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During the last 2-3 years a number of investigators have been concerned with the reactions of fluoro olefins with hydrogen sulfide [1-5]. In absence of catalysts the addition of hydrogen sulfide to tetrafluoroethylene, hexafluoropropene, and octafluoroisobutene cannot be brought about, even at 180°. In presence of substances which catalyze the addition of thiols to fluoro olefins (sodium hydroxide, alcoholic alkali, etc.) a complicated mixture of addition products is formed, from which difluorothioacetic O-ester has been isolated. The reaction of chlorotrifluoroethylene with hydrogen sulfide in presence of benzoyl peroxide goes when the reaction temperature is raised to $100-110^{\circ}$. Individual reaction products can be isolated only when a 100% excess of the olefin relative to the hydrogen sulfide is used.

$$2CF_2 = CFCl + H_2S \rightarrow S(CF_2CHFCl)_2$$

At a 1:1 molar ratio of reactants we were unable to isolate an addition product. The probable explanation is that α, α -difluoropolyhaloalkanethiols readily lose hydrogen fluoride at an elevated temperature and polymerize [1, 3]:

$$\begin{array}{c} \text{CHFClCF}_2\text{SH} \xrightarrow{\mathfrak{f}} \text{CHFClc} \xrightarrow{\text{S}} \rightarrow -(-\text{CFS}-)_{\overline{n}} \\ \xrightarrow{} \\ F \\ \text{CHFCl} \end{array}$$

It was shown in [4] that prolonged irradiation of a mixture of chlorotrifluoroethylene and hydrogen sulfide in presence of catalytic amounts of benzoyl peroxide (15 days, 500-W lamp) leads to the formation of an unsaturated sulfide:

$$CF_2 = CFCl + H_2S_{A}^{\nu} \rightarrow [S(CF_2CHFCl)_2] \xrightarrow{-2HF} S(CF = CFCl)_2 + [S(CF = CFCl)_2]_n$$

For the preparation of products of the addition of hydrogen sulfide to fluoro olefins at a 1:1 ratio, the conditions of the photochemical reaction have proved extremely convenient. We have studied the reaction of hydrogen sulfide with fluoro olefins for tetrafluoroethylene, chlorotrifluoroethylene [1], vinylidene fluoride, and hexafluoropropene [2]. The reaction of tetrafluoroethylene with hydrogen sulfide with a 4-6-h irradiation of an equimolecular mixture of reactants in presence of traces of acetone (sensitizer) leads to the formation of a mixture of addition products in a total yield of more than 90%. As main reaction products 2H-tetrafluoroethyle) sulfide are formed in 2:1 proportions. When there is a 100% excess of the olefin relative to hydrogen sulfide, the yield of the sulfide is more than 70%, and the thiol is completely absent. Also, a small amount of a mixture of high-boiling products of the telomerization of tetrafluoroethylene is formed.

$$CF_2 = CF_2 + H_2S \xrightarrow{h\gamma} | \xrightarrow{\rightarrow} CHF_2CF_2SH \\ (CHF_2CF_2)_2S \\ \xrightarrow{\rightarrow} H (CF_2)_nCF_2SH$$

The addition of hydrogen sulfide to tetrafluoroethylene was often accompanied by the explosion of the quartz tubes in which the reaction was conducted.

Under similar conditions (time of irradiation 4-6 h) the reaction of hydrogen sulfide with chlorotrifluoroethylene leads to the formation of 2-chloro-1,1,2-trifluoroethanethiol (up to 50%), bis (2-chloro-1,1,2trifluoroethyl) sulfide, bis (2-chloro-1,1,2-trifluoroethyl) disulfide, and a small amount of higher-boiling products; total yield about 100%.

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More prolonged irradiation (more than 6 h) of a 1:1 mixture of hydrogen sulfide and chlorotrifluoroethylene leads to a sharp fall in the yield of the thiol. As well as the main addition product -2-chloro-1,1,2-trifluoroethanethiol - a small amount of the product of addition in the opposite direction -1-chloro-1,2,2-trifluoroethanethiol - is formed, though we were unable to isolate it in the pure state. The presence of the latter compound is indicated by the products isolated in the reactions of the isomeric thiols with diethylamine and with potassium fluoride, which in the case of the second thiol were N,N-diethyl-2,2-difluorothioacetamide and difluorothioacetyl chloride, respectively:



Diflurothioacetyl chloride differs from fluorothioacetyl fluorides in their considerably higher stability. It can be kept in a glass vessel almost without change at room temperature for more than one month, whereas fluorothioacetyl fluorides polymerize spontaneously at room temperature during the first few days. The chlorine in the acid chloride can be titrated as chloride quantitatively after decomposition with aqueous alkali.

In the addition of hydrogen sulfide to chlorotrifluoroethylene under the action of x rays, Harris and Stacey did not observe the formation of 1-chloro-1,2,2-trifluoroethanethiol. However, study of the PMR spectrum of the sulfide obtained in this reaction showed the possibility of the presence (less than 3%) of an isomer containing the CHF₂ group [i.e., HCF₂CHClSCF₂CHFCl or (CHF₂CFCl)₂S] [3]. The reaction of hydrogen sulfide with vinylidene fluoride under the action of UV radiation also leads to the formation of two isomeric thiols, a small amount of a sulfide, but only very small amounts of telomeric products.

$$\mathrm{CH}_{2} = \mathrm{CF}_{2} + \mathrm{H}_{2}\mathrm{S} \xrightarrow{h\nu} \begin{array}{|} & \longrightarrow \mathrm{CH}_{3}\mathrm{CF}_{2}\mathrm{SH} \\ & \longrightarrow \mathrm{CHF}_{2}\mathrm{CH}_{2}\mathrm{SH} \\ & \longrightarrow \mathrm{(CH}_{3}\mathrm{CF}_{2})_{2}\mathrm{S} \end{array}$$

Reaction is practically complete in 3 h. Increase in the time of irradiation lowers the yield of thiols and raises the amount of telomeric products. In the reactions of hydrogen sulfide with vinylidene fluoride and chlorotrifluoroethylene no explosions were observed. We were unable to separate 1,1-difluoroethane-thiol and 2,2-difluoroethanethiol by fractional distillation, probably because these isomers form an azeo-tropic mixture. By decomposing the azeotropic mixture of thiols with alkali and determining the amount of fluoride ion in solution we showed that the mixture contained 36-42% of 1,1-difluoroethanethiol and 64-58% of 2,2-difluoroethanethiol.

 $\begin{array}{c} \mathrm{CHF_{2}CH_{2}SH} \xrightarrow{\mathrm{NaOH}} \mathrm{NaSCH_{2}CHF_{2}+H_{2}O} \\ \mathrm{CH_{3}CF_{2}SH} \rightarrow \mathrm{CH_{3}C}\left(\mathrm{S}\right)\mathrm{ONa} + 2\mathrm{NaF} + \mathrm{H_{2}O} \end{array}$

In the treatment of the azeotropic mixture with alcohols the corresponding thioacetic O-esters were formed, and pure 2,2-difluoroethanethiol, which does not react with alcohols, was isolated.

$$\mathrm{CHF_2CH_2SH}, \ \mathrm{CH_3CF_2SH} \xrightarrow{\mathrm{ROH}} \mathrm{CHF_2CH_2SH} + \mathrm{CH_3C}(\mathrm{S}) \ \mathrm{OR} + 2\mathrm{HF}$$

In the irradiation of a 2:1 mixture of hydrogen sulfide and vinylidene fluoride with x rays, Harris and Stacey [3] isolated only 2,2-difluoroethanethiol. Our results on the composition of the reaction products are confirmed in [5].

The reaction of hydrogen sulfide with hexafluoropropene under the same conditions always ended explosively. We were able to carry out the reaction in an inert perfluorinated solvent, which made it possible to interrupt the process at the stage at which 60% of the reactants had reacted. The irradiation of an equimolecular mixture of hexafluoropropene and hydrogen sulfide dissolved in octafluorocyclobutane in presence of traces of acetone for 28-30 h led to the formation of a mixture of addition products, from which we isolated two isomeric thiols and a small amount of a mixture of high-boiling products of the telomerization of hexafluoropropene.

 $CF_{3} - CF = CF_{2} + H_{2}S \xrightarrow{h_{v}} \rightarrow CF_{3}CHFCF_{2}SH$ $\rightarrow CF_{3}CF(SH) CHF_{2}$ $\rightarrow H [CF(CF_{3}) CF_{2}]_{n} SH$ $\rightarrow HS [CF(CF_{3}) CF_{2}]_{n} H$

Attempts to use other solvents, such as toluene, were unsuccessful. 2H-Hexafluoro-1-propanethiol is a stable compound, which can be distilled at atmospheric pressure without decomposition. 1H-Hexafluoro-2-propanethiol is an unstable compound which readily loses hydrogen fluoride with formation of 1H-penta-fluoro-2-propanethione:



1H-Pentafluoro-2-propanethione does not react with alcohols, in aqueous dioxane it is converted into 1H-pentafluoroacetone, and when kept it appears to be converted into a dimer:



Attempts to carry out the reaction of hydrogen sulfide with hexafluoropropene with a conversion of more than 60% always led to explosions, explicable by the explosive reaction arising from the radicalization of the unsymmetrical thione:



It may be regarded as established, therefore, that under conditions for photochemical reaction hydrogen sulfide reacts with fluoro olefins with formation of the corresponding thiols and sulfides together with a series of telomerization products. In reactions with unsymmetrical fluoro olefins isomeric thiols are formed, which confirms views expressed previously concerning the radical mechanism of this reaction.



EXPERIMENTAL*

<u>Addition of Hydrogen Sulfide to Tetrafluoroethylene</u>. A mixture of 2 g of H_2S , 4.5 g of tetrafluoroethylene, and 5 drops of acetone was irradiated in a sealed translucent quartz glass tube (volume 30 ml, external diameter 13 mm, wall thickness 3.5 mm) at room temperature (cooling with fan) from a distance of 25-30 cm for 5.5 h with a PRK-2 quartz mercury lamp (375 W, mean wavelength 3650 A). The quartz tube was cooled and opened. The products (6.5 g) were fractionated. We isolated: a) 2H-tetrafluoroethanethiol, 2.6 g; b.p. 31°; d_4^{20} 1.4910; n_D^{20} 1.3230. Found %: F 57.7; S 24.5. $C_2H_2F_4S$. Calculated %: F 57.1; S 23.9. b) Bis (2H-tetrafluoroethyl) sulfide, 3.2 g; b.p. 100-102°; d_4^{20} 1.6240; n_D^{20} 1.3280. Found %: F 64.83; S 13.74. Mol.wt. 235. $C_4H_2F_8S$. Calculated %: F 64.95; S 13.68. Mol. wt. 234. c) Telomerization products, 0.7 g (not identified)

* With the participation of I. Ya. Lyubchenko and K. V. Frosina.

Addition of Hydrogen Sulfide to Chlorotrifluoroethylene. A mixture of 20 g of chlorotrifluoroethylene, 6 g of dry H₂S, and 5 drops of acetone was irradiated in a sealed quartz tube (volume 230 ml) at room temperature for 6 h with a PRK-2 quartz mercury lamp. The cooled tube was opened. The addition products (26 g) were fractionated. We isolated: a) 2-chloro-1,1,2-trifluoroethanethiol, 9.1 g; b.p. 64° ; d_4^{20} 1.4750; n_D^{20} 1.3880. Found %: F 38.43; Cl 23.96; S 21.09. Mol. wt. 145. $C_2H_2F_3$ ClS. Calculated %: F 37.87; Cl 23.59; S 21.26. Mol. wt. 150.5. b) Bis(2-chloro-1,1,2-trifluoroethyl) sulfide, 2.6 g; b.p.71.5° (60 mm); d_4^{20} 1.6350; n_D^{20} 1.3920. Found %: F 42.83; Cl 26.30; S 13.71. Mol. wt. 258. $C_4H_2F_6$ Cl₂S. Calculated %: F 42.59; Cl 26.53; S 11.95. Mol.wt. 267. c) Bis(2-chloro-1,1,2-trifluoroethyl) disulfide, 8 g; b.p. 70° (2 mm); d_4^{20} 1.749; n_D^{20} 1.491. Found %: F 38.5; Cl 23.9; S 20.67. Mol. wt. 296. $C_4H_2F_6$ Cl₂S. Calculated %: F 38.2; Cl 23.8; S 21.4. Mol. wt. 299. d) Telomerization products, 6 g (not identified).

<u>Difluorothioacetyl Chloride</u>. 7.4 g of 2-chloro-1,1,2-trifluoroethanethiol and 2.9 g of calcined KF were sealed in a glass tube and kept for 12 h at room temperature. The tube was heated in a boiling water bath for 1.5 h. The tube was opened, and fractionation of the contents gave 0.47 g of a yellow-ish liquid; b.p. 56°; d_4^{20} 1.386; n_D^{20} 1.4319. Found %: F 29.27; S 24.49; Cl 27.12. C₂HF₂ClS. Calculated %: F 29.19; S 24.52; Cl 27.20.

Addition of Hydrogen Sulfide to Vinylidene Fluoride. A mixture of 3.9 g of vinylidene fluoride, 2.2 g of H₂S, and 2-3 drops of acetone was irradiated in a quartz tube (length 40 cm, external diameter 12 mm, wall thickness 1 mm) for 3 h with a PRK-2 lamp. The cooled tube was opened. The reaction products (6.1 g) were fractionated. We isolated: a) difluoroethanethiols (mixture of isomers), 4.3 g, b.p. $60-62^{\circ}$; n_{D}^{20} 1.4040; d_{4}^{20} 1.2362. Found %: F 38.68; S 32.99. $C_{2}H_{4}F_{2}S$. Calculated %: F 38.78; S 32.70. b) Bisdifluoroethyl sulfide, 0.8 g; b.p. 110-112°; n_{D}^{20} 1.3936; d_{4}^{20} 1.2983. Found %: F 45.44; S 20.52. $C_{4}H_{6}F_{4}S$. Calculated %: F 46.92; S 19.76.

Addition of Hydrogen Sulfide to Hexafluoropropene. A mixture of 20 g of hexafluoropropene, 4.8 g of H₂S, 3 g of octafluorocyclobutane, and 5 drops of acetone was irradiated in a sealed quartz tube (volume 100 ml) at room temperature for 30 h with a PRK-2 quartz mercury lamp. The cooled tube was opened. The addition products, which amounted to 15 g, were fractionated. We isolated: a) 1H-Penta-fluoro-2-propanethione, 3.6 g; b.p. 15° ; d_4^{20} 1.4463. Found %: F 58.21; S 19.38. C₃HF₅S. Calculated %: F 57.94; S 19.50. b) 2H-Hexafluoro-1-propanethiol, 4 g, liquid; b.p. $42-43^{\circ}$; n_D^{20} 1.3270; d_4^{20} 1.4766. Found %: F 60.77; S 17.89. C₃H₂F₆S. Calculated %: F 61.83; S17.39. c) Telomerization products – viscous liquid (not identified).

Fraction (a) was left for one week in a sealed tube in presence of KF, and pentafluoro-2-propanethione dimer was obtained; b.p. 62-63° (46 mm); n_D^{20} 1.3627. Found %: F 58.16; S 19.62. Mol. wt. 323. $C_6H_2F_{10}S_2$. Calculated %: F 57.97; S 19.50. Mol. wt. 328.

CONCLUSIONS

1. The photochemical reactions of hydrogen sulfide with tetrafluoroethylene and vinyldene fluoride lead to the formation of the corresponding fluorine-containing thiols and sulfides together with telomerization products

2. Orientation in the addition of hydrogen sulfide to unsymmetrical fluoro olefins is examined.

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