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THE FREE RADICAL MECHANISM OF NITRATION

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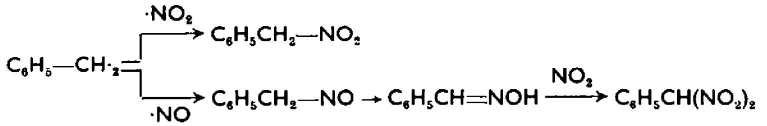
Abstract—The paper reviews the results of investigations† on the nitration mechanism of saturated, unsaturated, and aromatic compounds by the action of radicals such as $\dot{N}O_2$, $NO{\cdot}_3$, and other initiating agents, leading in the first instance to the formation of free alkyls. Some additional evidence and suggestions are advanced.

Only recently has it become possible to suggest sound nitration mechanisms. The first was proposed in 1936–37 for the nitration of a paraffin chain.[1] The action of NO_2 on the methyl group of toluene has been investigated by noting the effect of increasing the dilution of equal amounts of an equilibrium mixture of NO_2 and N_2O_4 with hydrocarbon. This is contrary to the well known rule—decrease in the activity of the nitrating agent with its lowered concentration. It was found that the reaction rate increases approximately proportionally to the square root of the dilution of nitrogen dioxide. On strong dilution, the main product proved, surprisingly, to be phenyldinitromethane, $C_6H_5CH(NO_2)_2$, first isolated on nitrating toluene, the yield of phenylnitromethane, $C_6H_5CH_2NO_2$ being substantially lower. Raising the temperature from 20 to 100° results in a decreased yield of dinitro-compound and a correspondingly increased yield of mononitro-derivative.

To explain these paradoxal phenomena it is suggested that nitration of the paraffin chain is initiated by NO_2, the reaction giving rise to a free alkyl, $C_6H_5CH_2{\cdot}$.

$$C_6H_5CH_2{-}H + {\cdot}NO_2 \rightarrow C_6H_5CH{\cdot}_2 + HNO_2 \qquad (1)$$

According to this assumption benzyl radical addition to ${\cdot}NO_2$ results in phenylnitromethane;



$$C_6H_5{-}CH{\cdot}_2 \xrightarrow{{\cdot}NO_2} C_6H_5CH_2{-}NO_2 \qquad (2)$$

$$C_6H_5{-}CH{\cdot}_2 \xrightarrow[{\cdot}NO]{} C_6H_5CH_2{-}NO \rightarrow C_6H_5CH{=}NOH \xrightarrow{NO_2} C_6H_5CH(NO_2)_2 \qquad (3)$$

and its combination with ·NO, in terms of (3), results in phenylnitrosomethane $C_6H_5CH_2{-}NO$, which is converted by NO_2 into phenyldinitromethane, either directly or through the oxime according to the Ponzio-Scholl reaction. The presence of NO is due to the decomposition of HNO_2, produced in (1) and to side oxidation reactions. At 20° the NO is retained in solution and the chief reaction is in accordance with (3), whereas at 100° most of the NO is eliminated resulting in the addition of the benzyl radical to NO_2 according to (2).

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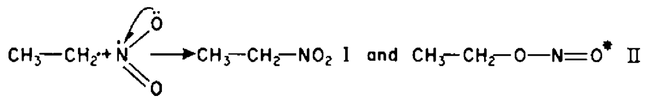
* Translated by A. L. Pumpiansky, Moscow.

† Other works are only referred to if not mentioned in the cited papers.

[1] A. I. Titov, *Zh. Obshch. Khim.* 7, 1695 (1937).

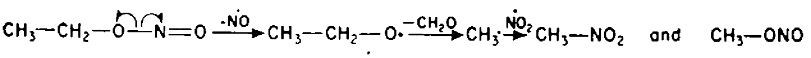
It is also suggested that nitration with nitric acid proceeds according to a similar mechanism by the intermediate reaction with nitrogen oxides. This is substantiated by the formation of phenyldinitromethane and phenylnitromethane by the action of nitric acid (*d* 1·42) on toluene under suitable conditions at 20–30° in the presence of a trace of NO_2 which autocatalyses the reaction.

In 1940,[2] based on this radical mechanism we indicated a probable route for the formation of lower nitro-compounds by nitration at high temperature of hydrocarbons, e.g. isobutane. Depending on the distribution of the unpaired electron $\dot{N}O_2$ throughout all nitrogen and oxygen atoms it may be concluded that the reaction of $\dot{N}O_2$ with a free alkyl R·, e.g. ethyl radical, gives rise not only to nitro-compound (I) but also to alkyl nitrite (II).



$$CH_3{-}CH_2\cdot + \dot{N}O_2 \longrightarrow CH_3{-}CH_2{-}NO_2 \ \text{I} \quad \text{and} \quad CH_3{-}CH_2{-}O{-}N{=}O^{*} \ \text{II} \qquad (4)$$

Between 300–500° the R—ONO* decomposes to produce a free ethoxy- and then methyl radical to form with $\dot{N}O_2$ nitromethane and methyl nitrite.



$$CH_3{-}CH_2{-}O{-}N{=}O \xrightarrow{\cdot\dot{N}O} CH_3{-}CH_2{-}O\cdot \xrightarrow{-CH_2O} CH_3\cdot \xrightarrow{\dot{N}O_2} CH_3{-}NO_2 \quad \text{and} \quad CH_3{-}ONO \qquad (5)$$

The composition of products of nitration of different paraffins is in accordance with this theory.

By the end of 1941 this investigation on the nitration of the paraffin chain initiated by NO_2 was complete and the "Nitration Theory"[3] was formulated. Since 1945 this work has been published as separate papers, each dealing with some aspect of the investigation and containing additional data. Later it was reported as a review.[4]

Based on the theory published,[5] nitric acid acts only as a source of nitrogen oxides and of NO_2 regeneration from lower oxides according to the equilibrium:

$$NO + 2HNO_3 \overset{t}{\rightleftarrows} 3NO_2 + H_2O \qquad (6)$$

and factors that determine its formation in the nitration. The inertness of nitric acid to the paraffin chain was proved by the interaction of HNO_3 with various types of paraffin chain in the absence or presence of NO_2. Under various conditions, using HNO_3 up to (*d.* 1·42) and 150°, in the absence of nitrogen oxides, the nitration does not take place[2,5,6,7] except alkylbenzenes which give rise to nitrotoluenes and nitrophenols[2]. It has also been shown that in the gaseous phase at about 300° the reaction is initiated by NO_2.[5] It was suggested that with anhydrous HNO_3 or at higher temperatures other agents,[6] in particular the $NO_3\cdot$ may initiate the reaction.

Nitration with nitric acid in the presence of nitrogen oxides proceeds at a rate proportional to the concentration of NO_2,[6] the product being of the same composition

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[2] A. I. Titov, *Zh. Obshch. Khim.* **10**, 1878 (1940).

[3] A. I. Titov, Dissertation, Moscow (1941).

[4] A. I. Titov, *Usp. Khim.* **21**, 881 (1952).

[5] A. I. Titov, *Zh. Obshch. Khim.* **16**, 1896 (1946).

[6] A. I. Titov and M. K. Matveyeva, *Zh. Obshch. Khim.* **23**, 238 (1953).

[7] A. I. Titov, *Zh. Obshch. Khim.* **19**, 1464 (1949).

as in the reaction with nitrogen oxides alone, under similar conditions.[2,6–8] Moreover, owing to the presence of H_2O in nitric acid and to the state of equilibrium (6) addition of HNO_3 of *d* 1·3–1·42 retards the reaction,[6,7] and almost completely in the nitration of toluene with HNO_3 of *d* 1·25 at room temperature even with added NO_2.[2]

The use of sealed apparatus in nitration according to Konovalov prevents the loss of NO_2 and NO during the reaction. The part played by nitrogen oxide in the equilibrium (6) is of great importance in nitration with strongly diluted HNO_3, particularly at the end of heating and explains the "nitrating effect of nitric acid under pressure",[9] postulated by Konovalov. In addition a rise in temperature results in a favourable shift in equilibrium (6) as well as in the dissociation $N_2O_4 \rightleftarrows 2NO_2$ (7). The failure of a number of workers to produce phenylnitromethane according to Konovalov and the varying yields obtained by the author himself[10,4,8] are due to the fact that the role of nitrogen oxides in this reaction was not fully understood.

Nitration by HNO_3 is slowed down by the diffusion of NO from the reaction sphere (organic phase) into the acidic layer and of NO_2 in the opposite direction as well as of HNO_3 at the interface.[9] This retardation is considerable at high reaction rates, particularly when active R—H is nitrated, or at elevated temperatures. Acceleration of diffusion by changing the position of the tubes from vertical to horizontal increases the yield several fold even if NO_2 is added. Diffusion must have been of still greater importance in the investigation of previous workers who did not introduce NO_2 into the reaction and it could have even been decisive in the failure to nitrate the paraffin chain of toluene attempted by Golleman, Shoryguin and other authors.[10]

Addition of nitrates e.g. $Ca(NO_3)_2$ [1,3] to aqueous nitric acid increases the yield by binding the water, shifting the equilibrium (6), decreasing ionization of N_2O_4 into NO^+ and NO_3^- and salting NO_2 out of the acidic phase. Thus, heating 4 ml of cyclohexane with 10 ml of HNO_3 (*d* 1·3) in the presence of traces of NO_2 for 3 hours at 100° in a sealed tube yields 0·1 g adipic acid and 0·5 g of nitrocyclohexane whereas with 5 g of $Ca(NO_3)_2$ added it results in 0·7 g of adipic acid and 1·0 g of nitrocompound.[3] On nitration of alkylbenzenes, nitrates retard the reaction in the nucleus owing to decreasing concentration of NO_2^+.

The overall yield of the reaction products varied in accordance with the equation:[1,5]

$$\frac{-dRH}{dt} = K_1[NO_2] \approx K_1\sqrt{K_2[N_2O_4]} \tag{8}$$

thus demonstrating the chemical inertness of N_2O_4 to the paraffin chain. The inertness of N_2O_3 is shown by the reaction being slowed down when N_2O_4 in toluene is saturated with nitrogen oxide, $NO_2 + NO \rightleftarrows N_2O_3$, and sharply accelerated when saturated with O_2 [5,11] which converts the NO formed into NO_2. In the latter case the overall yield increased five-fold.

From the calculation of energy and the conjugation in its structure it follows that $\dot{N}O_2$ (see Eq. 4) is moderately unsaturated and as electrophilic as atomic iodine. The approximate activation energy of the reaction of methane and NO_2 in terms of (1)

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[8] A. I. Titov, *Zh. Obshch. Khim.* **18**, 473 (1948).

[9] A. I. Titov and M. K. Matveyeva, *Sbornik rabot po obschey khimii* **1**, 241 (1953); *Dokl. Akad. Nauk SSSR* **83**, 101 (1952).

[10] P. P. Shoryguin and A. M. Sokolova, *Zh. Russk. Khim. Obshch.* **62**, 673 (1930).

[11] A. I. Titov, *Zh. Obshch. Khim.* **18**, 465 (1948).

is approximately 50 kcal,* for other cases it is assumed to decrease with the stabilization energy of the radical due to E_R conjugation. Thus, for example, for the reaction of NO_2 with toluene it is 28–33 kcal, with diphenylmethane 17–22 kcal, and with tritane 5–10 kcal.[4,5] In keeping with the calculations *n*-paraffins almost fail to react with NO_2 under normal conditions even after several months whereas the reaction with isoparaffins proceeds markedly[5,6,7] and with toluene the reaction goes to completion.[1] Nitration of diphenylmethane with NO_2 is complete in two days and tritane reacts very quickly with warming.[5,12] The difficulty encountered in nitrating hydrocarbons of the type $(CH_3)_3C—R$ such as *t*-butylbenzene is appreciated as is the inertness of tertiary hydrogens at bridge carbons in bicyclic compounds such as camphenilane and bicyclo-(2,2,1)-heptane,[4] which disappears at about 400° when the activity of all hydrogen atoms levels out.[13] The high reactivity of the paraffin chain of tetralin is probably due to its cryptoaromatic state, i.e. to the appearance of weak π-bonds between formally saturated carbon atoms thus leading to the weakening of CH-bonds in the tetramethylene group, $—(CH_2)_4^-$.[14] Similarly, the easy conversion of 1,4-dihydronaphthalene to naphthalene on reaction with NO_2,[15] and the increased reactivity of cyclohexane to NO_2 as compared to that of *n*-hexane,[4] is readily understood.

The nitration of the paraffin chain is considered to be a radical–molecular reaction. This assignment is substantiated by the course of the reaction with HNO_3 in the organic phase and is instanced by the increased yield of nitro-derivatives with increasing amount of hydrocarbon.[6] The greater polarity of the solvent[3] (substitution of CH_3NO_2 for CCl_4), addition of strong protonic and aprotonic acids ($AlCl_3$, $TiCl_4$) and of mercuric salts does not accelerate nitration and, finally, the reaction of NO_2 with paraffins can be effected in a gaseous phase.[5,6,16] It should however be borne in mind that due to the effective electrophilicity of NO_2 and the potential nucleophilicity of R—H the reaction in its transition state must be to some extent of a polar character:[4,5]

$$R - H + \cdot NO_2 \rightarrow \overset{+\delta}{\overbrace{R \cdots}} H \cdots \overset{-\delta}{NO_2} \rightarrow R\cdot + HNO_2 \qquad (9)$$

The processes of homolysis and electron pairing are combined with that of "neutralization". Hence the increasing polarization and polarizability in the type R—H should favour a transition complex. The weakening of these effects on introducing —COOH, $—CF_3$ and NO_2^- groups results in decreasing activity of R—H as, is seen for example, in the case of nitrotoluenes[3] and to a still greater extent with phenylnitromethane.[2] In contrast, phenyldinitromethane under the action of HNO_3 is readily converted in the presence of NO_2 to phenyltrinitromethane $C_6H_5—C(NO_2)_3$ but, as has been shown, this is due to its conversion into an electron dative anion[17] $C_6H_5—C(NO_2)_2^-$.

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* According to the new data (D. V. E. George, J. H. Thomas, *Trans. Farad. Soc.* **58,** 262 (1962)) early calculations of E of nitration of CH_4 (43 kcal/mole[3,5]) and the experimental results (52 kcal/mole, J. J. Boyd, *Ind. Eng. Chem.* **34,** 300 (1942)) gave too high magnitudes. But that does not change the essentiality of further conclusions based on the comparison of E_R.

[12] A. I. Titov, *Zh. Obshch. Khim.* **18,** 1312 (1948).

[13] R. Blickenstaff and H. Hass, *J. Amer. Chem. Soc.* **68,** 1431 (1946).

[14] A. I. Titov. In press

[15] A. I. Titov, *Zh. Obshch. Khim.* **22,** 1331 (1952).

[16] A. I. Titov, *Zh. Obshch. Khim.* **19,** 1472 (1949).

[17] A. I. Titov and V. V. Smirnov, *Dokl. Akad. Nauk. SSSR* **83,** 243 (1952).

Mesitylene[18] is superior even to diphenylmethane in its readiness to react with NO_2. The reaction proceeds much faster than with *o*-xylene, the activity of which is almost equal to that of toluene. Thus the reactivity of mesitylene cannot be explained as due to an induction effect and may be understood by taking into account the higher stability of tri-*m*-tolylmethyl as compared with the trityl or even of its tri-*p*-methyl derivative. The reaction also readily takes place with cumene, durene and hexaethylbenzene[3] owing to the high nucleophilicity and conjugation in the respective radicals.

R—Hg—R[19] reacts extremely readily with NO_2 and HNO_3 in the presence of nitrogen oxides even at $-10°$ owing to a decrease by 50 kcal in the bond energy when passing from CH_3—H to CH_3—$HgCH_3$. The reaction with aliphatic compounds proceeds to the stage of conversion to alkylmercuric nitrate R—Hg^+ NO_3^-, but with dibenzyl mercury both alkyls are involved owing to the stability of $C_6H_5CH_2\cdot$ ($E_R \approx 24{\cdot}5$ kcal). For the same reason NO_2 reacts very readily with benzylmercuric chloride, C_6H_5—CH_2-HgCl, to give under similar conditions the same compounds as toluene C_6H_5—CH_2—H. Thus the formation of benzyl radical in terms of (1) is proved:

$$C_6H_5\text{—}CH_2\text{—}HgCl + \cdot NO_2 \rightarrow C_6H_5\text{—}CH_2\cdot + NO_2HgCl \qquad (10)$$

Mercuric compounds are especially useful to investigate nitration under very mild conditions (*vide infra*). In particular, higher reactivity of hydrogen atoms in cyclohexane is confirmed by a reaction of cyclohexylmercuric bromide and NO_2 under normal conditions.[19]

The complexing of NO_2 and electrophilic agents, such as H^+, NO_2^+, etc, should increase its reactivity and this should be decreased when electrondonating solvents, such as ether, are involved. The influence of the medium and the walls of the reaction vessel may affect the formation of HNO_2 in terms of (9) owing to solvation or adsorption of H^+ and NO_2^-.[4]

When nitrating with NO_2 in a gaseous phase, the decomposition of nitrous acid in status nascendi to a hydroxyl radical and NO may take place.

$$R\text{—}H + \dot{N}O_2 \rightarrow R \cdots H \cdots O \cdots NO \rightarrow R\cdot + HO\cdot + \cdot NO \qquad (11)$$

the nitration then proceeding as a chain reaction. Apparently the hydroxyl radical and NO_2 combine so quickly that this is not possible. In any case, packing the reactor with short glass tubes when nitrating pentane and cyclohexane at 300° failed to produce the expected retardation effect.[6] At a high concentration of nitrogen dioxide (0·84 g of C_6H_{12} and 4·5 g of N_2O_4) in a sealed tube at 100°, the reaction proceeds violently,[6] possibly at the expense of active NO_2 radicals* and O=CH—$(CH_2)_4$—$CH_2\cdot$ appearing in the branching of the chain.

$$C_6H_{11}\cdot + N_2O_4 \xrightarrow{-\dot{N}O_2{*}} C_6H_{11}\text{—}O\text{—}NO{*} \xrightarrow{-NO} O{=}CH\text{—}(CH_2)_4\text{—}CH_2\cdot \qquad (12)$$

A careful study of the formation of phenyldinitromethane by the action of nitrogen oxides on toluene substantiates the nitration mechanism in terms of (1–3).[11] Contrary to usual rules but in agreement with (3) phenylnitromethane is not converted to the dinitro-derivative by the action of NO_2 and is recovered unchanged.[2]

The role of NO in the formation of *gem*-dinitro-compounds in terms of (3) is thus

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[18] A. I. Titov, *Zh. Obshch. Khim.* **19,** 258 (1949).

[19] A. I. Titov and D. E. Russanov, *Dokl. Akad. Nauk SSSR* **82,** 65 (1952).

fully substantiated,[11] as when a mixture of nitrogen dioxide and toluene are saturated with oxygen, converting the NO produced into NO_2, no phenyldinitromethane is formed in spite of the increased yield of mononitro-compound and, particularly, of oxidation products, primarily benzyl nitrate. In contrast, saturation with nitrogen oxide, in accordance with the equilibrium $NO_2 + NO \rightleftarrows N_2O_3$, lowers the absolute yields of all products while the relative yield of *gem*-dinitro-compound is increased. The lowering of the absolute yield of $C_6H_5CH(NO_2)_2$ in spite of an increase in the concentration of N_2O_3 indicates that nitrogen trioxide is unable to effect the nitrozation of the paraffin chain. The possibility of R· reacting with NO and NO_2 according to (3) and (2) determines the yields ratio of $C_6H_5CH(NO_2)_2/C_6H_5CH_2—NO_2$ (**n**) thus explaining the effect of initial concentration of N_2O_4 in the reaction mixture (I) and of temperature (II) on the magnitude of *n*.

TABLE 1

I Molar fraction of N_2O_4	0·04	0·15	0·46	
n	3·7	1·4	0·9	
II Reaction temperature	20°	40°	70°	95°
n	3·6	2·2	0·32	0·03

In the former instance the [NO] to [NO_2] ratio decreases due to increasing $[NO_2] = \sqrt{K_2[N_2O_4]}$, in the latter owing to a strong decrease in solubility of NO at higher temperatures and to the increased dissociation of N_2O_4.

An appreciation of the mechanism of $C_6H_5CH(NO_2)_2$ formation has resulted in an understanding of the conditions necessary to produce this compound in a yield up to 50% in the reaction of toluene with N_2O_4 [11] or HNO_3.[1] The use of NO under pressure together with increased temperature points to further improvement of yields.[11]

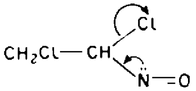
Experiments with diphenylmethane in CCl_4 have confirmed these conclusions.[12] In increased dissociation of N_2O_4 in CCl_4 and, therefore the increased ratio of NO_2/NO, results in the yield of mononitroderivative $(C_6H_5)_2CH—NO_2$ being higher and that of *gem*-dinitro-compound $(C_6H_5)_2C(NO_2)_2$ lower than when the reaction is carried out in toluene, the percentages being 22 and 27% respectively, together with regenerated diphenylmethane 32 and 38%, and saturated NO 20 and 48%. These experiments have also demonstrated the possibility of producing via such a route *gem*-dinitro-derivatives of xylenes, mesitylene,[18] ethylbenzene and tetralin.[14] Phenyldinitromethane is also produced by treating benzylmercuric chloride[19] with HNO_3, d_1 1·2, the reaction being similar to but much faster than with toluene.

There is also the possibility of oxidizing the intermediate nitroso-compounds to $R_3C—NO_2$ with NO_2 and their conversion via oximes to *gem*-trinitro-compounds of the type $ArC(NO_2)_3$, pseudo-nitrols, nitrolic acids, nitrile oxides, furoxanes, aldehydes and ketones, carboxylic acids, etc.[3,4,11] In some instances, nitration is determined by the formation of *gem*-trinitro-compounds,[18,20] in particular phenyltrinitromethane[20] and its conversion to *p*-nitrobenzoic acid, and benzyl *p*-nitrobenzoate.[3,17,21] *Gem*-trinitro-compounds in yields of over 6%, are formed when N_2O_4 solutions are kept in toluene[20] and *m*-xylene[18] at 20° and *p*-nitrobenzoic acid is produced on nitrating toluene in acetic acid[3] at 80° according to Shoryguin.[10] Diphenylfuroxane was

[20] A. I. Titov, *Zh. Obshch. Khim.* **18**, 534 (1948).

[21] A. I. Titov, *Zh. Obshch. Khim* **24**, 2040 (1954).

obtained in a fair yields (ten years after the prediction[3] (1941) of its formation) by the action of HNO_3, d_1 1·1, in the presence of NO_2, on benzyl mercuric chloride.[19] The formation of nitroso-compounds was observed in the vapour-phase nitration of ethyl chloride and dichloroethane,[22] probably due to the stabilizing effect of chlorine atoms, particularly in α-position,



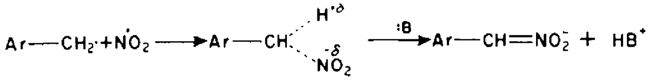
Gem-chlornitroso-compounds are also formed on introducing nitrogen oxide during photochemical chlorination of cyclohexane and *n*-pentane at room temperature.[5]

The possibility of alkyl radicals reacting with $\dot{N}O$ through oxygen, similarly to the reaction with $\dot{N}O_2$ to give rise to the monomeric hyponitrite R—ON has not yet been proved and has only recently been discussed. The same is true of the conversion of R—NO to diazo-compounds $R—N_2^+ \; NO_3^-$ by reaction with NO.[14]

The formation and production of mononitro-derivatives is mainly exemplified by nitration of toluene,[8] cyclohexane[6,9] and ethylbenzene.[14] According to Konovalov, phenylnitromethane is produced by the nitration of toluene with HNO_3, d_1 1·12, at 100° in sealed tubes for 48 hours. Shoryguin[10] failed in 1930 to explain why Hantzsch and other workers did not succeed in producing phenylnitromethane according to Konovalov. This must have been due to the lack of NO_2 formation and regeneration, in particular with tubes in vertical position (see p. 559).

The mechanism of phenylnitromethane formation according to (1) and (2) indicates the possibility of developing useful methods to produce α-nitroalkylbenzenes in open vessels in large amounts (up to 50–60% yields) both by nitration with N_2O_4 and HNO_3, d_1 1·5, in 2–4 hours.[8,12,14,18] According to the theory when nitrating with NO_2 it is necessary to attain the maximum content of NO_2 in the hydrocarbon with a minimum ratio of NO/NO_2 and N_2O_4/NO_2. This was ultimately achieved by using a very large excess of toluene, heating to 100° and introducing oxygen.[8] The difficulties of extracting the nitro-compound with alkali from a large excess of hydrocarbon was overcome by adding diethylamine to transform e.g. phenylnitromethane into the salt of the aci-form when still in toluene solution.[8] Addition of 1 g of the paraformaldehyde, to a mixture of 0·5–2·1 of hydrocarbon, 50 ml of HNO_3, d_1 1·4, and of 50 g of $Ca(NO_3)_2$ or KNO_3 led to the initial formation of NO_2 whereas gradual introduction of 50 ml of HNO_3, d_1 1·5, into the acidic layer at 90–100° and of a suitable amount of O_2 for 2–4 hours ensured a necessary concentration of NO_2. Nitrate addition decreases the nitration in the nucleus and together with an excess of RH minimizes the destructive effect of HNO_3 upon $R—NO_2$, ROH, R—ONO and other esters.[14] By this route tens and hundreds of grams of α-nitroalkylbenzenes, particularly those of *m*-xylene[18] and ethylbenzene[14] have been produced.

Under these conditions 3–7% *gem*-dinitro-[8] and up to 1% *gem*-trinitro-compounds are produced, partly due to NO, but essentially due to the partial formation of the aci-form or of the anion of the nitro-compound during the attack of the electrophilic NO_2 on the alkyl radical with participation of proton acceptors:



$$Ar—CH_2\cdot + \dot{N}O_2 \longrightarrow Ar—CH\begin{matrix} \cdot\cdot H^{+\delta} \\ \cdot\cdot \overset{-\delta}{N}O_2 \end{matrix} \xrightarrow{:B} Ar—CH{=}NO_2^- + HB^+ \qquad (13)$$

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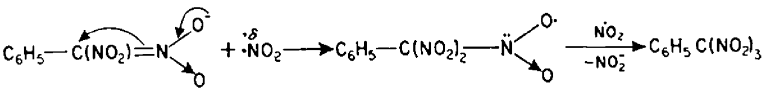
[22] A. I. Titov and V. V. Smirnov, in the press.

In fact, anions and aci-forms are readily converted to dinitro- and partly to trinitro-compounds by the action of NO_2.[17] Ionization of phenyldinitromethane in HNO_3 causes a striking change of reactivity in the series $C_6H_5CH_3$, $C_6H_5{-}CH_2NO_2$, $C_6H_5CH(NO_2)_2$.[17] The first compound undergoes nitration at a moderate rate, the second does not react and the third reacts readily according to the mechanism:



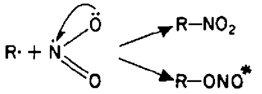
(14)

The radical-anion generated gives up an electron to the second molecule of NO_2 thus forming the trinitro-compound.

The effect of addition of NO_2, diffusion, the amount of hydrocarbon, stirring and other factors on nitration under pressure was investigated using cyclohexane.[6,9]

The theoretical aspects of nitration also involve the mechanisms with formation of degradation, dehydrogenation and oxidation products.

The most interesting compounds formed by degradation are the lower nitro-compounds by nitration at elevated temperatures. They result from the dual reactivity of $\dot{N}O_2$ with alkyl radicals

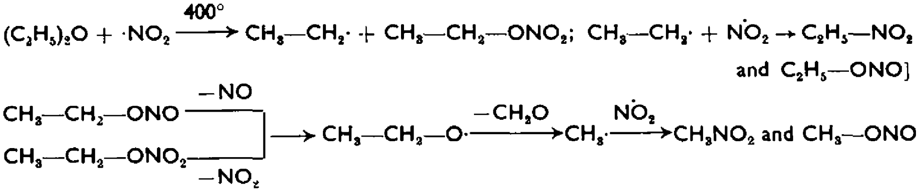


(15)

(16)

and the simultaneous or subsequent pyrolysis of alkyl nitrites R—ONO* in terms of (5) (see p. 558). This mechanism was first reported in 1940[2] and repeated in 1948[20] and 1952.[4] There are, however, some authors who advance the same conceptions without acknowledging the earlier references.

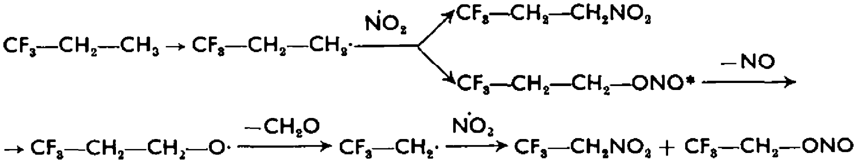
It is also possible to depict the mechanism of destructive nitration of alcohols, ethers, and ketones, e.g. diethyl ether[23] to form $C_2H_5{-}NO_2$ and $CH_3{-}NO_2$:



$$(C_2H_5)_2O + \cdot NO_2 \xrightarrow{400^\circ} CH_3{-}CH_2\cdot + CH_3{-}CH_2{-}ONO_2;\ CH_3{-}CH_2\cdot + \dot{N}O_2 \rightarrow C_2H_5{-}NO_2 \text{ and } C_2H_5{-}ONO]$$

$$\left.\begin{array}{l} CH_3{-}CH_2{-}ONO \xrightarrow{-NO} \\ CH_3{-}CH_2{-}ONO_2 \xrightarrow[-NO_2]{} \end{array}\right] \longrightarrow CH_3{-}CH_2{-}O\cdot \xrightarrow{-CH_2O} CH_3\cdot \xrightarrow{\dot{N}O_2} CH_3NO_2 \text{ and } CH_3{-}ONO \qquad (17)$$

The formation of trifluoronitroethane on nitration of *gem*-trifluoropropane,[24] bearing in mind the strongly electrophilic effect of the CF_3-group, can be shown as follows:



$$CF_3{-}CH_2{-}CH_3 \rightarrow CF_3{-}CH_2{-}CH_2\cdot \xrightarrow{\dot{N}O_2} \begin{array}{l} \nearrow CF_3{-}CH_2{-}CH_2NO_2 \\ \searrow CF_3{-}CH_2{-}CH_2{-}ONO^* \xrightarrow{-NO} \end{array} \qquad (18)$$

$$\rightarrow CF_3{-}CH_2{-}CH_2{-}O\cdot \xrightarrow{-CH_2O} CF_3{-}CH_2\cdot \xrightarrow{\dot{N}O_2} CF_3{-}CH_2NO_2 + CF_3{-}CH_2{-}ONO$$

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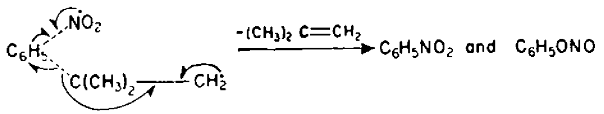
[23] H. Hass and D. Hudjin, *J. Amer. Chem. Soc.* **76**, 2692 (1954).

[24] E. McBee, H. Hass and J. Robinson, *J. Amer. Chem. Soc.* **72**, 3579 (1950).

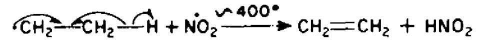
During the nitration of ethyl chloride[22] under similar conditions the formation of $CH_3—CHCl—NO_2$ and $CH_3—CHCl—NO$ was observed. In this case the possibility of the conjugation of the unpaired electron in the radical $CH_3—\dot{C}H—\ddot{C}l$ with the methyl group and the unshared pair of chlorine electrons is of predominant importance.

The isomerization of radicals such as the neophyl[25] $C_6H_5—C(CH_3)_2CH_2\cdot$ are considered to proceed at a low concentration of NO_2, e.g. when nitrating with dilute HNO_3.[14] Concurrently, an anomalous degradation with NO_2 attacking the nucleus of the neophyl radical takes place.


(19)

The phenyl nitrite gives rise to nitrophenols.

As will be shown, dehydrogenation of radicals by NO_2 is of great importance during nitration of aromatic and unsaturated compounds. The formation of olefins during nitration of paraffins (e.g. see [26]) proceeds similarly by the β-hydrogen abstraction from free alkyls by NO_2, O_2, NO and other radical-like agents.


$$\cdot CH_2—CH_2—H + \dot{N}O_2 \xrightarrow{\sim 400^\circ} CH_2{=}CH_2 + HNO_2 \tag{20}$$

This reveals the dual reactivity of alkyl radicals and a third reaction with NO_2. The readiness of the abstraction of β-hydrogen in alkyl radicals is accounted for by the decreasing dissociation energy of this bond by 58 kcal as compared with ethane $CH_3—CH_2—H$ and there can be no doubt that $D(\cdot CH_2—CH_2—H)$ equal to 40 kcal[27] is amply compensated for by the heat of H and NO_2 bonding, possibly with a simultaneous dissociation of HNO_2, at the moment of formation, to HO· and $\dot{N}O$. Steric factors also favour this reaction and its rate seems to be comparable in the gaseous phase at high temperature to that of the combination of R· and $\dot{N}O_2$ in terms of (15–16). The formation of destructive oxidation products takes place to a large extent, at the expense of the reaction of NO_2 and O_2 with olefins.[28]

The predicted formation of alkyl nitrites[2] according to (16) has been proved[3,20,29,30] and the postulation of the mechanism of formation of lower nitro-compounds[2,4] has been thus convincingly substantiated. Alkyl nitrites also proved to be the major source of oxidation products.

Oxidation is one of the main reactions involving the paraffin chain nitration, being predominant at a high concentration of nitrogen dioxide[29] or O_2.[20] The reaction of radicals with NO_2 at 100° gives rise to about 60% nitro-compound and 40% alkyl nitrite.[20]

Alkyl nitrites when nitrated in a liquid phase readily undergo hydrolysis, trans-esterification, and other equilibrium reactions in terms of the following scheme:[4,20]

[25] H. C. Duffin, E. D. Hughes and C. Ingold, *J. Chem. Soc.* 2734 (1959).

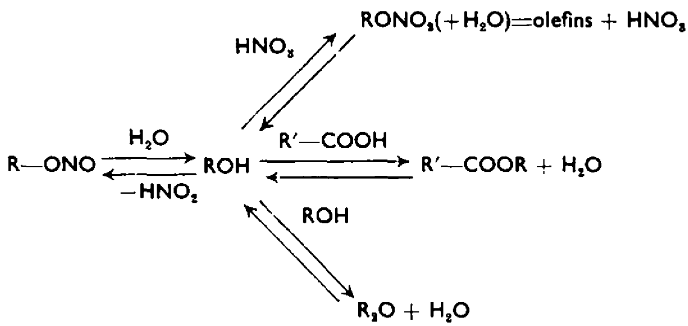
[26] G. B. Bachman and N. W. Standish, *J. Org. Chem.* **26**, 570 (1961).

[27] C. Walling, *Free Radicals in Solution*, N.Y. (1957).

[28] A. P. Altshuller and Cohen, *Ind. Eng. Chem.* **51**, 776 (1959).

[29] A. I. Titov and M. K. Matveeva, *Sbornik rabot po obschey knimii* **1**, 246 (1953).

[30] A. I. Titov and M. K. Matveeva, *Dokl. Akad. Nauk SSSR* **83**, 101 (1952).



(21)

(22)

(23)

yielding alcohols, alkyl nitrates, esters of organic acids, ether and olefins and their conversion products. Alcohols and alkyl nitrites are readily oxidized by NO_2 to aldehydes and ketones and subsequently to acids R′—COOH which esterify with alcohol according to (22).[21,29,30] Alkyl nitrates $\overset{+\delta}{R}$—ONO_2 with their cationic R are relatively stable to oxidation. Aldehydes and ketones may be transformed to lower *gem*-dinitro-compounds, nitriles, HCN, etc.[3,4] Olefins are converted to vicinal dinitroalkanes, nitroolefins, etc.[4] By creating conditions favourable to the formation of R—ONO, R—ONO_2 and ROH it is possible to obtain these compounds in fair yields. Thus, treating benzylmercuric chloride with HNO_3, *d* 1·2, in the presence of NO_2 at 20° gives 21 % benzyl nitrite and 7 % nitrate. When dibutylmerçury is nitrated with N_2O_4 at −5° the yield of alkyl nitrite is 15 %[19] but with a large excess of toluene, about 1 % concentration of nitrogen dioxide and saturation with O_2 at room temperature for 6 days in the presence of $CuSO_4$ the yield of benzyl nitrate is over 30%; which may be due partly to the reactions with O_2 and N_2O_4:

$$R\cdot + O_2 \rightarrow R{-}O{-}O\cdot \xrightarrow{NO_2} R{-}O{-}ONO_2 \xrightarrow[-NO_3\cdot]{\cdot NO_2} RONO_2 \tag{24}$$

$$R\cdot + O_2N.NO_2 \xrightarrow{-NO_2} R{-}ONO \xrightarrow{NO_2} RONO_2 + NO \tag{25}$$

With 2% NO_2 after 4 days, the yield of benzyl alcohol and its esters amounted to 42·3%, that of benzaldehyde 14·2% benzoic acid 4·4% phenylnitromethane 11·2% nitrotoluenes 13·6% and nitrocresols 2·2%.[20]

Nitration at 100° gives a lower yield of primary oxidation products for in this case radicals react almost exclusively with NO_2 whereas alcohol, esters and aldehyde were mostly oxidized to benzoic acid. Thus the percentage yield of one run[20] was as follows:

Table 2

Phenylnitromethane	52·5	Benzaldehyde	2·4
Phenyldinitromethane	2·7	Benzoic acid	11·2
Benzyl nitrite	6·2	Nitrotoluenes	2·0
Benzyl alcohol	7·1	Other products	12·4
Benzyl nitrate	1·8		

Similar results are obtained for other arylparaffins. The reaction of NO_2 and diphenylmethane yields crystalline dibenzhydryl ether.[12] An hour's heating in a sealed tube at

100° with a 20% solution of N_2O_4 in cyclohexane results together with nitrocyclohexane and dibasic acids, in cyclohexyl nitrite, cyclohexanol, dicyclohexyl adipate and nitrate (at 60°).[29,30] The formation of nitrites, alcohols and nitrates also takes place in the reaction with nitric acid[20] as well as in the vapour-phase nitration of pentane and cyclohexane.[29] Adipic acid probably originates from cyclohexyl nitrite mainly through the intermediate cyclohexanol,[29,30] and in part through its decomposition to NO and $O{=}CH{-}(CH_2)_4{-}CH_2\cdot$ (see Eq. 12) as confirmed by Konovalov's report on the formation of acetophenone during nitration of isopropylbenzene under similar conditions:[3,4]

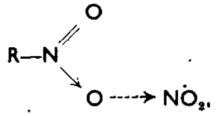
$$C_6H_5{-}C(CH_3)_2{-}ONO \xrightarrow[-NO]{t} C_6H_5{-}C(CH_3)_2{-}O\cdot \rightarrow C_6H_5COCH_3 + CH_3\cdot \tag{26}$$

It has thus been shown that the oxidation and degradation products are formed during nitration *via* alkyl nitrites. This is further proved for the oxidation products, in the case of toluene nitration at 100° under different conditions by the constant overall yield of benzoic acid (I) and oil (II) consisting essentially of benzyl nitrite and its neutral conversion products. This overall yield is ~45%[20,4] although the yields of I may range from 4·7 to 26·7 and that of II from 42 to 20%. Under more drastic conditions the oil is almost completely converted into benzoic acid. Similarly, the product of cyclohexane nitration under mild conditions when heated with HNO_3 in the presence of NO_2 is a mixture of nitrocyclohexane and adipic acid just as was the case when Markovnikov, Nametkin and other workers nitrated cyclohexane under drastic conditions.[29,30]

The oxidative route of the reaction increases with rising concentration of NO_2 as illustrated by the composition of products when a solution of N_2O_4 in cyclohexane was allowed to stand for 60 days under normal conditions.[29]

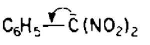
N_2O_4/C_6H_{12}	0·1	3·8	
$C_4H_8(COOH)_2/C_6H_{11}NO_2$	1·1	13·7	(27)

The concentration effect is accounted for by the predominance of the reaction of cyclohexyl radical with N_2O_4 according to (25) producing, due to the screening of the nitrogen atom in $O_2N{\cdot}NO_2$, cyclohexyl nitrite, which is converted to adipic acid. A marked increase in the oxidation is also observed in the reaction of diphenylmethane with NO_2 (20°) if CH_3NO_2 is substituted for CCl_4 as solvent. This is probably due to the appearance of solvates of the type



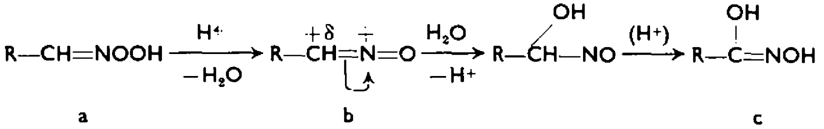
with the nitrogen atom screened.[3,4] It is possible that a relatively high concentration of NO_2 is partially present as $O_2N{\cdot}NO_2 \dashrightarrow \dot{N}O_2$. All this favours oxidative processes with no large excess of hydrocarbons[6,8] or solvents.[3,12]

To a lesser degree, oxidation products are formed by conversion of nitroso-compounds or oximes (see Eq. 3), to aldehydes, ketones and acids. In the absence of a large excess of hydrocarbons, *gem*-dinitro-compounds are readily converted to acids, when nitrated in acetic acid at elevated temperatures. In particular, phenyldinitromethane gives *p*-nitrobenzoic acid[3,17] via nitration of the anion



$C_6H_5\text{—}\bar{C}(NO_2)_2$

into *p*-nitrophenyldinitromethane 1,4-$NO_2C_6H_4CH(NO_2)_2$. Mononitro-compounds RCH_2NO_2, including phenylnitromethane, are stable to NO_2 and react rather slowly with HNO_3 to give acids probably through the intermediate aci-form (a), the organic analogue of NO_2^+ (b) and hydroxamic acid (c):[3]

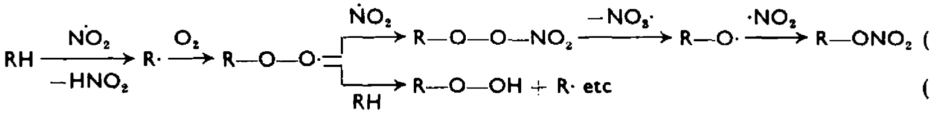


(28)

Thus RNO_2 is, generally not responsible for oxidation products.

It is evident from the above and from pages 559 and 563 that the slower rate of diffusion as compared with nitration lowers $[N_2O_4]$ in the organic phase to a greater extent than it does $[NO_2]$ and hence, the relative yield of R—NO_2 is increased. The same factor leads to increasing [NO] and hence results in more R—NO and its conversion products, in particular *gem*-dinitro-compounds. In some cases this diffusion effect is very pronounced.[9]

In the presence of oxygen NO_2 initiates oxidation.[3,20,4]

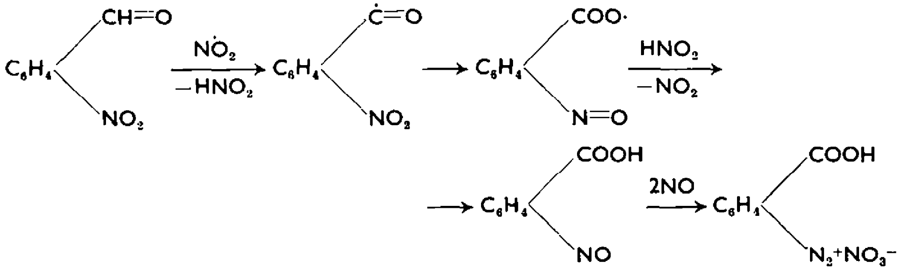


(29)

(30)

The reaction following scheme (29) results in pernitrates followed by nitrates and according to (30) leads to chain nitration, degradation and oxidation. According to schemes such as (30), NO_2 initiates chlorination of the paraffin chain. At high temperatures additions of Cl_2 and Br_2 also apparently accellerate nitration.[4,31]

Intramolecular oxidation of radicals at the expense of the *o*-nitro-group leading to the formation of diazo-compounds takes place on long standing with NO_2 solutions in *o*-nitrotoluene[3] or more quickly in *o*-nitrobenzaldehyde as follows:



(31)

Owing to NO being consumed in the reaction (31), the nitration with NO_2 of *o*-nitrotoluene gives no *gem*-dinitro-compounds; whereas *o*-nitrophenylnitromethane is, produced in fair yield. The formation of large quantities of picric acid by the action

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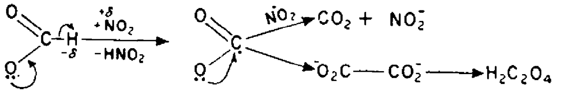
[31] G. Bachman, M. T. Atwood and M. Pollack, *J. Org. Chem.* **19**, 312 (1954).

of 22·5% HNO_3 on *o*-nitrotoluene[32] at 180° must have proceeded through similar stages. Under similar conditions (via the intermediate *o*-nitrotoluene) toluene yields only a small quantity of picric acid. As will be shown the reaction of R· and $ArNO_2$ is intermolecular. R—ONO, $R—ONO_2$[4], $CHBr_3$, CCl_4, maleic anhydride, etc. can also take part in the reaction.

The comparatively rapid oxidation by NO_2 of alcohols, aldehydes and similar compounds is accounted for by the greater stability of incipient radicals than that of free alkyls due to conjugation with unshared pairs of electrons O or N, e.g. in an acid radical $R—\dot{C}{=}\ddot{O}$. In particular, oxidation of formic acid by HNO_3 proceeds by the interaction of NO_2 and formiate anion[3] or HCOOH



(32)

(33)

with the intermediate formation of a radical-anion $\dot{C}O_2^-$ which is isoelectronic to $\dot{N}O_2$ and hence rather stable. Its presence or the formation of radical-acid $\dot{C}OOH$ is proved by the dimerization product, oxalic acid.[33]

Similarly the high reactivity of $Ar—CH_2—\ddot{N}{=}O$ in the nitration of alkylbenzenes is due to the conjugation of CH with the aryl nucleus and the unshared electron pair of nitrogen. Nitroso-compounds of this type are readily converted by NO_2 to a radical:

$$Ar—\dot{C}H—\ddot{N}{=}O \longleftrightarrow Ar—CH{=}\dot{N}{\rightarrow}O \longleftrightarrow Ar—CH{=}\dot{N}—\dot{O}$$

Depending on the NO_2 concentration this radical may be converted to *gem*-dinitro-compound, diarylfuroxan or other products.

Thus many problems related to paraffin chain nitration have been solved. The rapid reaction of anhydrous nitric acid with *n*- and isoparaffins under normal conditions, the possibility to nitrate rapidly with conc. nitric acid (*d* 1·42) at about 400° and some other problems were elucidated during 1941–1950 by studying the high reactivity of the paraffin chain toward nitric anhydride[3,6] and by allowing for its formation, as well as the formation of a radical-like nitrogen tri-oxide $O_2N—O\cdot$ during high-temperature nitration[6] and the concurrent action of nitrogen oxides[3] and O_2.

The reaction of N_2O_5 with paraffins and cyclohexane[34] is quick even at 0° in a solution of CCl_4 giving rise mainly to secondary alkyl nitrates and nitro-compounds. The reaction is obviously affected by a more active initiator than $\dot{N}O_2$. Probably this is $NO_3\cdot$, resulting from the homolytic dissociation of N_2O_5.

$$O_2N—O—NO_2 \rightleftarrows \dot{N}O_2 + \cdot O—NO_2 \tag{34}$$

Such a dissociation is proved by the fact that the nitrogen pentoxide reaction with paraffins is slowed down by addition of NO_2 shifting the equilibrium (34) toward the formation of N_2O_5, just as the reaction of NO_2 is itself retarded by NO owing to the formation of N_2O_3. This postulate is also substantiated by data reported by Ogg.[34]

The high reactivity of $NO_3\cdot$ as compared with $\dot{N}O_2$ and $\dot{N}O$ is due to its being less saturated and more electrophilic as, is shown by the equilibrium reactions with $NO_2\cdot$,

$$\underset{K_1>}{(1)\ NO_3\cdot + \dot{N}O_2 \rightleftarrows N_2O_5};\quad \underset{K_2>}{(2)\ \dot{N}O_3 + \dot{N}O_2 \rightleftarrows N_2O_4};\quad \underset{K_3}{(3)\ \dot{N}O + \dot{N}O_2 \rightleftarrows N_2O_3} \tag{35}$$

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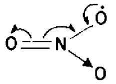
[32] P. Askenasy, E. Elöd and C. Trogus, *Liebigs Ann.* **461**, 109 (1928).

[33] M. Ballo, *Ber. Dtsch. Chem. Ges.* **17**, 6 (1884).

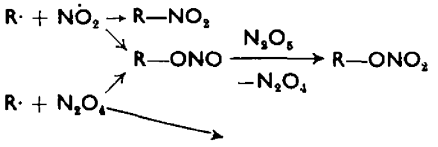
[34] A. I. Titov, *Dokl. Akad. Nauk SSSR* **81**, 1085 (1951).

and the strength of the corresponding acids $HONO_2 > HONO > HNO$. Accordingly, E in the reaction of RH and NO_3 in (36) should be ~25 kcal. lower than with NO_2 in terms of (1). The relative stability of $NO_3\cdot$ is based on the distribution of the unpaired electron throughout all oxygen atoms owing to an allyl type conjugation



The mechanism of the reaction of N_2O_5 with a paraffin chain may be regarded, in addition to (34) as:

$$R{-}H + NO_3\cdot \rightarrow R\cdot + HNO_3 \quad (36)$$



$$R\cdot + \dot{N}O_2 \rightarrow R{-}NO_2 \quad (37)$$

$$R{-}ONO \xrightarrow[-N_2O_4]{N_2O_5} R{-}ONO_2 \quad (38)$$

$$R\cdot + N_2O_4 \quad (39)$$

$$R\cdot + O_2N{-}O{-}NO_2 \rightarrow R{-}ONO_2 + NO_2 \text{ (or NO)} \quad (40)$$

The rapid conversion of nitrite to nitrate according to (38) proved experimentally. The part played by each of the above processes is dependent on the concentration of $\dot{N}O_2$, N_2O_4, N_2O_5 and their reactivity. In accordance with the theory, by slow addition of N_2O_5 and at elevated temperatures reaction (37) predominates and the yield of $R{-}NO_2$ is greatly increased approximating that obtained by nitration under similar conditions with N_2O_4 or aqueous HNO_3 in the presence of $\dot{N}O_2$. This evidence was confirmed by kinetic data and the participation in the reaction with R· of oxygen and CCl_4 [35] that had already been noted during radical nitration of paraffins[34] and olefins with NO_2 (*vide infra*).

The reactivity of concentrated or anhydrous HNO_3 with paraffins is due to the formation of N_2O_5, as evidenced by a number of facts, particularly the presence of NO_2^+ and NO_3^-.[3,4,34,36]

$$3HNO_3 \rightleftarrows N_2O_5 + H_2O.HONO_2;\ N_2O_5 \rightleftarrows NO_3\cdot + \dot{N}O_2 \quad (41)$$

Nitrogen trioxide may also result from NO_2^+ and NO_3^- due to interionic electron transfer.

$$NO_2^+ + NO_3^- \rightleftarrows \dot{N}O_2 + NO_3\cdot \quad (42)$$

This theory of nitration by anhydrous HNO_3 has recently been confirmed.[37]

At the same time the formation of N_2O_5 and $NO_3\cdot$ during high temperature nitration with nitric acid was postulated.[6,34]

$$2HNO_3 \xrightarrow{t} N_2O_5 + H_2O;\ N_2O_5 \rightarrow NO_3\cdot + \dot{N}O_2 \quad (43)$$

In 1953, Fréjacques[38] proved the bimolecular order of the pyrolysis of HNO_3 at 280–380° and showed that it proceeds via the intermediate production of N_2O_5.

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[35] J. C. D. Brand, *J. Amer. Chem. Soc.* 77, 2703 (1955).

[36] A. I. Titov, *Usp. Khim.* 27, 845 (1958). (Due to the illness of the author some misprints have occurred. These can easily be corrected by readers). See also: *Wiadomosci chemiczne* 15, 741 (1961).

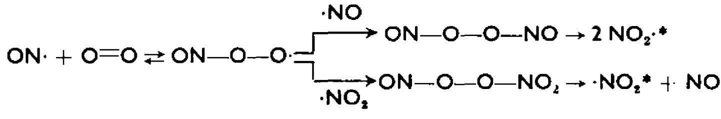
[37] M. L. Bender, J. Figueras and M. Kilpatrick, *J. Org. Chem.* 23, 410 (1958).

[38] C. Fréjacques, *Mem. Poudres* 35, appendix (1953), see 25.

Fréjacques thinks the conventional treatment of the pyrolysis of HNO_3 in terms of (44) to be wrong.

$$HONO_2 \rightarrow HO\cdot + \cdot NO_2 \tag{44}$$

It was shown in 1941[3]–1951[34] that the greatly increased reaction rate of NO_2 with the paraffin chain on saturation with O_2 is largely due to the formation of $NO_3\cdot$ and the active form of NO_2 during the conjugated oxidation of NO and NO_2:



$$ON\cdot + O{=}O \rightleftarrows ON{-}O{-}O\cdot \xrightarrow{\cdot NO} ON{-}O{-}O{-}NO \rightarrow 2\,NO_2\cdot^{*} \tag{45}$$

$$ON{-}O{-}O\cdot \xrightarrow{\cdot NO_2} ON{-}O{-}O{-}NO_2 \rightarrow \cdot NO_2{}^{*} + NO_3\cdot \tag{46}$$

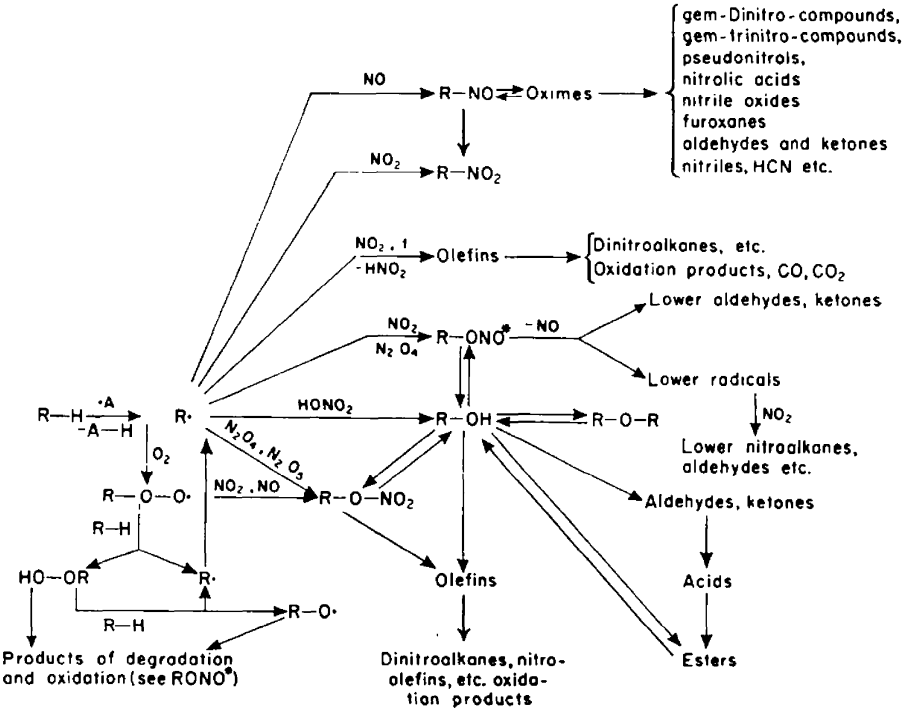
The increased rate of nitration in the gaseous phase in the presence of ozone[26] appears also due to the formation of $NO_3\cdot$.

Thus, according to the general theory of paraffin chain nitration the rate-determining step is the formation of a free alkyl radical following the scheme:

$$R{-}H + \cdot A \rightarrow R\cdot + H{-}A \tag{47}$$

where $\cdot A$ is $\cdot NO_2$, $NO_3\cdot$, $HO\cdot$, $Cl\cdot$, O_2, etc. The reaction of $R\cdot$ with NO_2, NO, O_2, N_2O_4, N_2O_5 and other suitable components of the reaction system including solvents such as $ArNO_2$, $CHBr_3$, CCl_4, etc. generally results in a mixture of $R{-}NO_2$, $R{-}ONO$, $R{-}NO$, $R{-}ONO_2$ etc. These compounds with the exception of $R{-}NO_2$ may, depending on the conditions undergo further, sometimes manifold, conversions thus accounting for the different composition of the end-products of nitration.

Schematically, the many chemical conversions that take place with paraffin chain nitration may be expressed as follows:



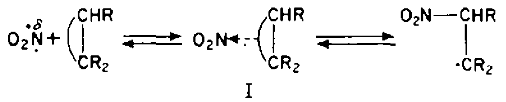
Hypotheses concerning the nature and mechanism of nitration of the paraffin chain suggested earlier do not adequately account for the experimental data obtained* and are in a sharp contrast to the discoveries in this field made since 1937.

As was shown in 1941[3] and 1946,[39] in contrast to the reaction with paraffins, nitration of unsaturated and aromatic compounds depending on their structure and mainly on the nature of the nitrating agent can take place according to the ionic or radical mechanisms. In the presence of strong acids nitration proceeds by the ionic mechanism via formation of a cation by addition NO_2^+ to the double bond. In contrast, "the reaction of unsaturated compounds with nitrogen oxides, particularly in neutral solvents, proceeds via, through the intermediate formation of radicals such as $O_2N{-}CR_2{-}\dot{C}R_2$; some reactions of nitrogen dioxide with aromatic compounds in a nonpolar medium also belong to this type of reaction."[3] In a subsequent paper[40] the reaction of olefins with nitrogen oxides has been demonstrated by a concise scheme with the formation of dinitro-compounds, nitro-nitrites and pseudo-nitrosites (nitronitroso-compounds):

$$R_2C{=}CR_2 + \dot{N}O_2 \rightleftarrows O_2N{-}CR_2{-}\dot{C}R_2 \xrightarrow{X=\dot{N}O,\dot{N}O_2} O_2N{-}CR_2{-}CR_2{-}X \qquad (48)$$

"The high rate and the reversibility of the initial phase is evidenced by the rapid conversion of *cis*-isomers (e.g. of maleic and oleic acids) in the presence of nitrogen dioxide, the action of which is similar to that of bromine atoms in a corresponding photochemical reaction. The high rate of the reaction of NO_2 with unsaturated compounds is due to the well known nature of the carbon–carbon double bond (π-bond) and the coordinative unsaturation of the carbon atoms."[40]

The above was extensively treated and experimentally proved in 1952.[41] During development of the work in 1946,[39,4] it was suggested that electrophilic NO_2 reacts with olefins via the intermediate complex I at the expense of its interaction with sterically available and mobile π-electrons represented in the scheme by a little bow.



(49)

For ethylene the activation energy of NO_2 addition in terms of the formula $E = -Q + 0{\cdot}13\ Q\pi$; Q being the reaction heat and $Q\pi$ the energy of the π-bond is 9 kcal at 20° whereas for styrene, due to the very high value of E_R in the radical $C_6H_5{-}\dot{C}H_2{-}CH_2NO_2$, ($\approx$25 kcal) there is no need for activation energy which is, in agreement with experimental data that styrene reacts instantly with NO_2 even at −20°.

The β-nitroalkyl radicals produced readily interact, in accordance with the theory, with $\dot{N}O$, $\dot{N}O_2$ similar to the nitration of paraffins.

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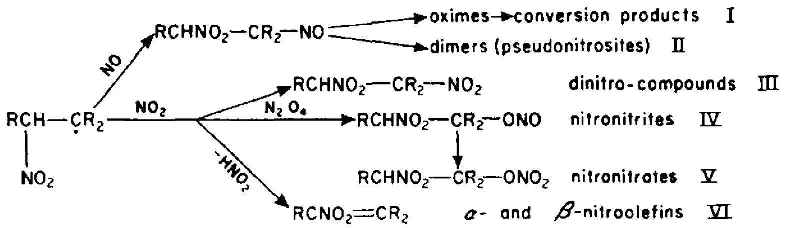
* These hypotheses are reviewed in.[4,5]

[39] A. I. Titov, *Zh. Obshch. Khim.* **18**, 190 (1948).

[40] A. I. Titov, *Zh. Obshch. Khim.* **16**, 1902–1903 (1946).

[41] A. N. Baryshnikova and A. I. Titov, *Dokl. Akad. Nauk SSSR* **91**, 1099 (1953).



(50)

The subsequent conversions of these compounds are in some respects similar to those considered above.

The suggested mechanism not only elucidates the known chemical and stereochemical data but also predicts new routes for this reaction. In particular, it offers an explanation for the formation of a mixture of stereoisomers by the action of NO_2 on unsaturated compounds, the identity of the products of nitration of *cis*- and *trans*-isomers and the catalytic effect of NO_2 on their conversion (see Eqs. 48 and 49). The reversibility of the reaction is substantiated by the kinetics in the gaseous[42] and liquid[43] phases. In some cases the stereospecificity of the reaction cannot be excluded.[43,44]

In accordance with the theory it has been possible to produce styrene pseudonitrosite by reaction II of scheme 50 with a low NO_2 concentration and NO saturation in a yield one and a half as high as that obtained by Wieland. It is hoped that by applying NO under pressure the yield will be even higher. A high yield is also possible when the reaction is carried out in styrene itself provided a very low NO_2 concentration is maintained owing to the extremely rapidity of the reaction of NO_2 with styrene. The structure of the monomeric pseudo-nitrosite C_6H_5—CH(NO)—CH_2NO_2 is in accordance with the radical mechanism and the primary attack of NO_2. If the reaction proceeded by an ionic mechanism, for instance via the initial interaction with NO^+ or N_2O_3, one would expect the isomeric nitrosite C_6H_5—CH(ONO)CH_2—NO to be formed. Finally, in acetic acid if the reaction proceeded by the ionic mechanism, conjugated addition[41] of NO^+ and CH_3COO^- should give rise to nitrosoacetate $C_6H_5CH(OOC—CH_3)—CH_2$—NO but this was proved not to be the case, the main product under these conditions remaining pseudo-nitrosite. Hence the reaction is of the radical type. This reaction may to some extent be regarded in terms of an interesting investigation carried out by Brown in 1957.[45] The addition of Cl· and NO to yield nitrosochlorides takes place on ultraviolet irradiation or on passing a mixture of NOCl and NO into halogenoolefins, in particular into vinylidene chloride or even C_2Cl_4.[22]

Further evidence for the intermediate formation of radicals by the action of nitrogen oxides on olefins is based on free alkyls being involved in their specific reactions with the third component which does not itself react with olefins and NO_2. Thus $ArNO_2$ may be converted into diazonium salts (see Eq. 31).

$$R\cdot + C_6H_5\text{—}NO_2 \xrightarrow{-R\text{—}O\cdot} C_6H_5\text{—}NO \xrightarrow{2NO} C_6H_5\text{—}N_2^+\,NO_3^- \qquad (51)$$

Styrene and cyclohexene react with NO_2 or dilute HNO_3 in nitrobenzene saturated

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[42] T. L. Cottrell and T. E. Gracham, *J. Chem. Soc.* 556 (1953); 3644 (1954).

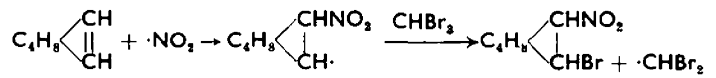
[43] J. C. D. Brand and I. D. R. Stevens, *J. Chem. Soc.* 629 (1958).

[44] J. J. Gardikes, A. H. Pagano and H. Shechter, *Chem. & Ind.* 632 (1958).

[45] J. F. Brown, Jr, *J. Amer. Chem. Soc.* **79**, 2480 (1957).

with NO and the phenyldiazonium nitrate formed may be identified as 1-azobenzene-2-naphthol.

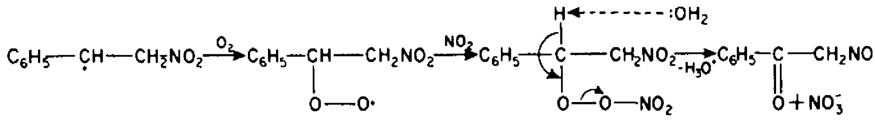
The reaction of cyclohexene in bromoform in the presence of low NO_2 concentration results in a fair yield of nitrobromocyclohexane.



(52)

These results are further substantiated by reaction in $BrCCl_3$ [43] as well as in the presence of $ClNO_2$, NOCl, I_2.[46] In the reaction of NO_2Cl and NOCl, Cl· as such or the incipient $\overset{\frown\frown}{Cl-NO_2}$ serve as initiators. This type of reaction should take place with halogeno derivatives possessing a positively polarized halogen. In particular the reaction takes place in CCl_4 solution; RONO, $RONO_2$,[4] etc. may also be involved.

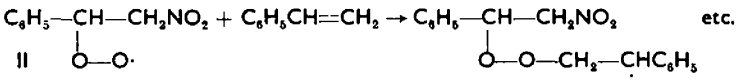
The introduction of O_2 into the reaction with radicals was effected in two ways with a low stryene concentration in CCl_4 and saturation with O_2 a vigorous absorption of oxygen takes place with formation of a "monomolecular" product which, on treatment with alcohol or water, results in a 50% yield of ω-nitroacetophenone.



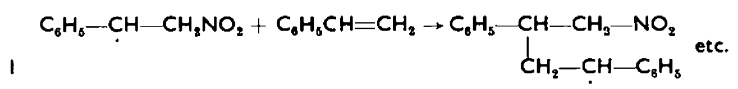
I II

(53)

The yield may be raised by introducing O_2 under pressure. The same reaction results in a high-molecular product when carried out in styrene or cyclohexene if additional olefin molecules are used according to the following schemes (54) and (55);



$$\underset{\text{II}}{C_6H_5-\underset{O-O\cdot}{CH}-CH_2NO_2} + C_6H_5CH{=}CH_2 \rightarrow C_6H_5-\underset{O-O-CH_2-\underset{\cdot}{C}HC_6H_5}{CH}-CH_2NO_2 \quad \text{etc.} \qquad (54)$$



$$\underset{\text{I}}{C_6H_5-\underset{\cdot}{C}H-CH_2NO_2} + C_6H_5CH{=}CH_2 \rightarrow C_6H_5-\underset{CH_2-\underset{\cdot}{C}H-C_6H_5}{CH}-CH_2-NO_2 \quad \text{etc.} \qquad (55)$$

as well as various combinations including those indicated by reaction (53). Later Stevens[47] reported that in this reaction and with other olefins α-nitroketones are formed in addition to the usual products.

The reaction rate and the orientation of $\overset{+\delta}{\cdot NO_2}$ in terms of (49) is governed by the tendency to form stable β-nitroalkyl radicals and by the electrophilicity of $\overset{-\delta}{NO_2}$. Thus, in reactions of the radical type the $\cdot NO_2$ adds on to carbon 3 when reacting with acrylic and metacrylic acids[48] and their esters,[49] to the carbons in the β-position to the phenyl group in compounds such as styrene, benzalacetophenone and even α,α-diphenyl-β-nitroethylene and to the CH_2 group in the case of propylene etc. With crotonic acid and its esters the NO_2 may attach itself to the α- and β-positions due to

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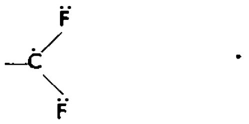
[46] T. E. Stevens and W. D. Emmons, *J. Amer. Chem. Soc.* **80**, 338 (1958).

[47] T. E. Stevens, *Chem. & Ind.* 499 (1960).

[48] N. V. Egorov, Dissertation, Moscow (1903).

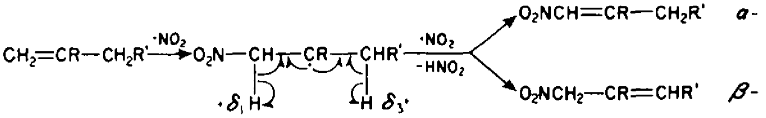
[49] H. Shechter and D. Ley, *Chem. & Ind.* 533 (1955).

the competitive orienting effect of the CH_3^- and O═C groups. The NO_2 addition to perfluoroisobutylene[50] takes place at the quaternary carbon in accordance with the possibility of the conjugation of the unpaired electron in the group



with unshared electron pairs of fluorine favoured by the similar dimensions of the atomic orbitals of C and F. The increased production of nitronitrite in the reaction of NO_2 and perfluoropropylene may be explained by the high electrophilicity of the β-nitroperfluoroalkyl radical formed. The NO_2 addition to nitro- and dinitroalkenes such as 2,3-dinitrobutene-2 takes place under drastic conditions due to their electrophilic character.[51,52]

α-Nitro-derivatives are reported[53] in the reaction of β-nitrostyrene and NO_2 in CCl_4 to result in $C_6H_5{-}CH{=}C(NO_2)_2$. It has also been found that bromine is substituted in β-bromostyrene[54] owing to the ready cleavage of bromine atoms from β,β-bromonitroalkyl radical in the reaction with the parent olefin. The formation of β-nitroolefin[55] should be represented as follows:



(56)

In the incipient nitroalkyl radical the unpaired electron is homolytically conjugated with CH-bonds of carbons 1 and 3 and hence their hydrogen is readily abstracted by NO_2 (see the explanation of Eq. 20). This readiness is decreased by the $+\delta$ hydrogen magnitude increasing due to the electrophilicity of NO_2, and as $\delta_1 \gg \delta_3$ it is essentially the H at carbon 3 that is split off giving rise to β-nitro-olefins. Similarly the addition of 2 NO_2, or NO_2 and NO to dienes-1,3 in 1,4 position,[56] may be accounted for in radicals of the type $O_2NCH_2{-}\dot{C}H{-}\dot{C}H{-}CH_2$ $\delta_2 > \delta_4$. In the reaction of NO_2 and 1-cyano-1,4-diphenylbutadiene the $2NO_2$ addition takes place in 4,3 position (see [57]) due to the radical exhibiting the electrophilic effect of the N≡C-group and to a high δ_1. Being of a cryptoaromatic character, cyclohexadienes and their derivatives are often dehydrogenated by NO_2 to give aromatic compounds.

The homolytic reactions of N_2O_5 with olefins have not been investigated, but the

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[50] I. L. Knunyants and A. V. Fokin, *Dokl. Akad. Nauk SSSR* **111**, 1035 (1956).

[51] Ch. E. Grabiel, D. E. Bisgrove, L. B. Clapp, *J. Amer. Chem. Soc.* **17**, 1293 (1955).

[52] M. B. Frankel and K. Klager, *J. Org. Chem.* **23**, 494 (1958).

[53] S. S. Novikov, V. M. Belikov, V. F. Demyanenko and L. V. Lapkina, *Izw. Akad. Nauk SSSR, Otd. Khim. Nauk* 1295 (1960).

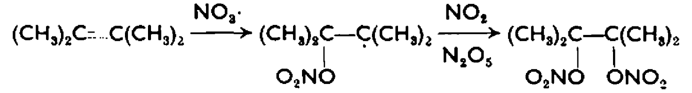
[54] T. E. Stevens, J. Org. Chem. **25**, 1658 (1960).

[55] A. D. Petrov and M. A. Bulyiguina, *Dokl. Akad. Nauk SSSR* **77**, 1033 (1951).

[56] A. A. Ivanov, *Zh. Obshch. Khim.* **16**, 647 (1946).

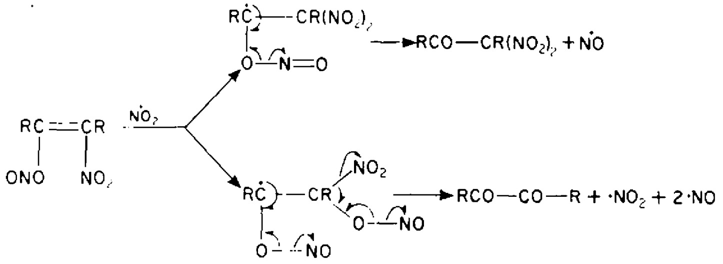
[57] A. V. Topchiev, *Nitration of Hydrocarbons and Other Organic Compounds*. Pergamon Press, N.Y. (1959).

formation of glycol dinitrates as observed by Demyanov appears to be initiated by $NO_3\cdot$.[58]



$$(CH_3)_2C{=}C(CH_3)_2 \xrightarrow{NO_3\cdot} (CH_3)_2\underset{O_2NO}{C}-\dot{C}(CH_3)_2 \xrightarrow[N_2O_5]{NO_2} (CH_3)_2\underset{O_2NO}{C}-\underset{ONO_2}{C}(CH_3)_2 \qquad (57)$$

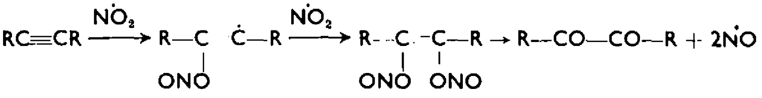
The NO_2 reactions with alkines are essentially similar to those with olefins.[41] Dinitroketones and diketones are produced via nitronitrites[59] similar to the pyrolysis of R—ONO but here scission is strongly facilitated by conjugation with the unpaired electron and by the energy factor, the starting radicals forming stable molecules



(58)

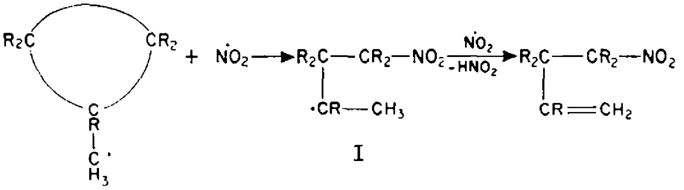
(59)

Owing to the increased electrophilicity of the triple bond, primary addition of NO_2 to O may take place, followed by the decomposition of dinitrite:



$$RC{\equiv}CR \xrightarrow{\dot{N}O_2} R-\underset{ONO}{C}\;\;\dot{C}-R \xrightarrow{\dot{N}O_2} R-\underset{ONO}{C}-\underset{ONO}{C}-R \rightarrow R-CO-CO-R + 2\dot{N}O \qquad (60)$$

The configuration of electronic orbitals of carbon atoms in the nucleus of cyclopropane compounds is approximately tetrahedral but with less overlapping and greater steric availability of electrons due to the eccentricity of the orbitals. The carbon–carbon bonds in cyclopropane may be considered as having the character of π-bonds in accordance with physical and chemical properties such as increased polarizability and formation of complexes with $C(NO_2)_4$.[41] This conclusion is substantiated by data on the nitration of tricyclene[41] which, in relation to this aspect may be represented as:



(61)

The addition of NO_2 to the π-like bond is followed by the dehydrogenation of the radical I. At an elevated temperature (>400°) hydrogen substitution by a nitro group may take place simultaneously.

The radical mechanism for the nitration of aromatic compounds was already formulated in 1941[3,39] as may be seen from the quotation on page 31 it having been

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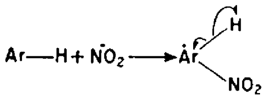
[58] A. N. Baryshnikova and A. I. Titov, *Dokl. Akad. Nauk SSSR* **114**, 777 (1957).

[59] J. P. Freeman and W. D. Emmons, *J. Amer. Chem. Soc.* **79**, 1712 (1957).

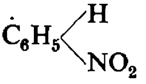
proved at the same time that "the chemical activity of nitrogen dioxide in benzene solution is proportional to its degree of hydrocarbon dilution."[3] The mechanisms of the reaction of ArH and NO_2 were recorded in 1945–46[60,61] and in more detail in 1948–51.[62,63]

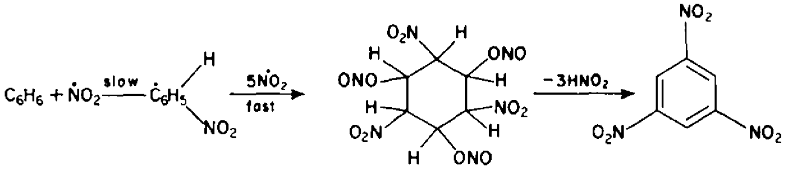
According to the theory the initial stage in the reaction of ArH with nitrogen oxides[62] or dilute nitric[63] acid is the addition of $\overset{+\delta}{\cdot NO_2}$ to the π-electron sextet to form a radical:



(62)

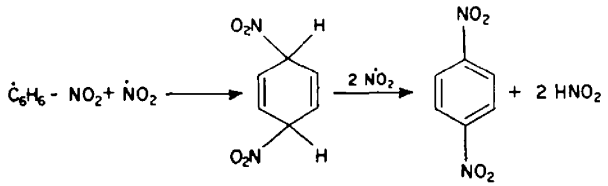
in which the CH-bond is strongly conjugated with the unpaired electron owing to the tendency to reduce the aromatic system (cryptoaromatic state). Saturation with O_2 greatly accelerated the reaction of nitrogen oxide and benzene at 20° partly due to the conversion of NO to NO_2 but mainly due to the formation of $NO_3\cdot$ and N_2O_5 (see Eqs. 46 and 69). Nitration proceeds quickly at 135–150° even at a very low concentration of NO_2 in benzene[62] or with HNO_3 (d1·1) in the presence of traces of nitrogen oxides,[63] that is with complete dissociation of N_2O_4 and N_2O_3. To retard the reaction proceeding by an ionic mechanism, nitrates were added and this would also favour the transition of NO_2 into the organic layer.[63] In accordance with the radical mechanism the reaction yields anomalous products such as *s*-trinitrobenzene, *p*-and *m*-dinitrobenzenes, 2,4-di- and 2,4,6-trinitrophenol and oxalic acid. Nitro- and dinitrobenzenes fail to react with NO_2 both under the conditions of a benzene reaction and more drastic conditions.

The formation of *m*-dinitrobenzene and *s*-trinitrobenzene is accounted for by the successive addition of, three and five molecules of NO_2 to nitrocyclohexadienyl radical  $\dot{C}_6H_5\langle{}^{H}_{NO_2}$ respectively (as shown in (62)) followed by an abstraction of two or three HNO_2 molecules from the adducts. e.g. in the formation of *s*-trinitrobenzene.



(63)

The formation of *p*-dinitrobenzene may be represented as $\dot{N}O_2$ addition through nitrogen to the radical $\dot{C}_6H_6$—NO_2 in *p*-position following by dehydrogenation of 1,4-dinitrocyclohexadiene-2,5.



(64)

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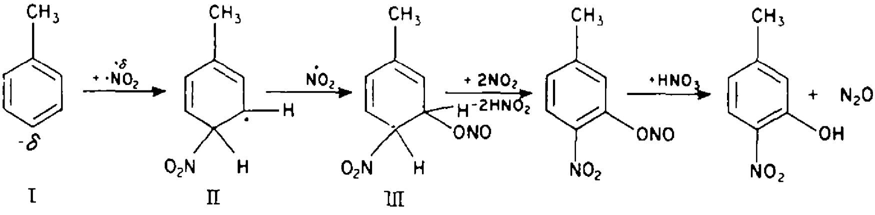
[60] A. I. Titov, *Zh. Obshch. Khim.* **17,** 382 (1947).
[61] A. I. Titov, *Zh. Obshch. Khim.* **18,** 190 (1948).
[62] A. I. Titov, *Zh. Obshch. Khim.* **22,** 1329 (1952).
[63] A. I. Titov and A. N. Baryshnikova, *Zh. Obshch. Khim.* **22,** 1335 (1952).

This point is substantiated by the ease with which NO_2 dehydrogenates 1,4-dihydronaphthalene,[62] dihydrophthalic acid, etc.

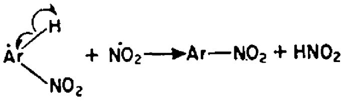
The formation of nitrophenols such as nitro-derivatives of *m*-cresol on nitration of toluene by NO_2 may be represented as:



(65)

The predominance in the nitrophenol mixture of *m*-substituted phenols formed in the reactions of toluene and chlorobenzene is characteristic of the radical nitration as opposed to ionic nitration which in the above cases yields derivatives of *o*- and *p*-substituted phenols.[62,64]

The formation of mononitro-derivatives, due to the readiness of alkyl radicals to hydrogenation in terms of (20) and the tendency to reduce the aromatic system (cryptoaromatic state) may be depicted as the abstraction of atomized H from the radical $Ar\dot{H}{-}NO_2$.



(66)

This reaction proceeds very readily with naphthalene. In the reaction of NO_2 with anthracene and phenanthrene it is evident that the radicals readily produce adducts of the type III of the (scheme 65). According to Meisenheimer (see [57]) anthracene in $CHCl_3$ adds $2NO_2$ in meso-positions and in nitrobenzene gives anthraquinone, possibly due to NO_2 reacting as a complex, $C_6H_5NOO \rightarrow NO_2$ and addition of oxygen (cf. p. 567).

When ArH or olefins are nitrated with dilute nitric acid, the molecules of HNO_3 serve only as a source of nitrogen oxides and a means of progressive regeneration of NO_2 from NO in accordance with (6). In this case factors previously considered, in particular diffusion (see pp. 559, 568), may come into play. Raising the concentration of HNO_3 from 30 to 50% in nitration of benzene has little affect on the absolute yield of *s*-trinitrobenzene but sharply decreases its relative yield due to a substantial increase in nitrobenzene formation[63] owing to the increased role of the reaction with NO_2^+.

The extremely high reactivity of $NO_3\cdot$ led us to expect that aromatic compounds are nitrated by nitric anhydride according to the radical mechanism. However, owing to the ready formation of NO_2^+ by ionization of N_2O_5, very few radical nitration products, under normal conditions during nitration of ArH, are produced.

The nitration with N_2O_5 by radical mechanism could be effected in a non-polar medium (CCl_4) at elevated temperatures being favoured by the homolytic dissociation of N_2O_5 to give $NO_3\cdot$.[58] The radical nature of the mechanism is revealed by the

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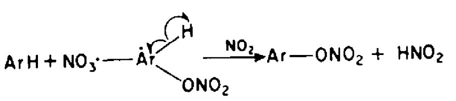
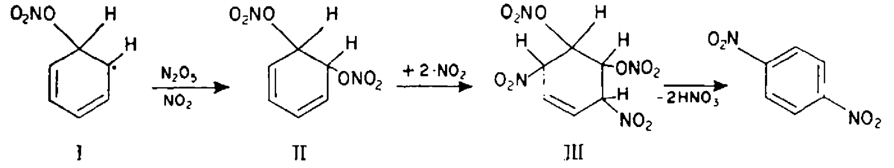
[64] A. I. Titov and N. G. Laptev *Organicheskie poluprodukty i krasitely; Uspekhi i problemy issledovanya okislitelynoguo nitrovanya aromaticheskikh soyedineniy* pp. 5–40. Moskva (1960).

predominance of anomalous products such as nitrophenols and polynitro-derivatives in spite of a large excess of ArH. Nitration with N_2O_5 proceeds many times faster than with N_2O_4 and even nitrobenzene stable to NO_2 with continued heating reacts with $NO_3\cdot$. The first step in nitration with N_2O_5 is undoubtedly the addition of $NO_3\cdot$



$$ArH + NO_3\cdot \longrightarrow \dot{A}r\langle^{H}_{ONO_2} \xrightarrow{NO_2} Ar{-}ONO_2 + HNO_2 \qquad (67)$$

and dehydrogenation of the adducts by NO_2 giving rise to arylnitrate and then to nitrophenols, sometimes as the main reaction products.[58,64] In accord with the radical mechanism, the reaction with chlorobenzene results in considerable yield of nitro-derivatives of *m*-chlorophenol. The mechanism of *p*-dinitrobenzene formation during nitration of benzene is depicted by the authors as follows:



(68)

The product of $NO_3\cdot$ addition to benzene by the action of N_2O_5 results either directly, or through an intermediate reaction with $\dot{N}O_2$ addition to oxygen, to dinitrate II which, in turn, with $\dot{N}O_2$ added to nitrogen results in a derivative of cyclohexene III and subsequent abstractions of HNO_3 converts it into *p*-dinitrobenzene.

The increased nitration rate and oxidation of benzene[62] and other aromatic hydrocarbons[3] by nitrogen oxides on saturation with O_2, is partly the result of $NO_3\cdot$ formation.[58,64] In a similar manner the formation of dinitrates of type II (see Eq. 68), in the reaction with anthracene and its analogues may be initiated.[65] The nitration of unsaturated and aromatic compounds may in these cases proceed simultaneously via the ionic mechanism in accordance with a dual dissociation of N_2O_5.

$$NO_3\cdot + \cdot NO_2 \overset{t}{\rightleftarrows} N_2O_5 \rightleftarrows NO_2^+ + NO_3^- \qquad (69)$$

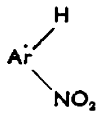
To a lesser degree the ionic reaction is also possible for N_2O_4 and N_2O_3.[36,64]

$$O_2N.NO_2 \overset{t}{\rightleftarrows} 2NO_2 \rightleftarrows ON{-}O{-}NO_2 \overset{HNO_3}{\rightleftarrows} NO^+ + NO_3^- \qquad (70)$$

In nitration with NO_2 and O_2 some part is also played by $NO_4\cdot$.[58,64]

$$O_2N\cdot + O_2 \rightleftarrows O_2N{-}O{-}O\cdot. \qquad (71)$$

Reactions with incipient radicals such as



$$\dot{A}r\langle^{H}_{NO_2}$$

may also involve N_2O_4, NO[62], nitro- and polynitro-compounds, polyhalogeno-derivatives ($CHBr_3$, CCl_4, etc), maleic anhydride and other suitable compounds.

Although the radical nitration of paraffins, unsaturated and aromatic compounds

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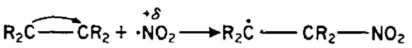
[65] J. Perronnet, *C.R. Acad. Sci. Paris* **249**, 2687 (1959); **250**, 872 (1960).

in typical cases is similar in some respects there are also differences. The reaction of the initiating agent, e.g. NO_2, with *n*-paraffins leads to the rupture of the strong σ-bond to give a product of hydrogen abstraction, alkyl radical R·.

$$R{-}H + \dot{N}O_2 \rightarrow R\cdot + HNO_2 \qquad (72)$$

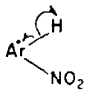
With unsaturated compounds the weak π-bond is broken resulting in the formation of the addition product, β-nitroalkyl radical.



$$R_2C{=}CR_2 + \cdot\overset{+\delta}{N}O_2 \longrightarrow R_2\dot{C}{-}CR_2{-}NO_2 \qquad (73)$$

The energy of the cleavage of the R—H bond is about 94–102 kcal and that of the opening of the π-bond only 58 kcal. The conversions of alkyl and β-nitroalkyl radicals are similar in some respects but also distinctly different due to the latter containing a nitro-group and because of their rapid formation. Thus, owing to the effect of the NO_2-group, the addition products of NO to β-nitroalkyl radical prove to be stable dimers (pseudo-nitrosites). The comparatively high rate of β-nitroalkyl radical formation at very low concentrations of NO_2 leads to a ready participation in the reaction of other olefin molecules (to form telomers), as well as O_2, polyhalogens compounds, $ArNO_2$, etc.

The NO_2 addition to benzene to give



proceeds slowly due to a supplementary loss of energy required to open the aromatic sextet, in this case about 25–30 kcal. The addition products of one or several molecules of NO_2 to ArH tend, due to their cryptoaromatic character, to dehydrogenate, giving, the corresponding, $ArNO_2$, polynitro-compounds and nitrophenols which may result from loss of HNO_2 and HNO_3 from the adducts.

The radical nitration mechanism holds for all types of hydrocarbons whereas ionic mechanism applies only to unsaturated and aromatic compounds.[3,36,39] The radical mechanism as opposed to the typical cases of the ionic mechanism is characterized by a greater diversity of routes and products which is both an advantage and disadvantage from the synthetic point of view—to control these processes a more profound knowledge is needed to meet the special requirements.

Previous views on the exclusively ionic character of nitration are erroneous though for the reactions of olefins and aromatic compounds it was considered applicable until recently.[66] The mechanism of nitration of paraffins by (1) and (2) proposed in 1959 is belated.[67]

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[66] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, pp. 209, 670. Bell, London (1953).

[67] E. D. Hughes, *Kekulé Symposium*, p. 218. Butterworths, London (1959).