Chemistry

A. V. Fokin, A. A. Skladnev, Yu. N. Studnev, and Academician I. L. Knunyants

1962

SovietRxiv

Abstract

Full Text

Chemistry

A. V. Fokin, A. A. Skladnev, Yu. N. Studnev, and Academician I. L. Knunyants

INTERACTION OF UNSYMMETRICAL FLUOROOLEFINS WITH HYDROGEN SULFIDE

We have previously shown the possibility of radical photochemical addition of hydrogen sulfide to tetrafluoroethylene and trifluorochloroethylene ([1]), leading to the corresponding fluoro-thiols and fluoro-sulfides. The addition of hydrogen sulfide to unsymmetrical perfluoroolefins had not been studied up to the present time.

The reaction of hydrogen sulfide with perfluoropropylene under the same conditions ended explosively. Only in an inert perfluorinated solvent was it possible to moderate the process and interrupt it at the stage when 60% of the reactants had entered into reaction. Irradiation of an equimolar mixture of perfluoropropylene and hydrogen sulfide, dissolved in perfluorocyclobutane, in the presence of traces of acetone (sensitizer) for 28–30 hr led to the formation of a mixture of addition products. About 40% of the reactants were recovered from the reaction unchanged.

Among the addition products, two isomeric mercaptans were detected: 2-monohydroperfluoropropyl mercaptan (I) and 2-monohydroperfluoroisopropyl mercaptan (II) in a ratio of 1 : 1. In addition, a small amount of a mixture of high-boiling telomerization products of perfluoropropylene was isolated:

$$CF_3{-}CF{=}CF_2 + HSH \begin{cases} \longrightarrow CF_3CFH{-}CF_2SH \quad (I) \\ \longrightarrow CF_3CF(SH){-}CF_2H \quad (II) \\ \longrightarrow H[CF(CF_3)CF_2]_{nSH} \\ \longrightarrow HS[CF(CF_3)CF_2]_{nH} \end{cases}$$

2-Monohydroperfluoropropyl mercaptan (I) is a stable compound, distilling without decomposition at ordinary pressure. In its chemical properties it is an analog of 2-monohydroperfluoroethyl mercaptan and, on interaction with compounds containing a labile hydrogen atom, is converted into the corresponding derivatives of thiopropionic acid by replacement of the fluorine atom at the α-carbon atom by the anion, followed by elimination of hydrogen fluoride:

$$CF_3CFHCF_2SH \xrightarrow[-HF]{(-HY)} \left[CF_3CFH{-}C\begin{pmatrix} Y \\ | \\ F \end{pmatrix}{-}SH\right] \xrightarrow{-HF} CF_3{-}CFH{-}C\begin{pmatrix} Y \\ | \end{pmatrix}{=}S,$$

where Y = OH; OR; SR; NR_2

2-Monohydroperfluoroisopropyl mercaptan (II) is an unstable compound that readily eliminates hydrogen fluoride with formation of monohydroperfluorothioacetone (III):

$$\begin{matrix} F_3C\backslash & F \\ & C \\ HF_2C/ & \backslash SH \end{matrix} \xrightarrow{-HF} \begin{matrix} F_3C\backslash \\ C{=}S \\ HF_2C/ \end{matrix} \text{(III)}$$

Monohydroperfluorothioacetone does not react with alcohols; in dioxane it is converted into monohydroperfluoroacetone; this is further confirmation that this compound is a ketone, and not the isomeric fluoroanhydride of α-monohydroperfluorothionpropionic acid (IV):

$$\underset{\text{(III)}}{CF_3{-}C(=S){-}CF_2H} \qquad \underset{\text{(IV)}}{CF_3CFH{-}C(=S){-}F}$$

Attempts to intensify the process led to explosions, explained by an explosive reaction occurring through radicalization of the (unsymmetrical) thioketone:

$$CF_3{-}C(=S){-}CF_2H \xrightarrow{h\nu} \begin{cases} CF_3\dot{C}{=}S + \dot{C}F_2H \\ CF_3^{\cdot} + \dot{C}(=S)CF_2H \end{cases}$$

The constants of the substances and the products of their transformations are given in Table 1.

Table 1

Substance	b.p., °C (mm)	d_4^{20}	n_D^{20}	Found, % F	Found, % S	Calculated, % F	Calculated, % S
CF_3CFHCF_2SH	42–43	1.4766	1.3279	60.77	17.89	61.83	17.39
$CF_3C(S)CF_2H$	45	1.4463	–	58.21	19.38	57.97	19.50
CH_3CF_2SH	60–62	d_4^{19} 1.2362	1.4040	38.68	32.99	38.78	32.70
CHF_2CH_2SH	62–63	1.2465	1.3930	39.10	32.61	38.78	32.70
$(CH_3CF_2)_2S$	110–112	1.2983	1.3936	45.44	20.52	46.92	19.76
$CF_3CFHCF_2CH_2OH$	73–74 (95)	1.3633	1.3522	46.15	19.21	46.81	19.74
$CF_3CFH(SC_2H_5)_2$	88–89	1.3167	1.3920	41.12	6.44	40.07	16.84
$CF_3CFHCF_2SC_2H_5$	75–76 (10)	1.2758	1.4662	34.78	14.63	35.16	14.77

The scheme for the formation of isomeric products of hydrogen sulfide addition to perfluoropropylene is confirmed by the analogous reaction of vinylidene fluoride with hydrogen sulfide. As a result of this reaction, two isomeric fluorothiols are formed–β,β-difluoroethyl mercaptan and α,α-difluoroethyl mercaptan:

$$HCH_2{=}CF_2 + HSH \xrightarrow{h\nu} \begin{cases} CH_2CF_2SH \\ CH_2(SH)CF_2H \end{cases}$$

The indicated isomers form an azeotropic mixture, which cannot be separated by fractionation. By decomposing a weighed portion of the azeotropic mixture of mercaptans with alkali and determining the amount of ionic fluorine in the solution, it was possible to establish that the mixture contains approximately 36 –42% α,α-difluoroethyl mercaptan and 64–58% β,β-difluoroethyl mercaptan.

$$HCF_2CH_2SH \xrightarrow{NaOH} NaSCH_2CF_2H + HOH$$

$$HCH_2CF_2SH \xrightarrow{2NaOH} HCH_2{-}C(S)ONa + 2NaF$$

On interaction of the azeotropic mixture with an alcohol, an ester of thioacetic acid is formed and pure β,β-difluoroethyl mercaptan is isolated:

$$HCH_2CF_2SH \xrightarrow{ROH} HCH_2C(=S)OR$$

Analogous formation of isomeric products was observed during inter-

interactions of unsymmetrical fluoroolefins with trifluoromethyl mercaptan (2).

A more detailed study of the addition of hydrogen sulfide to trifluorochloroethylene showed that, in this previously investigated case (1) as well, two isomers are formed: along with 2,2-fluorochloro-1,1-difluoroethyl mercaptan, a small amount of the isomeric 2,2-difluoro-1,1-fluorochloroethyl mercaptan is formed:

$$CFCl = CF_2 + HSH \begin{matrix} \nearrow HCFClCF_2SH \\ \searrow HSCFClCF_2H \end{matrix}$$

Typical experiment

Addition of hydrogen sulfide to perfluoropropylene

20 g of perfluoropropylene, 4.8 g of hydrogen sulfide (molar ratio 1 : 1.05), and 3 g of perfluorocyclobutane in the presence of 5 drops of acetone were irradiated in a sealed quartz ampoule at room temperature for 30 h with a PRK-2 mercury-quartz lamp of 375 W power and mean wavelength 3650 Å.

The cooled ampoule was opened. The addition products, 15 g in amount (yield 60%), were fractionated. The following were isolated:

a) monohydroperfluorothioacetone, 3.6 g, a colorless mobile liquid with b.p. 15°, 24% of the total amount of addition products; b) 2-monohydroperfluoropropyl mercaptan, a liquid with b.p. 42-43°, 4 g (26.6% of the total amount); c) telomerization products—a viscous liquid—4 g (not identified).

2.8 g (0.015 g-mol) of 2-monohydroperfluoropropyl mercaptan and 3 ml of water were heated on a boiling water bath for 30 h in a sealed tube. The cooled tube was opened, and the reaction mixture was extracted with ether. The ether extract was dried over ignited magnesium sulfate. The solvent was distilled off, and the residue was fractionated. 0.48 g of monohydroperfluorothiopropionic acid was isolated, b.p. 73-75° (95 mm), yield 19.5% of theoretical.

2.6 g (0.014 g-mol) of 2-monohydroperfluoropropyl mercaptan in 20 ml of abs. dry benzene, with vigorous stirring and cooling, was treated with an excess amount of abs. ethyl alcohol; the reaction mixture was kept at the boiling temperature of benzene for 1.5 h, cooled, washed with sodium bicarbonate solution and then with water; the benzene layer was separated from the aqueous layer, dried over ignited magnesium sulfate, and fractionated. 0.91 g of the ethyl ester of monohydroperfluorothiopropionic acid was isolated, b.p. 98-99°, yield 34.3% of theoretical.

11.8 g (0.08 g-mol) of 2,2-fluorochloro-1,1-difluoroethyl mercaptan, dissolved in dry ether, with vigorous stirring and cooling, was treated with 22 g of diethylamine dissolved in ether (1 : 4). The temperature of the reaction mixture was brought to room temperature; diethylamine hydrofluoride was filtered off, and the ether solution was evaporated and fractionated.

The following were isolated. a) 0.26 g of diethylamide of difluorothioacetic acid, b.p. 66° (2.5 mm), d_4^{20} 1.1389, n_D^{20} 1.4798. Literature data (3): b.p. 86° (6 mm), d_4^{20} 1.1346, n_D^{26} 1.4752. b) 6.1 g of diethylamide of fluorochlorothioacetic acid (yield 42.3%), b.p. 73-74° (2.5 mm), d_4^{20} 1.1963, n_D^{20} 1.5199. Literature data (3): b.p. 98° (8 mm), d_4^{20} 1.1954, n_D^{20} 1.5175.

Received
2 X 1961

References Cited

1. A. V. Fokin, A. A. Skladnev, I. L. Knunyants, DAN, 138, No. 5, 1132 (1961).

2. J. H. Harris, F. W. Stacey, J. Am. Chem. Soc., 83, 840 (1961).

3. N. N. Yarovenko, M. A. Raksha, ZhOKh, 29, No. 7, 2159 (1959).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.