CHLORINE FLUOROSULFATE

COMMUNICATION 3. INTERACTION WITH HYDROGEN CHLORIDE, NITROGEN TETRAOXIDE, SULFUR DIOXIDE, CARBON MONOXIDE, AND TETRACHLOROETHYLENE

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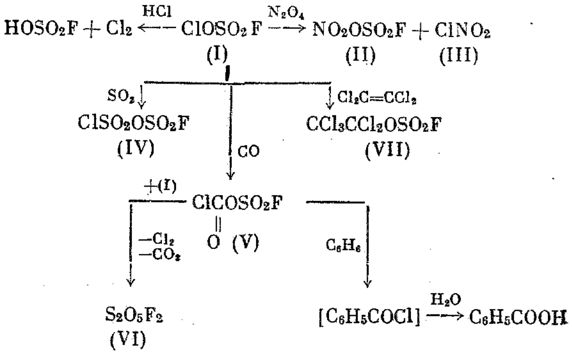
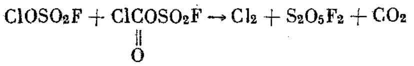
Chlorine fluorosulfate (I) is added energetically at the double bonds of fluoroolefins [1-3], perfluoro-2-aza-1-butene [4], and fluorinated isocyanates [5]. In the case of catalysis by fluorosulfonic acid, (I) reacts smoothly with certain freons, forming polyfluoroalkyl esters of fluorosulfonic acid [6]. Of the inorganic compounds, reactions of (I) with potassium and cesium fluorides [7], nitronium and cesium perchlorates [8] are known. In this work we conducted the reaction of (I) with certain inorganic compounds, as well as with tetrachloroethylene.

The passage of dry HCl through liquid (I) at ~20°C is accompanied by a negligible exothermic effect and the liberation of chlorine with the formation of practically pure fluorosulfonic acid. (I) reacts smoothly with N_2O_4, also at ~20°C, giving nitronium fluorosulfate (II) and nitryl chloride (III) with quantitative yields:



To prevent a vigorous heating, the reagents should be mixed in the gas phase, using an inert diluent, for example, nitrogen. The interaction of (I) with (III) or with nitric oxide at ~20°C is not observed. In this case it is interesting to note that the fluorosulfate of bromine with N_2O_4 forms nitronium fluorosulfate and bromine, while with (III) and nitric acid it interacts even at reduced temperatures [9].

(I) also interacts vigorously with SO_2 with the formation of pyrosulfuryl chloride—fluoride (IV). An attempt to produce trisulfuryl fluoride by the reactions of (I) with (IV) did not lead to success. Even after prolonged heating at 110-120°C, the initial reagents were recovered unchanged. A practically quantitative yield of chlorocarbonyl fluorosulfate (V), previously characterized only by the IR and NMR-^{19}F spectra [10], was obtained by the reaction of (I) with CO. The reaction proceeds with a substantial exothermic effect. To obtain high yields of (V) the temperature should be maintained no higher than 30°C, since at high temperatures (I) reacts with the (V) formed:



$$ClOSO_2F + Cl\underset{\underset{O}{\|}}{C}OSO_2F \rightarrow Cl_2 + S_2O_5F_2 + CO_2$$

Thus, in the reaction of (I) with CO, depending on the conditions, either (V) with a practically quantitative yield or pyrosulfuryl fluoride (VI) can be obtained.

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The fluorosulfate (V) is a rather reactive compound. When it is exposed in benzene at ~ 20°C for several days, followed by treatment with water, benzoic acid is obtained. The optimum conditions of the reaction were not determined.

The addition of (I) at the multiple bond of polychlorinated olefins was carried out for the first time for tetrachloroethylene as an example. The reaction could be conducted directedly only at —20°C by slow addition of (I) to tetrachloroethylene, dissolved in 1,1,2-trifluorotrichloroethane. The pentachloroethyl ester of fluorosulfonic acid (VII) is a colorless liquid, immiscible with water, soluble in most organic solvents.

EXPERIMENTAL METHOD

Reaction of (I) with Hydrogen Chloride. Dry HCl was bubbled through 13.5 g (I) at a rate such that (I) was not removed by the stream of HCl. The chlorine formed was collected in a trap, and after the liberation of 7.1 g of chlorine, the passage of HCl was stopped. We obtained 9.9 g (99%) fluorosulfonic acid in the form of a yellowish liquid; after distillation 9.5 g (95%), bp163°C; d_4^{20}1.741. Equivalent: found 100.7, calculated 100; cf. [11].

Reaction of (I) with Nitrogen Tetraoxide. A mixture of dry N_2O_4 (4.8 g) and nitrogen (1 : 3 by volume) was passed at a low speed into a reactor containing 6.8 g freshly redistilled (I), collecting the gaseous products in a trap (—78°C). In the reactor 6.7 g (92.4%) nitronium fluorosulfate [9] with mp 217°C was formed. By fractionating the gaseous products we obtained 3.5 g (86.2%) nitryl chloride [11] with bp —15°C.

Pyrosulfuryl Chloride—Fluoride (IV). In a reactor equipped with an effective reflux (CO_2) condenser we placed 13.5 g (I), and with mixing slowly passed through 6.4 g of gasous SO_2. The reaction mass was mixed for 1 h. Fractionation yielded 18.2 g (91.5%) pyrosulfuryl chloride—fluoride [12] in the form of a colorless free-flowing liquid, bp 100°C; d_4^{20}1.794.

Reaction of (I) with Carbon Monoxide. a. Chlorocarbonyl Fluorosulfate. An excess of dry CO was bubbled through 13.5 g (I), maintaining a temperature of the reaction mass 25-30°C. To prevent the removal of the reaction products, we used an effective reflux condenser. Fractionation yielded 15 g (92%) chlorocarbonyl fluorosulfate in the form of a colorless free-flowing liquid, bp 70°C; d_4^{20}1.675; nD^{20} 1.3667. Found: C 7.11; F 11.99; Cl 21.73; S 19.91%. $CClFO_4S$. Calculated: C 7.39; F 11.79; Cl 21.85; S 19.69%. NMR-^{19}F spectrum: singlet 126 ppm (external standard CF_3COOH). According to the data of [10], NMR-^{19}F spectrum: singlet 44.7 ppm (standard CCl_3F).

b. Pyrosulfuryl Fluoride. Into 13.5 g of boiling (I) 1.4 g of CO was slowly passed. The reaction mass was exposed for 1 h at 80-90°C and fractionated. We obtained 8.1 g (89%) pyrosulfuryl fluoride [12] in the form of a colorless free-flowing liquid, bp 51°C; d_4^{20}1.749.

Reaction of (I) with Chlorocarbonyl Fluorosulfate. A mixture of 8.1 g chlorocarbonyl fluorosulfate and 6.8 g (I) was heated at 80-90°C with a reflux condenser until the evolution of the calculated amount of chlorine (3.5 g) was ended. The CO_2 formed was quantitatively absorbed with barite water. Fractionation of the residue yielded 8.6 g (94.5%) pyrosulfuryl fluoride, bp 51°C; d_4^{20}1.749.

Reaction of Chlorocarbonyl Fluorosulfate in Benzene. A mixture of 3.2 g chlorocarbonyl fluorosulfate and 6 ml of benzene was exposed at ~20°C for seven days. Volatile products were removed under water-jet pump vacuum; 30 ml of water was added to the residue. After one day the solid substances formed was removed and washed with water. We obtained 0.9 g benzoic acid, mp. 121-122°C. A mixed sample gave no depression of the melting points.

Pentachloroethyl Ester of Fluorosulfonic Acid. To 16.6 g tetrachloroethylene, dissolved in 60 ml of 1,1,2-tetrafluorotrichloroethane, 13.5 g (I) was added dropwise with mixing at —20°C. In a period of 2 h the temperature was brought to ~20°C. After 12 h the solvent was removed at a residual pressure of 35 mm Hg. Fractionation of the residue yielded 23.2 g (77.5%) of the pentachloroethyl ester in the form of a colorless liquid, bp 80-81°C (24 mm); d_4^{20} 1.819; n_D^{20} 1.4670. Found: C 7.65; F 6.67; Cl 58.87; S 10.51%. $C_2Cl_5FO_3S$. Calculated: C 7.99; F 6.32; Cl 59.07; S 10.65%. NMR-^{19}F spectrum: singlet 130.5 ppm (external standard CF_3COOH).

CONCLUSIONS

1. As a result of simple conversion, fluorosulfonic acid, nitronium fluorosulfate, pyrosulfuryl chloride—fluoride, pyrosulfuryl fluoride, and chlorocarbonylfluorosulfate can be obtained from chloride fluorosulfate.

2. Chlorocarbonyl fluorosulfate is capable of interacting smoothly with chlorine fluorosulfate, as well as acylating benzene.

LITERATURE CITED

1. A. V. Fokin, Yu. N. Studnev, L. D. Kuznetsova, and V. L. Rud', Izv. Akad. Nauk SSSR, Ser. Khim., 471 (1974).
2. W. P. Gilbreath and G. H. Cady, Inorgan. Chem., 2, 496 (1963).
3. D. D. Moldavskii, V. G. Temchenko, V. I. Slesareva, and G. L. Antipenko, Zh. Organ. Khimii, 9, 673 (1973).
4. D. D. Moldavskii, V. G. Temchenko, and G. L. Antipenko, Zh. Organ. Khimii, 7, 44 (1971).
5. G. H. Sprenger, K. J. Wright, and J. M. Shreeve, Inorgan. Chem., 12, 2890 (1973).
6. A. V. Fokin, Yu. N. Studnev, A. I. Rapkin, and L. D. Kuznetsova, Izv. Akad. Nauk SSSR, Ser. Khim., 1892 (1974).
7. C. J. Schack and R. D. Wilson, Inorgan. Chem., 9, 311 (1970).
8. C. J. Schack and D. Pilipovich, Inorgan. Chem., 9, 1387 (1970).
9. A. M. Qureshi, H. A. Carter, and F. Aubke, Canad. J. Chem., 49, 35 (1971).
10. K. J. Wright and J. M. Shreeve, Inorgan. Chem., 12, 77 (1973).
11. G. Brauer, Handbook of Preparative Inorganic Chemistry [Russian translation], IL (1956), pp. 110, 253.
12. L. I. Ragulin, M. A. Belavantsev, G. A. Sokol'skii, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2304 (1968).