A. N. BARYSHNIKOVA and A. I. TITOV

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Abstract

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A. N. BARYSHNIKOVA and A. I. TITOV

NITRATION OF AROMATIC COMPOUNDS WITH NITROGEN PENTOXIDE BY A RADICAL MECHANISM

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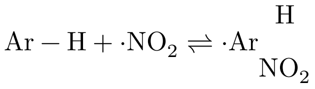
For the first time, nitration of unsaturated and aromatic compounds by a radical mechanism, using the reaction with nitrogen dioxide as an example, was described by us in 1941 (^{1}), and this investigation was then developed in works from 1945-1953 ($^{2-7}$). In them (^{5}) it was shown that the initial determining stage of the reaction is the addition of a nitrogen dioxide monomer, NO_2, at the π bond, ultimately leading to the formation of the radical


$$\mathrm{Ar}-\mathrm{H}+\cdot\mathrm{NO_2} \rightleftharpoons \cdot\mathrm{Ar}\overset{\mathrm{H}}{\underset{\mathrm{NO_2}}{}} \qquad (1)$$

Transformations of the resulting radical $\cdot\mathrm{Ar}\overset{\mathrm{H}}{\underset{\mathrm{NO_2}}{}}$ with NO, NO_2, N_2O_4, O_2 lead to a variety of products. For example, in the case of benzene (^{3,5}), nitrobenzene, *p*- and *m*-dinitrobenzene (up to 30%), s-trinitrobenzene (up to 30%), nitrophenols (up to 30%), and others are formed; chlorobenzene, along with other products, gives many nitro derivatives of metachlorophenol, etc. The predominant formation of anomalous products—polynitro compounds and nitrophenols—is characteristic of nitration by a radical mechanism.

The possibility of nitration by a radical mechanism with nitrogen pentoxide became apparent when, in addition to its decomposition by the ionic type (^{1}),

$$\mathrm{N_2O_5} \rightleftharpoons \mathrm{NO_2^+} + \mathrm{NO_3^-} \qquad (2)$$

we proposed (^{7,8}), and subsequently proved, the dissociation of N_2O_5 into radical-like nitrogen dioxide and nitrogen trioxide

$$\mathrm{N_2O_5} \rightleftharpoons \cdot\mathrm{NO_2} + \mathrm{NO_3^{\cdot}} \qquad (3)$$

Ideas about the radical dissociation of nitrogen pentoxide made it possible to find methods for controlling its rapid reaction with paraffins and to discover a number of features of this type of nitration, in particular inhibition by additions of nitrogen dioxide (8).

The extraordinarily high activity of nitrogen trioxide $NO_3^{\cdot}$ in reactions with paraffins (even at low temperatures)

$$\mathrm{R} - \mathrm{H} + \mathrm{NO}_3^{\cdot} \to \mathrm{R} \cdot + \mathrm{HNO}_3, \tag{4}$$

as compared with NO and NO_2, is explained by the great electrophilicity and high unsaturation of the unpaired electron of oxygen, $O_2N{-}O^{\cdot}$. It may be considered that the electrophilicities of these oxides will be proportional to the constants of electrolytic dissociation of nitric, nitrous, and hyponitrous acids

$$K_{\mathrm{HNO}_3} > K_{\mathrm{HNO}_2} > K_{\mathrm{HNO}}, \tag{5}$$

and unsaturation—by their equilibrium constants with NO_2

$$\begin{aligned} &1)\ \mathrm{NO} + \mathrm{NO}_2 \rightleftarrows \mathrm{N}_2\mathrm{O}_3; \\ &2)\ \mathrm{NO}_2 + \mathrm{NO}_2 \rightleftarrows \mathrm{N}_2\mathrm{O}_4; \\ &3)\ \mathrm{NO}_2 + \mathrm{NO}_3 \rightleftarrows \mathrm{N}_2\mathrm{O}_5 \quad K_1 < K_2 < K_3 \end{aligned} \tag{6}$$

Proceeding from the considerations developed above, one would have expected a very high activity of nitrogen pentoxide, as compared with nitrogen dioxide, in the nitration of aromatic compounds by the radical type. However, owing to the extremely rapid nitration of aromatic compounds by N_2O_5 under ordinary conditions by the ionic mechanism, relatively few products of the radical reaction are formed.

Nitration predominantly by the radical mechanism could be achieved by carrying out the process at elevated temperature in a nonpolar medium, which promoted dissociation of N_2O_5 according to equation (3) and suppressed the formation of the nitronium cation according to scheme (2). The predominance, in the reaction products, of anomalous products—polynitro derivatives and nitrophenols—despite a very large excess of the starting aromatic compound, characterizes the interaction of nitrogen pentoxide by the radical type. We give data from several experiments.

I. To 200 g of benzene at a bath temperature of 70°, over 40 min, a solution of 5 g of nitrogen pentoxide in 50 ml of carbon tetrachloride was added dropwise. After part of the reaction mass had been distilled off in vacuo, it was worked up by the method described earlier (5).

Extraction with a soda solution gave 0.9 g of a mixture of nitrophenols, consisting mainly of 2,4-dinitrophenol; from this mixture, and also from the alkaline-solution extracts, careful steam distillation gave 0.1 g each of ortho-nitrophenol. From the neutral residue, 1.25 g of nitrobenzene and 1.21 g of a mixture of dinitrobenzenes were isolated, consisting mainly of *p*- and *m*-dinitrobenzene; the *p*-isomer was obtained fairly pure (m.p. 163—165°) after a single recrystallization from alcohol. Carrying out the reaction at 0—20° gave about 7.5 g of nitrobenzene, 0.5 g of a mixture of dinitrobenzenes (chiefly the meta isomer), and only traces of nitrophenols.

II. To 200 ml of chlorobenzene at 100°, a solution of 5 g of nitrogen pentoxide in 50 ml of $C_2H_2Cl_4$ was added dropwise. By analogous treatment with soda solution, 1.4 g of a liquid mixture of nitrochlorophenols was isolated; on treatment of it at 100° with nitric acid of sp. gr. 1.4, crystalline trinitrometachlorophenol, m.p. 106—107°, can readily be isolated. The neutral reaction product consisted of 1.2 g of a mixture of nitrochlorobenzenes and of a higher-boiling residue. Nitration of nitrobenzene gave similar results.

III. Nitration of toluene with nitrogen pentoxide at elevated temperature, like the reaction with NO_2 (6,9), gave chiefly products of transformations in the side chain (phenylnitromethane, benzyl alcohol ethers, benzaldehyde) and mononitrotoluenes with a small admixture of dinitro derivatives. The reaction at ordinary or reduced temperature led to the formation almost exclusively of a mixture of mono- and dinitrotoluenes; very strong dilution with toluene or substantial additions of pyridine promoted the formation of dinitrotoluene, chiefly the 2,4-isomer. In the latter case the nitration proceeded, in essence, in an "alkaline medium."

The results of nitration with nitrogen pentoxide by the radical mechanism are similar to the data for the reaction with nitrogen dioxide. The difference consists primarily in the fact that the reaction with $NO_3^{\cdot}$, formed upon dissociation of N_2O_5, proceeds many times faster, and even nitrobenzene, quite resistant to the action of NO_3 even on very prolonged heating, is readily involved in it. The attack of $NO_3^{\cdot}$ on toluene, for understandable reasons, was directed predominantly at the α-hydrogen. These results are also analogous to the data for the reaction of aromatic compounds with nitrous acid (10,11), which decomposes with

with formation of a free hydroxyl, similar in chemical character to $NO_3\cdot$.

$$\mathrm{HO{-}O{-}NO} \longrightarrow \mathrm{HO}\cdot + \cdot\,\mathrm{NO_2}$$

A considerable part of the normal mono- and dinitro derivatives (for example, nitrobenzene and 2,4-dinitrotoluene) probably arose by a purely or cryptically ionic reaction, respectively with NO_2^+ and N_2O_5 (1,12).

Radical nitration by nitric anhydride of unsaturated and aromatic compounds undoubtedly begins with the addition of $NO_3\cdot$ at the π-bond. The simplest example of this type of reaction is the formation of glycol dinitrate observed by N. Ya. Dem' yanov (^{13,14}):

$$\begin{aligned}(CH_3)_2C = C(CH_3)_2 + NO_3\cdot \longrightarrow (CH_3)_2C(ONO_2) - \dot{C}(CH_3)_2 \\ \xrightarrow[-NO_2]{N_2O_5} (CH_3)_2C(ONO_2) - C(CH_3)_2(ONO_2)\end{aligned} \tag{7}$$

In the reactions investigated by us, the primary stage is likewise the formation of a radical of type (I) (see equation (8)). Owing to the strong tendency toward aromatization, this radical is readily dehydrogenated by nitrogen dioxide, which is constantly present in the reaction sphere, to phenyl nitrate, which then, naturally, is converted into phenol and its nitro derivatives (8, a). In parallel, nitrogen dioxide monomer adds to radical (I) with formation of adduct (II), elimination of nitric acid elements from which leads to the formation of a mononitro derivative (8, b).

$$\begin{aligned}&C_6H_6 + NO_3\cdot \longrightarrow \text{(I)} \\ &\quad \text{(I)} \xrightarrow[-HNO_2]{NO_2} C_6H_5ONO_2 \longrightarrow \text{phenol, nitrophenols} \quad (a) \\ &\quad \text{(I)} \xrightarrow{NO_2} \text{(II)} \xrightarrow{-HNO_3} C_6H_5NO_2 \quad (b)\end{aligned} \tag{8}$$

A more complex reaction is, for example, the formation of p-dinitrobenzene, the mechanism of which may be represented as follows:

$$\text{(I)} \xrightarrow[-NO_3\cdot]{+N_2O_5} \text{(II)} \xrightarrow{+2\cdot NO_2} \text{(III)} \xrightarrow{-2HNO_3} p\text{-}C_6H_4(NO_2)_2 \tag{9}$$

Radical (I), reacting with N_2O_5 at oxygen, forms dinitrate (II); addition to it of two $\cdot NO_2$ particles at nitrogen in the 1,4 position gives adduct (III), elimination of HNO_3 elements from which leads to the formation of paradinitrobenzene.

It should be noted that the acceleration we observed earlier of the reaction of benzene (^{5}) and other aromatic hydrocarbons (^{1}) with nitrogen oxides from the ...

the absence of oxygen is due in part to the formation, under these conditions, of $NO_3\cdot$, N_2O_5, and NO_2^+.

$$\begin{aligned}NO + O_2 \longrightarrow O{=}N{-}O{-}O\cdot \xrightarrow{NO_2} O{=}N{-}O{-}O{-}NO_2 \longrightarrow \\ \longrightarrow NO_2\cdot + \cdot ONO_2 \rightleftarrows N_2O_5 \rightleftarrows NO_2^+ + NO_3^-\end{aligned} \tag{10}$$

The participation of the radical $NO_4\cdot$ in this reaction is also possible:

$$O_2N\cdot + O{=}O \rightleftarrows O_2N{-}O{-}O\cdot$$

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Note: Figure translations are in progress. See original paper for figures.

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