REACTIONS OF FLUOROOLEFINS WITH HALOGENS IN STRONG ACID MEDIUM

A. V. Fokin, Yu. N. Studnev,
A. I. Rapkin, I. N. Krotovich,
A. S. Tamarinov, and O. V. Verenikin

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 ($HalOSO_2F$, 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 HSO_3F or in its mixtures with SbF_5.

We found that when tetrafluoroethylene (TFE) is bubbled through a suspension of I_2 in a fourfold excess of HSO_3F at 50°C, 2-iodotetrafluoroethyl fluorosulfate (I) is slowly formed

$$CF_2{=}CF_2 + I_2 \xrightarrow{HSO_3F} \underset{(I)}{ICF_2CF_2OSO_2F}$$

The reaction is considerably accelerated when SbF_5 is added, and is accompanied by a weak exothermal effect. Iodine completely disappears only when not less than an equimolar amount of SbF_5 is used, which indicates the direct participation of 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 SbF_5 are formed

$$CF_2{=}CF_2 + I_2 \xrightarrow{HSO_3F/SbF_5} (I) + \underset{(II)}{ICF_2CF_3}$$

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 I_2 in strong acids was confirmed in [2]. It is clear that 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 I_2, Br_2 is much less polarized in HSO_3F, and in this case the addition of the 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%.

$$CF_2{=}CF_2 + Br_2 \xrightarrow{HSO_3F} \underset{(III)}{BrCF_2CF_2Br} + \underset{(IV)}{BrCF_2CF_2OSO_2F}$$

Under these conditions Cl_2 does not react with TFE, but in a stronger acid (HSO_3F/SbF_5) it gives 1,2-dichlorotetrafluorethane (V) (~70%) and 2-chlorotetrafluoroethyl fluorosulfate (VI) (~8%).

$$CF_2{=}CF_2 + Cl_2 \xrightarrow{HSO_3F/SbF_5} \underset{(V)}{ClCF_2CF_2Cl} + \underset{(VI)}{ClCF_2CF_2OSO_2F}$$

The activity of Br_2 with respect to TFE also increases considerably in HSO_3F/SbF_5. In this case, the main product is fluorosulfate (IV), in a yield ~1.5 times higher than that of (III).

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2298-2302, October, 1985. Original article submitted June 29, 1984.

0568-5230/85/3410-2128$09.50

Although hexafluoropropylene (HFP) has a lower affinity towards electrophilic addition reactions, we succeeded in carrying out the processes under consideration with its participation. In the case of HFP, the composition and the ratio of the products formed differ from those obtained with TFE. In a closed volume, in an HSO_3F/SbF_5 medium, HFP exothermally reacts with ~0.5 mole of I_2 to form 2-iodohexafluoropropyl fluorosulfate (VII), heptafluoroisopropyl iodide (VIII), and 2-hydrohexafluoropropyl fluorosulfate (IX) in nearly equal amounts. In the presence of an equimolar amount of I_2, the yield of the addition product of HSO_3F to HFP (IX) appreciably decreases

$$\mathrm{CF_3CF{=}CF_2 + I_2 \xrightarrow{HSO_3F/SbF_5} \underset{(VII)}{CF_3CFICF_2OSO_2F} + \underset{(VIII)}{(CF_3)_2CFI} + \underset{(IX)}{CF_3CFHCF_2OSO_2F}}$$

A still more vigorous reaction of Br_2 with HFP in an HSO_3F/SbF_5 medium gives approximately equal amounts of heptafluoroisopropyl bromide (X), 1,2-dibromohexafluoropropane (XI), 2-bromo- (XII) and 2-hydrohexafluoropropyl fluorosulfates (IX), while in the absence of SbF_5, dibromide (XI) is mainly formed

$$\mathrm{CF_3CF{=}CF_2 + Br_2} \left| \begin{array}{l} \xrightarrow{\mathrm{HSO_3F/SbF_5}} \underset{(X)}{\mathrm{(CF_3)_2CFBr}} + \underset{(XI)}{\mathrm{CF_3CFBrCF_2Br}} + \\ \quad + \underset{(XII)}{\mathrm{CF_3CFBrCF_2OSO_2F}} + \underset{(IX)}{\mathrm{CF_3CFHCF_2OSO_2F}} \\ \xrightarrow{\mathrm{HSO_3F}} \underset{(XI)}{\mathrm{CF_3CFBrCF_2Br}} \end{array}\right.$$

In contrast to TFE hexafluoropropylene with an equimolar amount of Cl_2 forms (XIII) (~84%) as the main product of the joint addition, a small amount of heptafluoroisopropyl chloride (XIV) (~8%), and traces of the corresponding dichloride (XV). In the absence of SbF_5, HFP does not react with either Cl_2 or HSO_3F

$$\mathrm{CF_3CF{=}CF_2 + Cl_2 \xrightarrow{HSO_3F/SbF_5} \underset{(XIII)}{CF_3CFClCF_2OSO_2F} + \underset{(XIV)}{(CF_3)_2CFCl} + \underset{(XV)}{CF_3CFClCF_2Cl}}$$

These results indicate an electrophilic mechanism of the reaction of halogens with fluoroolefins in strongly acid media. There are apparently more favorable conditions in HSO_3F/SbF_5 for the ionic process, as the result of an attack by the positive halogen on the multiple bond of the fluoroolefin. This leads to the intermediate formation of the corresponding carbonium ion, as confirmed by increase in the yield of 2-haloperfluoroalkyl fluorosulfates (I), (IV), etc., and the formation of perfluoroalkyl halides (II), (X), (XIV). In all cases when SbF_5 was used and 2-haloperfluoroalkylfluorosulfate was formed, a solid compound was isolated, which is probably an adduct of SbF_5 with the corresponding hydrogen halide.

It is interesting to note that in the reactions of HFP with I_2 and Br_2 in an HSO_3F/SbF_5 medium, an adduct of HSO_3F with HFP (I) is obtained. However, in the case of TFE, no similar product was formed. It has already been shown that in HSO_3F under rigid conditions, adducts of HSO_3F with HFP (>150°C) [3] and with TFE (>100°C [4] are obtained in inappreciable yield.

In contrast to the available information on the absence of a reaction of HFP with the superacid HSO_3F/SbF_5 [5], at a molar ratio of $HSO_3F:SbF_5 = 2:1$, we obtained an adduct of HSO_3F with HFP (IX) in an 85% yield. A byproduct, 2-hydrohexafluoropropane (XVI), was also obtained.

$$\mathrm{CF_3CF{=}CF_2 \xrightarrow{HSO_3F/SbF_5} \underset{(IX)}{CF_3CFHCF_2OSO_2F} + \underset{(XVI)}{(CF_3)_2CFH}}$$

EXPERIMENTAL

The ^{19}F and ^{1}H NMR spectra were run on a Hitachi R-20 (56.45 and 60 MHz) spectrometer, with reference to CF_3COOH (external standard) and HMDS in $CHCl_3$. The GLC analysis was carried out on a LKhM-8MD chromatograph, using a column (3 m × 3 mm) with 5% SE-30 Chromaton N-AW-DMCS (0.20 – 0.25 mm), and a 3 m × 3 mm column with 5% QF-1 on Chezasorb AW-NMDS; carrier gas helium yielded at a flow rate of 18.5 ml/min.

Reaction of TFE with I_2. a) In HSO_3F. 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_2 and 26.6 g (226 mmoles) of HSO_3F. 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_4^{20} 2.078, n_D^{20} 1.3715. ^{19}F NMR spectrum of (I) was identical to that reported in [6].

b) In HSO_3F/SbF_5. A 19.5-g portion (76.8 mmoles) of I_2, 30 g (330 mmoles) of HSO_3F, and 16.7 g (77.7 mmoles) of SbF_5 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]). ^{19}F NMR spectrum of (II): $\delta_1 = 6.68$ t (CF_3), $\delta_2 = -12.90$ q (CF_2), $J_{12} = 4.2$ 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 $MgSO_4$. By fractionation, 18 g of (I), bp 100°C, was obtained. The overall yield of (I) was 21 g (84%). The constants and ^{19}F NMR spectrum were identical to those given above.

Reaction of TFE with Br_2. a) In HSO_3F. A 9-g portion (56.3 mmoles of Br_2 and 23.6 g (236 mmoles) of HSO_3F 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_4^{20} 2.149, n_D^{20} 1.3710 (cf [8]): ^{19}F NMR spectrum of (III): $\delta = -14.5$ s; and also 1.2 g (7.6%) of 2-bromotetrafluoroethyl fluorosulfate (IV), bp 73-75°C, d_4^{20} 1.900, n_D^{20} 1.3235. The ^{19}F NMR spectrum of (IV) was identical to that given in [9].

b) In HSO_3F/SbF_5. A 9-g portion (56.3 mmoles) of Br_2, 22.5 g (113 mmoles) of SbF_5, 22.6 (226 mmoles) of HSO_3F 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_2 in HSO_3F/SbF_5. An equimolar mixture of Cl_2 and TFE was bubbled, with stirring, for 6 h, through a solution of 10 g (46 mmoles) of SbF_5 in 20 g (200 mmoles) of HSO_3F, 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_4^{20} 1.660, n_D^{20} 1.3067 (cf. [10]).

Reaction of HFP with I_2 in HSO_3F/SbF_5. A mixture of 22.5 g (113 mmoles) of SbF_5, 22.6 g (226 mmoles) of HSO_3F, 14.2 g (56 mmoles) of I_2, 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_4^{20} 2.077, n_D^{20} 1.3237 (cf [11]); ^{19}F NMR spectrum of (VIII: $\delta_1 = -2.72$ d (CF_3), $\delta_2 = 70.17$ sept (CF), $J_{12} = 13.3$ Hz (cf. [12]; 6 g of (IX), bp 74-77°C, d_4^{20} 1.667, n_D^{20} 1.29 (cf. [3]); ^{19}F and ^1H NMR spectra: $\delta_1 = -2.26$ d.d.t (CF_3), $\delta_2 = 134.10$ d.t.q (CF), $\delta_3 = 5.11$ d.t.q (H), $\delta_4 = 1.13$ d.d.d.q (CF_2), $\delta_5 = -127.23$ t (SF), $J_{12} = 11.3$, $J_{13} = 5.0$, $J_{14} = 9.3$, $J_{23} = 43.8$, $J_{24} = 11.0$, $J_{34} = 5.1$, $J_{45} = 8.5$ Hz; 4.5 g of (VII), bp 117-119°C, d_4^{20} 2.120, n_D^{20} 1.3633. The constants and the ^{19}F NMR spectrum of (VII) are identical to those given in [6].

Reaction of HFP with Br_2. a) In HSO_3F. An excess of HFP was bubbled, with stirring, through a mixture of 9 g (56.3 mmoles) of Br_2 and 22.6 g (226 mmoles) of HSO_3F 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_4^{20} 2.120, n_D^{20} 1.3594 (cf. [8]). ^{19}F NMR spectrum of (XI): $\delta_1 = -4.07$ d.d.d (CF_3), $\delta_2 = 54.59$ d.d.q (CF), $\delta_3 = -20.81$ d.q (CF_2), $\delta_4 = -20.31$ d.q (CF_2), $J_{12} = 9.3$, $J_{13} = 10.2$, $J_{14} = 11.3$, $J_{23} = 15.8$, $J_{24} = 15.5$ Hz.

b) In HSO_3F/SbF_5. A mixture of 24.5 g (113 mmoles) of SbF_5, 22.6 g (226 mmoles) of HSO_3F, 9 g (56.3 mmoles) of 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°C) under a 30 mm vacuum. Yield, 36 g of a liquid containing (according to GLC and ^{19}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}F NMR spectrum of (X): $\delta_1 = 0.34$ d (CF_3), $\delta_2 = 65.41$ sept (CF), $J_{12} = 8.8$ Hz (cf. [12]). The ^{19}F NMR spectrum of (XII) was identical to that given in [13].

Reaction of HFP with Cl_2 in HSO_3F/SbF_5. A mixture of 24.5 g (113 mmoles) of SbF_5, 22.6 (226 mmoles) of HSO_3F, 10 g (140 mmoles) of 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°C (cf. [13]). ^{19}F NMR spectrum of (XIV): $\delta_1 = 2.44$ d (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°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°C, d_4^{20} 1.700, n_D^{20} 1.3070. The constants and ^{19}F NMR spectrum of (XIII) were identical with those given in [13].

Reaction of HFP with HSO_3F/SbF_5. A mixture of 24.5 g (113 mmoles) of SbF_5, 22.6 g (226 mmoles) of HSO_3F, and 35 g (233 mmoles) of HFP was shaken in a sealed ampul for 12 h at 20°C. The gaseous products were collected in a trap (−78°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°C, d_4^{20} 1.667, n_D^{20} ~1.29 (cf. [3]). The ^{19}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°C (cf. [14]). ^{19}F NMR spectrum of (XVI): $\delta_1 = 1.10$, d.d. (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 HSO_3F/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 HSO_3/SbF_5 to form 2-hydrohexafluoropropyl fluorosulfate and 2-hydrohexafluoropropane.

LITERATURE CITED

1. A. V. Fokin, Yu. N. Studnev, L. D. Kuznetsova, and I. N. Krotovich, Usp. Khim., 51, 1258 (1982).
2. R. J. Gillespie and J. B. Milne, Chem. Commun., 158 (1966).
3. H. H. Gibbs, W. L. Edens, and R. N. Griffin, J.Org. Chem., 26, 4140 (1961).
4. G. A. Sokol'skii, M. A. Belaventsev, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1804 (1965).
5. G. H. Olah and Y. K. Mo, J. Org. Chem., 37, 1028 (1972).
6. A. V. Fokin, Yu. N. Studnev, A. I. Rapkin, T. M. Potarina, and L. D. Kuznetsova, Izv. Akad. Nauk SSSR, Ser. Khim., 2641 (1980).
7. E. A. Nodiff, A. V. Grosse, and M. Hauptschein, J. Org. Chem., 18, 235 (1953).
8. R. N. Haszeldine, J. Chem. Soc., 4259 (1952).
9. A. V. Fokin, Yu. N. Studnev, A. I. Rapkin, A. S. Tamarinov, and Yu. V. Seryanov, Izv. Akad. Nauk SSSR, Ser. Khim., 1635 (1985).
10. A. V. Fokin, Yu. N. Studnev, L .D. Kuznetsova, and V. L. Rud', Izv. Akad. Nauk SSSR, Ser. Khim., 471 (1974).
11. M. Hauptschein and M. Braid, J. Am. Chem. Soc., 83, 2383 (1961).
12. J. W. Emsley and L. Phillips, in: Progress in Nuclear Magnetic Resonance Spectroscopy, Vol. 7, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, (eds.), Pergamon Press, Oxford (1971), p. 121.
13. D. D. Moldavskii, V. G. Temchenko, V. I. Slesareva, and G. L. Antipenko, Zh. Org. Khim., 9, 673 (1973).
14. T. Martini and C. Schumann, J. Fluorine Chem., 8, 535 (1976).