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Abstract

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A. I. TITOV

IONIC MECHANISM OF NITRATION OF UNSATURATED COMPOUNDS

NITROFLUORINATION OF OLEFINS AND THEIR HALOGEN-SUBSTITUTED DERIVATIVES

(Presented by Academician M. M. Shemyakin, 9 X 1962)

According to the theory developed since 1941, the nitration of unsaturated and aromatic compounds may proceed, chiefly depending on the nature of the reagent and the medium, by both a radical and an ionic mechanism. The nitration, for example, of olefins $CHR_1 = CR_2$ in the absence of strong protonic and aprotonic acids, especially in a low-polarity medium, usually proceeds by a radical mechanism through the primary addition of NO_2 and the formation of the free β-nitroalkyl radical $O_2N - CHR_1 - \dot{C}R_2$. Subsequent rapid reactions of this radical with $\dot{N}O_2$, NO, O_2, $CHBr_3$, $C_6H_5NO_2$, and other suitable components lead to the observed mixture of products ([1,3,6]). In the presence of an excess of strong acids, N_2O_4, HNO_3, $RONO_2$, etc., the reagents are converted into $O = N^+ = O$, and the reaction proceeds by the ionic type through the primary addition of NO_2^+ to π-electrons, for example, as substitution of H, similar in mechanism to normal nitration of ArH ([1–5]).

$$O = N^+ = O + \begin{matrix} CHR' \\ \| \\ CR_2 \end{matrix} \longrightarrow \left[O_2N^+ \cdots \begin{matrix} CR' - H^{+\delta} \\ \| \\ CR_2 \end{matrix} \right]_I \longrightarrow O_2N - \begin{matrix} CR' \\ \| \\ CR_2 \end{matrix} + H^+ \quad (1)$$

In this scheme the bracket indicates the π-bond, and the dashed line in complex I indicates the distribution of π-electron density; the π-donor bond with N causes shifts of electrons toward O. Normal nitration, in particular, predominates if $R' = -COOR$, $-COR$, which promotes an increase of $+\delta$ and stabilization of the π-bond by conjugation, and these factors favor the elimination of H^+. Similarly, one may represent the nitration of electron-donor olefins by means of $(NO_2)_3C \overset{+}{\leftarrow} NO_2$ in the presence of pyridine ([4,5]), which is necessary in this case as an acceptor of H^+. In a similar way one may represent nitration

by NO_2-O-NO_2 in CCl_4, etc., by reagents containing an O_2N-group that readily converts into NO_2^+ in the reaction complex ([1,2]).

However, as has, for example, been emphasized in work ([3]), reactions of nitrating and nitrosating agents with olefins and many of their derivatives by the ionic mechanism proceed predominantly by addition of the anion X^- to complex I of equation (1), with formation of $O_2N-CHR-CR_2-X$. The conjugate addition ([7]) of NO_2^+ and F^- along the π-bond with formation of $O_2N-CHR-CR_2-F$ was termed by us nitrofluorination, and it is the principal subject of this article.

From data on the equivalent electrical conductivity ([8]) of 0.13 N solutions in HF (HNO_3—622, KF—255, H_2O—242), it follows that HNO_3 in this

in case (4) is converted by more than 70% into NO_2^+.

$$KNO_3 + H_2F_2 \xrightarrow[-KHF_2]{} HNO_3 \overset{2H_2F_2}{\rightleftharpoons} O=\overset{+}{N}=O + \dot{H}_3O^+ + 2HF_2^-. \quad (2)$$

The equilibrium postulated by Hantzsch ([8])

$$HNO_3 + HF \rightleftharpoons H_2NO_3^+ + F^- \quad (3)$$

has no measurable significance, since according to all data ([1,4,5]) $H_2NO_3^+$ is practically completely cleaved by H_2F_2 (H—F $\cdots \rightarrow$ HF), as also by other donors of H^+, with formation of NO_2^+, similarly to the complete dissociation of isosteric H_2CO_3 ([1,4]):

$$O=\overset{+}{N}(OH)_2 \underset{(H^+)}{\rightleftharpoons} O_2N^+ \longleftarrow :\ddot{O}H_2 \xrightarrow{H^+} O_2N^+ + :\ddot{O}H_3, \quad (4)$$

$$O=C(OH)_2 \rightleftharpoons O_2C \longleftarrow :OH_2 \rightarrow CO_2 + :OH_2. \quad (5)$$

The structure of the second form of $H_2NO_3^+$ may also be represented as follows ([4,5]):

$$:\ddot{O}\rightarrow \overset{O}{\overset{\|}{N}}-OH_2.$$

Solutions of HNO_3, N_2O_4, KNO_3, and N_2O_5 in excess HF, owing to conversion into NO_2^+, are, according to our data, equivalent for purposes of synthesis. The ionization of N_2O_4 in HF is confirmed by the colorlessness of the solutions observed by us, i.e., by the absence of NO_2

$$2NO_2 \rightleftharpoons N_2O_4 \xrightarrow{3H_2F_2} NO_2^+ + NO^+ + H_3O^+ + 3HF_2^-. \quad (6)$$

The concentration of NO_2^+ can be increased by additions of HgF_2, BF_3, H_2SO_4, and similar activators, or of nitronium salts $NO_2^+X^-$. The NO_2^+ cation is more highly solvated and less active in H_2F_2 than in H_2SO_4 ([4],[5]).

Nitrofluorination was usually carried out by introducing a haloethylene into a solution of 0.1 g-mol of HNO_3 in 60 ml of HF at $-10°$. The reaction mechanism, using nitrofluorination of vinyl chloride as an example, is represented in outline as follows:

$$O_2N^+ + \left(\begin{array}{c} \overset{+\delta}{CH{-}Cl} \\ \| \\ CH_2 \end{array} \right) \longrightarrow \left(\begin{array}{c} CH{-}Cl \\ | \\ CH_2 \end{array} \right)_I \xrightarrow{O_2N^+} \xrightarrow{F^-} O_2N{-}CH_2{-}CHCl{-}F \quad (7)$$

The donor of F^- in the triple transition complex ([9]) (not shown in the scheme) is HF_2^-. Orientation proceeds according to Markovnikov' s rule owing to the influence of the $+\delta$ C−Cl bond and dynamic conjugation in complex I. Into reaction with a cation of type I there may be drawn $CR_2{=}CR_2$, with formation of telomers $O_2N{-}(-CR_2{-}CR_2-)-F$, HNO_3 as a donor of NO_3^- ([3],[4]), etc.

Sometimes, it must also be said, partial addition through oxygen occurs,

$$O = \overset{\downarrow}{N} = O^+$$

according to oxygen ([1],[4],[5]).

In the case of olefins, besides the insignificant formation of α-nitro derivatives according to scheme (1), their β-isomers apparently arise to a more noticeable extent, owing to conjugation of the type

$$\begin{array}{l} \qquad\quad CH_2 \\ \qquad\quad / \\ O_2N \quad + \quad \| \\ \qquad\quad \backslash \\ CH{-}CH_2 \leftarrow H^+ \end{array}$$

and to abstraction of a proton by a fluoride ion from the CH_3 group. Nitrofluorination of haloethylenes proceeded very smoothly, without resin formation, and often gave an almost quantitative yield of nitrofluorides.

The hypothesis of Roberts and Kimball ([7]) that the conjugate-addition reaction proceeds through the stage of formation of a cyclic onium cation is wholly

inapplicable for understanding nitrofluorination, owing to the absence on the nitrogen of NO_2^+ of an unshared electron pair.

Conjugate addition of O_2N^+ and RO^- under the action on olefins of

$$(NO_2)_3C{-}NO_2$$

in ROH undoubtedly proceeds through Ostromyslenskii complexes ([3–5]) of type I and, probably like nitrofluorination, gives predominantly trans adducts. The possibility of cis addition in a low-polarity medium, for example under the action of N_2O_5 ([10]) in CH_2Cl_2 or HNO_3 in acetic anhydride ([11]), is explained, in our opinion, by the formation from complexes of type I of six-membered cyclic adducts, owing to the predominance of the reaction of olefins in the first case with the ion pair

$$O_2N^+ \longleftarrow\!\!\!\!- ONO_2^-,$$

and in the second with the solvate

$$O_2N^+ \longleftarrow\!\!\!\!- O{=}C(OH){-}CH_3.$$

Nitrofluorination has been successfully carried out for mono-, di-, and trichloroethylenes, but under the same conditions it was not possible for C_2Cl_4, owing to its electrophilicity and steric hindrance. On the contrary, nitrofluorination of C_2F_4 proceeded readily, owing to dynamic conjugation in the complex with NO_2^+ of the type

$$C \leftarrow F,$$

which is strongly expressed in this case because of the closeness of the sizes of the orbitals of C and F ([4,5]). At the same time, side formation of $C_2F_5{-}N{=}O$ was observed owing to the presence of NO^+ in the nitrofluorinating mixture. The same difference in reactivity of C_2Cl_4 and C_2F_4 was also observed in nitrosochlorination—addition of NO^+ and Cl^- ([12]). Reactions with higher perfluoroalkenes should, naturally, proceed with greater difficulty than with C_2F_4, i.e., the reverse of what is observed for olefins.

The electronic structure of the cyclopropane ring in cyclopropane compounds, their ability to give colored complexes with $C(NO_2)_4$, and ring cleavage under the action of a series of electrophilic reagents ([3,4]) speak in favor of the possibility of applying the nitrofluorination method to them and of thereby obtaining 1,3-nitrofluorides. Finally, we note that nitrofluorination is one of the mildest and most convenient methods for introducing fluorine and for synthesizing new types of organofluorine compounds. Attention should be drawn to the broad

possibilities for introducing fluorine by means of other conjugate-addition reactions, for example under the action of halides ([7]), ROCl, BrCl, JCl, NO^+ in an HF medium, in particular with additions of BF_3 or HgF_2.

We give brief data on some experiments.

1. Into a steel reactor were charged 60 ml of HF and then 6.3 g of HNO_3, sp. gr. 1.52 (heating!). Then, at −10° and with vigorous stirring, 9.7 g of vinylidene chloride was gradually added. After a one-hour holding period the contents were poured onto a mixture of 200 g of ice and 20 ml of $CHCl_3$. Distillation of the washed and dried organic layer in vacuo gave 14.2 g of 1-fluoro-1,1-dichloro-2-nitroethane with b.p. 48° at 10 mm; d_4^{16} 1.537;

Found, %: N 8.6; F 11.7; Cl 45.1

The colorless product dissolves in aqueous NaOH and $NaHCO_3$. On boiling with conc. HCl until the layers disappear, it gives $NH_2OH \cdot HCl$ and Cl_2FC–COOH with b.p. 163°.

2. Analogously, from trichloroethylene, 1-fluoro-1,1,2-trichloro-2-nitroethane was synthesized, with b.p. 47° at 12 mm; d_4^{20} 1.668.

Found, %: N 7.2; F 9.6; Cl 54.4

On chlorination in the presence of water and $CaCO_3$ it was converted into $CFCl_2$ –CCl_2NO_2.

3. With very vigorous stirring in a shaker, 2 l of vinyl chloride was passed over three hours through the nitrofluorinating mixture (see item 1) at −10°. By the method described above, 7.5 g of O_2N–CH_2–CHClF was obtained, with b.p. 41° at 10 mm; d_4^{18} 1.474;

Found, %: N 10.88; F 14.8; Cl 27.9

On boiling the product with alcohol it was converted into $C_6H_{12}NO_2FCl$ with b.p. 68° at 3 mm, presumably CHFCl–$CH(NHOC_2H_5)OC_2H_5$.

4. The reaction with C_2F_4 was carried out by the same method. The evolved gases were washed with 20% NaOH and then with conc. H_2SO_4, and the reaction product was condensed in a trap at −60°; the end of the reaction was determined by an increase in the current of excess C_2F_4. On distillation, 6.2 g of $C_2F_5NO_2$ was obtained, with b.p. −2°, slightly bluish owing to the presence of traces of C_2F_5–NO (mol. wt. 166; % F 55.5). CF_3–CF_2–NO_2, unlike the above-mentioned chlorofluoronitro compounds, does not have a perceptible odor, probably owing to the weak positive polarization of the fluorine in it under the influence of the NO_2 group. It was reduced by the action of Zn dust in an NH_4Cl solution at −5° and with stirring to C_2F_5NHOH, the solution of which, on oxidation with $K_2Cr_2O_7$, gave blue C_2F_5–NO.

5. Similarly, 2-fluoro-1-nitropropane was obtained from propylene, with b.p. 33° at 4 mm.

Found, %: C 33.6; H 5.6; N 13.4; F 16.2

and from ethylene, CH_2NO_2—CH_2F, with b.p. 60° at 15 mm.

V. V. Smirnov and O. E. Dubov took part in the experimental part of the investigation in 1950–1952, and F. L. Maklyaev in the preparation of the article.

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* A number of misprints have been found in the article, easily corrected by the reader; for an edition of the work with almost no misprints, see A. I. Titov, *Wiadomosci chemiczne*, 1961, p. 741.

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