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Abstract

Full Text

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V. A. Ginsburg, E. S. Vlasova, M. N. Vasil' eva, N. S. Mirzabekova, S. P. Makarov, A. I. Shchekotikhin, A. Ya. Yakubovich

PHOTOREACTIONS OF HEXAFLUOROAZOMETHANE WITH UNSATURATED COMPOUNDS

(Presented by Academician M. I. Kabachnik on 26 IX 1962)

We have previously established (1) that, upon photolysis of polyfluoroazoalkanes, the corresponding polyfluoroalkyl derivatives of hydrazine and tetrazine are readily formed. The results of a study of the photolysis of hexafluoroazomethane in the presence of free-radical acceptors are set forth below.

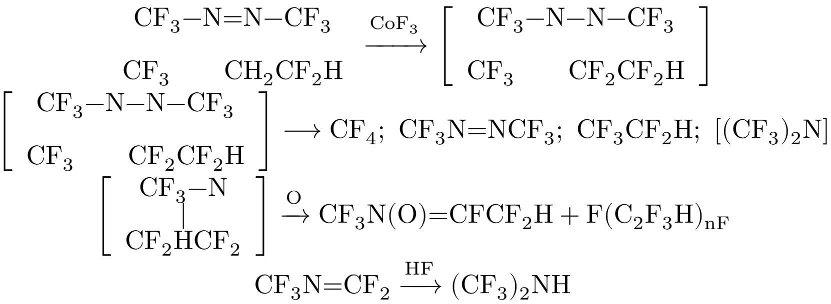
In the joint photolysis of hexafluoroazomethane and a number of substances containing various multiple bonds, such as: N_2O, $CH_3N{=}CO$, $CH_3N{=}C$, $CF_3C{\equiv}N$, $HC{\equiv}N$, $ClC{\equiv}N$, $CF_3N{=}O$, CO, CO_2, CS_2, SO_2, as well as with acetylene, olefins, and benzene, it was found that only unsaturated organic compounds enter into the reaction to an appreciable extent. Thus, upon irradiation with a mercury-quartz lamp of gaseous mixtures of hexafluoroazomethane with ethylene, vinylidene fluoride, and trifluoroethylene at room temperature and atmospheric pressure, telomers are readily formed (cf. (2)):

$$\mathrm{CF_3N_2CF_3} \xrightarrow{\mathrm{h}} \mathrm{N_2} + 2\mathrm{CF}_3^{\cdot}; \quad \mathrm{CF_3N_2CF_3} \xrightarrow{\mathrm{CF}_3^{\cdot}} \mathrm{(CF_3)_2N{-}\dot{N}(CF_3)} \rightarrow$$

$$\xrightarrow{\mathrm{n(C_2H_4)}} \mathrm{(CF_3)_2N{-}N(CF_3)(C_2H_4)}_{\mathrm{n}}^{\cdot} \xrightarrow{\mathrm{H}^{\cdot}} \mathrm{(CF_3)_2N{-}N(CF_3)(C_2H_5)_{nH}},$$

where $n = 1, 2, 3$ and higher.

In the case of vinylidene fluoride, attack by the perfluorotrimethylhydrazyl radical occurs primarily at the nonfluorinated carbon atom, as is proved by the following reactions of the telomer $(n = 1)$



$$CF_3{-}N{=}N{-}CF_3 \xrightarrow{CoF_3} \left[\begin{array}{c} CF_3{-}N{-}N{-}CF_3 \\ CF_3 \quad CF_2CF_2H \end{array}\right]$$
$$\begin{array}{c} CF_3 \quad CH_2CF_2H \end{array}$$
$$\left[\begin{array}{c} CF_3{-}N{-}N{-}CF_3 \\ CF_3 \quad CF_2CF_2H \end{array}\right] \longrightarrow CF_4;\ CF_3N{=}NCF_3;\ CF_3CF_2H;\ [(CF_3)_2N]$$
$$\left[\begin{array}{c} CF_3{-}N \\ | \\ CF_2HCF_2 \end{array}\right] \xrightarrow{O} CF_3N(O){=}CFCF_2H + F(C_2F_3H)_{nF}$$
$$CF_3N{=}CF_2 \xrightarrow{HF} (CF_3)_2NH$$

Similarly, in the photolysis of hexafluoroazomethane with benzene, tri-(trifluoromethyl)-phenylhydrazine is formed; in the case of acetylene the telomers formed contain CF_3NH groups (interaction with aniline) and have the structure:

$$CF_3NHN(CF_3)(CH{=}CH)_{nCF}3.$$

The structure of the product of the analogous reaction of hexafluoroazomethane with trichloroethylene may be represented by the formula

$$(CF_3)_2N{-}N(CF_3)(C_2Cl_3H)_{nCF}3.$$

The interaction under ultraviolet light of hexafluoroazomethane and polyfluoroolefins in the presence of oxygen proceeds unusually. Thus, upon irradiation of equimolecular mixtures of tetrafluoroethylene and oxygen containing 5-10% hexafluoroazomethane, a copolymer of tetrafluoroethylene and oxygen of composition $(C_2F_4O_2)_n$ is formed—a non-distillable viscous oil. Upon heating, this copolymer ···

Table 1

Newly synthesized compounds

No.	Compound	B.p., °C, mm Hg	d_{20}^{20}	n_D^{20}	Found, % C	Found, % H	Found, % F	Found, % Cl	Found, % N	Calculated, % C	Calculated, % H	Calculated, % F	Calculated, % Cl	Calculated, % N
1	$(CF_3)_2N{-}N(CF_3)(CH_2CH_2)_2H$ 85/80 1.5400 1.3180 27.34 2.1 61.02							—	9.47 9.15	28.28	2.7	58.9	—	9.6
2 *	$(CF_3)_2N{-}N(CF_3)(CH_2CH_2)_3H$ 125/60 1.3700 1.3194 33.52 3.81 53.02							—	3.13 8.62	33.8	4.05	53.5	—	8.7
3 *	$(CF_3)_2N{-}N(CF_3)(CH_2CF_2)_2H$ 80/20 1.8290 1.3421 22.74 0.91 65.75							—	5.08 10.73	23.40	0.64	67.0	—	9.4
4	$CF_3N(O){=}CFCF_2H$	19.0		1.37	16.70	0.96	64.31	—	7.83	7.7	15.8	0.55	63.0	—	7.7

No.	Compound	B.p., °C, mm Hg	d_{20}^{20}	n_D^{20}	Found, % C	Found, % H	Found, % F	Found, % Cl	Found, % N	Calculated, % C	Calculated, % H	Calculated, % F	Calculated, % Cl	Calculated, % N
5	$(CF_3)_2NN(CF_3)(C_2F_3H)$[illegible]	90 — 130	1.760	—	19.22 19.29	[illegible]	[illegible] 71.32	—	8.58 8.15	18.9	0.88	71.7	—	8.8
6	$(CF_3)_2NN(CF_3)(C_2F_3H)_2H$	70/10	[illegible]	—	[illegible]	[illegible]	[illegible] 67.83	—	6.67 [illegible]	[illegible]	0.77	73.5	—	7.2
7	$(CF_3)_2NN(CF_3)C_6H_5$	—	—	—	34.90	2.15	57.27	—	8.33	34.5	1.6	56.0	—	8.9
8	CF_3N[illegible]$CH)_2CF_3$ *	[illegible]	[illegible]	[illegible] 1.3440	48.80 [illegible]	[illegible]	[illegible] 60.15	—	9.13 [illegible]	[illegible]	1.4	59.5	—	9.75
9	$(CF_3)_2NN(CF_3)(C_2Cl_3$[illegible]	32 — 34/8	1.7941	[illegible]	[illegible]	[illegible]	50.55 [illegible]	[illegible]	[illegible]	16.6	—	52.5	24.5	6.45
10	$CF_2—CF_2$ \ / O	−57	—	—	19.05 19.40	—	65.09 65.05	—	—	20.5	—	65.5	—	—
11	$(C_2F_4O_2)_n$ **	—	1.820	—	18.04 17.87	traces	57.55 57.54	—	—	18.2	—	57.5	—	—
12	$CF_3O_3CF_3$	−13.5	—	—	12.30 11.95	—	60.33 60.53	—	—	12.9	—	61.3	—	—

* Telomers with a higher value of n are not distilled and have not been isolated in individual form.

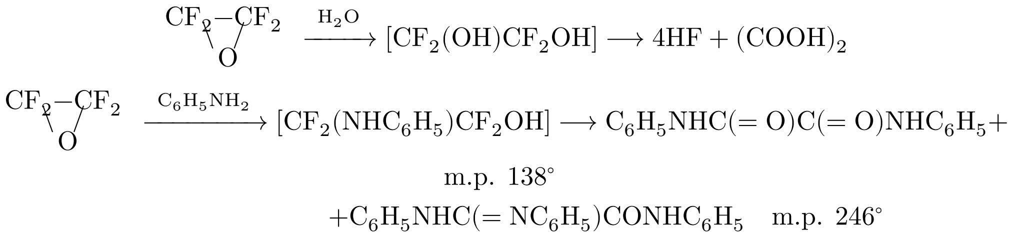
** Constants are given for the crude material; the product partially decomposes during distillation.

quantitatively decomposes into difluorophosgene; with aniline it forms diphenylurea

$$(C_2F_4O_2)_n \longrightarrow 2CF_2O$$

$$(C_2F_4O_2)_n \longrightarrow 2(C_6H_5NH)_2CO$$

Along with this, tetrafluoroethylene oxide is obtained, the structure of which is confirmed by a series of transformations and by mass spectrometry



$$\underset{\diagdown\ O\ \diagup}{CF_2-CF_2} \xrightarrow{H_2O} [CF_2(OH)CF_2OH] \longrightarrow 4HF + (COOH)_2$$

$$\underset{\diagdown\ O\ \diagup}{CF_2-CF_2} \xrightarrow{C_6H_5NH_2} [CF_2(NHC_6H_5)CF_2OH] \longrightarrow \underset{\text{m.p. }138^\circ}{C_6H_5NHC(=O)C(=O)NHC_6H_5} +$$

$$+C_6H_5NHC(=NC_6H_5)CONHC_6H_5 \quad \text{m.p. } 246^\circ$$

In the reaction of trifluoroethylene, oxygen, and hexafluoroazomethane, the less stable trifluoroethylene oxide was isolated—b.p. 42° (on hydrolysis the substance is converted into glyoxylic acid). It should be noted that, among fluorinated α-oxides, only trifluorochloroethylene oxide has been reliably described in the literature, in a patent ([3]) (cf. ([4–8])).

On photolysis of equimolecular amounts of a mixture of hexafluoroazomethane and oxygen under the same conditions, a compound of gross formula $C_2F_6O_3$ is formed, with pronounced oxidizing properties (liberation of 3–3.5 equivalents of iodine from neutral potassium iodide solutions, oxidation of nitric oxide to nitrogen dioxide and of sulfur dioxide to sulfuric anhydride). The substance is hydrolyzed by alcoholic alkalis, liberating 6 equivalents of fluoride ion and two molecules of soda. At 200° the product decomposes, forming difluorophosgene. These properties, together with NMR and mass-spectral data, indicate that the substance obtained is perfluorodimethylozone: CF_3OOOCF_3 (cf. ([7])).

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