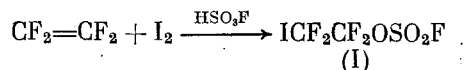


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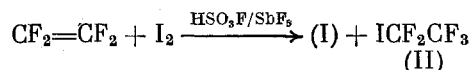
UDC 542.91:547.413.722:546.12

The reactions of fluoroolefins with electrophilic reagents are usually strongly hindered, and require rigid conditions and the use of catalysts. However, halogen fluorosulfates fluorosulfates ( $\text{HalOSO}_2\text{F}$ , Hal = I, Br, Cl) containing a positively polarized halogen atom under mild conditions, add to the multiple bond of fluoroolefins and give the corresponding 2-halopolyfluoroalkyl fluorosulfates [1]. The formation of these products can be assumed to be a result of a joint addition of both a positive halogen atom and the fluorosulfate anion, from sources that may be solutions of halogens, interhalide and other compounds in  $\text{HSO}_3\text{F}$  or in its mixtures with  $\text{SbF}_5$ .

We found that when tetrafluoroethylene (TFE) is bubbled through a suspension of  $\text{I}_2$  in a fourfold excess of  $\text{HSO}_3\text{F}$  at  $50^\circ\text{C}$ , 2-iodotetrafluoroethyl fluorosulfate (I) is slowly formed

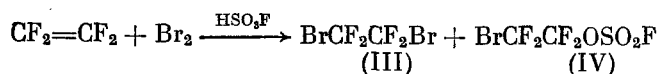


The reaction is considerably accelerated when  $\text{SbF}_5$  is added, and is accompanied by a weak exothermal effect. Iodine completely disappears only when not less than an equimolar amount of  $\text{SbF}_5$  is used, which indicates the direct participation of  $\text{SbF}_5$  in the process. As the result of the reaction, compound (I), a small amount of pentafluoroethyl iodide (II), and a white solid substance, which is probably a complex of HI with  $\text{SbF}_5$  are formed

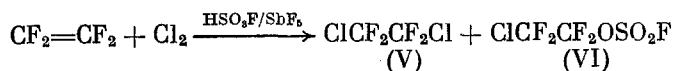


It is probable that the initial attack of iodine cation at the TFE double bond gives a carbocation, which is further stabilized by the capture of a fluorosulfate or fluoride anion. In fact, the formation of iodine cations in solutions of  $\text{I}_2$  in strong acids was confirmed in [2]. It is clear that  $\text{SbF}_5$  favors increase in the content of iodine cations in the solution, and appreciably influences the rate of the reaction by binding the HI formed; and also serves as the source of fluoride ion, leading to the formation of (II).

In contrast to  $\text{I}_2$ ,  $\text{Br}_2$  is much less polarized in  $\text{HSO}_3\text{F}$ , and in this case the addition of the  $\text{Br}_2$  molecule to the TFE multiple bond is the main reaction with the formation of 1,2-dibromotetrafluoroethane (III) (yield ~82%), while the yield of 2-bromotetrafluoroethyl fluorosulfate (IV) is only ~7%.



Under these conditions  $\text{Cl}_2$  does not react with TFE, but in a stronger acid ( $\text{HSO}_3\text{F}/\text{SbF}_5$ ) it gives 1,2-dichlorotetrafluoroethane (V) (~70%) and 2-chlorotetrafluoroethyl fluorosulfate (VI) (~8%).



The activity of  $\text{Br}_2$  with respect to TFE also increases considerably in  $\text{HSO}_3\text{F}/\text{SbF}_5$ . In this case, the main product is fluorosulfate (IV), in a yield ~1.5 times higher than that of (III).

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Reaction of TFE with I<sub>2</sub>. a) In HSO<sub>3</sub>F. An excess of TFE was bubbled for 24 h, with stirring and heating to 50°C, through a mixture of 14.3 g (56.3 mmoles) of I<sub>2</sub> and 26.6 g (226 mmoles) of HSO<sub>3</sub>F. The volatile products were collected in a trap (-78°C) under a 20-mm vacuum. Fractionation of the trap contents gave 4 g (21.8%) of 2-iodotetrafluoroethyl fluorosulfate (I), bp 100°C, d<sub>4</sub><sup>20</sup> 2.078, n<sub>D</sub><sup>20</sup> 1.3715. <sup>19</sup>F NMR spectrum of (I) was identical to that reported in [6].

b) In HSO<sub>3</sub>F/SbF<sub>5</sub>. A 19.5-g portion (76.8 mmoles) of I<sub>2</sub>, 30 g (330 mmoles) of HSO<sub>3</sub>F, and 16.7 g (77.7 mmoles) of SbF<sub>5</sub> were charged into a reactor with a trap (-70°C) at its outlet, and an excess of TFE was bubbled through with stirring until decoloration of the mixture. In the trap, 7 g of a liquid was collected, from which the following were isolated: 3 g of 2-iodotetrafluoroethyl fluorosulfate (I) and 3 g (15.8%) of pentafluoroethyl iodide (II), bp 12-13°C (cf. [7]). <sup>19</sup>F NMR spectrum of (II): δ<sub>1</sub> = 6.68 t (CF<sub>3</sub>), δ<sub>2</sub> = -12.90 q (CF<sub>2</sub>), J<sub>12</sub> = 4.2 Hz. The reaction mixture was filtered, the filtrate was poured onto ice, the organic layer was separated, washed with water (3 × 30 ml), and dried over MgSO<sub>4</sub>. By fractionation, 18 g of (I), bp 100°C, was obtained. The overall yield of (I) was 21 g (84%). The constants and <sup>19</sup>F NMR spectrum were identical to those given above.

Reaction of TFE with Br<sub>2</sub>. a) In HSO<sub>3</sub>F. A 9-g portion (56.3 mmoles of Br<sub>2</sub> and 23.6 g (236 mmoles) of HSO<sub>3</sub>F were charged into a reactor with a trap (-70°C) at its outlet, and an excess of TFE was bubbled through with stirring until the decoloration of the reaction mixture. Fractionation of the reaction mixture and the trap contents gave: 12 g (18.2%) of 1,2-dibromotetrafluoroethane (III), bp 46-48°C, d<sub>4</sub><sup>20</sup> 2.149, n<sub>D</sub><sup>20</sup> 1.3710 (cf [8]): <sup>19</sup>F NMR spectrum of (III): δ = -14.5 s; and also 1.2 g (7.6%) of 2-bromotetrafluoroethyl fluorosulfate (IV), bp 73-75°C, d<sub>4</sub><sup>20</sup> 1.900, n<sub>D</sub><sup>20</sup> 1.3235. The <sup>19</sup>F NMR spectrum of (IV) was identical to that given in [9].

b) In HSO<sub>3</sub>F/SbF<sub>5</sub>. A 9-g portion (56.3 mmoles) of Br<sub>2</sub>, 22.5 g (113 mmoles) of SbF<sub>5</sub>, 22.6 (226 mmoles) of HSO<sub>3</sub>F were charged into a reactor with a trap (-70°C) at its outlet, and excess TFE was bubbled through until decoloration of the reaction mixture. In the trap, 2 g of a liquid was collected. The volatile products from the reaction mixture were collected in a trap (-78°C) under a 30-mm vacuum. The contents of the traps were combined. The yield was 13.6 g of a liquid containing (according to the GLC data) ~60% of bromotetrafluoroethyl fluorosulfate (IV) and ~40% of 1,2-dibromotetrafluoroethane (III).

Reaction of TFE with Cl<sub>2</sub> in HSO<sub>3</sub>F/SbF<sub>5</sub>. An equimolar mixture of Cl<sub>2</sub> and TFE was bubbled, with stirring, for 6 h, through a solution of 10 g (46 mmoles) of SbF<sub>5</sub> in 20 g (200 mmoles) of HSO<sub>3</sub>F, and the volatile products were collected in a trap (-70°C). Fractionation of the trap contents gave: 24 g (70%) of 1,2-dichlorotetrafluoroethane, bp 3-4°C (cf. [7]) and 1.9 g (8.2%) of 2-chlorotetrafluoroethyl fluorosulfate (VI), bp 53-55°C, d<sub>4</sub><sup>20</sup> 1.660, n<sub>D</sub><sup>20</sup> 1.3067 (cf. [10]).

Reaction of HFP with I<sub>2</sub> in HSO<sub>3</sub>F/SbF<sub>5</sub>. A mixture of 22.5 g (113 mmoles) of SbF<sub>5</sub>, 22.6 g (226 mmoles) of HSO<sub>3</sub>F, 14.2 g (56 mmoles) of I<sub>2</sub>, and 20 g (133 mmoles) of HFP was shaken in a sealed ampul for 72 h at 20°C. After removal of excess HFP, the volatile products were collected in a trap (-78°C) under a 20 mm vacuum. Yield: 29.1 g of a liquid containing (according to GLC) ~12% of 2-iodohexafluoropropyl fluorosulfate (VII), ~58% of heptafluoroisopropyl iodide (VIII), and ~30% of 2-hydrohexafluoropropyl fluorosulfate (IX). Fractionation gave the following compounds in an individual state: 11 g of (VIII), bp 40-42°C, d<sub>4</sub><sup>20</sup> 2.077, n<sub>D</sub><sup>20</sup> 1.3237 (cf [11]); <sup>19</sup>F NMR spectrum of (VIII): δ<sub>1</sub> = -2.72 d (CF<sub>3</sub>), δ<sub>2</sub> = 70.17 sept (CF), J<sub>12</sub> = 13.3 Hz (cf. [12]); 6 g of (IX), bp 74-77°C, d<sub>4</sub><sup>20</sup> 1.667, n<sub>D</sub><sup>20</sup> 1.29 (cf. [3]); <sup>19</sup>F and <sup>1</sup>H NMR spectra: δ<sub>1</sub> = -2.26 d.d.t (CF<sub>3</sub>), δ<sub>2</sub> = 134.10 d.t.q (CF), δ<sub>3</sub> = 5.11 d.t.q (H), δ<sub>4</sub> = 1.13 d.d.d.q (CF<sub>2</sub>), δ<sub>5</sub> = -127.23 t (SF), J<sub>12</sub> = 11.3, J<sub>13</sub> = 5.0, J<sub>14</sub> = 9.3, J<sub>23</sub> = 43.8, J<sub>24</sub> = 11.0, J<sub>34</sub> = 5.1, J<sub>45</sub> = 8.5 Hz; 4.5 g of (VII), bp 117-119°C, d<sub>4</sub><sup>20</sup> 2.120, n<sub>D</sub><sup>20</sup> 1.3633. The constants and the <sup>19</sup>F NMR spectrum of (VII) are identical to those given in [6].

Reaction of HFP with Br<sub>2</sub>. a) In HSO<sub>3</sub>F. An excess of HFP was bubbled, with stirring, through a mixture of 9 g (56.3 mmoles) of Br<sub>2</sub> and 22.6 g (226 mmoles) of HSO<sub>3</sub>F until decoloration of the reaction mixture. The volatile products were collected in a trap (-78°C) under a 30-mm vacuum. Fractionation of trap contents gave 13.3 g (76.6%) of 1,2-dibromohexafluoropropane (XI), bp 71-72°C, d<sub>4</sub><sup>20</sup> 2.120, n<sub>D</sub><sup>20</sup> 1.3594 (cf. [8]). <sup>19</sup>F NMR spectrum of (XI): δ<sub>1</sub> = -4.07 d.d.d (CF<sub>3</sub>), δ<sub>2</sub> = 54.59 d.d.q (CF), δ<sub>3</sub> = -20.81 d.q (CF<sub>2</sub>), δ<sub>4</sub> = -20.31 d.q (CF<sub>2</sub>), J<sub>12</sub> = 9.3, J<sub>13</sub> = 10.2, J<sub>14</sub> = 11.3, J<sub>23</sub> = 15.8, J<sub>24</sub> = 15.5 Hz.

b) In  $\text{HSO}_3\text{F}/\text{SbF}_5$ . A mixture of 24.5 g (113 mmoles) of  $\text{SbF}_5$ , 22.6 g (226 mmoles) of  $\text{HSO}_3\text{F}$ , 9 g (56.3 mmoles) of  $\text{Br}_2$ , and 35 g (233 mmoles) of HFP was shaken in a sealed ampul for 48 h. After removal of excess HFP, the volatile products were collected in a trap ( $-78^\circ\text{C}$ ) under a 30 mm vacuum. Yield, 36 g of a liquid containing (according to GLC and  $^{19}\text{F}$  NMR data) ~33% of heptafluoroisopropyl bromide (X), ~28% of 1,2-dibromohexafluoropropane (XI), ~16% of 2-bromohexafluoropropyl fluorosulfate (XII), and ~23% of 2-hydrohexafluoropropyl fluorosulfate (IX).  $^{19}\text{F}$  NMR spectrum of (X):  $\delta_1 = 0.34$  d ( $\text{CF}_3$ ),  $\delta_2 = 65.41$  sept (CF),  $J_{12} = 8.8$  Hz (cf. [12]). The  $^{19}\text{F}$  NMR spectrum of (XII) was identical to that given in [13].

Reaction of HFP with  $\text{Cl}_2$  in  $\text{HSO}_3\text{F}/\text{SbF}_5$ . A mixture of 24.5 g (113 mmoles) of  $\text{SbF}_5$ , 22.6 g (226 mmoles) of  $\text{HSO}_3\text{F}$ , 10 g (140 mmoles) of  $\text{Cl}_2$ , and 35 g (233 mmoles) of HFP was shaken in a sealed ampul for 48 h. Fractionation of the evolved gases gave 3 g (8.2%) of heptafluoroisopropyl chloride (XIV), bp  $0-2^\circ\text{C}$  (cf. [13]).  $^{19}\text{F}$  NMR spectrum of (XIV):  $\delta_1 = 2.44$  d ( $\text{CF}_3$ ),  $\delta_2 = 64.22$  sept (CF),  $J_{12} = 7.5$  Hz. The volatile products from the ampul were collected in a trap ( $-78^\circ\text{C}$ ) under a vacuum of 30 mm. Fractionation of the trap contents gave 27.1 g (84.3%) of 2-chlorohexafluoropropyl fluorosulfate (XIII), bp  $75-77^\circ\text{C}$ ,  $d_4^{20} 1.700$ ,  $n_D^{20} 1.3070$ . The constants and  $^{19}\text{F}$  NMR spectrum of (XIII) were identical with those given in [13].

Reaction of HFP with  $\text{HSO}_3\text{F}/\text{SbF}_5$ . A mixture of 24.5 g (113 mmoles) of  $\text{SbF}_5$ , 22.6 g (226 mmoles) of  $\text{HSO}_3\text{F}$ , and 35 g (233 mmoles) of HFP was shaken in a sealed ampul for 12 h at  $20^\circ\text{C}$ . The gaseous products were collected in a trap ( $-78^\circ\text{C}$ ), and from the residue, volatile products were isolated under a 30-mm vacuum; their fractionation gave 24 g (85%) of 2-hydrohexafluoropropyl fluorosulfate (IX), bp  $74-77^\circ\text{C}$ ,  $d_4^{20} 1.667$ ,  $n_D^{20} \sim 1.29$  (cf. [3]). The  $^{19}\text{F}$  NMR spectrum of (IX) was identical to that given above.

The gases collected in the trap were purified from HFP by bubbling through MeOH containing a catalytic amount of KOH; fractionation of the residue gave 4 g of 2-hydrohexafluoropropane (XVI), bp  $-17^\circ\text{C}$  (cf. [14]).  $^{19}\text{F}$  NMR spectrum of (XVI):  $\delta_1 = 1.10$ , d.d. ( $\text{CF}_3$ ),  $\delta_2 = 137.65$  d. sept (CF),  $J_{12} = 11.3$ ,  $J_{13} = 6.0$ ,  $J_{23} = 39.5$  Hz (cf [12]).

#### CONCLUSIONS

1. In the reactions of tetrafluoroethylene and hexafluoropropylene in a  $\text{HSO}_3\text{F}/\text{SbF}_5$  medium, a joint addition of both halogen and the fluorosulfate group to the multiple bond of the fluoroolefin takes place with the formation of the corresponding 2-haloperfluoroalkyl fluorosulfates.

2. Under mild conditions, hexafluoropropylene reacts with the superacid  $\text{HSO}_3/\text{SbF}_5$  to form 2-hydrohexafluoropropyl fluorosulfate and 2-hydrohexafluoropropane.

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