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THEORY OF THE NITRATION OF SATURATED HYDROCARBONS AND OF SIDE CHAINS OF ARYL PARAFFINS

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/Comment: The author of this article has been identified with the Military Academy imeni K. Ye. Voroshilov, where he is known to have been active during 1947 - 1950.

Numbers in brackets refer to appended bibliography. Tables referred to are appended./

I. INTRODUCTION

The chemical nature of the reactions of nitration of saturated hydrocarbons and of side chains of aryl paraffins proved to be the same, thus permitting these reactions to be consolidated under the common term "nitration of the paraffin chain" and to be distinguished from the nitration of the aromatic nucleus.

It is well known that nitration of aromatic hydrocarbons proceeds very easily and smoothly. Undoubtedly this circumstance enabled the discovery of this reaction in 1834 by Mitscherlich soon after benzene became known to chemists.

The nitration of the paraffin chain is entirely different. For a long time attempts to accomplish this reaction were unsuccessful. Not until 50 years after Mitscherlich, did Konovalov (in 1888) find the well-known classical method of nitrating paraffin chains. This method consists of heating the hydrocarbon with dilute nitric acid in a sealed tube. Since then, investigation of the nitration of the paraffin chain has become a traditional line of work with Russian organic chemists. The fundamental work of M. I. Konovalov, V. V. Markovnikov, and S. S. Nametkin brilliantly answered many questions on the nitration of the paraffin chain for a variety of problems in classical organic chemistry and laid the groundwork for future development in this field.

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In the past, the investigation of the nitration of the paraffin chain was burdened with exceptionally great difficulties due to the necessity of carrying out the work in tens and hundreds of sealed tubes, the nonuniformity of the reaction product, frequent preponderance of oxidation products, and, as a rule, a very slow rate of reaction.

Because the conditions required for successful nitration do not lend themselves to satisfactory estimation, there were sharp diversities in results not only among various authors, but also for the same worker. Thus, M. I. Konovalov was successful in obtaining phenylnitromethane in good yield by heating toluene with nitric acid of s.g. 1.12 over a period of 48 hours on a water bath. Hantzsch, Holleman, and Van-Raalte [2], nitrating toleune in the side chain independently of each other, did not detect the formation of phenylnitromethane at all or obtained only a few drops of it. Shorygin [2] similarly was unsuccessful in obtaining satisfactory yields [of this product] and his attempts at clarifying the reasons for his failure were also unsuccessful. Konovalov [3] noted the strong fluctuation in yields of nitrocompounds; for example, the best results were obtained in tubes having a high pressure or by reusing previously used nitric acid.

In recent times a number of new methods for nitrating the paraffin chain have been discovered and new ways in which this reaction may proceed clarified.

Shorgyin and Topchiyev were the first to accomplish nitration of the paraffin chain in the gaseous phase [4, 5]; they were followed by Urbansky and Slon [6, 7] and by Hass and co-workers [8]. These investigations led to the development of a method of high-temperature nitration of the simplest paraffins using nitric acid in the vapor phase. Titov [9] published a series of new methods of nitration using nitrogen dioxide and concentrated nitric acid. As a result of Titov's investigations, ways of modifying and improving earlier methods were found, and a study of new directions in which this reaction may proceed was carried out. Nitroparaffins are becoming industrial products and their utilization in various phases of technology receives much attention [5]. All of this makes it necessary to clarify the essence of the nitration of the paraffin chain and thus acquire the ability to control all possible directions of this reaction. The author of the present report hopes - and experiment thus far supports this hope - that the theory being developed by him is correct and that it sets the course for the solution of this problem.

II. CONCEPTS OF MECHANISM OF REACTION DEVELOPED OVER PERIOD 1935 - 1945

Concepts in regard to the nature of the nitration of the paraffin chain developed during the period 1935 - 1945 usually failed to account for the complexity of this reaction and its peculiarities. Until the publication of our work and even after its publication, the conviction existed that the mechanism of the nitration process could be satisfactorily represented as an ordinary double decomposition reaction:

$$\text{R-H} + \text{HO-NO}_2 = \text{R-NO}_2 + \text{H-OH} \tag{1}$$

Thus, as late as 1942 Feiser maintained that "in the nitration of alkanes (according to Konovalov and Markovnikov) using dilute nitric acid and in the nitration of the side chain of toluene under the same conditions, substitution of this type undoubtedly takes place" [10].

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Ingold [11] at one time considered nitration of the paraffin chain as an organic reaction which proceeds according to the bimolecular type of electrophyllic substitution S_E2. He adopted the same mechanism for the nitration of the aromatic ring and for that of paraffinic chains and expressed it by a scheme analogous to (1), indicating the fate of the valence electrons of the ruptured bonds more precisely:

$$R{:}H + HO{:}NO_2 \rightarrow R{:}NO_2 + H{:}OH \qquad (2)$$

This view on the nature of nitration was generally accepted by the English chemical school and also among many American chemists (Remick [12] and others). Robinson [13] advocated a complex reaction mechanism involving participation of the quinoid form in the nitration of the side chain of aryl paraffins, but this hypothesis was not upheld experimentally.

Usanovich [14], striving to explain why nitric acid must be diluted in the Konovalov nitration, advanced a hypothesis which assumes preliminary combination of a hydrocarbon complex with a nitrate ion:

$$R\text{-}CH_3 + NO_3^- \rightleftarrows RCH_2NO_2(OH^-) \qquad (3)$$

followed by the formation of a nitrocompound upon reaction with an oxonium cation.

$$RCH_2NO_2(OH^-) + H_3O^+ \rightarrow RCH_2NO_2 + 2H_2O \qquad (4)$$

Until recently, Huckel shared understanding of the nitration of the paraffin chain in the sense of scheme (1). Being unaware of our work or at any rate not referring to it, he expressed some doubts as to the correctness of the traditional theory only in his last papers [15].

In 1938, after the appearance of our work, McCleary and Degering [16] proposed a chain mechanism involving participation of free radicals for the vapor phase nitration at high temperatures:

$$HONO_2 \xrightarrow{heat} HO\cdot + NO_2 \qquad (5)$$

$$R\text{-}H + HO\cdot \rightarrow R\cdot + H_2O \qquad (6)$$

$$R\cdot + HONO_2 \rightarrow R\text{-}NO_2 + HO\cdot \text{ etc.} \qquad (7)$$

According to this hypothesis, thermal decomposition of nitric acid initiates the formation of free hydroxyls (equation 5) which collide with hydrocarbons and form R·. Interaction of the radical with nitric acid yields nitrocompounds, at the same time regenerating free hydroxyls and thus continuing the reaction cycle.

The error of these and similar hypotheses is now indisputably proved by experimental investigation, partly by discovering the absence of any reaction between nitric acid as such and the paraffin chain [17]. In these same investigations it was established that nitration of the paraffin chain proceeds, as a rule, through a preliminary reaction of the hydrocarbon and a monomer of nitrogen dioxide NO_2. Some exceptions to this rule will be discussed later.

The central point of the paraffin chain nitration theory developed by the author is the assumption that the first elementary stage of the reaction is the formation of a free alkyl radical. As a rule, this occurs when a hydrocarbon collides with an electrophyllic and radical-like molecule of the monomer of nitrogen dioxide NO_2:

$$R\text{-}H + NO_2 \rightarrow R\cdot + HNO_2 \qquad (8)$$

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Conversion of the alkyl radical in the sphere of the reaction leads to the complex mixture of products observed; for example, the formation of nitrocompounds comes about by way of a combination of alkyl with NO_2:

$$R\cdot + NO_2 \longrightarrow R\text{-}NO_2 \qquad (9)$$

This theory permitted a rational explanation of the data accumulated by earlier workers and, what is even more important, led to the discovery of many new chemical phenomena in this field and of directions of the reaction which were unexpected from the old point of view.

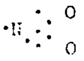
After we had experimentally clarified the role of NO_2 as a catalyst, we discovered that the idea to the effect that lower oxygen compounds of nitrogen play the part of a catalyst in the nitration with nitric acid was not altogether foreign to earlier investigators. In 1871 Mills [18] expressed this idea while investigating the nitration of chloroform. A number of observations led Konovalov to the thought that "nitrous acid promotes nitration (or, perhaps, the start of nitration)." This thought was expressed by Konovalov [19, 20] in 1893 and in 1901. Apparently, unfavorable results of some of the experiments and accidental circumstances precluded this idea from having an influence on the basic line of research and on the theoretical views of Konovalov. In his last paper, he arrived at the conclusion that no nitration catalysts have been found in the case of nitric acid, and that the search for them is a problem for future investigation [21]. In 1914, Nametkin [22] pointed out the importance of clarifying the role of nitrous acid to understand the mechanism of the action of nitric acid on saturated compounds.

The author started the study of the nitration of the paraffin chain by studying the reaction between nitrogen dioxide and toluene [23]. The first to observe a reaction between the oxides of nitrogen and a paraffin was Markovnikov in the case of octanaphthene [24]. He discovered, as he briefly stated, "the formation of compounds containing nitrogen in an oxidized form". In 1919 - 1921, Granacher obtained a mixture of carboxylic acids by the action of nitrogen dioxide on paraffin and undecane [25]. Schaarschmidt's investigation of this reaction [26] did not yield any results of value. Using toluene, he was able to isolate benzaldehyde, benzoic acid, and, as he figured, nitrocresols and nitrotoluenes. Working with m-xylene and mesitylene [27], Schaarschmidt observed only the formation of resinous products (compare page 21). The investigations of Monty, Martello, and Franco [28] on the action of nitrogen dioxide on diphenylmethane did not yield any results (compare page [illegible]); Pass and Jonson, checking the effect of sunlight and light from a mercury-vapor lamp on the reaction of toluene with nitrogen dioxide, detected only the formation of benzoic acid [29].

The first problem in the study of the action of nitrogen dioxide on toluene was clarification of the effect of the degree of dissociation of the dimer of nitrogen dioxide (see equation 10) on the course of the reaction

$$N_2O_4 \rightleftarrows 2NO_2 \qquad (10)$$

and the consequent appearance of a specific chemical effect produced by the monomeric form of nitrogen dioxide, i.e., by a particle with an unpaired electron [29]



With this aim the experiment was made of reacting nitrogen dioxide with toluene at a very high dilution of the nitrogen dioxide with the hydrocarbon. Quite unexpectedly, the main product of the reaction was phenyldinitromethane $C_6H_5CH(NO_2)_2$. Previously, this compound was not detected in the nitration of toluene, notwithstanding numerous investigations of this process. At a low dilution of nitrogen dioxide (1:2) the reaction led principally to the formation of benzoic acid.

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Contrary to the usual rule, raising the temperature in the case of high dilution lowered the yield of phenyldinitromethane. It was also found that sunlight and light from a mercury-vapor lamp do not greatly affect the direction of the reaction. The author expressed the thought that this line of investigation can be helpful in clarifying many questions concerning Konovalov's reaction, i.e., the nitration of the paraffinic chain with nitric acid.

At the time this investigation was going on, the work of Shorygin and Topchiyev was published [4]. This was a study of the reaction between toluene and an excess of nitrogen dioxide in the gaseous phase. In addition to the presence of the main reaction product - a mixture of nitrotoluenes - the authors established the formation of phenylnitromethane. The investigators assumed that phenylnitromethane is formed by addition of the dimer of nitrogen dioxide to the semicyclic double bond of the orthoquinoid form of toluene with a subsequent splitting off of nitric acid from the addition product. They also proved that nitroderivatives of cyclohexane and n-hexane form under analogous conditions. Illumination with a mercury-vapor lamp had no effect on the reaction, according to the data of these authors. Urbansky and Slon, carrying out the reaction according to the Shorygin-Topchiyev method at 200°, obtained nitroderivatives of some other paraffins [6, 7].

In his next work, the author of the present paper has shown that the activity of nitrogen dioxide in the reaction with the paraffinic chain of toluene strongly increases with an increase in the degree of dissociation of the dimer N_2O_4 to the monomeric molecule NO_2 [30]. Thus, when a mixture of 11 g of nitrogen dioxide and 25 g of toluene was left standing for a period of 6 days at 25-30°, the proportion of the nitrogen dioxide entering the reaction was about 28%. By increasing the amount of toluene to 500 g, this proportion was raised to 85%. The yield of phenylnitromethane in the first case was less than one g, and in the second case, with a greater dilution of nitrogen dioxide, it reached almost 8 g.

In this work, the idea was first advanced that the beginning stage of the reaction between oxides of nitrogen and toluene, which determines the rate of formation of the end products, is the formation of the free benzyl radical $C_6H_5CH_2\cdot$ on collision of a hydrocarbon molecule with a monomer of nitrogen dioxide.

$$C_6H_5CH_2\text{-}H + NO_2 \longrightarrow C_6H_5CH_2\cdot + HNO_2 \qquad (11)$$

The formation of phenylnitromethane, according to this work, takes place through the union of a free benzyl radical with NO_2

$$C_6H_5CH_2\cdot + NO_2 \rightarrow C_6H_5CH_2\text{-}NO_2 \qquad (12)$$

In support of the latter conclusion, the fact of the rapid combination of a monomer of nitrogen dioxide with a free triphenylmethyl radical and the formation of nitromethane on electrolysis of a solution of a mixture of actate and nitrate was mentioned. For this reaction, the author suggested the following probable mechanism back in 1931 [31]:

$$CH_3COO^- - e \rightarrow CH_3COO\cdot \rightarrow CH_3\cdot + CO_2 \qquad (13)$$

(e - electron, the dot - an unpaired electron or a free valency)

$$NO_2^- - e \rightarrow O{=}N\text{-}O\cdot \rightarrow O{=}N{=}O \qquad (14)$$

$$CH_3\cdot + \cdot NO_2 \rightarrow CH_3NO_2 \qquad (15)$$

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A support for the assumption that there is formation of free radicals during the reaction of nitrogen dioxide with hydrocarbons is furnished by the fact that the author observed great increase in the reaction rate in the series toluene, diphenylmethane, triphenylmethane parallel to increasing ease of formation of the corresponding radicals. Together with the above-stated manner of the formation of phenylnitromethane, a chain reaction mechanism involving a dimer of N_2O_4 was also considered to be probable:

$$R\cdot + N_2O_4 \rightarrow RNO_2 + NO_2^*; \quad R\text{-}H + NO_2^* \rightarrow R\cdot \text{ etc.} \qquad (16)$$

In that paper [31] a mechanism for the formation of phenyldinitromethane was also proposed. The validity of this mechanism was fully confirmed later.

The results of the investigation were utilized for the preliminary explanation of the characteristics of the nitration of saturated hydrocarbons and side chains of alkylbenzenes with nitric acid. It was postulated that the active agent in this reaction is the monomeric form of nitrogen dioxide, reacting by equations of the types (11) and (12). Nitric acid, according to this interpretation, is merely a medium for the regeneration of NO_2 in a reaction with the nitrous acid that arises in the first stage

$$R\text{-}H + NO_2 \rightarrow R\cdot + HNO_2 \qquad (17)$$

$$HNO_2 + HNO_3 \rightleftarrows 2NO_2 + H_2O$$

or by reaction with nitric oxide which forms copiously during the various side processes of oxidation

$$NO + 2HNO_2 \rightleftarrows 3NO_2 + H_2O \qquad (18)$$

These reactions lead to a progressive growth in the concentration of nitrogen dioxide and nitric oxide in the hydrocarbon layer. This is favored by carrying out the reaction in hermetically sealed apparatus such as the sealed tubes of Konovalov's method. Therefore, in the final analysis, nitration with nitric acid must have the same results as that with oxides of nitrogen under corresponding conditions.

To prove these conclusions, the investigation of the action of nitric acid on toluene under conditions theoretically favorable for the formation of phenyldinitromethane (these conditions will be described in more detail below) was undertaken. Experiment confirmed theoretical conclusions - at a relatively high concentration of nitric oxide, phenyldinitromethane was the main reaction product. For example, the reaction in a mixture of 100 milliliter nitric acid sg 1.42, 50 g anhydrous calcium nitrate and an excess of toluene left standing for a period of 20 days led to the formation of 21 g phenyldinitromethane, 9 g phenylnitromethane, 5 g benzaldehyde, and 38 g of residual oil that has not been examined further. The high concentration of nitric oxide in this experiment was manifested by the green color of the hydrocarbon layer in which the reaction took place. This was also when the first observations on the great part that diffusion plays in the nitration of the paraffinic chain with nitric acid were made.

III. PRINCIPAL POSTULATES OF THEORY OF NITRATION OF PARAFFIN CHAIN

The stated results served as a basis for broad experimental research on the nitration of the paraffin chain with oxides of nitrogen as well as with nitric acid and led to the formulation of a general theory for this reaction. The most important conclusions of the investigations are formulated in the following statements [32].

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1. Nitric acid molecules do not have an independent nitrating effect on the paraffin chain. In the reaction of nitration, nitric acid is merely a source and medium for the progressive regeneration of oxides of nitrogen.

2. The monomer of nitrogen dioxide serves as the active chemical agent in the nitration of the paraffin chain. This monomer is an electrophyllic molecule of the radical type.

3. The initial elementary stage of the nitration of the paraffin is the interaction between the monomer of nitrogen dioxide and the original organic compound, bringing about the formation of a free radical.

$$R\text{-}H + NO_2 \longrightarrow R\cdot + HNO_2 \qquad (19)$$

4. In the sphere of the nitration, the alkyl radical R· thus formed reacts with radical-like forms of the oxide and the dioxide of nitrogen with the formation of nitroso compounds, alkyl nitrites, and nitro compounds:

$$R\cdot + NO \longrightarrow RNO \qquad (20)$$

$$R\cdot + NO_2 \longrightarrow R\text{-}O\text{-}NO \qquad (21)$$

$$R\cdot + NO_2 \longrightarrow R\text{-}NO_2 \qquad (22)$$

5. At very high relative concentrations, other active components of the reaction system (i.e., N_2O_4, N_2O_5, $HONO_2$, O_2, etc.) can enter the reaction:

$$R\cdot + N_2O_4 \longrightarrow R\text{-}O\text{-}NO + NO_2 \qquad (23)$$

$$R\cdot + N_2O_4 \longrightarrow R\text{-}O\text{-}NO_2 + NO \qquad (24)$$

$$R\cdot + N_2O_5 \longrightarrow R\text{-}ONO_2 + NO_2 \qquad (25)$$

$$R\cdot + O{=}O \longrightarrow R\text{-}O\text{-}O \qquad (26)$$

$$R\cdot + HONO_2 \longrightarrow R\text{-}OH + NO_2 \qquad (27)$$

6. The formation of various other end products of the reaction depends on chemical transformations taking place under conditions favorable for the nitration of nitroso compounds R-NO, nitrous esters R-O-NO, alkyl nitrates $RONO_2$, alcohols R-OH, and to a lesser extent, of nitro compounds $R\text{-}NO_2$.

7. Peculiarities of the nitration of the paraffin chain with nitric acid are determined for the most part by the position of the equilibrium

$$2HNO_3 + NO \rightleftarrows 3NO_2 + H_2O \qquad (28)$$

and by factors which determine the establishment of this equilibrium in the sphere of the reaction.

We will now move on to a systematic justification of these basic conditions for the theory of nitration of paraffin chain and apply this theory to explain results known earlier, as well as newly discovered phenomena in this field - also in order to develop methods for obtaining different products. We will first explain and apply statements 1, 2, and 3 in the section which follows.

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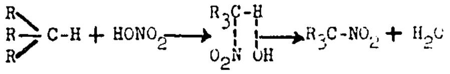
IV. THE FIRST STAGE OF NITRATION OF PARAFFIN CHAIN

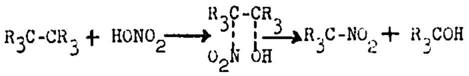
As proof of the chemical passivity of nitric acid toward the paraffin chain, experiments were made on the reaction between nitric acid and various hydrocarbons both in the presence and in the absence of oxides of nitrogen. The experiments were carried out under the most varied conditions [32]: at normal and elevated temperatures; with dilute and concentrated nitric acid (up to sg 1.42); in open vessels and in Konovalov's sealed tubes [33]; in heterogeneous and homogeneous liquid media [34], and in the gaseous phase [32]. It developed that in the absence of oxides of nitrogen at temperatures up to 150°, nitric acid of sg up to 1.4 practically did not react at all with n-paraffins, isoparaffins, saturated cycloparaffins, nor with the side chain of alkyl benzenes. In the latter case, nitration took place only in the aromatic nucleus.

In nitration experiments with nitric acid at higher temperatures or in cases when highly concentrated acid was used, the reaction proceeded to a greater or lesser extent. In some cases this could have been due to the impossibility of eliminating the formation of nitrogen oxides; in other cases, where anhydrous acid was used or where the nitration was carried out at still higher temperature, other active agents (NO_3, N_2O_5 and others) could originate in the sphere of the reaction and these agents are capable of reacting with the paraffin chain.

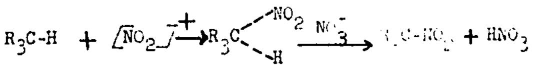
The passivity of paraffins to nitric acid and nitrating mixtures, and therefore to the nitronium cation ($O{=}\overset{+}{N}{=}O$) contained in them, can be explained by first considering the electron structure and chemical characteristics of saturated hydrocarbons. Paraffins have only homopolar bonds C-C and C-H, which have a very low polarity. Therefore, similarly to hydrogen molecules, they are not capable of undergoing reactions of the ion-complex type. In spite of their potential nucleophilic nature, paraffins do not form stable complexes with protonic and aprotonic acids. For example, they do not dissolve in liquid hydrogen fluoride, do not yield molecular compounds with polynitro derivatives, and are not mercurated by mercury salts, differing in these respects from olefins and aromatic hydrocarbons. For paraffins, typical chemical reactions are those with reagents containing unpaired electrons, e.g., with halogen atoms during halogenation or with various radicals during oxidation and cracking processes. In all these cases, the action of the reagent is directed only towards the peripheral hydrogen atoms and not towards the shielded and coordination-saturated carbon atoms. This permits us to understand why paraffins do not react with nitric acid or with the nitronium cation by the following schemes:

(a)  (29)

$$R_3C\text{-}H + HONO_2 \longrightarrow \begin{matrix} R_3C\text{-}H \\ O_2N \quad OH \end{matrix} \longrightarrow R_3C\text{-}NO_2 + H_2O \qquad (29)$$

(b)  (30)

$$R_3C\text{-}CR_3 + HONO_2 \longrightarrow \begin{matrix} R_3C\text{-}CR_3 \\ O_2N \quad OH \end{matrix} \longrightarrow R_3C\text{-}NO_2 + R_3COH \qquad (30)$$

(c)  (31)

$$R_3C\text{-}H + [NO_2]^{+} \longrightarrow R_3C\begin{smallmatrix} NO_2 \\ H \end{smallmatrix} \xrightarrow{NO_3^-} R_3C\text{-}NO_2 + HNO_3 \qquad (31)$$

Schemes (a) and (b) were suggested by several authors as mechanisms for the nitration of the paraffin chain [34].

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To prove that the nitration of the paraffin chain proceeds according to the stated conditions under preliminary interaction with the monomer of nitrogen dioxide and under conditions of chemical passivity of other common oxides of nitrogen, various experimental data were utilized. As already stated, parallel experiments on the interaction of the same quantity of nitrogen dioxide with different amounts of toluene showed that the yield of reaction products increases when the dioxide is diluted (see page 5). Changes in the yield of reaction products agreed favorably with the suggestion that all of the products of nitration form through an initial interaction of the hydro-carbon R-H with NO_2 in accordance with the equation:

$$\frac{-d[RH]}{dt} = k_1[NO_2] = k_1\sqrt{k_2[N_2O_4]} \qquad (32)$$

in which k_2 is the equilibrium constant for the dissociation of N_2O_4.

These results also proved the chemical passivity of the nitrogen dioxide dimer towards the paraffin chain.

The absence of any chemical interaction between the paraffin chain and nitric oxide and N_2O_3 became known from the results of parallel experiments on nitrating with nitrogen dioxide saturated with nitric oxide and with nitrogen dioxide in the absence on NO. In accordance with the theory, saturation with nitric oxide and the subsequent reaction $NO + NO_2 \rightleftarrows N_2O_3$ lowered the concentration of NO_2 a great deal and therefore the yield of the products was greatly reduced [32]. That the nitration of the paraffin chain proceeds through a preliminary interaction with NO_2 is also evident from the fact that the reaction takes place readily at high temperatures at conditions of full dissociation of N_2O_4 and N_2O_3.

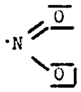
Proofs that nitric acid is chemically inert toward the paraffin chain have been stated above. It was demonstrated that nitration with nitric acid takes place only in the presence of oxides of nitrogen at a rate proportional to the quantity of the latter. This kind of nitration gave a product of the same composition as did the interaction of the hydrocarbon with nitrogen dioxide alone, as seen, for example, in the case of the product of the reaction with toluene at 100° (see Table 1) [35]. Analogous data were obtained in various other cases. From this it follows that nitration with nitric acid under these conditions takes place solely through the preliminary reaction with NO_2. Nitrogen dioxide serves as a transmitter of the nitrating action of nitric acid under circumvention of the high energy barrier which would have to be surmounted in the direct reaction of nitric acid with the paraffin chain.

To prove that the reaction between NO_2 and the paraffin chain takes place according to the scheme

$$R\text{-}H + NO_2 \longrightarrow R^{\cdot} + HNO_2 \qquad (33)$$

with the formation of radicals, the chemical nature of the nitrogen dioxide monomer should first be clarified.

According to Lewis and Langmuir, the electronic structure of NO_2 may be expressed as follows:



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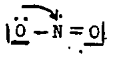
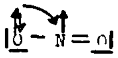
in which the dot represents a single electron and the dashes represent pairs of electrons that are either shared or are found in the shell of one atom. Noting the conjugation of the single electron with the mobile p-electrons, the structure of NO_2 may be expressed more accurately by the following formula:



$$|\ddot{O}-\dot{N}=O| \qquad (34)$$

Denoting the electrons participating in the conjugation as↓ and↑ under indication of their spins, formula (34) may be expressed as follows:



$$|O-N=O| \qquad (35)$$

Assumption of this type of conjugation allowed one to foresee the interaction of NO_2 with radicals through the N as well as the O atom [see formula (34) and equations (21) and (22)].

The presence of a solitary unpaired electron in NO_2 permits it to be considered as a free radical. This conclusion is supported by the paramagnetism of NO_2 and the band character of the absorption spectrum of NO_2. The radical character of NO_2 is also manifested in its rapid interaction with other particles containing unpaired electrons, such as $(C_6H_5)C\cdot$, Fe ·, metallic silver etc.

From the calculation of the free energy of the reactions

$$X + H_2 = HX + H\cdot \qquad (X = Cl\cdot;\ Br\cdot;\ I\cdot;\ \cdot NO_2) \qquad (36)$$

it follows that NO_2 is close to atomic iodine in its chemical unsaturation. In its affinity to the electron, the nitrogen dioxide monomer stands between iodine and bromine. The electrophility of $\overset{+\delta}{NO_2}$ is seen in its ability to react quickly with bases, ammonia (even at -80°), amines, and many anions, so that NO_2 may be regarded as an aprotonic acid.

The electronic structure of NO_2 [see formula (34)] and the data on energy just stated, permit one to understand the reasons for the relative stability of NO_2 as a radical and its low chemical activity in comparision with Cl and Br atoms.

Thus, theory and experiment agree in the conclusion that NO_2 is a particle of the radical type and that its degree of electrophility is moderate. On the other hand, all the known information on the reactions of the paraffin chain R-H with atoms (Cl·, Br·) and radicals (R-O-O·, CH_3·) permits one to maintain that they occur, as a rule, under the breaking off of a hydrogen atom and the formation of a free radical R· as in the scheme $R\text{-}H + Br\cdot \longrightarrow R\cdot + HBr$. Consideration of both conditions leads one to accept the interaction of NO_2 with the paraffin chain according to the formerly postulated scheme [equation (19)]. In the light of the theory of the transitional state and noting the electrophility of NO_2, the course of the reaction may be described in more detail:

$$R\text{-}H + NO_2 \longrightarrow \overbrace{R\ldots H}^{+\delta}\ldots\overset{-\delta}{NO_2} \longrightarrow R\cdot + HNO_2 \qquad (37)$$

This conclusion is in agreement with all the experimental results. The most direct experimental proof of the formation of free radicals during the nitration of the paraffin chain will be presented in the discussion of the mechanism of the formation of geminate dinitro compounds of the phenyldinitromethane type (see p 23).

[redacted]

The rate of the formation of the free radical R· during the reaction of a hydrocarbon with NO_2 determines the observed rate of nitration, since transformations of the radical in the sphere of the nitration must take place almost instantly. According to general chemical knowledge, as well as conclusions drawn from studies of the transition state the nitration rate of the paraffin chain increases strongly as the energy stability of the corresponding radical R· increases. Utilizing the data of Rice and other authors, it is possible to find the decrement in activation energy ΔE during the transition from methane to other hydrocarbons. On the basis of the magnitude of ΔE, the respective nitration rate constants (k') were calculated [32]. Finally, starting from probable considerations, it is possible to estimate the magnitude of the activation energy of the nitration of methane as 45-50 kcal, which permits calculation of the activation energies of nitration of other hydrocarbons in the gaseous phase. The results of these calculations are listed in Table 2. In this table, the hydrogen atoms reacting with NO_2 are underlined, and k' for the hydrogen atoms of the methyl group of butane is taken as equal to unity.

The calculated rate constants are found to be in agreement with Konovalov's observation that nitration of n-paraffins takes place at the secondary carbon and of isoparaffins at the tertiary. More recently, Urbansky's and Slon's assertion that nitration of n-pentane with nitrogen dioxide takes place at the primary carbon [6, 7] was refuted by our investigations [36]. Carrying out the reaction at higher temperatures must bring about an equalization in the mobility of the hydrogen atoms at various carbons.

In agreement with the values for the activation energy found in the table, n-pentane practically does not react at all with nitrogen dioxide at ordinary temperatures even after it has been left standing for several months [32]. The reaction with diisoamyl $(CH_3)_2CH-CH_2-CH_2-CH_2-CH_2-CH(CH_3)_2$ takes place at a very slow rate [33], but toluene reacts much faster. The reaction between NO_2 and diphenylmethane, after immediate stirring, is completed after the mixture has been left standing for 2 days, but triphenylmethane reacts very fast on heating [37]. In the light of the above, the increasing reaction rate in the series: toluene, metaxylene, mesitylene (38) becomes clear, since the methyl group in the meta position increases the stability of the respective free radicals considerably. In a similar way, the effect of the naphthyl group on the ease of nitration of the paraffin [alkyl] groups of 1,4-dimethylnaphthalene can be explained.

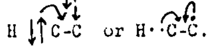
Increase in the chemical activity of hydrogen in respect to $\cdot NO_2$ and $NO_3\cdot$ in the series of the type

$$CH_3-H;\ CH_3CH_2-H;\ (CH_3)_2CH-H;\ (CH_3)_3C-H$$

is connected with the increasing ease of the formation of the free radicals

$$CH_3\cdot;\ CH_3CH_2\cdot;\ (CH_3)_2CH\cdot;\ (CH_3)_3C\cdot$$

This serves to explain the increase in the possibility of homogeneous conjugation of a solitary p-electron with spatially accessible electrons of neighboring C-H bonds at the expense of their p-components in the following manner:


$$H \downarrow\uparrow C-C \quad \text{or} \quad H\cdot \cdot C-C. \qquad (38)$$

The predominant interaction of NO_2 with paraffins in the 2-position under formation of 2-nitroalkanes is connected with the possibility of maximum manifestation of the above-mentioned conjugation in the radical $CH_3-\dot{C}H-CH_2-R$ as compared with other possible alkyls. The extreme inertness of hydrogens at carbons connected with tertiary radicals that has been noted by Markovnikov [39] is easily understood from this viewpoint; the difficulty of nitrating the paraffin chain in tert-butyl benzene that has been noted by Konovalov [40] is similarly explained.

[redacted]

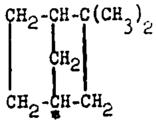
Methane's great inertness toward nitration is based on the complete absence of conjugation in the solitary electron of the free methyl radical due to the fact that the axis of its orbit is perpendicular to the axes of the C-H bonds. This circumstance permits the assumption that the activation energy of nitration cited earlier for methane is probably too low.

In the series of phenylated methyl radicals

$$CH_3\cdot;\ C_6H_5CH_2\cdot;\ (C_6H_5)_2CH\cdot;\ (C_6H_5)_3C\cdot \qquad (39)$$

the very strong conjugation between the solitary p-electron and the neighboring mobile π-electrons of the aromatic nucleus results in an even greater increase in the stability of the radicals and a corresponding facilitation of the reaction with NO_2 during the transition from methane to toluene and then to diphenylmethane and triphenylmethane.

Konovalov [41] and Nametkin [42] observed interesting cases of the passivity of hydrogen atoms at tertiary carbons shared by two rings, as in camphenilane:



(40)

This anamolous behavior is explained by the difficulty with which the corresponding radical is freed as a result of the rigidity of the tetrahedral configuration of the valence electrons of such carbons($\overset{*}{C}$). This, in turn, makes it impossible for the remaining bonds to assume a planar distribution and in this manner assure to a greater degree conjugation of the resulting unpaired electron with electrons of the neighboring C-H bonds. This restriction, in regard to nitration, will apply only to those carbons of bicyclic compounds for which Bredt's restriction of the formation of double bonds applies, since both restrictions are of the same nature. For example, both restrictions are not applicable to the tertiary carbon atoms in decalin. This follows from Nametkin's nitration results [43], the study of spacial models, and the existance of 1, 9- and 9, 10-octalins.

It can be concluded from a series of observations that there is an increased activity of the hydrogen atoms of cyclohexane during interaction with NO_2 Judging from Nametkin's results on the nitration of hydrindane [44], the activity of the hydrogen atoms in cyclohexane is greater than the activity of the hydrogen atoms in cyclopentane. The greater activity of cyclohexane can be explained in the form of a working hypothesis as a weakening of C-H bonds produced by the strengthening of the conjugation of their p-components in a six-membered ring, which is somewhat similar to the effect of the conjugation of p-electrons in aromatic nuclei (cryptoaromatic character). This hypothesis is confirmed by a number of physical and chemical properties of cyclohexane and its analogs.

The following results of experimental investigations also confirmed that radical-molecular reactions are the initial and determining stage leading to the nitration of the paraffin chain [32].

1. Nitration of the paraffin chain with nitric acid in the presence of nitrogen dioxide takes place in the hydrocarbon and not in the acid phase, since the yield is not changed by increasing the amount of acid but it is increased by additions of hydrocarbon.

2. The degree of polarity of the medium does not have a great effect on the rate of the reaction; nitration of the paraffin chain also takes place readily in the gaseous phase.

3. Additions of strong protonic (H_2SO_4) and aprotonic ($AlCl_3$, $TiCl_4$) acids do not noticeably accelerate the nitration of the paraffin chain.

However, if one considers the electrophlic character of the nitrogen dioxide monomer and the potential nucleophility of the paraffin chain with respect to NO_2, it follows that in the process of their interaction purely electrical forces will also play a significant role and the process in the transitional stages

$$R\text{-}H + NO_2 \longrightarrow \overset{+\delta}{\overbrace{R \ldots H}} \ldots \overset{-\delta}{NO_2} \longrightarrow R^{\cdot} + HNO_2 \qquad (41)$$

will bear marks of an ion-complex reaction. Increase of the electron density in the hydrogen sphere and a raise in the polarity of the C-H bond must favor the formation of the transition complex. Hence introduction of an electron-donor group - alkyl, alkoxy, etc. - into the R-H molecule facilitates nitration, with the exception of such cases where this kind of substitution will lead to a considerable decrease in the stability of the radicals, as in the transition from isopropyl benzene to tertiary butyl benzene. Electrophylic groups present in the R-H molecule, especially such groups as - NO_2, -COOH, will act in an opposite direction. In accordance with this, nitro derivatives react with NO_2 with greater difficulty than the hydrocarbons themselves or they do not react at all, as can be seen from the data of Konovalov, Nametkin, the author of the present article, and other investigators. However geminate dinitro compounds of the phenyl dinitromethane type nitrate readily under proper conditions following ionization and the subsequent transformation into electron-donor (nucleophilic) anions $[C_6H_5C(NO_2)_2]^-$ in a way similar to that which leads to the nitration of nitrophenols [45].

In connection with the above, it can be foreseen that the nature of the medium and any additions must all have an effect on the reactivity of NO_2 by changing its electrophility, as shown by the following schemes:

$$\overset{-\delta}{O_2N} \leftarrow \text{-----} \overset{+\delta}{O}(C_2H_5)_2; \qquad O{=}\overset{+\delta}{N} \rightarrow O \text{-----}\rightarrow \overset{-\delta}{H}{}^{+} \qquad (42)$$

As a result of complex formation with ether, the activity of NO_2 must decrease, but in consequence of combination with a hydrogen ion it increases. The influence of the medium or of a third particle (A) can also act as a means of aiding the removal of HNO_2

$$R\text{-}H + {\cdot}NO_2 + A \longrightarrow R^{\cdot} + HNO_2 \ldots A \qquad (43)$$

through the adsorption of H^+ and NO_2^- ions on ionic lattices, hydration through interaction with water, etc.

The rate constant for the reaction in the liquid phase, according to the general rule, must be several times greater than for that in the gaseous phase. The observed reaction rate will then rise sharply as a result of an enormous increase in the number of collisions between the paraffin molecules and particles of the nitrating agent [46].

We shall stop briefly to consider other possible ways in which NO_2 can react with the paraffin chain. From purely energetical, spatial, and chemical considerations, the reaction according to the scheme

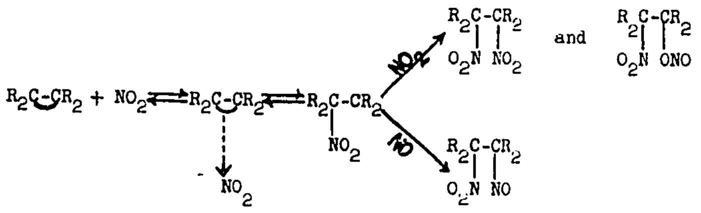
$$R\text{-}H + NO_2 \longrightarrow H^{\cdot} + R\text{-}NO_2 \qquad (44)$$

can be considered as practically nonexistent.

Spatial-energetical factors also bring about a low probability of the fission of the hydrocarbon chain

$$R_3C\text{-}CR'_3 + NO_2 \longrightarrow R_3C\cdot + R'_3C\text{-}NO_2. \qquad (45)$$

This reaction can occur only at high temperatures or whenever there is a considerable weakening of the bond between the carbon atoms as in hexaarylethanes after a threefold σ,π-conjugation. Apparently this type of process occurs only during the interaction of NO_2 with the dinitrile of tetraphenyl succinic acid $(C_6H_5)(CN)C\text{-}C(CN)(C_6H_5)_2$, since the reaction rate of this nitrile with NO_2 is greater than the rate of dissociation of the dinitrile into the free diphenylcyanomethyl radical [$(C_6H_5)_2(CN)C$] [47]. It may be assumed that to some degree an analogous process often takes place in the first stages of the interaction between oxides of nitrogen and the π- bonds of olefinic compounds [32, 48]:



$$R_2C{=}CR_2 + NO_2 \rightleftharpoons \underset{\underset{NO_2}{\downarrow}}{R_2C\text{-}CR_2} \rightleftharpoons \underset{NO_2}{R_2C}\text{-}CR_2 \begin{cases} \xrightarrow{NO_2} \underset{O_2N\ \ NO_2}{R_2C\text{-}CR_2} \text{ and } \underset{O_2N\ \ ONO}{R_2C\text{-}CR_2} \\ \xrightarrow{NO} \underset{O_2N\ \ NO}{R_2C\text{-}CR_2} \end{cases} \qquad (46)$$

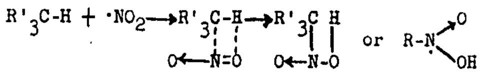
I ($\smile$-π-bond)

II transition complex

The great rate of change and reversibility of these stages can be deduced on the basis of the known facts of rapid transformation of the energetically unstable cis-compounds into the stable trans-isomers during the action of NO_2. The nitrogen dioxide monomer behaves similarly to bromine atoms during photochemical isomerization.

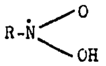
In reactions with NO_2 and NO_3, cyclopropane and its derivatives must behave analogously to olefins. According to our views, the state of the carbon - carbon bonds in this ring is close to that of the π-bond. Apparently, this kind of reaction, accompanied by fission of a three-membered ring, was accomplished by Namekin and Zabrodina in the nitration of tricyclene [49].

The reaction of the paraffin chain with NO_2 according to the following scheme [37] is also possible to some extent



$$R'_3C\text{-}H + \cdot NO_2 \longrightarrow \underset{O\leftarrow \dot{N}=O}{R'_3C\text{-}H} \longrightarrow \underset{O\leftarrow N\text{-}O}{R'_3C\ \ H} \text{ or } R\text{-}\dot{N}\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix} \qquad (47)$$

($\leftarrow$ is the symbol for a semipolar bond)

with the formation of organic analogs of nitrogen dioxide


$$R\text{-}\dot{N}\begin{smallmatrix}\diagup O\\ \diagdown OH\end{smallmatrix}$$

Only careful stereochemical investigations - showing retention of the configuration at the central asymmetric carbon may establish the feasibility of this type of interaction.

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In addition to interaction of the paraffin chain with the common form of NO_2, the formation of radicals can also take place under proper conditions as the result of the reaction of hydrocarbons with other particles.

Thus, from the observations of Dem'yanov [50] and Adkins [51], it is clear that nitric acid anhydride reacts with paraffins very rapidly. Direct interaction of nitric acid anhydride with the paraffin chain according to the scheme

$$R\text{-}H + O_2N\text{-}O\text{-}NO_2 \rightarrow R\cdot + HONO_2 + NO_2 \qquad (48)$$

is not certain from the point of view of general principles of radical - molecular reactions. We propose that the active agent in this reaction is nitrogen trioxide in the radical state formed during the equilibrium dissociation of nitric acid anhydride:

$$O_2N\text{-}O\text{-}NO_2 \rightleftarrows NO_2 + \cdot ONO_2 \qquad (49)$$

Interaction of nitrogen trioxide NO_3 with the paraffin chain by analogy to the corresponding reaction of the nitrogen dioxide monomer NO_2 can be represented by the following scheme:

$$R\text{-}H + \cdot ONO_2 \rightarrow R\cdot + HONO_2 \qquad (50)$$

The high activity of nitrogen trioxide in this reaction follows from purely energetical considerations and from the high electrophility of $NO_3\cdot$ as compared with $\cdot NO_2$. The energetical considerations are based on the fact that nitric acid has a greater heat of formation than nitrous acid. The electrophility of $NO_3\cdot$ and $\cdot NO_2$ in the first approximation will be proportional to the strengths of the corresponding acids - nitric and nitrous. It is clear that the ideas developed above apply to nitration with the participation of $NO_3\cdot$.

Quite recently, Ogg proved that the equilibrium between nitric acid anhydride and its dissociation products is established very rapidly by determining the rate of formation of $N^{15}O_2$ in the reaction

$$N_2^{15}O_5 + N^{14}O_2 \rightleftarrows O_2N^{15}\text{-}O\text{-}N^{14}O_2 + N^{15}O_2 \qquad (51)$$

on the basis of measurements of the intensity of absorption bands of the formed nitrogen dioxide monomer $N^{15}O_2$ in the infrared spectrum [52]. In agreement with the accepted mechanism of the reaction

$$N_2^{15}O_5 \rightarrow N^{15}O_2 + N^{15}O_3;\ N^{15}O_3\cdot + \cdot N^{14}O_2 \rightarrow O_2N^{15}\text{-}O\text{-}N^{14}O_2 \qquad (52)$$

its velocity turned out to be that of a first order reaction with respect to N_2O_5 and that of a zero order reaction with respect to NO_2. This result proves that a determining factor in the exchange is the dissociation of N_2O_5. Analogous information was obtained by studying the very rapid reaction:

$$N_2O_5 + NO = 3NO_2, \qquad (53)$$

whose mechanism is represented by the scheme

$$N_2O_5 \rightarrow NO_3\cdot + \cdot NO_2;\ NO_3\cdot + \cdot NO \rightarrow 2\cdot NO_2. \qquad (54)$$

Since the equilibrium $N_2O_5 \rightleftarrows NO_3\cdot + \cdot NO_2$ (55)

exists, additions of nitrogen dioxide inhibit reaction (54). On the basis of Ogg's work on the oxidation of NO [53], the possibility that NO_3 arises from this reaction may be assumed.

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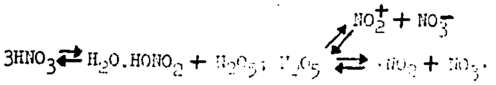
All this when summed up leads to the necessity of assuming the participation of NO_3 in a number of cases of nitration of paraffins with nitric acid and nitrogen dioxide. Thus, for example, the ability of highly concentrated or anhydrous nitric acid to react with n-paraffins and more rapidly with isoparaffins under normal conditions as observed by Markovnikov [54] establishes the presence of nitrogen trioxide in such an acid. Nitrogen trioxide must form as a result of the following reaction:



$$3HNO_3 \rightleftarrows H_2O.HONO_2 + N_2O_5;\ N_2O_5 \rightleftarrows \cdot NO_2 + NO_3\cdot;\quad N_2O_5 \rightleftarrows NO_2^+ + NO_3^- \qquad (56)$$

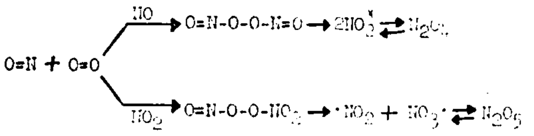
The formation of N_2O_5 in anhydrous nitric acid is indicated by a number of data [5].

In high temperature nitrations with nitric acid (at 400-500°) in the gaseous phase, the formation of NO_3 can come about as a result of the following sequence of reactions:

$$2HNO_3 \rightarrow N_2O_5 + H_2O;\ N_2O_5 \rightarrow NO_3\cdot + \cdot NO_2 \qquad (57)$$

Apparently, this circumstance leads to the observed high nitration rate in the case of nitric acid as compared with nitrogen dioxide [56].

In our experiments on nitration in the presence of oxygen carried out in the liquid phase [74], and in Hass's experiments done in the gaseous phase [56], the process of the oxidation of nitrogen oxides must have led to the formation of NO_3, and hence to acceleration of the reaction with the paraffin chain due to the following reactions:



$$O{=}N + O{=}O \xrightarrow{NO} O{=}N{-}O{-}O{-}N{=}O \rightarrow 2NO_2^* \rightleftarrows N_2O_4$$
$$O{=}N + O{=}O \xrightarrow{NO_2} O{=}N{-}O{-}O{-}NO_2 \rightarrow \cdot NO_2 + NO_3\cdot \rightleftarrows N_2O_5 \qquad (58)$$

It is probable that active molecules of nitrogen dioxide (NO_2^*) also form.

In the nitration of methane using a mixture of chlorine and nitrogen dioxide and applying Topchiyev's interesting method [ ], the formation of radicals could have occurred from the action of atomic chlorine formed by schemes (a), (b), and (c):

$$(a)\ Cl_2 \xrightarrow{heating} 2Cl\cdot;\ b)\ Cl_2 + NO \rightarrow NOCl + Cl\cdot;\ c)\ Cl_2 + NO_2 \rightarrow NO_2Cl + Cl\cdot. \qquad (59)$$

V. INITIAL CONVERSIONS OF RADICALS WITHIN SPHERE OF NITRATION

Both experiment and theory lead to the conclusion that the combination of alkyl radicals R· with other radicals or atoms having unpaired electrons takes place many times faster (by a factor of the order of 10^5 or greater) than the reaction of alkyl radicals with saturated molecules. Within the sphere of nitration there is usually present a noticeable and sometimes strikingly large concentration of the oxide and dioxide of nitrogen. Therefore, it must be assumed that any alkyl radicals that are formed must react with these oxides of nitrogen.

Variations in affinity toward the electron of these oxides of nitrogen and alkyl radicals must favor their union. This general conclusion is supported not only by the results of investigation of the nitration of the paraffin chain, but also by other independent experimental data. Below, independent data will be stated for the most part, while the proofs deriving from our work will gradually become apparent during the perusal of the following section.

As far back as 1911, Schlenk observed rapid combination of nitric oxide with triphenylmethyl to form triphenylnitrosomethane [57]. Investigating this reaction quantitatively, Ziegler and his co-workers concluded that the phase

$$(C_6H_5)_3C\cdot + NO \rightarrow (C_6H_5)_3C\text{-}NO \qquad (60)$$

must be passed instantaneously. Over the past 10-15 years, enough material has been collected by investigating the photolysis and pyrolysis of organic compounds to prove conclusively that the combination of nitric oxide with ordinary alkyl radicals is extremely rapid. The method of capturing formed radicals with the help of nitric oxide has now acquired a great significance. Forsyth considers that the combination of the methyl radical with nitric oxide requires only the low activation energy of 6.4 kcal [58].

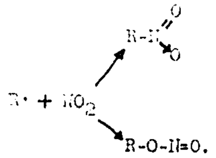
Combination of radicals with nitrogen dioxide also takes place very rapidly. In agreement with theory, Schlenk observed that an increased degree of dissociation of N_2O_4 into NO_2 leads to an acceleration of the reaction between the dioxide and the triphenylmethyl radical. The high combination rate of the methyl radical with NO_2 follows from the possibility of obtaining nitromethane by electrolysis of a solution of acetate and nitrate (see p 5). The ability of nitrogen dioxide to interrupt the chain reaction of the chlorination of n-pentane [59] is undoubtedly based on the capture of the alkyl radicals formed.

In accordance with the chemically most acceptable electronic structure, nitric oxide $\cdot\overline{N}{=}\underline{O}$, reacts with radicals to form nitroso compounds exclusively

$$R\cdot + \cdot\overline{N}{=}\underline{O} \rightarrow R\text{-}N{=}O \qquad (61)$$

This is followed by the formation of transformation products of the latter.

Starting with electronic conceptions of the structure of the nitrogen dioxide monomer (see p 10) and the possibility of finding a single electron at the nitrogen atom as well as at the oxygen atoms, the author proposed as far back as 1940 that interaction of alkyl radicals with NO_2 proceeds in two directions, yielding both a nitro compound and an ester of nitrous acid [35]:



$$R\cdot + NO_2 \rightarrow R\text{-}N\overset{\displaystyle O}{\underset{\displaystyle \searrow O}{\nearrow\!\!\!\!\!=}} \qquad (62)$$

$$R\cdot + NO_2 \rightarrow R\text{-}O\text{-}N{=}O. \qquad (63)$$

According to experimental data, the reaction of radicals and NO_2 at 100° yields about 60% of nitro compound and 40% of alkyl nitrite [60]. This ratio may change under the influence of solvation and complex formation that involves NO_2, bringing about the shielding of one of the atoms of the dioxide. It may be assumed, for example, that the formation of NO_2 complexes with nitro compounds of the type $R\text{-}N\overset{\nearrow O}{\underset{\searrow O \dashrightarrow \overset{-\delta}{\overline{N}}O_2}{}}$ involves lowering of the activity of the nitrogen atom.

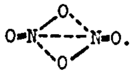
These circumstances could have an effect on the ratio of effective collisions of the radical with NO and NO_2.

The reactions between radicals and saturated molecules taking place in the sphere of the nitration can be represented by the scheme

$$R\cdot + A\text{-}B \rightarrow R\cdots A\cdots B \rightarrow R\text{-}A + B\cdot . \qquad (64)$$

It should be noted that the possibility that this type of reaction will actually take place will be greater the weaker the A-B bond and the more stable the formed radical B. A rise of the electrophility of the corresponding atom of group A and an increase in its spatial availability for attack by a radical should facilitate this reaction.

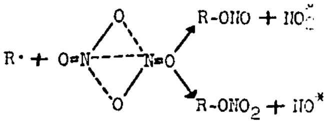
Of all formally saturated (diamagnetic) molecules, the nitrogen dioxide dimer has apparently the greatest chance of reacting with alkyl radicals. According to our conceptions [60, 61], the structure of N_2O_4 in a nonpolar solution is expressed by the formula



(65)

In this scheme, the broken lines indicate bonds of a secondary character, O•••N bands of an electrostatic and covalent character, and N•••N simple covalent bonds. The secondary character of the NO_2 bonds holding NO_2 molecules together in the dimer follows from the insignificant change of the ultraviolet absorption spectrum as a result of dimerization and the immeasurably high dissociation rate of N_2O_4. The weakness of the NO_2-NO_2 bond in the dimer also agrees with the low heat of decomposition of the dimer (0.6 kcal). All of this indicates a high degree of independence of NO_2 in the dimer.

The proposed structure of N_2O_4 is found to agree with data on the symmetry of the dimer molecule, with the big distance between nitrogen atoms in the molecule, with the low polarity of N_2O_4 as a solvent and with the increasing degree of dissociation of the dissolved nitrogen dioxide as the polarity of the medium increases. In view of the shielding of the nitrogen atoms in this form of N_2O_4, attack on its radical must be directed toward the oxygen atoms and must lead to the formation of alkyl nitrites and to some extent of alkyl nitrates.



(66)

The shielding of nitrogen by three atoms results in a loss of reactivity by it. This follows from the peculiarities of the interaction of organic analogs of NO_2 with radicals, which proceeds exclusively through oxygen, as the reaction between nitrogen diphenyloxide and the radical of triphenylmethyl shows [62]:

$$(C_6H_5)_2N\text{-}\bar{O}| + \cdot C(C_6H_5)_3 \rightarrow (C_6H_5)_2N\text{-}O\text{-}C(C_6H_5)_3 . \qquad (67)$$

As indicated above, the reaction of NO_2 itself with triphenylmethyl takes place along both possible directions — through the nitrogen atoms and through the oxygen atoms.

Since the effectiveness of the collisions between the radicals and N_2O_4 is undoubtedly considerably less than for NO and NO_2, reaction (66) can play a noticeable part only at high ratios of $\frac{[N_2O_4]}{[NO_2]}$ and $\frac{[N_2O_4]}{[NO]}$, i.e., at moderate or low temperatures and a high analytical concentration of nitrogen dioxide. This has been confirmed by experiment.

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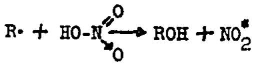
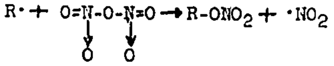
According to the above, the effectiveness of collisions between the radicals and molecules of nitric acid must be very small. On the basis of a consideration of spatial factors and energy calculations, it may be assumed that the most probable direction for the reaction is formation of alcohols by the scheme:



$$R\cdot + HO\text{-}N\overset{O}{\underset{O}{\rightleftarrows}} \longrightarrow ROH + NO_2^{*} \qquad (68)$$

The role of this process can only be significant at a sufficiently high temperature, a high concentration of nitric acid, and a low content in the reaction sphere of nitrogen dioxide and nitric oxide, which intercept radicals rapidly.

The reaction of radicals with nitric acid anhydride must lead to the formation of alkyl nitrate according to the considerations presented above:



$$R\cdot + O{=}\underset{\downarrow\atop O}{N}\text{-}O\text{-}\underset{\downarrow\atop O}{N}{=}O \longrightarrow R\text{-}ONO_2 + \cdot NO_2 \qquad (69)$$

In some special cases of nitration, as for example in experiments where the reaction mass is saturated with oxygen or at high temperatures (~300°), when there is a significant shift of the equilibrium in (70) to the right

$$2NO_2 \rightleftarrows 2NO + O_2 \qquad (70)$$

it is necessary to take into account the possibility that the radicals may react with oxygen. According to its magnetic and other properties, the oxygen molecule possesses a biradical character, which, it is true, is comparatively weakly expressed in its chemical behavior. Nevertheless, it combines rapidly with free triarylmethyls and alkyl radicals, giving peroxide radicals:

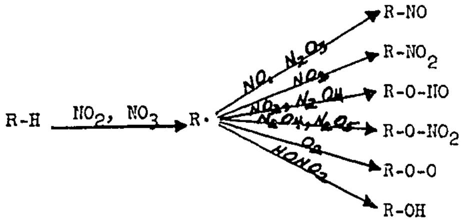
$$R\cdot + O_2 \longrightarrow R\text{-}O\text{-}O\cdot . \qquad (71)$$

From a series of observations, it may be concluded that effective collisions of radicals with N_2O_3 yield mainly nitroso compounds.

Since nitro compounds and alkyl nitrites inhibit reactions passing through an intermediate formation of radicals [63], they apparently also are capable of reacting with free radicals formed during the nitration. However, the effectiveness of their collisions must be very low in comparison with those of NO and NO_2 and even with the activity of oxygen molecules.

VI. MECHANISMS OF FORMATION OF END PRODUCTS OF THE REACTION

In Section IV it was shown that the beginning stage in all cases of nitration of the paraffin chain is the formation of free radicals due to the reaction of hydrocarbons with the nitrogen dioxide monomer. In Section V the probable primary conversions of these radicals within the sphere of nitration were considered. The basic conclusions from both sections may be summarized by means of the scheme:



(72)

[redacted]

Comparison of the experimental data obtained by us permits us to assume that the relative effectiveness of collisions of the radicals with NO and NO_2 respectively is pretty close together, and that in the first approximation this effectiveness is 3-5 times less for nitric oxide than for the dioxide. The effectiveness of collisions of the radicals with N_2O_4 and N_2O_3 is many tens of times less than in the case of the radical-like oxides NO and NO_2, and for nitric acid it is apparently very insignificant. Therefore, according to theory, under normal conditions of nitration the first conversion products of the formed radicals must be mononitro derivatives $R-NO_2$ or nitroso compounds R-NO, esters of nitrous acid R-ONO, and to some extent alkyl nitrates and alcohols. The ratio of these products in the process of transformation of radicals and the subsequent chemical behavior of these products under the selected conditions of nitration determine the composition of the end product of the reaction.

Among these compounds, only nitro derivatives proved to be stable under ordinary conditions of nitration, so that they are preserved almost entirely intact until the end of the reaction. Nitroso compounds are extremely unstable within the sphere of the nitration, but their intermediate formation was unquestionably proved by studying their conversion products, whose yields attain 50% of the theoretical [59]. Esters of nitrous acid possess an intermediate degree of stability, and hence it was possible to demonstrate, under special conditions of nitration, the formation of over 40% of alkyl nitrites and of their closest conversion products — alcohols, alkyl nitrates and other esters [60]. Alkyl nitrates are quite stable in many types of nitration.

The results of the investigation summed up in scheme (72) were a starting point for comprehending the mechanism of the formation of the observed nitration products of paraffin chains and for understanding the basic rules of this process. These results also led to the discovery of new directions of this reaction and to unexpected (in the ordinary sense) chemical phenomena. These results permitted the application of rational methods for obtaining a series of products.

To illustrate the above, we will first describe preparation of the usual product of the reaction, i.e., of the mononitro derivative. Then by the way of studying the formation of geminate dinitro compounds, we will demonstrate the possibility that the reaction may proceed mainly in the direction of intermediate formation of nitroso derivatives and we will shed light on their eventual fate. Finally, we will present proof of the formation of alkyl nitrites and nitrates and will explain their predominating role in processes leading to formation of products of oxidation and destruction.

Formation of Mononitro Derivatives

In accordance with the theory which has been developed [64], the principal manner in which mononitro compounds are formed in nitration with oxides of nitrogen and with nitric acid can be represented by the following scheme:

$$R\text{-}H + NO_2 \xrightarrow{-HNO_2} R\cdot \xrightarrow{NO_2} R\text{-}NO_2 \text{ and } R\text{-}ONO\ (\sim 40\%). \qquad (73)$$

Competitive reactions under ordinary conditions of nitration will be combination of the radical with NO to produce nitroso compounds and then the varied products of their transformation, as well as the interaction with N_2O_4 leading to the formation of alkyl nitrites and of the latter's products of oxidation and decomposition.

From these ideas it follows that to create an adequate total reaction velocity when nitrating with the oxides of nitrogen, and to direct the process towards the formation of mononitro derivatives, it is necessary to maintain a high content of NO_2 in the sphere of the reaction and to assure low relative concentrations of NO/NO_2 and N_2O_4/NO_2. When working with open vessels and nitrating in the liquid phase the desired values of these ratios were obtained by raising the temperature to 100°. At this temperature the solubility of nitric oxide decreases sharply and an almost complete dissociation of N_2O_4 takes place. A sufficient amount of NO_2 in the sphere of the reaction was maintained by using large volumes of hydrocarbon.

Using a large excess of either hydrocarbon or solvent led to difficulties in the alkali extraction of nitro compounds due to the extremely low velocity of the process. These difficulties were overcome by adding small amounts of amines. The amines, dissolving in the organic layer, rapidly converted the pseudoacidic form of the nitro compound into a salt of the aci form:

$$C_6H_5CH_2NO_2 + NH(C_2H_5)_2 \qquad [C_6H_5CH{=}NO_2]^- [NH_2(C_2H_5)_2]^+ . \tag{74}$$

The latter immediately went into the aqueous layer, where as a result of its interaction with the caustic, the amine was regenerated. It then was again extracted by the organic layer and thereupon reacted with a fresh portion of the nitro compound, etc. This continued until the nitro compound was completely converted into the sodium salt of the aci form. As a result of this procedure, the duration of the extraction was shortened by a factor of ten.

Further effectiveness of the nitrating action of nitrogen dioxide was achieved by introducing oxygen into the sphere of the reaction. The favorable effect due to this procedure is made apparent in the following cases. For example the reactions of nitration and oxidation with nitrogen dioxide

$$2C_6H_5CH_3 + 3NO_2 = 2C_6H_5CH_2NO_2 + H_2O + NO \tag{75}$$

and

$$C_6H_5CH_3 + 3NO_2 = C_6H_5COOH + H_2O + 3NO \tag{76}$$

are accompanied by the formation of nitric oxide, which leads to an inefficient utilization of NO_2. The presence of nitric oxide in the gas mixture lowers the partial pressure of the nitrogen dioxide and, therefore, the concentration of NO_2 in the hydrocarbon as well. This then lowers the observed rate of the nitration. Introduction of oxygen in the necessary quantity converts the NO into NO_2 and thereby improves the efficiency of the utilization of nitrogen dioxide and speeds up the reaction. Moreover, introduction of oxygen can raise the activity of the NO_2 and bring about the formation of the highly active NO_3 (see p 16).

These theoretical conclusions were checked and confirmed on the basis of an investigation of the nitration of toluene to phenylnitromethane [64]. We shall present some data on the yield of phenylnitromethane, illustrating the influence of some of the most important factors. On passing 43 g of nitrogen dioxide and 8 liters of oxygen into 175 ml of toluene over a period of 2 hours at 100°, 15.3 g of phenylnitromethane were obtained; increasing the amount of toluene to 1750 ml raised the yield of the product to 41.7 g. Passing 43 g of nitrogen dioxide into 1750 ml of the hydrocarbon over a period of 4 hours yielded 34.2 g of phenylnitromethane; simultaneous introduction of 10 liters of oxygen raised the yield to 56.1 g. The ratio of the yield of phenylnitromethane to the total yield of the products of the reaction comprised approximately 50%. When oxygen was employed, the degree of consumption of nitrogen dioxide for the synthesis of all products of the reaction that contained nitrogen exceeded 90% of the theoretical.

Nitration of meta-xylene with nitrogen dioxide [38] proceeded very smoothly and went faster than the nitration of toluene. Thus, when 36 g of NO_2 were passed through 200 ml of the hydrocarbon over a period of 3 hours at 100°, 26.4 g of very pure meta-tolylnitromethane were obtained with a yield amounting to 55% of the total quantity of reaction products. Due to its high reactivity, the nitration of diphenylmethane was carried out at 70-75° in a solution of carbon tetrachloride, thus aiding the dissociation of N_2O_4; the yield of diphenylnitromethane was 53.4% of the theoretical based on the starting hydrocarbon. Experiments on the nitration of 2,7-dimethyloctane in the liquid phase [46] and of n-pentane and cyclopentane in the gas phase [36] also gave encouraging results.

To nitrate most successfully the paraffin chain with nitric acid in the liquid phase, according to theory, the following principal conditions had to be fulfilled: (1) establishment and maintenance of the required concentration of NO_2 with the aid of nitric acid; (2) adherence to conditions developed for the nitration with nitrogen dioxide.

It was also necessary to hinder the development of a destructive action of nitric acid on the newly formed nitro compounds. In the case of alkyl benzenes it was necessary, in as far as possible, to lower the nitrating effect of nitric acid on the aromatic nucleus of these hydrocarbons.

In earlier work, success in nitrating with nitric acid in the liquid phase depended on purely accidental circumstances. Fluctuations in the amount of oxides of nitrogen in nitric acid and in the extent to which it was possible to raise it, could have been reasons for the wide differences in the results of previous workers. In the author's experiments, establishment of a primary concentration of NO_2 was achieved by first adding nitrogen dioxide or a substance easily forming oxides of nitrogen on reacting with nitric acid, e.g., paraformaldehyde or sodium nitrite [64].

To maintain the necessary concentration of nitrogen dioxide during nitration with nitric acid, it is possible to employ various methods. In accordance with the equilibrium

$$NO + 2HNO_3 \underset{}{\overset{\text{heat}}{\rightleftarrows}} 3NO_2 + H_2O \qquad (77)$$

this can be achieved by sustaining the necessary concentration of nitric acid, increasing the pressure of nitric oxide, and finally, by raising the temperature.

Under the conditions of Konovalov's reaction, nitric oxide, accumulating as a result of oxidation, remains in the sealed tube where its pressure constantly increases. This assures, to some degree, the maintenance of the NO_2 concentration by lowering the concentration of nitric acid. Accordingly, Konovalov noted that the reaction went best in those tubes where a high pressure was found to exist when they were opened [3]. Maintenance of a sufficient reaction rate was also aided by applying sometimes a gradual increase in temperature.

In our experiments on nitrating the paraffin chain of alkylbenzenes in open vessels at a constant temperature, the concentration of NO_2 was maintained by gradually adding nitric acid of sg 1.5. To avoid nitration of the nucleus with strong nitric acid, the latter was introduced directly into the lower acid layer and not allowed to come in contact with the hydrocarbon. Using a very large excess of hydrocarbon, in addition to the previously stated advantages, almost completely canceled the destructive action of nitric acid on mononitro derivatives, an action which was especially strongly developed in the case of alpha-nitroalkylbenzenes. Passing oxygen into the sphere of the reaction at a rate just necessary for the conversion of nitric oxide into nitrogen dioxide, increased the effectiveness of the nitration even more.

[redacted]

As a result of these innovations it is possible to obtain significant quantities of alpha-nitroalkyl benzenes by nitration with strong nitric acid in open vessels for 2-4 hours at 100°. The results were very different from those obtained in previous investigations.

To illustrate what has been stated, we will cite some figures showing the influence of the amount of hydrocarbon and of the passage of oxygen on the yield of phenylnitromethane produced by nitration with 50 ml of nitric acid of sg 1.5 [64].

Volume of toluene	200 ml	500 ml	1750 ml
Yield of $C_6H_5CH_2NO_2$ (without the use of O_2) ..	23.6 g	35.3 g	53.9 g
Yield of $C_6H_5CH_2NO_2$ (with the use of O_2)	-	48.4 g	76.4 g

Increasing the volume of hydrocarbon raised the molar ratio of phenylnitromethane in the reaction product from 45 to 55%. The total utilization of nitric acid achieved in the last experiment was 90% of the theoretical amount. Experiments carried out on the nitration of meta-xylene [38], cyclohexane [65], 2,7-dimethyloctane [46] and n-heptane [33] with nitric acid also gave encouraging results.

Some other ways of the formation of mononitro compounds in the process of nitration of the paraffin chain will be discussed below.

Formation of Geminal Dinitro Derivatives and of Other Transformation Products of Nitroso Compounds

At the beginning of the investigation it was found that the yield of phenyldinitromethane and other geminal dinitro derivatives of aryl paraffins shows a very paradoxal dependence on the conditions of nitration. Contrary to the universal law, it appeared that the yield of dinitro-substituted compounds increased when the concentration of the nitrating agent -- nitrogen dioxide -- was lowered and also when the temperature was lowered. This can be seen from the following data [59]:

Molecular portion of N_2O_4	$\frac{N_2O_4}{N_2O_4 + C_6H_5CH_3}$	0.46	0.15	0.04	(t - 20°)
Ratio of yields in gram-moles	$\frac{C_6H_5CH(NO_2)_2}{C_6H_5CH_2NO_2}$	0.9	1.4	3.7	
Temperature of reaction in °C		95	70	40	20
Ratio of yields in gram-moles	$\frac{C_6H_5CH(NO_2)_2}{C_6H_5CH_2NO_2}$	0.03	0.32	2.2	3.6

Nitration with strong nitric acid at 100° gave phenylnitromethane almost exclusively and only a very small amount of the geminal dinitro compound while at the normal temperature the reaction yielded phenyldinitromethane as the main product. It is well known that in prior cases of a similar type entirely different behavior was observed.

It was soon established that phenylnitromethane, again contrary to customary ideas, does not appear as an intermediate product in the formation of the geminal dinitro derivative since, under the conditions leading to formation of the latter, or even more rigorous conditions, phenylnitromethane has not been found to change and only to the most insignificant degree was converted to benzoic acid. Thus, it would seem that the most obvious assumption in regard to the formation of the dinitro compound from the mononitro derivative must be rejected.

All of these apparently unexpected phenomena could be explained from the point of view of the theory of nitration of the paraffin chain developed by the author of this article. It was recognized that the source for the formation of geminal dinitro compounds were nitroso compounds formed as a result of the collision of a radical with nitric oxide, which is always present in the sphere of the reaction (see page 17):

$$C_6H_5CH_2\text{-}H \xrightarrow[-HNO_2]{NO_2} C_6H_5CH_2\cdot \xrightarrow{NO} C_6H_5CH_2\text{-}N{=}O \qquad (78)$$

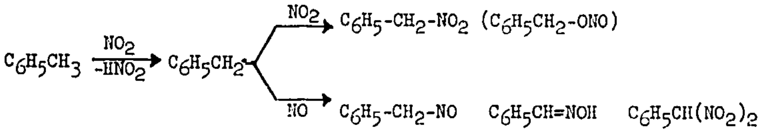
It is known that primary and secondary nitroso compounds isomerize into oximes very easily:

$$C_6H_5CH_2\text{-}N{=}O \rightarrow C_6H_5CH{=}NOH, \qquad (79)$$

and oximes of the type $\overset{R}{\underset{Ar}{>}}C{=}NOH$ react with nitrogen dioxide very rapidly even in very dilute solutions and at temperatures below 0° to form dinitro compounds

$$C_6H_5CH{=}NOH \xrightarrow{NO_2} C_6H_5CH(NO_2)_2. \qquad (80)$$

According to experiment and in agreement with this mechanism, the formation of geminal dinitro compounds takes place without passing through the intermediate stage of mononitro derivatives. Bearing in mind that from the point of view of the theory developed by the author, the ratio of yields of the dinitro and mononitro derivatives depends on the number of collisions between the formed radical and nitric oxide or nitrogen dioxide, respectively,



$$C_6H_5CH_3 \xrightarrow[-HNO_2]{NO_2} C_6H_5CH_2\cdot \begin{cases} \xrightarrow{NO_2} C_6H_5\text{-}CH_2\text{-}NO_2 \;(C_6H_5CH_2\text{-}ONO) & (81) \\ \xrightarrow{NO} C_6H_5\text{-}CH_2\text{-}NO \quad C_6H_5CH{=}NOH \quad C_6H_5CH(NO_2)_2 & (82) \end{cases}$$

it is easy to understand the apparently paradoxical influence of reaction conditions on this ratio. Thus, for example, the decrease in the yield of the dinitro compound when the concentration of nitrogen dioxide or nitric acid is lowered, is explained by a drop in the concentration of NO and an increase in the concentration of NO_2. A similar effect due to an increase in temperature is analogously explained by a great decrease in solubility of nitric oxide and a sharp increase in the degree of dissociation of N_2O_4 into NO_2 molecules, which again leads to an increase in the ratios

$$\frac{NO_2}{NO} \text{ and } \frac{C_6H_5CH_2NO_2}{C_6H_5CH(NO_2)_2}.$$

A deciding factor for establishing the validity of the assumed mechanism of formation of geminate dinitro compounds were the results of experiments on nitration in the absence of nitric oxide. In agreement with theory, the interaction of toluene with nitrogen dioxide in the absence of nitric oxide led to an increased amount of the mononitro derivative and of other reaction products with the exception of phenyldinitromethane, which did not form at all under these conditions. Removal of nitric oxide from the sphere of the reaction in these experiments was achieved by saturating the reaction mixture with oxygen throughout the entire nitration process.

In the formation of a nitroso compound and therefore of a geminal dinitro compound, NO_2 and NO play an active role, but not N_2O_4, N_2O_3 or HNO_2, as one could have assumed if the formation of nitro compounds followed the scheme

$$C_6H_5CH_3 + O{=}N{-}O{-}N{=}O \rightarrow C_6H_5CH_2{-}NO + HNO_2 \qquad (83)$$

or

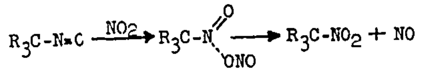
$$C_6H_5CH_3 + HO{-}N{=}O \rightarrow C_6H_5CH_2{-}NO + H_2O. \qquad (84)$$

This is proved by the fact that when the concentration of nitric oxide and therefore also of N_2O_3 and HNO_2 has increased, the absolute yield of dinitro compound decreases after reaching a maximum, even though its relative quantity in the reaction products continues to grow. Reduction of the absolute yield of geminal dinitro compounds upon saturation with nitric oxide is incompatible with the formation of nitroso derivatives according to equations (83) and (84) since the concentration of N_2O_3 and HNO_2 must reach a maximum under the circumstances. According to the author's theory, saturation with NO shifts the equilibrium $NO_2 + NO \rightleftarrows N_2O_3$ to the right, bringing about a drop in the concentration of NO_2 and therefore also a decrease in the rate of formation of radicals and in the yield of all components of the reaction product including dinitro compounds. When this happens, the probability of collisions between radicals being formed in a smaller quantity and NO continues to grow steadily, resulting in a slight increase in the relative yield of geminal dinitro compounds. In accordance with the theory, saturation of the reaction mixture with oxygen eliminates nitric oxide and thus sharply increases the general rate of nitration (see also page 16).

The results of the above-stated investigation can be taken as proof that theory of nitration of the paraffin chain is correct on the whole. These results were used to work out a method of preparing phenyldinitromethane directly from toluene and oxides of nitrogen in a yield amounting to 50% of the total amount of reaction products. This method was successfully employed for obtaining alpha, alpha-dinitro derivatives from meta and ortho-xylenes, mesitylene /38/, diphenylmethane /37/, ethyl benzene, and tetralin /59/. It developed that it was also possible to obtain geminal dinitro compounds in satisfactory yield by reacting concentrated nitric acid with hydrocarbons under appropriate conditions at an ordinary temperature /30/. The author is confident that under the guidance of the theory it is possible to achieve further increases in the yields of geminal dinitro compounds /59/.

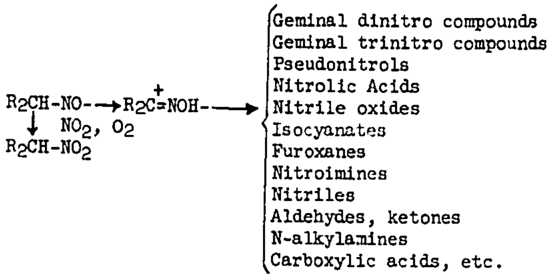
We shall consider briefly the other directions of the chemical transformations of nitroso compounds under the conditions of nitration.

The principal product of conversion of tertiary nitroso compounds in all cases of nitration of paraffin chains must be the corresponding nitro derivatives /59/



$$R_3C{-}N{=}O \xrightarrow{NO_2} R_3C{-}N\begin{smallmatrix}{\nearrow}O\\ \searrow ONO\end{smallmatrix} \longrightarrow R_3C{-}NO_2 + NO \qquad (85)$$

This circumstance serves to explain the great facility of nitration at the tertiary carbon which has already been noted by Konovalov. It is possible that some primary and secondary nitroso compounds are also transformed under the right conditions in this manner. Primary and secondary nitroso compounds can easily change into geminate dinitro and trinitro compounds, nitrolic acids and pseudonitrols through isomerization into oximes; they can also undergo a Beckman rearrangement and hydrolysis, thus being converted into nitriles, etc. The possible immediate transformations of the formed nitroso compounds in the sphere of the nitration can be expressed by the following scheme:



$$\begin{array}{l} R_2CH\text{-}NO \longrightarrow R_2\overset{+}{C}{=}NOH \longrightarrow \left\{\begin{array}{l}\text{Geminal dinitro compounds}\\ \text{Geminal trinitro compounds}\\ \text{Pseudonitrols}\\ \text{Nitrolic Acids}\\ \text{Nitrile oxides}\\ \text{Isocyanates}\\ \text{Furoxanes}\\ \text{Nitroimines}\\ \text{Nitriles}\\ \text{Aldehydes, ketones}\\ \text{N-alkylamines}\\ \text{Carboxylic acids, etc.}\end{array}\right. \\ \quad \downarrow NO_2,\ O_2 \\ R_2CH\text{-}NO_2 \end{array}$$

The presence of geminal dinitro and trinitro compounds in the reaction products was proved in our work, while furoxane was discovered earlier by Gabriel [66]. The presence of nitrolic acids is probably responsible for the appearance of a reddish brown color in the first alkaline extraction from the nitration product obtained from a substance such as pentane [36]. Nitroso compounds of the type $\genfrac{}{}{0pt}{}{Ar}{R}\!>\!CHNO$ are converted almost entirely to dinitro compounds during nitration in solution. In this respect they differ favorably from nitroso derivatives of the type R_2CHNO. For this reason and also because of the high activity of hydrogen on the alpha-atom, aryl paraffins are the most suitable object for investigating the role of the formation of nitroso compounds in the nitration of the paraffin chain.

Under ordinary conditions of nitration in the liquid phase at an elevated temperature, the formation of nitroso compounds will not play a big part, as seen from the investigation. Formation of these compounds can be very significant in nitrations by Konovalov's method in those cases where the pressure of the nitric oxide reaches a very high magnitude or the nitration takes place under specially selected conditions. The significance of the formation of nitroso compounds during nitration in the gaseous phase has not as yet been experimentally investigated; at high temperatures it is necessary to take into consideration the equilibrium

$$R_3CNO \rightleftarrows R_3C\cdot + NO. \tag{86}$$

Formation of Products of Oxidation, Dehydrogenation, and Destruction of the Paraffin Chain [60]

Oxidation is one of the principal reactions in the nitration of the paraffin chain. In some cases it is the only reaction. The formation of the products of the destruction of the paraffin chain, discovered by Konovalov and Nametkin, plays an especially important part in vapor phase nitration at high temperatures. There are sufficient reasons to assume that the chief source for the formation of the products of oxidation and destruction during nitration of the paraffin chain is the alkyl nitrites formed by the interaction of radicals with NO_2 and N_2O_4:

[redacted]

50X1-HUM

$$\begin{tikzcd}
 & & R\text{-}ONO \ (\text{and } R\text{-}NO_2) & (87) \\
R\text{-}H + NO_2 \arrow[r, "-HNO_2"'] & R\cdot \arrow[ur, "NO_2"] \arrow[dr, "N_2O_4"'] & & \\
 & & R\text{-}ONO \ (\text{and } R\text{-}O\text{-}NO_2) & (88)
\end{tikzcd}$$

According to the author's data, the reaction of the radicals with NO_2 at 100° gives ~40% of alkyl nitrite and 60% of the nitro compound, and the reaction with N_2O_4 -- oxidation products exclusively.

At an appreciable concentration of oxygen, as for instance when it has been especially introduced, or in high temperature nitrations (following the decomposition of NO_2 and HNO_3), the formation of oxidation products can also commence with the formation of peroxides

$$R\cdot + O_2 \rightarrow R\text{-}O\text{-}O.$$

The alkyl nitrite that is formed during the nitration in the liquid phase must quickly enter the equilibrium reactions of hydrolysis, re-esterification, etc.:

$$\begin{tikzcd}
 & & RONO_2| + H_2O| \arrow[r, shift left] & \text{olefins and } HNO_3 \arrow[l, shift left] & \\
R\text{-}ONO \arrow[r, shift left, "H_2O"] & R\text{-}OH \arrow[l, shift left, "-HNO_2"] \arrow[ur, shift left, "HNO_3"] \arrow[r, shift left, "R'COOH"] \arrow[dr, shift left] & ROCOR'| \arrow[l, shift left] \quad H_2O| & & (89) \\
 & & R\text{-}O\text{-}R| + H_2O| \arrow[ul, shift left, "R\text{-}OH"] & &
\end{tikzcd}$$

These processes will bring about the formation of alcohol, alkyl nitrate, esters of organic acids present in the sphere of the reaction, as well as of ether and olefins.

By creating favorable conditions for the formation and conservation of alcohols and their derivatives, the author was not only able to prove the prediction by the theory of the presence of these compounds in the reaction mixture, but was also able to prepare them in significant quantities [60]. With this aim, the reaction was often carried out at a normal temperature and always with a very large excess of hydrocarbon. Introduction of oxygen and use of suitable dehydrating agents also aided in raising the yield of primary products of oxidation, due to the increased degree of esterification of alcohols achieved in this manner. Alkyl nitrates $R\text{-}ONO_2$ were found to be especially stable in many cases. This stability is due to a considerable increase in the positive charge of the R group, which makes it stable to the action of oxidizing agents.

The formation of an alcohol and of its derivatives during nitration of the paraffin chain was studied very carefully in the case of the reaction with toluene. A 2% solution of nitrogen dioxide in the hydrocarbon at a normal temperature was saturated with oxygen at room temperatures. After 4 days, a yield of benzyl alcohol and its esters exceeding 40% of the sum of the reaction products was obtained from this mixture In some experiments the yield of the benzyl nitrate alone exceeded 30% of the theoretical. The composition of the other reaction products for the experiment using 40 g of N_2O_4 and 2 liters of toluene saturated with oxygen is given in Table 3.

Due to the significant role of the reactions of N_2O_4 and O_2 with the radicals under these conditions, the total yield of oxidation products in experiments of this type exceeded 60%. Saturation with oxygen increased the rate of the reaction (see p 16).

Nitration at an elevated temperature naturally gave less oxidation products, since the radicals reacted almost exclusively with NO_2. Moreover, a considerable part of the alcohols and esters was converted into acids, as can be seen, for instance, from the composition of the products of the nitration of toluene at 100° (Table 4).

The author has also demonstrated that there is formation of alcohols, alkyl nitrites, and nitrates, as well as of other esters in the nitration of m-xylene [38], of diphenylmethane [37], of ethyl benzene, of cyclohexane [60], of n-pentane [36] and of other hydrocarbons. The investigation was carried out under varied conditions of nitration of the paraffin chain, including nitration by the method of Konovalov in sealed tubes with the use of dilute nitric acid. The simplest method of determination of nitrates formed during the nitration of aryl paraffins, was by reacting them with diethyl amine under formation of the corresponding tertiary amines, which are easily identified:

$$(C_6H_5)_2CHONO_2 + NH(C_2H_5)_2 = (C_6H_5)_2CH\text{-}N(C_2H_5)_2 + [NH_2(C_2H_5)_2]NO_3 \qquad (90)$$

Even in the products of the nitration of diphenylmethane, the presence of benzhydryl nitrate, benzhydrol and dibenzhydryl ester was proved [37].

The question of the different ways of formation of oxidation products -- aldehydes, ketones, and especially carboxylic acids -- during nitration of the paraffin chain attracted the special attention of M. I. Konovalov and S. S. Nametkin. Discovery of the formation of alcohols, alkyl nitrites, and other esters permitted the explanation of the inherent mechanism of these reactions. Undoubtedly, carbonyl compounds and acids form principally by the way of conversion of alcohols and alkyl nitrites, and through them of the more stable esters. This conclusion is proved by the fact that under mild conditions of nitration the reaction product consists almost exclusively of alcohols and esters, while under more rigid conditions the yield of acids is increased. This is also confirmed by the ease with which acids are obtained from the primary product of the reaction, when this reaction proceeds toward oxidation, if the so-called residual oil containing alcohols and esters is heated with nitric acid in the presence of nitrogen dioxide. The stable nitro compounds do not change under these conditions.

From the accepted mechanism for the formation of oxidation products, it follows that as long as the degree of probability of the formation of alkyl nitrite and nitrate in the process of the conversion of radicals remains constant, the sum of the relative amounts of neutral oxidation products (the so-called residual oil) and acids must be equal to this probability and therefore also remain constant. This must have been the case if radical reacted exclusively with NO_2 at the same temperature. In keeping with this condition, during the nitration of the paraffin chain of toluene at 100° the sum of the yields of residual oil and benzoic acid was found to remain equal to ~45% of the theoretical, although the yield of benzoic acid fluctuated between 20 and 42%, depending on the conditions of the reaction [60].

In earlier methods of nitration, alcohols and esters were transformed into acids almost completely. In accordance to Konovalov's principle on the predominance of the formation of 2-nitro alkanes during the nitration of n-paraffins, there must also be formed 2-alkyl nitrite, which must then be converted into alkanone-2 and finally into acetic acid and an acid of normal structure containing two less carbon atoms than the original hydrocarbon. This conclusion is supported by the results of Granacher's work on the oxidation of n-undecane with nitrogen dioxide [25]. The theoretical conclusion that the composition of the mixture of dibasic acids obtained from the oxidation of cyclohexanol with nitric acid is similar to the one obtained from the nitration of cyclohexane by Nametkin's method [68] is justified, since in the latter case, according to the theory, these acids also form through a stage of the oxidation of cyclohexanol:

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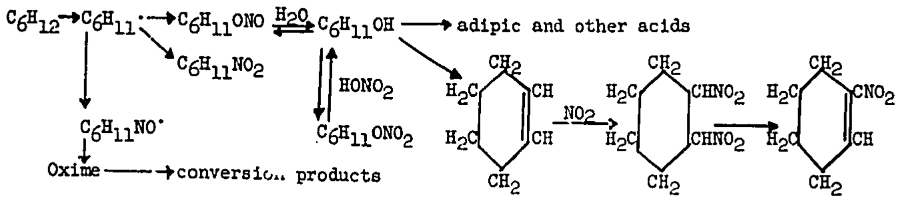


(91)

These conceptions in regard to the mechanism for the formation of oxidation products during nitration of cyclohexane were utilized in working out a method for obtaining adipic acid from cyclohexane /63/.

If all possible conversions of the alkyl nitrites and nitrates formed during nitration in the liquid phase are considered, it is also possible to foresee the formation of lower geminal dinitro compounds, nitriles, hydrocyanic acid, hydroxyacids, olefins and their conversion products, etc.

Knowledge to the effect that intermediate formation of alkyl nitrites takes place permitted us to outline a plausible mechanism for the formation of nitro compounds with a smaller number of atoms than the original hydrocarbon as a result of high temperature nitration in the gas phase /35/. This could have been demonstrated by the analysis of the nitration of isobutane at 420° as an example. In this case, along with primary and tertiary nitroisobutane, isobutyl nitrites must be formed in the same ratio and be present in a form rich in energy:

$$R\cdot + NO_2 \begin{cases} \nearrow R\text{-}NO_2^* \\ \searrow R\text{-}ONO^* \end{cases}$$

Primary isobutyl nitrite, exposed to pyrolysis, must lead to the formation of the isopropyl free radical, according to Rice /69/:

$$(CH_3)_2CH\text{-}CH_2ONO \xrightarrow[-NO]{heat} (CH_3)_2CH\text{-}CH_2O\cdot \longrightarrow (CH_3)_2CH\cdot + CH_2O, \qquad (92)$$

The combination of this radical with NO_2 will yield 2-nitropropane and isopropyl nitrite:

$$(CH_3)_2CH\cdot + NO_2 \nearrow CH_3\text{-}CHNO_2\text{-}CH_3 \qquad (93)$$

$$(CH_3)_2CH\cdot + NO_2 \searrow CH_3\text{-}CH(ONO)\text{-}CH_3 \qquad (94)$$

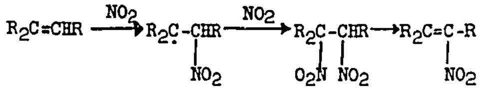
It can be shown analogously that the pyrolysis of tertiary isobutyl nitrite and isopropyl nitrite will lead to the formation of nitromethane and acetone. For example,

$$(CH_3)_2C\begin{matrix}\nearrow CH_3\\ \searrow ONO\end{matrix} \xrightarrow{-NO} (CH_3)_2C\begin{matrix}\nearrow CH_3\\ \searrow O\cdot\end{matrix} \longrightarrow (CH_3)_2CO + CH_3\cdot;\ CH_3\cdot + NO_2 \rightarrow CH_3NO_2 \qquad (95)$$

In agreement with the theory, high temperature nitration of isobutane yielded 65% of primary and 7% of tertiary nitroisobutane, 20% of 2-nitropropane, 3% of nitromethane, and 5% of acetone /70/. A similar agreement of theoretical conclusions with experimental data was established in other cases.

It should be noted that the first one to notice destruction of the carbon skeleton during nitration was Konovalov; he discovered the formation of acetophenone during the nitration of isopropyl benzene /71/.

Another possible way for the formation of lower nitro paraffins and other products of destruction is conversion of olefins arising from alcohols and alkyl nitrates under nitrating conditions; experimental data on this direction of the reaction are still lacking in the literature. The reaction with olefins must also lead to the formation of vicinal dinitro alkanes and nitro olefins, as shown in the scheme below:



$$R_2C{=}CHR \xrightarrow{NO_2} \underset{NO_2}{R_2\underset{|}{C}}\text{-}CHR \xrightarrow{NO_2} R_2\underset{O_2N}{\underset{|}{C}}\text{-}\underset{NO_2}{\underset{|}{CHR}} \longrightarrow R_2C{=}\underset{NO_2}{\underset{|}{C}}\text{-}R \qquad (96)$$

The possibility of the formation of lower nitro compounds by the way of fission of a C-C bond was pointed out earlier:

$$R_3C\text{-}CR_3 + NO_2 \rightarrow R_3C\text{-}NO_2 + R_3C. \qquad (97)$$

However, reliable evidence for the actual occurrence of this reaction during nitration is still lacking, if one does not count the splitting of the C-C bond in the dinitrile of tetraphenylsuccinic acid (p 14). The absence or only insignificant occurrence of a similar fission in the chlorination of paraffins at temperatures even as high as 600°

$$R_3C\text{-}CR_3 + Cl\cdot \rightarrow R_3C\text{-}Cl + R_3C\cdot \qquad (98)$$

also leads us to the conclusion that this type of conversion does not have a reasonable chance to occur. It is probably precluded by spatial hindrances. This type of fission of the C-C bond takes place readily only in reactions with atomic hydrogen due to the small dimensions of the latter /72/.

The problem of the catalytic action of nitrogen dioxide on the oxidation reactions of hydrogen, carbon monoxide, and paraffins with oxygen, is closely related to the problem of the formation of oxidation products. It is well known that small additions of nitrogen dioxide to mixtures of a paraffin and oxygen lower the temperature of ignition by 100-200°. After the amount of NO_2 has been increased, this effect reaches a maximum beyond which there is no explosion and only a slow stationary reaction takes place. We clarified these phenomena as follows in 1941 - 1946 from the viewpoint developed above /60/. Nitrogen dioxide after an effective collision with hydrocarbon forms a radical which at a very high ratio of O_2/NO_2, initiates a chain reaction between the paraffin and oxygen consisting of the following links:

$$R\text{-}H + NO_2 \xrightarrow[-HNO_3]{} R\cdot;\ R\cdot + O_2 \rightarrow R\text{-}O\text{-}O\cdot \qquad (99)$$

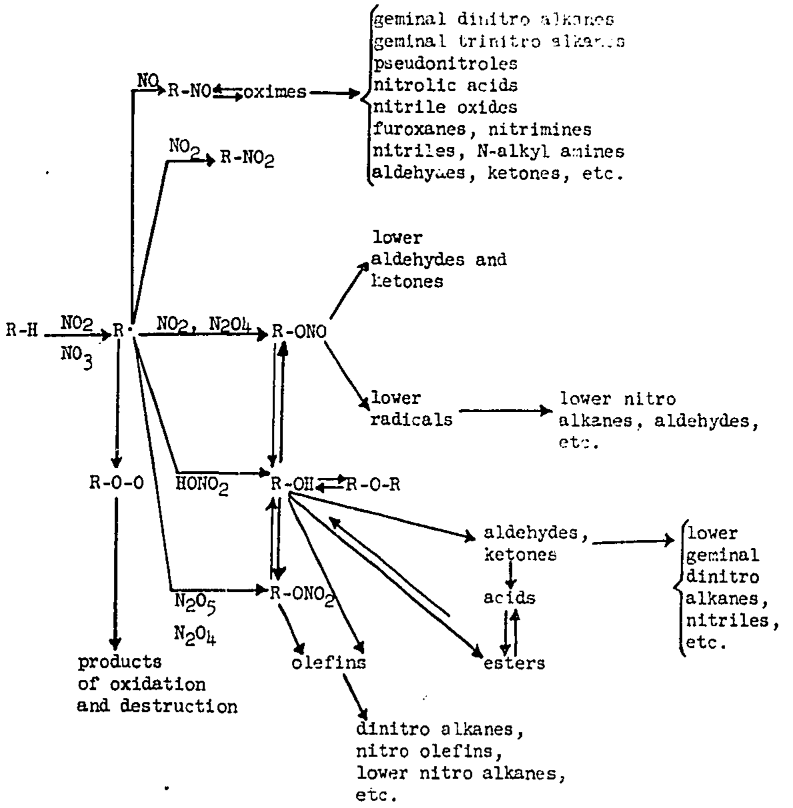
and

$$R\text{-}O\text{-}O\cdot + H\text{-}R \rightarrow R\text{-}O\text{-}O\text{-}H + R\cdot. \qquad (100)$$

Along with initiating the oxidation reaction, the NO_2 molecules, combining with radicals, rupture oxidation chains and shorten them. When the concentration of nitrogen dioxide is increased, the NO_2 will completely prevent formation of oxidation chains and the reaction will not be much different from stationary nitration. The concepts just stated can also be used to solve other questions concerning the use of oxides of nitrogen as accelerators of the oxidation with oxygen. Apparently unaware of our work, Voyevodskiy and Kondrat'yev quite recently proposed an analogous theory for the action of NO_2 in the oxidation of paraffins with oxygen /73/.

Aside from the principal way of obtaining oxidation products discussed, i.e., by the nitration of the paraffin chain through the stage of the formation of alkyl nitrites or of peroxides of the type R-O-O·, the formation of oxidation products is also possible by way of the conversion of nitroso compounds [74] and nitro derivatives [59]. However, as a rule these two ways of conversion do not play a significant role. Nitroso compounds are converted into oxidation products through the oxime isomerization stage and further transformation of the latter into aldehydes, ketones, geminal di- and trinitro compounds etc., as described above in some detail. Mononitro derivatives, which are very stable anyway, can convert to carbonyl compounds and acids due to the action of the hydrogen ion only under very rigorous conditions.

In conclusion, we submit a scheme expressing the theory for the nitration of the paraffin chain in the most general form.



(101)

The research conducted revealed the complexity and multifariousness of the chemical constituents of the nitration of the paraffin chain, and demonstrated how varied the courses of this reaction and how numerous its reaction products can be. It also demonstrated how important it is to understand the reaction mechanism in order to control all of its aspects and to uncover new chemical phenomena. Undoubtedly, future investigation will reveal many unknown aspects of this reaction and explain interesting details of its directions and stages, especially of those which were only touched on in our review. The aims and ways for future investigation of the nitration of the paraffin chain are now clear and this is the main task which could have been accomplished by theory.

SUPPLEMENT

When this article had already been prepared for printing, several other works were published which broaden the experimental foundation for the theory of the nitration of the paraffin chain and extend this theory's range of usefulness.

In the author's work together with Shchitov, the reaction between n-paraffins or cycloparaffins and nitric acid anhydride was investigated [75]. It was found that this reaction proceeds at a satisfactory rate even at 0° in an inert solvent; if the reagents are merely mixed, they react rapidly under evaluation of heat. The proposed mechanism for the beginning stage of this new nitration reaction

$$N_2O_5 \rightleftarrows NO_3\cdot + \cdot NO_2 \qquad (102)$$

and

$$R\text{-}H + \cdot ONO_2 \rightarrow R\cdot + HONO_2 \qquad (103)$$

is proved by the discovery of the inhibiting action of NO_2; addition of the latter, shifting the equilibrium of (102) to the left, lowered the concentration of active NO_3. In agreement with the theory, at low temperature the newly formed alkyl radical reacted for the most part to form alkyl nitrate-2, due to the low concentration of NO_2.

$$n\text{-}C_6H_{14} \xrightarrow[-HNO_3]{NO_3} 2\text{-}C_6H_{13}\cdot \xrightarrow[-NO_2]{N_2O_5} 2\text{-}C_6H_{13}ONO_2 \qquad (104)$$

At a higher temperature, the role of the combination of the radical with NO_2 to form a 2-nitro alkane predominated.

Thus, the assumption concerning the role of NO_3 in a number of nitrations (see p 15), is upheld by experiment.

In work done together with Rusanov [76] it was demonstrated that alkyl mercury compounds RHgR and RHgX react with NO_2 to form the radical

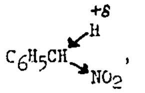
$$RHgR \xrightarrow{NO_2} R\cdot + RHgNO_2 \qquad (105)$$

Further transformations of the radical sphere of the reaction took place according to the theory. The reaction of R_2Hg as well as of $C_6H_5\text{-}CH_2HgCl$ proceeded energetically even in solvents at low temperatures because of the ease of the fission of the bond $R\cdot\cdot HgX$ with the formation of radicals, especially in the case where $R = C_6H_5CH_2$. This circumstance permits the use of alkyl mercury compounds as convenient models for studying nitration of the paraffin chain under varied conditions which are otherwise difficult to bring about, or cannot be brought about at all. In this work it was proved that alkyl nitrites form during the nitration of dibutyl mercury and diphenyl furoxan in the reaction of $\dot{N}O_2$ with benzyl mercuric chloride.

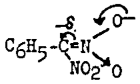
In work carried out together with Smirnov [77], the reasons for the paradoxical changes in the rate of nitration of paraffin chains in the following series were explained:

$$C_6H_5CH_3,\ C_6H_5CH_2NO_2,\ C_6H_5CH(NO_2)_2 \qquad (106)$$

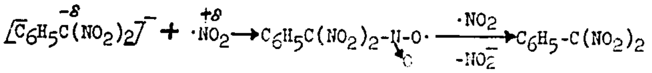
While the nitration of phenylnitromethane



$C_6H_5CH\begin{smallmatrix} \swarrow \overset{+\delta}{H} \\ \searrow NO_2 \end{smallmatrix}$, practically does not occur because of the strong electron-attracting effect of NO_2, phenylinitromethane reacts rapidly with nitric acid in the presence of nitrogen dioxide -- even more rapidly than with toluene. It has been demonstrated that the high activity of phenyldinitromethane is based on its ionization with the formation of the phenyldinitromethanate-anion



possessing an electron-donating, coordination-unsaturated carbon atom $(\overset{-\delta}{C})$:



$$[\overset{-\delta}{C}_6H_5C(NO_2)_2]^- + \overset{+\delta}{\cdot NO_2} \rightarrow C_6H_5C(NO_2)_2\text{-}\underset{\searrow O}{N}\text{-}O\cdot \xrightarrow[-NO_2^-]{\cdot NO_2} C_6H_5\text{-}C(NO_2)_2 \qquad (107)$$

Thus, in the series (106) the first member is nitrated by a radical mechanism, the last by an ionic mechanism, while the second member reacts with difficulty by either of these two mechanisms.

We will note that in this investigation nitration with nitrogen dioxide in an alkaline medium was achieved for the first time, as well as the nitration of metal derivatives of nitro and dinitro compounds.

In work done together with Matveyeva [78], investigation was carried out on a number of questions concerning the nitration theory by using as an example the reaction with cyclohexane. The authors (Titov and Matveyeva) demonstrated the formation in this reaction of cyclohexyl nitrite and of its immediate transformation products -- nitrate, adipinate, and cyclohexanol -- and with this they definitively clarified the mechanism of the formation of adipic acid in the nitration of cyclohexane (see p 28). Guided by the theory, researchers were able to establish the great role of the diffusion of NO, NO_2, and HNO_3 in the rate and direction of nitration with nitric acid. For example it was shown that the total yield of nitration products from Konovalov's method under use of horizontally placed tubes was two to three times greater than when using the yield obtained when vertically placed tubes were used and the yield of adipic acid was even five times greater. The diffusion effect was not taken into account by previous investigators. In fact explicit indications that the nitration was conducted in vertically placed tubes were encountered in the literature.

[Appended tables and bibliography follow.]

Table 1. Nitration of Toluene

Product	Amount of Product in Mole, % Reacted NO_2	Reacted HNO_3
Phenylnitromethane	52.5	55.2
Phenyldinitromethane	2.7	3.7
Benzoic acid	11.2	11.9
Residual oil	33.6	29.2

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Table 2. Activation Energies of Nitration

Hydrocarbon	Δ E (kcal)	Nitration Rate Constant k'	Activation Energy E (kcal)
$\underline{CH_4}$	-	-	48
$\underline{CH_3}\text{-}\underline{CH_3}$	2.0	-	46
$\underline{CH_3}\text{-}CH_2\text{-}\underline{CH_3}$	3.0	-	45
$CH_3\text{-}\underline{CH_2}\text{-}CH_3$	4.0	-	44
$\underline{CH_3}\text{-}CH_2\text{-}CH_2\underline{CH_3}$	3.5	1	45
$CH_3\text{-}\underline{CH_2}\text{-}\underline{CH_2}\text{-}CH_3$	5.0	6	43
$(\underline{CH_3})_3CH$	3.5	1	45
$(CH_3)_3\underline{CH}$	8.0	$2 \cdot 10^2$	40
$C_6H_5\text{-}\underline{CH_3}$	15.0	$5 \cdot 10^6$	33
$(C_6H_5)_2\underline{CH_2}$	26.0	$1 \cdot 10^{13}$	22
$(C_6H_5)_3\underline{CH}$	38.0	$1 \cdot 10^{20}$	10

Table 3. Products Formed in the Nitration of Toluene at Room Temperature Under Saturation With Oxygen

Reaction Products	Yield	
	G	%
Phenylnitromethane	7.7	11.2
Benzyl alcohol and its esters	29.6	43.2
Benzaldehyde	7.5	14.2
Benzoic acid	2.7	4.4
Nitrotoluene	9.4	13.6
Nitrocresol	2.2	2.2
Other products substituted in the CH_3 group	7.7	11.2

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Table 4. Products Formed in the Nitration of Toluene at 100°

Reaction Products	%	Reaction Products	%
Phenylnitromethane	52.5	Benzoic acid	11.2
Phenyldinitromethane	2.7	Other products substituted in the CH_3 group	2.4
Benzyl nitrite	6.4		
Benzyl alcohol	7.1	o-Nitrotoluene	1
Benzyl nitrate	1.8	p-Nitrotoluene	1
Benzaldehyde	2.4	Loss due to separation	10

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