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## Abstract

## Full Text

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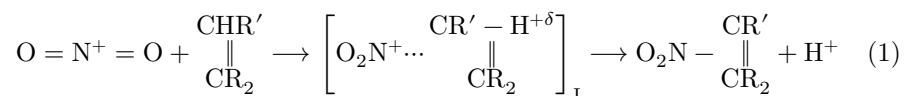
A. I. TITOV

# 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  $\text{CHR}_1 = \text{CR}_2$  in the absence of strong protonic and aprotic acids, especially in a low-polarity medium, usually proceeds by a radical mechanism through the primary addition of  $\text{NO}_2$  and the formation of the free  $\beta$ -nitroalkyl radical  $\text{O}_2\text{N} - \dot{\text{C}}\text{HR}_1 - \text{CR}_2$ . Subsequent rapid reactions of this radical with  $\dot{\text{N}}\text{O}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{CHBr}_3$ ,  $\text{C}_6\text{H}_5\text{NO}_2$ , and other suitable components lead to the observed mixture of products<sup>(1,3,6)</sup>. In the presence of an excess of strong acids,  $\text{N}_2\text{O}_4$ ,  $\text{HNO}_3$ ,  $\text{RONO}_2$ , etc., the reagents are converted into  $\text{O} = \text{N}^+ = \text{O}$ , and the reaction proceeds by the ionic type through the primary addition of  $\text{NO}_2^+$  to  $\pi$ -electrons, for example, as substitution of H, similar in mechanism to normal nitration of  $\text{ArH}$ <sup>(1-5)</sup>.

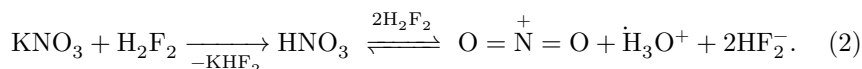


In this scheme the bracket indicates the  $\pi$ -bond, and the dashed line in complex I indicates the distribution of  $\pi$ -electron density; the  $\pi$ -donor bond with N causes shifts of electrons toward O. Normal nitration, in particular, predominates if  $\text{R}' = -\text{COOR}$ ,  $-\text{COR}$ , which promotes an increase of  $+\delta$  and stabilization of the  $\pi$ -bond by conjugation, and these factors favor the elimination of  $\text{H}^+$ . Similarly, one may represent the nitration of electron-donor olefins by means of  $(\text{NO}_2)_3\text{C}^+ \leftarrow \text{NO}_2$  in the presence of pyridine<sup>(4,5)</sup>, which is necessary in this case as an acceptor of  $\text{H}^+$ . In a similar way one may represent nitration

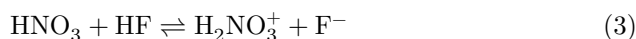
by  $\text{NO}_2 - \text{O} - \text{NO}_2$  in  $\text{CCl}_4$ , etc., by reagents containing an  $\text{O}_2\text{N}$ -group that readily converts into  $\text{NO}_2^+$  in the reaction complex <sup>(1,2)</sup>.

However, as has, for example, been emphasized in work <sup>(3)</sup>, reactions of nitrating and nitrosating agents with olefins and many of their derivatives by the ionic mechanism proceed predominantly by addition of the anion  $\text{X}^-$  to complex I of equation (1), with formation of  $\text{O}_2\text{N} - \text{CHR} - \text{CR}_2 - \text{X}$ . The conjugate addition <sup>(7)</sup> of  $\text{NO}_2^+$  and  $\text{F}^-$  along the  $\pi$ -bond with formation of  $\text{O}_2\text{N} - \text{CHR} - \text{CR}_2 - \text{F}$  was termed by us nitrofluorination, and it is the principal subject of this article.

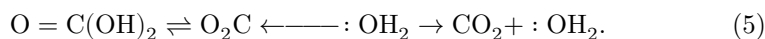
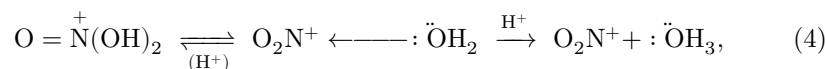
From data on the equivalent electrical conductivity <sup>(8)</sup> of 0.13 *N* solutions in HF ( $\text{HNO}_3$ —622,  $\text{KF}$ —255,  $\text{H}_2\text{O}$ —242), it follows that  $\text{HNO}_3$  in this in case (4) is converted by more than 70% into  $\text{NO}_2^+$ .



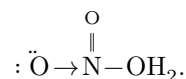
The equilibrium postulated by Hantzsch <sup>(8)</sup>



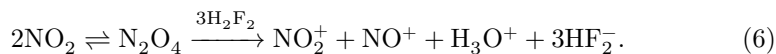
has no measurable significance, since according to all data <sup>(1, 4, 5)</sup>  $\text{H}_2\text{NO}_3^+$  is practically completely cleaved by  $\text{H}_2\text{F}_2$  ( $\text{H}-\text{F} \cdots \rightarrow \text{HF}$ ), as also by other donors of  $\text{H}^+$ , with formation of  $\text{NO}_2^+$ , similarly to the complete dissociation of isosteric  $\text{H}_2\text{CO}_3$  <sup>(1, 4)</sup>:



The structure of the second form of  $\text{H}_2\text{NO}_3^+$  may also be represented as follows <sup>(4, 5)</sup>:

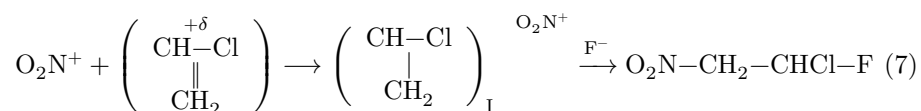


Solutions of  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{KNO}_3$ , and  $\text{N}_2\text{O}_5$  in excess HF, owing to conversion into  $\text{NO}_2^+$ , are, according to our data, equivalent for purposes of synthesis. The ionization of  $\text{N}_2\text{O}_4$  in HF is confirmed by the colorlessness of the solutions observed by us, i.e., by the absence of  $\text{NO}_2$



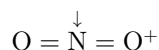
The concentration of  $\text{NO}_2^+$  can be increased by additions of  $\text{HgF}_2$ ,  $\text{BF}_3$ ,  $\text{H}_2\text{SO}_4$ , and similar activators, or of nitronium salts  $\text{NO}_2^+\text{X}^-$ . The  $\text{NO}_2^+$  cation is more highly solvated and less active in  $\text{H}_2\text{F}_2$  than in  $\text{H}_2\text{SO}_4$  (4, 5).

Nitrofluorination was usually carried out by introducing a haloethylene into a solution of 0.1 g-mol of  $\text{HNO}_3$  in 60 ml of  $\text{HF}$  at  $-10^\circ$ . The reaction mechanism, using nitrofluorination of vinyl chloride as an example, is represented in outline as follows:



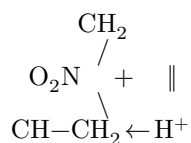
The donor of  $\text{F}^-$  in the triple transition complex (9) (not shown in the scheme) is  $\text{HF}_2^-$ . Orientation proceeds according to Markovnikov's rule owing to the influence of the  $+\delta$  C-Cl bond and dynamic conjugation in complex I. Into reaction with a cation of type I there may be drawn  $\text{CR}_2=\text{CR}_2$ , with formation of telomers  $\text{O}_2\text{N}-(-\text{CR}_2-\text{CR}_2-)-\text{F}$ ,  $\text{HNO}_3$  as a donor of  $\text{NO}_3^-$  (3, 4), etc.

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



according to oxygen (1, 4, 5).

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

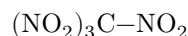


and to abstraction of a proton by a fluoride ion from the  $\text{CH}_3$  group. Nitrofluorination of haloethylenes proceeded very smoothly, without resin formation, and often gave an almost quantitative yield of nitrofluorides.

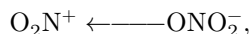
The hypothesis of Roberts and Kimball (7) that the conjugate-addition reaction proceeds through the stage of formation of a cyclic onium cation is wholly

inapplicable for understanding nitrofluorination, owing to the absence on the nitrogen of  $\text{NO}_2^+$  of an unshared electron pair.

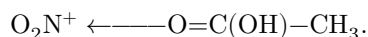
Conjugate addition of  $\text{O}_2\text{N}^+$  and  $\text{RO}^-$  under the action on olefins of



in ROH undoubtedly proceeds through Ostromyslenskii complexes (<sup>3-5</sup>) 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  $\text{N}_2\text{O}_5$  (<sup>10</sup>) in  $\text{CH}_2\text{Cl}_2$  or  $\text{HNO}_3$  in acetic anhydride (<sup>11</sup>), 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



and in the second with the solvate



Nitrofluorination has been successfully carried out for mono-, di-, and trichloroethylenes, but under the same conditions it was not possible for  $\text{C}_2\text{Cl}_4$ , owing to its electrophilicity and steric hindrance. On the contrary, nitrofluorination of  $\text{C}_2\text{F}_4$  proceeded readily, owing to dynamic conjugation in the complex with  $\text{NO}_2^+$  of the type



which is strongly expressed in this case because of the closeness of the sizes of the orbitals of C and F (<sup>4,5</sup>). At the same time, side formation of  $\text{C}_2\text{F}_5-\text{N}=\text{O}$  was observed owing to the presence of  $\text{NO}^+$  in the nitrofluorinating mixture. The same difference in reactivity of  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{F}_4$  was also observed in nitrosochlorination—addition of  $\text{NO}^+$  and  $\text{Cl}^-$  (<sup>12</sup>). Reactions with higher perfluoroalkenes should, naturally, proceed with greater difficulty than with  $\text{C}_2\text{F}_4$ , 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  $\text{C}(\text{NO}_2)_4$ , and ring cleavage under the action of a series of electrophilic reagents (<sup>3,4</sup>) 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 ( $\text{I}^+$ ),  $\text{ROCl}$ ,  $\text{BrCl}$ ,  $\text{JCl}$ ,  $\text{NO}^+$  in an  $\text{HF}$  medium, in particular with additions of  $\text{BF}_3$  or  $\text{HgF}_2$ .

We give brief data on some experiments.

1. Into a steel reactor were charged 60 ml of  $\text{HF}$  and then 6.3 g of  $\text{HNO}_3$ , sp. gr. 1.52 (heating!). Then, at  $-10^\circ$  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  $\text{CHCl}_3$ . 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.  $48^\circ$  at 10 mm;  $d_4^{16}$  1.537;

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

The colorless product dissolves in aqueous  $\text{NaOH}$  and  $\text{NaHCO}_3$ . On boiling with conc.  $\text{HCl}$  until the layers disappear, it gives  $\text{NH}_2\text{OH} \cdot \text{HCl}$  and  $\text{Cl}_2\text{FC}-\text{COOH}$  with b.p.  $163^\circ$ .

2. Analogously, from trichloroethylene, 1-fluoro-1,1,2-trichloro-2-nitroethane was synthesized, with b.p.  $47^\circ$  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  $\text{CaCO}_3$  it was converted into  $\text{CFCl}_2-\text{CCl}_2\text{NO}_2$ .

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  $-10^\circ$ . By the method described above, 7.5 g of  $\text{O}_2\text{N}-\text{CH}_2-\text{CHClF}$  was obtained, with b.p.  $41^\circ$  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  $\text{C}_6\text{H}_{12}\text{NO}_2\text{FCl}$  with b.p.  $68^\circ$  at 3 mm, presumably  $\text{CHFCl}-\text{CH}(\text{NHOC}_2\text{H}_5)\text{OC}_2\text{H}_5$ .

4. The reaction with  $\text{C}_2\text{F}_4$  was carried out by the same method. The evolved gases were washed with 20%  $\text{NaOH}$  and then with conc.  $\text{H}_2\text{SO}_4$ , and the reaction product was condensed in a trap at  $-60^\circ$ ; the end of the reaction was determined by an increase in the current of excess  $\text{C}_2\text{F}_4$ . On distillation, 6.2 g of  $\text{C}_2\text{F}_5\text{NO}_2$  was obtained, with b.p.  $-2^\circ$ , slightly bluish owing to the presence of traces of  $\text{C}_2\text{F}_5-\text{NO}$  (mol. wt. 166; % F 55.5).  $\text{CF}_3-\text{CF}_2-\text{NO}_2$ , 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  $\text{NO}_2$  group. It was reduced by the action of  $\text{Zn}$  dust in an  $\text{NH}_4\text{Cl}$  solution at  $-5^\circ$  and with stirring to  $\text{C}_2\text{F}_5\text{NHOH}$ , the solution of which, on oxidation with  $\text{K}_2\text{Cr}_2\text{O}_7$ , gave blue  $\text{C}_2\text{F}_5-\text{NO}$ .

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,  $\text{CH}_2\text{NO}_2\text{—CH}_2\text{F}$ , 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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5 X 1962

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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.*

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