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Abstract

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Pyrolysis and Photolysis of Polyfluoronitrosoalkanes, the Reaction of Nitroso Compounds with Nitric Oxide

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Pyrolytic and photochemical reactions of nitrosoalkanes, including polyhalogenated ones, have been little studied. Trichloronitrosomethane decomposes on heating with formation of trichloromethylcarbylamine dichloride ([1]); when heated on charcoal, trifluoronitrosomethane is converted into trifluoronitro- and hexafluoroazoxymethane ([2]). In the photochemical decomposition of trifluoronitrosomethane, the nitrite of N,N-bistrifluoromethylhydroxylamine has been isolated ([2,3]).

We found that polyfluoronitrosoethanes at 100-150° (in a steel autoclave) decompose according to a common scheme, with formation, as the main products, of the corresponding nitroalkanes and azomethines:

$$3R_{fCF}2NO \rightarrow R_{fCF}2NO_2 + R_{fCF}2N{=}CFR_f.$$

For the properties of the newly synthesized compounds, see Table 1. In the thermal decomposition of trifluoronitrosomethane under these conditions, trifluoronitromethane (b.p. −32°), trifluoromethylcarbylamine difluoride (b.p. −32°), and bistrifluoromethylamine—the product of addition of hydrogen fluoride (formed by the action of traces of moisture) to carbylamine difluoride (b.p. −6°)—were isolated.

$$CF_3N{=}CF_2 \xrightarrow{HF} (CF_3)_2NH.$$

Along with these compounds, tetrafluoromethane, difluorophosgene, and nitrogen oxides are formed. The mechanism of the pyrolytic decomposition of polyfluoronitrosoalkanes may be expressed by a series of equations including the primary homolysis of the nitroso compound into R_f- and NO-radicals and their subsequent recombinations:

$$R_{fCF}2NO \rightarrow R_{fCF}2 + NO;$$

$$R_{fCF}2NO + R_{fCF}2 \rightarrow [(R_{fCF}2)_2\dot{N}O] \rightarrow R_{fCF}2N{=}CFR_f + \dot{O}F;$$

$$R_{fCF}2NO + \dot{O}F \rightarrow R_{fCF}2NO_2 + F;$$

$$R_{fCF}2 \xrightarrow{F} R_{fCF}3.$$

In the pyrolysis of trifluoronitrosomethane at 250–300° (in a stream, contact time 1–2 min), other reaction products are formed as a result of free-radical and oxidation–reduction transformations represented by the following schemes:

$$CF_3NO \begin{cases} \longrightarrow NO + CF_3 \xrightarrow{CF_3NO} [(CF_3)_2\dot{N}O] \xrightarrow{\dot{C}F_3} (CF_3)_2NOCF_3 \\ \longrightarrow CF_3NO_2 + [CF_3N\lhd] \rightarrow CF_2{=}NF \rightarrow (CF_2NF)_n. \end{cases}$$

In this case, fluorophosgene and fluoropicrin are also formed in accordance with the schemes presented above. The evolving monomer, dimer, and polyme-

Table 1

Properties of newly synthesized compounds

Compound	b.p., °C/mm	d_{20}^{20}	n_D^{20}	Found, % C	Found, % H	Found, % N	Found, % F	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % F	Calculated, % Cl
$NO_2CF_2CF_2N{=}CFCF_2NO_2$ 1	52°/5	1.719	1.3570	16.81, 17.08	–	14.54, 14.32	45.28, 45.80	–	16.70	–	14.60	46.4	–
$ClCF_2CF_2N{=}CFCF_2Cl$	75	1.621	1.33	17.11, 17.94	–	5.41, 5.35	50.95, 51.8	25.80, 24.02	18.02	–	5.25	50.0	26.0
$(CF_3)_2NOCF_3$	−3.5	d_4^9 1.616	–	15.19, 15.20	–	6.17, 6.7	72.34, 71.68	–	15.20	–	5.93	72.14	–
$CF_2{=}NF$ 2	−36	–	–	14.40	–	16.22, 16.48	67.3, 66.90	–	14.48	–	16.90	68.67	–
$(CF_2{=}NF)_2$ 3	6	–	–	14.18, 13.60	–	–	68.64, 69.81	–	14.48	–	–	68.67	–
$CF_3N(NO)ONO$ 4	decomposes				–	–	–	–	–	–	–	–	–
$CF_3N(NO)ONa$	100 (decomp.)	2.086	–	8.65	–	18.02	37.70	–	7.9	–	18.4	37.5	–
$CF_3N(NO)OH{\cdot}NH(C_2H_5)_2$	m.p. 62 (decomp.)	–	–	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	29.5	5.9	20.7	27.0	–

Compound	b.p., °C/mm	d_{20}^{20}	n_D^{20}	Found, % C	Found, % H	Found, % N	Found, % F	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % F	Calculated, % Cl
$CF_3N(NO)OH \cdot NH_3$	m.p. 86	—	—	8.60 8.39 70 3.05 28.00 28.25 39.39 — 75					8.2	27	28.5	38.6	—
$CF_3N(NO)OH \cdot CuCl$	—	—	—	6.71 6.60 — 11.95 12.73 25.22 24.0 15.29 15.25						—	12.2	24.8	15.5
$CF_3NHOCOCH_3$	m.p. 35 (in a sealed capillary)	—	—	25.74 26.10 4.38 9.79 9.81 39.81 39.70 —					25.20	2.80	9.80	39.90	—
$CF_3NHOCOC_2H_5$	m.p. 62			47.25 47.98 3.15 6.46 6.34 28.02 27.75 —					47.0	2.90	6.80	28.0	—
$(C_6H_5NH)_2C{=}NOCOC_6H_5$	m.p. 125	—	—	71.40 71.26 5.32 12.33 12.06 —				—	72.5	5.12	12.70	—	—

Notes: [1] In the IR spectrum, intense absorption at 5.65 μ, corresponding to vibration of the C=N bond. [2] Molecular weight: found 89.0; calculated 83.0. [3] Molecular weight: found 167.3, calculated 166. [4] Obtained as an ethereal solution. Decomposes above −55°.

perfluoroformimine (b.p. up to 90-95°), on treatment with aniline, form one and the same crystalline anilide, N-phenyl, N′-tri-(phenylamino)-methylhydrazine, m.p. 134°. With pyridine, the monomer and dimer of perfluoroformimine, $CF_2{=}NF$ and $(CF_2NF)_2$, form distillable complexes, from which, under the action of concentrated sulfuric acid at 0° in vacuum, the starting monomer and dimer are liberated. The ability to undergo the indicated complex formation may be used for purifying these products from accompanying impurities. The preferential decomposition of nitroso compounds during pyrolysis at the site of the C–N bond is consistent both with the data of mass-spectral investigation (formation upon electron impact of the ion NO^+, $m/e = 30$, of maximum intensity) and with the direction of decomposition of nitroso compounds in the ultraviolet. In the latter case, for example, in the photolysis of trifluoronitrosomethane, we, as well as Haszeldine, showed the formation of the nitrite N,N-bistrifluoromethylhydroxylamine (b.p. +10°).

$$CF_3NO \xrightarrow{h\nu} CF_3^{\bullet} + NO; \qquad CF_3NO \xrightarrow{CF_3^{\bullet}} [(CF_3)_2\dot{N}O] \xrightarrow{NO} (CF_3)_2NONO.$$

Since, in the investigations carried out, contact took place between nitroso compounds and nitric oxide arising in the reaction, it was of interest to study specif-

ically the behavior of polyfluorinated nitrosoalkanes toward it. It turned out that nitric oxide at room temperature reacts extremely readily with the nitroso compounds studied. Thus, when trifluoronitrosomethane and NO are mixed in the gas phase, the mixture immediately turns brown (formation of N_2O_4) and a vacuum arises in the vessel, although during the first hours of the reaction no appreciable decomposition of the nitroso compound is observed. Thus, the nitroso compound catalyzes the oxidation-reduction disproportionation of nitric oxide. After several weeks, trifluoronitromethane and some amount of N,N-bistrifluoromethylhydroxylamine nitrite accumulate in the reaction system. The interaction of CF_3NO with NO may be expressed by the scheme:

$$CF_3NO + 2NO \rightarrow [CF_3N(NO)ONO] \underset{NO^+}{\longrightarrow} CF_3^{\bullet} + N_2 + 2NO_2$$

$$[CF_3N(NO)ONO] \xrightarrow[\xrightarrow{+NO_2}]{+NO} CF_3NO_2 \qquad CF_3^{\bullet} + N_2 + 2NO_2 \xrightarrow[CF_3NO+NO]{} (CF_3)_2NONO$$

The scheme given is confirmed by the reaction of $CF_3NO + NO$ in solutions (ether, petroleum ether, methanol) at low (-100°) temperatures. In this case 1 mole of CF_3NO binds exactly 2 moles of nitric oxide, forming a bisnitroso derivative of trifluoromethylhydroxylamine that rapidly decomposes at -50°. Under the action of bases, the bisnitroso derivative formed is converted into comparatively stable salts of N-nitroso, N-trifluoromethylhydroxylamine:

$$CF_3N(NO)ONO \xrightarrow[-CH_3ONO]{+HN(C_2H_5)_2} [CF_3N(NO)OH] \xrightarrow{HN(C_2H_5)_2} CF_3N(NO)OH \cdot (C_2H_5)_2NH.$$

On warming to room temperature in the presence of alcohol, the second nitroso group is also split off, with formation of N-trifluoromethylhydroxylamine (isolated in the form of the N,O-dimethyl derivative upon reaction with diazomethane)

$$CF_3N(NO)ONO \xrightarrow{2CH_3OH} CF_3NHOH + 2CH_3ONO;$$

$$CF_3NHOH \xrightarrow{CH_2N_2} CF_3N(CH_3)OCH_3.$$

When the reaction of trifluoronitrosomethane with nitric oxide is carried out in alcohol in the presence of cuprous or ferrous salts, on cooling with solid carbon dioxide, complex derivatives are separated from the solution, for example,

$$CF_3N \begin{matrix} NO \\ OHCuCl \end{matrix}$$

analogous to "cupferron."

Salts of N-nitroso-N-trifluoromethylhydroxylamine are reactive. They are readily oxidized to trifluoronitromethane and react with acyl chlorides, forming O-acyl-N-trifluoromethylhydroxylamines. On boiling the salt with methanol, a mixed ether CF_3OR is formed:

$$CF_3N(NO)OMe \xrightarrow{ClCOR} [CF_3N(NO)OCOR] \xrightarrow{H_2O} CF_3NHOCOR \xrightarrow[-3HF]{C_6H_5NH_2} (C_6H_5NH)_2C{=}NOCOR,$$

where $R = CH_3, C_6H_5$; Me = Na, etc.

Like trifluoronitrosomethane, other polyfluorinated nitroso compounds also enter into reaction with NO, for example 2-chloro-2-nitrosopropane. In an alcohol medium these transformations lead to fluoroanhydrides of the corresponding polyfluoroalkylhydroxamic acids:

$$R_{fCF}2NO + 2NO \rightarrow [R_{fCF}2N(NO)ONO] \xrightarrow{CH_3OH} R_{fCF}2NHOH] \xrightarrow{-HF} R_fCF{=}NOH.$$

The study of the reactions of polyfluorinated nitrosoalkanes has shown that the nitroso group in these compounds is an active acceptor of free radicals, adding them at the site of the double bond; moreover, nitroso derivatives of hydroxylamine are readily formed with NO, i.e., nitrosoalkanes in this transformation behave analogously to the corresponding aromatic compounds ([5–8]).

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