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Abstract

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REACTIONS OF FLUOROOLEFINS

THE INTERACTION OF FLUOROOLEFINS WITH HYDROGEN SULFIDE

A number of reactions of fluoroolefins with electrophilic substances (halogens, fluoroalkyl halides, nitrosyl fluoride, nitrogen oxides), as well as polymerization reactions and others, proceed by a radical mechanism and require the input of energy for homolytic cleavage of the reagents and for overcoming the energy barrier in the form of heat or light or the addition of catalysts. These features of fluoroolefins are apparently connected with the electron depletion of their π-bond, caused by the strong electronegativity of fluorine, as a result of which the carbon atoms connected by the double bond are, to a certain extent, radicalized. In accordance with this assumption, fluoroolefins should react comparatively readily with easily radicalized agents and radical-like molecules. In this light, the question of the behavior of perfluoroolefins toward hydrogen sulfide, which under the influence of various factors rather readily undergoes homolytic cleavage, is of particular interest.

It is not possible to add hydrogen sulfide to tetrafluoroethylene, trifluorochloroethylene, perfluoropropylene, and perfluoroisobutylene, even at a temperature of 180°, in the absence of catalysts. In the presence of substances catalyzing the addition of thiols to fluoroolefins (^1) (caustic soda, alcoholic alkali, sulfur, pyridine), a complex mixture of addition products is formed, from which it is not possible to isolate individual substances.

The addition of hydrogen sulfide to tetrafluoroethylene and trifluorochloroethylene was carried out by us under the conditions of a photochemical reaction induced by ultraviolet light.

The photochemical decomposition of hydrogen sulfide under the influence of ultraviolet irradiation was established by Evers and Forbes (^2), who studied this reaction in a solution of dry carbon tetrachloride:

$$H_2S + h\nu \rightarrow H\cdot + \cdot SH,$$

$$H\cdot + CCl_4 \rightarrow HCl + \cdot CCl_3.$$

A substitution of this kind of a chlorine atom in carbon tetrachloride is one of the well-studied reactions of atomic hydrogen. The addition of hydrogen sulfide to simple olefins, for example butylene, diallyl, and vinyl chloride, under ultraviolet irradiation leads to the formation of mercaptans and thioethers (ˆ3). In all cases the sulfur atom adds to the carbon atom bearing the larger number of hydrogen atoms:

$$CH_2{=}CHCl + {\cdot}SH \rightarrow HSCH_2{-}\dot{C}HCl.$$

When an equimolar mixture of tetrafluoroethylene and hydrogen sulfide was irradiated in the presence of traces of acetone (sensitizer), the reaction over the course of 4-6 hr led to the formation of a mixture of addition products with an overall yield of more than 90%. The main reaction products formed were 2-monohydrotetrafluoroethyl mercaptan and 2,2′-dihydroperfluorodiethyl sulfide in a ratio of 2 : 1. In the case of a twofold excess of olefin relative to hydrogen sulfide, the yield of sulfide is more than 70%, with complete absence of mercaptan. In addition, a small amount of a mixture of high-boiling telomerization products of tetrafluoroethylene, initiated by radical particles of hydrogen sulfide, is formed.

$$CF_2{=}CF_2 + HSH \begin{cases} \nearrow\ HCF_2CF_2SH \\ \rightarrow\ HCF_2CF_2{-}S{-}CF_2CF_2H \\ \searrow\ H(CF_2)_{nCF}2SH \end{cases}$$

In the case of trifluorochloroethylene, the reaction, carried out under the same conditions, leads to 1,1,2-trifluoro-2-chloroethyl mercaptan, 2,2′-dihydro-2,2′-dichloroperfluorodiethyl sulfide, and 2,2′-dihydro-2,2′-dichloroperfluorodiethyl disulfide (Table 1)

$$CFCl{=}CF_2 + HSH \begin{cases} \nearrow\ HCFClCF_2SH \\ \nearrow\ HCFClCF_2{-}S{-}CF_2CFClH \\ \searrow\ HCFClCF_2{-}S{-}S{-}CF_2CFClH \\ \searrow\ H(CFClCF_2)_{nSH}\cdot \end{cases}$$

The conditions for the addition of hydrogen sulfide to fluoroolefins, the nature of the products obtained (and primarily of the telomers), as well as the numerous cases of explosions as a result of the occurrence of a chain reaction, serve as evidence for the radical character of the reaction.

$$H_2S \xrightarrow{h} HS\cdot + \cdot H,$$

$$HS\cdot + CF_2{=}CF_2 \rightarrow HSCF_2CF_2\cdot,$$

$$HSCF_2CF_2\cdot + HSH \rightarrow HSCF_2CF_2H + \cdot SH,$$

$$CF_2{=}CF_2 + \cdot H \rightarrow HCF_2CF_2\cdot,$$

$$HCF_2{-}CF_2\cdot + HSH \rightarrow HCF_2CF_2SH + \cdot H,$$

$$HCF_2CF_2SH \xrightarrow{h} HCF_2CF_2S\cdot + \cdot H,$$

$$HCF_2CF_2S\cdot + CF_2{=}CF_2 \rightarrow HCF_2CF_2SCF_2CF_2\cdot,$$

$$HCF_2CF_2SCF_2CF_2\cdot + HSH \rightarrow HCF_2CF_2S{-}CF_2CF_2{-}H + \cdot SH,$$

$$HCF_2CF_2S\cdot + HSH \rightarrow HCF_2CF_2SSH + \cdot H,$$

$$HCF_2CF_2SSH + CF_2{=}CF_2 \rightarrow HCF_2CF_2SSCF_2CF_2H$$

In the case of an unsymmetrically constructed perfluoroolefin, for example trifluorochloroethylene, there are two possible modes of addition of hydrogen sulfide, with formation of trifluorochloroethyl mercaptan

$$HSCF_2CFClH\ (I), \qquad HCF_2CFClSH\ (II).$$

Trifluorochloroethyl mercaptan having structure I, upon interaction with water, could lead to the formation of fluorochlorothioacetic acid III, whereas with structure II, as a result of hydrolysis, the formation of difluorothioacetic acid IV should be expected

$$HCFCl{-}C({=}S)OH \quad (III), \qquad HCF_2C({=}S)OH \quad (IV).$$

The production of fluorochlorothioacetic acid as the sole product of hydrolysis of fluorochloroethyl mercaptan was confirmation

order of addition of hydrogen sulfide to trifluorochloroethylene, whose sulfhydryl group adds to the "most fluorinated" and less negatively polarized carbon atom.

Analogously to water, the action of amines, alcohols, and mercaptans on the new β-monohydroperfluoromercaptans leads, respectively, to substituted amides, esters, and thioesters of thioacetic acids. In all these reactions, monohydroperfluoromercaptans react as mixed anhydrides of α-difluoroalkanol and hydrogen sulfide; they are strong acylating agents, similar to the previously studied β-nitroperfluoroalkylnitriles (^{4}), and in all cases the reaction proceeds by replacement of fluorine at the α-carbon atom, with subsequent elimination of hydrogen fluoride

$$\mathrm{CF_2H{-}CF_2SH} \xrightarrow{\mathrm{H(Y)}} \mathrm{CF_2HCF(Y)SH} \xrightarrow{-\mathrm{HF}} \mathrm{CF_2H{-}C({=}\,S)(Y)},$$

where $Y = \mathrm{OH, OR, SR, NR_2}$, etc.

The constants of the substances obtained as a result of transformations of β-monohydroperfluoromercaptans are given in Table 2.

Table 1

Formula of substance	B.p., °C (mm)	d_4^{20}	n_D^{20}	Found, % F	Found, % Cl	Found, % S	Calculated, % F	Calculated, % Cl	Calculated, % S
$HSCF_2CF_2H$	31	1.4910	1.3230*	57.70	–	24.50	57.10	–	23.90
$S(CF_2CF_2H)_2$	100–102	1.6240	1.3280	64.83	–	13.74	64.95	–	13.68
$HSCF_2CFClH$	64	1.4750	1.3880	38.43	23.96	21.09	37.87	23.59	21.26
$S(CF_2CFClH)_2$	71.5 (60)	1.6350	1.3920	42.83	26.30	13.71	42.59	26.53	11.95
$S_2(CF_2CFClH)_2$	70 (2)	1.7496	1.4910	38.50	23.90	20.67	38.29	23.80	21.40

* d_4 and n_D were determined at a temperature of 0°.

Table 2

Formula of substance	B.p., °C (mm)	d_4^{20}	n_D^{20}	Found, % F	Found, % Cl	Found, % S	Calculated, % F	Calculated, % Cl	Calculated, % S
HCF_2CSOH	70 (5)	1.688	1.4880	35.20	–	28.50	33.93	–	27.35
$HCF_2ClCSOH$	43 (3)	1.470	1.4320	15.02	–	25.00	14.90	–	24.90
HCF_2CSOCH_3	94	1.331	1.4012	30.84	–	24.10	30.20	–	25.40
$HCF_2CSOC_2H_5$	105	1.180	1.3888	27.76	–	23.46	27.20	–	22.80
$HCFClCSOCH_3$	59 (60)	1.327	1.4726	13.42	23.86	22.76	13.42	24.91	22.46
$HCFClCSOC_2H_5$	71 (60)	1.246	1.4636	14.10	22.72	19.04	13.20	22.69	20.40

Formula of substance	B.p., °C (mm)	d_4^{20}	n_D^{20}	Found, % F	Found, % Cl	Found, % S	Calculated, % F	Calculated, % Cl	Calculated, % S
$HCFClCSOC_4H_9$	80–83 (23)	1.162	1.4572	9.85	20.38	–	10.28	19.30	–
$HCFClCSOC_6H_{11}$	86 (5)	1.064	1.4564	8.46	16.98	–	8.92	16.65	–
$HCF_2CSN(C_2H_5)_2$	70 (10)	1.143	1.4970	23.07	–	18.70	22.75	–	19.60
$HCFClCSN(C_2H_5)_2$	93 (7)	1.199	1.5220	12.00	17.20	16.97	10.35	19.34	17.44
$HCF_2CSOCCH_3$	65 (4)	1.358	1.3869	24.60	–	20.30	24.60	–	20.6
$HCFClCSOCOCH_3$	60 (2)	1.351	1.3935	11.80	20.40	17.80	11.15	20.80	18.75
$HCF_2CSSC_2H_5$	80 (60)	1.261	1.4990	24.60	–	40.40	24.40	–	41.00
$HCFClCSSC_2H_5$	60 (40)	1.330	1.4885	10.29	21.70	–	11.05	20.58	–

Thus, also in the case of addition of hydrogen sulfide to fluoroolefins, despite the radical character of the reaction, a definite order of addition is observed.

The α-fluorothiols obtained are stable compounds, distilling with slight decomposition, whereas the oxygen analogs of these substances are unknown.

Before the present study, only two representatives of perfluorothiols had been described—trifluoromethyl- and perfluoropropylmercaptans, obtained by Haszeldine and Kidd in 1953 upon ten-day irradiation with ultraviolet light of hexafluorodimethyl and bis(perfluoropropyl) sulfides with mercury, followed by treatment of the resulting mercaptide with hydrochloric ···

hydrogen at 90° in a sealed tube (^{5}).

$$(CF_3S)_2 \xrightarrow{Hg,\,h\nu} Hg(SCF_3)_2 \xrightarrow[-HgCl_2]{HCl} CF_3SH.$$

The infrared spectrum of trifluoromethyl mercaptan, studied by Dininny (^{6}), showed the presence of vibrations corresponding to the sulfhydryl group in the region of 2618 cm^{-1}. The infrared spectra of the β-monohydroperfluoro- and β-monohydrotrifluorochloroethyl mercaptans obtained by us contain clearly expressed peaks at 2608 and 2612 cm^{-1}, characteristic of the sulfhydryl group.

Typical experiment*

1. **Addition of hydrogen sulfide to trifluorochloroethylene.** 20 g of trifluorochloroethylene and 6 g of dry hydrogen sulfide in the presence of 5 drops of acetone were irradiated in a sealed quartz ampoule at room temperature for 6 hr with a PRK-2 mercury-quartz lamp of 375 W power with an average wavelength of 3650 Å. The cooled ampoule was opened. The addition products, in an amount of 26 g (yield 100%), were fractionated. Isolated:
    a) 2,2-fluorochloro-1,1-difluoroethyl mercaptan, liquid, b.p. 64°, 11 g, 42.5% of the total amount.
    b) 2,2′-dihydro-2,2′-dichloroperfluorodiethyl sulfide, liquid, b.p. 71.5° (60 mm), 2.6 g, 10% of the total amount.
    c) 2,2′-dihydro-2,2′-dichloroperfluorodiethyl disulfide, viscous liquid, b.p. 70° (2 mm), 8 g, 31% of the total amount.
2. 7 g of 2,2-fluorochloro-1,1-difluoroethyl mercaptan was treated with 1.8 g of water (twofold excess) with vigorous stirring and cooling. The reaction mixture was kept for 30 min at 70°; the oily liquid was separated from the aqueous layer, dried with calcined magnesium sulfate, and fractionated. 1.6 g of fluorochlorothioacetic acid was isolated, b.p. 43° (3 mm), yield 18% of theory.
3. 13.5 g of 2,2-fluorochloro-1,1-difluoroethyl mercaptan, with vigorous stirring and cooling, was treated with an equimolar amount of ethyl alcohol; the reaction mixture was kept at 100° for 1 hr, cooled, washed with a solution of sodium bicarbonate and with water, separated from the aqueous layer, dried with calcined magnesium sulfate, and fractionated. Ethyl fluorochlorothioacetate was isolated in 66% yield, liquid, b.p. 71° (60 mm).
4. 4.4 g of 2,2-fluorochloro-1,1-difluoroethyl mercaptan, dissolved in dry ether, with vigorous stirring and cooling was treated with 8.4 g of diethylamine in ether. The temperature of the reaction mixture was brought to room temperature, diethylamine hydrofluoride was filtered off, and the ethereal solution was evaporated and fractionated. 2.7 g of diethylamide of fluorochlorothioacetic acid was isolated (yield 51%), b.p. 93° (7 mm).

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