CHEMISTRY

Academician I. L. KNUNYANTS, E. G. BYKHOVSKAYA, V. N. FROSIN, and Ya. M. KISEL

1960

SovietRxiv

Abstract

Full Text

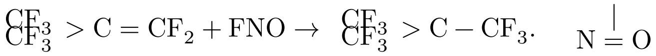
CHEMISTRY

Academician I. L. KNUNYANTS, E. G. BYKHOVSKAYA, V. N. FROSIN, and Ya. M. KISEL

INTERACTION OF FLUOROOLEFINS WITH NITROSYL FLUORIDE

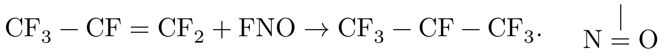
Nitrosyl fluoride was first obtained by Ruff in 1905 (^{1}). However, up to now only its physical properties (^{2}) and reactions with certain inorganic substances (boron, silicon, red phosphorus, AsF_3, H_2SO_4, etc. (^{1,3})) and with benzene (^{4}) have been studied.

We have shown that nitrosyl fluoride reacts readily with fluoroolefins, adding at the site of the double $C = C$ bond.* Thus, in the interaction of nitrosyl fluoride with perfluoroisobutylene, tert-perfluoronitrosoisobutane is formed in quantitative yield (b.p. +24°)



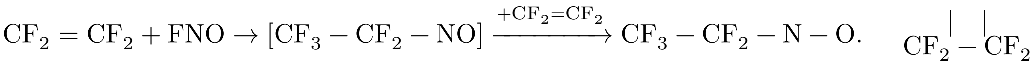
$$\begin{matrix}CF_3\\CF_3\end{matrix} > C = CF_2 + FNO \rightarrow \begin{matrix}CF_3\\CF_3\end{matrix} > \underset{\overset{|}{N = O}}{C} - CF_3.$$

From perfluoropropylene and FNO, 2-nitroso-perfluoropropane was obtained (b.p. −13°)



$$CF_3 - CF = CF_2 + FNO \rightarrow CF_3 - \underset{\overset{|}{N = O}}{CF} - CF_3.$$

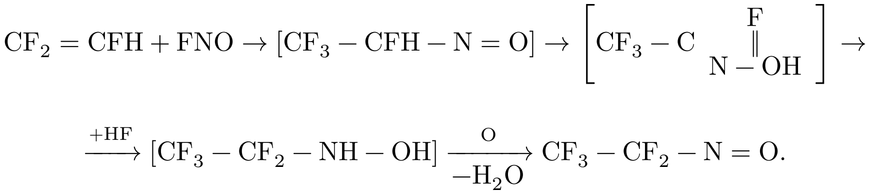
Perfluoroethylene also reacts with nitrosyl fluoride, but perfluoronitrosoethane could not be isolated, since under the reaction conditions the latter interacts with excess perfluoroethylene, giving perfluoro-2-ethyl-1,2-oxazetidine, which is the main product of the reaction



$$CF_2 = CF_2 + FNO \rightarrow [CF_3 - CF_2 - NO] \xrightarrow{+CF_2=CF_2} \begin{array}{c} CF_3 - CF_2 - N - O. \\ \qquad\qquad\quad | \quad\;\; | \\ \qquad\qquad\quad CF_2 - CF_2 \end{array}$$

The formation of oxazetidines was observed by Haszeldine in the interaction of trifluoronitrosomethane with tetrafluoroethylene (^{5}) and other fluoroolefins.

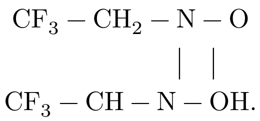
The reaction between nitrosyl fluoride and trifluoroethylene unexpectedly led to the formation of perfluoronitrosoethane, a blue gas with b.p. (−42–43°). Its formation can be explained by the following sequence of transformations:



$$CF_2=CFH+FNO \rightarrow [CF_3-CFH-N=O] \rightarrow \left[CF_3-C\begin{array}{l}F\\ \| \\ N-OH\end{array}\right] \rightarrow$$

$$\xrightarrow{+HF} [CF_3-CF_2-NH-OH] \xrightarrow[-H_2O]{O} CF_3-CF_2-N=O.$$

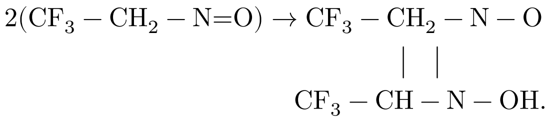
Nitrosyl fluoride and vinylidene fluoride react still more complexly. The sole product of this reaction was a compound with b.p. 80° and empirical formula $(C_2F_3H_2ON)_x$. Study of the properties of the compound obtained made it possible to assign it the following structure:



$$\begin{array}{c}CF_3-CH_2-N-O\\ \qquad\quad |\quad\; | \\ CF_3-CH-N-OH.\end{array}$$

It is probably formed as a result of the following transformations:

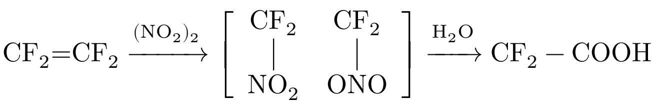
$$CF_2=CH_2+FNO \rightarrow [CF_3-CH_2-N=O];$$



$$2(CF_3-CH_2-N=O) \rightarrow \begin{array}{c}CF_3-CH_2-N-O\\ \qquad\quad |\quad\; | \\ CF_3-CH-N-OH.\end{array}$$

The principal reaction between nitrosyl fluoride and fluoroolefins, consisting in the addition of FNO to fluoroolefins at the site of the double bond, is often accompanied by side reactions of oxidation, fluorination, and nitration of the starting fluoroolefins by nitrosyl fluoride and nitrogen oxides; the latter are formed as a result of decomposition of FNO. Thus, in the reaction between nitrosyl fluoride and tetrafluoroethylene, the formation of hexafluoroethane and nitrodifluoroacetic acid was observed:

$$CF_2-CF_2 \xrightarrow{2F\cdot} CF_3-CF_3;$$



$$CF_2=CF_2 \xrightarrow{(NO_2)_2} \left[\begin{array}{cc}CF_2 & CF_2\\ | & | \\ NO_2 & ONO\end{array}\right] \xrightarrow{H_2O} CF_2-COOH$$

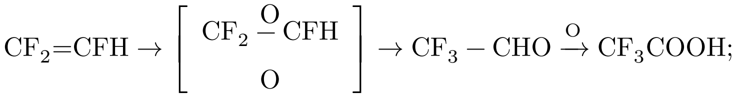
---

* Nitrosyl fluoride was obtained by the reaction between gaseous fluorine and nitric oxide.

$$|$$

$$NO_2.$$

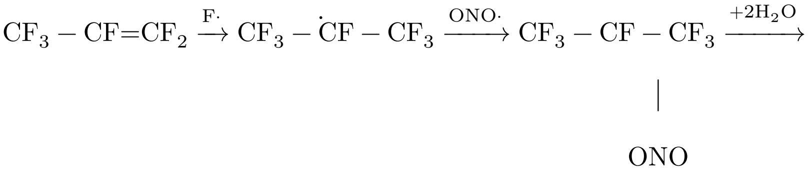
As a result of the interaction of nitrosyl fluoride with trifluoroethylene, in addition to φ-nitrosoethane, trifluoroacetaldehyde, trifluoroacetic acid, and pentafluoroethane were isolated:



$$CF_2{=}CFH \rightarrow \left[\begin{array}{c} CF_2 \overset{O}{-} CFH \\ O \end{array} \right] \rightarrow CF_3 - CHO \xrightarrow{O} CF_3COOH;$$

$$CF_2{=}CFH \xrightarrow{2F\cdot} CF_3 - CF_2H.$$

In the reaction between nitrosyl fluoride and φ-propylene, along with φ-nitrosopropane, hexafluoropropanol-2 nitrite was obtained, which was converted by hydrolysis into hexafluoroacetone:



$$CF_3 - CF{=}CF_2 \xrightarrow{F\cdot} CF_3 - \dot{C}F - CF_3 \xrightarrow{ONO\cdot} CF_3 - \underset{ONO}{\underset{|}{CF}} - CF_3 \xrightarrow{+2H_2O}$$

$$\rightarrow CF_3 - CO - CF_3 \cdot H_2O + HNO_2 + HF.$$

The reactivity of fluoroolefins toward FNO varies. Whereas the hydrofluoroolefins $CF_2{=}CFH$ and $CF_2{=}CH_2$ studied by us react with nitrosyl fluoride explosively, and, for a successful reaction, dilution of the reagents with an inert solvent is necessary, perfluoroolefins react with nitrosyl fluoride under more stringent conditions. Thus, φ-isobutylene interacts with FNO at room temperature without solvent. With tetrafluoroethylene and φ-propylene, nitrosyl fluoride reacts only on heating and in the presence of a catalyst (activated charcoal). In the absence of a catalyst, only products of nitration (and fluorination) of the φ-olefins are formed.

Experimental Part

φ-Isobutylene and FNO. Into a steel, hermetically sealable test tube were charged 35 ml of perfluoroisobutylene, 10 ml of nitrodifluoride and 1 g of calcined potassium fluoride. The tube was shaken on a “shaker”at room temperature for 24 hours. After opening the tube, the unreacted starting materials were distilled off. The residue was a dark-blue liquid with b.p. 24°/760 mm, d_4^0 1.6630. Molecular weight found 249, calculated for C_4F_9NO 249.

Found, %: C 19.40; N 5.28; F 69.21
Calculated, %: C 19.28; N 5.62; F 68.67

φ-Propylene and FNO. A. Into a steel tube were charged 2 g of activated carbon impregnated with calcium sulfate, 25 ml of perfluoropropylene, and 10 ml of nitrosyl fluoride. The tube was heated at 140—150° for 7 hours. On distillation of the reaction mass the following compounds were obtained:

1) Perfluoronitrosopropane—a blue gas with b.p. −13°. Molecular weight found 197, calculated for C_3F_7NO 199.

Found, %: N 6.66; F 67.06
Calculated, %: N 7.03; F 66.83

2) Perfluoropropanol-2 nitrite—a yellow liquid with b.p. +25°/749 mm. When poured into water it decomposes with evolution of nitrogen oxides. The water was extracted with ether; after distillation of the ether the residue was perfluoroacetone hydrate. Colorless liquid with b.p. 50°/90 mm; d_4^{20} 1.3950; n_D^{20} 1.3252. Literature data (7): b.p. 57°/93 mm; d_4^{20} 1.4085; n_D^{20} 1.3288. The compound obtained gives a semicarbazone with m.p. 153°. Literature data (7): m.p. 153°.

$C_4H_5F_6N_3O_2$. Found, %: C 19.48; H 2.20; N 16.84
Calculated, %: C 19.91; H 2.04; N 17.12

B. Into a steel tube were charged 25 ml of perfluoropropylene and 10 ml of nitrosyl fluoride. The tube was heated for 7 hours at 100—110°. After distillation of the unreacted starting materials, the reaction mass was poured into ice water; in the process part of the product decomposed with evolution of nitrogen oxides, and a heavy blue liquid remained. The aqueous solution was extracted with ether. After distillation of the ether, α-nitroperfluoropropionic acid was obtained. Colorless liquid, b.p. 56°/35 mm, d_{20}^{20} 1.4866; n_D^{20} 1.3578. Literature data (6): b.p. 119°; d_1^{20} 1.638; n_D^{20} 1.3560. Molecular weight, found by titration with alkali, 194; calculated for $C_3HF_4NO_4$ 191. Blue liquid—nitronitrosopropane; b.p. 53—54°; d_4^{20} 1.6507. Molecular weight: found 227, calculated for $C_3F_6N_2O_3$ 226.

Found, %: C 16.02; N 12.00; F 50.50
Calculated, %: C 15.92; N 12.39; F 50.44

φ-Ethylene and FNO. Into a steel tube were charged 2 g of activated carbon impregnated with calcium sulfate, 20 ml of tetrafluoroethylene, and 10 ml of nitrosyl fluoride. The tube was heated for 10 hours at 70—80°. After cooling and opening the tube, the gaseous reaction products were distilled off, and the residue was poured into ice water; the oil that separated was isolated, dried with sodium sulfate, and distilled. Perfluoro-2-ethyl-1,2-oxazetidine—colorless liquid, b.p. 24°/737 mm; d_4^0 1.634; $n_D^0 < 1.3$. Molecular weight found (by V. Meyer’ s method) 252, calculated for C_4F_9NO 249.

Found, %: C 19.65; N 5.75; F 68.35
Calculated, %: C 19.28; N 5.62; F 68.67

The wash water was extracted with ether; after distillation of the ether, nitrodifluoroacetic acid was obtained—a colorless liquid with

b.p. 70°/25 mm; d_4^{20} 1.4358; n_D^{20} 1.3660. Literature data (^{8}): b.p. 72°/25 mm; d_4^{20} 1.4381; n_D^{20} 1.3670. In the gaseous reaction products, hexafluoroethane was found—a gas with b.p. −79°, freezing point −101°. Literature data (^{9}): b.p. −79°, freezing point −100.6°; F found 81.72%, F calculated 82.61%; mol. wt. found 137, calculated 138.

Trifluoroethylene and FNO. Into a steel tube were introduced 10 ml of trifluoroethylene, 5 ml of nitrosyl fluoride, and 20 ml of cyclobutane. The tube was left for two days at room temperature. After the tube was opened, the gaseous products were condensed and fractionated on a Podbielniak column. As a result, in addition to cyclobutane, the following were found: 1) pentafluoroethane—a colorless gas with b.p. $-48 \div -50°$ and m.p. −103°. Literature data (^{10}): b.p. −48.5°; m.p. −102°; 2) perfluoronitrosoethane—a blue gas, with b.p. $-42 \div -43°$. Mol. wt. found 144, calculated for C_2F_5NO 149.

Found %: C 15.34; N 9.06; F 62.74
Calculated %: C 16.10; N 9.39; F 63.75

The liquid reaction product (collected from 7 tubes) was distilled on a rectification column. As a result of the distillation the following products were isolated:

1) Trifluoroacetic acid—a colorless liquid, b.p. 72°, d_4^{20} 1.542; $n_D < 1.3$. Literature data (^{11}): d_4^{15} 1.535; $n_D < 1.3$.

Found %: F 49.44
Calculated %: F 50.00

2) Trifluoroacetaldehyde (collected in a “trap”). A colorless gas, b.p. −21°. Literature data (^{12}) −21°. Mol. wt.: found 98, calculated for C_2F_3HO 98; readily polymerizes into beautiful white crystals. When the gas is passed into a solution of 2,4-dinitrophenylhydrazine, a crystalline hydrazone precipitates, the m.p. of which after recrystallization from 50% alcohol is 150—151°. Literature data (^{12}) 150—151°.

Found %: N 19.70
$C_8H_5F_3N_4O_4$. Calculated % N 20.15

Fluorinated vinylidene and FNO. Into a steel tube were introduced 10 ml of vinylidene fluoride, 8 ml of nitrosyl fluoride, and 25 ml of Freon-22. The tube was left for two days at room temperature. The residue after opening the tube and distilling off the solvent and unreacted starting materials was redistilled—a colorless mobile liquid, insoluble in water and in aqueous alkali solutions. After fusion with dry KOH it gives a qualitative reaction for nitrous acid. B.p. 79—80°; d_4^{21} 1.6160; n_D^{21} 1.3437. Mol. wt.: found 217, calculated for $C_4H_4F_4N_2O_2$ 226. One mobile hydrogen atom was found in the compound.

Found %: C 21.52; H 1.85; N 12.75; F 50.73
Calculated %: C 21.24; H 1.89; N 12.39; F 50.44

Received
30 I 1960

CITED LITERATURE

1. O. Ruff, K. Stauber, *Zs. anorg. u. allgem. Chem.*, **47**, 190 (1905).
2. C. U. Stephenson, E. A. Jones, *J. Chem. Phys.*, **20**, 135 (1952); D. W. Magnuson, *J. Chem. Phys.*, **19**, 1071 (1951).
3. A. A. Wolff, *J. Chem. Soc.*, **1950**, 1053.
4. O. Ruff, K. Stauber, W. Neuman, *Zs. anorg. u. allgem. Chem.*, **208**, 293 (1932).
5. R. N. Haszeldine, D. A. Barr, *J. Chem. Soc.*, **1955**, 1881.
6. . . , . . . , , **112**, 67 (1957).
7. A. L. Henne, J. W. Separd, E. J. Young, *J. Am. Chem. Soc.*, **72**, 3577 (1950).
8. . . , . . . , , **111**, 1035 (1956).
9. B. Atkinson, A. B. Trenwith, *J. Chem. Soc.*, **1953**, 2083.
10. W. S. Young, N. Fukuhara, L. A. Bigelow, *J. Am. Chem. Soc.*, **62**, 1171 (1940).
11. F. Swarts, *Bull. Classe sci. Acad. roy. Belg.*, **8**, 342 (1922).
12. A. L. Henne, R. L. Pelley, R. M. Alm, *J. Am. Chem. Soc.*, **72**, 3370 (1950).

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