ketone 2 : 2 : 4-trimethylpentanone-3 and products of its oxidation.

If the action of nitric acid is directed to a tertiary hydrogen atom, however, a tertiary nitro compound is formed straight away. Tertiary aliphatic nitro compounds can be intermediate products in the transition to oxidation products.

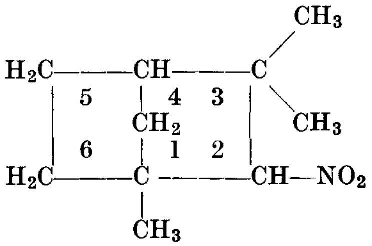
NAMETKIN was the first to investigate in detail the nitration of saturated bicyclic hydrocarbons with nitric acid. These compounds remained for a long time uninvestigated owing to their limited availability. NAMETKIN established that bicyclic hydrocarbons possessed certain peculiarities which distinguish them from paraffins and monocyclic naphthenes.

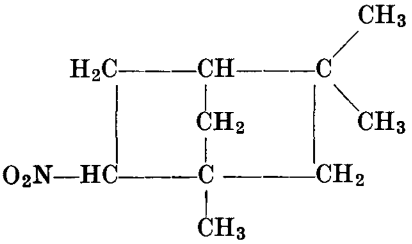
As already mentioned above, nitration of paraffins and naphthenes containing a tertiary hydrogen atom gives tertiary nitro compounds as the main reaction product. The majority of bicyclic hydrocarbons contain a tertiary hydrogen atom at the carbon atom common to both rings. NAMETKIN's studies showed that during nitration with dilute nitric acid of bicyclic hydrocarbons consisting of two fused five-membered rings these hydrogen atoms were never substituted by the nitro group. Tertiary nitro compounds can only be obtained from hydrocarbons containing the >CH—CH$_3$ group. For example, nitration of *iso*bornylane [99] gives 2-nitro*iso*bornylane which has the following structure:



It is interesting that during nitration of bicyclic naphthenes consisting of two six-membered rings or one six-membered and one five-membered ring tertiary nitro compounds are formed in which the nitro group does join the carbon atom common to both rings. By nitrating decalin NAMETKIN [100] obtained tertiary nitrodecalin, whilst hydrindan gave tertiary nitrohydrindan [101].

Another characteristic peculiarity of bicyclic hydrocarbons established by NAMETKIN is their ability to form structurally isomeric nitro compounds. Nitration of paraffins and monocyclic naphthenes is always strictly directed, so that of a number of possible secondary nitro compounds only one is always formed. Nitration of normal paraffin hydrocarbons leads to the formation of β-nitro compounds. In aliphatic–aromatic hydrocarbons the nitro group goes to the position α to the benzene ring. Nitration of bicyclic hydrocarbons is accompanied by substitution in both rings simultaneously. As the result of nitrating fenchane [102] two nitro compounds are obtained—2-nitrofenchane and 6-nitrofenchane:





Two secondary structurally isomeric nitro compounds are also obtained by nitrating camphenilane [103].

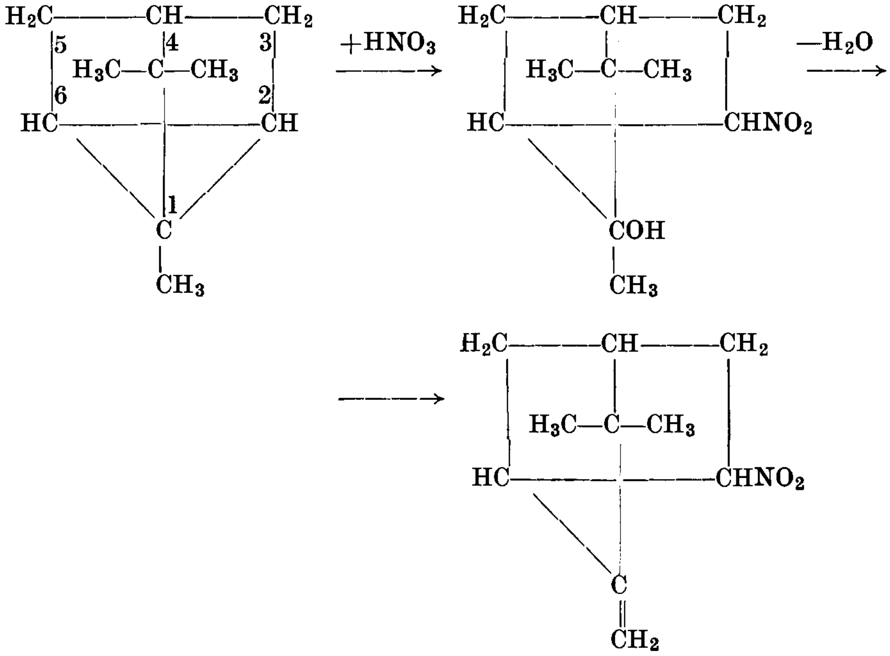
Nitration of bicyclic hydrocarbons sometimes gives mixtures of stereoisomeric nitro compounds. When the symmetrical hydrocarbon camphane [104] was nitrated α- and α′-nitrocamphanes were obtained, which gave the same ketone on oxidation—inactive camphor. A mixture of stereoisomeric nitro compounds was also obtained by the action of nitric acid on *iso*camphane [105].

Nametkin and Zabrodina [106] obtained interesting results by treating a saturated tricyclic hydrocarbon—tricyclene—with nitric acid. Unexpectedly the only product of nitration proved to be an unsaturated nitro compound, α-nitrocamphene. Nametkin explains its formation according to the following scheme:

(1) Initially opening of the three-membered ring occurs at the bonds 1–2 or 1–6 and nitric acid adds on to the available bond forming a nitro alcohol.

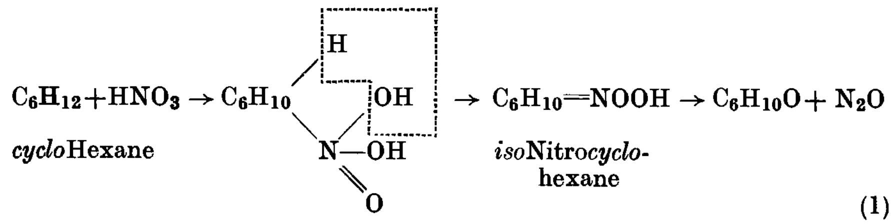
(2) Subsequently the unstable nitro alcohol is dehydrated, forming α-nitrocamphene.

The process is expressed by the equation:



Nametkin extended this scheme of reaction to the nitration of hydrocarbons not containing a three-membered ring. The reaction proceeds in two stages: (1) combination of hydrocarbon with nitric acid; (2) elimination of water from the intermediate product.

For example, in the case of the combination of nitric acid with *cyclo*hexane the elimination of water can occur in two directions: (a) with the formation of a secondary nitro compound, (b) with the formation of an *iso*nitro compound which then breaks down into a ketone and N_2O:

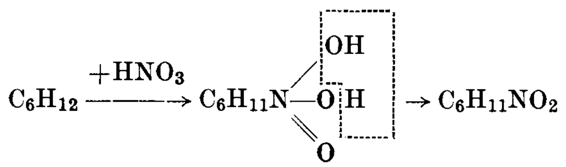


$$C_6H_{12}+HNO_3 \rightarrow C_6H_{10}\left\langle\begin{array}{l}H\\ N(OH)_2{=}O\end{array}\right. \rightarrow C_6H_{10}{=}NOOH \rightarrow C_6H_{10}O + N_2O \qquad (1)$$

*cyclo*Hexane

*iso*Nitro*cyclo*hexane

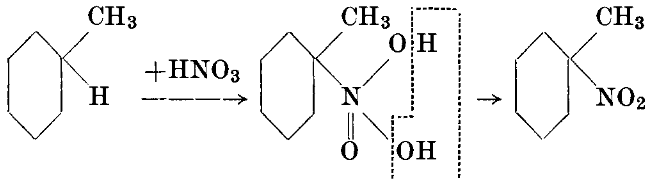
(1)



$$C_6H_{12} \xrightarrow{+HNO_3} C_6H_{11}N\begin{matrix}\diagup OH\\ -OH\\ \diagdown\!\!\diagdown O\end{matrix} \rightarrow C_6H_{11}NO_2 \qquad (2)$$

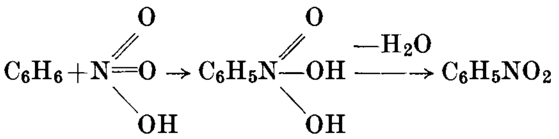
Analogous transformations are observed on combination of nitric acid with methyl*cyclo*hexane.

Elimination of water from the addition product of nitric acid and a tertiary carbon atom can only lead to the formation of a tertiary nitro compound:



tert.-Methylnitro-*cyclo*hexane

Nametkin has suggested that nitration of aromatic hydrocarbons may also proceed through a stage of addition of the hydrocarbon to nitric acid with the formation of aromatic nitro compounds by the elimination of water from the intermediate product:



$$C_6H_6 + N\begin{matrix}\diagup\!\!\diagup O\\ =O\\ \diagdown OH\end{matrix} \rightarrow C_6H_5N\begin{matrix}\diagup\!\!\diagup O\\ -OH\\ \diagdown OH\end{matrix} \xrightarrow{-H_2O} C_6H_5NO_2$$

Shorygin and **Sokolova** [107] also studied the nitration of aliphatic–aromatic compounds, using nitric acid in acetic acid solution as the nitrating agent. The aim of their investigations was to find the most favourable conditions for the nitration of the aliphatic side-chain of toluene to give phenylnitromethane. The experiments were carried out both in sealed tubes and in open vessels. In the first case a mixture of toluene (10 ml), nitric acid (sp. gr. 1·5; 10·7 ml) and glacial acetic acid (29·3 ml) was heated for 24 hr giving a 14·5 per cent yield of phenylnitromethane. Experiments at atmospheric pressure were carried out as follows: a mixture of toluene (150 ml; 130 g), nitric acid (sp. gr. 1·5; 120 ml) and glacial acetic acid (480 ml) was heated in a flask with a reflux condenser on an oil-bath to 110°C for 3½ hr. Under these conditions, which proved to be optimal on the evidence of preliminary investigations, the yield of phenylnitromethane was 14 per cent. There was concurrent nitration of the ring (yield of nitrotoluenes was 24 per cent) and formation of oxidation products (yield of benzoic acid 31·5 per cent).

Shorygin and **Sokolova** treated the reaction products as follows: the oily layer, which separated when the reaction mixture was poured into water, was shaken with a 5 per cent solution of soda in order to extract the benzoic acid. The oily residue, containing phenylnitromethane and nitrotoluenes was steam-distilled. The distilled oil was treated with a 20 per cent NaOH solution to extract phenylnitromethane, after which it was distilled, toluene coming over first (109–111°C) and then *o*- and *p*-nitrotoluenes (217–238°C). Phenylnitromethane was isolated from the alkaline solution by acidifying with a 20 per cent solution of hydrochloric acid.

Titov has made a detailed and penetrating study of the mechanism of nitration of saturated and aliphatic–aromatic hydrocarbons. He comes to the following conclusions [108] concerning the nitration of saturated hydrocarbons and their derivatives.

(1) During the nitration of paraffins nitric acid shows no direct chemical action but merely serves as a source of formation and regeneration of nitrogen oxides.

(2) The active chemical agent in this reaction is the radical-like molecule of the monomeric form of nitrogen dioxide NO_2. As distinct from the colourless diamagnetic N_2O_4, the monomeric form NO_2 is paramagnetic and coloured, which proves the radical-like structure of its molecule.

(3) The initial chemical process during the nitration of the paraffin chain is the formation of the hydrocarbon radical by the interaction of the monomeric form of nitrogen dioxide and the organic reactant:

$$RH + NO_2 \rightarrow R\cdot + HNO_2$$

On the grounds of the experimental data Titov considers that saturated hydrocarbons and their residues in other compounds react as a rule with free radicals (A) with insignificant activation energy (not greater than 10 kcal/mole) with detachment of a hydrogen atom and formation of a hydrocarbon radical:

$$RH + A \rightarrow R\cdot + AH$$

The fact that the rate of nitration shows an increase parallel to the increase in relative stability of the radical R• and parallel to the decrease in the energy of activation for the detachment of the hydrogen atom confirms the initial appearance of radicals.

(4) The alkyl radicals formed in the first stage of the reaction react rapidly with the radical-like molecules of nitrogen oxide and nitrogen dioxide to form nitroso and nitro compounds and alkyl nitrites:

$$R\cdot + NO \rightarrow RNO \qquad (1)$$

$$\begin{tikzcd} & RNO_2 & \\ R\cdot + NO_2 \arrow[ur] \arrow[dr] & & (2) \\ & RONO & \end{tikzcd}$$

The most likely transformations and interactions between the free radicals and the other components of the reaction system are, in TITOV's opinion, the following:

(*a*) $R\cdot + N_2O_4 \rightarrow RONO + NO_2$
(*b*) $R\cdot + N_2O_3 \rightarrow RNO + NO_2$
(*c*) $R\cdot + N_2O_3 \rightarrow RONO + NO$
(*d*) $R\cdot + N_2O_3 \rightarrow RNO_2 + NO$
(*e*) $R\cdot + HONO_2 \rightarrow ROH + NO_2$

However, it is unlikely that such transformations of hydrocarbon radicals do take place; they only acquire significance at very considerable concentrations of N_2O_4, N_2O_3, and HNO_3 or at high temperatures.

The author maintains that all the variety of end products of the interaction of nitrogen oxides and nitric acid with saturated hydrocarbons and their derivatives results from further transformations of nitroso compounds, esters of nitrous acid, alcohols and, to a lesser extent, nitro compounds which occur under the conditions existing during the nitration.

The peculiarities of nitration with nitric acid are first of all determined by the state of equilibrium expressed by the scheme $2\ HNO_3 + NO \rightleftarrows 3NO_2 + H_2O$ and those factors on which the establishment of this equilibrium depends.

TITOV's experimental findings prove that nitric acid in the absence of nitrogen oxides practically does not react either with normal paraffins or *iso*paraffins, *cyclo*paraffins and side-chains of alkyl benzenes. In the presence of nitrogen oxides the chemical action shows an increase parallel to the increase of the nitrogen dioxide content. By studying the action of various mixtures of nitrogen oxides (NO, NO_2, N_2O_3, N_2O_4) and of nitrous and nitric acids TITOV found that the only chemically active agent in the nitration of saturated hydrocarbons was the monomeric nitrogen dioxide NO_2.

The rate of reaction is decreased by saturating the reaction mixture with nitrogen oxide by shifting the equilibrium $NO_2 + NO \rightleftarrows N_2O_3$ from left to right. If, however, oxygen is introduced into the reaction mixture in order to eliminate nitrogen oxide from the sphere of reaction, acceleration of the reaction takes place.

The rate of nitration of paraffin hydrocarbons is determined by the rate of the initial formation of hydrocarbon radicals. This reaction is of the molecular–radical type, which is proved by the observation that an increase in the volume of the acid phase is not reflected on the course of the reaction; an increase in the volume of the hydrocarbon phase enhances the course of the reaction. It follows from this that the nitration of paraffins with nitric acid occurs not in the acid but in the hydrocarbon phase. This provides an explanation for the well-known facts that (a) the rate of reaction is not appreciably altered by the degree of polarity of the reaction medium, (b) the presence of strongly protonic and aprotonic acids (H_2SO_4, $AlCl_3$, $TiCl_4$) does not accelerate the nitration of the paraffin chain.

TITOV [109, 110] supposes that, analogously with the saturated hydrocarbons, the main agents involved in the nitration of the aliphatic side-chain of aromatic hydrocarbons with nitric acid are nitrogen oxides (NO_2 and NO) present in the sphere of reaction. The role of nitric acid is confined to the regeneration of nitrogen dioxide and increasing its concentration by oxidizing lower oxides of nitrogen formed during the reaction. In the initial stage of nitration a primary breakdown of the hydrocarbons occurs under influence of nitrating agents giving free radicals:

$$C_6H_5CH_3+NO_2 \rightarrow C_6H_5CH_2\cdot +HNO_2$$

The correctness of the assumption that free radicals are formed by the action of NO_2 on aliphatic–aromatic hydrocarbons is confirmed by the author's observation [111] that the rate of reaction increases rapidly in the series toluene, diphenylmethane, triphenylmethane—parallelling the ease of formation of the corresponding radicals. The free radicals react further with radical-like molecules of nitrogen oxide and dioxide:

$$C_6H_5CH_2\cdot +NO \rightarrow C_6H_5CH_2NO \qquad (I)$$

$$C_6H_5CH_2\cdot +NO_2 \rightarrow C_6H_5CH_2NO_2 \qquad (II)$$

$$C_6H_5CH_2\cdot +NO_2 \rightarrow C_6H_5CH_2ONO \qquad (III)$$

The nitroso compounds formed according to scheme (I) then give dinitro derivatives, the reaction proceeding through an intermediate stage of rearrangement of the nitroso compounds into oximes:

$$C_6H_5CH_2NO \rightarrow C_6H_5CH{=}NOH \qquad (1)$$

$$C_6H_5CH{=}NOH \xrightarrow{+N_2O_4} C_6H_5CH(NO_2)_2 \qquad (2)$$

TITOV obtained the following data by studying the nitration of toluene with NO_2 only on the one hand and with nitric acid containing NO_2 on the other (Table 13).

Table 13. *Nitration of toluene with* NO_2 *and nitric acid*

Reaction product	Content (mole %)	
	Nitration with NO_2	Nitration with HNO_3
Phenylnitromethane	52·5	55·2
Phenyldinitromethane	2·7	3·7
Benzoic acid	11·2	11·9
Oily residue	33·6	29·2

Thus, in both cases a mixture of practically identical composition is obtained.

TITOV's experiments showed that the nitration of the aliphatic side-chain of aromatic hydrocarbons gave predominantly either ω-mononitro compounds or ω-dinitro compounds, depending on the conditions of the reaction. The formation of the two sorts of compounds proceeds by quite distinct routes, and therefore the mononitro compounds do not represent an intermediate stage in the formation of ω-dinitro compounds. This is confirmed by the fact that phenylnitromethane, treated with nitrogen dioxide remains unchanged, treated with dilute nitric acid gives benzyl alcohol and benzoic acid, and undergoes nitration in the ring when treated with concentrated nitric acid. At low temperatures dinitro derivatives are mainly formed. For example, a mixture of nitric acid sp. gr. 1·42 (100 ml) containing NO_2 (0·3 g) and toluene (1000 ml) was allowed to stand in a loosely stoppered flask for 20 days at a temperature of about 25°C. Under these conditions the main reaction product was phenyldinitromethane. Raising the temperatute to 50°C led to an increased yield of phenylnitromethane and a decreased yield of phenyldinitromethane. At a temperature around 100°C the only product of nitration of the side-chain was phenylnitromethane. Thus when nitric acid (sp. gr. 1·38; 300 ml) was added over a period of 2½ hr to toluene (500 ml) heated on a boiling water-bath in a flask fitted with a reflux condenser, phenylnitromethane was obtained with a 52 per cent yield together with oxidation products: benzoic acid (yield 24·5 per cent) and benzaldehyde (yield 3 per cent).

Titov explains the lowering of the yield of phenyldinitromethane with rising temperature by the accompanying decrease in the solubility of nitrogen oxide which is essential for the formation of nitroso compounds, and by the enhanced dissociation of N_2O_4 which converts oximes into dinitro compounds (see the scheme given above for the formation of the latter). Another factor which has a negative effect on the yield of phenyldinitromethane is the high concentration of NO_2 leading to decreased chances for the collision of free radicals with NO as well as lowering the concentration of the latter by shifting the equilibrium from left to right in the equation:

$$NO+NO_2 \rightleftarrows N_2O_3$$

On the other hand, increased yield of phenyldinitromethane is obtained by increasing the concentration of nitrogen oxide, e.g. by specially saturating the reaction mixture with it.

Formation of ω-moninitro compounds occurs by the action of the monomeric molecule NO_2 (when a large excess of the hydrocarbon being nitrated is used NO_2 dissolves in it). In the initial stages of the reaction only an insignificant amount of nitrogen dioxide is present, dissolved in nitric acid. To raise this initial concentration Titov usually adds trihydroxymethylene to the reaction mixture which readily forms NO_2 by interaction with nitric acid.

Descriptions of some of Titov's experiments, giving good yields of phenylnitromethane by nitration of toluene, are given below.

Toluene, trihydroxymethylene (0.5 g) and a buffering mixture of nitric acid (sp. gr. 1·38; 8 g) and 50 per cent sulphuric acid (40 g) were placed in a flask and heated on a water-bath for 3½ hr, during which time nitric acid (sp. gr. 1·5; 50 ml) was added from a dropping-funnel to the reaction mixture. In this way concentrated nitric acid did not come into contact with toluene and the possibility of nitration in the ring was eliminated.

In these experiments the relative quantities of toluene and nitric acid were varied, and the optimal ratio, giving a 54·6 per cent yield of the product, was found to be 1750 ml toluene to 50 ml nitric acid.

The reaction products were treated as follows. After washing with water, the hydrocarbon layer was stirred vigorously for 4 hr with 200 ml of 20 per cent potassium carbonate solution with a further addition of 50 ml of 50 per cent potassium carbonate solution during the second and third hours. The potassium salt of phenyldinitromethane which precipitated out was filtered with suction and washed with water, alcohol and ether. The phenyldinitromethane remaining in solution was isolated as phenyldinitrobromomethane by treating it with bromine. After removal of the brominated compound benzoic acid was isolated from the mother liquor.

In order to extract phenylnitromethane the reaction mixture was stirred for 4 hr with 100 ml of 10 per cent alkali.

Titov concludes that the following requirements should be fulfilled for successful nitration of the toluene side-chain with nitric acid:

(1) Initial presence of nitrogen oxides in the sphere of reaction.

(2) Their accumulation up to a certain limit with the help of nitric acid.

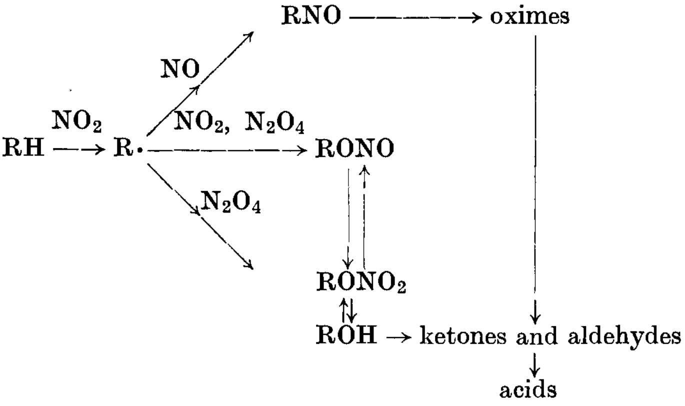
(3) Creation of conditions hindering the nitration of the aromatic ring by nitric acid and its destructive action on the phenylnitromethane formed.

Oxidation of the paraffin chain by nitrogen oxides and nitric acid during the nitration of saturated hydrocarbons not infrequently constitutes one of the main reactions. Titov regards its mechanism as follows:

$$RONO + H_2O \rightleftarrows ROH + HNO_2$$

$$ROH + HNO_3 \rightleftarrows \underset{\text{Alkyl nitrate}}{RONO_2} + H_2O$$

By creating conditions favouring the preservation of alcohols and their nitrous and nitric acid esters it is possible to direct the reaction towards good yields of these products. For example, by using a large excess of hydrocarbon, dehydrating agents and oxygen to remove nitrogen oxide from the sphere of reaction, it is possible to direct the interaction between toluene and NO_2 at ordinary temperatures towards the predominant formation of benzyl nitrate, benzyl alcohol and, from the latter, the acid:



Titov [112] confirmed his theory of the nitration of paraffin and aliphatic–aromatic hydrocarbons also by his experiments on the nitration of diphenylmethane and *cyclo*hexane. Depending on the conditions of the reaction the main product resulting from the nitration of diphenylmethane is either diphenylmononitromethane or diphenyldinitromethane. Titov represents the formation of these substances in the following way. Benzhydryl is first formed from diphenylmethane and NO_2:

$$(C_6H_5)_2CHH+NO_2 \rightarrow (C_6H_5)_2CH\cdot+HNO_2$$

then

$$(C_6H_5)_2CH\cdot+NO_2 \rightarrow (C_6H_5)_2CHNO_2$$

or

$$(C_6H_5)_2CH\cdot+NO \rightarrow (C_6H_5)_2CHNO \rightarrow (C_6H_5)_2C{=}NOH \rightarrow (C_6H_5)_2C(NO_2)_2$$

In addition to the products of nitration the author demonstrated the formation of oxidation products: benzhydryl nitrate, benzhydrol, dibenzhydryl ether and benzophenone in accordance with the following schemes:

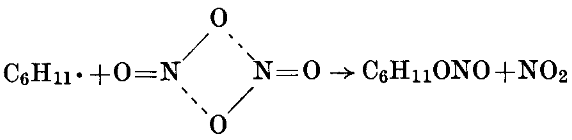
$$(a)\quad (C_6H_5)_2CH\cdot \xrightarrow{ONO,\ N_2O_3,\ N_2O_4} (C_6H_5)_2CH{-}ONO \rightarrow$$

$$\xrightarrow[-HNO_2]{+H_2O} (C_6H_5)_2CHOH \underset{H_2O}{\overset{HNO_3}{\rightleftarrows}} (C_6H_5)_2CHONO_2$$

$$(b)\quad 2(C_6H_5)_2CHOH \overset{H\cdot}{\rightleftarrows} (C_6H_5)_2CH{-}O{-}CH(C_6H_5)_2$$

$$(c)\quad (C_6H_5)_2CHOH \xrightarrow{NO_2} (C_6H_5)_2CO+NO+H_2O$$

In one of his recent works Titov [113] using the nitration of *cyclo*hexane with nitric acid and nitrogen oxides as an example, shows that increasing the ratio $N_2O_4 : NO_2$ enhances progressively the role of *cyclo*hexyl nitrite formed in the reaction of the hexyl radical with the dimer of nitrogen dioxide.



(1)

The *cyclo*hexyl nitrite formed reacts with water in the acid medium giving *cyclo*hexanol, which is readily oxidized to *cyclo*hexanone and then, by stronger oxidation, to adipic acid. With a large excess of *cyclo*hexane and duration of process = 1 hr, TITOV obtained a mixture of the following composition:

	(Mole-%)
Nitro*cyclo*hexane	50
*cyclo*Hexanol	8
*cyclo*Hexyl nitrite	8
Other esters	14
Adipic acid	20
TOTAL	100

Increased concentration of the dimer of nitrogen dioxide is accompanied by an increase in the yield of oxidation products exceeding the increase in the yield of nitro*cyclo*hexane, since it corresponds to an enhancement of the reaction between *cyclo*hexyl and N_2O_4 as in equation (1). The positive effect of raised pressure on the nitration of saturated and aliphatic–aromatic hydrocarbons was observed by KONOVALOV who noted the sharp lowering of yield when the reaction was carried out in open vessels. TITOV has made some interesting studies on the effect of sealing hermetically the reaction vessels and on the role of diffusion processes during the nitration of saturated hydrocarbons with nitric acid in the liquid phase. The active nitrating agent—nitrogen dioxide, in Konovalov's method, remains predominantly in the hydrocarbon layer, where the reaction takes place. The rate of reaction consequently depends on the NO_2 content of this layer. Gaseous nitrogen oxide which also remains in the sphere of reaction assists in the maintenance of the necessary concentration of nitrogen dioxide by virtue of its participation in the equilibrium:

$$2HNO_3+NO \rightleftarrows 3NO_2+H_2O \qquad (I)$$

At the beginning of the reaction the nitrogen dioxide content of the hydrocarbon layer, especially during nitration with dilute acid, is very low. As the reaction:

$$RH+NO_2 \rightarrow R\cdot +HNO_2 \qquad (II)$$

proceeds the NO_2 content of the hydrocarbon layer drops and constant replenishment of the NO_2 used up is necessary to maintain the reaction. The acid layer, into which NO penetrates from the hydrocarbon layer, serves as a source of this NO_2 replenishment. Regeneration of nitrogen dioxide in the upper acid layer, adjacent to the hydrocarbon layer, involves nitric acid which must, therefore, be available from the deeper layers. Due to the lag of diffusion processes in the absence of stirring the concentration of NO_2 in the hydrocarbon layer falls below the limit required by equation (I). The NO_2 deficiency is more keenly felt the quicker the rate of reaction between the hydrocarbon and NO_2. When replenishment of NO_2 in the hydrocarbon layer is insufficient the rate of nitration drops. Towards the end of nitration by Konovalov's method when the concentration of NO is high owing to oxidative side-reactions and the concentration of nitric acid is markedly lowered, the role of NO as a nitrogen dioxide content regulator becomes particularly important. When relatively inactive hydrocarbons (e.g. di*iso*amyl, *cyclo*hexane) are nitrated by Konovalov's method at ordinary temperature there is practically no lagging of the diffusion processes in relation to the nitration reaction. In the case of nitration of such hydrocarbons as, for instance, diphenylmethane, this lag becomes very appreciable, so that the reaction only occurs in a thin layer at the interface between the acid and the hydrocarbon layers. Raising the temperature accelerates the diffusion processes (1°C rise in temperature increases the diffusion coefficient by 2–3 per cent), but at the same time the rate of reaction is increased to a much greater extent. Hence nitration at high temperature enhances the diffusion lag.

Titov studied the effect of diffusion on the rate of reaction during nitration of *m*-xylene in reaction vessels of different cross-sections and found that the reaction proceeded 2·6 times more readily in a vessel with cross-section 100 cm^2 than in one of 20 cm^2. Likewise the yield in horizontal tubes was 2–3 times higher than in vertical ones. It was shown that stirring (using a revolving autoclave) increased the yield of reaction products 1·5 times over that obtained without stirring.

Titov draws the following conclusions from his experiments:

(1) The role of sealed tubes in the nitration of the paraffin chain by Konovalov's method is reduced to the preservation of nitrogen oxide and dioxide in the sphere of reaction.

(2) During the nitration of paraffins with nitric acid in the liquid phase there is a lagging of the diffusion processes compared to the course of the reaction; this leads to the slowing down of the latter and alters the interrelation of the reaction products, favouring the formation of mono- and dinitro compounds with a decreased yield of oxidation products.

(3) The diffusion lag and the phenomena this entails become more marked with increased chemical activity of the hydrocarbon and at higher temperatures, and also depends on the type of apparatus used for the reaction.

In considering the differences in the nitration of aromatic and saturated hydrocarbons Titov [114] reaches the following conclusions:

(1) Aromatic compounds are easily nitrated with concentrated nitric acid or nitrating mixture, the presence of NO_2 in these reagents being of no significance, whilst in the case of saturated hydrocarbon it is the active nitrating agent. Saturated hydrocarbons are not obviously affected by nitric acid itself.

(2) Under heterogeneous conditions the nitration of aromatic compounds occurs in the acid layer; that of saturated hydrocarbons occurs in the hydrocarbon layer.

(3) Addition of strongly protonic or aprotonic acids ($AlCl_3$, $TiCl_4$, BF_3) to the reaction mixture markedly accelerates the nitration of aromatic compounds but has no apparent effect on paraffin hydrocarbons.

(4) The rate of nitration of aromatic compounds is considerably lower in the vapour phase than in the liquid; in the case of saturated hydrocarbons the rate of nitration in both phases is almost the same.

(5) Addition of mercury salts during the nitration of aromatic hydrocarbons with nitric acid of moderate concentration accelerates the reaction; it has no effect on the course of reaction in the case of saturated hydrocarbons.

(6) The nitration of aromatic compounds (with nitric acid, nitrating mixture) usually gives yields of the nitro derivatives close to the theoretical, whereas in the case of saturated hydrocarbons the yield of the mononitro derivatives does not exceed 60 per cent of the theoretical, and a considerable amount of oxidation products is formed.

(7) Owing to the incomplete coordination and the presence of multiple bonds in aromatic rings, their nitration begins with an interaction of the nitrating agent with a carbon atom; in the case of saturated hydrocarbons the nitrating agent (NO_2) reacts with a hydrogen atom.

(8) Nitration of the aromatic ring is an ionic-complex reaction, whilst that of saturated compounds is a radical–molecular reaction.

Titov and Shchitov [115] showed that in a number of cases of nitration of paraffins with nitric acid and NO_2, especially at high temperature, it was necessary to admit the $NO_3\cdot$ radical into the reaction. The radical is formed from nitric anhydride according to the scheme:

$$O_2N\text{—}O\text{—}NO_2 \rightleftarrows NO_2\cdot + ONO_2\cdot$$

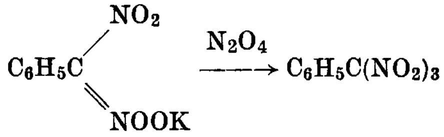
The authors investigated the interaction of normal paraffins and *cyclo*paraffins with nitric anhydride. The reaction proceeds at a satisfactory rate even at 0°C in inert solvents. On mixing the reagents the interaction occurs rapidly and with evolution of heat.

The authors consider that $NO_3\cdot$, formed from nitric anhydride, reacts with the hydrocarbon forming the hydrocarbon radical according to the scheme:

$$RH + ONO_2\cdot \rightarrow R\cdot + HONO_2$$

The authors suppose that the formation of the extremely active radical-like particle NO_3 explains the higher rate of nitration sometimes observed when using nitric acid rather than NO_2.

Phenyltrinitromethane was first obtained by Titov and Smirnov in 1952 [116] by the action of N_2O_4 on the potassium salt of phenyldinitromethane:



$$C_6H_5C\begin{matrix} \diagup NO_2 \\ \diagdown NOOK \end{matrix} \xrightarrow{N_2O_4} C_6H_5C(NO_2)_3$$

To a suspension of the potassium salt of phenyldinitromethane in carbon tetrachloride at −12°C was added a solution of N_2O_4 in the same solvent. The ratio was 2·4 moles N_2O_4 to 1 mole of the salt. The reaction was almost instantaneous. The mixture was treated with water and soda solution; after removal of the solvent by vacuum distillation the crude phenyltrinitromethane was purified by treating it with concentrated sulphuric acid. The yield was 70 per cent of the theoretical.

An attempt to prepare phenyltrinitromethane by the action of N_2O_4 not on the salt but on the free phenyldinitromethane was unsuccessful. The reaction only takes place when base is added (even pyridine). This indicates that phenyldinitromethane reacts with N_2O_4 only in the aci-form.

Phenyltrinitromethane can also be prepared by the action of nitric acid (sp. gr. 1·4) containing nitrogen oxides on phenyldinitromethane, giving a 50 per cent yield of the theoretical. *p*-Nitrobenzoic acid is also formed with a 35 per cent yield of the theoretical. In the absence of nitrogen oxides the reaction does not take place.

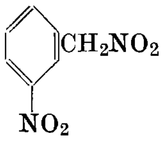
The Italian chemist **Ponzio** [117] has proposed an interesting method for the introduction of two nitro groups into the side-chain of the aromatic ring. The method is based on the action of N_2O_4 on benzaldoxime according to the scheme:

$$C_6H_5CH{=}NOH \xrightarrow{N_2O_4} C_6H_5CH(NO_2)_2$$

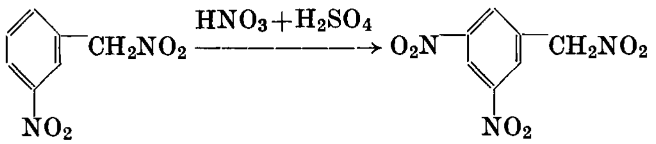
In this reaction an excess of N_2O_4 is of major importance. If the process is carried out with an equimolecular amount of N_2O_4 side reactions develop. **Ponzio** submits the following method for the reaction: to an ethereal solution of benzaldoxime N_2O_4 is added in the ratio of 2 moles to 1 mole of the oxime. The process is carried out at first with cooling, then at room temperature. The phenyldinitromethane formed is extracted with a 5 per cent aqueous solution of alkali and then precipitated out by acidifying with 10 per cent sulphuric acid. The yield is 75 per cent of the theoretical.

The conversion of oximes to nitro compounds by oxidation with hypobromite and subsequent reducing debromination has been studied [118]. The reaction fails completely with the aldoximes and ketoximes of aliphatic and aromatic ketones. Only alicyclic ketoximes give the corresponding nitro compounds. N-bromimide of succinic acid is recommended as a brominating agent. Sodium boronhydride $NaBH_4$ gives the best results as a reducing agent.

It is pertinent to mention the action of concentrated nitric acid on phenylnitromethane and phenyldinitromethane. When phenylnitromethane is nitrated it is slowly added to 7–10 times the amount by weight of nitric acid (sp. gr. 1·49–1·53) at 10–15°C (the reaction mixture has to be cooled). The reaction mixture is poured onto ice and the *m*-nitrophenylnitromethane which precipitates out:

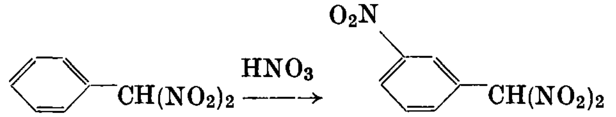


is recrystallized from alcohol or glacial acetic acid. The yield is approximately 40 per cent of the theoretical. It should be noted that on nitration with concentrated nitric acid alone only one nitro group enters the ring, predominantly in the *m*-position. In order to introduce a second nitro group into the ring it is necessary to use a mixture of nitric acid (sp. gr. 1·5) and oleum containing 20–25 per cent free SO_3:



Eight to ten times the amount by weight of the nitrating mixture is used in the reaction which is carried out at 65–70°C. The yield is approximately 75 per cent of the theoretical [119].

The nitration of phenyldinitromethane with concentrated nitric acid [120] gives *m*-nitrophenyldinitromethane according to the scheme:



The reaction is carried out as follows: nitric acid (sp. gr. 1·5) cooled to − 15°C is added to phenyldinitromethane (ratio by weight of nitric acid to phenyldinitromethane 10 : 1) and the mixture is allowed to stand at room temperature for 1 hr. It is then poured into water. The precipitate obtained is filtered off, washed with water and recrystallized from methyl alcohol. *m*-Nitrophenyldinitromethane is obtained as yellow crystals. The yield is 93 per cent of the theoretical.

In the last 15–20 years data have been published concerning the nitration of saturated hydrocarbons with nitric acid by the so-called vapour phase method. A peculiarity of this method, which uses atmospheric pressure, is the high temperature of the reaction, markedly exceeding the temperatures used in Konovalov's method of nitration. This peculiarity confers a distinctive character on the vapour phase method, since under these conditions not only nitration of the paraffins occurs but also their (or that of the free radicals, *vide infra*) pyrolysis, forming compounds (or radicals) of lower molecular weight. These when nitrated give nitro compounds with fewer carbon atoms than the parent paraffin.

Industrial production of nitroparaffins by continuous nitration of paraffins in the vapour phase, begun in 1940, has opened up a new field of organic chemistry. To ensure good yields of nitroparaffins and to avoid the risk of explosion it is most important to regulate the ratio of the reagents in such a way that the ratio of the hydrocarbon to nitric acid be at least 2 : 1. In addition to the nitro derivatives with different numbers of carbon atoms the vapour phase method of nitration also gives oxidation products.

The work of HASS, HODGE and VANDERBILT [121] gives data for the nitration of the paraffins: ethane, propane, *n*-butane and *iso*butane. The appropriate nitroparaffins were synthesized by passing the hydrocarbon vapour through nitric acid at the rate of 150 l/hr (molar ratio of hydrocarbon to acid 2 : 1) the mixture so formed entered a reaction vessel which was heated on a nitrite–nitrate bath to 420°C (the vessel being a glass tube 10 mm in diameter). Nitration of ethane gave nitromethane and nitroethane; nitration of propane gave four products: nitromethane, nitroethane, 1-nitropropane and 2-nitropropane, the two latter forming the bulk of the products (65 per cent of the total yield of nitroparaffins). The main products given by the nitration of butane were 1- and 2-nitrobutanes (77 per cent of the total yield of nitroparaffins); 1-nitropropane, nitroethane and nitromethane were also formed by nitration of the products of pyrolysis. Nitration of *iso*butane gave the following results; of the two nitro derivatives with the same number of carbon atoms as the parent paraffin, primary 1-nitro*iso*butane was obtained with a yield 65 per cent of the total yield of nitro derivatives, whilst tertiary 2-nitro*iso*butane amounted only to 7 per cent. 2-Nitropropane (yield 20 per cent) and nitromethane were also found among the reaction products. The results of these experiments are summarized in Table 14.

Table 14. *Vapour phase nitration of paraffins*

Hydrocarbon	Reaction product (%)									
	Acetone	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	1-Nitro*iso*butane	2-Nitro*iso*butane	Yield (%) after one passage
Ethane	—	10–20	80–90	—	—	—	—	—	—	9
Propane	—	9	26 (?)	32	33	—	—	—	—	21
Butane	—	6	12	5	—	27	50	—	—	28
*iso*Butane	5	3	—	—	20	—	—	65	7	25

The same authors nitrated *iso*butane by the Konovalov method at 150°C, and obtained as the only reaction product crystalline 2-nitro*iso*butane which, on nitration by the vapour phase method is formed with a yield of only 7 per cent. Comparison of these two methods demonstrates clearly the peculiarities of vapour phase nitration: owing to the high temperatures the reaction becomes less selective and gives isomers of which the primary, obtained with a much better yield than the tertiary, is evidently the more stable under the conditions of the reaction. As already mentioned above, high temperatures also lead to the formation of nitro compounds with fewer carbon atoms than the parent paraffin as the result of pyrolysis.

In 1952 Bachmann *et al.* [122–125] conducted a thorough investigation into vapour phase nitration of propane and butane with nitric acid. They established that not only nitro compounds, but also oxygen-containing compounds and unsaturated hydrocarbons were formed during such nitration. At a temperature of 425°C (optimum) and time of contact 1·6 sec the conversion reaches 36 per cent. These authors studied the effect of adding oxygen and halogens on the yield and composition of nitration products obtained from butane [123] and propane [124, 125]. They found that the addition of 2 moles O_2 to 1 mole HNO_3 did not alter the optimum temperature (425°C) for the nitration of butane, increased the yield of nitro products calculated on the nitric acid passed through, but lowered the yield calculated on the converted butane. It was also found that the successive introduction of 1, 2 and 3 moles of oxygen caused a general increase of carbonyl compounds, olefines and CO, whilst the amount of CO_2 reached a minimum at the maximal yield of nitroparaffins obtained with 1–2 moles O_2 to 1 mole HNO_3.

Bachmann explains the results obtained with the addition of oxygen as follows: the addition of oxygen increases the concentration of free radicals which, combining with nitrogen dioxide, give nitroparaffins. It is always only a part of the alkyl radicals which undergoes conversion to nitroparaffin, the rest react with oxygen. When the amount of oxygen is increased beyond the optimal limit the rate of oxidation rises and an additional part of the radicals is involved in this at the expense of nitroparaffin formation. The presence of olefines in experiments conducted without oxygen confirms the participation of free radicals in nitration.

Addition of 0·015 mole bromine to 1 mole HNO_3 increases the yield of nitroparaffins from 23 to 28 per cent calculated on the nitric acid passed through and from 23 to 50 per cent calculated on converted butane [124]. Additions of oxygen enhance the positive effect of bromine. Thus the yield of nitroparaffins calculated on HNO_3 reaches the maximal value of 48 per cent with 2 moles O_2 to 1 mole HNO_3, whilst the yield of nitroparaffins calculated on the converted butane reaches the maximal value of 57 per cent in the presence of 1 mole O_2 to 1 mole HNO_3.

The authors consider that the positive effect of bromine is associated with its ability to generate radicals according to the scheme:

(1) $Br_2 \rightleftharpoons 2Br\cdot$
(2) $C_nH_{2n+2} + Br\cdot \rightarrow C_nH_{2n+1}\cdot + HBr$
(3) $C_nH_{2n+1}\cdot + Br_2 \rightarrow C_nH_{2n+1}Br + Br\cdot$
(4) $2C_nH_{2n+1}Br \rightarrow C_nH_{2n} + C_nH_{2n+1}\cdot + HBr + Br\cdot$
(5) $HBr + [O] \rightarrow HO\cdot + Br\cdot$

The advantage of bromine over oxygen Bachmann explains by the ease of breakdown of alkyl halides with regeneration of bromine atoms. The positive effect of added oxygen in nitration in the presence of bromine is explained by Bachmann in terms of oxidation of HBr to $Br\cdot$.

Bachmann's findings show that in order to obtain maximal yields of the nitro product (in the presence of 0·1 mole O_2 to 1 mole of propane) twice as much chlorine is needed than bromine (0·05 mole Cl_2 to 1 mole HNO_3; 0·025 mole Br_2 to 1 mole HNO_3). This is explained as follows, using the scheme below to express the reactions of chlorine and bromine:

(1) $X_2 \rightarrow 2X\cdot$
(2) $RH + X\cdot \rightarrow R\cdot + HX$
(3) $R\cdot + NO_2 \rightarrow RNO_2$
(4) $R\cdot + X_2 \rightarrow RX + X\cdot$
(5) $HX + NO_2\cdot \rightarrow X_2 + H_2O +$ lower oxides of nitrogen
(6) $RX + NO_2\cdot \rightarrow X_2 +$ oxidation products of $R +$ lower oxides of nitrogen

Hydrogen bromide and alkyl bromide are oxidized more rapidly than the corresponding chlorine derivatives. Therefore the number of molecules of halogen capable of conversion to free radicals is larger in the case of bromine than chlorine. The lowering of the yield of nitro product when the concentration of halogen exceeds the optimal level is explained by the expenditure of NO_2 according to equations (5) and (6).

Bachmann has also investigated the effect of the parameter S/V (ratio of surface of the reactor to its volume) on the yield of nitroparaffins using the nitration of butane in the presence of oxygen for his experiments [123]. The curve of the relation of the yield of RNO_2, calculated on HNO_3 passed through, to the amount of oxygen showed a maximum for all the values of S/V investigated (20, 28, 300). The maximal yield (43 per cent RNO_2) remained constant at all the three values of S/V, but depending on the parameter S/V this yield was reached at various levels of O_2 content; with maximal yield, the highest value of S/V corresponded to the lowest level of O_2 (1 mole O_2 to 1 mole HNO_3). Increasing the parameter S/V caused a decrease in the ratio converted butane–butane passed through. Bachmann puts forward the following explanation for these findings. Reduction in the amount of converted butane with increased S/V is explained by the disappearance of part of the radicals on the surface. However, in spite of the disappearance of these, the amount of nitroparaffins formed from the radicals does not decrease (the level of the maximum is preserved). Consequently, increasing S/V allows the formation of greater amounts of nitroparaffins at the expense of curtailed oxidation chain reaction, i.e. by suppressing the oxidative direction of the reaction.

Bachmann and Pollack [126] studied the vapour phase nitration of propane with chlorine as catalyst and compared the results obtained with the data published in 1952 on vapour phase nitration in the presence of oxygen and chlorine.

As the authors remark, the usual vapour phase nitration of propane gives a mixture of nitroparaffins consisting of 25 per cent 1-nitropropane, 40 per cent 2-nitropropane, 10 per cent nitroethane and 25 per cent nitromethane. If a mixture of oxygen and chlorine is used as catalyst the conversion to nitroparaffins is increased by 32 per cent, whilst the use of chlorine alone increases it by 46 per cent. Bromine acts similarly to chlorine, but the disadvantage in using it consists of the reducing action of the HBr formed, which converts the nitro compounds into ammonium and hydroxylammonium salts.

An optimal conversion of 13 per cent is obtained on vapour phase nitration of natural gas of the following composition: 75·56 per cent CH_4, 6·36 per cent C_2H_6, 3·45 per cent C_3H_8, 13·65 per cent N_2, 0·69 per cent C_4H_{10} and with the following ratios of reactants: natural gas : HNO_3 : H_2O : Cl_2 = 13·6 : 1 : 1·6 : 0·4, time of contact 1·7–1·8 sec and temperature 450°C. The same conversion results from nitration without chlorine using the ratios (molar): C_3H_8 : HNO_3 : H_2O : CH_4 = 0·483 : 1 : 1·6 : 14·0. Therefore, if methane predominates in the mixture chlorine has no catalytic effect.

According to an American patent [127] propane is nitrated by 40–70 per cent nitric acid at 190°C and pressure of approximately 9 atm. To 2 moles propane 1 mole of acid is taken and a mixture of nitropropanes obtained [$(CH_3)_2CHNO_2$ and $(CH_3)_2C(NO_2)_2$ with a yield of 8–10 per cent calculated on nitric acid].

Nitration of propane with nitric acid has received much attention both from the point of view of apparatus (creating isothermic conditions for the reaction) and of the use of catalysts (oxygen, air) to intensify the process [128]. Hass and Alexander [129] studied the effect of oxygen on the nitration of propane with nitric acid at 410°C. They succeeded in increasing the conversion of propane from 28 to 62 per cent. At 395°C and with the introduction of 3·8 moles oxygen to 1 mole HNO_3 the conversion of propane to nitro products increases from 20 to 76 per cent.

A recently published patent [130] indicates appreciable rises in the yield of nitroalkanes and valuable oxidation side-products obtained by vapour phase nitration of aliphatic hydrocarbons CH_4, C_2H_6, C_3H_8, C_4H_{10} (normal and *iso*-) in the presence of oxygen.

Addition of oxygen has no marked effect on the nitration of methane. At the temperature of 435°C changing the molar ratio O_2 : HNO_3 from 0 to 5 increases the conversion of nitric acid to nitromethane from 17·6 to 24·2 per cent. [129].

When nitration is carried out under pressure and in the presence of oxygen the conversion of HNO_3 to CH_3NO_2 falls rapidly with increasing oxygen concentration. This can be seen from the data in Table 15 [131] obtained at 444°C and 7·8 atm.

Table 15. *Conversion of* HNO_3 *to* CH_3NO_2 *under pressure in the presence of oxygen*

CH_4/HNO_3	11·8	12·0	12·3	11·9	10·5
O_2/HNO_3	0·0	0·38	0·37	0·60	1·30
Concentration O_2	0·0	2·4	2·4	3·9	8·8
Conversion	21·1	18·1	20·4	19·3	0·0
Yield	21·3	21·2	23·6	22·4	0·0

At high concentrations of oxygen no nitromethane is formed, instead of which formaldehyde is chiefly obtained.

Tiutiunnikov, Mankovskaia and Iavlinskii [132] studied the vapour phase nitration of the liquid petroleum distillates. The mixture of hydrocarbons consisted of 24·2 per cent naphthene and 72·6 per cent paraffin hydrocarbons. The yield of nitro products from a single operation was 60–65 per cent of the hydrocarbon mixture. The nitro products obtained contained: 90 per cent mononitro compounds consisting of 20 per cent primary nitro compounds, 40 per cent secondary and 40 per cent tertiary compounds; 67 per cent nitric acid was used in 1 : 1 ratio to ligroin; duration of contact was 4–5 sec, temperature of nitration 330–350°C. As the authors point out, the yield of nitro products increased by 90 per cent when the hydrocarbon vapours were swept through by means of an air current; this was evidently connected with the catalytic action of atmospheric oxygen.

HASS and PATTERSON [133] investigated the nitration of pentane. Pentane vapour was introduced into the reaction vessel at a rate of 260 ml/hr where it was mixed with nitric acid vapour admitted at the rate of 70 ml/hr (molar ratio pentane to nitric acid 2·3 : 1). Nitration was carried out at 400°C. The following products were obtained: 1-, 2-, 3-nitropentanes (yield 65 per cent of the total nitroparaffins), 1-nitrobutane, 1-nitropropane, nitroethane and nitromethane. Total yield of nitroparaffins, calculated on reacted nitric acid, was 31 per cent.

SEIGLE and HASS [134] developed a method of vapour phase nitration of *iso*pentane. With a molar ratio of hydrocarbon to acid 1·7 : 1 and temperature 420°C the authors obtained nine nitroparaffins: 3-methyl-1-nitrobutane, 2-methyl-1-nitrobutane, 3-methyl-2-nitrobutane, 2-methyl-2-nitrobutane, 2-nitrobutane, 2-methyl-1-nitropropane, 2-nitropropane, nitroethane and nitromethane. The same products were obtained at 380°C but with lower yields.

HASS and ROBINSON [135] indicate a method for vapour phase nitration of 1 : 1 : 1-trifluoropropane by introducing trifluoropropane and nitric acid into a reactor at 395°C at the rate of 0·42 and 0·52 mole/hr with duration of contact 2·5–3·5 sec. The yield is 39 per cent of a mixture of 1 : 1 : 1-trifluoronitroethane and 1 : 1 : 1-trifluoro-3-nitropropane in the ratio 2 : 3. 11·9 per cent of the original substance is converted into nitro compounds.

When chloro derivatives of hydrocarbons are treated with nitric acid in the vapour phase chloronitro hydrocarbons are formed. These are used as insecticide solvents and as intermediate products [136].

The work of DANZIG and HASS on 2 : 3-dimethylbutane [137] should also be mentioned in connexion with vapour phase nitration of paraffins. The aim of their investigation was to establish whether dinitroparaffins as well as mononitroparaffins were formed in the course of vapour phase nitration similarly to the case of Konovalov's method. On nitration of 2 : 3-dimethylbutane in a sealed tube at 125° KONOVALOV [138] obtained, apart from 2 : 3-dimethyl-2-nitrobutane, 2 : 3-dimethyl-2 : 3-dinitrobutane whose formation could be explained by the substitution of tertiary hydrogen atoms on the second and third carbon atoms by nitro groups. DANZIG and HASS conducted their experiments at temperatures of 400–430°C and with molar ratio of hydrocarbon to nitric acid 1·58 : 1.

They found that the optimal conversion of 2 : 3-dimethylbutane to nitroparaffins occurred at 410°C and duration of contact 1–2 sec. Further increase in temperature decreased the conversion, with the formation of oxidation side products whose yield was highest at 430°C. At 408°C the conversion calculated on nitric acid was 17·5 per cent. No dinitro derivatives were found in DANZIG and HASS' experiments. Only mononitroparaffins were formed: 2 : 3-dimethyl-1-nitrobutane, 2 : 3-dimethyl-2-nitrobutane, 3-methyl-2-nitrobutane, 2-nitropropane and nitromethane, together with oxidation products (ketones) and products of cracking (2 : 3-dimethyl-1-butene and 2 : 3-dimethyl-2-butene).

MCCLEARLY [139], using butane, showed the influence of temperature on the composition of reaction products obtained by nitration (Table 16).

Table 16. *Nitration of butane—yield of reaction products* (%) *depending on temperature*

Temperature (°C)	Nitromethane (%)	Nitroethane (%)	1-Nitropropane (%)	2-Nitrobutane (%)	1-Nitrobutane (%)
395	2·1	12·7	4·9	49·0	30·5
393	6·1	19·0	7·0	41·0	27·0
393	5·0	11·0	5·0	46·0	32·0
445	5·9	18·2	6·5	37·0	31·8
450	9·0	25·0	7·0	28·0	31·0

As can be seen from this table, raising the reaction temperature decreases the formation of nitrobutanes and correspondingly increases the amount of lower nitroparaffins, including nitromethane.

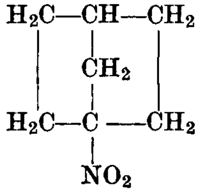
It should be noted that the preparation of nitromethane by direct nitration of methane is a fairly difficult problem owing to low conversion and difficulty of recovery of the unreacted hydrocarbon. There is a patent which recommends that methane be diluted with inert gas, e.g. nitrogen, and recirculation be used. The yield of nitromethane increases with greater dilution with nitrogen. Thus, conversion of 100 per cent methane is 2·2 per cent, whereas that of 10 per cent methane increases almost threefold [140].

Owing to the greater difficulty of nitrating methane nitromethane is mostly obtained during nitration of propane with nitric acid. Depending on the conditions of reaction the nitromethane content of the reaction products varies between 9–49 per cent [141]. To remove nitromethane from the mixture of reaction products distillation with *n*-hexane is recommended. The latter gives an azeotropic mixture with nitromethane, lower aliphatic alcohols and water.

Aliphatic esters, alcohols, ketones and carboxylic acids when subjected to vapour phase nitration give yields of nitro derivatives not exceeding 20 per cent (from 5 per cent to 20 per cent); the temperature used in the reaction is 400°C [142].

Aliphatic–aromatic hydrocarbons have also been subjected to vapour phase nitration. Bullock and Mitchell [143] nitrated toluene with nitric acid in the vapour phase and obtained a mixture of isomeric nitro derivatives which contained 55 per cent of *o*-nitrotoluene, 5 per cent *m*-nitrotoluene and 40 per cent *p*-nitrotoluene. Negligible amounts of polynitro products and oxidation products were also obtained. The ratio of the isomers is approximately the same as that obtained by ordinary nitration.

Norcamphane served as an example of vapour phase nitration of bicyclic naphthenes; treated with nitric acid at 400–410°C it gave tertiary nitronorcamphane, as shown by Hass and Blickenstaff [144]:



Formation of this product showed that during vapour phase nitration the tertiary hydrogen atom at the carbon atom common to both rings loses its inert character.

A summary of the published experimental data on the nitration of paraffins in the vapour phase leads to the following conclusions concerning the distinctive features of this method:

(1) Vapour phase nitration is achieved at ordinary pressure and at high temperatures, from 250 to 600°C; in most cases the synthesis of nitroparaffins is carried out at 400–450°C which is, evidently, the optimal range of temperatures.

(2) As distinct from nitration by the Konovalov method which gives one or two reaction products, vapour phase nitration gives a series of isomeric nitro compounds (at high temperatures the reaction becomes less selective).

(3) Vapour phase nitration gives, in addition to nitro derivatives corresponding to the hydrocarbon being nitrated, a series of nitroparaffins with fewer carbon atoms than the parent paraffin. In order to explain this fact the formation of free radicals from the paraffins has been proposed. These, in the course of further pyrolysis, give radicals with lower molecular weight; the products of pyrolysis, combining with the nitro group, give nitroparaffins with different numbers of carbon atoms. The relative yield of nitroparaffins formed by the nitration of the products of pyrolysis increases at higher temperatures.

(4) Mononitroparaffins are formed exclusively during vapour phase nitration, with primary nitro compounds predominating. Raising the temperature increases the yield of primary nitro compounds and decreases that of secondary and tertiary ones. These findings lead to the following conclusions: (a) polynitroparaffins are readily pyrolysed; as the result of this they cannot exist at the high temperatures used in vapour phase nitration; (b) of the mononitroparaffins the most stable are the primary ones.

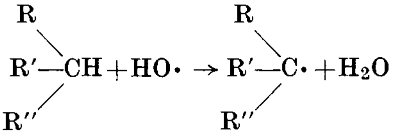
(5) Conversion (amount of nitroparaffins formed in relation to nitric acid passed through the reactor) is constant for a fairly wide range of temperature with suitably chosen duration of contact. When duration of contact is kept constant the curve conversion-temperature shows a maximum; at temperatures below the optimum, nitration is incomplete, whilst at higher temperatures pyrolysis of nitroparaffins takes place.

(6) The nitration reaction is accompanied by oxidation processes involving the paraffins and their nitro derivatives, as the result of which alcohols, aldehydes, ketones, carboxylic acids as well as CO and CO_2 are formed. Optimal utilization of nitric acid in the synthesis of nitroparaffins reaches 40 per cent. By means of regeneration of nitrogen oxides formed in the oxidation reactions, the yield of nitroparaffins calculated on nitric acid can be raised (in large industrial plants synthesizing nitroparaffins where regeneration of nitrogen oxides to nitric acid is carried out the yield of nitroparaffins is 90 moles/100 moles nitric acid).

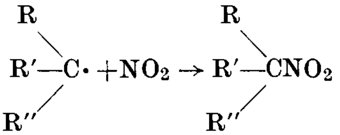
(7) Methane is the most difficult of the paraffins to nitrate; at higher temperatures and with longer duration of contact it still gives smaller conversion to nitro derivatives than the other homologues (at 450°C and contact duration 0·42 sec the yield of nitromethane is 15 per cent). Up to propane there is progressively increasing ease of nitration, but hydrocarbons following propane exhibit no appreciable differences in their reactivity to nitration.

(8) The mechanism of vapour phase nitration has not been sufficiently studied. In the view of McCleარly and Degering [139] first of all nitric acid breaks up into nitrogen dioxide and OH· radical [equation (1)]; the latter acts on the hydrocarbon with the formation of free radicals [equation (2)] which react with NO_2 or nitric acid [equations (3) and (4)]:

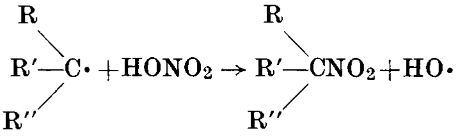
$$\mathrm{HONO_2 \rightarrow NO_2 + HO\cdot} \qquad (1)$$



$$\mathrm{R'{-}\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}H + HO\cdot \rightarrow R'{-}\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}\cdot + H_2O} \qquad (2)$$



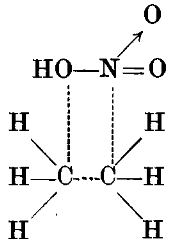
$$\mathrm{R'{-}\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}\cdot + NO_2 \rightarrow R'{-}\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}NO_2} \qquad (3)$$



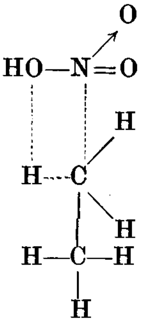
$$\mathrm{R'{-}\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}\cdot + HONO_2 \rightarrow R'{-}\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}NO_2 + HO\cdot} \qquad (4)$$

In this way are formed nitro compounds with the same number of carbon atoms as the paraffin being nitrated. In order to explain the formation of nitro compounds with fewer carbon atoms McClearly and Degering suggest further breaking up of radicals under the influence of high temperatures and subsequent nitration of the products of pyrolysis by NO_2 or nitric acid.

Another theory proposed by Ewell (145) is based on the assumption that hydrocarbons, combining with nitric acid, form two kinds of intermediate complexes. Subsequent breakdown of complexes of the first type gives alcohols and nitroparaffins with fewer carbon atoms than the compound being nitrated; breakdown of the complexes of the second type leads to the formation of water and nitroparaffins corresponding to the parent hydrocarbon. For example, the nitration of ethane proceeds, according to Ewell, by way of the following intermediate complexes:



(I)



(II)

As the reaction proceeds the first complex breaks down into nitromethane and methanol, whilst the second one gives nitroethane and water.

Burton's work [146] offers confirmation of the theory of complexes. He showed that when optically active 3-methylhexane was nitrated, optically active 2-nitrobutane was also formed.

Vapour phase nitration as already mentioned, is usually carried out at atmospheric pressure. In some cases, however, it may be done under pressure to enhance the effectiveness of the reaction. Hass, Hibsmann and Pierson [147] nitrated ethane under pressure of 7 atm and obtained a 33 per cent yield of nitroparaffins after a single passage through the reaction chamber (at atmospheric pressure the conversion is 9 per cent).

Recent patent literature has communications on vapour phase nitration with nitric acid in the presence of catalysts. Levy [148] passed a mixture of paraffins with nitric acid at 300–450°C through a reaction chamber with a catalyst consisting of compounds of arsenic or antimony mixed with silicates. Optimal conversion was obtained with the ratio of paraffins to nitric acid 0·5 : 1 and duration of contact 1–5 secs.

There are also suggestions [149] for the vapour phase nitration of both aliphatic and aromatic hydrocarbons in reactors with pulverized contact (size of particles 5—600μ) suspended in a stream of the reagents.

Published data are available [150] on continuous nitration of *cyclo*hexane by nitric acid. Glass apparatus is used through which the liquid passes at rates which can be regulated over a wide range. The pressure maintained is 7 atm. Neither the reactants nor the products of reaction come in contact anywhere with metallic parts and are fed in by a stream of nitrogen. The optimal conditions for this nitration are: temperature

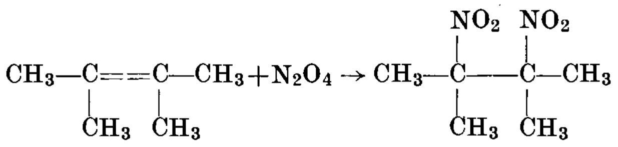
120°C and ratio $HNO_3/C_6H_{12} = 0{\cdot}91$. Yield of nitro*cyclo*hexane is 13·9 per cent.

It should be mentioned that the synthesis of some of the lower nitroparaffins by the vapour phase method is at present being used on an industrial scale.

3. PREPARATION OF POLYNITROPARAFFINS

Preparation of polynitroparaffins by direct nitration with nitric acid is not as common as in the case of mononitroparaffins. A brief summary of the various methods used is given in this section.

Olefines treated with N_2O_4 add on $—NO_2$ groups giving polynitroparaffins. For example, 2 : 3-dimethyl-2-butene reacts with N_2O_4 to give 2 : 3-dimethyl-2 : 3-dinitrobutane:

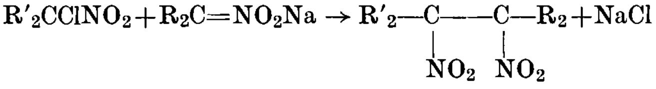


$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle CH_3}{\underset{|}{C}}—CH_3 + N_2O_4 \rightarrow CH_3—\overset{\displaystyle NO_2}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—\overset{\displaystyle NO_2}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—CH_3$$

Seigle and Hass [151] have developed a method by which dinitroparaffins can be prepared from secondary nitroparaffins by their successive treatment with base and halogen. The essence of this method is the condensation of sodium salts of the aci-form of nitroparaffin with the product of the interaction of these salts with halogen, associated with elimination of sodium halide:

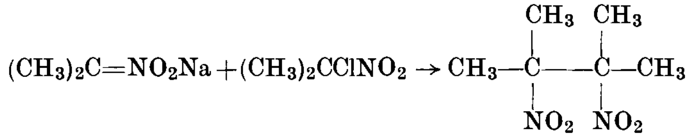
$$R_2CHNO_2 + NaOH \rightarrow R_2C{=}NO_2Na + H_2O \qquad (1)$$

$$R'_2C{=}NO_2Na + Cl_2 \rightarrow R'_2CClNO_2 + NaCl \qquad (2)$$



$$R'_2CClNO_2 + R_2C{=}NO_2Na \rightarrow R'_2—\underset{\displaystyle NO_2}{\underset{|}{C}}—\underset{\displaystyle NO_2}{\underset{|}{C}}—R_2 + NaCl \qquad (3)$$

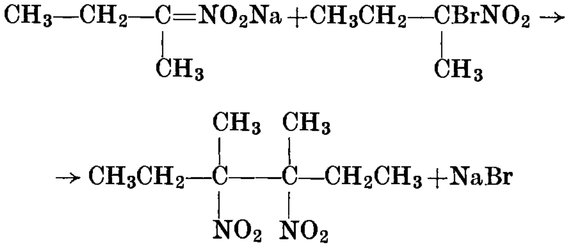
For example, the sodium salt of the aci-form of nitropropane $(CH_3)_2C{=}NO_2Na$ on heating for 7 hr with $(CH_3)_2\,CClNO_2$ gives 2 : 3-dimethyl-2 : 3-dinitrobutane (yield 9 per cent):



$$(CH_3)_2C{=}NO_2Na + (CH_3)_2CClNO_2 \rightarrow CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle NO_2}{\underset{|}{C}}}}—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle NO_2}{\underset{|}{C}}}}—CH_3$$

The reaction proceeds more effectively if a bromo derivative is substituted for the chloro derivative in treating the sodium salt of the aci-form of the nitroparaffin (yield of dinitroparaffin 29 per cent); still better results are obtained when the iodo derivative is used (yield 43 per cent). Similarly, the sodium salt of the aci-form of nitrobutane $(C_2H_5)(CH_3)C$

$=NO_2Na$ reacting with $(C_2H_5)(CH_3)CBrNO_2$ gives 3 : 4-dimethyl-3 : 4-dinitrohexane with a 16 per cent yield:

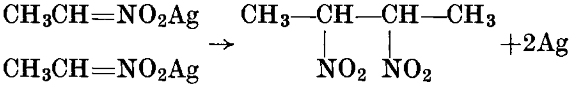


$$CH_3{-}CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}NO_2Na + CH_3CH_2{-}\underset{CH_3}{\underset{|}{C}}BrNO_2 \rightarrow$$

$$\rightarrow CH_3CH_2{-}\overset{CH_3}{\overset{|}{\underset{NO_2}{\underset{|}{C}}}}{-}\overset{CH_3}{\overset{|}{\underset{NO_2}{\underset{|}{C}}}}{-}CH_2CH_3 + NaBr$$

The sodium salt of nitro*cyclo*hexane, on refluxing for 3 hr in 80 per cent alcohol solution with $(CH_3)_2CBrNO_2$ gives 1-nitro-1-(2-nitro*iso*propyl)-*cyclo*hexane with a 19 per cent yield. Primary nitro compounds do not undergo this reaction.

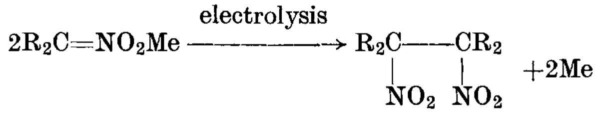
Angeli and Alessandri [152] found that the silver salt of nitroethane underwent spontaneous breakdown with subsequent condensation of the products to give 2 : 3-dinitrobutane:



$$\begin{matrix} CH_3CH{=}NO_2Ag \\ CH_3CH{=}NO_2Ag \end{matrix} \rightarrow CH_3{-}\underset{NO_2}{\underset{|}{CH}}{-}\underset{NO_2}{\underset{|}{CH}}{-}CH_3 + 2Ag$$

This synthesis is apparently a general one and can be used for the transition from mono- to polynitroparaffins. For example, the silver salts of nitropentane and phenylnitromethane give 5 : 6-dinitrodecane and 1 : 2-dinitro-1 : 2-diphenylethane respectively.

Dinitroparaffins can also be synthesized electrochemically, viz. by the electrolysis of salts of the aci-form of nitroparaffins [153–154]:

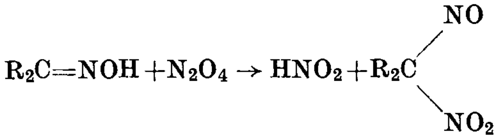


$$2R_2C{=}NO_2Me \xrightarrow{\text{electrolysis}} R_2\underset{NO_2}{\underset{|}{C}}{-}\underset{NO_2}{\underset{|}{C}}R_2 + 2Me$$

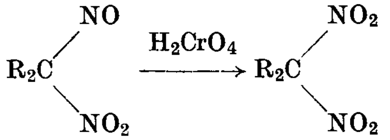
Electrolysis is carried out in a cell with a copper cathode and a polished platinum anode at 6–10 V and temperature 23–27°C. Under these conditions 2-nitrobutane gives mainly 3 : 4-dinitro-3 : 4-dimethylhexane and a small amount of 2 : 2-dinitrobutane [155].

Dinitro compounds can also be prepared by the action of various oxidizing agents on salts of the aci-form of secondary nitroparaffins. Persulphates give the best results. The following have been obtained by this method: 2 : 3-dimethyl-2 : 3-dinitrobutane (yield 51 per cent) from 2-nitropropane, 3 : 4-dimethyl-3 : 4-dinitrohexane (yield 37 per cent) from 2-nitrobutane, 1 : 1-dinitrobi*cyclo*hexyl (30 per cent yield) from nitro*cyclo*hexane. At the same time attempts to convert 1 : 1-dinitroethane into tetranitrobutane and trinitromethane into hexanitroethane by the oxidative dimerization method proved unsuccessful. Primary nitro alkanes as distinct from secondary ones, only react with persulphate to give *iso*oxazole derivatives [156].

Synthesis of dinitroparaffins with both nitro groups attached to the same carbon atom can be achieved by a method which consists of oxidizing pseudo-nitrol $R_2C(NO)(NO_2)$ with chromic acid; pseudonitrols [157] are obtained by the action of N_2O_4 on oximes:



$$R_2C{=}NOH + N_2O_4 \rightarrow HNO_2 + R_2C\begin{array}{l} \diagup NO \\ \diagdown NO_2 \end{array} \tag{1}$$



$$R_2C\begin{array}{l} \diagup NO \\ \diagdown NO_2 \end{array} \xrightarrow{H_2CrO_4} R_2C\begin{array}{l} \diagup NO_2 \\ \diagdown NO_2 \end{array} \tag{2}$$

According to data in patents [158] when pseudonitrols dissolved in CCl_4 are treated with nitrogen oxides or 70 per cent nitric acid 2 : 2-dinitropropane is formed with 27–36 per cent yield.

When paraffins are nitrated at 180°C it is possible to obtain a mixture of the corresponding mono- and dinitro derivatives together with oxidation products and unchanged hydrocarbon. The ratios of the reaction products depend on the ratio of hydrocarbon to nitric acid. Thus, for example, nitration of dodecane [159] at 180–190°C with nitric acid sp. gr. 1·4 gives the following products (Table 17).

Table 17. *Nitration of dodecane*

Ratio dodecane/HNO_3		Products of reaction (%)		
	Dodecane	Nitro-dodecanes	Polynitro-dodecanes	Fatty acids
1:4	24	4	47	25
1:2	33	25	38	4
1:1	43	10	15	2
2:1	58	36	5	1

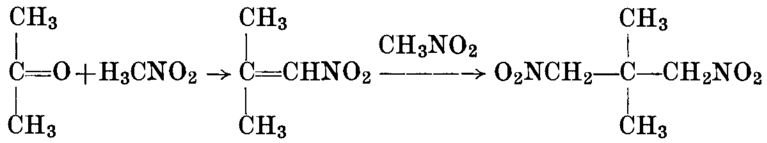
As can be seen from the table, with a large excess of nitric acid (hydrocarbon : acid = 1 : 4) dinitro derivatives and fatty acids are mainly formed: with insufficient nitric acid (hydrocarbon: acid = 2 : 1) only 42 per cent of dodecane enters the reaction, and the predominant reaction products are mononitro derivatives.

Paraffins of more than eight carbon atoms are successfully nitrated in a stream of NO_2, air and CO_2 at 160–190°C. NO_2, CO_2 and air are passed through dodecane (300 g) at 175–180°C during 110 min. The reaction product is fractionated; 130 g of mononitrododecane, 40 g of polynitroparaffins, 20 g fatty acids and 130 g unreacted dodecane are obtained.

Hydrocarbons containing twelve to twenty carbon atoms are similarly nitrated to form corresponding nitroparaffins [160].

Polynitro compounds with fewer carbon atoms than the parent substances are formed when nitrogen dioxide is used as nitrating agent and a longer reaction time is allowed at temperature 200–250°C. Thus, when *iso*butane reacts with NO_2 at 200–250°C 2 : 2-dinitropropane is formed in addition to 2-methyl-2-nitropropane and 2-methyl-1 : 2-dinitropropane [161].

Nitroparaffins condense with ketones to give dinitroparaffins. For example, the reaction between nitromethane and acetone proceeds according to the scheme:



$$\underset{CH_3}{\overset{CH_3}{C}}{=}O + H_3CNO_2 \rightarrow \underset{CH_3}{\overset{CH_3}{C}}{=}CHNO_2 \xrightarrow{CH_3NO_2} O_2NCH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2NO_2$$

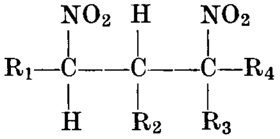
The reaction is conducted in the presence of basic catalysts, preferably secondary amines. Nitro olefines are found among the reaction products in addition to the dinitro alkanes. Lowering the reaction temperature and raising the concentration of ketone favours the formation of dinitro alkanes [162].

According to data in a patent [163] condensation of the potassium salt of dinitromethane with dialdehydes gives tetranitrodiols of the general formula:

$$(NO_2)_2CHCH(OH)(CH_2)_n(OH)CHCH(NO_2)_2 \text{ where } \quad n = 1\text{–}2$$

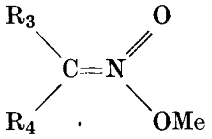
Tetranitrodiols serve as starting material in the synthesis of various polynitro compounds.

Polynitroparaffins of the general formula:



$$R_1{-}\underset{H}{\overset{NO_2}{C}}{-}\underset{R_2}{\overset{H}{C}}{-}\underset{R_3}{\overset{NO_2}{C}}{-}R_4$$

where R_1, R_2, R_3 = H or alkyl and R_4 = alkyl, nitroalkyl, alkoxyl are prepared by [164] the interaction of alkali salts of nitroparaffins of the general formula:

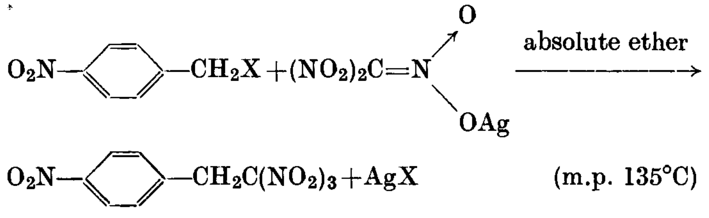


where Me = Na, K, with nitroolefines of general formula $O_2NCH{=}CHR$, with subsequent decomposition of the condensation product obtained by weak acid, such as acetic acid. Thus, K-salt of 2-nitropropane and 1-nitro-1-butene give 1 : 3-dinitro-2-ethyl-3-methylbutane. Interaction of the potassium salt of 2-nitropropane with 2-nitrobutene-1 gives [165] 3 : 5-dinitro-3-methylhexane with a yield approximately 90 per cent.

Alkali salts of polynitroparaffins are also able to react with nitroolefines to form polynitro compounds. According to data available in the literature

[166] 1 : 1 : 1 : 3-tetranitropropane is formed by the condensation of nitroform with nitroethylene. Interaction of the potassium salt of 1 : 1-dinitroethane with 2-nitropropylene gives 2 : 2 : 4-trinitropentane with a 93 per cent yield [163, 167].

Another method of preparation of polynitro compounds consists of a reaction between the silver salt of trinitromethane with alkyl halides and nitroalkyl halides. The reaction generally succeeds with methyl halide derivatives of the aromatic series [168]:



Analogous methods give 2 : 4 : 6-trinitro-2 : 2 : 2-trinitroethylbenzene $C_8H_4O_{12}N_6$ (m.p. 153°C). Of the aliphatic polynitro compounds preparation of 1 : 1 : 1 : 2- and 1 : 1 : 1 : 3-tetranitropropane is described in the literature [169].

Interaction of 1-bromo-1-nitroethane or 1-bromo-2-nitroethane with $AgC(NO_2)_3$ in ether gives 1 : 1 : 1 : 2-tetranitropropane—a liquid with sp. gr. approximately 1·6 and b.p. approximately 235°C.

Finally, polynitroparaffins, in isolated cases, can be prepared by nitration of salts of nitroparaffins. Thus the dipotassium salt of tetranitroethane treated with a mixture of concentrated sulphuric and nitric acids gives hexanitroethane, m.p. 142°C. According to an American patent [170] mononitroparaffins with three to five carbon atoms and the nitro group associated with a secondary carbon atom, treated with nitric acid at 150–250°C and pressure of approximately 10 atm give dinitroparaffins with the $—NO_2$ group at a secondary carbon atom. For example, $(CH_3)_2CH(NO_2)$ under these conditions forms $(CH_3)_2C(NO_2)_2$, whilst primary nitropropane $O_2NCH_2CH_2CH_3$ does not form dinitro compounds.

Other patents [171] describe nitration of a mixture of mononitroparaffin and parent hydrocarbon. Concentration of nitric acid is 40–70 per cent. Pressure is 56–85 atm; ratio $HNO_3 : (RNO_2+RH) = 0{\cdot}5 : 1{\cdot}0$. To ensure better control of the process the use of N_2, H_2O, CO_2 as diluents is recommended.

4. PROPERTIES OF NITROOLEFINES*

Two types of nitroolefines are known: α-nitroolefines containing the nitro group at an unsaturated carbon atom, and nitroolefines containing the nitro group in the allyl position.

Nitroolefines are slightly yellowish, clear liquids with a pungent odour. On keeping they polymerize into dark, viscous tars. The tendency to

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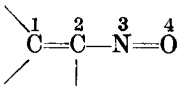
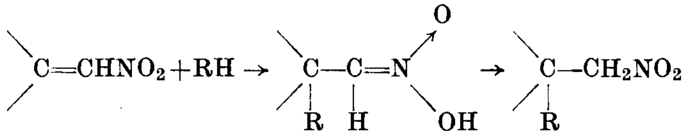
* For some of the properties of nitroolefines, see also Section 1, Chapter 3.

polymerize diminishes with increasing molecular weight. The rate of polymerization rises sharply in the presence of alkali.

α-Nitroolefines add on alcohols, amines, nitroparaffins and other substances. This property is determined by the presence in the nitro olefines molecule of a conjugated system of double bonds:



Substances containing a mobile hydrogen atom add on to nitroolefines in positions 1 and 4. The pseudo-acid so formed isomerizes to the corresponding nitro compound:

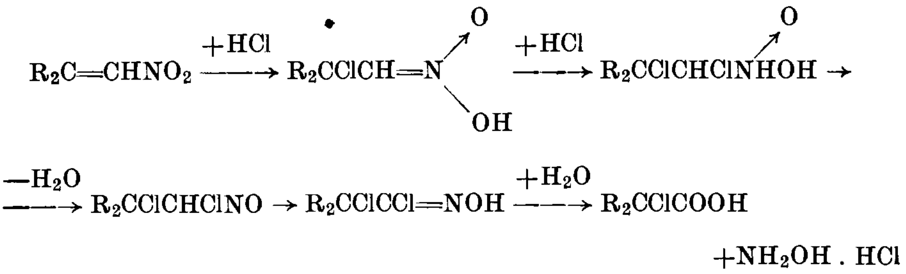


The ability of nitroolefines to undergo addition reactions makes them useful starting material in the synthesis of nitro- and aminoketones, dinitroparaffins, esters of nitroalcohols and other compounds.

Reduction of nitroolefines gives amines, oximes, ketones and nitroparaffins. The nature of the reducton products is determined by the reaction conditions (see Section 1 of this chapter).

Action of Mineral Acids on Nitroolefines

When nitroolefines are treated with concentrated hydrochloric acid hydroxylamine hydrochloride and α-hydroxy- or α-chlorocarboxylic acid are formed [172]. The same products may be obtained by treating nitroolefines with an ethereal solution of hydrogen chloride. The interaction of lower nitroolefines with ethereal and aqueous solutions of HCl was studied by Heath and Rose [173]. The authors suggest that in the first stage of the reaction hydrogen chloride adds on to the nitroolefine in positions 1–4. The aci-form of chloronitroparaffin so formed is converted by the action of hydrochloric acid into hydroxylamine hydrochloride and α-chloro- or α-hydroxycarboxylic acid. The reaction proceeds according to a scheme analogous to that for the conversion of a primary nitroparaffin into a carboxylic acid:



$$R_2C{=}CHNO_2 \xrightarrow{+HCl} R_2CClCH{=}N(\rightarrow O)OH \xrightarrow{+HCl} R_2CClCHClNH(\rightarrow O)OH \rightarrow$$

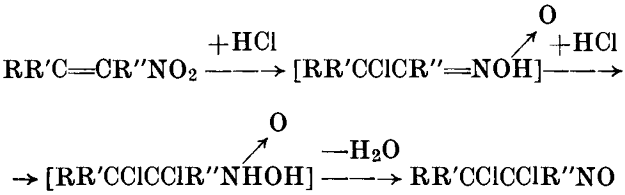
$$\xrightarrow{-H_2O} R_2CClCHClNO \rightarrow R_2CClCCl{=}NOH \xrightarrow{+H_2O} R_2CClCOOH + NH_2OH\,.\,HCl$$

The authors confirm this reaction mechanism by the following facts:

When 1-nitropropene-1 and 1-nitro-2-methylpropene-1 were treated with an ethereal solution of HCl the corresponding 1 : 2-dichlorooximes were isolated as intermediate products.

2-Chloro-1-nitropropane (addition product of HCl and 1-nitropropene in positions 1 and 2) does not react with ethereal solution of HCl, whilst 1-nitropropene under the same conditions is converted into α-chloropropionic acid and hydroxylamine hydrochloride. This excludes the possibility of the addition of HCl to the nitroolefine in position 1, 2 in the first stage of the reaction.

When the authors treated nitroolefines not containing a hydrogen atom on the carbon atom carrying the nitro group with hydrochloric acid or an ethereal solution of HCl they obtained dark blue liquids with lachrymatory properties; these were taken to be dichloronitroso compounds according to the schemes:



$$RR'C{=}CR''NO_2 \xrightarrow{+HCl} [RR'CClCR''{=}\overset{\overset{O}{\nearrow}}{N}OH] \xrightarrow{+HCl}$$

$$\rightarrow [RR'CClCClR''\overset{\overset{O}{\nearrow}}{N}HOH] \xrightarrow{-H_2O} RR'CClCClR''NO$$

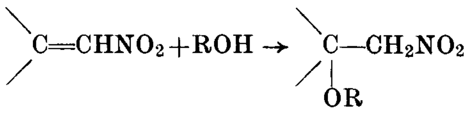
Nitroolefines are easily soluble in sulphuric acid (3 vols. H_2SO_4 to 1 vol. H_2O). Solution is accompanied by decomposition giving nitroparaffin and aldehyde. Nitroparaffin, under the action of sulphuric acid, is converted into a carboxylic acid and hydroxylamine H_2SO_4 [174]:

$$RCH{=}C(NO_2)R' + H_2O \xrightarrow{H_2SO_4} RCH(OH)CHNO_2R' \rightarrow RCHO + R'CH_2NO_2$$

$$R'CH_2NO_2 + H_2O + H_2SO_4 \rightarrow R'COOH + NH_2OH \,.\, H_2SO_4$$

Interaction of Nitroolefines with Alcohols

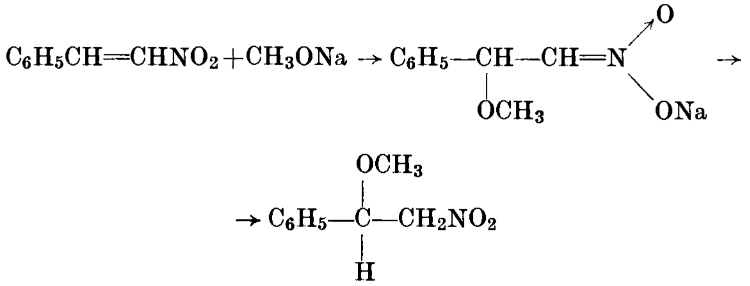
Addition of a molecule of alcohol to nitroolefines leads to the formation of ether of nitroalcohol:



$$>C{=}CHNO_2 + ROH \rightarrow >\underset{\displaystyle OR}{\underset{|}{C}}{-}CH_2NO_2$$

The reaction occurs at room temperature in the presence of an alkali catalyst.

Condensation of alcohols with nitroolefines was first performed by MEISENHEIMER and HEIM [175]. The authors obtained the methyl and ethyl ethers of α-phenyl-β-nitroethyl alcohol by treating ω-nitrostyrene with an alcoholic solution of alcoholate and then saturating the reaction mixture with carbon dioxide. In this case the reaction proceeds in two stages: at first a sodium derivative of the aci-form of the ester of α-phenyl-β-nitroethyl alcohol is formed from which carbon dioxide liberates the free ether:



Addition of alcoholate to aryl substituted homologues of nitroethylene is described in several communications [176].

Lambert *et al.* [177] condensed alcoholates with the lower nitroolefines. Nitroethylene, nitropropylene and nitro*iso*butylene treated with an alcoholic solution of sodium methylate and butylate gave the corresponding ethers of nitro alcohols on acidifying the reaction mixture with acetic acid. The interaction of 2-nitropropene-1 with sodium methylate gives, in addition to the methyl ether of 2-nitropropyl alcohol, the methyl ether of 2 : 4-dinitro-2-methylamyl alcohol. The latter is formed as the result of addition of nitropropene to the initial condensation product—ether of mononitroalcohol:

$$CH_3C(NO_2){=}CH_2 + CH_3OH \rightarrow CH_3CH(NO_2)CH_2OCH_3 \rightarrow$$

$$\rightarrow CH_3CH(NO_2)CH_2C(CH_3)(NO_2)CH_2OCH_3$$

The interaction of alcoholates with nitrooctene has been described by Bahner [178].

Interaction of Nitroolefines with Nitroparaffins

Nitroolefines add on primary and secondary nitroparaffins with the formation of 1 : 3-dinitroparaffins:

$$RR'CHNO_2 + CHR''{=}CR'''NO_2 \rightarrow RR'C(NO_2)CHR''CHR'''NO_2$$

In spite of the fact that this reaction offers a convenient method for the synthesis of dinitroparaffins only a small number of published works is devoted to it.

Lambert and Piggott [179] studied the addition of nitroethane and 2-nitropropane to 2-nitropropene-1, 2-nitrobutene-2 and nitro*cyclo*hexene. The authors conclude that the reaction is a general one, but the yields show wide variation depending on the nitro derivatives. Thus, the interaction of 2-nitrobutene-2 with 2-nitropropane in the presence of sodium ethylate gives 2 : 4-dinitro-2 : 3-dimethylpentane with a 47 per cent yield, whilst the interaction of 2-nitropropane with 2-nitropropene-1 gives a 26 per cent yield of the addition product.

Besides the dinitroparaffins high polymer side products are frequently formed since nitroolefines tend to polymerize under the influence of alkaline reagents.

HASS [180] has described the addition product of nitromethane and 1-nitro-2-methylpropene-1.

Data on the addition of phenylnitromethane to nitrostilbene are also available in the literature [181].

BAHNER and KITE [182] found that the condensation of alkali salts of nitroparaffins with nitroolefines gives appreciably higher yields of dinitro compounds than those obtained by condensing nitroparaffins with nitroolefines in the presence of alkaline catalyst.

Interaction of Nitroolefines with Amines and other Organic Bases

The addition of primary and secondary amines to nitroolefines leads to the formation of nitroamines. This reaction was first performed by WIELAND and SAKKELARIOUS [183] who treated an ethereal solution of nitroethylene with aniline, and obtained a crystalline addition product N-(α-nitroethyl)-aniline:

$$CH_2{=}CHNO_2+C_6H_5NH_2 \rightarrow C_6H_5NHCH_2CH_2NO_2$$

A detailed study of the interaction of ω-nitrostyrene with organic bases has been made by WORRAL [184]. This author investigated the action of forty different organic bases on ω-nitrostyrene, establishing that nitrostyrene reacts with the following bases: aniline, *p*-toluidine, phenylhydrazine, diphenylhydrazine, β-naphthylhydrazine, *p*-tolylhydrazine, semicarbazide and piperidine. According to WORRAL's data nitrostyrene reacts most readily with derivatives of hydrazine. Introduction of a negative substitutent into the molecule of an aromatic amine or an aryl-substituted hydrazine lowers the reactivity of the base. For example, aniline and phenylhydrazine interact vigorously with nitrostyrene, whilst *p*-chloroaniline, *p*-nitroaniline and *p*-bromophenylhydrazine do not form addition products.

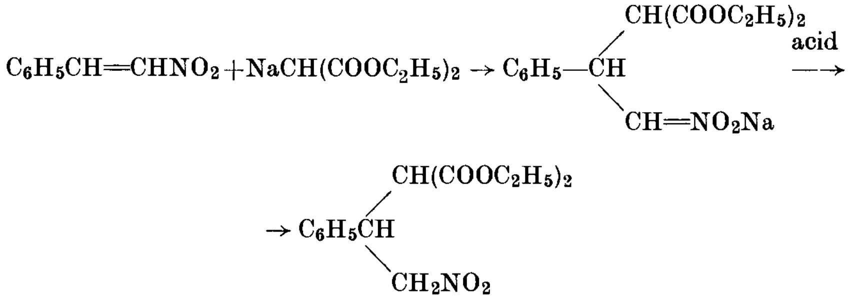
Condensation products were obtained by DORNOW and ROBERG [185] from amines and α-nitrostilbene.

Addition of aliphatic and aromatic amines to the lower nitroolefines is described by LAMBERT *et al.* [177].

Addition products of nitro*cyclo*hexene and phenylhydrazine, semicarbazide [186], thiosemicarbazide and *p*-toluidine have also been obtained.

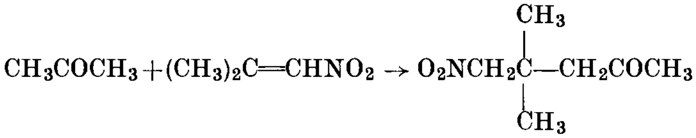
Interaction of Nitroolefines with Compounds containing Methylene Groups, Activated Carbonyl and Carboxylic Groups

Nitroolefines undergo condensation with substances containing mobile hydrogen atoms in methylene and methyl groups. Thus, for example, condensation of ω-nitrostyrene with the sodium derivative of malonic ester gives the ethyl ester of 1-nitro-2-phenyl-3-carbethylbutyric acid [187]



Perkalin and Sopova [188] obtained the condensation products of ω-nitrostyrene and acetoacetic ester, benzoylacetone and acetylacetone. The reaction occurred at room temperature in benzene solution. Triethylamine was used as catalyst. The yield of condensation products was 77–98 per cent. The authors remark that ω-nitrostyrene does not react with methylethylketone in which the methylene group is activated only by one carbonyl group.

The survey by Hass [189] mentions that condensation of acetone with 1-nitro-2-methylpropene-1 gives 5-nitro-4 : 4-dimethylpentanone-2:



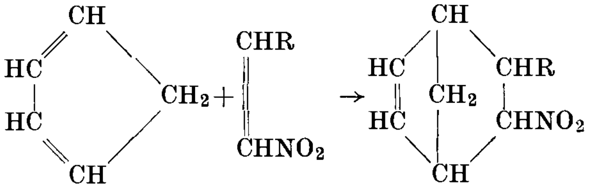
$$CH_3COCH_3 + (CH_3)_2C{=}CHNO_2 \rightarrow O_2NCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2COCH_3$$

The experimental procedure is not given in this communication.

Dornow and Roberg [190] succeeded in combining α-nitrostilbene with malonic ester, acetoacetic ester, acetylacetone, benzoylacetone and phenylacetone. The sodium derivative of malonic ester was used; other ketones only combined with α-nitrostilbene in the presence of sodium ethylate. The yield of condensation products was not high (not exceeding 29 per cent).

Interaction of Nitroolefines with Dienes

Since nitroolefines contain an active double bond they undergo the Diels-Alder condensation. On treating nitroethylene, 1-nitropropene-1 and 1-nitropentene-1 with *cyclo*pentadiene condensation reaction products are formed as shown in the following scheme [191]:



1-Nitropentene-1 also condenses with butadiene, methylbutadiene and 2 : 3-dimethylbutadiene.

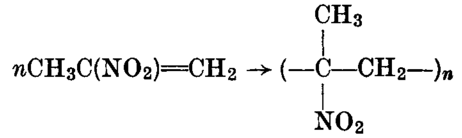
Mono- and bicyclic nitro compounds have been obtained by condensing 2-nitrobutene-2 and 2-nitropropene-2 with butadiene and *cyclo*pentadiene [192].

Wildman prepared the phenyl-substituted nitro derivatives of cyclohexene by condensation of α-nitro styrene with butadiene and methylbutadiene [193].

Polymerization of Nitroolefines

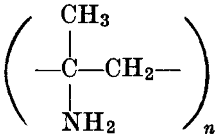
Nitroolefines have a great tendency to polymerize [183, 194]. Thus, nitroethylene $CH_2{=}CHNO_2$ obtained by dehydration of nitroethyl alcohol over H_3PO_4 polymerizes at room temperature in the course of 2–3 days, giving a clear, viscous liquid. At the same time the product obtained by dehydrating nitroethyl alcohol over $KHSO_4$ does not polymerize [195].

2-Nitropropene polymerizes in the presence of an aqueous solution of potassium bicarbonate [196] giving a high-molecular product soluble in organic solvents:



$$nCH_3C(NO_2){=}CH_2 \rightarrow (\text{—}\underset{NO_2}{\overset{CH_3}{C}}\text{—}CH_2\text{—})_n$$

This polymer on hydrogenation with Raney nickel catalyst gives the corresponding polyvinylamine:



$$\left(\text{—}\underset{NH_2}{\overset{CH_3}{C}}\text{—}CH_2\text{—}\right)_n$$

which is readily soluble in water, but contrary to the polymer of 2-nitropropene is insoluble in most organic solvents.

5. NITRATION OF UNSATURATED HYDROCARBONS*

Unsaturated compounds undergo nitration fairly readily giving predominantly mononitro compounds.

Nitration of unsaturated hydrocarbons with dilute nitric acid was first studied by Konovalov. The reaction was performed under conditions elaborated for the nitration of paraffins. The substances investigated were: menthene, octene-1, trimethylethylene [197], bornylene, pinene [198] and camphene [199], Nitration of menthene with nitric acid (sp. gr. 1·075) in a sealed tube gave two isomeric mononitro compounds. Nitromenthenes were soluble in alkali; the alkaline solution gave, on the addition of ferric chloride, red ether soluble precipitates (reaction-characteristic) of primary and secondary nitro groups). Nitration of octene-1

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* Some methods of preparation of nitroolefines are described in Section 1, Chapter III.

under analogous conditions gave a nitro compound of composition $C_8H_{15}NO_2$. The nitro compound was soluble in alkali and on treatment with ferric chloride gave the characteristic reaction for primary or secondary nitro group. Trimethylethylene is considerably more difficult to nitrate with dilute nitric acid than menthene and octene. The nitro products formed were soluble in alkali.

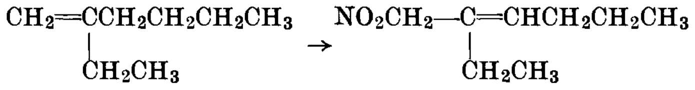
Alkali soluble nitro compounds were also obtained on nitration of unsaturated bicyclic hydrocarbons—bornylene, camphene and pinene.

Konovalov concludes on the basis of his results that the nitrating action of nitric acid is directed not to the hydrocarbon groups linked by a double bond but to those adjacent to them.

Konovalov's work remained unfinished. Not all the nitro compounds were isolated in the pure state, nor was the position of the nitro groups in the hydrocarbon molecule conclusively ascertained. It was shown later that on nitration of camphene [200] with nitric acid (sp. gr. 1·075) two structurally isomeric nitro compounds were formed: secondary α-nitrocamphene and ω-nitrocamphene, with the nitro group attached to the carbon atom linked by a double bond.

Nitration of di*iso*butylene [201] gives a mixture of isomeric mononitro compounds. The reaction was carried out with concentrated nitric acid at a temperature slightly above 60°C. The reaction can also be performed with 70 per cent nitric acid at 70–90°C, and by dilute nitric acid (20 per cent) at 70°C if it is taken in excess and nitrogen oxides are added to it. The latter indicates that under these reaction conditions the olefines are nitrated by nitrogen oxides generated by the nitric acid, i.e. the reaction probably proceeds by the same mechanism as the nitration of saturated hydrocarbons.

2-Ethylhexene-1 undergoes nitration as readily as di*iso*butylene. When 2-ethylhexene-1 is nitrated with 80 per cent nitric acid at 70–75°C 1-nitro-2-ethylhexene-2 is formed with a yield of about 85·9 per cent.

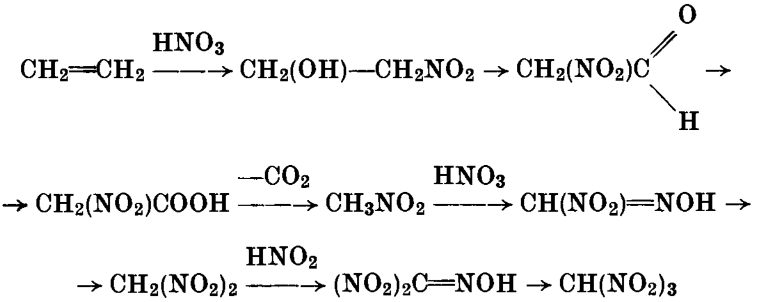


$$\begin{array}{l} CH_2{=}CCH_2CH_2CH_2CH_3 \\ \quad\;| \\ \quad CH_2CH_3 \end{array} \rightarrow \begin{array}{l} NO_2CH_2{-}C{=}CHCH_2CH_2CH_3 \\ \qquad\qquad\;| \\ \qquad\qquad CH_2CH_3 \end{array}$$

More drastic conditions are required for the nitration of octene-1 to 1-nitrooctene-2 (temperature 90–100°C).

Nitration of olefines under these conditions is analogous to their chlorination, viz. the introduction of the nitro group is accompanied by a shift of the double bond to the β-position.

McKee [202] investigated the interaction of ethylene with concentrated nitric acid in order to find a means of preparing tetranitromethane. As the result of this investigation it was found that trinitromethane was the main nitrogen-containing reaction product of the interaction of ethylene and concentrated nitric acid. The reaction also gave β-nitroethyl alcohol, oxalic acid and carbon dioxide. Trinitromethane was not isolated in the pure state, but was subjected to further nitration to give tetranitromethane (by heating in the presence of sulphuric acid). McKee passed a stream of dry ethylene through a Drexell flask containing concentrated nitric acid. The concentration of nitric acid was varied within the range 95–100 per cent in different experiments. When ethylene was passed through nitric acid there was slight evolution of heat and copious evolution of carbon dioxide. The reaction mixture was poured into water, neutralized and extracted with ether. On vacuum distillation of the reaction products β-nitroethyl alcohol was isolated. β-nitroethyl alcohol and trinitromethane were obtained in the ratio 1 : 2·4. On adding mercury nitrate to the reaction mixture the yield of nitro compound was raised by nearly one and a half times. The authors consider that mercury nitrate suppresses the oxidation of ethylene. McKee explains the formation of trinitromethane from ethylene and nitric acid by means of the following scheme:



$$CH_2{=}CH_2 \xrightarrow{HNO_3} CH_2(OH){-}CH_2NO_2 \rightarrow CH_2(NO_2)C\substack{/\!\!/O\\ \diagdown H} \rightarrow$$

$$\rightarrow CH_2(NO_2)COOH \xrightarrow{-CO_2} CH_3NO_2 \xrightarrow{HNO_3} CH(NO_2){=}NOH \rightarrow$$

$$\rightarrow CH_2(NO_2)_2 \xrightarrow{HNO_2} (NO_2)_2C{=}NOH \rightarrow CH(NO_2)_3$$

Haitinger [203] obtained a small amount of an unsaturated nitro compound $C_4H_7NO_2$ by treating *iso*butylene with concentrated nitric acid. The nitro compound was soluble in alkali, and on heating with water in a sealed tube decomposed into acetone and nitromethane. Reduction of nitro*iso*butylene gave a mixture of neutral compounds, a small amount of amine and ammonia.

Guthrie [204] passed amylene through boiling fuming nitric acid. The main reaction product was a crystalline substance of composition $C_5H_{10}(NO_2)_2$ whose nature was not determined. The same compound was formed by treating amylene with nitrogen dioxide [205]. Evidently it was a dinitro compound.

Konovalov [206] studied the interaction of di*iso*butylene and tri-*iso*butylene with nitric acid. Di*iso*butylene reacted with nitric acid (sp. gr. 1·4) very violently and the experiments invariably terminated in an explosion. Nitration in acetic acid medium was also unsuccessful, since the hydrocarbon polymerized. When di*iso*butylene was heated on a water-bath with nitric acid (sp. gr. 1·28) a green liquid was formed which was partially soluble in alkali. On reduction with iron and acetic acid it gave a mixture of amines, from which an amine of composition $C_8H_{15}NH_2$ was successfully isolated. In addition to the amines a ketone-like substance was also obtained. Mono- and diamines were also formed on reduction of the product of nitration of tri*iso*butylene.

Bouis [207] treated caprylene with concentrated nitric acid. The reaction proceeded very vigorously and, therefore, either the reaction mixture had to be cooled or dilute nitric acid was first added. The reaction gave a liquid product whose nitrogen content was intermediate between that required for mono- and dinitrocaprylene.

Nitration of *cyclo*hexene [186] with nitric acid sp. gr. 1·2 at 60–65°C for 3 hr gave 1-nitro*cyclo*hexene-1, secondary nitro*cyclo*hexene and pseudonitrosite of *cyclo*hexene. Adipic acid was present in the acid layer. The average yield of isomeric nitro*cyclo*hexenes, calculated on the *cyclo*hexene which had reacted, was 16 per cent. It could be expected that the interaction of ethylene [208] with 96·6 per cent nitric acid (free of nitrogen oxides) at 0–25°C would give trinitromethane and β-nitroethyl alcohol or its ester. However, these compounds were not detected, whilst the reaction products obtained could not be determined owing to their instability.

Passing acetylene [209] through concentrated nitric acid gives trinitromethane which can be further nitrated to tetranitromethane.

Nitration of butadiene [210] with nitric acid at 30°C (1 part nitric acid sp. gr. 1·49–1·50 is added slowly, with stirring, to 3·5 parts butadiene) gives nitrobutadiene (lachrymatory) containing an admixture of the dimer.

On nitration of retene $C_{18}H_{18}$ it is possible to obtain a mixture of mononitroretenes with a yield of up to 75 per cent of the theoretical [211]. The procedure was as follows: to concentrated nitric acid (75 ml) was added retene (20 g) in glacial acetic acid (200 ml) at a temperature not lower than 6–7°C. The oil which was formed was poured into 1·5 l. of water and extracted with petroleum ether. The products of the reaction can be separated by chromatography (Al_2O_3.) The main products are: 9-nitroretene (28–31 per cent), 3-nitroretene (17–18 per cent), 4-nitroretene (11–13 per cent). 5(?)- or 8(?)-nitroretene is also formed in small amounts.

Unsaturated compounds such as, for example, styrene, cinnamic acid and their derivatives are nitrated in a way similar to that used for purely aromatic compounds.

SIMON [212] nitrated styrene with concentrated nitric acid and obtained a tarry substance which on steam-distillation yielded crystalline ω-nitrostyrene. BLYTH and HOFMAN [213] obtained a better yield of nitrostyrene by introducing styrene into ice-cooled fuming nitric acid.

TITOV [214] studied the mechanism of nitration of unsaturated compounds. He considers that, depending on the reaction conditions, the nitration of olefines as well as of aromatic compounds proceeds along the lines of ionic or radical reactions. Interaction in both cases begins with an attack by the electrophilic nitrating agents on the mobile and sterically accessible π-electrons. The mobility of π-electrons is determined by the relatively low energy of their linkage with the nuclei of the carbon atoms, and their accessibility by the peripheral disposition of their orbits relative to the bonds between the carbon atoms.

Free radicals are formed during the action of nitrogen oxides on olefines, as confirmed experimentally by TITOV.

* * *

To conclude this chapter devoted to the nitration of paraffins and the aliphatic side-chain of aliphatic–aromatic hydrocarbons with nitric acid an evaluation should be made of the various schemes proposed for the mechanism of this reaction.

All the schemes proposed in contemporary literature (TITOV, McCLEARLY and DEGERING, BACHMANN *et al.*) have one feature in common, viz. the view that such nitration is, in TITOV's terminology, a molecular–radical process. By this term TITOV understands a reaction which proceeds by way of free radical (R and NO_2) formation from the parent substances with subsequent recombination of the radicals. The radical nature of the process prevents a chain reaction, since the recombination of the alkyl radical with nitrogen dioxide is not accompanied by the appearance of new free radicals and so represents the end of the chain.

Thus according to modern concepts, there is a fundamental distinction between the mechanisms of aromatic and aliphatic (including the aliphatic side-chain of aliphatic–aromatic compounds) nitration with nitric acid: the former is an ionic reaction (as seen from the survey of Chapter 2), the latter, molecular–radical. Such a sharp difference in mechanisms must doubtless be reflected in considerable experimental differences. And in fact, as has been shown above, it is found that, firstly, nitrogen dioxide which is an active nitrating agent for aliphatic hydrocarbons has no influence on the nitration of aromatic hydrocarbons with nitric acid or nitrating mixture; secondly, addition of strong acids markedly accelerates the rate of nitration of aromatic compounds, but has little effect on the nitration of aliphatic hydrocarbons, and thirdly, the rate of vapour phase nitration of aromatic hydrocarbons is much slower than the rate of liquid phase nitration, whereas in the case of aliphatic hydrocarbons the rates of nitration in the two phases are almost identical. Another difference can be added to these: the positive catalytic action, observed by various authors, exhibited by some metallic oxides and salts in aromatic nitration and the practically complete absence of any effect of the same substances in the case of vapour phase nitration of aliphatic hydrocarbons.

The ionic mechanism of aromatic nitration may be taken as generally accepted and has been substantiated to a considerable degree. As regards aliphatic nitration the experimental differences cited above only show that an ionic mechanism cannot be applied to this process. It should be emphasized that whilst these experimental differences exclude an ionic mechanism they do not provide conclusive evidence as to whether aliphatic nitration is a molecular, a molecular–radical or a chain reaction. This problem could only be solved definitely if direct and objective means were available for the confirmation (and identification) of free radicals in the course of so complex a chemical reaction. Unfortunately, the still limited development of free radical chemistry makes the solution of the problem in this way at present impossible. Another, more oblique, possibility of revealing the character (molecular or free-radical) of the reaction could arise from the examination of the kinetics of aliphatic nitration, including such experimentally determined characteristics of the reaction as its order with respect to each of the reactants, activation energy, change of rate depending on time, temperature and pressure, effect of surface, additions, etc.

It has to be stated, however, that up to the present the study of aliphatic nitration developed mainly along the lines of synthesis, i.e. in the direction of searching for methods of obtaining valuable nitrogen-containing and other intermediate and final products formed in the course of this reaction. Investigation of its kinetic properties has lagged far behind, and is in its very initial stages. This excludes the possibility of elucidating the nature of the process by this means with a sufficient degree of reliability, at the present time at any rate.

As the result the concepts presented in the literature concerning the molecular–radical as against a purely molecular nature of aliphatic nitration cannot be considered as unequivocally proved. The following can serve as an illustration of this: BACHMANN *et al.* [215] in an attempt to find confirmation for the free radical nature of vapour phase nitration of aliphatic hydrocarbons both with nitric acid and nitrogen dioxide are forced to admit that so far the most convincing proof of such a mechanism is the fact itself that this process takes place in the vapour phase. Such an argument cannot be regarded as tenable as far as proving the nature of the mechanism is concerned.

In spite of all this, the author of the present book inclines towards the free radical concept of aliphatic nitration. In the course of studying this reaction one experimental fact was obtained by him the most natural explanation of which would suggest, in the author's opinion, participation of free radicals in the reaction. The author has in mind the discovery in his joint work with ALANIIA [216] of the rapid thermic reaction of simultaneous nitration and chlorination of methane in its mixtures with nitrogen dioxide and chlorine under conditions in which the reaction practically ceases if either chlorine or nitrogen is absent. This can be explained by the formation of nitrosyl chloride NOCl in the simultaneous presence of chlorine and nitrogen dioxide. Nitrosyl chloride, owing to the low energy of the N—Cl bond (approximately 38 kcal/mole) decomposes fairly easily giving NO and an atom of chlorine which gives alkyl radicals on interaction with the hydrocarbon ($RH+Cl\cdot - R\cdot + HCl$) at a lower temperature than nitrogen dioxide. Thus the process of nitration must include the formation and subsequent conversion of alkyl radicals.

The author of the present book also considers important and confirmatory of the free radical theory of aliphatic nitration the work of HASS and RILEY [217] who showed that during vapour phase nitration of lead tetraethyl with nitric acid, lead nitrate, nitroethane and ethyl nitrate were formed. Thermal decomposition of lead tetraethyl, giving ethyl radicals, is now well known and is one of the extensively used methods for the formation of free alkyl radicals. Therefore it can hardly be doubted that in the experiments of HASS and RILEY nitroethane and ethyl nitrate were formed as the result of interaction of nitrogen dioxide with ethyl radicals; the formation of nitroethane needs no explanation, whilst that of ethyl nitrate can be seen as the result of a primary formation of ethyl nitrite ($C_2H_5+ONO \rightarrow C_2H_5ONO$) followed by oxidation to ethyl nitrate.

Generally, the works cited point to the undoubted reality of the formation of nitro products by the interaction of alkyl radicals with nitrating agents.

Thus, despite the absence up to now of a direct and objective method for the demonstration of free radicals in aliphatic nitration, their actual participation in this reaction can be accepted on the strength of indirect evidence.

A more detailed examination of the two main hypotheses proposed for the nitration of aliphatic hydrocarbons (TITOV's and BACHMANN's) allows the following remarks to be formulated:

(1) These authors try to substantiate their molecular radical schemes by the presence of just those stable intermediate and final substances which are actually found as products of nitration of aliphatic hydrocarbons.

Methodologically such confirmation of a scheme is, of course, obligatory but not unequivocal. Actually, at the present stage of penetration into the true nature of aliphatic nitration reaction mechanism the formation of the same stable reaction products can be explained not by one, but by several schemes with participation of different free radicals.

(2) It must be emphasized that the formation of the main intermediate products included in the schemes—nitroso compounds and alkyl nitrites—remains to a certain extent hypothetical. Nitroso compounds have not been isolated among the reaction products and therefore the formation from them of dinitrocompounds through oximes is only presumptive; as regards alkyl nitrites, they probably are formed, but their intermediate role has not been proved by anyone.

It is worth remarking here that according to TITOV's (chiefly with reference to the liquid phase reaction) and BACHMANN's (for vapour phase reaction) schemes under consideration, alkyl nitrite is that intermediate product whose further conversion leads to the formation of oxidation products—alcohols and carbonyl compounds. Moreover, TITOV supposes that within the framework of the liquid phase reaction which takes place at low temperature the initial stage of conversion of alkyl nitrite is its hydrolysis; in the high-temperature vapour phase reaction, according to BACHMANN, this stage is its monomolecular decomposition with the formation of the alkoxyl radical, which initiates a chain with a small number of links. This suggestion was put forward by BACHMANN on the strength of published works on the thermal decomposition of alkyl nitrites occurring in the absence of water—conditions which cannot be said to exist during vapour phase nitration with nitric acid. Thus, if TITOV's contention regarding the hydrolysis of alkyl nitrite in the course of liquid phase nitration is accepted, it becomes very doubtful that no such hydrolysis occurs under the conditions of the vapour phase reaction. The question therefore arises whether it is possible, accepting the intermediate role of alkyl nitrites, to consider natural such a totally different course of their further conversion (depending on temperature) as postulated in the two schemes.

(3) BACHMANN's scheme does not clarify the course of formation of

olefines, obtained during vapour phase nitration of aliphatic hydrocarbons; the course suggested by Titov cannot be, as will be shown presently, considered satisfactory. The question concerning the formation of olefines is of more vital importance than would appear at first sight for the elucidation of the true reaction mechanism of nitration. It is simplest to assume that unsaturated hydrocarbons are formed by way of decomposition of alkyl radicals with cleavage of either the C—C or the C—H bonds:

$$\mathrm{CH_3\dot{C}H_2CH_3 \rightarrow CH_3\cdot + C_2H_4}$$

$$\mathrm{CH_3\dot{C}HCH_3 \rightarrow H\cdot + C_3H_6}$$

It is known, however, that such cracking of saturated hydrocarbons occurs at measurable rates only at temperatures exceeding considerably those used in vapour phase nitration and consequently cannot be the source of olefines in this case. It follows from this that in the course of nitration conditions are created which favour the formation of olefines. It may be supposed that such a favourable condition could be the formation of olefines not from the alkyl radical but during one of the stages of its further transformation. This means that each of such stages of conversion including the final formation of the olefine must proceed at a rate faster than the decomposition of the alkyl radical. Titov evidently has just this in mind when he gives the following sequence of stages:

$$\mathrm{R \xrightarrow{NO_2} RONO \underset{HNO_2}{\overset{H_2O}{\rightleftarrows}} ROH \overset{HNO_3}{\rightleftarrows} RONO_2 \rightleftarrows \text{olefines} + HNO_3}$$

Here the alkyl radical, after undergoing a series of transformations, forms alkyl nitrate which then gives the corresponding olefine by elimination of nitric acid.

It is difficult to evaluate whether such a course is more feasible than the formation of olefines directly from alkyl radicals, all the more because not a single of the published works on thermal decomposition of alkyl nitrates [218] mentions positively the formation of olefines.

Without prejudging whether it is correct to assume that olefines are formed not directly from alkyl radicals but during one of the stages of their subsequent transformation, and whether it is possible to marshall better chemical evidence than Titov's in support of such a hypothesis, the author of the present book wants to draw attention to the well known fact that the temperature of cracking of aliphatic hydrocarbons (forming olefines) is considerably lowered in the presence of oxygen. The mechanism of this action of oxygen is still not clear, but the fact itself is indisputable, and would seem to this author to be a possible reason for the formation of olefines at measurable rates at the temperatures of vapour phase nitration. If this explanation were correct it would imply the presence of free oxygen in the reaction zone during vapour phase nitration. It is difficult to overestimate the effect of this on the course of the whole process, especially in view of the numerous experimental confirmations of the positive influence of added oxygen on aliphatic nitration. In particular, it is possible to consider the formation of the alkyl radical, which initiates nitration, in a somewhat different way [see below, (5)] from that presented in the schemes under consideration.

(4) Bachmann's and Titov's schemes for vapour phase nitration do not account for the way in which CO and CO_2 are formed during the process. Within the framework of these schemes the formation of products of profound oxidation and destruction of the paraffin chain, such as the oxides of carbon, is most naturally regarded as the result of further action by the nitrating agent on the aldehydes and olefines formed during the nitration. It may be thought that both these classes of compounds are more susceptible to the action of nitrogen dioxide, for example, than the aliphatic hydrocarbons.

Of contemporary literature on the interaction of nitrogen dioxide and aldehydes the work of McDowell and Thomas [219] may be cited. They studied the reaction of nitrogen dioxide and acetaldehyde without finding any oxides of carbon. Pollard and Wyatt [220] investigated the interaction of nitrogen dioxide and formaldehyde at temperatures 118–184°C; nitrogen oxide, water, CO and CO_2 were formed in this case. The authors suggest the following reaction mechanism which includes the formation of an intermediate binary complex between formaldehyde and nitrogen dioxide:

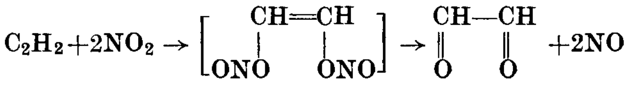
(1) $\mathrm{HCHO+NO_2 \rightarrow (HCHO\,.\,NO_2)}$

(2) $\mathrm{(HCHO\,.\,NO_2)+NO_2 \rightarrow CO+H_2O+NO+NO_2}$

(3) $\mathrm{(HCHO\,.\,NO_2)+NO_2 \rightarrow CO_2+H_2O+2NO}$

Although the authors consider that the experimental results are explained by the scheme put forward by them, it should be remarked that it has the character of stoichiometric equations rather than that of an aggregate of truly elementary processes. In stage (3) for example, the cleavage of six and formation of four bonds are included in one elementary act; the existence of so complex an elementary act is difficult to visualize.

Two communications which appeared more recently, Cottrell and Graham [221] and Thomas [222] are devoted to the study of the interaction of nitrogen dioxide with unsaturated hydrocarbons, viz. ethylene in the former and acetylene in the latter. In both works carbon oxides are reported to have been found among the reaction products. No reaction mechanism is offered in the first work; in the second the following scheme is proposed:

(1) 

$$\mathrm{C_2H_2+2NO_2} \rightarrow \left[\begin{array}{cc} \mathrm{CH{=}} & \mathrm{CH} \\ | & | \\ \mathrm{ONO} & \mathrm{ONO} \end{array}\right] \rightarrow \begin{array}{cc} \mathrm{CH{-}} & \mathrm{CH} \\ \| & \| \\ \mathrm{O} & \mathrm{O} \end{array} \mathrm{+2NO}$$

(2) $\mathrm{CHO{-}CHO+NO_2 \rightarrow \dot{C}O{-}CHO+HNO_2}$

(3) $\mathrm{C{\cdot}O{-}CHO+NO_2 \rightarrow CO_2+HC{\cdot}O+NO}$

(4) $\mathrm{C{\cdot}O{-}CHO \rightarrow CO+HC{\cdot}O}$

(5) $\mathrm{HC{\cdot}O+HNO_2 \rightarrow H_2O+CO+NO}$

The suggested mechanism is reduced to a preliminary formation of aldehyde (glyoxal) and its subsequent oxidation by the oxygen of nitrogen dioxide, which is converted to nitrous acid and nitrogen oxide, a fairly complex and not very convincing process. Whilst stage (2) with its elimination of a hydrogen atom from the carbonyl group giving a free radical CO—CHO and HNO_2 could be considered feasible, stages (3) and (5) appear to be insufficiently well founded.

Thus the proposed contemporary mechanisms for the reaction of nitrogen dioxide with aldehydes and unsaturated hydrocarbons, suggesting direct action of nitrogen dioxide both on the parent substances and on the intermediate products, offer no well substantiated ways for the formation of carbon oxides. This may, of course, be a temporary state of affairs; other schemes may be put forward which, whilst retaining the same principles of direct action by nitrogen dioxide, would show other labile intermediate products with more feasible ways of forming carbon oxides.

The author of the present book does not, however, exclude the possibility of the formation of carbon oxides under the conditions of vapour phase nitration by way of oxidation of aldehydes not by nitrogen dioxide, but by free oxygen. Although such a mechanism of carbon oxides formation is so far only hypothetical it is difficult to visualize that oxidative degradation of aldehydes would take place by reaction with nitrogen dioxide and not with free oxygen if the presence of the latter in the sphere of reaction is assumed (see (3) above). The readiness with which aldehydes are oxidized by oxygen is well known, and the radical-chain schemes proposed for this are quite logical. Therefore this author considers it essential to keep the possibility of this way of carbon oxides formation in mind when attempting to elucidate the mechanism of aliphatic nitration.

(5) The absence of a chain reaction mechanism asserted by BACHMANN and TITOV cannot be considered as finally established. Kinetic studies are crucial for the determination of the chain character of a chemical reaction, and, as already mentioned, these studies in the case of nitration are still far from complete.

It should be added that the assumption of the presence of free oxygen in the sphere of nitration makes one especially wary of denying the chain character of this process. It is, of course, possible that the chain reaction is not concerned with the stage during which nitrogen-containing products are formed; these are most likely to result from the recombination of the radicals (R and NO_2) as proposed in both the schemes. However, the oxidation reaction utilizing oxygen for the further transformation of such intermediate products as aldehydes, alcohols, etc., may well be of the chain type. In such a case there would be an interesting situation of a purely radical and a chain reaction occurring simultaneously within the framework of the general reaction of nitration. It should not be thought that these two reactions must develop independently, with no mutual influence. The free radicals involved, for example, in the chain oxidation of aldehydes are doubtless able to interact also with the parent hydrocarbon even if not, perhaps, so effectively. Such interaction could result in the formation of the alkyl radical ($RH + A^{\bullet} \rightarrow R^{\bullet} + AH$, where $A^{\bullet}$ is a free radical) which by recombining with nitrogen dioxide would support the purely radical direction of the reaction.

It is therefore not at all necessary to suppose with TITOV that the primary formation of alkyl radicals can only result from the reaction of the parent hydrocarbon with nitrogen dioxide:

$$RH + NO_2 \rightarrow R + HNO_2$$

It is relevant to mention that such an elementary process has not been generally stated by anyone; at least there is no reference to it in STEACIE's book *Atomic and Free Radical Reactions* (2nd Ed.) 1954.

The assumption regarding the presence of free oxygen in the reaction sphere during nitration gives rise to yet another possible way of formation of the alkyl radical:

$$RH + O_2 \rightarrow R^{\bullet} + HO_2$$

Such an elementary process is suggested in a number of modern schemes for hydrocarbon oxidation; it is also accepted by N. N. SEMENOV [223].

All the hypotheses concerning the possible course of aliphatic nitration developed in this conclusion, together with the critical remarks on the schemes proposed by BACHMANN and TITOV, led the author of the present book to conduct an investigation in his laboratory aimed at obtaining additional experimental material needed for more detailed and substantiated insight into the true mechanism of nitration. This investigation includes: (1) elucidation of the whole kinetic picture of the course of aliphatic nitration, (2) determination of the kinetics concerned with the expenditure of initial products and accummulation of intermediate and final products over the whole course of conversion and, finally, (3) study under pure conditions of some of the main elementary processes whose existence is assumed in the reaction.

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CHAPTER IV

NITRATION OF AMINES

NITRO derivatives of amines—N-nitroamines—acquired a great deal of importance in the last decade, although small quantities of these compounds had been prepared in the last century. However the methods of preparation of nitroamines have only been developed in detail recently. These new developments have made N-nitroamines readily available and some of them are produced industrially (dinitrohydroxydiethylnitroamine ethylenedinitroamine, etc.)

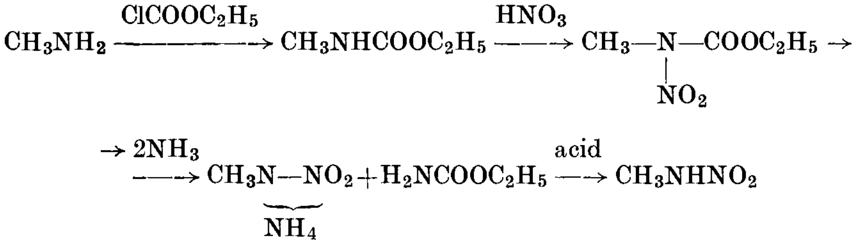
N-nitrocompounds cannot be obtained from tertiary amines which do not possess a hydrogen atom linked with the amino nitrogen.

Primary nitroamines, as distinct from the basic amines, are acidic and more strongly so than the corresponding carboxylic acids. The ability of N-nitroamines to form salts is explained by their isomerization similar to that of nitroparaffins. For example, the structure of the potassium salt of phenylnitroamine can be expressed by the formula $C_6H_5N{=}NOOK$.

Nitroamines are white, fairly stable crystalline substances. Some of the arylnitroamines, nitrated in the ring, are pale yellow in colour. However, the intensity of their coloration is markedly less than that of the corresponding derivatives of aniline. Some nitroamines decompose explosively on heating. At the same time many secondary aliphatic nitroamines can be distilled under reduced pressure [1].

Primary aliphatic nitroamines are quickly decomposed by concentrated acids and consequently cannot be obtained by direct nitration of the corresponding amines. The general method for the preparation of such N-nitroamines consists of acetylating the amine with subsequent nitration of the secondary amide formed to give a nitro amide, and decomposition of the latter with alkali giving the nitroamine salt. Nitroamines are obtained on careful acidifying of their salts [1].

Urethanes are often used as intermediates in the preparation of nitroamines. When an ethereal solution of crude alkylnitrourethane is treated with gaseous ammonia (or aliphatic amine) the products are the salt of the nitroamine and ether-soluble urethane. Thus, methylnitroamine can be obtained according to the following scheme [2]:

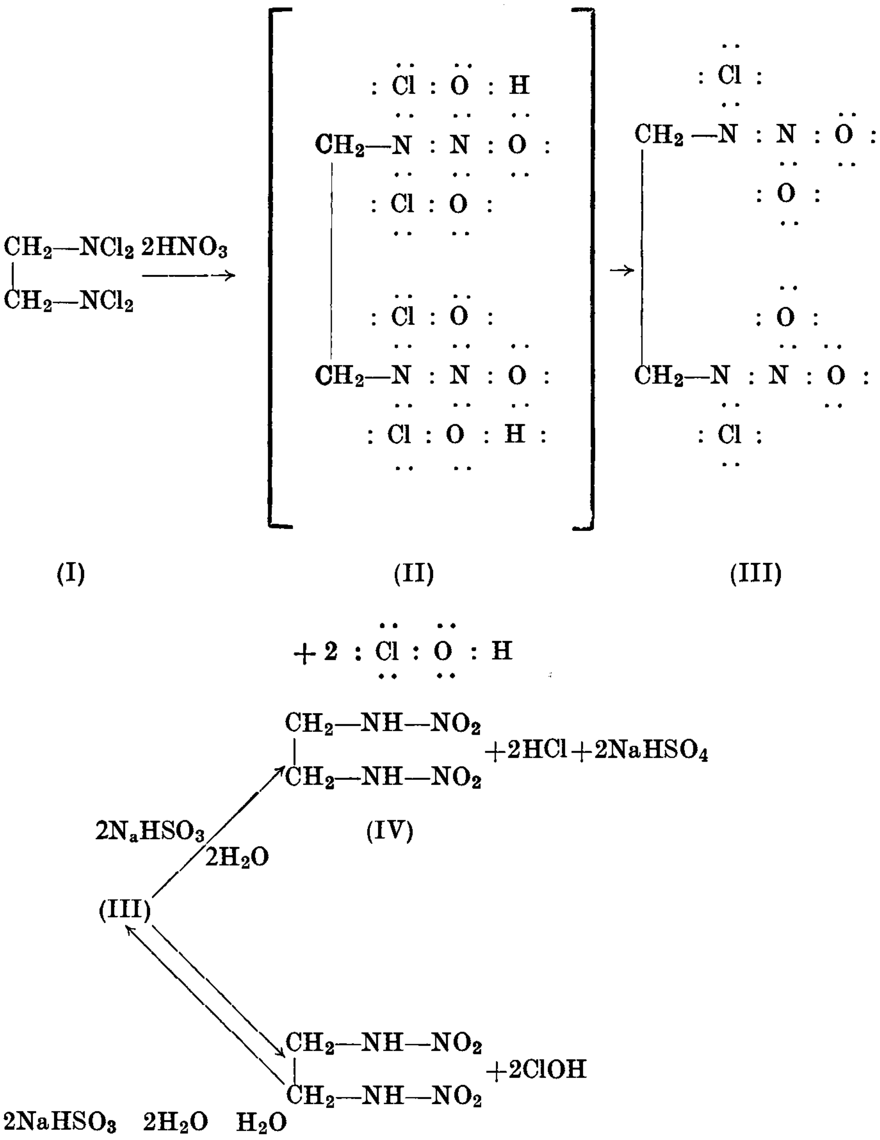


$$CH_3NH_2 \xrightarrow{ClCOOC_2H_5} CH_3NHCOOC_2H_5 \xrightarrow{HNO_3} CH_3{-}\underset{NO_2}{\underset{|}{N}}{-}COOC_2H_5 \rightarrow$$

$$\rightarrow \xrightarrow{2NH_3} CH_3\underbrace{N{-}NO_2}_{NH_4} + H_2NCOOC_2H_5 \xrightarrow{acid} CH_3NHNO_2$$

A new method for the nitration of primary amines has recently been developed by SMART and WRIGHT [3]. The primary amine is treated with chlorine to give N-dichloroamine which is then nitrated with nitrating mixture of 98–99 per cent nitric acid and acetic anhydride. N-Chloro-N-nitroamine is formed as the result of this procedure; it is a very unstable substance and on hydrolysis in a reducing medium (for example sodium bisulphite solution) gives nitroamine.

A typical example of the preparation of primary nitroamines is the nitration of ethylenediamine. In the first stage of the reaction when chlorine and ethylenediamine interact N-tetrachloro-1 : 2-diaminoethane is obtained (I); when this is nitrated with nitric acid and acetic anhydride N : N′-dichloro-N : N′-dinitro-1 : 2-diaminoethane (III) is formed. This latter compound, treated with sodium bisulphite, gives a good yield of ethylene-N : N′-dinitroamine (IV).



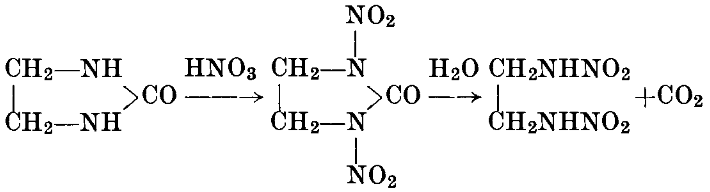
In the authors' opinion when N-tetrachloro-1 : 2-diaminoethane is nitrated with nitric acid an N : N'-coordination compound (II) is first formed, which can be regarded as a salt of a weak electron donor. This compound spontaneously loses hypochlorous acid to give N : N'-dichloro-N : N'-dinitro-1 : 2-diaminoethane (III), which is evidently too weak an electron donor and generally cannot form salts. This is confirmed by the fact that no tetranitroamine is formed.

The proposed scheme does not reflect the role of acetic anhydride in the nitration. The presence of acetic anhydride is essential for maintaining the reaction products in an anhydrous medium. When a large excess of nitric acid was used in the absence of acetic anhydride the reaction mixture proved to be very unstable.

Hydrolysis of N : N'-dichloro-N : N'-dinitro-1 : 2-diaminoethane (III) with water gives nitroamine and hypochlorous acid. This evidently represents a reversible reaction. Therefore, in order to obtain a good yield of ethylenedinitroamine the authors suggest that the conversion of N : N'-dichloro-N : N'-dinitro-1 : 2-diaminoethane to ethylene-N : N'-dinitroamine be carried out by means of reducing reagents (e.g. sodium bisulphite) which decompose hypochlorous acid during the hydrolysis.

The following N-nitroamines have been obtained by the method of Smart and Wright: ethylenedinitroamine, *sec.*-butylnitroamine, *n*-butylnitroamine, *n*-octylnitroamine, *iso*propylnitroamine and *cyclo*hexyl nitroamine.

Ethylenedinitroamine is obtained on an industrial scale by the nitration of ethyleneurea (imidazolidone-2) with subsequent hydrolysis of ethylenedinitrourea by boiling with water [4]:

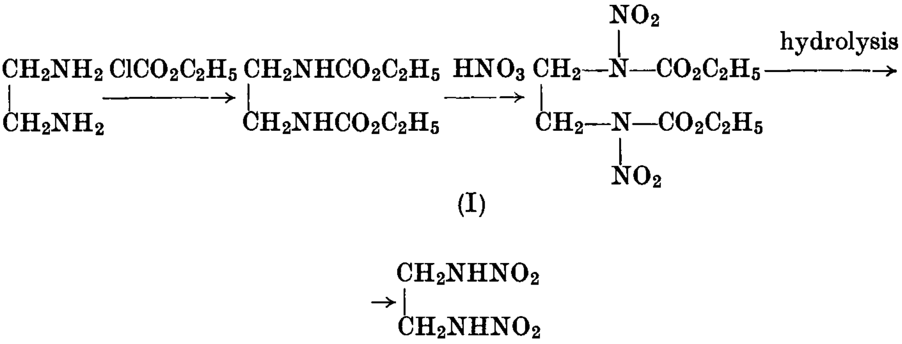


$$\begin{array}{l}CH_2\text{—}NH\\ |\\ CH_2\text{—}NH\end{array}\!>CO \xrightarrow{HNO_3} \begin{array}{l}\qquad\;\; NO_2\\ \qquad\;\;\; |\\ CH_2\text{—}N\\ |\\ CH_2\text{—}N\\ \qquad\;\;\; |\\ \qquad\;\; NO_2\end{array}\!>CO \xrightarrow{H_2O} \begin{array}{l}CH_2NHNO_2\\ |\\ CH_2NHNO_2\end{array} + CO_2$$

The nitration of ethyleneurea is carried out with nitrating mixture composed of 74 per cent sulphuric acid, 15·4 per cent nitric acid and 10·6 per cent water. To 10 parts by weight of nitrating mixture cooled to below 10°C is added 1 part by weight of ethyleneurea in small portions at such a rate that the temperature does not rise above 10°C. On cessation of the reaction the mixture is poured onto ice and the ethylenedinitrourea which separates out is filtered off and washed with water. It is then boiled with water until no more gas is evolved. On cooling the solution to room temperature ethylenedinitroamine precipitates out in lustrous crystals which are filtered, washed with water and dried.

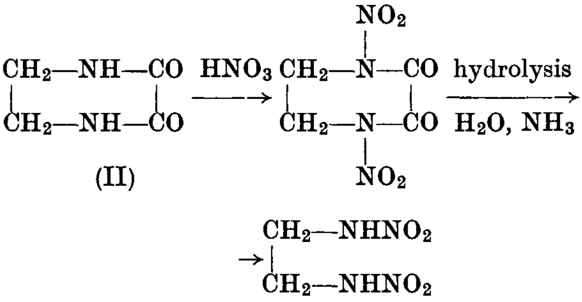
Ethyleneurea in its turn can be prepared by many methods: by condensation of carbon dioxide with ethylenediamine, interaction of ethylenediamine with urea, condensation of diethylcarbonate or phosgene with ethylenediamine, and so on [5].

Still other methods for the synthesis of ethylenedinitroamine have been developed. For example: nitration and subsequent hydrolysis of ethylene-bis-urethane (I) and N : N′-ethyleneoxamide (II) [6]:



$$\begin{array}{l}CH_2NH_2\\|\\CH_2NH_2\end{array}\xrightarrow{ClCO_2C_2H_5}\begin{array}{l}CH_2NHCO_2C_2H_5\\|\\CH_2NHCO_2C_2H_5\end{array}\xrightarrow{HNO_3}\begin{array}{l}\quad\;\; NO_2\\\quad\;\;|\\CH_2{-}N{-}CO_2C_2H_5\\|\\CH_2{-}N{-}CO_2C_2H_5\\\quad\;\;|\\\quad\;\; NO_2\end{array}\xrightarrow{\text{hydrolysis}}\begin{array}{l}CH_2NHNO_2\\|\\CH_2NHNO_2\end{array}$$

(I)



$$\begin{array}{l}CH_2{-}NH{-}CO\\|\qquad\qquad\;|\\CH_2{-}NH{-}CO\end{array}\xrightarrow{HNO_3}\begin{array}{l}\quad\;\; NO_2\\\quad\;\;|\\CH_2{-}N{-}CO\\|\qquad\quad\;|\\CH_2{-}N{-}CO\\\quad\;\;|\\\quad\;\; NO_2\end{array}\xrightarrow[H_2O,\ NH_3]{\text{hydrolysis}}\begin{array}{l}CH_2{-}NHNO_2\\|\\CH_2{-}NHNO_2\end{array}$$

(II)

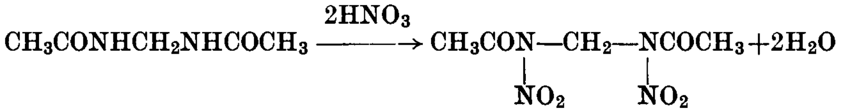
These methods have, however, no industrial application.

Among the nitro derivatives of primary amines a most interesting substance should be mentioned—methylenedinitroamine, which was originally isolated from the products of nitration of urotropine [7].

Methylenedinitroamine is obtained on nitration of methylene-bis-N-acetamide in acetic anhydride with subsequent hydrolysis; methylene-bis-N-acetamide is formed when acetamide is condensed with paraformaldehyde. The series of reactions follows the scheme given below:

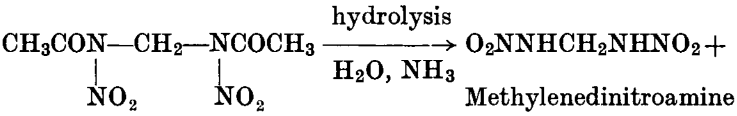
$$4CH_3CONH_2+HCHO \rightarrow 2CH_3CONHCH_2NHCOCH_3+2H_2O$$

Methylene-bis-N-acetamide



$$CH_3CONHCH_2NHCOCH_3 \xrightarrow{2HNO_3} \begin{array}{l}CH_3CON{-}CH_2{-}NCOCH_3+2H_2O\\\qquad\quad\;\, |\qquad\quad\;\; |\\\qquad\quad NO_2\qquad NO_2\end{array}$$

Methylene-bis-N(N-nitro)acetamide



$$\begin{array}{l}CH_3CON{-}CH_2{-}NCOCH_3\\\qquad\quad\;\, |\qquad\quad\;\; |\\\qquad\quad NO_2\qquad NO_2\end{array}\xrightarrow[H_2O,\ NH_3]{\text{hydrolysis}} O_2NNHCH_2NHNO_2+$$

Methylenedinitroamine

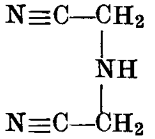
$$+CH_3COONH_4$$

Methylenedinitroamine is isolated from the reaction mixture by its precipitation as the barium salt followed by decomposition of the salt with hydrochloric acid.

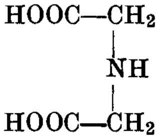
Nitration of secondary amines—dimethylamine and piperidine—was studied in the last century by BAMBERGER [8, 9]. N-nitrodimethylamine and N-nitropiperidine were obtained by the action of acetic anhydride on the nitric acid salts of dimethylamine and piperidine. No yields are given in these communications.

WRIGHT and co-workers [10] repeated BAMBERGER's synthesis and obtained N-nitropiperidine with a 22 per cent yield and N-nitrodimethylamine with only a 5 per cent yield.

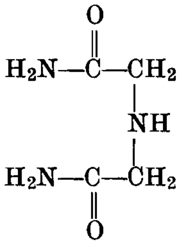
On the other hand it has been established that a series of secondary aliphatic amines can be easily nitrated by anhydrous nitric acid to give N-nitroamines [11]. This method was used for the preparation of N-nitro derivatives of imino-bis-acetonitrile (I), imino-bis-acetic acid (II), diamide of imino-bis-acetic acid (III) and 2 : 6-dioxopyridazine (IV):



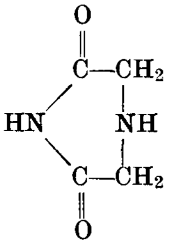
(I)



(II)



(III)



(IV)

Compared to dimethylamine and piperidine the compounds cited above are very weak bases.

Nitration by this method is very extravagant, since a considerable excess of anhydrous nitric acid is required. Moreover it is not a general method and many secondary amines do not give N-nitro derivatives under these conditions.

WRIGHT and co-workers [10] developed a new method of catalytic nitration of secondary amines with nitric acid in acetic anhydride medium. They established during nitration of diethanolamine that hydrogen chloride added to the reaction mixture in small quantity was a very potent catalyst for the nitration of secondary amines with nitric acid in acetic anhydride medium and greatly enhanced the yield of $\beta : \beta'$-dinitrooxydiethylnitroamine.

Originally the authors obtained a 98 per cent yield of $\beta : \beta'$-dinitrooxydiethylnitroamine by the interaction of dinitrooxydiethylammonium nitrate with acetic anhydride in the presence of chloroacetate, zinc chloride or dinitrooxydiethylammonium chloride as catalysts. However, this method proved inconvenient because of the need to obtain and isolate dinitrooxydiethylammonium nitrate.

In connexion with this a method has been developed for the single stage nitration of diethanolamine. The catalyst used in this process is diethanolamine hydrochloride.

In order to obtain a good yield of $\beta : \beta'$-dinitrooxydiethylnitroamine, the reagents: diethanolamine, nitric acid, acetic anhydride and diethanolamine hydrochloride, were taken in the molar ratios of 1 : 3·2 : 3·4 : 0·05.

Nitric acid and diethanolamine were added to acetic anhydride with stirring over a period of 45 min at 5-15°C at such a rate that no free diethanolamine would accumulate in the reaction mixture. When the addition of the reagents was complete the reaction mixture was heated to 40°C for 40 min. It was then poured into cold water. The precipitate of $\beta : \beta'$-dinitrooxydiethylnitroamine was filtered off and washed with dilute ammonia solution. The yield of crude product was 90 per cent, m.p. 49·5–51·5°C.

The crude product was purified by treating its suspension in water with steam to remove $\beta : \beta'$-dinitrooxydiethylnitrosoamine and recrystallizing from acetone.

The catalytic method was successfully applied to the nitration of other secondary amines as well. Nitrates of secondary amines were treated with acetic anhydride containing zinc chloride. The conversion of the nitrates of dimethylamine, diethylamine, piperidine and morpholine to nitroamines was 65, 60, 58 and 65 per cent of the theoretical respectively. Di-*n*-butylamine hydrochloride was also nitrated with nitric acid in acetic anhydride medium [10, 12].

Wright and collaborators [13] established that the ease of nitration of secondary amines depended on the basicity of the amino group. It was found that the basic properties of those amines which undergo nitration in the absence of catalysts with good yields were considerably weaker than that of morpholine. In the case of very strong amines (e.g. di-*n*-butylamine) it was found best to take an equimolecular amount of catalyst.

The relative basicity of some secondary amines was determined by colorimetric titration. *o*-Nitroaniline was used as indicator; it is not appreciably dissociated in glacial acetic acid and is orange–yellow in colour. In sulphuric and perchloric acids in concentrations sufficient to convert the indicator into an ammonium ion, *o*-nitroaniline is almost colourless. If one equivalent of a secondary amine is added to one equivalent of a solution of sulphuric or perchloric acid in acetic acid containing the indicator, the ratio of undissociated (coloured) molecules of indicator to the total amount of indicator will be highest when the amine being investigated exhibits maximum ability to acquire protons.

The authors did not attempt to assess the degree of association of the indicator in acetic acid as nitrophenylammonium acetate, and therefore expressed the results of titration only as a ratio of the intensity of indicator colour in the presence of a definite amount of the amine in sulphuric (or perchloric) acid to the intensity of colour of the same amount of indicator in acetic acid.

Table 18 gives the relative proton accepting ability of some amines with respect to sulphuric and perchloric acids. This table shows that all the amines (nos. 14–17 inclusive) which undergo nitration with good yields in the absence of hydrogen chloride catalyst [11] are the worst electron acceptors. Strongly basic amines such as dimethylamine and piperidine, on the contrary, give extremely poor yields of nitro compounds in the absence of catalyst (6 and 22 per cent respectively) [10].

Thus those amines which are the poorest electron acceptors are the easiest to nitrate.

Table 18. *Relative proton accepting ability with respect to sulphuric and perchloric acids*

No.	Amine	Intensity of indicator colour in CH_3COOH	
		Sulphuric acid	Perchloric acid
1	Di*iso*propylamine	1·06	0·675*
2	Di*iso*butylamine	1·06	0·536*
3	Di*cyclo*hexylamine	1·05	0·531
4	Di-*n*-butylamine	1·04	0·527
5	Diethylamine	1·02	0·516*
6	Di-*n*-octylamine	1·02	0·516
7	Dimethylamine	1·01	0·511*
8	Lysidine	0·99	0·500
9	Methylethanolamine	0·98	0·495*
10	Di*iso*amylamine	0·945	0·478
11	Morpholine	0·915	0·463*
12	Imino-bis-propionitrile	0·85	0·430*
13	Diethanolamine	0·77	0·389*
14	Imino-bis-acetonitrile	—	0·310
15	Imino-bis-methylacetonitrile (solid diastereomer)	—	0·182
16	Imino-bis-methylacetonitrile (liquid diastereomer)	—	0·084
17	Imino-bis-dimethylacetonitrile	—	0·0825

* The amines marked with an asterisk were not titrated with perchloric acid, the figures being recalculated according to the data obtained with sulphuric acid. The tendency to acquire a proton is approximately the same in piperidine as in methylethanolamine.

The following facts were established by WRIGHT and collaborators [12, 13] in their studies of the reactivity of secondary aliphatic amines with respect to nitration:

(1) The reactivity of secondary amines decreases with increased tendency on the part of the amine to accept protons.

(2) Weakly basic amines (nos. 14–17 inclusive) give good yields of N-nitro derivatives when nitrated in the absence of catalyst.

(3) in order to obtain good yields of N-nitroamine from more basic amines (nos. 1–13 inclusive) it is necessary to carry out the nitration in the presence of a catalyst (hydrogen chloride, zinc chloride, etc.). The amount of catalyst has to be increased as the proton-accepting ability of the amine increases. An equimolecular amount of hydrogen chloride is required for the nitration of the most basic of these amines: di*iso*propylamine.

Electropositive chlorine, in the form of hypochlorous acid or chloroacetate for example, was detected in the reaction mixture during the nitration of secondary amines in the presence of hydrogen chloride or zinc chloride [12]. Such compounds with positively charged chlorine can produce the conversion of secondary amine to the corresponding less basic chloroamine. If freshly prepared solution of nitric acid and hydrogen chloride in acetic anhydride will give chloramines from amines, then chloroacetate must likewise be present in the reaction mixture during the nitration of secondary amines in the presence of hydrogen chloride, and will act as a chlorinating agent.

This supposition was checked during the nitration of diethanolamine and its derivatives. The yield of $\beta : \beta'$-dinitrooxydiethylnitroamine was higher when $\beta : \beta'$-dioxydiethylammonium chloride and $\beta : \beta'$-dinitrooxydiethylammonium chloride were nitrated (94 and 97 per cent respectively), than when diethanolamine was nitrated in the presence of a small amount of hydrogen chloride (92 per cent) [10].

Nitration of dinitrooxydiethylchloroamine with nitric acid gave a 78 per cent yield of $\beta : \beta'$-dinitrooxydiethylnitroamine, but the reaction mixture was unstable, evidently as the result of perchlorous acid formation. On the other hand, when this chloroamine was nitrated with nitric acid in acetic anhydride the yield of $\beta : \beta'$-dinitrooxydiethylnitroamine (96 per cent) practically coincided with the yield obtained using dinitrodiethylammonium chloride, and the reaction mixture was perfectly stable. This increase in yield and stability of the reaction mixture is apparently associated with the fact that acetic anhydride converts hypochlorous acid into chloroacetate. The fairly high yield of $\beta : \beta'$-dinitrooxydiethylnitroamine obtained by nitration of the chloroamine with nitric acid resembles the nitration of weak amines of the imino-bis-acetonitrile type [12, 14]. Consequently, acetic anhydride in catalytic nitration acts as a stabilizing agent.

The presence of chloroamine in the reaction mixture was not, however, revealed although the presence of electropositive chlorine was established. Wright and collaborators [15] determined the amount of electropositive chlorine, formed from zinc chloride and nitric acid in acetic anhydride, and found that the amount formed was 39 per cent of the amount expected from the following equation:

$$\text{(I)}\quad ZnCl_2+2HNO_3+3(CH_3CO)_2O \rightleftarrows Zn(OCOCH_3)_2+N_2O_3+ \\ +2ClOCOCH_3+2HOCOCH_3$$

On the basis of this it is possible to suppose that chloroamine could be isolated from a nitration mixture which, according to equation (I), would contain an amount of nitric acid sufficient for the formation of chloroacetate but insufficient for subsequent nitration. Such a mixture was prepared according to equations (II) and (III) and gave a 30 per cent yield of the expected chloroamine.

$$\text{(II)}\quad 2HCl+2HNO_3+3(CH_3CO)_2O \rightarrow 2ClOCOCH_3+N_2O_3+4HOCOCH_3$$

$$\text{(III)}\quad (NO_3{-}CH_2{-}CH_2)_2NH+ClOCOCH_3 \rightarrow (NO_3{-}CH_2{-}CH_2)_2NCl+ \\ +HOCOCH_3$$

$\beta:\beta'$-Dinitrooxydiethylnitrosoamine was also obtained with a yield of 36 per cent of the theoretical. The reaction evidently followed the equations:

$$\text{(IV)}\quad (CH_3CO)_2O+N_2O_3+2HCl \rightarrow 2NOCl+2HOCOCH_3$$

$$\text{(V)}\quad NOCl+(NO_3{-}CH_2{-}CH_2)_2NH \rightarrow (NO_3{-}CH_2{-}CH_2)_2N{-}NO+HCl$$

Therefore chloroamine can be converted to nitroamine according to equation (VI)

$$\text{(VI)}\quad (NO_3{-}CH_2{-}CH_2)_2NCl+HNO_3 \rightarrow (NO_3{-}CH_2{-}CH_2)_2N{-}NO_2+ +HOCl$$

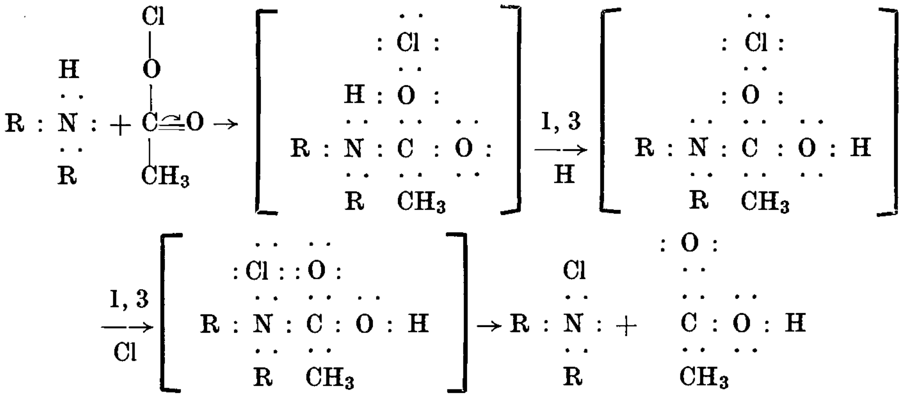
Since neither nitrous acid nor nitrous anhydride is formed in reaction (VI) it can be assumed that these substances will not be found among the reaction products, and in fact they were absent from the reaction products.

According to equation (VI) hypochlorous acid is formed during the nitration of chloroamine. If hypochlorous acid is stabilized by conversion to chloroacetate it can be used to obtain further amounts of chloroamine and the catalytic nitration of secondary amines can be regarded as a chain reaction, since the electropositive chlorine is regenerated in the process of the reaction.

Although secondary amines can be nitrated in the absence of acetic anhydride the yield of N-nitro derivatives rises appreciably when this reagent is used. The use of acetic anhydride is especially necessary during catalytic nitration of strongly basic amines. This is explained by the fact that hypochlorous acid is rapidly destroyed by nitric acid and so has no time to react with the amine in those cases when the rate of chloroamination is relatively low.

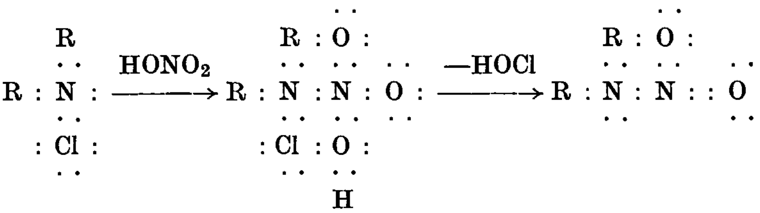
WRIGHT and collaborators consider that the nitration of secondary amines involves the formation of a complex of the amine and nitric acid. They presume that such complexes are not formed with strongly basic amines which give normal electrovalent salts. Therefore the strongly basic properties of such amines are weakened by conversion to the corresponding chloroamines in catalytic nitration.

Consequently, the first stage of catalytic nitration of secondary amines consists of the formation of the chloroamine. The combination of chloroacetate in the active state with the amine proceeds according to the following scheme:



The addition product of chloroacetate and the amine can then undergo a 1 : 3-rearrangement of hydrogen and 1 : 3-rearrangement of chlorine. Decomposition of the complex, following the hydrogen and chlorine rearrangements, leads to the formation of chloroamine and acetic acid.

In the second stage of the reaction a covalent bond is formed between the nitrogen atoms of the chloroamine and nitric acid. This compound eliminates hypochlorous acid spontaneously to give the nitroamine. Hypochlorous acid is thus set free and is stabilized by acetylation:



$$\begin{array}{cccc} & & R & \\ & & \cdot\cdot & \\ R & : & N & : \\ & & \cdot\cdot & \\ & : & Cl & : \\ & & \cdot\cdot & \\ & & & \end{array} \xrightarrow{HONO_2} \begin{array}{cccccccc} & & & & \cdot\cdot & & & \\ & & R & : & O & : & & \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & \\ R & : & N & : & N & : & O & : \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & \\ & : & Cl & : & O & : & & \\ & & \cdot\cdot & & \cdot\cdot & & & \\ & & & & H & & & \end{array} \xrightarrow{-HOCl} \begin{array}{ccccccc} & & & & \cdot\cdot & & \\ & & R & : & O & : & \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot \\ R & : & N & : & N & :: & O \\ & & \cdot\cdot & & & & \cdot\cdot \end{array}$$

Examination of side products of the reaction obtained on nitration of chloroamines showed that the nitration of chloroamine occurred at a slower rate than its formation in the reaction mixture.

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CHAPTER V

NITRATION WITH NITROGEN OXIDES

A. Nitration with Nitrogen Oxides without Catalysts

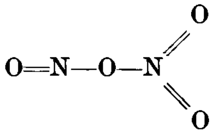
THE method of nitration with nitrogen oxides which began to be developed as far back as the 1870's only acquired actual importance since 1910–1915 with the industrial manufacture of nitric acid from atmospheric nitrogen through nitrogen oxides. Beginning with this period the problem of utilizing nitrogen oxides for the nitration of organic substances attracted the attention of many research workers who devoted to it numerous publications. This is explained chiefly by the fact that nitration with nitrogen oxides has certain technical advantages over nitration with nitric acid and nitrating mixtures, since the need of converting nitrogen oxides into nitric acid is obviated, and it is well known that the synthesis of nitric acid from nitrogen oxides is a fairly complicated process consisting of oxidation (with oxygen) of the lower oxides of nitrogen to nitric anhydride in the presence of water giving a dilute solution of nitric acid which is then concentrated with the help of H_2SO_4.

N_2O_4 usually used for nitration (b.p. 21·3°C at 760 mm) is regarded as an equilibrium mixture according to the equation:

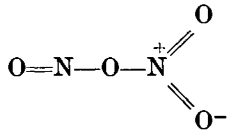
$$N_2O_4 \rightleftarrows 2NO_2$$

At low temperatures the dimer predominates. Determination of vapour density shows that at temperatures above 140°C complete dissociation of N_2O_4 occurs, whilst at 27°C about 20 per cent N_2O_4 is present as the monomer. The appearance of N_2O_4 alters depending on the temperature, and hence the state of the equilibrium, from colourless crystals at −50°C to black fumes at 183°C.

The structure of N_2O_4 cannot be considered as precisely established. Of all the suggested formulae the following merit most attention:



and



A number of the chemical reactions of N_2O_4 and in particular its reaction with water according to the equation:

$$N_2O_4+H_2O \rightarrow HNO_3+HNO_2$$

speak in favour of this formula.

CLUSIUS and VEECHI [1] consider, on the basis of studies of the interaction of labelled tetramethylammonium nitrate $(CH_3)_4N^{15}NO_3$ with liquid N_2O_4, that N_2O_4 exists partially in the form of nitrosyl nitrate $NO\,.\,NO_3$ which is, in turn, able to undergo ionization:

$$N_2O_4 \rightleftarrows NO\,.\,NO_3 \rightleftarrows NO^{+}+NO_3^{-}$$

Formation of nitrogen trioxide NO_3 is considered permissible by some authors. Thus Walsh [2] in explaining the mechanism of the oxidation of various compounds by nitrogen dioxide considers that oxygen is formed as the result of dissociation of NO_3 according to the following scheme:

$$N_2O_4 \rightarrow NO_3 + NO$$

$$NO_3 \rightarrow NO + O_2$$

Balandin [3], Zabolotskii [4], Blacet [5] regard NO_3 as a primary product of nitrogen oxide oxidation by ozonized oxygen.

1. NITRATION IN THE LIQUID PHASE

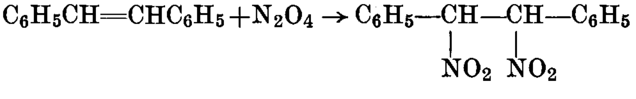
1. *Nitration of unsaturated compounds*—Among the works devoted to the nitration of organic compounds with nitrogen oxides those dealing with the preparation of nitro compounds from unsaturated aliphatic compounds should be mentioned first. The reaction products are usually unstable solids or oils from which it is at times very difficult to isolate the pure substance.

Wieland [6, 7] studied the interaction of aliphatic unsaturated compounds with N_2O_4 and nitrogen oxide gases.* He found that the products of this reaction were dinitro compounds which were formed according to the scheme:

$$R{-}CH{=}CH{-}R' + N_2O_4 \rightarrow R{-}CHNO_2{-}CHNO_2{-}R'$$

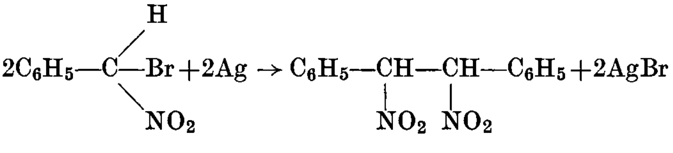
where R and R′ are saturated hydrocarbon radicals. Similar dinitro compounds are also obtained on nitration of mixed aliphatic aromatic unsaturated compounds with the general formula of $C_6H_5{-}CH{=}CH{-}R$ and $Ar{-}CH{=}CH{-}Ar$ using N_2O_4.

Thus, for example, diphenyldinitroethane is obtained when stilbene reacts with N_2O_4:



$$C_6H_5CH{=}CHC_6H_5 + N_2O_4 \rightarrow C_6H_5{-}\underset{NO_2}{\underset{|}{CH}}{-}\underset{NO_2}{\underset{|}{CH}}{-}C_6H_5$$

Wieland proved the structure of this dinitro compound by synthesizing it from phenylbromonitromethane interacting with silver:



$$2C_6H_5{-}\overset{H}{\underset{NO_2}{C}}{-}Br + 2Ag \rightarrow C_6H_5{-}\underset{NO_2}{\underset{|}{CH}}{-}\underset{NO_2}{\underset{|}{CH}}{-}C_6H_5 + 2AgBr$$

The product obtained from stilbene proved to be identical with diphenyldinitroethane obtained from phenylbromonitromethane. Wieland also

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* Wieland considered these gases to be a mixture of N_2O_3 and N_2O_4 the active part being played, in his opinion, by the free radicals $NO\cdot$ and $NO_2\cdot$.

studied the nitration of unsaturated hydrocarbons containing conjugated double bonds by means of N_2O_4:

$$R-CH=CH-CH=CH-R'$$

Treating a suspension of 1 : 4-diphenylbutadiene in absolute ether with a solution of N_2O_4 in a mixture of ether and petrol, with cooling, gave WIELAND 1 : 4-diphenyl-1 : 4-dinitrobutene-2:

$$C_6H_5-CH=CH-CH=CH-C_6H_5+N_2O_4 \rightarrow$$

$$\rightarrow C_6H_5CH(NO_2)-CH=CH-CH(NO_2)C_6H_5$$

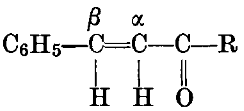
Thus the nitro groups add on not to two adjacent carbon atoms (in positions 1, 2) but to the terminal carbon atoms in a system of conjugated double bonds (1, 4) which agrees with THIELE's rule.

When diphenyldinitrobutene is treated with alcoholic alkali it splits out a molecule of HNO_2 and gives 1 : 4-diphenyl-1-nitrobutadiene:

$$C_6H_5CH(NO_2)-CH=CH-CH(NO_2)C_6H_5 \rightarrow$$

$$\rightarrow C_6H_5C(NO_2)=CH-CH=CHC_6H_5+HNO_2$$

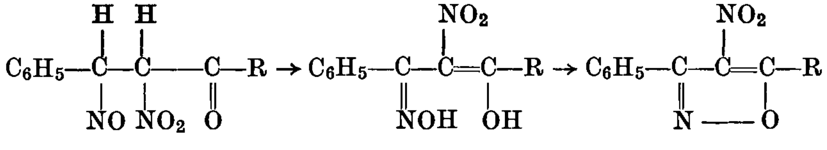
WIELAND showed further that when nitrogen oxide gases act on unsaturated compounds containing a carbonyl group and corresponding to the general formula given below:



$$C_6H_5-\underset{\overset{|}{H}}{\overset{\beta}{C}}=\underset{\overset{|}{H}}{\overset{\alpha}{C}}-\underset{\overset{\|}{O}}{C}-R$$

three types of compounds result.

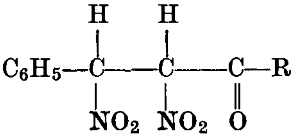
(1) The nitro group adds on to the α-atom of the hydrocarbon, whilst the nitroso group adds on to the β-atom (I); as the reaction proceeds intramolecular rearrangements result in the conversion of compound (I) into the oxime (II) which loses water readily to give the azoxazole (III):



$$C_6H_5-\underset{\overset{|}{NO}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{NO_2}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{\|}{O}}{C}-R \rightarrow C_6H_5-\underset{\overset{\|}{NOH}}{C}-\overset{\overset{NO_2}{|}}{C}=\underset{\overset{|}{OH}}{C}-R \rightarrow C_6H_5-\underset{\overset{\|}{N}}{C}-\overset{\overset{NO_2}{|}}{C}=\underset{\overset{|}{O}}{C}-R$$

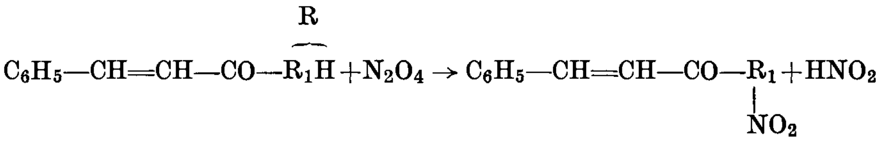
(I) (II) (III)

(2) Nitro groups add on across the double bond linking carbon atoms α and β, giving dinitrocompounds:



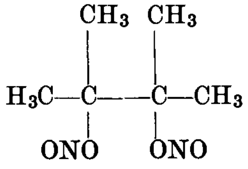
$$C_6H_5-\underset{\overset{|}{NO_2}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{|}{NO_2}}{\overset{\overset{H}{|}}{C}}-\underset{\overset{\|}{O}}{C}-R$$

(3) Direct nitration occurs in the radical linked with the keto group (R) which gives an unsaturated nitroketone:



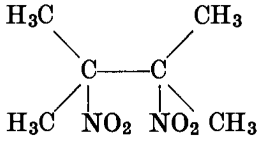
$$C_6H_5\text{—}CH{=}CH\text{—}CO\text{—}\overbrace{R_1H}^{R}+N_2O_4 \rightarrow C_6H_5\text{—}CH{=}CH\text{—}CO\text{—}\underset{\substack{|\\ NO_2}}{R_1}+HNO_2$$

The interaction of N_2O_4 with tetramethylethylene was studied by a number of workers. SCHMIDT [8] affirms that when ether is used as solvent the main reaction product is a dinitrite of the structure:



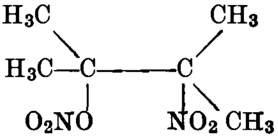
$$H_3C\text{—}\underset{\substack{|\\ ONO}}{\overset{\substack{CH_3\\ |}}{C}}\text{——}\underset{\substack{|\\ ONO}}{\overset{\substack{CH_3\\ |}}{C}}\text{—}CH_3$$

This assertion was subsequently disproved by DEMIANOV and SIDORENKO [9, 10], who also studied the nitration of unsaturated compounds with nitrogen oxides. When these authors nitrated tetramethylethylene (until a small excess of hydrocarbon remained) with an ethereal solution of nitrogen oxides, obtained by the action of nitric acid on As_2O_3, a dinitro compound resulted whose composition was:



(I)

and a product of empirical formula $C_6H_{12}N_2O_5$ (II), m.p. 101–104°C. The structure of dinitro compound (I) was proved by its reduction to the diamine; the second reaction product (II) gave a mixture of diamine and oxamine on reduction, which led DEMIANOV and SIDORENKO to ascribe to it the following structure:



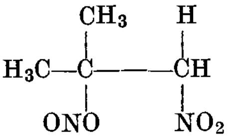
(II)

The same workers obtained addition products of NO_2 with *iso*butylene, hexylene, diallyl and other unsaturated aliphatic hydrocarbons, using N_2O_5, N_2O_4 and N_2O_3 as nitrating agents.

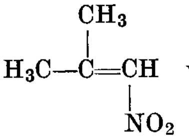
MICHAEL and CARLSON [11] made a detailed study of the interaction of tetramethylethylene and N_2O_4. When the reaction was carried out in ethereal solution the authors obtained up to 22 per cent of 2 : 3-dinitro-2 : 3-dimethylbutane, whereas in the absence of the solvent or in petroleum ether solution the dinitro product was obtained in small quantity. The authors mention the formation in all their experiments of the nitronitrate to which Demianov and Sidorenko ascribe structure (II).

According to the findings of these authors this product results from the addition of N_2O_4 and subsequent oxidation. Michael and Carlson conclude that no dinitrite is formed.

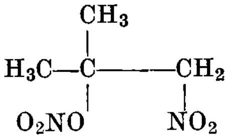
Michael and Carlson also studied the action of N_2O_4 on *iso*butylene under various conditions. In ethereal solution the reaction products were reduced and the composition of the reduction products gave an insight into the nature of the original product of interaction with N_2O_4. In this way it was found that in ethyl ether solution the following compounds were obtained:



$H_3C-\overset{CH_3}{\underset{ONO}{C}}-\overset{H}{\underset{NO_2}{CH}}$ with yield of 16–23 per cent of the theoretical

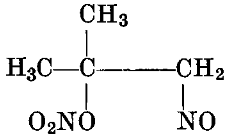


$H_3C-\overset{CH_3}{C}=\underset{NO_2}{CH}$ with yield of 5–12 per cent of the theoretical



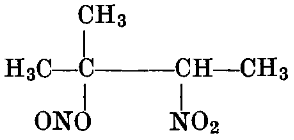
$H_3C-\overset{CH_3}{\underset{O_2NO}{C}}-\underset{NO_2}{CH_2}$ with yield of 12 per cent of the theoretical

In the absence of solvent or in petroleum ether solution nitroso nitrate with a yield of approximately 13 per cent of the theoretical was obtained:



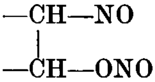
$$H_3C-\overset{CH_3}{\underset{O_2NO}{C}}-\underset{NO}{CH_2}$$

If *iso*butylene was replace by trimethylethylene [12] the following compound was obtained with a yield of 35 per cent of the theoretical when ether was used as solvent:



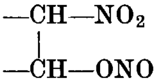
$$H_3C-\overset{CH_3}{\underset{ONO}{C}}-\underset{NO_2}{CH}-CH_3$$

Schaarschmidt and Hoffmeier [13, 14] found that when liquid N_2O_4 acts on unsaturated hydrocarbons a mixture of products of various nature results, its composition in every individual case depending on the nature of the olefine and the reaction temperature used. These workers consider that four types of compounds can result from the addition of N_2O_4 to olefines:



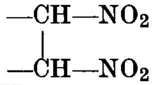
$$\begin{array}{l}\text{—CH—NO}\\ \;\;|\\ \text{—CH—ONO}_2\end{array}$$

(I) Nitrosates (nitroso nitrates)



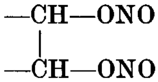
$$\begin{array}{l}\text{—CH—NO}_2\\ \;\;|\\ \text{—CH—ONO}\end{array}$$

(II) Nitrous esters of nitro alcohols (nitro nitrites)



$$\begin{array}{l}\text{—CH—NO}_2\\ \;\;|\\ \text{—CH—NO}_2\end{array}$$

(III) Dinitro compounds



$$\begin{array}{l}\text{—CH—ONO}\\ \;\;|\\ \text{—CH—ONO}\end{array}$$

(IV) Nitrous esters of glycols (dinitrites)

Of these compounds the only stable one is (III) in which both nitrogen atoms are directly linked with carbon atoms; compounds of the other types (I), (II), (IV) readily undergo transformations and give other reaction products.

Compounds of type (I) (nitroso nitrate), similarly to chlorine addition products which split out HCl, split out HNO_3; the latter oxidizes the nitrosoolefine formed. Compounds of type (II) (nitronitrite) can break down into nitroolefine and nitrous acid, which decomposes further according to the equation

$$3HNO_2 = HNO_3 + H_2O + 2NO$$

The nitrous acid, or more probably the nitric acid formed as shown in the equation above, oxidizes the nitroolefine. Dinitrite (IV) readily splits out nitrous acid with simultaneous formation of an extremely unstable olefine-nitrite.

When SMITH [15] passed pure ethylene through purified liquid nitrogen dioxide at 0°C he obtained a good yield of $\alpha : \beta$-dinitroethane. According to this author, when N_2O_4 is passed through an ethereal solution of tetramethylethylene 2 : 3-dinitro-2 : 3-dimethylbutane is formed with a yield of approximately 22 per cent. 1 : 2-Dinitropropane and 1 : 2-dinitro-*iso*butane can be obtained similarly [16].

A process for the preparation of 1 : 2-dinitro*cyclo*hexane from N_2O_4 and *cyclo*hexene at 300°C and pressures up to 100 atm has been described [17].

LEVY [18] obtained dinitroethane by passing simultaneously ethylene (at the rate of 30 l/hr) and oxygen (at the rate of 8 l/hr) into liquid N_2O_4 (3 l.) at 0°C during $10\frac{1}{2}$ hr. 228·5 l. of ethylene and 24·4 l. of oxygen were adsorbed in the course of the reaction. After removal of excess N_2O_4 with dry air the oil obtained was strongly cooled (solid CO_2 and CH_3OH) and approximately 400 g of 1 : 2-dinitroethane were isolated; the yield —33 per cent (approximately) of the theoretical calculated on ethylene and about 40 per cent calculated on N_2O_4.

LEVY and collaborators [19] also investigated the reaction between propylene, butylene, *cyclo*hexene, 2 : 4 : 4-trimethylpentene-1 and 2 : 4 : 4-trimethylpentene-2 and N_2O_4. In the case of gaseous olefines a stream of the hydrocarbon was passed through a solution of N_2O_4 in ether. Liquid olefines were added to N_2O_4 or, conversely, an ethereal solution of N_2O_4 was added to the hydrocarbon. The reactions were carried out at low temperatures (from −5 to 0°C). In some experiments a gentle stream of oxygen was passed through the reaction mixture in order to avoid the formation of nitrogen trioxide.

The studies showed that the interaction of N_2O_4 with olefines led to the formation of two substances: a dinitro compound and a nitro-nitrite. In the case of an asymmetrical olefine molecule the ONO group always joined the carbon atom linked with the fewest number of hydrogen atoms. Thus, for example, when nitrogen tetraoxide adds on to propylene the products formed are dinitropropane $CH_3CH(NO_2)CH_2NO_2$ and α : β-nitro*iso*propyl nitrite $CH_3CH(ONO)CH_2NO_2$.

Owing to the instability of the nitro nitrites these compounds were not isolated in the pure state, but were hydrolysed to form nitro alcohols. In some experiments nitro nitrates were found amongst the reaction products which were formed by the oxidation of nitro nitrites.

According to LEVY and SCAIFE when olefines interact with N_2O_4 in the absence of solvent not only addition reactions occur but also oxidation of the olefine. Ethers and esters were used as solvents, among them: diethyl ether, dioxane, ethyl acetate, etc. The authors suppose that these form a complex with the N_2O_4 molecule and so suppress oxidation of the latter [20].

The action of nitrogen dioxide (NO_2) on ethylene oxide [21] gives 2-nitroethyl alcohol if the reaction is carried out as follows: ethylene oxide (50 g) and $CHCl_3$ (250 g) cooled to 0°C are slowly added to NO_2 (92 g) and $CHCl_3$ (1000 g) at 0°C. The mixture is allowed to stand for 12–15 hr at room temperature after which $CHCl_3$ is distilled off at 50°C and 135 g of nitroethyl nitrate are obtained; this, after treatment with a 10 per cent solution of Na_2CO_3, gives 2-nitroethyl alcohol.

β-Nitroethyl alcohol is also formed when ethylene oxide is treated with sodium nitrite [22] with simultaneous passage of carbon dioxide: CO_2 and ethylene oxide are passed through a solution of $NaNO_3$ (200 g) in 1 l. of water at 25–30°C. The precipitate of $NaHCO_3$ is filtered off. The filtrate is distilled, giving 235 g. $O_2N—CH_2—CH_2—OH$ (85 per cent), b.p. 107–110°C at 20 mm.

β-Nitroethyl alcohol can also be obtained by passing ethylene oxide through a solution of barium nitrite. Ethylene oxide (130 g) is bubbled through a solution of $Ba(NO_2)_2$ (400 g) in H_2O (100 ml); 2-nitroethanol is obtained with a 93 per cent yield.

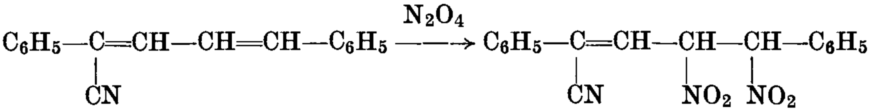
BILTZ [23] heated tetrachloroethylene (or tetrabromoethylene) with N_2O_4 in a sealed tube at 100°C for 3 hr and obtained a good yield of *sym.*-dinitrotetrachloroethane. Under similar conditions α : α-diphenyl-β : β-dichloroethane $(C_6H_5)_2C{=}CCl_2$ gives diphenyldinitrodichloroethane $(C_6H_5)_2C(NO_2)—C(NO_2)Cl_2$.

When ethylene reacts with nitrogen dioxide (NO_2) containing an admixture of NO at temperatures 20–60°C and pressure above 50 atm an unstable addition compound is formed which readily decomposes at 50–100°C in the presence of steam, and 2-nitroethanol, which is isolated by the usual method [24].

1 : 4-Addition takes place when N_2O_4 interacts with hydrocarbons containing a system of conjugated double bonds. Thus, for example, the reaction with 1 : 3-butadiene both in various solvents and in the vapour phase gives 1 : 4-dinitro-2-butene [25].

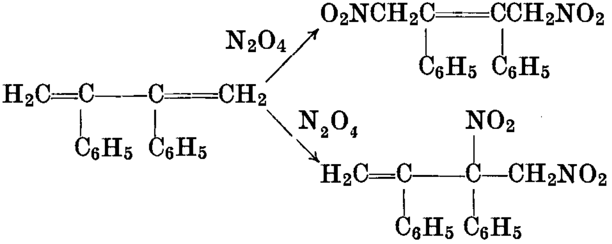
As has been mentioned previously **Wieland** observed a similar course of reaction [6,7].

In some cases NO_2 adds on to the 1 : 2 position of a conjugated system. For example, the action of N_2O_4 on 1-cyano-1 : 4-diphenyl-1 : 3-butadiene gives 1-cyano-1 : 4-diphenyl-3 : 4-dinitro-1-butene [26]:



$$\underset{\displaystyle CN}{C_6H_5{-}\overset{|}{C}}{=}CH{-}CH{=}CH{-}C_6H_5 \xrightarrow{N_2O_4} \underset{\displaystyle CN}{C_6H_5{-}\overset{|}{C}}{=}CH{-}\underset{\displaystyle NO_2}{\overset{|}{CH}}{-}\underset{\displaystyle NO_2}{\overset{|}{CH}}{-}C_6H_5$$

Allen [27] notes addition both in positions 1 : 2 and 1 : 4 of a conjugated system; for example the action of N_2O_4 on 2 : 3-diphenyl-1 : 3-butadiene is expressed by the equation:



$$H_2C{=}\underset{\displaystyle C_6H_5}{C}{-}\underset{\displaystyle C_6H_5}{C}{=}CH_2 \xrightarrow{N_2O_4} O_2NCH_2\underset{\displaystyle C_6H_5}{C}{=}\underset{\displaystyle C_6H_5}{C}CH_2NO_2$$

$$H_2C{=}\underset{\displaystyle C_6H_5}{C}{-}\underset{\displaystyle C_6H_5}{C}{=}CH_2 \xrightarrow{N_2O_4} H_2C{=}\underset{\displaystyle C_6H_5}{C}{-}\overset{\displaystyle NO_2}{\underset{\displaystyle C_6H_5}{C}}{-}CH_2NO_2$$

2. *Nitration of aromatic and heterocyclic compounds*—The study of nitrating aromatic compounds with nitrogen oxides dates relatively far back. In 1871 **Hasenbach** [28] found that benzene treated with N_2O_4 for 7 days at room temperature gave nitrobenzene and oxalic acid.

Nitrous anhydride, which reacts readily with unsaturated compounds, only reacts with aromatic hydrocarbons as the result of decomposition into nitrogen oxide and dioxide according to the equation [29]:

$$N_2O_3 \rightarrow NO+NO_2$$

Leeds [30] saturated benzene with nitrogen dioxide over several days in the cold; he obtained nitrobenzene, oxalic acid and picric acid. The greater part of benzene, evidently, remained unchanged. When NO_2 reacts with boiling benzene, however, two more products are formed in addition to the ones mentioned above; of these **Leeds** identified only one (monohydroxy derivative m.p. 205°C). The same author nitrated toluene with nitrogen dioxide, as well as xylene, cymene, naphthalene, anthracene and phenol. After toluene had been saturated with nitrogen dioxide for 3 months in the cold *o*-nitrotoluene and the following oxidation products were obtained: methyldinitrodihydroxybenzene $C_6H(CH_3)(NO_2)_2(OH)_2$ (needles, m.p. 110°C), oxalic and dihydroxybenzoic acids. Xylene under identical conditions gives *o*-nitroxylene and oxidation products: oxalic, *p*-toluic and phthalic acids, whilst cymene gives α-nitrocymene, oxalic and *p*-toluic acids. Nitration of naphthalene with nitrogen dioxide gives mononitronaphthalene, dinitronaphthalene, tetrahydroxynaphthalene and naphthodiquinone. Phenol, which nitrates very easily, gives picric acid. When a solution of anthracene in glacial acetic acid is saturated with nitrogen dioxide the only reaction product formed is anthraquinone with a yield of 58 g from 50 g anthracene.

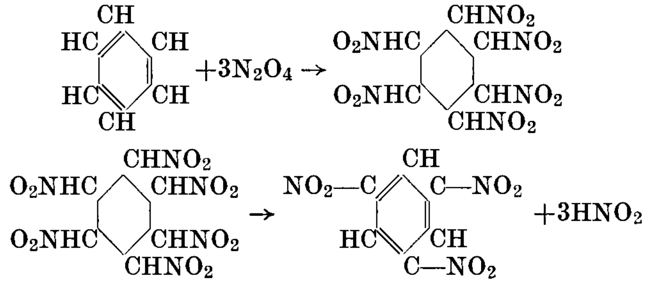
Friedberg [31] modified Leeds' method by using higher temperatures. He nitrated benzene by first dissolving nitrogen oxides in carbon disulphide and mixing the solution so obtained with benzene; a mixture of nitro- and *p*-dinitrobenzene was obtained.

Nitration of anthracene with nitrogen dioxide was also studied by Liebermann and Lindenmann [32] and by Meisenheimer [33], who, unlike Leeds, obtained nitro compounds. Liebermann and Lindenmann passed nitrogen dioxide in a slow stream through anthracene mixed with 4 parts of glacial acetic acid, the reaction temperature being maintained no higher than 10–15°C. The nitro compound formed was separated from excess anthracene by treating the mixture with boiling benzene, in which the former was insoluble (only anthracene passed into solution). Meisenheimer obtained 9 : 10-dinitro-9 : 10-dihydroanthracene by the action of liquid N_2O_4 on anthracene mixed with chloroform. At the same time N_2O_4 acting on anthracene suspended in benzene or dissolved in nitrobenzene gives no nitro derivatives of anthracene [34]. In the first case only traces of anthraquinone are formed, in the second a large yield of anthraquinone is obtained.

These examples clearly demonstrate the dependence of the nature of the reaction products formed during nitration with N_2O_4 on the nature of the solvent used. 1-Chloroanthracene [35] treated with dry N_2O_4 in carbon tetrachloride medium gives an addition product which on heating with pyridine becomes 1-chloro-9(or 10)-nitroanthracene.

1 : 5-Dichloroanthracene gives 1 : 5-dichloro-9 : 10-dinitro-9 : 10-dihydroanthracene, which is converted to 1 : 5-dichloro-9-nitroanthracene on heating with pyridine.

Wieland [36] nitrated aromatic hydrocarbons, phenols and amines with nitrogen dioxide. Nitration of benzene, carried out at 80°C in sealed tubes, gave only a small yield of nitrobenzene. Using equimolecular quantities of benzene and NO_2 the main reaction products (in addition to oxidation products CO_2, oxalic acid, etc.) were 1 : 3 : 5-trinitrobenzene and picric acid, part of the benzene remaining unchanged. Experiments on the nitration of nitrobenzene showed that the latter did not undergo nitration under conditions similar to those used for the nitration of benzene. Analysing these results, Wieland concludes that nitration of benzene is not a step reaction. He supposes that benzene combines with six particles of NO_2 at once (analogously to the combination of benzene with chlorine and bromine in sunlight) to form hexanitro*cyclo*hexane; the latter decomposes further to give trinitrobenzene and three molecules of nitrous acid:



Nitration of naphthalene in ether solution in the cold gives a small yield of nitro compounds, whilst in the absence of solvent the reaction proceeds energetically to form α-nitronaphthalene.

Phenols react readily with NO_2 giving considerably better yields than those obtained by nitration with nitric acid. To nitrate these compounds WIELAND used solutions of nitrogen dioxide in mixtures of benzene with petroleum ether or gasoline and carried out the reaction with efficient cooling and vigorous stirring. He obtained the following results: phenol gave *p*- and *o*-nitrophenols, the former predominating, the total yield of nitro products with respect to phenol being 125 per cent calculated on the weight of phenol taken. Nitration of *o*-, *p*- and *m*-cresols gives a mixture of isomeric nitro compounds. When NO_2 acts on 1 : 3 : 4-xylenol a 5-nitro derivative is formed with a good yield (m.p. 72°C), whilst its action on α-naphthol gives a mixture of 2-nitronaphthol and 2 : 4-dinitro naphthol.

Nitration of acetanilide with N_2O_4 in ethereal medium in the cold gave WIELAND diazobenzoyl nitrate and acetic acid. It should be remarked that when WITT [37] treated aniline in benzene solution with N_2O_4 he also obtained benzene diazo nitrate with a quantitative yield (compare with the works of TOPCHIEV on the interaction of aniline and acetanilide with N_2O_4 in chloroform).

WIELAND nitrated diphenylamine either in absolute ether solution or a mixture of benzene and petroleum ether in the ratio of 4 : 1. In the former case the main reaction product was diphenylnitrosoamine (crystal line compound, m.p. 66°C), in the latter case—*p*-nitrodiphenylnitrosoamine. To explain the formation of diphenylnitrosoamine WIELAND suggests that N_2O_4 consists not only of molecules with a $O_2N—NO_2$ structure but also molecules with the structure $O{=}N—O—NO_2$ with which diphenylamine reacts according to the equation:

$$(C_6H_5)_2NH + O{=}N{-}O{-}NO_2 \rightarrow (C_6H_5)_2N{-}NO + HONO_2$$

The interaction of di-*p*-tolylhydroxylamine with N_2O_4 in cold ether or benzene solution leads to the formation of *o* : *o*′-dinitro-*p*-tolylamine [38]. In the same communication WIELAND points out that diphenylamine oxide reacts with N_2O_4 to form *p* : *p*′-dinitrodiphenylamine oxide.

The course of the reaction is considerably affected by the relative amount of N_2O_4 used. This was very convincingly demonstrated in the work of BATTEGAY and KERN [39], who investigated the nitration of monomethylaniline and dimethylaniline with N_2O_4. When monomethylaniline reacted with an equimolecular amount of N_2O_4 in benzene solution for 5 days a 55·4 per cent yield of *p*-nitro-N-nitrosomonomethylaniline was obtained (m.p. 100°C). If, however, an excess of N_2O_4 was used under similar conditions the main reaction product was 2 : 4-dinitromonomethylaniline with a yield of 50–60 per cent (m.p. 175°C). Nitration of dimethylaniline with N_2O_4 dissolved in benzene, at reaction temperature not exceeding 10°C (molar ratio of reagents 1 : 1) gave *p*-nitrodimethylaniline and *p*-nitrosodimethylaniline (as the nitrate). BATTEGAY and KERN explain the formation of these products by the following reactions:

$$C_6H_5N(CH_3)_2+N_2O_4 \rightarrow O_2NC_6H_4N(CH_3)_2+HNO_2$$

$$C_6H_5N(CH_3)_2+HNO_2 \rightarrow ONC_6H_4N(CH_3)_2+H_2O$$

$$N_2O_4+H_2O \rightarrow HNO_2+HNO_3$$

$$ONC_6H_4N(CH_3)_2+HNO_3 \rightarrow HON{=}C_6H_4{=}N(CH_3)_2NO_3$$

When the ratio of N_2O_4 to dimethylaniline was increased to 2 : 1 the main product was 2 : 4-dinitrodimethylaniline formed together with a small amount of *p*-nitrodimethylaniline.

SCHAARSCHMIDT and SMOLLA [40] nitrated certain aromatic compounds with liquid N_2O_4 in the cold using the reagents in the ratio of 1 part N_2O_4 to 3 parts hydrocarbon. Under these conditions benzene gave nitrobenzene, picric acid and a small amount of dinitrobenzene; toluene gave nitrotoluene, dinitrocresol, nitrophenol, benzaldehyde, oxalic and benzoic acids. Increasing the duration of reaction increased considerably the relative yield of benzoic acid whilst the yield of nitro derivatives showed some decrease.

Xylene and mesitylene undergo a vigorous exothermic reaction with N_2O_4. Instead of nitro compounds this reaction produces tarry masses which, according to analytical data, contain nitrogen and considerable quantities of oxygen. These results indicate that when N_2O_4 interacts with xylene and mesitylene the predominant reactions are those of oxidation.

SCHAARSCHMIDT, BALZERKEWICZ and GANTE [41] nitrated dimethylaniline with N_2O_4 dissolved in carbon tetrachloride. A solution of N_2O_4 (9·3 g; 0·1 mole) in carbon tetrachloride (20 g) was added gradually to a solution of dimethylaniline (12·3 g; 0·1 mole) in carbon tetrachloride (100 g) with stirring and external cooling with a mixture of ice and salt. When all the N_2O_4 had been added the reaction mixture was left in the cooling mixture for a further 3 hr. On completion of the reaction the mixture was stirred with water and the organic part extracted with ether. After distilling off the solvents and recrystallizing the residue from alcohol *p*-nitro-N-dimethylaniline was obtained as yellow needles, m.p. 162°C, with an 86 per cent yield.

Halogenated aromatic compounds cannot be satisfactorily nitrated in the absence of sulphuric acid, $AlCl_3$ and other catalysts. Fluorobenzene does not react with N_2O_4 in carbon tetrachloride solution even after prolonged (72 hr) contact. Iodobenzene under similar conditions gives a mixture of *o*- and *p*-iodonitrobenzene with a yield of 45 per cent of the theoretical. Chlorobenzene and bromobenzene form the corresponding chloronitro and bromonitro derivatives, but with smaller yields.

An extensive and systematic study of the nitration of organic substances with nitrogen oxides has been conducted by the author of the present book since 1934 (in collaboration with SHORYGIN up to 1939 [42]). This reaction was studied both in the liquid and vapour phases on numerous examples of various organic compounds (aromatic hydrocarbons, phenols, amines, heterocyclic compounds, etc.), taking into account the influence of various factors (irradiation, temperature, ratios of reagents, etc.) on the process of nitration. The experimental data obtained are given below, with a detailed description of the experiments and the methods of investigating the products of the reaction.

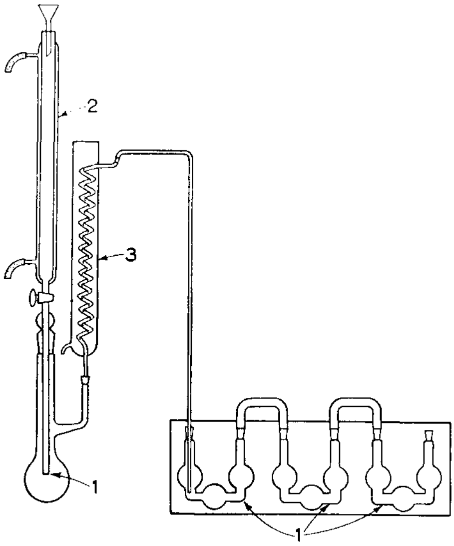


Fig. 1. Scheme for the nitration of hydrocarbons with nitrogen dioxide in the liquid phase.

Nitration in the liquid phase was carried out in the special apparatus shown in Fig. 1, which consisted of the reaction flask (1), connected by ground glass joints with a burette (2) (externally cooled by water) for liquid N_2O_4 and with a condenser (3), filled with a mixture of ice and salt. Condensation of the reaction products took place in the tubes (4), also cooled by a mixture of ice and salt. The substance being nitrated was poured into the reaction flask (either cooled or heated on a metal bath, depending on the conditions of the reaction) and N_2O_4 was then added dropwise.

Nitration of naphthalene—The experiments were conducted at various temperatures and with various ratios of the reagents. Some N_2O_4 was added dropwise from the burette over 30–40 min. At the end of the reaction the contents of the flask and receiving vessels were transferred to a Würtz flask and unreacted N_2O_4 was distilled off at 22–40°C. The residue was poured into a saturated solution of soda, when a dirty-yellow precipitate separated out: the latter was filtered off, washed with water and treated with cold benzene (or carbon disulphide), which dissolved α-mononitronaphthalene. After distilling off the solvent and recrystallization from hot alcohol α-mononitronaphthalene was obtained in long yellow needles, m.p. 57–58·5°C, Polynitronaphthalenes, undissolved in benzene, were extracted with boiling acetone which took up 1 : 8-dinitronaphthalene and 1 : 3 : 8-trinitronaphthalene (1 : 5-dinitronaphthalene being insoluble in acetone).

The acetone extract was treated with hot alcohol after distilling off the acetone; on cooling the alcoholic solution 1 : 8-dinitronaphthalene crystallized out; the latter was purified by a second recrystallization from alcohol (m.p. 172°C). The alcohol-insoluble 1 : 3 : 8-trinitronaphthalene was dissolved in hot chloroform from which, on cooling, a yellow product in the form of rhomboid plates was obtained (m.p. 218°C). 1 : 5-Dinitronaphthalene (see above) was obtained in the pure state after recrystallization from benzene and glacial acetic acid (yellow crystals, m.p. 215°C).

The results of the most characteristic of the experiments on the nitration of naphthalene are given in Table 19.

As can be seen from the data in Table 19 at 18–20° naphthalene gives α-mononitronapthalene with a 90–96 per cent yield (calculated on the naphthalene taken) both with the theoretical and excessive amounts of N_2O_4. At 60°C naphthalene is nitrated by the theoretical amount of N_2O_4 with the formation of α-mononitronaphthalene exclusively (yield 92·6 per cent of the theoretical); if an excess of N_2O_4 is used, however, not only α-mononitronaphthalene (yield 78–90 per cent) but also 1 : 5-dinitronaphthalene is formed (yield 12 per cent).

Table 19. *Nitration of naphthalene* (10 g) *with liquid* N_2O_4

No. of expt.	Temperature (°C)	Amount liquid N_2O_4 (ml)	Yield					
			α-Mononitronaphthalene		1:5-Dinitronaphthalene		1:8-Dinitronaphthalene	
			(g)	(% of theoretical)	(g)	(% of theoretical)	(g)	(% of theoretical)
1	18–20	6	13·0	96	—	—	—	—
2	18–20	12	12·0	90	—	—	—	—
3	18–20	20	12·5	92·6	—	—	—	—
4	60	6	12·5	92·6	—	—	—	—
5	60	12	11·0	80	2·0	12	—	—
6	60	20	10·5	78	2·0	12	—	—
7	150	6	12·0	90	—	—	—	—
8	150	40	4·0	30	6·0	36	3·0	18
9	150	50	4·0	30	6·0	36	3·0	18

At 150°C nitration with the theoretical amount of N_2O_4 gives exclusively α-mononitronaphthalene; if a large excess of N_2O_4 (seven to eight times the theoretical amount) is used polynitronaphthalenes are also found among the reaction products: 1 : 5-dinitronaphthalene (yield 36 per cent), 1 : 8-dinitronaphthalene (yield 18 per cent) and a small amount of 1 : 3 : 8-trinitronaphthalene (yield 2 per cent).

An analysis of the results mentioned above leads to the conclusion that in order to obtain the optimal yield of α-mononitronaphthalene (96 per cent of the theoretical) it is necessary to perform the reaction at

18–20°C using the theoretical amount of N_2O_4. A large excess of the latter and high temperature (above 150°C) favour the formation of polynitro derivatives.

Nitration of diphenyl—Nitration was carried out at room temperature over a period of 1–2 hr, using an excess of N_2O_4. At the end of the experiment, after removal of N_2O_4, the unreacted diphenyl was distilled off with steam. The residue was dissolved in glacial acetic acid, from which *o*- and *p*-nitrodiphenyl were obtained by fractional crystallization: the *p*-isomer separated out on cooling the solution, the *o*-isomer on diluting the mother liquor with water. These products were purified by several recrystallizations from alcohol, giving *p*-nitrodiphenyl, m.p. 113–114°C, and *o*-nitrodiphenyl, m.p. 37°C.

Nitration of anthracene—Anthracene was nitrated in chloroform solution (in the absence of solvent the reaction proceeds very vigorously, with the formation of tar). To anthracene (5 g) in chloroform (100 ml) N_2O_4 (30 ml) was added drop by drop over 45–50 min at a temperature around 0°C (cooling with ice). The nitration gave 9 : 10-dinitroanthracene, which was purified by repeated recrystallization of the crude product from acetic acid and alcohol. The yield was 6 g, i.e. 80 per cent of the theoretical.

Nitration of phenanthrene—Phenanthrene (5 g) in chloroform (100 ml) was treated with liquid N_2O_4 (30 ml) over 45 min at 0°C. Excess N_2O_4 was removed from the reaction mixture by blowing through with dry CO_2. After distilling off chloroform the residue was poured into cold water and the oil which then separated out was dissolved by heating with alcohol. The products of reaction (moninitrophenanthrenes) were separated by fractional crystallization. The alcoholic solution of the oil was cooled and the crystals which precipitated on the walls of the beaker were separated from the oil. The oil was dissolved in alcohol, cooled; a second fraction of crystals separated out. The oily residue remaining after these crystals were separated off was again dissolved in alcohol, and so on. As the result of this treatment 2-mononitrophenanthrene in the form of pale yellow crystals, m.p. 99°C, was obtained (yield 1·7 g, 32 per cent of the theoretical) was obtained, as well as 9-mononitrophenanthrene with a yield of 0·7 g (11 per cent of the theoretical) in the form of orange–yellow crystals, m.p. 116–117°C, 4-mononitrophenanthrene in the form of yellow needles, m.p. 80–82°C (yield 3 per cent) and a small amount of 3-mononitrophenanthrene (m.p. 170–171°C).

It must be noted that the method of fractional crystallization used for the separation of the nitrophenanthrenes led to considerable losses of the original product; when the yield of crude product was 7–7·5 g the total yield of the recrystallized products was 2·6 g (SCHMIDT and HEINLE [43]. who nitrated phenanthrene with a mixture of nitric acid and acetic anhydride obtained the crude nitro product with a yield which was two to two and a half times smaller).

Nitration of phenol—In order to discover the optimal reaction conditions experiments were conducted at various temperatures. Phenol (5 g) was treated with 20–30 ml liquid N_2O_4 for 30 min. At the end of nitration the unreacted N_2O_4 was driven off and the reaction mixture was distilled with steam; on cooling the aqueous distillate yellowish crystals separated out. The residue was treated with ether; the extracted product, after distilling off the ether, was treated with alcohol and the alcoholic solution decolorized by boiling with animal charcoal; on adding water to the alcoholic solution 2 : 4-dinitrophenol was isolated, which gave crystals on sublimation (golden–yellowish needles, m.p. 113–114°C).

The crystals which separated out from the aqueous distillate were identified as 2 : 4-dinitrophenol (they melted, after sublimation, at 113–114°C). Mononitrophenols were not detected in the reaction products.

It must be mentioned that the nitration of phenol with N_2O_4 is an exothermic reaction: in the absence of cooling the temperature rises to 100–105°C.

The results of experiments on nitration of phenol are given in Table 20.

Table 20. *Nitration of phenol with liquid* N_2O_4
(5 g phenol, 25 ml N_2O_4)

No. of expt.	Temperature (°C)	Yield 2:4-Dinitrophenol	
		(g)	(%) of theoretical
1	0	7·5	76
2	58–60	7·0	71
3	98–100	6·0	61
4	150–154	4·0	41

As the data of Table 20 show, the optimal temperature for this reaction is 0°C (the highest yield of 2 : 4-dinitrophenol being 76 per cent).

Nitration of m-*cresol*—Nitration was carried out similarly to nitration of phenol. The aqueous distillate obtained on distilling the reaction product with steam yielded 4 : 6-dinitro-*m*-cresol (m.p. 63–65°C).

The residue remaining after steam-distillation of 4 : 6-dinitrocresol was extracted with ether and then distilled; the 2 : 4 : 6-trinitro-*m*-cresol so obtained was purified from the admixture of tarry substances by repeated recrystallizations from hot ligroin (m.p. 107–109°C). The nitration of *m*-cresol is accompanied by evolution of considerable heat (without cooling the temperature in the reaction flask rises up to 115°C).

Varying the temperature of the reaction gave the following results (Table 21).

The main product of nitration is 2 : 4 : 6-trinitrocresol, the highest yield of which is obtained at reaction temperature of 98–100°C (31–33 per cent); lowering the temperature to 0°C (external cooling) diminishes the yield of trinitrocresol somewhat whilst increasing the yield of the other reaction product—4 : 6-dinitrocresol.

Table 21. *Nitration of* m-*cresol with liquid* N_2O_4
(10 g *m*-cresol, 40–50 ml N_2O_4, duration of reaction 50–55 min)

No. of expt.	Temperature (°C)	Yield 4:6-dinitrocresol (g)	(% of theoretical)	Yield 2:4:6-Trinitrocresol (g)	(% of theoretical)
1	0	1·5–2·0	8 –10	6·0	26·7
2	98–100	1·0–1·5	5·5– 8	7·0–7·4	31·1–33
3	About 115	1·0–1·5	5·5– 8	7·0	31

Nitration of β-naphthol—Nitration was carried out in chloroform solution (1 : 20), since without solvent there was marked tarring of the product. To β-naphthol (5 g) in chloroform (100 ml) liquid N_2O_4 (25–30 ml) was gradually added, the nitration taking 55–60 min. At the end of the nitration excess N_2O_4 was driven off and the reaction mixture treated with soda solution; the aqueous–alkaline layer was separated from the chloroform layer, and acidified with hydrochloric acid; the precipitate which separated out was filtered off, dried and dissolved in alcohol; water was added to the alcoholic solution (decolorized by boiling with animal charcoal) whereupon 1 : 6-dinitro-β-naphthol precipitated out (m.p. 195–196°C). A small amount of 1 : 6-dinitro-β-naphthol was also obtained from the chloroform solution.

Results of the most typical experiments are presented in Table 22.

Table 22. *Nitration of β-naphthol with liquid* N_2O_4
(5 g β-naphthol, 25–30 ml N_2O_4, duration of nitration 55–60 min)

No. of expt.	Temperature (°C)	Yield 1:6-dinitro-β-naphthol (g)	(% of theoretical)
1	0	6·5	81
2	0	5·5	69
3	55–60	5·0	62·5
4	55–60	4·5	56·2

As Table 22 shows the optimal temperature for the nitration of β-naphthol is 0°C (yield of 1 : 6-dinitro-β-naphthol up to 81 per cent of the theoretical). Raising the temperature to 55–60°C appreciably increases the amount of tarry products whilst the yield of 1 : 6-dinitronaphthol correspondingly diminishes.

Nitration of aniline—To aniline (10 g) in chloroform (100 ml) N_2O_4 (30 ml) was added over a period of 40–45 min with external cooling of the reaction mixture with ice and salt. At the end of nitration N_2O_4 was driven off (at 40°C) and chloroform distilled off at 80°C; the residue was steam-distilled. The yellowish crystals which separated out from the aqueous distillate were purified by sublimation, which gave golden–yellowish needles of 2 : 4-dinitrophenol (m.p. 113–114°C). This product was identified by the absence of depression when a mixed melting-point was done with 2 : 4-dinitrophenol. The residue remaining in the flask after steam-distillation of 2 : 4-dinitrophenol was made alkaline and extracted with ether. The ether was distilled off from the ethereal extract and the nitroaniline remaining as residue was recrystallized from alcohol and water (needles, m.p. 145–147°C). Experiments on nitration of aniline under the above-mentioned conditions gave 5 g 2 : 4-dinitrophenol, corresponding to 25 per cent of the theoretical, and about 1 g *p*-nitroaniline, corresponding to 7 per cent of the theoretical. The yield of both products is diminished about twofold if the reaction is performed without cooling.

The results obtained coincide with the data given by RINKES [44]. But it must be mentioned that RINKES did not detect the formation of *p*-nitroaniline during the nitration of aniline with N_2O_4.

VARMA and KRISHAMURTY [45] studied the action of nitrogen oxides (from a mixture of HNO_3 and As_2O_3) on aromatic amines and found that the latter underwent diazotization with subsequent nitration resulting in the formation of nitrophenols. Nitration of aniline hydrochloride in aqueous solution at 0°C gave 2 : 5-dinitrophenol. RINKES, however, showed that when aniline was nitrated with nitrogen dioxide 2 : 4-, and not 2 : 5-dinitrophenol was formed.

Nitration of dimethylaniline—N_2O_4 (30 ml) was added over 45–50 min to dimethylaniline (5 g) in chloroform (50 ml). At the end of the reaction N_2O_4 and chloroform were distilled off, and the residue dissolved in glacial acetic acid; the solution was poured into cold water when a pale-yellow precipitate of *p*-nitrodimethylaniline separated out; after recrystallization from alcohol pure *p*-nitrodimethylaniline was obtained in yellow needles, m.p. 164–166°C. A small amount of the *m*-isomer was also obtained.

Varying the reaction temperature showed that the optimal temperature was 0°C (yield of *p*-nitrodimethylaniline 4·7 g, corresponding to approximately 70 per cent of the theoretical). Raising the temperature to 55–60°C diminished the yield of *p*-nitrodimethylaniline to about 55 per cent.

According to data in the literature [46], when NO_2 acts on dimethylaniline in carbon tetrachloride (molar ratio of dimethylaniline to NO_2 $= 1{\cdot}6$) nuclear substitution predominates, giving *p*-nitrodimethylaniline. The reaction conditions were as follows: to a suspension of 0·05 moles of dimethylaniline in 50 ml carbon tetrachloride a solution of NO_2 in CCl_4 was added dropwise. The initial reaction temperature was 15°C, duration of experiment $2\frac{1}{2}$ hr, final temperature 5°C. The yield of *p*-nitrodimethylaniline is not indicated. *p*-Nitrodimethylaniline on reacting further with excess NO_2 gives 2 : 4-dinitrodimethylaniline and then 2 : 4-dinitro-N-nitrosomonomethylaniline. The yield of the latter is 62 per cent of the theoretical. 2 : 4 : 6-Trinitrodimethylaniline does not react with NO_2.

The interaction of 2 : 4 : 6-trichlorodimethylaniline and NO_2 under similar conditions gives 2 : 4 : 6-trichloro-N-nitrosomonomethylaniline with an 86 per cent yield. N : N-dimethyl-*p*-toluidine reacts with NO_2 to form a product of simultaneous substitution in the ring and the side chain, viz. 4-methyl-2 : 6-dinitro-N-nitrosomonomethylaniline with a 44 per cent yield.

Nitration of acetanilide—A solution of acetanilide (5 g) in chloroform (150 ml) was nitrated with N_2O_4 (30–40 ml) over a period of 35–40 min at 60–70°C. At the end of the reaction excess N_2O_4 and chloroform were distilled off and the residue was steam-distilled. The aqueous distillate was extracted with ether. After removal of ether *o*-nitroacetanilide was obtained; it was recrystallized from hot water and alcohol (m.p. 91–92°C).

The residue in the flask remaining after distillation with steam was extracted with ether; the ether-insoluble product was washed with cold water and sodium bicarbonates olution and then dissolved in hot water: *p*-nitroacetanilide was obtained from the hot aqueous solution and recrystallized from alcohol (m.p. 204–206°C).

An additional amount of *o*-nitroacetanilide was obtained from the ethereal extract (m.p. 92–93°C).

The yields obtained were: *p*-nitroacetanilide 3·5–4 g, corresponding to 53–60 per cent of the theoretical, *o*-nitroacetanilide 2 g (30 per cent of the theoretical).

Experiments on the nitration of amines thus gave the following results: aniline gave a small amount of *p*-nitroaniline, but the main reaction product was 2 : 4-dinitrophenol (presumed mechanism of reaction—diazotization of the amino group with subsequent nitration of the ring) whilst amines with protected amino groups (dimethylaniline and acetanilide) formed only ring-substituted nitro derivatives, i.e. the acyl- and dialkylamino groups remained unchanged.

Nitration of quinoline—Of heterocyclic compounds quinoline was studied with respect to nitration in the liquid phase. The experiments were performed using the ratio, by weight, of quinoline to N_2O_4, 1 : 5 and varying the reaction temperature.

At the end of the reaction the contents of the flask were poured into water (the residue from the condensation tubes remaining after distilling off N_2O_4 was also added to this); the precipitate which then separated out was filtered off from the acid filtrate, which contained mononitroquinoline and quinoline (as salts) in solution, and treated with a 40 per cent KOH solution; dinitroquinoline was extracted from the alkaline liquid with benzene. The benzene solution, dried over solid KOH, was boiled for several hours with animal charcoal to decolorize the initially dark solution; the solvent was then distilled off and the product purified by repeated precipitation with water from alcoholic solution and with ligroin from benzene solution. As the result of this treatment yellowish needles of dinitroquinoline were obtained, m.p. 170–180°C. Evidently this product was a mixture of 5 : 7-dinitroquinoline with other nitro derivatives (according to KAUFMANN and HUSSY [47] pure 5 : 7-dinitroquinoline melts at 180°C). NaOH was added to the acid filtrate and the alkaline solution extracted with a mixture of ether and benzene. After drying the ether–benzene extract over KOH ether was distilled off and then quinoline (under vacuum). The residue—crude 7-mononitroquinoline—was purified by two distillations with steam (m.p. of purified 7-mononitroquinoline 130–131°C); mixed melting point of the latter with 7-mononitroquinoline prepared by the Skraup method from *m*-nitroaniline, glycerol, sulphuric and arsenic acids was 130–131°C.

Results of the experiments on nitration of quinoline with N_2O_4 at different temperatures are given in Table 23.

Table 23. *Nitration of quinoline*
(20 g quinoline, 100 ml N_2O_4)

No. of expt.	Temperture (°C)	Duration of nitration (min)	Yield					
			Mononitroquinoline		Dinitroquinoline		Recovered quinoline	
			(g)	(% of theor. calc. on quinoline)	(g)	(% of theor. calc. on quinoline)	(g)	(% of quinoline taken)
1	14– 16	55	Trace only		—	—	18	90
2	95–100	60	3	11	—	—	15	75
3	100–105	60	3	11	—	—	14	70
4	150–155	65	1	3·7	3·5	10·3	13	65
5	155–160	60	0·5	1·85	3·5	10·3	14	70
6	150–160	55	1	3·7	4	11·8	12	60
7	155–160	90	0·5	1·85	3	9	12	60
8	150	95	1	3·7	2	5·9	12·5	62·5

As these data show the nitration of quinoline with N_2O_4 gives a small yield of nitro derivatives (calculated on the quinoline taken); at reaction temperatures around 100°C only mononitroquinoline is formed (yield 11 per cent); at higher temperatures (150–160°C) the main reaction product is dinitroquinoline (yield 10–12 per cent), whilst the yield of mononitroquinoline is appreciably reduced. In spite of the large excess of N_2O_4 (five times the amount of quinoline) the main bulk of quinoline does not enter into the reaction (at 155–160°C up to 60–70 per cent). At room temperature nitration of quinoline does not take place.

2. NITRATION IN THE VAPOUR PHASE

Nitration of organic compounds with nitrogen dioxide in the vapour phase was carried out in a special apparatus (Fig. 2) fitted with a mercury lamp which made it possible to study the effect of ultraviolet irradiation on the course of this reaction. The apparatus consisted of a quartz mercury vapour lamp (7) (Heraeus–Hanau), surrounded by two jackets (concentric), of which the outer one (5) served as reaction vessel, and the inner one (6) (adjacent to the lamp) as cooler or heater, depending on the temperature conditions of the experiment; air was sucked out of the inner jacket by means of a water pump through the conical flask (16) and heated or cooled liquid (from flask (1) on bath (2) filled with water or vaseline oil) was drawn through the inner jacket; the temperature of this liquid was measured by two thermometers (3) and (15). Vaporization of the hydrocarbon and N_2O_4, which were added dropwise from burettes (10) and (14) took place in the flasks (8) and (12), heated in baths (9) and (13) up to the required temperatures (burette (14) with N_2O_4 was surrounded by a water jacket to prevent evaporation of N_2O_4).

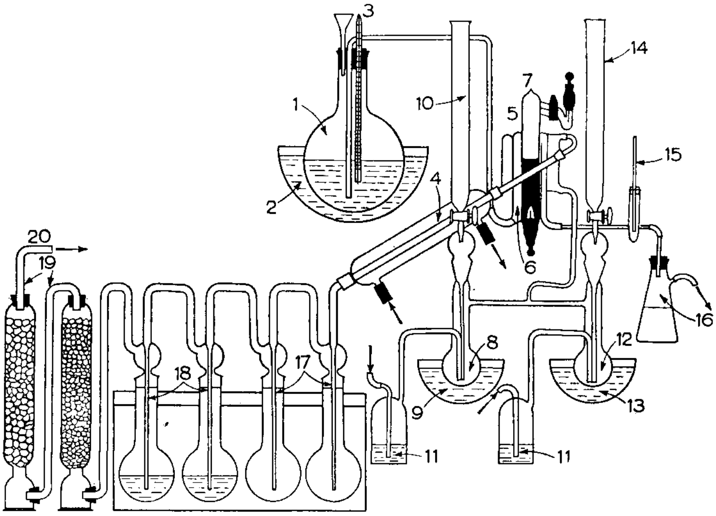


Fig. 2. Scheme for nitration of hydrocarbons with nitrogen dioxide in the vapour phase.

In order to regulate the rate at which the hydrocarbon and N_2O_4 vapours entered the reaction chamber a stream of CO_2 was passed through flasks (8) and (12) after preliminary dehydration in bottles (11) containing sulphuric acid. The vapours of the reaction products were condensed first in the condenser (4), then in externally cooled flasks (17) and absorption flasks (18) with soda solution, the residue was finally adsorbed on activated charcoal in towers (19). The passage of gases and vapours through the condensation–absorption system was facilitated by suction [pump (20) situated at the end of the system]. All the parts of the apparatus were connected by soldered or ground glass joints.

Nitration of benzene—Benzene (40 g), N_2O_4 (180 g) and CO_2 (40–50 l.) were passed through the reaction chamber over 2 hr. At the end of the experiment the unreacted N_2O_4 was distilled off at 25–40°C and the residue was distilled to separate nitrobenzene from unreacted benzene. As in the case of toluene, no dinitro derivatives of benzene were found among the reaction products. Results of the most typical experiments are given in Table 24.

Table 24. *Nitration of benzene with nitrogen dioxide*
(40 g benzene, 180 g N_2O_4)

No. of expt.	Temperature (°C)	Yield of nitrobenzene (g)	(% of theoretical)	Recovered benzene (g)	(% of theoretical)	Remarks
1	10–12	8	12·7	33	82·5	With irradiation
2	25–30	18	28·6	25	62·5	
3	55–60	20	31·7	20	50·0	
4	80–85	8	12·7	22	55·0	
5	10–12	8	12·7	32	80·0	Without irradiation
6	25–30	17	27·0	25	62·5	
7	55–60	20	31·7	22	55·0	
8	80–85	8	12·7	20	50·0	

The data in Table 24 show that ultraviolet irradiation does not improve the yield of nitrobenzene. This indicates that ultraviolet light exerts a positive effect on nitration only in those cases where the symmetry of a molecule is disturbed by the presence of a side chain which makes tautomeric rearrangement possible giving a tautomeric system of conjugated double bonds (as occurs in the case of toluene, see below).

Optimal results (yield of nitrobenzene around 32 per cent of the theoretical) were obtained at 55–60°C.

In another series of experiments on the nitration of benzene the ratio of N_2O_4 to benzene was varied. These experiments showed that when 100 g N_2O_4 was taken to 40 g benzene (molar ratio 2 : 1) the yield of nitrobenzene remained unchanged as compared to the yields of the preceding series of experiments (see Table 24) where this ratio was 4 : 1. When the amount of N_2O_4 was reduced to 50 g (ratio 1 : 1) the yield of nitrobenzene was appreciably diminished (to 6·5 per cent). Therefore excess N_2O_4 is needed for optimal results (2 moles N_2O_4 to 1 mole benzene).

Nitration of toluene—Experiments on the nitration of toluene with nitrogen dioxide were carried out both with and without irradiation by ultraviolet light.

The procedure employed was as follows: toluene (40 g), N_2O_4 (200 g) and CO_2 (40–45 l.) were passed through the reaction chamber over a period of 2 hr. At the end of the experiment the contents of the condensation flasks (17) (Fig. 2) were transferred to a flask connected by ground glass joints to a condenser through which water cooled to 0°C was circulated, and the unreacted N_2O_4 was distilled off at 25–40°C for use in other experiments. The residue was poured into a large amount of water, to which were added the washings from rinsing out all the parts of the apparatus, the contents from absorption flasks (18) and the condensate obtained on superheated steam distillation of products adsorbed in columns

(19) by the activated charcoal. The reaction products separated into two layers on standing—an oily and an aqueous one. The oily layer was separated off, the aqueous layer was treated with ether and the ethereal extract was added to the oily layer. The oil and ethereal extract were washed with soda solution and with water, and after distilling off the solvent the rest was steam-distilled. The oil distilled over completely, indicating the absence of dinitrotoluenes. The oil which separated out in the aqueous distillate was separated from the water and treated with a 20 per cent solution of NaOH. After standing overnight the alkaline solution was separated from the oil which did not dissolve in NaOH and the latter was treated with ether (ethereal solution A). When the alkaline extract was acidified with hydrochloric acid the crystalline aci-form of phenylnitromethane precipitated out; it gradually acquired an oily consistency as the result of transition to the neutral form. The latter was extracted with ether (ethereal solution B). Pure phenylnitromethane (b.p. 140–142°C at 35 mm) was obtained after distilling off the solvent from ethereal solution B.

The NaOH-insoluble oil and ethereal solution A gave a mixture of isomeric mononitrotoluenes, b.p. 217–238°C.

Results of the most typical experiments are presented in Table 25. These data show that when toluene is nitrated with nitrogen dioxide the principal products are mononitrotoluenes together with phenylnitromethane. Optimal results with ultraviolet irradiation were obtained at 14–15°C (yield of mononitrotoluenes 46 per cent, phenylnitromethane 9 per cent). Raising the temperature to 58–60°C left the yield of phenylnitromethane almost unchanged whilst the yield of nitrotoluenes was appreciably reduced (to 17 per cent).

Table 25. Nitration of toluene with nitrogen dioxide
(40 g toluene, 200 g N_2O_4)

No. of expt.	Temperature (°C)	Yield phenylnitromethane		Yield nitrotoluenes		Recovered toluene		Remarks
		(g)	(% of theoretical)	(g)	(% of theoretical)	(g)	(% of toluene taken)	
1	14–15	5	8·5	27	46·2	16	40	With irradiation
2	58–60	5·5	9·4	15	25·5	23	57·5	
3	105–110	3	5	10	17	15	37·5	
4	14–15	4	7	19	32·5	22	55	Without irradiation
5	58–60	5	8·5	11	18·8	27	67·5	
6	105–110	3	5	11	18·8	20	50	
7	140–145	2·5	4·2	10	17	16	40	

Without irradiation the nitration proceeds less effectively. It must be remarked that the relative amounts of phenylnitromethane and nitrotoluenes in the experiments with irradiation remain the same as in the experiments without irradiation despite the increase in the yields.

Valjashko, Blizniukov and Lutskii [48] used the following method for the nitration of toluene with nitrogen dioxide: N_2O_4 (3 moles) interacted with toluene (1 mole) in a sealed glass tube at temperature up to 70°C. The reaction was very energetic even at room temperature. Explosions were observed at temperature of 70°C. The main direction of the reaction was the entry of the NO_2 group into the methyl group, the side direction was its entry into the ring to form mononitrotoluenes. Oxidation products—benzoic and oxalic acids—were formed in the course of the nitration. Catalysts which usually direct the nitro group into the ring proved ineffective under these conditions. The reaction between N_2O_4 and toluene was damped down by filling the tubes with stainless steel shavings, diluting the reaction mixture with CCl_4 and decreasing the amount of N_2O_4 to 1·7–1 mole to 1 mole of toluene. Acceleration of ring nitration was achieved by adding 0·27–0·4 moles of acetic anhydride to 1 mole of toluene, giving 2·5–3 per cent of 2 : 4 : 6-trinitrotoluene and up to 30 per cent of nitrotoluenes. The mononitrotoluenes formed do not undergo further nitration. Nitration of the ring gives only mono- and trinitrotoluenes, without the intermediate formation of dinitrotoluene. Replacement of acetic anhydride by acetic acid does not produce acceleration of the reaction.

Nitration of ethylbenzene—Ethylbenzene (15 g; b.p. 136–138°C), N_2O_4 (70–80 g) and CO_2 (15–20 l.) were passed through the reaction chamber over a period of 50–55 min. At the end of nitration N_2O_4 was driven off from the condensation flasks (17) (Fig. 2) and their contents were mixed with the contents of absorption flasks (18) and with the condensate obtained on distilling the products adsorbed on activated charcoal with super-heated steam. The mixture separated into two layers on standing: an oily layer and an aqueous one. The oily layer was separated off and the ethereal extract from the aqueous layer added to it. After washing with 5 per cent soda solution and then with water ether was distilled off and the oil distilled with steam; methyl phenylnitromethane and mononitroethylbenzene passed into the aqueous distillate. No dinitroethylbenzene was detected in the residual liquid left after the distillation of the above-mentioned nitro compounds.

In order to separate methylphenylnitromethane from mononitroethylbenzene the oil in the aqueous distillate was treated with 20 per cent solution of caustic soda with vigorous shaking for 20 min and allowed to settle out overnight. The alkaline solution was then separated from the oil undissolved in NaOH, washed with ether to extract residual nitroethylbenzene and acidified with hydrochloric acid until acid to Congo indicator; whitish flakes of the aci-form of methylphenylnitromethane separated out from the solution. This form did not change to the neutral form even on long standing.

After 10–12 hr methylphenylnitromethane was extracted with ether; after drying the ethereal extract over calcium chloride the ether was distilled off and the product purified by vacuum distillation. Methylphenylnitromethane so obtained was in the form of colourless crystals melting at 97–99°C*. The ethereal extract obtained by treating with ether the alkaline solution (see above) was added to the alkali-insoluble oil, the ether was distilled off and the residue fractionally distilled. Ethylbenzene distilled over first at 136–138°C followed by the mixture of nitroethylbenzenes over the range 223–246°C.

Results of the most characteristic experiments on the nitration of ethylbenzene are given in Table 26.

Table 26. *Nitration of ethylbenzene with nitrogen dioxide*
(15 g ethylbenzene, 70–80 g N_2O_4)

No. of expt.	Temperature (°C)	Yield methylphenylnitromethane (g)	Yield methylphenylnitromethane (% of theoretical)	Yield nitroethylbenzenes (g)	Yield nitroethylbenzenes (% of theoretical)	Recovered ethylbenzene (g)	Recovered ethylbenzene (% of ethylbenzene taken)	Remarks
1	10–12	4·5	21·4	5	24	7	46·7	With irradiation
2	78–80	8	40	5	24	2·5	16·7	
3	10–12	3	14·3	3	14·3	8	53·3	Without irradiation
4	78–80	6	28·6	4·5	21·4	2	13·4	

It can be seen from the data of this table that nitration of ethylbenzene with nitrogen dioxide leads to the formation of mononitroethylbenzenes together with a product of NO_2 substitution in the side chain—methylphenylnitromethane. At 10–12°C and with ultraviolet irradiation the yield of nitroethylbenzenes exceeds somewhat the yield of methylphenylnitromethane (total yield of nitrocompounds 45 per cent); on raising the temperature to 78–80°C the total yield of nitro compounds reaches 64 per cent, the yield of methylphenylnitromethane almost doubling (up to 40 per cent), the yield of nitroethylbenzene remaining unchanged. The same phenomenon is observed in experiments without irradiation (increase mainly in the yield of side-chain substituted nitro compounds on raising the temperature); these experiments gave generally lower yields of nitro derivatives than those obtained with irradiation.

Nitration of m-*xylene*—Nitration of *m*-xylene with nitrogen dioxide and separation of the reaction products were carried out similarly to nitration of toluene and ethylbenzene.

m-Xylene (20 g; b.p. 139–140°C), N_2O_4 (140–150 g) and CO_2 (20–25 l.) were passed through the reaction chamber over 50–60 min at 12–14°C. Nitration yielded tolylnitromethane (yellowish oil, b.p. 128–132°C at 19 mm), a mixture of mononitroxylenes which distilled at 225–245°C and a small amount of dinitro-*m*-xylenes.

Experiments with ultraviolet irradiation gave 21 g mononitroxylenes

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* These findings do not agree with those of Konovalov [49]: methylphenylnitromethane obtained by him by nitrating ethylbenzene with nitric acid (sp. gr. 1·075) did not solidify even at −15°C and had a b.p. of 135°C at 25 mm.

(73·9 per cent of the theoretical, calculated on *m*-xylene), 7 g tolylnitromethane (24·6 per cent of the theoretical) and a small amount (0·5 g) of dinitro-*m*-xylenes. Experiments without irradiation gave lower yields of mononitro derivatives: 16 g mononitroxylenes, corresponding to 56·3 per cent of the theoretical, and 6 g tolylnitromethane (21 per cent of the theoretical); the yield of dinitro-*m*-xylenes proved to be rather higher than in experiments with irradiation (3·5 per cent of the theoretical).

These results indicate that the nitration of *m*-xylene with nitrogen dioxide in the vapour phase occurs quite satisfactorily at 12–14°C when the principal reaction products are mononitroxylenes. With ultraviolet irradiation an almost quantitative total yield of nitro derivatives of *m*-xylene was obtained; without irradiation it amounted to 81 per cent.

Nitration of pyridine—A study was also made by the present author of the nitration of pyridine with nitrogen dioxide; according to data in the literature pyridine undergoes nitration with difficulty. Thus FRIEDL [50] nitrated pyridine with a mixture of 18 per cent fuming sulphuric acid and potassium nitrate at 330°C at the same time passing a strong stream of air through the reaction mixture. He obtained β-nitropyridine (m.p. 41°C) with a yield of 15 per cent of the theoretical.

SCHAARSCHMIDT, BALZERKEWICZ and GANTE [41] nitrated pyridine with N_2O_4 both without catalyst and in the presence of $AlCl_3$ but did not obtain positive results.

Nitration of pyridine by the present author was carried out as follows: pyridine (20 g; previously dried and distilled over BaO), N_2O_4 (100–150 g; b.p. 22–25°C) and CO_2 (15–20 l.) were passed through the reaction chamber over a period of 1 hr. At the end of nitration all the parts of the apparatus were washed through with pure N_2O_4, the washings were mixed with the contents of the condensation flasks and poured into a flask fitted with a ground-glass thermometer and Liebig condenser cooled by ice water. The unreacted N_2O_4 was distilled off with gentle heating to 25–40°C. The residue in the flask was treated with soda solution and extracted with ether; the solvent was removed from the ethereal solution, and then the unreacted pyridine; the remaining brown mass was dissolved in nitric acid (sp. gr. 1·4). After prolonged standing crystals of the nitric acid salt of β-nitropyridine appeared in this solution. On adding soda to the aqueous solution of the salt the free base was obtained; this was recrystallized from a mixture of benzene and ligroin. β-Nitropyridine so obtained was in the form of colourless needles, m.p. 41–42°C.

Experiments at higher temperatures (200–300°C) were carried out in a hard glass tube (combustion tube) filled with glass beads [51].

Attempts at nitrating pyridine with N_2O_4 in the vapour phase at temperatures above 300°C led to a powerful explosion which destroyed the apparatus. Very powerful explosions also occurred when pyridine was mixed with liquid N_2O_4 at room temperature.

Table 27 gives the results of experiments on the nitration of pyridine with nitrogen dioxide at various temperatures.

The following conclusions can be drawn from the experiments on the nitration of pyridine: (1) ultraviolet irradiation exerts no effect on the yield of nitro compounds which is explained by the symmetrical structure of the pyridine molecule (analogous to benzene and naphthalene); (2) the optimal temperature for nitration is 115–120°C; raising the temperature to 220–230°C does not alter the yield of nitropyridine; (3) the greater part of pyridine does not enter into reaction during nitration (60–65 per cent).

Table 27. *Nitration of pyridine with nitrogen dioxide*
(20 g pyridine, 100–150 g N_2O_4)

No. of expt.	Temperature (°C)	Yield β-nitropyridine (g)	Yield β-nitropyridine (% of theoretical)	Recovered pyridine (g)	Recovered pyridine (% of pyridine taken)	Remarks
1	14– 15	1·0	3·2	13	65	With irradiation
2	58– 60	1·5	4·8	12	60	
3	115–120	2·0	6·4	12	60	
4	14– 15	1·0	3·2	11	55	Without irradiation
5	58– 60	1·5	4·8	13	65	
6	115–120	2·0	6·4	12	60	
7	220–230	2·0	6·4	10	50	

When pyridine is nitrated with nitrogen dioxide the nitric acid salt of pyridine $C_6H_5N \cdot HNO_3$ is also found among the reaction products; its formation can be explained by the action of nitric acid, formed according to the following equation, on pyridine:

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

(pyridine, being hygroscopic, contains water with which N_2O_4 reacts).

The nitric acid salt of pyridine is also formed by the action of N_2O_4 vapour on liquid pyridine at room temperature and by dropwise addition of liquid N_2O_4 to well-cooled (ice–salt mixture) pyridine, separating out in both cases as a red crystalline precipitate; on recrystallizing this precipitate from hot alcohol pyridine nitrate is obtained in the pure state (colourless crystals, m.p. 117–118°C).

3. NITRATION OF AROMATIC COMPOUNDS WITH NITROUS FUMES

In order to investigate the possibility of using nitrogen oxides (nitrous fumes), formed on a large scale in the manufacture of nitric acid from atmospheric nitrogen, for aromatic nitration a series of experiments was staged on an artificial mixture of gases, corresponding in composition to the industrial nitrous fumes (10 per cent N_2O_4, 80 per cent N_2, 5 per cent O_2 and 5 per cent H_2O).

This mixture was prepared as follows: liquid N_2O_4 was introduced from a water-jacketed burette (cooled) into a Würtz flask heated on a water-bath; the N_2O_4 vapours formed passed on to a second flask where they were mixed with a gas mixture admitted from a gasometer and composed of definite proportions, by volume, of N_2, O_2, H_2O; from the mixing flask the gases were led into the reaction chamber into which the vapour of the substance being nitrated was also admitted (from an evaporator).

Nitration of benzene.—Benzene was added dropwise from a water-cooled burette (fitted with a ground-glass joint) to a Würtz flask which was heated to the boiling temperature of benzene and served as evaporator; benzene vapour was led off by a tube to a nitrator-flask, 500 ml in volume, where the vapour met the nitrous fumes admitted from the mixer. The reaction products, together with unreacted benzene and excess N_2O_4, were condensed first in the condenser, then in a system of interconnected receiving vessels (ground-glass joints) cooled by dry ice to -80°C. At the end of the experiment the contents of the receiving flasks were pooled together and excess N_2O_4 was distilled at 25–40°C; the residue was distilled to separate unreacted benzene and nitrobenzene.

Results of the most characteristic experiments on nitration of benzene with nitrous fumes at different temperatures are given in Table 28; in each experiment a mixture of 40 g benzene with nitrous fumes containing 47 g N_2O_4 was passed through the reaction chamber over a period of 2 hr.

Table 28. *Nitration of benzene with nitrous fumes*
(40 g benzene, 47 g N_2O_4)

No. of expt.	Temperature (°C)	Yield nitrobenzene (g)	(% of theoretical)	Recovered benzene (g)	(% of benzene taken)
1	15– 18	5	8	35	87·5
2	55– 60	8	12·9	32	80·0
3	90–100	4·5	7·25	35	87·5

As these data show the optimal results (yield of nitrobenzene calculated on benzene taken about 13 per cent) are obtained at 55–60°C; the greater part of benzene (80 per cent) remains unchanged (yield calculated on benzene which entered the reaction is 65 per cent).

Nitration of naphthalene—Naphthalene (10 g) and nitrous fumes corresponding to 8 g N_2O_4 were passed through a reaction chamber during 2 hr at 18–20°C. As the result of nitration 13 g α-mononitronaphthalene was obtained, corresponding to 96 per cent yield. There were no dinitro compounds among the products of reaction.

Conclusions

The following basic conclusions can be arrived at on analysing the results of experiments on nitration of a number of aromatic and heterocyclic compounds with nitrogen oxides:

(1) Nitration of benzene, naphthalene and phenanthrene gives mainly mononitro derivatives; naphthalene is the easiest to nitrate; the yield of α-mononitronaphthalene at 18–20°C is 96 per cent (without admixture of polynitro derivatives). At temperatures above 60°C polynitro derivatives are also formed. Nitration of phenanthrene at 0°C gives a mixture of mononitrophenanthrenes with a total yield of 48 per cent. Benzene

undergoes nitration less readily than the other two compounds; the yield of nitrobenzene is 32 per cent at reaction temperature of 55–60°C.

(2) As distinct from the hydrocarbons mentioned, anthracene gives 9 : 10-dinitroanthracene as the main reaction product (yield 80 per cent of the theoretical) when subjected to nitration; the optimal temperature for the reaction is 0°C.

(3) Ultraviolet irradiation exerts no effects on nitration of aromatic hydrocarbons with symmetrical molecular structures (benzene, naphthalene and so on).

(4) Nitration of aromatic compounds with a side-chain (aliphatic–aromatic compounds) leads to the simultaneous formation of mononitro derivatives substituted in the side-chain and in the ring, with predominance of the latter. For example, when toluene is irradiated with ultraviolet rays 46 per cent of mononitrotoluenes and 9 per cent phenylnitromethane are obtained (reaction temperature 14–15°C), whilst ethylbenzene gives 40 per cent nitroethylbenzenes and 24 per cent methylphenylnitromethane (at 78–80°C).

(5) Ultraviolet irradiation during nitration of aromatic compounds with asymmetric structure increases the yield of nitro derivatives as compared with experiments without irradiation (for example, *m*-xylene gives a 99 per cent total yield of nitro derivatives when irradiated and an 81 per cent yield without irradiation).

(6) Phenols undergo nitration relatively readily, giving dinitro- and trinitro derivatives. Phenol gives 2 : 4-dinitrophenol with a 76 per cent yield, *m*-cresol—a mixture of 2 : 4 : 6-trinitro- and 4 : 6-dinitro-*m*-cresols with a total yield of 41 per cent, and β-naphthol—1 : 6-dinitro-β-naphthol with an 81 per cent yield. The optimal temperatures are: for phenol 0°C *m*-cresol 98–100°C and β-naphthol 0°C.

(7) Nitration of amines proceeds differently depending on whether the amino group is protected or not. Aniline gives a small yield of *p*-nitro aniline and 2 : 4-dinitrophenol as the predominant product, which indicates that a possible reaction mechanism consists of diazotization of the amino group and subsequent nitration of the ring; amines with protected amino groups are much easier to nitrate; dimethylaniline gives *p*-nitrodimethylaniline with a 72 per cent yield at 0°C, and acetanilide gives a mixture of *p*- and *o*-nitroacetanilide, the yield of the *p*-isomer being 60 per cent and of the *o*-isomer—30 per cent at 60–70°C.

(8) Nitration of heterocyclic compounds occurs with considerably more difficulty than that of aromatic compounds; quinoline gives an 11 per cent yield of mononitroquinoline at 95–100°C; at 155–160°C dinitroquinoline is mainly formed with a 10–12 per cent yield; nitration of pyridine leads to a small yield (6 per cent) of β-nitropyridine (optimal temperature 115–120°C). During nitration of both quinoline and pyridine much of the substance being nitrated (65–70 per cent) does not enter the reaction and can be recovered. It should be mentioned that pyridine is nitrated with nitrogen oxide in the vapour phase even at room temperature, whereas according to FRIEDL's method of nitration with HNO_3 mixed with fuming sulphuric acid the reaction only occurs at 330°C.

(9) Experiments on nitration with a gaseous mixture corresponding in composition to industrial nitrous fumes show that the latter can be used for the nitration of aromatic compounds; thus, for example, naphthalene is nitrated with nitrous fumes at 18–20° analogously to nitration with pure N_2O_4 with a yield of 96 per cent of the theoretical.

4. NITRATION OF ALIPHATIC-AROMATIC AND ALIPHATIC HYDROCARBONS WITH NITROGEN OXIDES

Titov [52] who devoted a number of works to the nitration of organic compounds with nitrogen dioxide, has established that under suitable conditions nitration of aliphatic-aromatic substances can give satisfactory yields of ω-nitro derivatives, the relative yields of nitro and dinitro derivatives depending on the concentration of NO and NO_2 in the reaction mixture and on temperature used during nitration. The influence of the former factor is proved by him experimentally in the following way: the same amounts of nitrogen dioxide (25 ml) and anhydrous $CuSO_4$ (20 g) were mixed with various amounts of toluene and the mixture was allowed to stand at 20°C for 30 days. The results proved to be:

	Amount of toluene (ml)		
	1000	250	50
Yield phenyldinitromethane (g)	23·5	7·3	2·6
Yield phenylnitromethane (g)	5·0	3·9	2·1

These data show that with increased dilution, i.e. with decreased concentration of NO_2 (at low temperatures) the yield of dinitro derivatives, in this case phenyldinitromethane, rises, which coincides with Titov's inferences. Actually, lowering the concentration of NO_2 creates more favourable conditions for the combination of radicals with NO, i.e. for the formation of nitroso compounds which, in Titov's opinion, serve as the source of dinitro compound formation:

$$C_6H_5CH_3 \xrightarrow{NO_2} C_6H_5CH_2\cdot \xrightarrow{NO} C_6H_5CH_2NO \rightarrow$$

$$\rightarrow C_6H_5CH{=}NOH \xrightarrow{+N_2O_4} C_6H_5CH(NO_2)_2$$

The influence of temperature has been established by Titov in experiments in which it was varied from 20 to 95°C.

	Reaction temperature (°C)			
	20	40	70	95
Yield phenyldinitromethane (g)	23·5	18·4	6·8	1·4
Yield phenylnitromethane (g)	5·0	7·2	15·9	13·4

TITOV explains the increase in the yield of phenyldinitromethane on lowering the temperature by increased solubility of nitrogen oxide and decreased dissociation of the dimeric form N_2O_4 to NO_2, the presence of the former being essential for the conversion of the nitroso compound into phenyldinitromethane (see scheme of reaction above).

The yield of phenyldinitromethane can be raised relative to phenylnitromethane by saturating the reaction mixture with nitrogen oxide. For instance, a mixture of nitrogen dioxide (18·4 g) and toluene (2 l.) was preliminarily saturated with nitrogen oxide and then allowed to stand at room temperature for 6 days (experiment no. 2). Compared to the control experiment (no. 1) without nitrogen oxide saturation, the following results were obtained:

	Expt. No. 1	Expt. No. 2
Yield phenylnitromethane (g)	3·7	2·3
Yield phenyldinitromethane (g)	14·8	11·7
Ratio of amounts of dinitro- and mononitro derivatives	4:1	5:1

A description of one of TITOV's experiments on the nitration of toluene with nitrogen dioxide to give phenyldinitromethane with good results is as follows: a mixture of toluene (1500 ml), nitrogen dioxide (10 g) and anhydrous $CuSO_4$ (30 g) was saturated with nitrogen oxide (increase in weight 1 g) with cooling and then allowed to stand for 15 days at a temperature about 25–30°C; during the first 9 days 10 g nitrogen dioxide was added after every 3 days. The following yields of reaction products were obtained:

	(g)	(%)
Phenylnitromethane	4·6	10·3
Phenyldinitromethane	28·1	46·7
Benzoic acid	4·3	10·6

In contrast to ω-dinitro compounds which are formed as the result of interaction with NO, ω-mononitro compounds are formed by the action of the monomeric form of nitrogen dioxide on the side-chain of the aliphatic–aromatic hydrocarbon (liquid N_2O_4 commonly used is an equilibrium mixture of monomeric NO_2 and dimeric N_2O_4 forms of nitrogen dioxide and also contains a small amount of NO).

The most important factor determining the direction of reaction towards the formation of ω-mononitro derivatives is the fairly high temperature (optimal temperature 100°C) which favours a shift of the equilibrium:

$$N_2O_4 \rightleftarrows 2NO_2$$

from left to right giving high concentration of NO_2 in the reaction mixture.

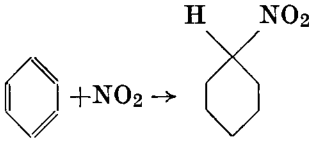
Formation of ω-mononitro compounds is favoured by the introduction of oxygen into the reaction sphere; this converts nitrogen oxide to the dioxide. For example, a mixture of toluene (1750 ml) with anhydrous $CuSO_4$ (20 g) was saturated during 4 hr with nitrogen dioxide with heating on a boiling water-bath. Oxygen was simultaneously passed through the mixture (experiment no. 2). Compared with the control experiment (no. 1) without the addition of oxygen, the following results were obtained:

	Yield as % of theoretical calculated on reacted toluene	
	Expt. no. 1	Expt. no. 2
Phenylnitromethane	51	52·5
Phenyldinitromethane	2·7	2·7
Benzoic acid	7·1	11·2

The yield calculated on bound nitrogen taking into account recovered N_2O_4 was 93 per cent in the experiment with introduction of oxygen (no. 2) and 63 per cent of the theoretical in the experiment without added oxygen (no. 1).

Another factor favouring the formation of ω-mononitro derivatives (in this case phenylnitromethane) is lowering the concentration of the solution (at high temperatures). Other factors being equal (temperature 100°C, amount NO_2 43 g, duration of saturation 2 hr, oxygen consumption 8 l.) the experiment in which 1750 ml toluene was taken gave an absolute yield of phenylnitromethane three times higher than the experiment in which 175 ml toluene was taken.

Nitration of benzene with nitrogen dioxide is also regarded by Titov as a free-radical process. The role of the primary radical in his opinion is played by the radical-like complex—a product of the addition of the electrophilic and radical-like molecule of NO_2 to the benzene ring:



The yield of nitro derivatives increases as the dilution of the same amount of nitrogen oxides (N_2O_4) with benzene increases. Titov isolated the following from the products of reaction: nitrobenzene, *m*- and *p*-dinitrobenzenes, *sym.*-trinitrobenzene, 2 : 4-dinitrophenol, 2 : 4 : 6-trinitrophenol and oxalic acid.

Following the publication of the works of Shorygin and Topchiev on nitration of aromatic compounds with nitrogen dioxide, Urbansky *et al.* [53, 54] studied the nitration of saturated aliphatic hydrocarbons with nitrogen dioxide in the vapour phase. A mixture of N_2O_4 and the hydrocarbon vapours was passed through a glass tube filled with glass rings, which was heated in an electric furnace to a temperature of about 200°C. Volatile reaction products were condensed. Excess N_2O_4 was removed in the cold by a stream of air and the residue, consisting of nitro products and unreacted hydrocarbon, was washed with water. After drying over Na_2SO_4 the mixture was freed from the hydrocarbon by distilling it off. The remaining mixture of nitro products was fractionated under vacuum.

The experimental data showed that the yields of nitro products varied from 30 to 80 per cent depending on the conditions of nitration and the size of reactor. The ratio of mono- and dinitro derivatives was usually 60 : 40.

Nitration of propane gave nitropropane (b.p. 31–34°C) and $\alpha : \alpha'$-dinitropropane (b.p. 42°C) with a total yield of nitro derivatives of 70 per cent of the theoretical; nitration of pentane gave a mixture of 60 per cent mono- and 40 per cent dinitropentane, from which nitropentane (b.p. 164–165°C at 750 mm) and dinitropentane (in the residue) were isolated. Hexane and heptane undergo nitration with the formation of mononitrohexane (b.p. 66–72°C at 14 mm) and mononitroheptane (b.p. 199–200°C at 750 mm) respectively and also of dinitro compounds. Nitration of methane gave a small yield of nitromethane and polynitro compounds up to tetranitromethane inclusive.

It has also been shown that nitration of saturated hydrocarbons under conditions described above gives as main reaction products primary nitro compounds containing the CH_2NO_2 group (these products are identified by forming nitrolic acids and reducing these to aldehydes with zinc and acetic acid). In addition to mononitro products corresponding to the general formula $O_2NCH_2—(CH_2)_n—CH_3$ nitration also gives dinitro derivatives of the general formula $O_2NCH_2—(CH_2)_n—CH_2—NO_2$.

Consideration of the analysis of the liquid and gaseous reaction products leads URBANSKY *et al.* to propose the following scheme for the nitration of aliphatic hydrocarbons:

$$2RCH_3+4NO_2 \rightarrow 2RCH_2NO_2+H_2O+\underbrace{N_2O_3}_{NO_2+NO}$$

Besides the nitro derivatives, aldehydes and fatty acids, formed as the result of the oxidative action of nitrogen oxides, are also found among the reaction products.

Nitration of aliphatic hydrocarbons with nitrogen dioxide entails a risk of explosion according to these authors (explosions did occur during some of the experiments).

HASS and others [55] nitrated propane with nitrogen oxides (N_2O_4) at 790–795°C and obtained approximately equal amounts of nitroethane, 1- and 2-nitropropane. Lower temperatures favour the formation of 2-nitropropane. In addition to the nitroparaffins various oxidation products are also formed, such as aldehydes and acids. A considerable part of the original substance remains unchanged.

TITOV [56] obtained almost exclusively secondary nitropentane when he nitrated *n*-pentane with nitrogen dioxide at 260–270°C; only a trace of primary nitropentane was formed.

According to patent data [57] paraffin hydrocarbons can be nitrated similarly to aromatic hydrocarbons by means of nitrous fumes obtained during the catalytic oxidation of ammonia. The reaction products are oxidized by oxygen or air to form nitroparaffins (it is supposed that the primary stage of the process consists of the formation of nitroso compounds).

SHORYGIN and TOPCHIEV [58] have established that the interaction of *n*-hexane and N_2O_4 diluted with carbon dioxide gives a small yield of 2-nitrohexane. The reaction was carried out at 10–80°C over 1 hr. Under these conditions *cyclo*hexane gives approximately 15 per cent of mononitro*cyclo*hexane.

The same authors [42] demonstrated as far back as 1935 that it was possible to nitrate paraffin hydrocarbons with nitrogen oxides at low temperatures. Lately TOPCHIEV has developed an original method for the nitration of saturated hydrocarbons in the vapour phase by the simultaneous action of chlorine and nitrogen oxides. Using this method for the nitration of methane gave good results, whereas other methods such as nitric acid or nitrogen oxides alone only react with methane at relatively high temperatures and give small yields of nitro derivatives.

The work was carried out on natural Saratov gas, containing 92–93 per cent methane, 2·8 per cent ethane, 1·49 per cent propane, 0·56 per cent butane, etc. To purify the methane from the higher homologues the gas was passed through an activated charcoal column prior to being admitted to the reactor. Experiments on the interaction of chlorine an nitrogen oxides with methane [59] were carried out in the vapour phase over the range of temperature from 25–30°C (room temperature) to about 300°C, with a ratio of methane : nitrogen oxides = 4 : 1 and methane : chlorine = 1 : 3. The liquid reaction products were dissolved in ether, the ether washed with water, then with a 2 per cent solution of sodium bicarbonate and then dried over calcium chloride.

After distilling off the ether on a water-bath the oil was transferred to a flask fitted with a fractionating column and subjected to fractional distillation; the following fractions were isolated: b.p. 100–103°C (45–49°C at 22 mm), 120–124°C, 128–132°C and 133–137°C. The fractions obtained were purified by a second distillation. The experiments showed that at 150–230°C using the ratios chlorine : methane = 1:3 and methane : nitrogen oxides = 4 : 1 nitromethane, nitroform, chloronitromethane and chlorotrinitromethane were formed with a total yield of 77–93 per cent with respect to nitrogen oxides which had entered the reaction. At 230°C chloroform, methyl alcohol and formic acid were formed in addition to the products listed above.

The nitromethane obtained had a melting point of −29°. No interaction of methane and chlorine under these conditions (without N_2O_4) was observed; nor was nitration of methane observed in the absence of chlorine. At 150–230°C and normal pressure the reaction was directed mainly towards oxidation.

On the basis of other work carried out in TOPCHIEV's laboratory [60] it has been established that nitration of *cyclo*hexane with nitrogen dioxide in the vapour phase in the presence of halogens at low temperatures (140–200°C) proceeds much more rapidly than in the absence of halogens. The role of the halogens consists, on the one hand, of catalytic acceleration (at low concentrations of halogen) of the reaction between *cyclo*hexane and NO_2:

$$C_6H_{12}+1{\cdot}5\ NO_2 \xrightarrow{X_2} C_6H_{11}NO_2+0{\cdot}5\ NO+0{\cdot}5\ H_2O$$

and, on the other hand, of active participation in the reaction:

$$C_6H_{12}+NO_2+1{\cdot}5\ X_2 \rightarrow C_6H_{11}NO_2+HX+X_2$$

When large concentrations of halogen are used there is an increase of yield with respect to nitrogen dioxide. Thermodynamic calculations indicate that there is very little probability of free *cyclo*hexyl radical formation as an intermediate product in the reaction of *cyclo*hexane with NO_2. Evidently in the chain reaction being studied the role of active centres must be played not by radicals by by radical-like complexes [61]. The small yield of nitro*cyclo*hexane is explained by the fact that the main reaction is accompanied by side-reactions during which nitro*cyclo*hexane undergoes decomposition (at higher temperatures). The products of decomposition enter into reaction with NO_2 and halogen.

BACHMANN and collaborators [62] studied the effect of chlorine, bromine and iodine on the nitration of propane with nitrogen oxides and with nitric acid.

When propane is nitrated with nitrogen dioxide in the presence of bromine at 325°C, duration of contract 2 min and composition of mixture $C_3H_8 : NO_2 : O_2 : Br_2 = 4{\cdot}2 : 1{\cdot}0 : 0{\cdot}5 : 0{\cdot}031$ the yield of nitro compounds rises from 41·7 to 50·2 per cent. Similar increase in yield occurs when iodine is used ($NO_2 : I_2 = 1 : 0{\cdot}0085$).

The concentration of halogen must not be excessive, since it tends to reduce the yield and conversion. On the other hand, data in the literature [63] concerning activation of photochemical nitration of saturated hydrocarbons recommend that the chlorine content of the mixture be 33–50 per cent.

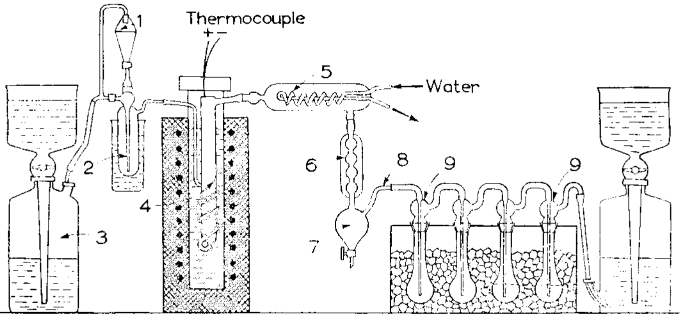


Fig. 3. Scheme for nitration of hydrocarbons with nitrogen dioxide in the vapour phase.

In the laboratory of the author of the present book a study was made of the nitration of n.heptane, *iso*octane (2 : 2 : 4-trimethylpentane) and *iso*pentane with nitrogen dioxide in the vapour phase [64].

The reaction was carried out at 300, 325, 350 and 375°C in the apparatus illustrated in Fig. 3; the reaction mixture was diluted with nitrogen, air and oxygen. A mixture of the hydrocarbon and nitrogen dioxide was placed in the dropping funnel (1), from which it was added dropwise to the evaporator (2). The temperature in the evaporator was maintained electrically at a level somewhat above the boiling point of the hydrocarbon. Nitrogen, air or oxygen was admitted to evaporator (2) from gas-containing vessel (3). The mixture of hydrocarbon vapour, nitrogen dioxide and diluent gas entered reactor (4) immersed in a molten mixture of sodium nitrite and potassium nitrate. From reactor (4) the reaction mixture was rapidly led off into condenser (5), and then into condenser (6) attached to a receiving vessel (7). Liquid reaction products were collected in vessel (7), whilst the gaseous products entered a system of absorption flasks (9) [via tube (8)] cooled by an ice–salt mixture. In the first two flasks liquid products carried over by the gases were collected, whilst in the next two flasks, filled with water, unreacted nitrogen dioxide was absorbed. Gases which did not react with water were collected in a gasometer. Carbon dioxide and nitrogen oxide content of the gases was determined.

The liquid reaction products were separated in a separating funnel into a hydrocarbon layer with reaction products dissolved in it and an aqueous–acid layer. The hydrocarbon layer was washed with water, treated with a 5 per cent sodium bicarbonate solution and again washed with water. The washed reaction products were dried over anhydrous sodium sulphate and then fractionally distilled to remove unreacted hydrocarbons. The remainder of unreacted hydrocarbon was distilled off under vacuum.

Results of experiments on the nitration of heptane and *iso*octane with nitrogen dioxide in the vapour phase are given in Table 29, whilst Table 30 gives the results of experiments using dilution of the reaction mixture.

The nitro products obtained were fractionated under vacuum.

Tables 29 and 30 show that the nature of the diluent (nitrogen, air) and its amount do not influence appreciably the yield of nitro compounds obtained during nitration of paraffin hydrocarbons in the vapour phase. In all cases the yield of nitro compounds depended only on the nature of the hydrocarbon being nitrated.

The conversion of nitrogen dioxide into nitro compounds was not altered significantly by raising the reaction temperature from 300 to 375°C provided the time during which the mixture was in the reactor was reduced as the temperature was raised. In all cases conversion of nitrogen into nitro compounds was about 20 per cent for heptane and *iso*octane and about 18 per cent for *iso*pentane.

The composition of reaction products obtained during nitration of heptane showed no significant changes on raising the temperature from 300 to 375°C, whereas in the case of *iso*octane considerable alteration of the fractional composition accompanie changes in experimental temperature.

Table 29. *Nitration of heptane and* isooctane *with nitrogen dioxide in the vapour phase*

	Heptane				*iso*Octane			
Reaction temperature (°C)	300	325	350	375	300	325	350	375
Duration of contact (sec)	3·7	1·9	1·2	0·7	6·0	5·1	2·8	1·8
Taken:								
Hydrocarbon (g)	170	170	170	170	170	170	170	170
Nitrogen dioxide (g)	40	40	40	40	40	40	40	40
Nitrogen (l.)	13	7·5	10	15	10	15	11	11
Obtained:								
Hydrocarbon (g)	146	148	142	143	146	144	142	146
Aqueous layer (g)	10	8·5	7·5	9·4	12	10	10	10
Gas (l.)	28	24	26	33	23	27	27	32
Nitro compounds (g)	20	21	21	21	22	22	21	18
Conversion with respect to NO_2 (%)	19·8	20·5	20·5	20·5	21·5	21·5	20·8	17·8

Table 30. *Nitration of heptane,* isooctane *and* isopentane *with nitrogen dioxide, with dilution of reaction mixture with nitrogen and air*

	Heptane		*iso*Octane		*iso*Pentane		
Reaction temperature (°C)	325	325	325	325	325	325	325
Duration of contact (sec)	1·9	2·5	5·1	5·9	1·7	2·5	2·4
Taken:							
Hydrocarbon (g)	170	170	170	170	140	140	140
Nitrogen dioxide (g)	40	40	40	40	40	40	40
Nitrogen (l.)	7·5	—	15	—	9	—	—
Air (l.)	—	10	—	16	—	9	—
Obtained:							
Nitro compounds (g)	21	21	22	22	15	16	15
Conversion with respect to NO_2 (%)	20·5	20·5	21·5	21·5	17·2	18·1	17·2

When heptane was nitrated the bulk of the reaction products distilled over within the range of 57–63°C (up to 70 per cent by weight of the total amount of nitro compounds) and consisted of mononitroheptane, chiefly secondary. The mononitroheptane content of the reaction products did not change appreciably on altering the temperature from 300 to 375°C. The nature of these mononitroheptanes also showed no substantial changes with changes in reaction temperature, the main bulk of reaction products being secondary nitroheptanes (chiefly 2-nitroheptane), although some increase in the amount of primary nitroheptane must have occurred, judging by the more pronounced nitrolic acid reaction.

Nitration of isooctane led to the formation of nitro compounds the main bulk of which (55 per cent) distilled over within the range of 60–69°C at 5 mm. Raising the reaction temperature from 325 to 350°C caused a noticeable reduction in the yield of tertiary nitro*iso*octane. Mononitro compounds obtained at 325°C consisted of 25 per cent *tert.*-nitro*iso*octane, whereas the experiment conducted at 350°C led to a *tert.*-nitro*iso*octane content of only 20 per cent. The main bulk of nitro compounds formed during nitration of *iso*octane in the vapour phase consisted of primary nitro*iso*octanes (up to 48 per cent by weight of the total amount of nitro compounds).

Nitration of *iso*pentane resulted in a fairly complex mixture of mononitro compounds. Together with the expected 2-methyl-2-nitrobutane, 2-methyl-3-nitrobutane and 2-methyl-4-nitrobutane quite a considerable amount (up to 16 per cent) of nitro compounds with fewer carbon atoms than in *iso*pentane was formed. These nitro compounds of lower molecular weight gave both the nitrolic acid formation and pseudonitrol formation reactions. It would appear that the lower molecular weight nitro compounds consisted mainly of 2-nitrobutane and 2-methyl-2-nitropropane.

When heptane, *iso*octane and *iso*pentane are nitrated with nitrogen oxides in the vapour phase dinitro derivatives of these hydrocarbons are formed in addition to the mononitro compounds. In the case of heptane about 25 per cent of the total weight of nitro compounds consisted of dinitroderivatives. These exhibited the properties of primary nitro compounds. The yield of dinitro compounds formed during the nitration of *iso*octane was 40 per cent of the total weight of nitro compounds obtained. These also showed the properties of primary nitro compounds. Finally, nitration of *iso*pentane gave a yield of dinitro compounds of 35 per cent of the total weight of nitro compounds.

The results cited show that the yield of dinitro compounds during the nitration of hydrocarbons in the vapour phase depends on the structure of the hydrocarbon being nitrated. The yield of dinitro compounds is considerably higher in the case of hydrocarbons with an *iso*-structure as compared with those of normal structure.

Nitration of *iso*-hydrocarbons proceeds at a markedly lower rate than that of normal hydrocarbons. During nitration in the presence of air the time of contact is approximately one and a half times longer than that required for nitration in the presence of nitrogen.

Only about 20 per cent of nitrogen dioxide is used up during nitration in the vapour phase for the formation of nitro compounds; the remainder acts as an oxidizing agent. By oxidizing the hydrocarbon nitrogen dioxide is mainly reduced to nitric oxide. The amount of nitric oxide in the gaseous reaction products drops sharply when oxygen or air is introduced into the reaction sphere during nitration. Simultaneously with the reduction in the amount of nitric oxide in the reaction products there is a rise in the higher oxides of nitrogen trapped in the absorption system.

Approximately 50 per cent of the hydrocarbon is used in the formation of nitro compounds during nitration in the vapour phase, the remainder being oxidized. Oxidative processes tend to be more profound during nitration in the vapour phase than in the liquid phase. Very few water-insoluble acids are formed in the former case, the main substances found among the oxidation products being the lower carboxylic acids, dicarboxylic acids and water.

In addition to these a small amount of carbonyl compounds is also formed. No detailed study was made of the oxidation products.

When oxygen or air is introduced into the sphere of the reaction rather more oxidation products are formed than during nitration in the presence of nitrogen. Evidently part of the oxygen is used in the oxidation of the hydrocarbon.

Nitration of paraffin hydrocarbons with nitrogen dioxide in the vapour phase in the presence of nitrogen or air proceeds smoothly. On the other hand, when oxygen is introduced into the reaction sphere the process becomes dangerous from the point of view of explosive mixture formation.

A study was made in the same work [64] of the nitration of *n*-heptane and *iso*octane (2 : 2 : 4-trimethylpentane) with nitrogen oxides in the liquid phase. The reaction was performed both at atmospheric and at raised pressure. Apparatus illustrated in Fig. 4 was used for the experiments at atmospheric pressure.

Oxygen from gasometer (1) was introduced into flask (2) containing nitrogen oxides. The mixture of oxygen with nitrogen oxides entered the heating vessel (3). Heated to 250–400°C the mixture then entered reactor (5) by way of capillary (4). The reactor contained the boiling hydrocarbon. Hydrocarbon vapour condensed in condenser (6), the condensate running back into the reactor. Gaseous reaction products were led into the absorption system (7). Nitrogen dioxide was absorbed in the flasks containing water. The remaining gases were collected in a gasometer. Their carbon dioxide and nitric oxide content was determined. The amount of unreacted nitrogen oxides was determined by titrating with alkali the contents of the absorption flasks.

Results of the experiments on the nitration of *n*-heptane and *iso*octane with nitrogen dioxide at atmospheric pressure in the presence of oxygen are given in Table 31.

Nitration of *n*-heptane and *iso*octane at raised pressure was carried out in sealed tubes. Into each tube were placed 4 g nitrogen dioxide and 15 ml hydrocarbon. The sealed tubes were placed into metal containers which are immersed in a boiling water bath. Heating was continued until all the nitrogen dioxide entered the reaction. This occurred in both cases 90 min after the immersion of the sealed tubes in boiling water. At the end of the reaction the tubes were cooled with ice water and opened. The carbon dioxide and nitric oxide content of the gaseous reaction products was determined. Practically all the nitrogen oxides were used up in the nitration of *n*-and *iso*octane. The amount of carbon dioxide reached 10 per cent of the gaseous reaction products (by volume).

Table 31. *Nitration of* n-*heptane and* isooctane *with nitrogen dioxide at atmospheric pressure in the presence of oxygen at* 100°C

	Heptane	*iso*Octane	
Temperature NO_2 (°C)	300	250	400
Duration of experiment (hr)	12	12	12
Taken:			
Hydrocarbon (g)	170	170	170
Nitrogen dioxide (g)	60	40	40
Oxygen (l.)	7·5	5	5
Obtained:			
Hydrocarbon (g)	147	149	145
Aqueous layer (g)	6	6	7
Gas (l.)	4	7	7
Nitro compounds (g)	20	21	23
Nitrogen dioxide (g)	50	30	28
Mononitro compounds (%)	66	27	35
Dinitro compounds (%)	34	73	65
Conversion with respect to NO_2 (%)	12·5	21·5	22·8
Yield calculated on reacted NO_2 (%)	75	86	76

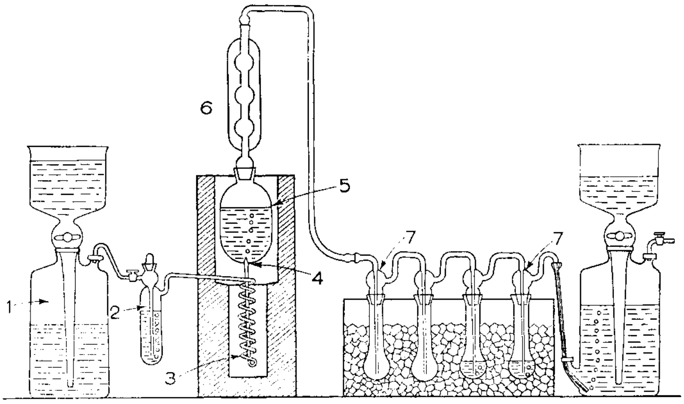


Fig. 4. Scheme for nitration of hydrocarbons with nitrogen dioxide in the liquid phase.

Results of experiments on the nitration of *n*-heptane and *iso*octane with nitrogen dioxide at raised pressure are given in Table 32.

Tables 31 and 32 show that the yield of nitro compounds, calculated on nitrogen oxides taken, is considerably higher when nitration is performed under pressure. This difference in the yields can be explained by the appreciably higher concentration of the reactants during nitration under pressure. The yield of nitro compounds calculated on nitrogen oxides which had entered the reaction, however, is higher on nitration without pressure in the presence of oxygen. This can be explained by the fact that nitric oxide formed in the process of the reaction is oxidized by the oxygen to nitrogen dioxide rather than participating in oxidation of the hydrocarbon.

The liquid reaction products obtained on nitration of *n*-heptane and *iso*octane were transferred to a separating funnel where the aqueous layer was separated from the hydrocarbon layer containing the nitro compounds and part of the oxidation products. The hydrocarbon layer was then washed with water, 5 per cent sodium bicarbonate solution and again with water, and dried over anhydrous sodium sulphate. The unreacted hydrocarbon was fractionally distilled off. The nitro compounds remaining after this were fractionally distilled under vacuum.

Table 32. *Results of experiments on nitration of* n-*heptane and* isooctane *with nitrogen dioxide under pressure at* 100°C

	Heptane	*iso*Octane	
Taken:			
Hydrocarbon (g)	160	189	222
Nitrogen dioxide (g)	64	58	92
Molar ratio hydrocarbon: NO_2	1·15	1·3	0·975
Obtained:			
Hydrocarbon (g)	105	140	140
Aqueous layer (g)	20	18	22
Loss with gas (g)	17	15	10
Nitro compounds (g)	60	57	112
Mononitro compounds (%)	50	50	32
Dinitro compounds (%)	50	50	68
Yields of nitro compounds calculated on nitrogen oxides (%)	37	39	50
Yield of nitro compounds calculated on hydrocarbon (%)	66	70	82

Introduction of oxygen into the sphere of reaction during nitration of *n*-heptane led to a considerable reduction in the yield of dinitro compounds. No such effect was observed in the case of *iso*octane, when the yield of dinitro compounds remained high (about 70 per cent). The yield of nitro compounds, calculated both on nitrogen oxides and on hydrocarbon which had entered the reaction, was sufficiently high and little different from the yield obtained by nitration with nitric acid.

The main bulk of nitro compounds obtained by nitration of *iso*octane with nitrogen dioxide in the liquid phase consisted of dinitro compounds. On fractionating the reaction products under vacuum dinitro compounds remained in the distilling flask and were then distilled with a small fractionating column. Dinitro*iso*octane was a pale yellow, heavy oil, b.p. 117–123°C at 3 mm, d_4^{20} 1·117 and n_D^{20} 1·4744. Nitrogen determination (Dumas) gave values corresponding to dinitro*iso*octane. The dinitro compounds obtained by nitration of *iso*octane had the properties of primary nitro compounds.

Approximately 25 per cent by weight of the total amount of nitro compounds formed on nitration of *iso*octane boiled within the range 63–69°C at 5 mm of mercury. This fraction of nitro compounds was in the form of slightly yellowish oil with d_4^{20} 0·9584 and refractive index n_D^{20} 1·4360. It was insoluble in alkali. Nitrogen estimation (Dumas) gave values corresponding to mononitro*iso*octane. This nitro compound could only be *tert.*-nitro*iso*octane (2 : 2 : 4-trimethyl-4-nitropentane).

About 50 per cent of the nitro compounds formed on nitration of heptane with nitrogen dioxide in the liquid phase boiled over within the range 64–66°C at 6 mm. When *n*-heptane was nitrated at normal pressure in the presence of oxygen approximately 66 per cent of the nitro compounds boiled over within this range. Nitrogen determination, reduction to amine and positive pseudonitrol reaction indicated that this nitro compound was 2-nitroheptane.

A considerable amount of dinitro compounds, boiling at 85–90°C at 5 mm, was formed during nitration of heptane with nitrogen dioxide in the liquid phase. Nitrogen estimations gave results corresponding to those calculated for dinitroheptane.

Dinitro derivatives of heptane dissolved in alkali to the extent of two-thirds; the alkali-insoluble residue could only be a dinitro compound with the nitro groups at one secondary carbon atom. Since nitration of normal hydrocarbons gives mainly nitro derivatives with the nitro group at the second carbon atom it may be assumed that the alkali-insoluble portion of dinitro compounds is 2 : 2-dinitroheptane. The structure of the alkali-soluble dinitro derivatives was not established.

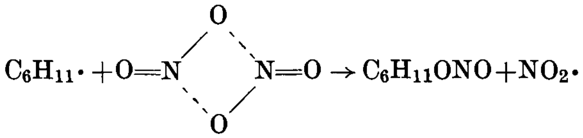
Nitration of *n*-heptane and *iso*octane with nitrogen dioxide in the liquid phase was accompanied by the formation of a considerable amount of oxidation products. Among these, in the case of heptane, were found: carbon dioxide, water, acetic, valeric, caproic and oxalic acids, as well as a certain amount of carbonyl compounds. In the case of *iso*octane the oxidation products included carbon dioxide, water, trimethylacetic, *tert.*-butylacetic and acetic acids, a dicarboxylic acid of undetermined structure and a certain amount of carbonyl compounds.

Titov studied the nitration of *cyclo*hexane with nitrogen oxides [61]. On the basis of his experiments (interaction of *cyclo*hexane with nitrogen dioxide at temperatures from 20 to 330°C in sealed tubes or open vessels, in the liquid or vapour phases) Titov reached the following conclusions:

(1) The initial stages of oxidation and nitration during the interaction of *cyclo*hexane and nitrogen dioxide take place fairly rapidly and give the same products of nitration as those obtained with nitric acid (by the Konovalov–Nametkin method):

$$C_6H_{12}+NO_2 \rightarrow C_6H_{11}\cdot +HNO_2$$

$$\begin{tikzcd}
C_6H_{11}\cdot +NO_2 \arrow[r] \arrow[dr] & C_6H_{11}NO_2 \\
 & C_6H_{11}ONO
\end{tikzcd}$$



$$C_6H_{11}\cdot + O{=}N\overset{O}{\underset{O}{\diamond}}N{=}O \rightarrow C_6H_{11}ONO + NO_2\cdot$$

(2) The absence of appreciable acceleration of the reaction between NO_2 and *cyclo*hexane on the addition of strong protonic or aprotonic acids (H_2SO_4, $TiCl_4$, $AlCl_3$) indicates that the primary stage of the reaction is radical in nature, and shows the unimportant role of the ionic aspect of this stage.

(3) With a high concentration of the nitrogen dioxide dimer it is possible to have fairly long chains of reaction as in the following scheme:

$$RH + NO_2\cdot \rightarrow R\cdot + HNO_2$$

$$R\cdot + N_2O_4 \rightarrow RONO + NO_2\cdot$$

$$NO_2\cdot + RH \rightarrow R\cdot + HNO_2$$

etc.

(4) Nitration and oxidation of *cyclo*hexane proceed according to the scheme proposed earlier for the nitration of paraffins.

According to data in the literature [65] nitration of saturated hydrocarbons with nitrogen tetroxide has been achieved in the liquid phase using a flowing system. The reaction is carried out at temperatures 150–200°C and pressure above 20 atm in stainless steel apparatus. The main part of the apparatus is a reactor, consisting of a steel tube 1 m long and with an internal diameter of 4 mm; the tube is heated by water (under pressure). The following results were obtained.

(1) Nitration of *n*-dodecane: dodecane (1000 g) and N_2O_4 (300 g) were passed through the reactor at 190°C, 40 atm and rate of 204 vols. of reaction mixture per unit volume of reactor per hour. After appropriate treatment of the reaction products 560 g nitrodecane and 12 g fatty acids were obtained.

(2) Nitration of *n*-heptane: C_7H_{16} (1000 g) and N_2O_4 (380 g) interacted at 170°C and 40 atm (volume rate 155) to give 630 g crude nitroheptane and 8 g acids.

(3) Nitration of 2 : 2 : 4 trimethylpentane: C_8H_{18} (1000 g) and N_2O_4 (400 g) reacting at 170°C and 40 atm gave 645 g crude nitro*iso*octane.

(4) Nitration of *cyclo*hexane: C_6H_{12} (1500 g) and N_2O_4 (500 g) reacting at 150°C and 40 atms (time of reaction 30 sec) gave 570 g crude nitro*cyclo*hexane. The products of nitration can in turn be subjected to similar nitration giving di- and polynitro derivatives.

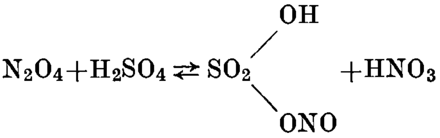
Activation energy values for the process have been obtained from experimental data. These are 5850 cal/mole for *n*-heptane and 7500 cal/mole for *iso*octane.

Hass *et al.* [66] obtained nitro*cyclo*propane by nitrating *cyclo*propane in the following way: excess *cyclo*propane (2396 g) and N_2O_4 (316 g) were passed through a tube at 420–455°C. Duration of contact was 2·36–2·44 sec, 45 g of nitro*cyclo*propane was obtained by treating the condensates collected at 0–80°C (after removal of nitrogen oxides and *cyclo*propane) with water, neutralizing and extracting with ether and finally fractionating. The yield was 15 per cent calculated on N_2O_4.

B. Nitration with Nitrogen Oxides in the presence of Catalysts

It was shown in the previous section that nitrogen dioxide (in its monomeric and dimeric forms) adds on readily to unsaturated aliphatic compounds to give the corresponding nitro products, but reacts rather slowly with aromatic compounds. The reason for such inertness of the latter lies evidently in their relatively greater saturation as compared to unsaturated compounds of the aliphatic series. In order to enhance the reactivity of aromatic substances with respect to the NO_2 group nitration is usually carried out in the presence of catalysts which activate the aromatic ring. For example, the mixture of benzene, toluene, naphthalene or chlorobenzene vapour with nitrous fumes (containing nitrogen oxides) when passed through sulphuric acid (catalyst) at raised temperatures gives nitro derivatives [67].

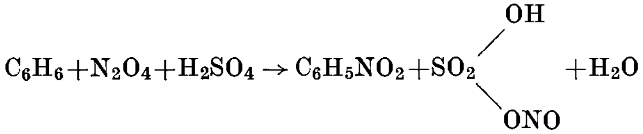
Pinck [68] suggested that sulphuric acid be added during nitration of aromatic compounds with nitrogen oxides; in his opinion it not only acted as a dehydrating agent but also activated the process of nitration by liberating HNO_3:



$$N_2O_4 + H_2SO_4 \rightleftarrows SO_2\left\langle\begin{matrix}OH\\ ONO\end{matrix}\right. + HNO_3$$

When excess sulphuric acid is used the reaction proceeds, practically, from left to right, since nitric acid is being continually removed from the sphere of reaction by interacting with the hydrocarbon to form nitro-compounds. Nitrosyl sulphuric acid and excess sulphuric acid which had not reacted with N_2O_4 act as dehydrating agents.

In Pinck's conception the reaction between aromatic hydrocarbons with N_2O_4 in the presence of sulphuric acid follows the equation (using benzene as an example):



$$C_6H_6 + N_2O_4 + H_2SO_4 \rightarrow C_6H_5NO_2 + SO_2\left\langle\begin{matrix}OH\\ ONO\end{matrix}\right. + H_2O$$

As the equation shows only 50 per cent of nitrogen oxides is used in this process for the conversion of hydrocarbons to nitro compounds, the rest reacts with sulphuric acid forming nitrosyl sulphuric acid.

The practical application of nitrogen dioxide in the presence of sulphuric acid as a method for the nitration of aromatic compounds depends on the extent to which it is possible to regenerate nitrogen dioxide, bound in nitrosyl sulphuric acid.

An American patent [69] suggests anodic oxidation of nitrosyl sulphuric acid using a porous diaphragm to regenerate nitrogen oxides in the process of nitration. Nitric and sulphuric acids are formed as the result of the reaction. The yield calculated on nitric acid is 92 per cent.

Oxidation of nitrosyl sulphuric acid proceeds according to the equation:

$$2ONOSO_3H+O+H_2O \rightarrow H_2SO_4+HNO_3 \qquad (1)$$

Nitrosyl sulphuric acid used is subjected to the action of sulphur dioxide according to the equation:

$$2ONOSO_3H+SO_2+2H_2O \rightarrow 3H_2SO_4+2NO \qquad (2)$$

The liberated nitric oxide is oxidized by air to nitrogen dioxide and used for nitration. The concentration of sulphuric acid is enhanced since water enters the reaction as seen from equation (2).

Pinck nitrated benzene in the following way: to a solution of 1·05 mole N_2O_4 in 1·25–1·75 mole sulphuric acid benzene (1 mole) was added from a dropping funnel with constant stirring, the reaction temperature being maintained over the range 5–15°C; when all the benzene had been added the temperature was raised to 40–60°C. Total duration of nitration was 5 hr.

By varying the temperature from 40 to 60°C, the amount of sulphuric acid from 1·25 to 1·75 mole to 1 mole of benzene and its concentration from 85 to 95 per cent at a constant ratio of N_2O_4 : benzene = 1·05 : 1 Pinck demonstrated that the optimal yield of nitrobenzene (94·4 per cent) was reached at 55–60°C, using a large excess of H_2SO_4 (1·75 mole) its concentration being about 95 per cent.

The main factor responsible for high yields of nitro derivatives obtained by nitration according to Pinck's method is the large excess of sulphuric acid which discourages oxidative side-reactions; under these conditions nitration can be carried out at higher temperatures (up to 60°C) which accelerates the reaction.

Nitrotoluene was synthesized by stirring (for 3½ hr at 50–55°C) the reaction mixture obtained by adding 1 mole toluene to a solution of 1·05 mole N_2O_4 in 1·6 mole 95 per cent sulphuric acid; at the end of the reaction excess toluene was distilled off under vacuum (yield of nitrotoluene 87·5 per cent of the theoretical).

The yield of pure α-nitronaphthalene obtained by adding 1 mole naphthalene to a solution of 1·1 mole N_2O_4 in 1·5 mole sulphuric acid was 88·4 per cent of the theoretical. Pinck also used the method developed by him for the synthesis of dinitro compounds from mononitro derivatives. Thus, for example, by adding slowly 1 mole nitrobenzene to a solution of 1·05 mole N_2O_4 in 2·8 mole fuming sulphuric acid containing 4·28 per cent free SO_3 a 93·4 per cent yield of dinitrobenzene was obtained.

Schaarschmidt, Balzerkewicz and Gante [41] obtained a nitro derivative of anthraquinone by nitrating anthraquinone with nitrogen oxides in the presence of oleum containing 5 per cent SO_3.

Battegay [70] who studied the reaction of nitrating aromatic compounds with N_2O_4 in the presence of sulphuric acid came to the cocnlusion that there was a certain similarity between that reaction and the Friedl–Crafts reaction. In the former case activation of the aromatic ring, in his view, is achieved by combination of H_2SO_4 with the aromatic ring to form an unstable complex analogous to the complex formed with $AlCl_3$ which is thought to be an intermediate product in the Friedl–Crafts reaction. To prove this similarity Battegay chlorinated (and brominated) benzene in the presence of relatively small amounts of 90 per cent sulphuric acid, the reaction proceeding as readily as in the presence of $AlCl_3$ and $FeCl_3$ as activators; even at low temperatures chlorination in the presence of sulphuric acid led to quantitative yields of chloro derivatives (at temperatures below 0° the main reaction product was $C_6H_6Cl_6$). In contrast to Pinck (see above), Battegay added liquid N_2O_4 to the compound being nitrated or saturated the hydrocarbon with NO_2 in the presence of concentrated sulphuric acid. Absorption of nitrogen oxides occurred rapidly and was accompanied by some evolution of heat. The reaction temperature was maintained at 15–20°C by means of external cooling. For the nitration of aromatic compounds with nitrogen oxides Battegay preferably used liquid N_2O_4 added from an ice-cooled vessel to the apparatus containing the mixture of the substance being nitrated and sulphuric acid. During the nitration the mixture was stirred vigorously.

Battegay's experiments led to the conclusion that the optimal concentration of sulphuric acid used depended on the nature of the substance being nitrated: thus for benzene, toluene and xylenes it was 78–80 per cent whereas for the nitration of nitro compounds to give polynitro derivatives the concentration of sulphuric acid required was approximately 100 per cent.

It has also been shown that the final concentration of sulphuric acid should not be below a certain value (e.g. for benzene 61 per cent). Since dilution of sulphuric acid occurs in the course of the reaction when nitrosyl sulphuric acid and water are formed it is necessary to use an amount of sulphuric acid such that its concentration during nitration remains above a certain limiting value, beyond which the absorption of nitrogen oxides is incomplete.

Table 33 gives results of Battegay's experiments on a number of organic compounds.

Whilst nitrating aromatic compounds with N_2O_4 in the presence of sulphuric acid, Battegay noted the colour of the used acids, which was very persistent. The intensity of this coloration depended on the concentration of the acid; for example, the acid remaining after nitration of benzene was orange-red in the presence of 73–74 per cent H_2SO_4 and dark red in the presence of 82 per cent sulphuric acid and higher. If the acid remaining after nitration of benzene with N_2O_4 was washed with benzene to free it from traces of nitrobenzene and then the solvent was distilled off under vacuum, a coloured residue was obtained; this was decolorized by the addition of cold water, with the appearance of benzene and decomposition products of nitrosyl sulphuric acid. Decolorization also occurred on the addition of excess nitric acid with the appearance of nitrobenzene.

Table 33. *Nitration of aromatic compounds with nitrogen dioxide in the presence of* H_2SO_4

Compound undergoing nitration	Taken for reaction: Compound being nitrated (g)	N_2O_4 (g)	H_2SO_4 (g)	Concentration H_2SO_4 (%)	Yield of nitro products calculated on N_2O_4 taken (%)
Benzene	50	50	350	80·2	95
Toluene	50	50	609	77·6	94
o-Xylene	50	44	400	78·8	77
m-Xylene	50	44	600	77·6	89
p-Xylene	50	44	400	78·8	95
Chlorobenzene	150	52	370	84·5	95
Nitrobenzene	61	47	250	100·0	94
Anthraquinone	20	9·5	100	Oleum ($5\%\ SO_3$)	84·5

BATTEGAY submits that the used acids contain a coloured complex consisting of three components: C_6H_6, $HNSO_5$ and H_2SO_4 which requires for its formation a certain concentration of sulphuric acid (for benzene not below 74 per cent). The mechanism of this complex formation consists of sulphuric acid combining with its residual valencies with benzene and enhancing the reactivity of the benzene ring, as the result of which the latter acquires the ability to combine with the nitrosyl sulphuric acid molecule:

$$xH_2SO_4+yC_6H_6 \rightarrow [xH_2SO_4 \ldots\ldots yC_6H_6]$$

$$[xH_2SO_4 \ldots\ldots yC_6H_6]+zHNSO_5 \rightarrow$$

$$\rightarrow [xH_2SO_4 \ldots\ldots yC_6H_6 \ldots\ldots zHNSO_5]$$

Assuming the ability of H_2SO_4 to activate the benzene ring, as demonstrated by the formation of coloured complexes in the used acids and also by the structural analogy between nitrosyl sulphuric acid and N_2O_4,* BATTEGAY postulates the following mechanism for the reaction between N_2O_4 and aromatic compounds: the molecular complexes formed in the first stage and composed of the hydrocarbon being nitrated, N_2O_4 and H_2SO_4 are rapidly converted to dinitro compounds or to nitro nitrites

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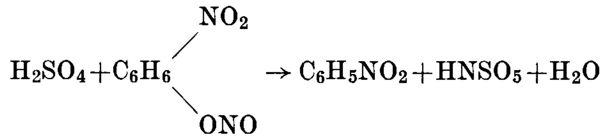
* According to BATTEGAY the nitrating agent during nitration of aromatic compounds with N_2O_4 is the NO_2ONO form of the dioxide ("nitrosyl nitrate").

which, being extremely unstable derivatives of dihydrobenzene, decompose further to form the corresponding nitro compound and nitrosyl sulphuric acid:

$$C_6H_6+N_2O_4+H_2SO_4 \rightarrow C_6H_6 \,....\, N_2O_4 \,...\, H_2SO_4$$



$$H_2SO_4+C_6H_6\begin{matrix} NO_2 \\ ONO \end{matrix} \rightarrow C_6H_5NO_2+HNSO_5+H_2O$$

Titov and Baryshnikova [71] suggest the following scheme for the course of nitration of aromatic compounds with nitrogen dioxide in the presence of sulphuric acid:

$$RH+N_2O_4 \rightarrow RNO_2+HNO_2 \qquad (1)$$

$$N_2O_4+H_2SO_4 \rightleftarrows HNO_3+HNSO_5 \qquad (2)$$

$$2HNSO_5+H_2O \rightleftarrows N_2O_3+2H_2SO_4 \qquad (3)$$

$$2HNO_3+N_2O_3 \rightleftarrows 2N_2O_4+H_2O \qquad (4)$$

$$H_2SO_4\,.\,qH_2O+H_2O \rightleftarrows H_2SO_4\,.\,(q+1)H_2O \qquad (5)$$

Overall scheme:

$$RH+N_2O_4+nH_2SO_4\,.\,mH_2O \rightarrow RNO_2+ONOSO_3H+$$

$$+(n-1)H_2SO_4\,.\,(m+1)H_2O \qquad (6)$$

Nitration occurs at the expense of nitric acid formed during the interaction of nitrogen dioxide and sulphuric acid. The main role in the activation of the reaction is played by the enormous capacity of concentrated sulphuric acid for transferring a proton to the benzene ring and so activating it. Such a reaction mechanism is based on the concept that nitration of aromatic compounds is associated with saturation of the sulphuric acid field of force with elements of nitrous acid and water. To achieve the most complete utilization of N_2O_4 the ratio of free sulphuric acid and water $[(n-1)/(m+1)$ as in equation (6)] towards the end of nitration must not be lower than a certain minimal value characteristic for each compound (experimental findings show this ratio to be approximately 4 : 1 for benzene, 5 : 1 for chlorobenzene and 1·8 : 1 for toluene).

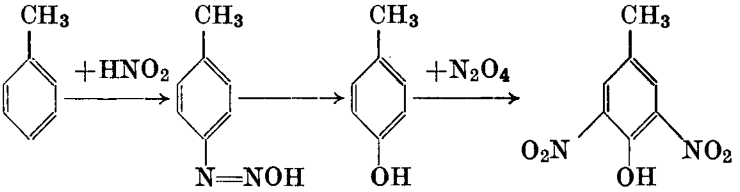
The degree of utilization of sulphuric acid can be increased—as can be seen from equations (2) to (6)—by increasing the concentration of NO_2 or removing N_2O_3 from the sphere of reaction.

Titov and Baryshnikova nitrated aromatic compounds with N_2O_4 in the presence of sulphuric acid by adding a solution of N_2O_4 in sulphuric acid to the hydrocarbon taken in excess to make it possible to maintain automatically the necessary concentration of sulphuric acid without using a large excess of the latter. Nitration of benzene with N_2O_4 was carried out as follows: to hydrocarbon (29·2 g) was added a solution of N_2O_4 (13·8 g) in 94 per cent sulphuric acid (39·2 g) with mechanical stirring and at a temperature of 40°C (approximately); when all the N_2O_4 had been added (over a period of 20 min) heating was continued for a further 1 hr at 50°C, after which the nitrobenzene layer was poured off and fractionated. Optimal results (yield of nitrobenzene 98·4 per cent of the theoretical) are obtained at nitration temperature 40–50°C and concentration of sulphuric acid at the end of nitration 80·6 per cent. When the latter is increased to 89·5 per cent the yield of nitrobenzene decreases owing to enhancement of side reactions.

The rate of nitration of chlorobenzene with a solution of N_2O_4 in sulphuric acid is appreciably less than the rate of nitration of benzene, especially at low temperatures; at 0°C, duration of reaction 5 hr and residual concentration of sulphuric acid 69 per cent the yield of nitrochlorobenzene is 72 per cent (under the same conditions benzene gives a 90 per cent yield of nitrobenzene). Experiments have shown that to increase the rate of nitration of chlorobenzene it is necessary, after the first stage of the reaction with a solution of N_2O_4 in 95 per cent sulphuric acid, to add gradually concentrated sulphuric acid so that towards the end of the nitration the concentration of free H_2SO_4 is not less than 82–84 per cent (total expenditure of sulphuric acid is 2·5 moles to 1 mole nitro product). By this means the yield of nitrochlorobenzene can be raised to 98–99 per cent at reaction temperature 40–50°C.

Nitration of toluene with a solution of N_2O_4 in sulphuric acid takes place very vigorously even at 10°C and low concentrations of sulphuric acid. Good results are obtained when toluene is nitrated with a 36·3 per cent solution of N_2O_4 in 94 per cent sulphuric acid at 0–15°C and residual concentration of sulphuric acid 64·5 per cent; under these conditions the yield of pure nitro product is 98 per cent of the theoretical.

When toluene was nitrated another reaction product besides nitrotoluenes was found and on examination shown to be 2 : 6-dinitrocresol. Titov explains its formation by the following reactions:



To support this mechanism Titov cites data in the literature [72, 73] concerning the formation of diazo derivatives by the action of nitrous acid on aromatic compounds; moreover, it has been established that when large amounts of toluene are nitrated diazo compounds are formed and have even been isolated from the reaction mixture.

Titov [74] has also shown that mononitro derivatives of aromatic compounds can be nitrated with N_2O_4 solution in sulphuric acid to give polynitro compounds. For example, to nitrobenzene (12·3 g) a solution of N_2O_4 (10·1 g) in 45 per cent oleum (25 g) was added, from a dropping funnel with vigorous stirring, over a period of 3 hr at 5–7°C. When all the nitrating mixture had been added the reaction mixture was maintained at the original temperature for 1 hr and then heated, raising the temperature gradually to 100°C over a period of 1 hr. After this the temperature was reduced to 40°C and 100 ml of water added to the reaction mixture. Without cooling the contents of the reaction flask were transferred to a beaker and when dinitrobenzene solidified it was filtered off. Crude dinitrobenzene was purified by treating with water and then with a weak solution of soda at about 80°C. Optimal results (yield of dinitrobenzene 97–98 per cent) were obtained at reaction temperature 5–15°C and ratio of reactants 0·14–0·15 mole H_2SO_4 and 0·11 mole N_2O_4 to 0·1 mole $C_6H_5NO_2$.

Nitration of nitrotoluenes under conditions similar to those described for nitrobenzene gave optimal results (yield of 2 : 4-dinitrotoluene 98 per cent of the theoretical) when oleum calculated on 1 mole sulphuric anhydride to 1 mole N_2O_4 was used. Nitration of 2 : 4-dinitrotoluene gave an 85 per cent yield of 2 : 4 : 6-trinitrotoluene. Experiments on nitration of nitrochlorobenzenes showed that in order to obtain optimal results (yield of dinitro product 98·5 per cent of the theoretical) it was necessary to use an excess of N_2O_4 amounting to about 10 per cent.

Schaarschmidt [75] used metallic chlorides ($AlCl_3$ and $FeCl_3$) as benzene ring activators during nitration of aromatic compounds with N_2O_4. For example, to a mixture of 3 moles hydrocarbon and $\frac{2}{3}$ mole $AlCl_3$ was added liquid N_2O_4 with cooling and energetic stirring, or the mixture was saturated with gas containing NO_2 at ordinary temperature. Following the gradual solution of $AlCl_3$ an intensely coloured red solution of the complex made up of $AlCl_3$, C_6H_6 and N_2O_4 in excess hydrocarbon was obtained. As distinct from unsaturated compounds which form very unstable addition products (see above) the product of interaction of N_2O_4 with aromatic hydrocarbon consists mainly of extremely stable nitronitrite. When this product is heated in benzene solution on a water-bath no perceptible signs of decomposition are observed. On further investigation Schaarschmidt established that the complex consisting of aluminium chloride, hydrocarbon and N_2O_4 was very easily decomposed by water even in the cold giving a small amount of chloro-substituted hydrocarbon (e.g. chlorobenzene). Schaarschmidt explains the formation of the latter as follows: water decomposes a small amount of aluminium chloride which leads to splitting off of HNO_2; the latter further hydrolyses a certain amount if $AlCl_3$ and oxidizes hydrochloric acid, which is a product of partial hydrolysis of $AlCl_3$, to chlorine which chlorinates the hydrocarbon.

Schaarschmidt proved, using benzene as an example, that the complex made up of C_6H_6, $AlCl_3$ and N_2O_4 was saturated: N_2O_4, chlorine and bromine did not react with the complex, Experimental findings have demonstrated that when 1 mole benzene is nitrated with 1 mole N_2O_4 1 mole nitrobenzene is obtained if not less than $\frac{2}{3}$ mole $AlCl_3$ is used. Nitration of chlorobenzene (1 mole) can also give a yield of nitrochlorobenzene approaching the theoretical if the molar ratio of $AlCl_3$ to N_2O_4 is $\frac{2}{3}$: 1. On the basis of these results Schaarschmidt takes the complexes formed during nitration to be $2AlCl_3 . 3C_6H_6 . 3N_2O_4$ in the case of benzene and $2AlCl_3 . 3C_6H_5Cl . 3N_2O_4$ in the case of chlorobenzene.

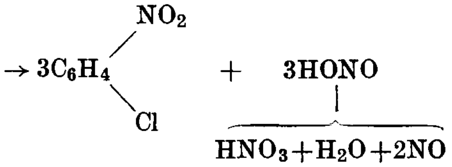
The effect of $AlCl_3$ on nitration with N_2O_4 depends on the nature of the compound being nitrated. Nitration of chlorobenzene takes place at ordinary temperature and can be achieved also at lower temperatures. Nitration of benzene consists of two phases: formation of addition product with N_2O_4 occurs at temperatures below 10°C, whereas decomposition of the complex, i.e. formation of the nitro compound, requires moderate heating above 10°C. $FeCl_3$ acts less energetically but gives more favourable results. During the reaction with toluene nitration is accompanied by oxidative processes as the result of which nitrocresols are formed (as esters of nitric and nitrous acids).

According to Schaarschmidt the reaction mechanism of nitration of aromatic compounds with N_2O_4 in the presence of $AlCl_3$ consists of the following: $AlCl_3$ combines with the aromatic compound activating the benzene ring, which then adds on N_2O_4 to form a triple complex; when the latter is decomposed with water $AlCl_3$ is split off; the remaining addition product of N_2O_4 and benzene, being an extremely unstable derivative of dihydrobenzene, decomposes into the nitro compound which remains dissolved in excess hydrocarbon, and nitrous acid which passes into the aqueous phase; nitrous acid decomposes further according to the equation $3HNO_2{=}HNO_3+H_2O+2NO$.

The process indicated above can be represented by the following scheme (using chlorobenzene as an example):

$$2AlCl_3+3C_6H_5Cl \rightarrow [2AlCl_3 \ldots 3C_6H_5Cl] \xrightarrow{+3N_2O_4}$$

$$\rightarrow 2AlCl_3 . 3C_6H_5Cl . 3N_2O_4 \xrightarrow{H_2O} 2AlCl_3 . H_2O+\underset{\text{(Unstable derivative of dihydrobenzene)}}{3(C_6H_5Cl . N_2O_4)} \rightarrow$$



The nitration of benzene with N_2O_4 in the presence of $AlCl_3$ was performed by Schaarschmidt as follows: to a suspension of sublimed $AlCl_3$ (140 g) in benzene (200 g) was slowly added in a thin stream a solution of N_2O_4 (92 g) in benzene (100 g) at 10–15°C. After adding all the nitrating agent the reaction mixture was heated to 30–35°C and slowly poured onto crushed ice. Nitrobenzene (in benzene solution together with $AlCl_3$) was so obtained. The benzene solution was separated from the aqueous phase, washed with water and then dilute NaOH solution, then distilled to separate nitrobenzene from benzene. The yield of crude nitrobenzene (with an admixture of tarry products) was **118** g.

Halogen substituted derivatives of benzene [76] give the following amounts (%) of *o*- and *p*-isomers on nitration will nitrogen oxides in the presence of catalysts ($AlCl_3$ or $FeCl_3$):

	p-	*o*-
$C_6H_4NO_2F$	91	9
$C_6H_4NO_2Cl$	78	22
$C_6H_4NO_2Br$	95	5
$C_6H_4NO_2I$	95	5

When chlorobenzene is nitrated with nitrogen dioxide in the presence of concentrated sulphuric acid the main reaction product is *p*-nitrochlorobenzene.

TITOV [74] reached the following conclusions concerning the nitration of aromatic compounds with nitrogen dioxide in the presence of $AlCl_3$:

(1) $AlCl_3$ passes into solution in amount three times smaller than that required for the formation of the Schaarschmidt complex.

(2) On further addition of N_2O_4 the reaction proceeds less energetically.

(3) The action of water on the complex considered essential by SCHAARSCHMIDT is not obligatory.

According to TITOV's observations, on heating in the absence of water the reaction proceeds according to the equation:

$$2AlCl_3+3RH+3N_2O_4 \rightarrow 3RNO_2+3NOCl+Al_2Cl_3(OH)_3$$

TITOV postulates a stage mechanism for nitration with nitrogen dioxide in the presence of $AlCl_3$, the first stage, which ends simultaneously with the moment of complete solution of aluminium chloride, corresponding to the most intense coordinate saturation of the aluminium atom field in $AlCl_3$:

$$RH+N_2O_4+2AlCl_3 \rightarrow RNO_2 . AlCl_3+AlCl_2(OH) . NOCl \rightleftarrows$$
$$\rightleftarrows RNO_2 . AlCl_2(OH)+AlCl_3 . NOCl \qquad (1)$$

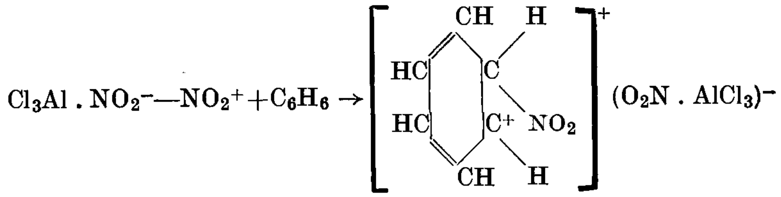
During the subsequent stages this saturation takes place less energetically:

$$RNO_2 . AlCl_3+N_2O_4+RH \rightarrow AlCl_2(OH) . 2RNO_2 . NOCl \qquad (2)$$

$$AlCl_2(OH) . NOCl+N_2O_4+RH \rightarrow AlCl(OH)_2 . RNO_2 . 2NOCl \qquad (3)$$

When heated the complex dissociates into its components. The mechanism of the activating action of aluminium chloride TITOV visualizes as follows. Aluminium, owing to its pronounced incomplete coordination in halogen salts, exerts a profound polarizing effect on molecules capable of deformation and can even cause their ionization:

$$AlCl_3+N_2O_4 \rightarrow Cl_3Al . NO_2^-—NO_2^+$$



In the compound formed hydrogen linked to the same carbon atom as the nitro group is very mobile and is easily split off as an ion, which leads to the formation of nitrobenzene.

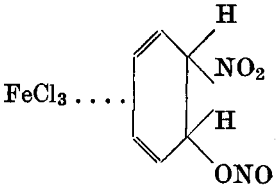
Good results have been obtained on nitration of chlorobenzene, benzene and toluene with N_2O_4 in the presence of $AlCl_3$.

A mixture of chlorobenzene (55 g; 0·35 mole) and $AlCl_3$ (10·7 g; 0·08 mole) was saturated with nitrogen dioxide with constant shaking; this was accompanied by a vigorous exothermic reaction. When all the $AlCl_3$ had dissolved the reaction proceeded more gently. Saturation with nitrogen oxides was continued until 10·5 g N_2O_4 (0·114 mole) had been absorbed, corresponding to 95 per cent of the theoretical amount. The reaction mixture, which had acquired a jelly-like consistency, was gradually heated to boiling with simultaneous passing of CO_2 through it. After boiling the liquid phase was separated from the precipitate of basic aluminium salts and fractionally distilled giving 17·2 g of a mixture of nitrochlorobenzenes, corresponding to a yield of 96 per cent of the theoretical. Similar results were obtained on nitration of benzene.

Nitration of toluene, which in SCHAARSCHMIDT's experiments was unsatisfactory and accompanied by the formation of oxidation products, was achieved by TITOV with a yield of 88 per cent of the theoretical of nitrotoluenes by altering the order of mixing the components: $AlCl_3$ was added to a mixture of N_2O_4 and toluene which diminished the likelihood of side reactions with nitrous acid.

BOGDANOV [77] studied the nitration of aromatic compounds with N_2O_4 in the presence of $FeCl_3$ and concluded that simultaneous passage of chlorine activated the reaction. In his opinion, chlorine acting on the triple complex made up of $FeCl_3$, C_6H_6 and N_2O_4 deprives ferric chloride of its additional valencies and converts it to a compound with a higher chlorine content. Owing to this the triple complex undergoes decomposition with the formation of the unstable derivative of dihydrobenzene $C_6H_6 \cdot N_2O_4$ which decomposes further to give nitrobenzene and nitrous acid. The product formed from $FeCl_3$, with higher chlorine content, is also unstable and decomposes into chlorine and ferric chloride which again enters into reaction with benzene and N_2O_4.

In BOGDANOV's view when benzene is nitrated in the presence of $FeCl_3$ a complex is formed at the beginning of the reaction



which later decomposes into ferric chloride, nitrobenzene and nitrous acid.

Simultaneous nitration and chlorination of 53·32 g benzene for 5 hr at 20°C in the presence of 5·6 g iron gave BOGDANOV a 35·6 per cent yield of nitrobenzene (calculated on benzene taken).

The next development in the work on nitration of organic compounds with nitrogen dioxide in the presence of catalysts was the work of TOPCHIEV who used boron trifluoride as catalyst.

The pure N_2O_4 needed for the experiments was prepared by interaction of nitrosyl sulphuric acid and potassium nitrate. Crystalline nitrosyl sulphuric acid, which was synthesized by saturating a solution of concentrated nitric acid in dichloroethane at 25–30°C with SO_2, was mixed with powdered potassium nitrate in a porcelain dish and the mixture quickly transferred to a wide-necked round-bottomed flask connected to a condensation–absorption system composed of a Liebig condenser and two wide U-shaped tubes immersed in a cooling mixture. The flask was heated on a water-bath to 50–60°C when N_2O_4 was formed according to the equation:

$$NO_2SO_3H+KNO_3 \rightarrow N_2O_4+KHSO_4$$

The reaction proceeded smoothly and sufficiently quickly being usually complete after 1½-2 hr. With excess nitrate (2 moles to 1 mole nitrosyl sulphuric acid) the yield of N_2O_4 reached 85 per cent.

Nitration of benzene with N_2O_4 in the presence of BF_3 was achieved by adding N_2O_4 dropwise from a burette to a reaction flask containing benzene through which BF_3 was passed at the same time.*

Nitration was carried out without external heating; because of the exothermic nature of the reaction the temperature was raised to 55 66°C at the beginning of nitration and then maintained within these limits during 1½–2 hr.

After 10–15 min from the beginning of the experiment the reaction mixture turned a dark yellow colour which became dark brown in a little while and a precipitate separated out on the walls of the flask.

At the end of the experiment unreacted N_2O_4 and benzene were distilled off on a water-bath. The residue was steam-distilled and the nitrobenzene was extracted from the distillate with ether from which it was isolated by fractional distillation (after removal of solvent).

Nitrobenzene (22 g) was obtained with a ratio of reactants of 0·5 mole N_2O_4 to 1 mole benzene; this yield corresponds to 18 per cent of the theoretical calculated on benzene taken for the reaction.

MCKEE and WILHELM [78] used silica gel as catalyst for the nitration of aromatic compounds with nitrogen dioxide. Benzene was nitrated as follows: nitrogen oxides obtaned by the interaction of As_2O_3 with HNO_3 were passed through a rheometer and led from the latter to an evaporator in which benzene was vaporized after entering it at a definite rate. The mixture of benzene vapour and nitrogen dioxide formed in the evaporator was led into the reaction chamber (a glass tube coated with the catalyst, 110 cm long) which was heated in a long electric muffle. The liquid reaction products and unreacted benzene were collected in a receiving vessel connected to a reflux condenser and cooled with ice, whilst nitrogen oxides formed during the reaction together with excess nitrogen dioxide

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* The method of preparation for boron trifluoride is described in Chapter VI.

went through the absorption system containing water, then through solutions containing oxidizing agents where NO was oxidized to NO_2, which was then taken up by a 10 per cent NaOH solution.

Experiments in which the volume rate, the ratio of reactants and reaction temperature were varied showed that the conversion of benzene to nitrobenzene increased with a rise of temperature (but not above 310°C) a decrease in volume rate and increased ratio of NO_2 to benzene. If the temperature was raised beyond 310°C the conversion decreased as the result of enhanced oxidizing side-reactions which became particularly marked at 380°C. Reduced yields at temperatures above 310°C are also explained by diminished activity of the catalyst.

It has been found that at 310°C and rate of admission of benzene 0·5 ml/min conversion to nitrobenzene amounts to 30·1 per cent (calculated on benzene taken) when during 1 hr 31·1 g NO_2 and 26·4 g C_6H_6 (molar ratio nitrogen dioxide to benzene 2 : 1) are passed through the reaction chamber. If the molar ratio $NO_2 : C_6H_6$ is increased to 7 : 1 (54·5 g NO_2 to 13·2 g benzene) conversion at the same temperature reaches 83·6 per cent.

It is interesting to note that the action of nitrogen oxides on benzene gives not only nitrobenzene but also nitrophenol which at temperatures above 330°C constitutes the main reaction product. Taking the results of analysis of the liquid and gaseous reaction products obtained during the nitration of benzene with nitrogen oxides as a basis, McKee and Wilhelm suppose that this reaction proceeds according to the following equation:

$$2C_6H_6+3NO_2 \rightarrow 2C_6H_5NO_2+NO+H_2O$$

These workers consider that the action of silica gel is explained partly by its dehydrating properties (as is well known silica gel is used successfully as catalyst in syntheses of esters, alkylation of ammonia and aniline in the vapour phase by alcohols and in other reactions in which, as in the case under discussion, there is liberation of water). There is no doubt, however, that silica gel also has specific properties with respect to nitration of aromatic compounds with NO_2 since other dehydrating catalysts, such as magnesium oxide, do not exert any catalytic effect on this reaction.

Experiments on the nitration of toluene gave less favourable results than in the case of benzene. McKee and Wilhelm obtained only a 6·8 per cent yield of the theoretical of nitrotoluene by passing 31 g NO_2 and 31 g toluene (molar ratio 2 : 1) through the catalytic chamber at 275°C during 1 hr.

Levy [79] developed a method for the nitration of paraffins with dry NO_2 in the presence of catalyst containing arsenic or antimony compounds. For example, a mixture of 30 per cent *iso*butane and 70 per cent butane was passed at the rate of 5 l/hr through a mixing chamber into which NO_2 was admitted at the rate of 10 l/hr. The mixture of reactants passed through a drying column with P_2O_5 to a converter containing the catalyst which consisted of sodium arsenite mixed with glass. Nitration was carried out at 200°C and duration of contact 120 sec. After removal of excess

NO_2 a product was isolated which consisted of a mixture of trimethylnitromethane $(CH_3)_3CNO_2$ (60 per cent), 2-nitrobutane (20 per cent) and 2 : 3-dinitrobutane (20 per cent).

The total yield of nitro compounds was 45 per cent of butane passed through or 90 per cent of butane which had entered the reaction. LEVY used the same method for the nitration of normal butane (free of *iso*butane) and propane.

FRÖLICH [80] obtained formaldehyde by passing methane and nitrogen oxide (N_2O_4) through a pyrex tube at 440–680°C in the presence of various catalysts (platinum, vanadium pentoxide, pumice and nickel) with a 25 per cent yield, calculated on utilized methane. Methanol was not detected among the reaction products.

According to an American patent [81] a mixture of equal volumes of propane and N_2O_4 was passed at 270°C during 80 sec (time of contact) through a catalyst consisting of Al with 1·7 per cent Cu and 1·3 per cent Fe. Nitroparaffins and oxidation products were thus obtained.

Another American patent [82] shows that when aromatic hydrocarbons are nitrated with nitrogen oxides at 130–430°C in the presence of such catalysts as metallic metaphosphate, phosphoric acid, boron fluoride mononitro derivatives of the aromatic hydrocarbons are formed.

It should be noted that unlike nitrogen dioxide neither nitrous nor nitric oxide reacts with aromatic hydrocarbons.

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82. *Amer. Pat.* 222994 (1947); *Chem. Abstr.* 1605 (1948).

CHAPTER VI

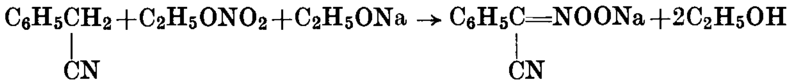
NITRATION OF ORGANIC COMPOUNDS WITH ORGANIC AND INORGANIC NITRATES AND NITROXYL CHLORIDE

1. NITRATION WITH ORGANIC NITRATES

THERE is relatively little reference in the literature to the use of organic nitrates as nitrating agents. The majority of works devoted to the use of organic nitrates for nitration deal with ethyl nitrate, benzoyl nitrate and acetyl nitrate.

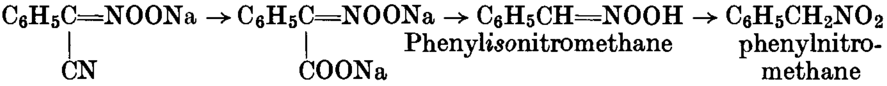
Ethyl nitrate $C_2H_5ONO_2$ is a liquid sp. gr. 1·105 (at 20°C) soluble in water, alcohol and ether. Its boiling point is 87·5°C. It is obtained from nitric acid and ethyl alcohol in the presence of urea nitrate. On superheating ethyl nitrate decomposes explosively.

Like many esters of organic acids ethyl nitrate condenses with compounds containing an active methylene group in the presence of sodium or sodium ethoxide. This leads to the formation of the sodium salt of the *iso*nitro compound. For example [1]:



$$\underset{\displaystyle CN}{C_6H_5CH_2} + C_2H_5ONO_2 + C_2H_5ONa \rightarrow \underset{\displaystyle CN}{C_6H_5C}{=}NOONa + 2C_2H_5OH$$

Benzyl cyanide

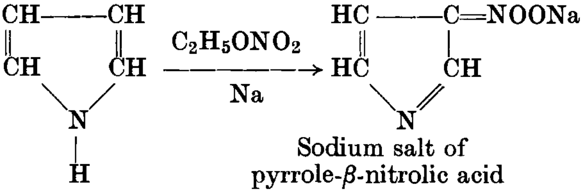


$$\underset{\displaystyle CN}{C_6H_5C}{=}NOONa \rightarrow \underset{\displaystyle COONa}{C_6H_5C}{=}NOONa \rightarrow C_6H_5CH{=}NOOH \rightarrow C_6H_5CH_2NO_2$$

Phenyl*iso*nitromethane phenylnitromethane

THIELE [2] obtained nitro*cyclo*pentadiene by the action of ethyl nitrate on *cyclo*pentadiene. Sodium (2·3 g) was dissolved in absolute alcohol (25 g) and to this solution ethyl nitrate (1·1 g) was added. When cooled to room temperature *cyclo*pentadiene (6·6 g) was added to the mixture and the transparent brown liquid formed was allowed to stand for several hours. The sodium salt which separated out in the form of small reddish-brown plates was filtered with suction and washed with ether. Free nitro*cyclo*pentadiene is liberated by acidifying the not too dilute solution of the salt; it is obtained as almost colourless, quickly solidifying droplets of oil. The substance decomposes readily.

Pyrrole and its derivatives [3] as well as indole give salts of the corresponding nitrolic acids when nitrated with ethyl nitrate:



Sodium salt of pyrrole-β-nitrolic acid

Pyrrole

When benzothiazole is treated with ethyl nitrate in concentrated sulphuric acid at 0–5°C, 6-nitrobenzothiazole is obtained in the form of yellow needles, m.p. 173–174°C. 2-Aminobenzothiazole gives 2-amino-6-nitrobenzothiazole when treated with ethyl nitrate in concentrated sulphuric acid [4].

Mononitrotoluenes can be prepared by nitration with ethyl nitrate [5] using the following method: 98 per cent sulphuric acid is gradually added to a stirred mixture of toluene and ethyl nitrate at 40°C. The reaction temperature is maintained at a level not above 60°C; more ethyl nitrate is then added and the mixture stirred for 10 min. After cooling the mixture is diluted with water, the aqueous layer is separated off, the upper layer is washed with water, dissolved in sodium carbonate solution and distilled. Mononitrotoluenes are obtained with a yield 94·5 per cent of the theoretical. *p*-Nitrotoluene can be isolated on fractional distillation. Ethyl nitrate reacts vigorously with benzene in the presence of aluminium chloride to give nitrobenzene (for further details see Chapter I).

Benzoyl nitrate is a mixed anhydride of benzoic and nitric acids. Benzoyl nitrate is prepared by the method of FRANCIS which consists of the action of benzoyl chloride on silver nitrate at 15°C.

$$C_6H_5COCl + AgONO_2 \rightarrow AgCl + C_6H_5COONO_2$$

Benzoyl nitrate so obtained always contains an admixture of 15–20 per cent of benzaldehyde and is an oily liquid sp. gr. 1·3 (at 0°C). Water readily decomposes it into benzoic and nitric acids:

$$C_6H_5COONO_2 + H_2O \rightarrow C_6H_5COOH + HNO_3$$

Like other mixed anhydrides benzoyl nitrate decomposes into the appropriate simple anhydrides when it is subjected to distillation:

$$2C_6H_5COONO_2 \rightarrow (C_6H_5CO)_2O + N_2O_5 \rightarrow (C_6H_5CO)_2O + N_2O_4 + O$$

The studies made by FRANCIS [6] showed that nitration with benzoyl nitrate gave good results when it was added, with cooling, to an excess of the substance being nitrated. In those cases in which the nitration proceeds too energetically the compound undergoing nitration is dissolved in carbon tetrachloride. Sometimes benzoyl nitrate is also dissolved in this solvent, since it is then possible to maintain the reaction mixture at a sufficiently high temperature and so obtain optimal yields of nitro compounds. For example, thiophene gives a theoretical yield of the corresponding mononitro derivative when nitration is carried out in CCl_4 solution.

The nitrating ability of benzoyl nitrate is demonstrated by its behaviour with respect to alcohols and aromatic amines. Thus, benzoyl nitrate converts ethyl alcohol readily into ethyl nitrate, whilst with secondary aromatic amines it gives excellent yields of the corresponding nitroamines. Benzoyl nitrate reacts vigorously with aromatic hydrocarbons. Benzene, toluene and particularly easily *m*-xylene give the appropriate mononitro derivatives. When toluene, xylene and mesitylene are nitrated the nitro group enters the ring and not the side chain. Nitration of mesitylene in carbon tetrachloride solution even at low temperatures gives a theoretical yield of mononitromesitylene when benzoyl nitrate is used. On the other hand, bromobenzene and benzoyl chloride react with benzoyl nitrate only with difficulty and give merely traces of the corresponding *p*-nitro derivatives.

When benzoyl nitrate acts on phenol a mixture of *o*- and *p*-nitrophenols is obtained, the *o*-isomer predominating, The nitration proceeds even more easily when phenol ethers are treated with benzoyl nitrate, anisole and phenetole; these give the corresponding *o*-nitro derivatives with yields approaching the theoretical. It should be noted that when phenol and its ethers are nitrated with other commonly used nitrating agents the predominating products are the *p*-nitro derivatives.

Unlike phenol, α- and β-naphthols only give small yields of 2 : 4-dinitro-α-naphthol (m.p. 138–139°C) and 1 : 6-dinitro-β-naphthol (m.p. 195°C) when treated with benzoyl nitrate. However α- and β-naphthol ethers are easily nitrated with benzoyl nitrate in carbon tetrachloride solution; when benzoyl nitrate acts on the ethyl ether of α-naphthol the 4-nitro derivative of this ether is obtained; the methyl and ethyl ethers of β-naphthol are nitrated in position 1, i.e. give the corresponding ethers of 1-nitro-2-naphthol. With respect to the majority of aromatic aldehydes (benzaldehyde, anisaldehyde, salicylaldehyde, etc.) benzoyl nitrate acts chiefly as an oxidizing agent; nitro compounds are formed in these reactions in negligible quantities. But treatment of β-naphthaldehyde with benzoyl nitrate gives a quantitative conversion to the corresponding nitro derivative (m.p. 194–195°C); vanillin also gives a quantitative yield of 3-nitrovanillin (m.p. 178°C). Coumarin gives 5-nitrocoumarin when nitrated with benzoyl nitrate; m.p. 185°C.

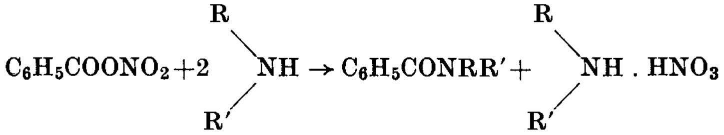
The experimental data obtained by FRANCIS thus showed that benzoyl nitrate possessed the following distinctive features as a nitrating agent: (1) the reaction takes place in complete absence of water, which is particularly important in nitration of thiophene; (2) in some cases nitration with benzoyl nitrate results in the exclusive formation of *o*-nitro derivatives or in their predominance as distinct from the usually employed methods of nitration—anisole, phenetole and phenol are instances of such effect.

BUTTLER [7] studied the action of benzoyl nitrate on amines. It reacts with primary amines to give benzoyl derivatives:

$$C_6H_5COONO_2+2RNH_2 \rightarrow C_6H_5CONHR+RNH_2 \,.\, HNO_3$$

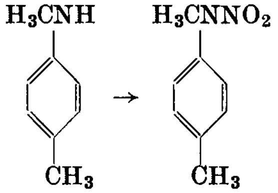
m-Chloroaniline treated with benzoyl nitrate gives *m*-chloroanilide of benzoic acid (m.p. 120°C); similarly *p*-chloroaniline gives *p*-chloroanilide of benzoic acid (m.p. 190°C). When *p*-anisidine, *o*-toluidine and xylidines are treated with benzoyl nitrate the corresponding anisidide, toluidide and xylidides of benzoic acid are formed.

Secondary amines react with benzoyl nitrate to give benzoyl derivatives:

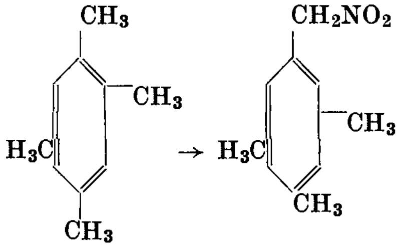


$$C_6H_5COONO_2 + 2\,\overset{R}{\underset{R'}{>}}NH \rightarrow C_6H_5CONRR' + \overset{R}{\underset{R'}{>}}NH \cdot HNO_3$$

In some cases, however, benzoyl nitrate reacts with secondary amines to give the corresponding nitroamines. Thus, for example, N-methyl-*p*-toluidine gives N-methyl-*p*-tolylnitroamine (m.p. 74·5°C) with a theoretical yield:



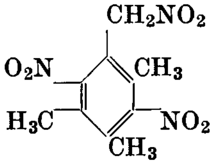
WILSTÄTTER [8], using Francis' method, obtained ω-mononitrodurene from durene. When durene is nitrated in chloroform solution with 100 per cent nitric acid in the presence of sulphuric acid, only the dinitro derivative is obtained. WILSTÄTTER treated durene with benzoyl nitrate in carbon tetrachloride solution with strong cooling (exothermic reaction). The reaction product was diluted with ether and washed with solutions of soda and then caustic soda to remove benzoic acid. After removal of ether and carbon tetrachloride (under vacuum) the nitro compound was steam-distilled and then recrystallized from methyl alcohol. Mononitrodurene was obtained in long colourless prisms, m.p. 52·5°C:



Durene 1'-Nitrodurene

Investigation of the structure of this compound revealed that when benzoyl nitrate reacted with durene the nitro group entered the side chain and not the ring.

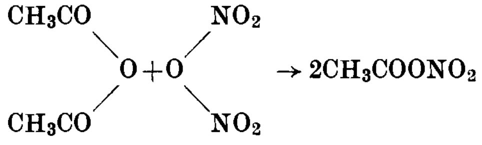
It is interesting that the ω-mononitro derivative of durene obtained by WILSTÄTTER undergoes quantitative ring nitration when treated with a mixture of nitric and sulphuric acids, forming 1' : 3 : 6-trinitrodurene (hexagonal prisms, m.p. 139°C):



Acetyl nitrate has certain advantages over benzoyl nitrate as a nitrating agent; its use is accompanied by the formation not of water or mineral acid but of volatile acetic acid which can be easily removed from the reaction mixture:

$$RH+CH_3COONO_2 \rightarrow RNO_2+CH_3COOH$$

Acetyl nitrate is prepared from nitric anhydride (obtained by distillation of nitric acid with phosphorus pentoxide) and acetic anhydride:



$$\begin{matrix} CH_3CO & & & & NO_2 \\ & \diagdown & & \diagup & \\ & & O+O & & \\ & \diagup & & \diagdown & \\ CH_3CO & & & & NO_2 \end{matrix} \rightarrow 2CH_3COONO_2$$

Acetyl nitrate is a very hydroscopic, colourless liquid which fumes in air; sp. gr. 1·24 (15°C).

Acetyl nitrate was synthesized by PICTET and KHOTINSKY [9] in the following way: nitric anhydride, obtained by distilling concentrated nitric acid over P_2O_5, was added in equal portions to acetic anhydride in which it dissolved without appreciable increase in the temperature of the reaction mixture. To separate acetyl nitrate from excess acetic anhydride the reaction product was distilled under vacuum at 70 mm and 22°C (distillation at ordinary pressure being accompanied by interaction of acetyl nitrate and acetic anhydride forming tetranitromethane). Water decomposes acetyl nitrate rapidly to acetic and nitric acids with evolution of heat. Acetyl nitrate is very similar to benzoyl nitrate in its action on organic compounds. It reacts with alcohols forming corresponding esters of nitric acid. It is a very energetic nitrating agent with respect to aromatic compounds: it is usually used at low temperatures and as a very dilute solution in carbon tetrachloride or acetic anhydride. Its high nitrating activity is explained by the fact that nitration takes place without formation of water or of strong mineral acids.

The action of acetyl nitrate on certain aromatic compounds has been studied. Benzene, toluene, benzyl chloride, benzoic acid, phenol, anisole, acetanilide, naphthalene, quinoline give the corresponding mononitro derivatives with theoretical or almost theoretical yields. When acetyl nitrate acts on benzene derivatives *o*-nitro compounds are formed predominantly (see nitration with benzoyl nitrate above). Thus, nitration of toluene, phenol and benzyl chloride results in a mixture of *o*- and *p*-nitro derivatives.

Table 34 gives the *o*- and *p*-nitro derivative content of reaction products obtained by nitration with acetyl nitrate.

As the table shows, acetanilide gives the *o*-nitro derivative exclusively. Acetyl nitrate also exerts an acetylating action on amines. Interaction of acetyl nitrate with aniline in carbon tetrachloride solution with strong cooling (ice–salt mixture) gives a theoretical yield of equimolecular amounts of acetanilide and aniline nitrate.

6-Nitro-*o*-toluidine is obtained by nitrating acetyl-*o*-toluidine with acetyl nitrate in the following way: to a mixture of acetyl nitrate (66 g) and glacial acetic acid (150 g) at −10°C acetyl-*o*-toluidine (85 g) was added and the mixture allowed to stand overnight. When a solution of salt was added to the reaction mixture the nitro product precipitated out (92 g); it was saponified with hydrochloric acid and steam-distilled. Yield of 6-nitro-*o*-toluidine—53 per cent.

Table 34

Substance being nitrated	*o*-Isomer content (%)	*p*-Isomer content (%)
Toluene	88	12
Phenol	52	48
Benzyl chloride	60	40
Acetanilide	100	0

Thiophene reacts with acetyl nitrate in the absence of solvents to give nitrothiophene (m.p. 44°C); the reaction must be carried out with strong cooling. Anthracene likewise gives a nitro derivative. Interaction of acetyl nitrate and chloroform gives chloropicrin. Tetranitromethane is formed when acetyl nitrate interacts with acetic acid and acetic anhydride.

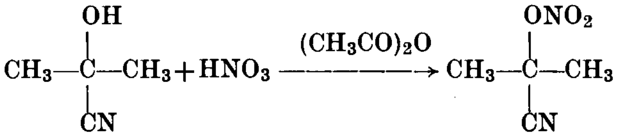
It should be noted, however, that compounds which are difficult to nitrate, such as nitrobenzene, quinone and pyridine, cannot be nitrated with acetyl nitrate even at high temperatures. Instead of prepared acetyl nitrate it is possible to use a mixture of concentrated nitric acid with acetic anhydride [10]. Izmailskii and Kozin [11] used this method for the preparation of the 8-nitro derivative of 1′-chloro-1-methylnaphthalene.

Introduction of one chlorine atom into the methyl group of α-methylnaphthalene diminishes the activating effect of the methyl group to such an extent that the reaction is directed chiefly towards the unsubstituted ring of naphthalene. Nitration of 1′-chloro-1-methylnaphthalene with a mixture of acetic anhydride and nitric acid (sp. gr. 1·52) at 5–10°C gives 8-nitro-1′-chloro-1-methylnaphthalene.

Acetyl nitrate is recommended for nitration of easily saponified esters when it is essential to avoid water being present, e.g. in the preparation of methyl ester of nitroopianic acid and other esters.

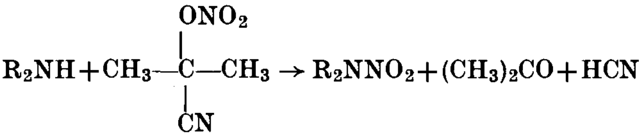
Ingold *et al.* [12] nitrated benzene and toluene under various conditions (various temperatures and concentrations of acetic anhydride) and also studied the kinetics of nitration of halogen substituted benzenes and of benzene with acetyl nitrate using different solvents and different nitration temperatures. Emmons and Freeman [12a] used acetonecyanhydrin nitrate as a nitrating agent. These authors found that acetonecyanhydrin nitrate was a unique nitrating agent for amines in alkaline medium.

Acetonecyanhydrin nitrate is easily prepared by treating acetonecyanhydrin with fuming nitric acid in acetic anhydride. This method gives a 65–67 per cent yield:



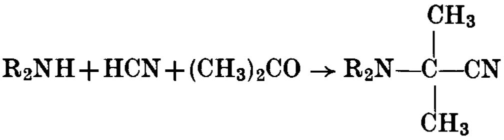
$$CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}-CH_3+HNO_3 \xrightarrow{(CH_3CO)_2O} CH_3-\overset{\overset{\displaystyle ONO_2}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}-CH_3$$

Acetonecyanhydrin nitrate is a mobile, colourless liquid, easily distilled under vacuum. In alkaline medium it reacts readily with primary and secondary amines forming nitroamines. Primary aliphatic and alicyclic nitroamines are obtained with 50–60 per cent yield, whilst secondary nitroamines give 55–80 per cent yields. The reaction proceeds as follows:



$$R_2NH+CH_3-\overset{\overset{\displaystyle ONO_2}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}-CH_3 \rightarrow R_2NNO_2+(CH_3)_2CO+HCN$$

Emmons and Freeman also demonstrated that hydrogen cyanide and acetone formed in the reaction products react in their turn with excess amine forming the corresponding α-aminonitrile:

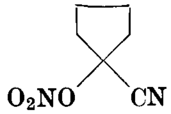


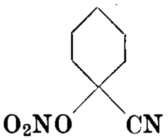
$$R_2NH+HCN+(CH_3)_2CO \rightarrow R_2N-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CN$$

These authors studied the influence of various solvents on this nitration reaction. Secondary amines are themselves good solvents, although the reaction can be carried out in acetonitrile and tetrahydrofurane solutions. The amine was taken in fivefold excess and was heated for 5 hr with acetonecyanhydrin nitrate.

When solvents with low dielectric constant or excess amine were used the yield of nitroamine was only 20–25 per cent. Heating a threefold excess of primary amine with acetonecyanhydrin nitrate for 6 hr in acetonitrile or tetrahydrofurane solution gave good yields of nitroamines.

The authors also used nitro esters of *cyclo*pentanone and *cyclo*hexanone cyanhydrins for nitration of amines:



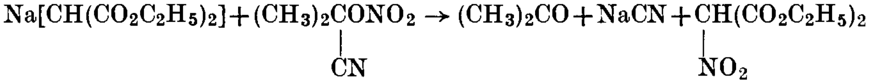


In another communication [12b] Emmons and Freeman studied the nitration of malonic and acetoacetic esters and their alkyl derivatives with acetonecyanhydrin nitrate in alkaline medium.

The authors used sodium hydride as the base.

Malonic ester was first converted into its sodium derivative to which was added acetonecyanhydrin nitrate. The reaction followed the equation:

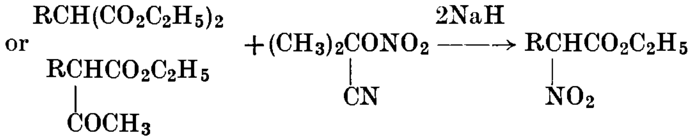
$$CH_2(CO_2C_2H_5)_2 \xrightarrow{NaH} Na[CH(CO_2C_2H_5)_2]$$



$$Na[CH(CO_2C_2H_5)_2] + \underset{CN}{(CH_3)_2CONO_2} \rightarrow (CH_3)_2CO + NaCN + \underset{NO_2}{CH(CO_2C_2H_5)_2}$$

The reaction was usually performed with excess sodium derivative of malonic ester in tetrahydrofurane solution. When a threefold excess of the sodium derivative of malonic ester was used the yield of nitro derivative of diethylmalonic ester was 45 per cent.

When nitration of sodium derivatives of malonic and acetoacetic esters and their alkyl derivatives was carried out in excess sodium hydride the nitro compounds formed were immediately subjected to further reaction giving α-nitro esters:



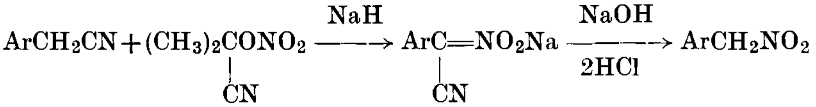
$$\begin{matrix} RCH(CO_2C_2H_5)_2 \\ \text{or} \\ \underset{COCH_3}{RCHCO_2C_2H_5} \end{matrix} + \underset{CN}{(CH_3)_2CONO_2} \xrightarrow{2NaH} \underset{NO_2}{RCHCO_2C_2H_5}$$

The yield of α-nitro esters, depending on the particular derivative of malonic or acetoacetic ester, varied between 42–70 per cent.

The authors consider that the method developed by them for the nitration of malonic and acetoacetic esters and their alkyl derivatives with simultaneous alkaline decomposition of the nitro derivatives obtained is the most general method of synthesis for α-nitro esters and takes place in a single stage. This method is suitable for the nitration of malonic and acetoacetic ester derivatives containing groups (e.g. aromatic rings) which react with the usual nitrating mixtures.

Arylacetonitriles can also be nitrated with acetonecyanhydrin nitrate forming appropriate nitroacetonitrile derivatives.

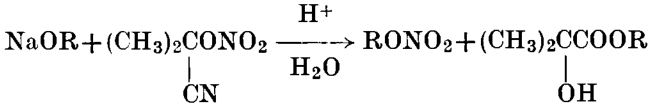
The authors did not isolate nitroacetonitrile derivatives in the pure state but converted them into arylnitromethanes in the usual way:



$$ArCH_2CN + \underset{CN}{(CH_3)_2CONO_2} \xrightarrow{NaH} \underset{CN}{ArC{=}NO_2Na} \xrightarrow[2HCl]{NaOH} ArCH_2NO_2$$

Phenylacetonitrile was converted by this method into phenylnitromethane with a 70 per cent yield, whilst *o*-chlorophenylnitromethane was obtained from *o*-chlorophenylacetonitrile with a 42 per cent yield.

Emmons and Freeman also studied the nitration of a number of alcoholates with acetonecyanhydrin nitrate [12c]. They established that this reaction led to the formation of two compounds—nitro ester and the corresponding ester of α-hydroxy*iso*butyric acid:



$$NaOR + \underset{CN}{(CH_3)_2CONO_2} \xrightarrow[H_2O]{H^+} RONO_2 + \underset{OH}{(CH_3)_2CCOOR}$$

2. NITRATION WITH INORGANIC NITRATES

Very little information is available in the literature concerning the nitration of aromatic hydrocarbons in the side chain and of naphthene and paraffin hydrocarbons with inorganic nitrates. Only a few works deal with this reaction.

In 1894 KONOVALOV [13] showed that copper nitrate reacted vigorously (without addition of water) with *iso*octanaphthene in sealed tubes at 160–170°C or on boiling in an open vessel. Nitro products and acids resulted from this reaction.

In 1901 KONOVALOV [14] published his work on the nitration of the side chain in diphenylmethane and ethylbenzene using various inorganic nitrates. The experiments were performed in sealed tubes. For each experiment 5 ml hydrocarbon was taken (ethylbenzene or diphenylmethane), and 40 ml water; nitrate was added to this mixture in such amount that complete hydrolysis of the salt would give a 12 per cent solution of nitric acid. In some experiments KONOVALOV used 10 per cent solution of the salt. Bismuth nitrate $Bi(NO_3)_3$ as well as its basic salt $Bi(NO_3)(OH)_2$, silver nitrate $AgNO_3$, mercury nitrate $Hg(NO_3)_2$, a mixture of aluminium alum and aluminium nitrate nitrated diphenylmethane on heating (with water) to 110–125°C for 6 hr.

Bismuth nitrate and mixture of aluminium alum with aluminium nitrate react with diphenylmethane even on heating (with water) to 100–106°C for 6 hr. Silver nitrate and mercury nitrate do not form nitro compounds with diphenylmethane at this temperature. Lead nitrate does not form nitro compounds with diphenylmethane on heating to 125°C.

When diphenylmethane was nitrated with inorganic nitrates no gaseous products were observed in a single experiment. This indicates absence of appreciable oxidation of the hydrocarbons during the nitration. Sodium and potassium nitrates (which were used as 10 per cent solutions) did not form nitro compounds with ethylbenzene after heating the reaction mixture at 125°C for 7 hr.

As KONOVALOV's experiments showed, the nitrating ability of potassium nitrate was greatly influenced by the addition of a small amount of potassium nitrite to the reaction mixture. Thus, for example, interaction of ethylbenzene with 10 per cent solution of potassium nitrate with a small admixture of potassium nitrite results in the formation of nitroethylbenzene.

KONOVALOV reached the following conclusions on the basis of his investigations:

(1) Nitrates of the alkali metals and of ammonia are either completely non-hydrolysed by water at 125°C or only hydrolysed very feebly, so that the concentration of nitric acid formed is very low and consequently these salts do not give nitro compounds when their solutions are heated with hydrocarbons.

(2) Bismuth, aluminium, mercury and silver nitrates are hydrolysed at 125°C and lower temperatures to a considerable degree and hence can

be used (especially the bismuth and aluminium salts) for nitration of hydrocarbons at raised temperatures.

(3) When hydrocarbons are nitrated with solutions of metallic nitrates no appreciable oxidation of the hydrocarbons is observed, which constitutes a distinct advantage over nitration under similar conditions using dilute nitric acid.

NAMETKIN [15] used aluminium nitrate for nitrating naphthene hydrocarbons.

A mixture of *cyclo*hexane (78 g) and aluminium nitrate (210 g) was heated in sealed tubes at 110–115°C. Strong pressure developed in the tubes. Following the usual treatment of the reaction products 27 g mononitro derivative was obtained (56·7 per cent of theoretical yield). Nitration with nitric acid does not give such a good yield of nitro*cyclo*hexane and Nametkin considers his method as the best for the preparation of nitro*cyclo*hexane.

Methyl*cyclo*hexane is easily nitrated in sealed tubes both by nitric acid sp. gr. 1·2 and dry aluminium nitrate. The main reaction product in both cases is the tertiary nitro compound. When nitration is achieved by nitric acid the mixture of primary and secondary nitro compounds which is formed in small amounts contains predominantly the secondary nitro derivative, whereas if aluminium nitrate is used the primary compound is found to predominate. The yields of crude nitro product, calculated on the reacted hydrocarbon, are 58 per cent in the case of nitric acid nitration and 72 per cent in the case of aluminium nitrate nitration.

*cyclo*Pentane was nitrated with aluminium nitrate in sealed tubes at 110–115°C. Each tube contained hydrocarbon (10 ml) and the salt (20 g). A quantity of 2 g pure nitro*cyclo*pentane was obtained (from three tubes). Glutaric acid was detected among the reaction products.

Like KONOVALOV, NAMETKIN explains the nitrating properties of aluminium nitrate by hydrolysis at the reaction temperature with formation of nitric acid. Aluminium nitrate $Al(NO_3)_3 . 9H_2O$ melts, without decomposition, at 73°C. Hydrolysis occurs at higher temperatures. At 140°C aluminium nitrate undergoes complete decomposition into aluminium hydroxide and nitric acid. At temperatures above 73°C and below 140°C there is, evidently, a certain equilibrium between the salt and the products of its hydrolysis. In the presence of hydrocarbon this equilibrium must be continuously upset by the entry of HNO_3 into reaction, and the hydrolysis must therefore go on in an attempt to restore it. Thus when aluminium nitrate is used the acid does not enter the reaction all at once but does so gradually. Therefore the yields of nitro compounds obtained by this method are better than those observed when nitration is carried out by an amount of nitric acid equivalent to the amount of acid that would be formed on complete hydrolysis of aluminium nitrate taken for reaction.

Amongst paraffin hydrocarbons KONOVALOV [16] studied the nitration of di*iso*amyl $(CH_3)_2CHCH_2CH_2CH_2CH_2CH(CH_3)_2$ with inorganic nitrates.

Negative results were obtained when di*iso*amyl was heated to its boiling temperature for 8 hr with a 32 per cent solution of mercury nitrate.

When di*iso*amyl was boiled with a 13 per cent solution of aluminium nitrate for 10 hr alkali-soluble nitro compounds were found among the reaction products.

Heating di*iso*amyl (60 g) to 110°C with dry bismuth nitrate (60 g) for 8 hr gave 63 g of an oil which was soluble in alkali to the extent of about 40 g. Primary and secondary nitro compounds were detected in this solution. The alkali-insoluble portion consisted mainly of di*iso*amyl. Approximately 1 g of tertiary nitro compounds was isolated from this residue.

KONOVALOV also studied the nitration of di*iso*amyl with aluminium nitrate in sealed tubes. Nitration was carried out both with a solution of aluminium nitrate and with the dry salt. Di*iso*amyl was heated with a 13 per cent solution of aluminium nitrate at 130–150°C for 8 hr. As the result of the reaction a small amount of a mixture of primary, secondary and tertiary nitro compounds was obtained. Of 10 g of hydrocarbon 7 g did not enter the reaction.

When di*iso*amyl was nitrated with dry aluminium nitrate for 8 hr at 130°C the main product was a mixture of primary and secondary nitro compounds. Of 10 g hydrocarbon taken 5 g entered the reaction. Only 0·5 g of tertiary nitro product was obtained.

The author of the present book has studied the possibility of using inorganic nitrates for the preparation of nitro compounds of both the aliphatic and the aromatic series. Thus, a study was made of the nitration of *n*-heptane and *iso*octane (2 : 2 : 4-trimethylpentane) with salts of nitric acid*. Nitration of these hydrocarbons was effected by aluminium nitrate $Al(NO_3)_3 . 9H_2O$, bismuth nitrate $Bi(NO_3)_3 . 5H_2O$, copper nitrate $Cu(NO_3)_2 . 6H_2O$, ferric nitrate $Fe(NO_3)_3 . 9H_2O$ and zinc nitrate $Zn(NO_3)_2 . 6H_2O$. The reaction was carried out in sealed tubes at 140°C (160°C in the experiment using zinc nitrate).

The duration of experiments was 8 hr during nitration of *iso*octane and *n*-heptane with bismuth, copper and iron nitrates, and 20-40 hr when aluminium and zinc nitrates were used. In the former case evolution of nitrogen oxides was observed.

At the end of the experiment the ampoules were cooled and then opened. The hydrocarbon layer, containing the nitro products in solution, was separated from the aqueous layer which contained the unreacted salt. The hydrocarbon layer was washed with water, 5 per cent sodium bicarbonate solution, again with water and then dried over anhydrous sodium sulphate. Unreacted hydrocarbon was distilled off at atmospheric pressure and the residue was distilled under vacuum.

The product remaining after removal of hydrocarbon was a nitro derivative mixed with a small amount of carbonyl compounds.

Results of experiments on the nitration of *n*-heptane and *iso*octane with nitric acid salts are given in Table 35.

The nitro compounds obtained were fractionally distilled under vacuum. The main bulk of the products in the case of *n*-heptane (85–90 per cent)

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* Unpublished data.

distilled over the range 59–62°C at 6 mm. The relative amount of this fraction was independent of the nature of the nitrating salt. In the case of *iso*octane the products of nitration distilled (75 per cent) at 60–63°C at 5 mm. The distilled reaction products were investigated in the usual way.

Table 35. *Nitration of* n-*heptane and* iso*octane with nitric acid salts*

Hydrocarbon	*iso*-Octane	*n*-Heptane				
Salt	Al^{+++}	Al^{+++}	Bi^{+++}	Cu^{++}	Fe^{+++}	Zn^{++}
Taken:						
Hydrocarbon (g)	124	109	109	109	109	109
Salt (g)	117	104	104	104	104	104
Molar ratio hydrocarbon:NO_2	1·2:1	1·34:1	1·7:1	1·58:1	1·02:1	1·58:1
Temperature of experiment (°C)	140	140	140	140	140	160
Duration of experiment (hr)	20	20	8	8	8	40
Nitro compounds obtained (g)	32	22	24	26	45	5
Yield calculated on NO_2 (%)	25	20	28	36	45	—

The following points were established during the nitration of *n*-heptane and *iso*octane with various salts of nitric acid:

(1) Nitration of *iso*octane with aluminium nitrate occurs at a somewhat faster rate than that of *n*-heptane. For example, the yield of nitro compounds in the case of *iso*octane was 25 per cent calculated on aluminium nitrate and 20 per cent in the case of *n*-heptane.

(2) The rate of the reaction depends to a greater extent on the nature of the salt or rather the cation used than on the nature of the hydrocarbon undergoing nitration. Ferric nitrate was found to be the most active with respect to *n*-heptane nitration, whilst zinc nitrate gave the lowest yield of nitro compounds.

(3) Nitration with different salts of nitric acid leads to the formation of the same reaction products. Nitration of *n*-heptane results in the formation of secondary nitroheptane as the main reaction product whilst nitration of *iso*octane gives mainly the tertiary nitro derivative. In addition to these a small amount of the primary nitro compounds is also formed.

(4) A small amount of dinitro compounds is formed in addition to mononitro derivatives when *n*-heptane and *iso*octane are nitrated with salts of nitric acid. The formation of dinitro compounds is considerably less pronounced in the former case (approximately 10 per cent by weight) than in the latter case (about 18 per cent by weight). In both cases the dinitro compounds formed are primary. When *n*-heptane is nitrated a small amount of secondary dinitro compounds is also formed.

(5) Nitration of *n*-heptane and *iso*octane with salts of nitric acid is accompanied by oxidation of the hydrocarbon being nitrated. The products of oxidation have not been investigated.

Nitration of aromatic compounds with metallic nitrates is usually achieved in the presence of other components which, presumably, play the role of activators.

MENKE [17] analysing the action of nitrating mixtures composed of nitric acid and acetic anhydride on aromatic compounds concluded that acetic anhydride not only acted as a dehydrating agent but also actively accelerated the process.

Assuming that replacement of nitric acid by its salts would still leave the nitrating mixture sufficiently active owing to the catalytic properties of acetic anhydride, MENKE studied nitration of aromatic compounds with mixtures of acetic anhydride and nitrates with sufficiently low temperatures of decomposition (among these being nitrates of iron, copper, nickel, cobalt, aluminium, cerium and a number of nitrates of metals belonging to groups I, II, III, IV and VIII of the periodic table). MENKE's experiments showed that alkali metal nitrates did not exhibit nitrating action or only reacted weakly.

MENKE nitrated aniline as follows: aniline (8 parts) was added dropwise with stirring and cooling with ice (the temperature not being allowed to exceed 30°C) to a mixture of $Cu(NO_3)_2 . 3H_2O$ (10 parts by weight) and acetic anhydride (30 parts). After half an hour, counting from the beginning of addition of aniline, the reaction mixture was poured into 150 parts of water. The crystalline mass which was formed was separated off, powdered and washed with water to remove the included copper nitrate. After recrystallizing the crude product from 50 per cent alcohol, 11 parts of pure *o*-nitroacetanilide were obtained, m.p. 92°C.

Since acetic anhydride reacts with aniline at ordinary temperatures to give acetanilide, the reaction of nitration with $Cu(NO_3)_2$ and acetic anhydride can be regarded as nitration of acetanilide. The results demonstrate the difference between nitrating acetanilide with a mixture of nitrate and acetic anhydride and a mixture of nitric and sulphuric acids, since in the latter case both *o*- and *p*-nitroacetanilides are formed.

Nitration of phenol is achieved by dissolving phenol (5 g) in acetic anhydride and adding the solution dropwise to a mixture of ferric nitrate (15 g) and acetic anhydride (25 g) at 70–85°C. The reaction product is picric acid.

Similarly, nitration of benzene at 80°C gives nitrobenzene, and chlorobenzene at 40–45°C gives *p*-nitrochlorobenzene. Toluene gives *o*-nitrotoluene when treated with a mixture of $Fe(NO_3)_3$ and acetic anhydride at 40°C.

It has been shown further that if nitrate is used in a mixture not with acetic anhydride but with acetyl chloride (or acetyl bromide) halogenation of the aromatic compound occurs together with nitration. For example, phenol treated with $Cu(NO_3)_2$ and acetyl chloride (cooled with ice–salt mixture) gives 4 : 6-dichloro-2-nitrophenol.

The mixture of copper nitrate and acetic anhydride can also be used to prepare nitroacetoacetic ester from acetoacetic ester.

Aromatic compounds can also be nitrated by mixtures of nitrates and acetic acid. It should be remarked, however, that such mixtures are less active nitrating agents than mixtures of nitrates with acetic anhydride.

It is thought that this difference can be explained by the hypothesis that in the former mixture the intermediate product, acting as nitrating agent, is not acetyl nitrate as in the case of the mixture with acetic anhydride but acetylorthonitric acid (MENKE).

Some compounds (phenol, *o*-nitrophenol, dimethylaniline) are nitrated by nitrate–acetic acid mixture even at room temperature. On the other hand naphthalene undergoes nitration by copper nitrate or iron nitrate and acetic acid only at 105°C, and acetanilide at 75°C (nitrates react with the two latter compounds at 30°C when mixed with acetic anhydride).

Phenol can be taken to illustrate nitration of aromatic compounds with a mixture of nitrate and acetic acid. A solution of phenol (5 g) in glacial acetic acid (10 g) is added dropwise with vigorous stirring to a mixture of $Cu(NO_3)_2$ (8 g) and glacial acetic acid (25 g); it is essential that the reaction temperature be maintained at 26°C by means of efficient cooling. After 20 min from the first addition of phenol the reaction is stopped. When the reaction mixture is poured into 10 ml of water the product crystallizes out; it is filtered off and washed with cold water. This treatment gives pure *o*-nitrophenol, m.p. 44–45°C (as has been pointed out above, nitration of phenol with a mixture of nitrate and acetic anhydride gives picric acid and not *o*-nitrophenol). Thus nitration of phenol with metallic nitrate mixed with either acetic anhydride or acetic acid gives different products depending on the second component of the nitrating mixture.

Nitration of aromatic compounds with metallic nitrates in the presence of acetic anhydride has been thoroughly studied by BACHARACH [18–20]. He set out to find out experimentally: (1) whether this method of nitration was general for all aromatic compounds or only applicable to a certain group of these compounds and (2) whether there was a definite relationship between the nature of the nitrate and the structure of the nitro compound obtained, i.e. whether the nitro group was oriented to one or other position depending on the nitrating agent employed.

In order to answer the first question a study was made of the action of copper nitrate and iron nitrate in the presence of acetic anhydride on benzaldehyde, benzoic acid, nitrobenzene and *p*-toluidine. Experiments on benzaldehyde, benzoic acid and nitrobenzene, conducted at various temperatures, gave negative results. *p*-Toluidine, on the other hand, nitrated extremely easily.

On the basis of his results and findings of other workers* BACHARACH concludes that nitration of aromatic compounds with inorganic nitrates gives positive results only in those cases where the compounds undergoing nitration contain *o*- and *p*-directing substituents; compounds containing *m*-directing substituents are not nitrated by inorganic nitrates mixed with acetic anhydride.

To elucidate the relation between the structure of the nitro compound

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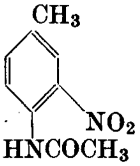
* MENKE [17], SPIEGEL and HAYMANN [21]; the last two authors nitrated aniline, phenol and anisole with bismuth nitrate in the presence of acetic anhydride and in all cases obtained mixtures of *o*- and *p*-nitro derivatives.

formed and the nature of the nitrate employed Bacharach nitrated *p*-toluidine with nitrates of iron, manganese, cobalt, nickel, copper, mercury, silver, sodium and lithium in the presence both of acetic acid and of acetic anhydride. The experiments showed that *p*-toluidine reacted first with acetic anhydride or acetic acid to form acetotoluidide and then nitration took place. All the nitrates cited above gave the same reaction product—3-nitro-*p*-acetotoluidide:



except sodium and silver nitrates, which proved to be inactive.

It has also been demonstrated that the greatest rate of reaction is observed when copper nitrate is used (duration of process 10 min at 30°C). The duration of *p*-toluidine nitration by metallic nitrates of the iron group is 15–20 min at 65–85°C (analogous results are obtained during nitration with mercury nitrate). The least active agent is lithium nitrate; its nitrating action is only observed on refluxing the reaction mixture for 2 hr.

When aniline is nitrated with lithium nitrate *p*-nitroacetanilide is formed and not the *o*-isomer, which, according to Menke, is given by nitration of aniline with nitrates of heavy metals. Considering these results Bacharach concludes that nitrates which react at relatively low temperatures (e.g. nitrates of heavy metals) lead to the formation of *o*-nitro compounds, whereas nitrates which react only at high temperatures, e.g. lithium nitrate, give *p*-nitro derivatives. This does not, however, hold in all cases; *p*-toluidine, for example, gives the same nitro derivative with all nitrates.

Bacharach also studied the action of nitrates on some two-ring compounds. When $Cu(NO_3)_2 . 3H_2O$ was used it was first treated with acetic anhydride until a green amorphous mass was obtained and then a solution of the hydrocarbon being nitrated in acetic anhydride was added to the amorphous mass with stirring. Nitration with lithium nitrate was achieved by boiling for several hours and adding 4 per cent of copper nitrate to enhance its activity.

Diphenyl treated with copper nitrate gave *p*-nitro and $p : p'$-dinitrodiphenyl; dibenzyl gave $p : p'$-dinitrodibenzyl. Lithium nitrate did not react with diphenyl and dibenzyl. Benzil and stilbene were not nitrated by lithium and copper nitrates, whilst benzoin was only oxidized by them to benzil. Experiments on ring compounds thus confirmed the conclusions cited above concerning susceptibility to nitration with mixtures of nitrate and acetic anhydride being confined to those aromatic rings which contained *o*- and *p*-directing substituents.

Bacharach's further investigations, however, showed that in some cases compounds containing *m*-directing substituents could also undergo nitration with nitric acid or with a mixture of nitrate and acetic anhydride.

Thus, for example, quinoline which gives only 5- and 8-nitro derivative- when treated with a mixture of nitric and sulphuric acids, gives 7-nitros quinoline when nitrated with lithium nitrate. Nitration of phenylacetic acid with copper nitrate in acetic anhydride gives *m*-nitrophenylacetic acid with a yield 50 per cent of the theoretical and *o*-nitrophenylacetic acid with a 10 per cent yield (when treated with nitric acid phenylacetic acid gives a mixture of *m*-nitrophenyl acetic acid with a 14 per cent yield and *o*- and *p*-nitro derivatives of phenylacetic acid with an 80 per cent yield).

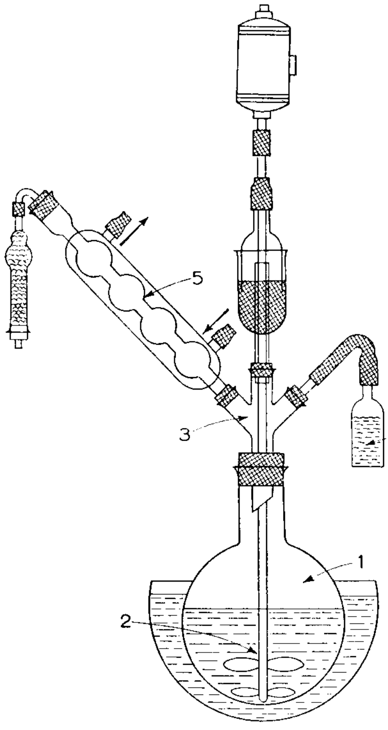


Fig. 5. Apparatus for nitration of organic compounds with nitrates in the presence of $AlCl_3$.

The reaction mechanism of nitration with metallic nitrates in the presence of acetican hydride and acetic acid consists, according to BACHARACH, of the formation of an intermediate compound—diacetylorthonitric acid, which acts as the nitrating agent. This acid was obtained by him in the following way: a mixture of 20 parts $Cu(NO_3)_2 . 3H_2O$ and 50 parts acetic anhydride was allowed to stand for 20 min at 30–35°C. The reaction product, consisting of a liquid part and a green amorphous mass (copper acetate), was separated by filtration. From the filtrate a substance was isolated by twice repeated distillation under vacuum whose properties corresponded to those described by PICTET for diacetyl-*o*-nitric acid (b.p. 45°C, n_D^{20} 1·37542).

When aniline was treated with an equivalent amount of diacetyl-*o*-nitric acid at 35°C a mixture of nitro derivatives was formed in the course of a few minutes; the mixture contained *p*-nitroacetanilide and the *o*-isomer.

As the result of systematic studies by the author of the present book a method has been developed for nitration of aromatic compounds with inorganic nitrates in the presence of certain activators. A description is given below of experiments on nitration of organic compounds with nitrates in the presence of the following activators: $AlCl_3$, $FeCl_3$, $SiCl_4$ and BF_3*.

I. NITRATION IN THE PRESENCE OF $AlCl_3$

Nitration was performed in a round-bottomed flask (1) (Fig. 5) 0·5 l. in volume, fitted with a three-necked adapter (3) through whose central neck passed the shaft of the mechanical stirrer (2); the two remaining necks were connected to a reflux condenser (5) and a measuring vessel (4) from which the activator was added.

During the experiments anhydrous nitrate in the form of a powder was placed in the flask, followed by the hydrocarbon undergoing nitration, and after starting the stirrer gradual addition of the activator was begun. Experiments were carried out both in the cold and with heating.

The effect of the following nitrates on aromatic hydrocarbons in the presence of aluminium chloride has been studied: KNO_3, $NaNO_3$, NH_4NO_3, $Ba(NO_3)_2$, $Pb(NO_3)_2$ and $AgNO_3$.

Nitration of Benzene

In these experiments carefully purified benzene, treated with concentrated sulphuric acid to remove thiophene and other admixtures was used. The nitrates were dehydrated, fused and pulverized prior to use.

Nitration with potassium nitrate. In the early experiments the molar ratio of nitrate to benzene was 1 : 1; however, these experiments showed that with this ratio of reactants the reaction mixture was too solid in consistency which impeded stirring. Therefore in subsequent experiments nitration was carried out in the presence of excess benzene which thus acted as solvent. The reaction products obtained on nitration of benzene with potassium nitrate were subjected to the same treatment as that described in Chapter V when benzene was nitrated with nitrogen oxides.

The first series of experiments was designed to elucidate the dependence of the process of nitration on the amount of activator and the period over which it was added (Tables 36 and 37). Benzene (1 mole) was placed in the reaction vessel as well as potassium nitrate (0·5 mole) and the reaction was performed over 3 hr, in some experiments the amount of aluminium chloride added over 30 min (Table 36) being varied, in others the period over which the activator was added was varied, its amount remaining constant (Table 37).

The experiments were carried out without external heating but owing to the exothermic nature of the reaction the temperature of the reaction mixture rose to 30–40°C during the nitration.

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* Attempts to achieve the nitration of aromatic hydrocarbons (benzene, toluene, xylene and mesitylene) in the absence of activators gave negative results: even when nitration was carried out for 3 hr at various temperatures the hydrocarbons remained unchanged.

Data given in Tables 36 and 37 indicate that the optimal results are achieved when 20 g (0·15 mole) activator is admitted over a period of 30 min.

Table 36. *Dependence of yield of nitrobenzene on amount of* $AlCl_3$ *activator used*
(78 g benzene, 50 g KNO_3)

No. of expt.	$AlCl_3$ taken (g)	Yield nitrobenzene (g)	Yield nitrobenzene (% of theoretical calculated on benzene taken)	Recovered benzene (g)	Recovered benzene (% of benzene taken)	Yield of nitrobenzene calculated on reacted benzene (% of theoretical)	Yield of nitrobenzene calculated on nitrate (% of theoretical)
1	63	23	18·7	53	67·9	58·3	37·3
2	34	23·1	18·8	55	70·5	63·6	37·6
3	20	23·3	18·9	58	74·3	73·6	37·9
4	20	22·7	18·4	57	73·0	68·5	37·0
5	10	12·5	10·1	62	79·5	49·5	20·3
6	10	11	8·9	65	83·5	53·6	17·9
7	3	5	4·1	70	89·7	39·6	8·2
8	3	4·2	3·4	72	92·3	44·3	6·8
9	7	2·2	1·8	73	93·7	27·9	3·6

The dependence of the yield of nitrobenzene on the duration of the nitrating process without heating was also studied. The yield was found to be unchanged when the duration was increased from 20 to 90 min; on increasing it from 90 min to 3 hr the yields of nitrobenzene gradually increased, but again diminished on prolonging the process beyond 3 hr which thus proved to be the optimal period (Table 38).

Table 37. *Dependence of nitrobenzene yield on length of time over which* $AlCl_3$ *activator was added*
(78 g benzene, 50 g KNO_3, 20 g $AlCl_3$)

No. of expt.	Time over which $AlCl_3$ added (min)	Yield nitrobenzene (g)	Yield nitrobenzene (% of theoretical, calculated on benzene taken)	Recovered benzene (g)	Recovered benzene (% of benzene taken)	Yield nitrobenzene calculated on reacted benzene (% of theoretical)	Yield calculated on nitrate (% of theoretical)
1	5	16·0	13·0	61	78·2	59·6	26·0
2	30	23·3	19·9	58	74·3	73·8	37·9
3	60	21·5	17·5	56	71·8	61·9	34·9
4	60	22·0	17·9	54	69·3	58·1	35·8
5	120	20·5	16·7	57	73·0	61·8	33·4
6	120	19·8	16·1	58	74·3	62·7	32·2

Experiments on the nitration of benzene with potassium nitrate in the presence of $AlCl_3$ thus showed that when 0·15 mole of the activator was added with a molar ratio of benzene to KNO_3 of 2 : 1 a 38·5 per cent yield of nitrobenzene (calculated on nitrate or 74·5 per cent calculated on reacted benzene) was obtained when the reaction took place over a period of 3 hr without external heating.

Table 38. *Dependence of nitrobenzene yield on duration of nitration*
(78 g benzene, 50 g KNO_3, 20 g $AlCl_3$)

No. of expt.	Duration of experiment (min)	Yield nitrobenzene		Recovered benzene		Yield nitrobenzene calculated on reacted benzene (% of theoretical)	Yield nitrobenzene calculated on nitrate (% of theoretical)
		(g)	(% of theoretical calculated on benzene taken)	(g)	(% of benzene taken)		
1	20	16	13	60	76·9	56·1	26·0
2	20	16·5	13·4	58	74·3	52·1	26·8
3	30	16·8	13·6	61	78·2	62·3	27·3
4	30	15·9	12·9	62	79·5	62·6	25·9
5	60	16·6	13·5	60·5	77·4	59·8	27·0
6	60	16·0	13·0	61·0	78·4	59·3	26·0
7	90	16·8	13·6	59·0	75·6	55·8	27·3
8	90	16·1	13·1	60·7	77·8	58·7	26·2
9	120	20·1	16·3	58·5	75·2	65·0	32·7
10	120	21·1	17·1	57·1	73·1	63·7	34·3
11	180	22·7	18·4	56·2	71·9	65·7	36·9
12	180	23·6	19·1	58·0	74·3	74·5	38·4
13	240	22·4	18·2	57·0	73·0	67·3	36·4
14	240	23·2	18·8	59·0	75·5	77·0	37·7

A most unexpected result was obtained on attempting to activate the process by raising the reaction temperature (Table 39).

Experiments with external heating on a bath led to a reduction in the yield of nitrobenzene; for example, at 90–100°C (temperature of the bath) the yield dropped to 20–23 per cent calculated on nitrate. This phenomenon is evidently accounted for by partial decomposition of the benzene–aluminium chloride complex (which interacts with potassium nitrate) at high temperatures; the mechanism of the reaction is discussed below.

Nitration with ammonium, sodium, barium, lead and silver nitrates—Nitration was carried out under the same conditions and with the same quantitative ratio of reagents as those found to be optimal for nitration with potassium nitrate. Results of the experiments are summarized in Table 40.

Comparison of data in Tables 39 and 40 shows that of all the nitrates investigated the most active nitrating agent in the presence of $AlCl_3$ is $AgNO_3$; the other nitrates are less active, barium and lead being the least effective. If the nitrates investigated are arranged in order of diminishing nitrating activity with respect to benzene the following series is obtained:

$$AgNO_3 > KNO_3 > NaNO_3 > NH_4NO_3 > Pb(NO_3)_2 > Ba(NO_3)_2$$

Table 39. *Dependence of nitrobenzene yield on reaction temperature*
(78 g benzene, 50 g KNO_3, 20 g $AlCl_3$)

No. of expt.	Temperature of bath (°C)	Yield of nitrobenzene		Recovered benzene		Yield nitrobenzene calculated on reacted benzene (% of theoretical)	Yield calculated on nitrate (% of theoretical)
		(g)	(% of theoretical calculated on benzene taken)	(g)	(% of benzene taken)		
1	without heating	23·1	18·9	57	73·0	69·7	37·6
2		21·2	17·2	56	71·0	60·9	34·5
3	45– 50	18·7	15·2	58	74·3	59·2	30·4
4		17·9	14·5	59	75·6	59·7	29·1
5	90–100	14·2	11·5	57	73·0	42·9	23·1
6		12·8	10·4	60	76·8	45·1	20·8

Table 40. *Nitration of benzene with ammonium, sodium, barium, lead and silver nitrates in the presence of* $AlCl_3$
(78 g benzene, 20 g $AlCl_3$)

No. of expt.	Nitrate	Yield nitrobenzene		Recovered benzene		Yield nitrobenzene calculated on reacted benzene (% of theoretical)	Yield nitrobenzene calculated on nitrate (% of theoretical)
		(g)	(% of theoretical calculated on benzene taken)	(g)	(% of benzene taken)		
1	NH_4NO_3	16·3	13·2	60	76·8	57·4	26·5
2	N_4HNO_3	16·0	13	58	74·2	50·7	26·0
3	$NaNO_3$	20·7	16·8	60	76·8	72·9	33·6
4	$NaNO_3$	21·0	17·1	59	75·5	70·1	34·1
5	$Ba(NO_3)_2$	25·0	20·3	60	76·8	83·5	20·3
6	$Ba(NO_3)_2$	26·0	21·1	57	73·0	78·6	21·1
7	$Pb(NO_3)_2$	27·0	21·9	58	74·2	85·6	21·9
8	$AgNO_3$	34·3	27·9	45	57·6	65·9	55·7
9	$AgNO_3$	35·7	29·0	48	61·5	75·5	58·0

Nitration of Toluene

As Table 41 shows, when toluene is nitrated without external heating for 6 hr the yield of nitrotoluene reaches 38 per cent calculated on nitrate and 72·6 per cent calculated on reacted toluene. Raising the temperature by external heating and reducing the duration of the process exert unfavourable effects on the yield of nitrotoluene.

Table 41. *Nitration of toluene with potassium nitrate in the presence of* $AlCl_3$
(92 g toluene, 50 g KNO_3, 20 g $AlCl_3$)

No. of expt.	Duration of experiment (min)	Temperature of bath (°C)	Yield nitrotoluene		Recovered toluene		Yield nitrotoluene calculated on reacted toluene (% of theoretical)	Yield nitrotoluene calculated on nitrate (% of theoretical)
			(g)	(% of theoretical calculated on toluene taken)	(g)	(% of toluene taken)		
1	180	without heating	19·0	13·7	71	77·2	60·6	28
2	240		21·0	15·3	69	75·0	61·1	30·6
3	300		22·5	16·4	70	76·0	68·4	32·8
4	360		26·0	18·9	68	73·9	72·6	37·9
5	600		25·8	18·8	67	72·8	69·1	37·6
6	180	45– 50	18·0	13·4	66	71·7	46·4	26·2
7	360		17·3	12·6	64	69·5	41·4	24·7
8	360	105–110	15·2	11·1	63	68·4	35·1	22·1
9	360		14·9	10·8	61	66·3	32·2	21·7

Nitration of m-Xylene

The following quantities of reagents were used for the nitration of *m*-xylene: 0·2 mole *m*-xylene, 0·1 mole KNO_3 and 0·03 g-mole $AlCl_3$; the reaction products were separated from unreacted *m*-xylene and the mononitroxylenes from dinitro-*m*-xylene by the same methods as those described for nitration with nitrogen oxides (see Chapter V).

Experiments on nitration of xylene (Table 42) showed that the optimal yield of isomeric mononitroxylenes (29 per cent calculated on nitrate) was obtained when the reaction was performed without external heating. At raised temperatures the yield of mononitroxylenes was reduced while that of dinitro-*m*-xylene increased, reaching a maximum value (10–11 per cent) at 105–110°C.

II. NITRATION IN THE PRESENCE OF $FeCl_3$ AND $SiCl_4$

Nitration of benzene in the presence of $SiCl_4$ was carried out with the same quantitative ratios of reagents as in the presence of $AlCl_3$; during nitration in the presence of $FeCl_3$ the quantities of reagents were one-quarter compared with those usually employed (0·25 mole benzene, 0·125 mole KNO_3 and 0·037 mole $FeCl_3$).

Results of the experiments are given in Table 43.

Table 42. Nitration of m*-xylene with* KNO_3 *in the presence of* $AlCl_3$ (21 g *m*-xylene, 10 g KNO_3, 4 g $AlCl_3$)

No. of expt.	Temperature of bath (°C)	Yield mononitroxylene			Yield dinitroxylene		
		(g)	(% of theoretical calculated on xylene taken)	(% of theoretical calculated on nitrate taken)	(g)	(% of theoretical calculated on xylene taken)	(% of theoretical calculated on nitrate taken)
1	Without heating	4·1	13·6	27·0	1·5	3·8	7·65
2		4·2	13·9	27·8	1·2	3·1	6·2
3	45– 50	3·4	11·3	22·5	1·8	4·6	9·2
4	105–110	2·4	7·9	15·9	2·0	5·1	10·2
5		2·6	8·6	17·2	2·1	5·3	10·6

Table 43. Nitration of benzene with KNO_3 *in the presence of* $FeCl_3$ *and* $SiCl_4$

No. of expt.	Activator	Yield nitrobenzene		Recovered benzene		Yield nitrobenzene calculated on reacted benzene (% of theoretical)	Yield calculated on nitrate taken (% of theoretical)
		(g)	(% of theoretical calculated on benzene taken)	(g)	(% of benzene taken)		
1	$FeCl_3$	3·1	10·3	16	84	65·3	20·2
2	$FeCl_3$	3·3	11·0	15	80	52·5	21·4
3	$SiCl_4$	5·2	3·3	69	88·4	36·6	8·45
4	$SiCl_4$	4·8	3·8	72	92·2	50·7	7·8

Comparing these results with the data obtained on nitration in the presence of $AlCl_3$ (see Table 37) it may be concluded that $FeCl_3$ is a less active catalyst than $AlCl_3$ which gives yields of nitrobenzene around 38 per cent calculated on nitrate and 70 per cent calculated on reacted benzene. $SiCl_4$ is an even less active catalyst (yield calculated on nitrate is one-fifth of that obtained in the presence of $AlCl_3$).

III. NITRATION IN THE PRESENCE OF BF_3

Boron fluoride is known to have extensive application as catalyst in organic syntheses owing to its ability to form intermediate complexes with aromatic compounds possessing active properties. Thus, for example, NIEUWLAND and collaborators [22] used BF_3 as catalyst during condensation of propylene with organic acids (acetic, chloroacetic, dichloroacetic, benzoic, etc.) to give the corresponding esters. The reaction was carried out at 70°C and pressure 25 mm above atmospheric (without catalyst this reaction only occurred at high temperatures and pressures).

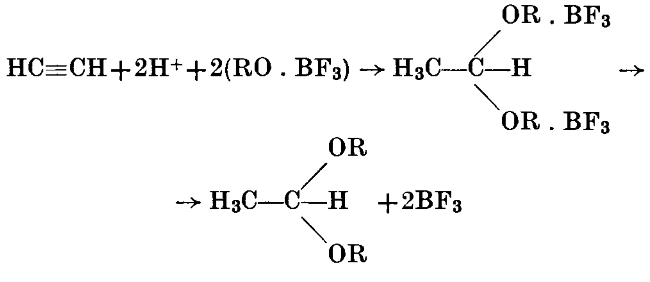
According to the same investigator [23], olefines also condense with hydroxyacids (salicylic, *p*-hydroxybenzoic, *m*-hydroxybenzoic, etc.) in the presence of BF_3. Propylene, for example, condenses with salicylic acid to form *iso*propylsalicylate and ring-alkylated esters of salicylic acid. The process occurs so that propylene first condenses with salicylic acid giving *iso*propylsalicylate, which then isomerizes with the *iso*propyl group entering the benzene ring. The mechanism of the action of boron fluoride in this case evidently consists of forming a complex with salicylic acid by combining with the oxygen atom of the hydroxyl in the —COOH group; this increases the mobility of the carboxyl group hydrogen atom which makes condensation of the acid with the olefine possible. The ester formed then combines with BF_3. This weakens the bond between oxygen and the hydrocarbon radical, facilitating isomerization.

Boron fluoride can be used for condensation of olefines with aromatic hydrocarbons [24]. Benzene, for instance, condenses with propylene in sulphuric acid medium forming mono- and di*iso*propylbenzene; the product is *p*-di*iso*propylbenzene in this case, as distinct from *m*-di*iso*propylbenzene which is formed when the reaction is carried out in the presence of $AlCl_3$. Benzene also condenses with ethylene and butylene.

Boron fluoride is also used as catalyst during condensation of olefines with phenols [25], the condensation being accompanied by isomerization as in the case of salicylic acid. In the presence of boron fluoride acetylene condenses with monatomic alcohols [26], glycols and hydroxy-acids [27] and with carboxylic acids [28].

The mechanism of condensation of alcohols with acetylene leading to the synthesis of acetals consists, it is supposed, of the following: the molecular complex formed by interaction of alcohol with BF_3 reacts in the ionized form with acetylene; a new complex is thus formed which decomposes into acetal and boron fluoride:

$$2ROH + 2BF_3 \rightarrow 2ROH\,.\,BF_3 \rightarrow 2H^+ + 2(RO\,.\,BF_3)^-$$



$$HC\equiv CH + 2H^+ + 2(RO\,.\,BF_3) \rightarrow H_3C\text{—}\overset{\displaystyle OR\,.\,BF_3}{\underset{\displaystyle OR\,.\,BF_3}{C}}\text{—}H \rightarrow$$

$$\rightarrow H_3C\text{—}\overset{\displaystyle OR}{\underset{\displaystyle OR}{C}}\text{—}H \;+ 2BF_3$$

In the same way hydroxy compounds condense with acetylene derivatives in the presence of BF_3 [29, 30].

It must also be noted that boron fluoride can be successfully used instead of $AlCl_3$ in the Friedl–Crafts reaction owing to its tendency to form complexes with organic compounds. Thus benzene homologues, for example, can be prepared by condensing it with alkyl halides with the help of boron fluoride: benzene, toluene and anisole give the corresponding ketones when treated with acetic anhydride in the presence of BF_3 [31].

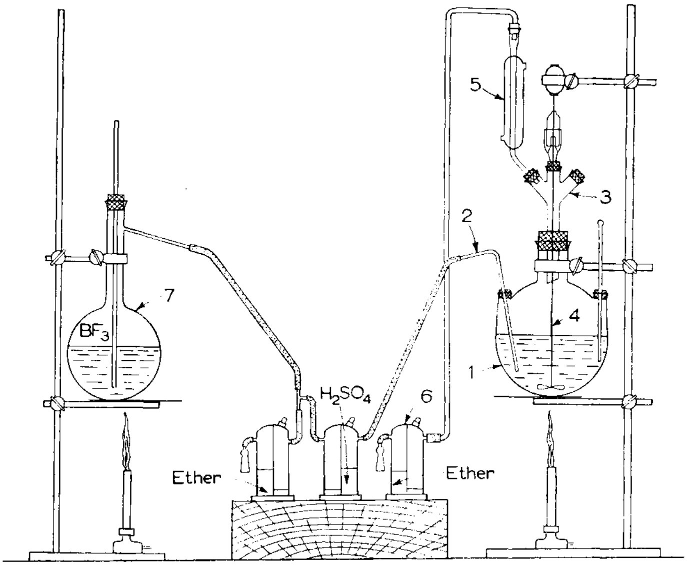


Fig. 6. Apparatus for nitration of organic compounds with nitrate in the presence of BF_3.

Considering the above-mentioned catalytic properties of boron fluoride and its ability to replace $AlCl_3$ in the Friedl–Crafts reaction the author of the present book made an attempt to use boron fluoride as a catalyst for nitration of organic compounds with nitric acid salts. Results of some of these experiments are given below.

A round-bottomed, three-necked flask (1) (Fig. 6) was used as nitrator; it was fitted with a three-necked adapter (3) with the shaft of the stirrer (4) passing down the central neck; one of the side tubes of the adapter was connected to a condensation–absorption system consisting of a condenser (5) and a Tishchenko flask (6) with ether in which the unreacted boron fluoride was absorbed. Boron fluoride entered the reaction vessel from apparatus (7), where it was synthesized, along tube (2) which passed through the left neck of the reaction flask (1). Boron fluoride needed for the experiments was obtained by mixing 20 g B_2O_3, 40 g CaF_2 and 200 g H_2SO_4 sp. gr. 1·84. The reaction followed the equation:

$$3CaF_2+3H_2SO_4+B_2O_3 \rightarrow 3CaSO_4+3H_2O+2BF_3$$

The starting materials used for the preparation of boron fluoride were pure crystalline CaF_2 (fluorite) and boric anhydride obtained by heating commercial boric acid at 800–1000°C (in a muffle) until no more bubbles of H_2O were evolved. These were pulverized and mixed together. The mixture was placed into a 500 ml Würtz flask and covered with sulphuric acid. During the reaction the flask was shaken from time to time to facilitate the passage of boron fluoride through the thick reaction mixture. The boron flouride so formed was led through a Tishchenko bottle with sulphuric acid prior to entering the nitrator.

Nitration of Benzene

Experiments on the nitration of benzene with potassium nitrate were conducted as follows: the mixture of 0·5 mole KNO_3 and 1 mole benzene was saturated, with stirring, by BF_3 which was admitted from the Würtz flask in which it was synthesized. The experiments were carried out both with and without external heating (on a water or a vaseline bath). When nitration was performed without external heating the temperature of the reaction mixture rose rapidly to 34–38°C owing to the exothermic nature of the reaction, and then more slowly to 55–57°C. At the end of saturation with boron fluoride the dark brown reaction mixture separated into a liquid portion and a precipitate which settled to the bottom of the flask. The liquid was separated from the precipitate, washed with water, then with soda solution and after drying over calcium chloride it was distilled (benzene distilled over first, followed by nitrobenzene at 207–210°C). The solid precipitate was steam-distilled to obtain the nitrobenzene adsorbed by it.

Tables 44 and 45 show the results of experiments on nitration of benzene with potassium nitrate in the presence of BF_3 conducted with different duration (Table 44) and at different temperatures (Table 45).

Data in Table 44 indicate that nitration of benzene with potassium nitrate in the presence of BF_3 gives better yields of nitrobenzene if the duration of the process is increased from 30 min to 3 hr. As regards the influence of temperature on the yield of nitrobenzene prepared by this method, Table 45 shows that the best results are obtained without external heating.

Nitration of Toluene and m-*Xylene*

Tables 46 and 47 give results of experiments on nitration of toluene and *m*-xylene.

Table 44. *Nitration of benzene with potassium nitrate in the presence of* BF_3 *without external heating*
(78 g benzene, 50 g KNO_3 and BF_3 obtained from 40 g CaF_2)

No. of expt.	Duration of experiment (min)	Maximal temperature of exothermic reaction (°C)	Yield nitrobenzene		Recovered benzene		Yield nitrobenzene calculated on reacted benzene (% of theoretical)	Yield calculated on nitrate (% of theoretical)
			(g)	(% of theoretical calculated on benzene taken)	(g)	(% of benzene taken)		
1	30	35–36	3	2·4	70	89·6	23·8	4·9
2	40	35–38	5	4·1	68	87·2	31·7	8·1
3	50	35–38	8	6·5	63	80·6	33·8	13·0
4	120	45–58	12	9·7	58	74·3	38·1	19·5
5	150	55–57	17	13·8	57	73·0	51·4	27·6
6	180	55–57	21	17·0	54	69·2	55·5	34·1
7	300	55–57	20·6	16·7	53	67·9	52·3	33·5

Table 45. *Nitration of benzene with potassium nitrate in the presence of* BF_3 *at different temperatures*
(78 g benzene, 50 g KNO_3 and BF_3 obtained from 40 g CaF_2)

No. of expt.	Temperature (°C)	Yield nitrobenzene		Recovered benzene		Yield nitrobenzene calculated on reacted benzene (% of theoretical)	Yield calculated on nitrate (% of theoretical)
		(g)	(% of theoretical calculated on benzene taken)	(g)	(% of benzene taken)		
1	without heating	21	17·1	55	70·5	57·9	34·1
2	max. temp. of exothermic reaction 57°C	21·2	17·2	54	69·2	56·0	34·4
3	90–95 (temp. of bath)	11	9·0	63	80·8	46·5	17·9
4	90–95 (temp. of bath)	12·2	9·9	62	79·5	48·3	19·8

Analysis of the results of these experiments can lead to the conclusion that the process is analogous to nitration with nitrates in the presence of aluminium chloride; the optimal conditions are reached when the reaction is carried out without external heating for 3 hr. Raising the temperature lowers the yield of nitro products, evidently as a consequence of decomposition of the aromatic compound—BF_3 complex at high temperatures.

Table 46. *Nitration of toluene with* KNO_3 *in the presence of* BF_3
(92·1 g toluene, 50 g KNO_3 and BF_3 obtained from 40 g CaF_2)

No. of expt.	Maximal temperature of exothermic reaction (°C)	Yield nitrotoluene		Recovered toluene		Yield of nitrotoluene calculated on reacted toluene (% of theoretical)	Yield calculated on nitrate (% of theoretical)
		(g)	(% of theoretical calculated on toluene taken)	(g)	(% of toluene taken)		
1	40	23·8	17·4	71	77·1	76·2	34·7
2	40	24·3	17·7	69	75·0	70·9	35·5

Table 47. *Nitration of* m-*xylene with* KNO_3 *in the presence of* BF_3
(11 g *m*-xylene, 10 g KNO_3 and BF_3 obtained from 40 g CaF_2)

No. of expt.	Maximal temperature of exothermic reaction (°C)	Yield mononitroxylene		Yield dinitroxylene	
		(g)	(% of theoretical calculated on nitrate taken)	(g)	(% of theoretical calculated on nitrate taken)
1	35	3·6	23·8	1·1	5·6
2	35	3·4	22·6	1·3	6·6

Preparation of Dinitro Derivatives

In order to discover whether it would be possible to introduce several nitro groups into the aromatic ring by means of nitrates in the presence of BF_3, experiments on nitration of nitrobenzene with potassium nitrate were carried out.

Boron fluoride (obtained from 20 g CaF_2 and 10 g B_2O_3) was passed, with stirring, into a mixture of nitrobenzene (0·8 mole) and KNO_3 (0·25 g) for a period of 3 hr. At the end of the experiment the liquid layer was poured off, the precipitate left in the flask was washed with ether and the ethereal solution was pooled with the liquid layer. After drying over calcium chloride first ether and then nitrobenzene were distilled off from the liquid; the residue was cooled and the solid so obtained was recrystallized several times from alcohol, giving crystals of dinitrobenzene m.p. 87–88°C.

The experiments showed (Table 48) that nitration without external heating, i.e. at 25–30°C gave only very small yields of dinitrobenzene (1·2 per cent calculated on nitrate and 18 per cent calculated on reacted nitrobenzene). The yield increased when external heating was applied (bath temperature 95–100°C) the maximal yield being 9 per cent calculated on nitrate and 40 per cent calculated on reacted nitrobenzene.

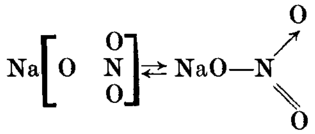
These results indicate that introduction of a second nitro group into the aromatic ring by means of nitration with KNO_3 in the presence of BF_3 is considerably more difficult than introduction of the first.

Table 48. ***Preparation of dinitro derivatives of benzene***
(nitration of nitrobenzene with KNO_3 in the presence of BF_3)

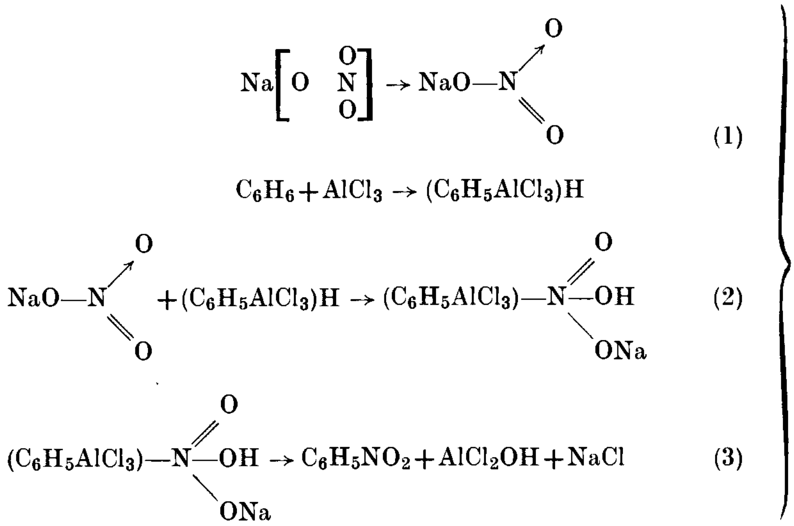
No. of expt.	Temperature of bath (°C)	Dinitrobenzene obtained (g)	Dinitrobenzene obtained (% of theoretical calculated on nitrobenzene taken)	Recovered nitrobenzene (g)	Recovered nitrobenzene (% of nitrobenzene taken)	Yield of dinitrobenzene calculated on reacted nitrobenzene (% of theoretical)	Yield of dinitrobenzene calculated on nitrate (% of theoretical)
1	Without heating	0·5	0·36	98	98	18·4	1·2
2	95–100	3·2	2·3	94	94	39·2	7·6
3	95–100	3·8	2·8	93	93	39·9	9·1

IV. MECHANISM OF NITRATION OF AROMATIC COMPOUNDS WITH INORGANIC NITRATES IN THE PRESENCE OF ACTIVATORS ($AlCl_3$ AND BF_3)

The author of the present book proposes the following interpretation of the mechanism of nitrating aromatic compounds with inorganic nitrates in the presence of $AlCl_3$ which brings it in line with the Friedl–Crafts reaction. Accepting HANTZSCH's concept of the structure of nitric acid, an equilibrium can be supposed to exist between the pseudo form and the true form of nitric acid salts, the equilibrium being shifted towards the true form, i.e. the latter being predominant:



When the reaction is carried out in the presence of $AlCl_3$ the equilibrium is disturbed with a shift towards the formation of the pseudo form since this form can react with the aluminium chloride activated molecule of benzene (with the $C_6H_5AlCl_3H$ complex). When the pseudo form of nitrate interacts with this complex the hydrogen from the outer sphere of the complex migrates to the oxygen of the nitrate which is linked with nitrogen by a semi-polar bond [equation (2)]; the addition product formed then decomposes according to equation (3) giving the nitro derivative:



(I)

We have also checked experimentally the possibility of the reaction following a different course, based on the assumption that free nitric acid could be formed as the result of hydrolysis of $AlCl_3$ under the influence of moisture penetrating into the reaction vessel from the outside, and subsequent decomposition of nitrate by HCl. In such a case nitric acid could act as the nitrating agent

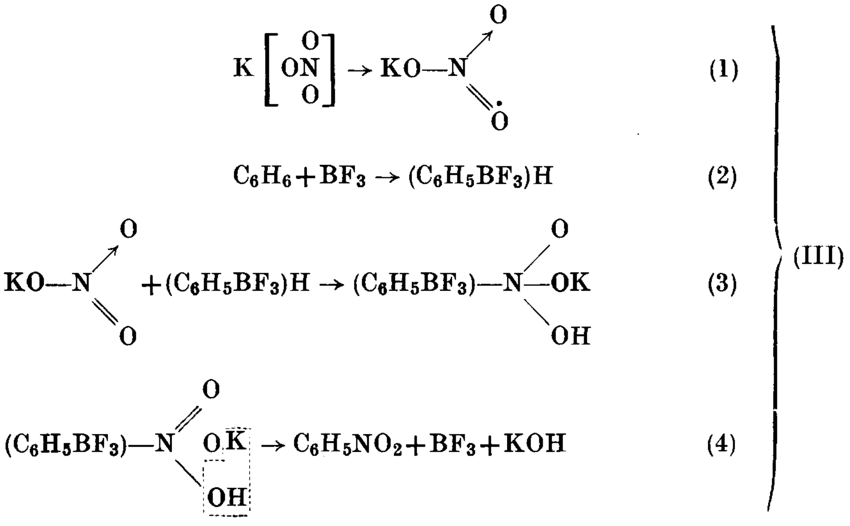
$$\left.\begin{aligned} &AlCl_3+3HOH \rightarrow Al(OH)_3+3HCl \\ &HCl+KNO_3 \rightarrow HNO_3+KCl \\ &C_6H_6+HNO_3 \rightarrow C_6H_5NO_2+H_2O \end{aligned}\right\} \text{(II)}$$

To check this scheme (II) experiments were staged on nitration of aromatic compounds with nitrates in the presence of HCl. The reaction mixture (1 mole benzene and 0·5 mole KNO_3) was saturated with dry hydrogen chloride at 40–45°C, i.e. at that temperature which prevails in the reaction mixture when the reaction is conducted in the presence of $AlCl_3$ (without external heating). It was found experimentally that in the presence of HCl only insignificant amounts of nitrobenzene were formed.

In another series of experiments the reaction was carried out with $AlCl_3$ as activator and simultaneous saturation of the mixture with hydrogen chloride. Introduction of hydrogen chloride lowered the yield of nitrobenzene considerably. It was thus shown that the assumption that free nitric acid formed from nitrate acted as the nitrating agent in this reaction was untenable on experimental evidence

The mechanism of nitration with nitrates in the presence of BF_3 in our opinion corresponds to the scheme proposed by us for nitration in the presence of $AlCl_3$. Taking benzene as an example the reaction with KNO_3 can be visualized as follows:

As equations (I) and (III) indicate the reaction mechanism in the presence of activators (BF_3 and $AlCl_3$) consists of the following stages: (1) transition of the true form of nitrate to pseudo form; (2) formation of a complex compound between the substance undergoing nitration and the activator; (3) formation of a triple complex aromatic compound–activator–nitrate; (4) decomposition of the triple complex leading to the formation of nitrobenzene and regeneration of the activator (one of the reaction products is the hydroxide of the metal whose nitrate acts as the nitrating agent).



The following conclusions can be reached concerning the distinctive features of nitration with inorganic nitrates on the basis of the experimental material obtained:

(1) Nitration with nitrates in the presence of activators ($AlCl_3$ and BF_3) gives sufficiently good yields, and the unreacted aromatic compound can be easily recovered by distillation from the reaction mixture.

(2) The most active nitrate is that of silver, $AgNO_3$; the less active alkali metal nitrates (KNO_3 and $NaNO_3$) nonetheless give satisfactory results. When benzene, for example, is nitrated with KNO_3 in the presence of $AlCl_3$ a 70 per cent yield calculated on reacted benzene is obtained (38 per cent calculated on nitrate); with $NaNO_3$ the yield is 73 per cent (34 per cent calculated on nitrate). Ammonium, barium and lead nitrates are still less reactive.

(3) The most active catalysts are $AlCl_3$ and BF_3 (the latter rather less so than the former), $FeCl_3$ is less active and $SiCl_4$ is little active.

(4) Nitration with nitrates proceeds most satisfactorily at normal temperature and excess of the aromatic compound which acts as solvent; nitrate is used in the solid state and hence stirring during the reaction is essential.

(5) Nitration with inorganic nitrates is not accompanied by oxidative reactions.

In no experiments on nitration of aromatic compounds with inorganic nitrates (by our method) were oxidation products detected. This method is more convenient than nitration with organic nitrates which is associated with side-products resulting from decomposition of the nitrate on interaction with the compound being nitrated.

The question of practical application of nitration with inorganic nitrates requires further study and development.

3. NITRATION WITH NITROXYL CHLORIDE

Nitroxyl chloride $ClNO_2$ can be regarded as chloroanhydride of nitric acid. Nitroxyl chloride is prepared as follows [32]: to fuming nitric acid (400 g) at 0°C is added dropwise 30 per cent oleum (644 g) followed by chlorosulphonic acid (370 g) over 12 hr; the mixture is allowed to stand at 20°C for 1 hr. Nitroxyl chloride is collected in a dry-ice cooled receiving vessel; b.p. 15–16°C, yield 91 per cent of the theoretical.

Nitroxyl chloride can be used for nitration of moderately active aromatic compounds, usually in the presence of catalysts (HF, $AlCl_3$, BF_3). Highly reactive aromatic compounds are strongly oxidized by nitroxyl chloride; thus phenol gives traces of *o*- and *p*-nitrophenol, anisole—traces of *o*-nitrophenol, diphenyl ether—7 per cent 4-nitrodiphenyl ether, N-dimethylaniline forms a tar, naphthalene gives 1-nitronaphthalene with a yield 26–31 per cent of the theoretical. When naphthalene is nitrated a mixture of α-nitronaphthalene and α-chloronitronaphthalene is obtained [32].

Benzoic acid, chlorobenzoic acid, *p*-toluic acid, nitrobenzene, *p*-nitrotoluene, acetophenone and benzaldehyde do not react with nitroxyl chloride.

Price and collaborators [33] achieved nitration with nitroxyl chloride in the following way. To aromatic compound (0·2 mole) in CS_2 (100 ml) was added $AlCl_3$ (0·25 mole) at 0°C and nitroxyl chloride (0·25 mole). The mixture was stirred for 1–2 hr at 0°C and allowed to stand at 20°C until nitroxyl chloride disappeared. It was then poured onto ice and nitrobenzene obtained from benzene with a 27–35 per cent yield (without catalyst; after mixing all the components, boiling was continued for 12 hr). With catalyst (HF or $AlCl_3$) and ratio of reactants 0·5 mole benzene and 0·55 mole nitroxyl chloride and 250 ml liquid HF the yield of nitrobenzene reached 70–89 per cent.

Toluene gives *o*- and *p*-nitrotoluene (47 and 24 per cent), bromotoluene gives 2- and 3-nitro-4-bromotoluene (23 and 16 per cent), bromobenzene—*p*- and *o*-nitrobromobenzene (67 and 8 per cent), dichlorobenzene—2 : 4-dichloronitrobenzene (31 per cent) and salicylic acid gives 5-nitrosalicylic acid (58 per cent).

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