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SYNTHESIS AND PYROLYSIS OF FLUOROSULFATES

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SUMMARY

Peroxydisulfuryl difluoride has been found to substitute a fluorosulfato group for isolated hydrogen in a fluorinated chain. The reaction is initiated by $FSO_2O\bullet$ radicals and proceeds under mild conditions. Some pyrolyses of fluorosulfates are also described.

INTRODUCTION

Bis(fluorosulfato) derivatives of polyfluoroalkanes have been prepared previously by the addition of peroxydisulfuryl difluoride to fluoro-olefins[1,2]. Mono(fluorosulfates) have been obtained from olefins by addition of halogen fluorosulfates[3,4], from fluoroalkyl chlorides and bromides by substitution of chlorine or bromine with peroxydisulfuryl difluoride[2,4] and from fluoroalkyl iodides by reaction with fluorosulfonic acid[5]. This paper describes the formation of polyfluoroalkyl fluorosulfates by replacement of isolated hydrogen atoms with peroxydisulfuryl difluoride under mild conditions. Differing pyrolytic reactions for α-fluoro- and α-chloro-alkyl fluorosulfates are also presented.

RESULTS AND DISCUSSION

Syntheses by hydrogen replacement

Although hydrogen on a highly fluorinated chain is generally resistant to radical abstraction, peroxydisulfuryl difluoride is capable of such abstraction under mild conditions, thereby allowing functionalization of polyfluorinated alkanes at sites determined by the position of single hydrogen atoms. Thus, replacement of the lone hydrogen in 1-hydroheptafluoropropane proceeded at a convenient rate at 40–50° to give 1-fluorosulfatoheptafluoropropane in 72% yield.

$$CF_3CF_2CF_2H + FSO_2OOSO_2F \rightarrow CF_3CF_2CF_2OSO_2F + HOSO_2F$$

The utility of this reaction with a functional group also present in the molecule has been demonstrated by replacement of the hydrogen atom in ω-hydrododecafluoroheptanenitrile. Peroxydisulfuryl difluoride was shown in separate experiments to be unreactive toward hexafluoroacetone, hexafluoropropene epoxide and pentafluoropropionyl fluoride, indicating that carbonyl, epoxy and acid fluoride functions will similarly survive the hydrogen replacement reaction.

$$H(CF_2)_6CN + FSO_2OOSO_2F \rightarrow FSO_2O(CF_2)_6CN + HOSO_2F$$

Peroxydisulfuryl difluoride is known to dissociate reversibly at moderate temperatures, forming reactive fluorosulfonyloxy radicals[6,7]. Many reactions of the peroxide have been attributed to the free radical in equilibrium and the above substitution for hydrogen is apparently initiated with a radical abstraction to form fluorosulfonic acid and fluoroalkyl radical. The fluoroalkyl radical can then combine with fluorosulfonyloxy radical and may also be capable of propagating a radical chain reaction by direct displacement on the peroxide oxygen of peroxydisulfuryl difluoride.

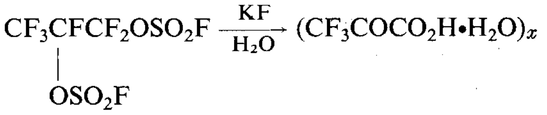
Two pieces of chemical evidence are now available to substantiate the formation of intermediate carbon radicals in reactions with peroxydisulfuryl difluoride. For the case of hydrogen abstraction, treatment of a film of vinylidene fluoride/hexafluoropropylene copolymer at 50° with vapors of peroxydisulfuryl difluoride resulted in a crosslinked polymer containing fluorosulfato groups. The latter groups could be removed by treatment with aqueous pyridine, but the hydrolyzed polymer was still crosslinked as indicated by its stiffness and insolubility in acetonitrile. The crosslinks are probably established by the same mechanism as more conventional peroxide cures, *i.e.* formation of radical sites within the polymer matrix followed by radical combination reactions. Another reaction attributable to carbon radical intermediates came from addition of peroxydisulfuryl difluoride to hexafluoropropylene as described below to form 1:2 as well as 1:1 adducts.

Addition to fluoro-olefins

1,2-Bis(fluorosulfato)hexafluoropropane, the 1:1 adduct of peroxydisulfuryl difluoride with hexafluoropropylene, has been prepared previously[8], but the mixture of 1:2 adducts has apparently not been reported despite the fact that the latter can be substantial products. Introduction of hexafluoropropylene as a vapor into a flask at 25° containing peroxydisulfuryl difluoride resulted in an exothermic vapor-phase reaction giving 1:1 and 1:2 adducts in 62% and 22% yields, respectively. The formation of isomeric 1:2 adducts in this reaction accords with a radical chain reaction similar to that observed between bis(trifluoromethyl) peroxide and hexafluoropropylene[9].

$$FSO_2OOSO_2F + CF_2{=}CFCF_3 \rightarrow FSO_2OCF_2CF(CF_3)OSO_2F$$
$$+ FSO_2O(C_3F_6)_2OSO_2F$$

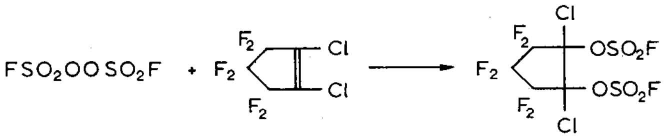
Treatment of 1,2-bis(fluorosulfato)hexafluoropropane with potassium fluoride was previously shown to give 2-fluorosulfatotetrafluoropropionyl fluoride readily, but attempted removal of the second fluorosulfato group with rubidium fluoride to form trifluoropyruvyl fluoride led only to fragmentation products[8]. This reaction has now been shown to be feasible by the use of potassium fluoride with a small amount of water. The hygroscopic product, apparently one derived by self-condensation of trifluoropyruvic acid hydrate, is indicated to have a high degree of symmetry by the presence of a single resonance for CF_3 in its NMR spectrum.



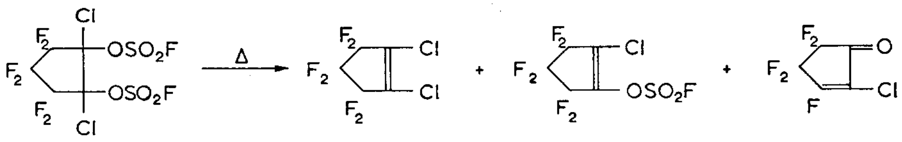
$$\underset{\displaystyle OSO_2F}{CF_3CFCF_2OSO_2F} \xrightarrow[H_2O]{KF} (CF_3COCO_2H{\bullet}H_2O)_x$$

In the absence of base, 1,2-bis(fluorosulfato)hexafluoropropane is quite stable to heat. Pyrolysis in a flow system over nickel gauze required 450° to give substantial amounts of products. Under these conditions, sulfuryl fluoride and one other major product [presumably $CF_3CF(OSO_2F)COF$] are formed.

At low temperatures, where peroxydisulfuryl difluoride is essentially undissociated, reaction with 1,2-dichlorohexafluorocyclopentene is extremely slow. A mixture of the two compounds, however, when prepared at —30° and warmed to about 15°, reacted violently. Controlled reaction was achieved by adding the peroxide drop-wise to the cyclopentene preheated to 50° to give 71% of the *cis*- and *trans*-1,2-bis(fluorosulfato) derivatives.



Pyrolysis of the *cis* and *trans* mixture over nickel gauze occurred readily at 250° to give three major products, 1,2-dichlorohexafluorocyclopentene, 1-chloro-2-fluorosulfatohexafluorocyclopentene and 2-chloropentafluorocyclopentenone-3. The first two products appear to involve elimination of $FSO_2O\bullet$. In view of the vigor with which $FSO_2O\bullet$ adds to 1,2-dichlorohexafluorocyclopentene, it is surprising to find the cyclopentene regenerated by elimination of the elements of $F_2S_2O_6$. Perhaps $FSO_2O\bullet$, although very electrophilic, enjoys significant resonance stabilization.



EXPERIMENTAL

Unless otherwise specified, ^{19}F NMR spectra were taken on 20% solutions in CCl_4 on a Varian spectrometer operating at 56.4 Mcps. Chemical shifts are reported in ppm from trichlorofluoromethane as an internal reference, with the downfield direction taken as positive. Mass spectra were taken on a CEC 21-490S instrument.

Peroxydisulfuryl difluoride

The directions followed for construction of a copper reactor with silver-coated catalyst bed and conditions for carrying out the reaction of F_2 with SO_3 were those of Shreeve and Cady[10]. Fluorine was passed over NaF pellets to remove HF before introduction into the reactor. Optimum conditions found for this system were F_2 flow rate of 4–4.5 through an R-2-15-AAA rotameter, N_2 at 11.8 on an R-2-15-AAA rotameter to sweep in SO_3 from a reservoir held at 22–23° and a reactor temperature of 160°. The crude product, brought to 25° to remove volatiles, amounted to a production of 11–12 g $F_2S_2O_6$ per hour. The product, b.p. 65–66°, can be fractionated in a spinning-band column, but purity is limited by attack on Halocarbon grease. For crude products containing the desired low level of SO_3 as impurity, simple evaporation of volatiles gives $F_2S_2O_6$ of good purity. Purified product does not fume noticeably, freezes solid at −80° and is colorless or nearly so until heated to about 50° where the concentration of $FSO_2O\bullet$ is sufficient to impart a brown color. Storage in glass at −80° seems satisfactory.

1-Fluorosulfatoheptafluoropropane

A flask containing 10.6 g (0.054 mole) of $F_2S_2O_6$ was blanketed with N_2 and fitted with a −80° condenser. The peroxide was stirred and heated at 60° while introduction of gaseous $CF_3CF_2CF_2H$ was begun. $CF_3CF_2CF_2H$ was added in portions so as to maintain a temperature of 40–50° in the pot. When the temperature dropped below 35° and rose to only 37° after heating for 2 h the addition was stopped. A total of 11.5 g (0.068 mole) of $CF_3CF_2CF_2H$ had been added. Distillation gave 10.4 g (72%) of 1-fluorosulfatoheptafluoropropane, b.p. 46–47°. The IR spectrum agreed with that quoted in the literature[5]. The ^{19}F NMR spectrum exhibited peaks at 50.2 (triplet, $J = 8$ Hz, 1F, $OSO_2\underline{F}$), −81.9 (triplet, $J = 8$ Hz, 3F, $C\underline{F}_3$), −85.0 (doublet, $J = 8$ Hz, into overlapping quartets, $J = 8$ Hz, 2F, $C\underline{F}_2O$) and −130 ppm (singlet, 2F, $C\underline{F}_2$).

ω-Fluorosulfatododecafluoroheptanenitrile

ω-H-Dodecafluoroheptanamide was dehydrated by heating and stirring a mixture of 100 g (0.29 mole) of the amide with 112 g of P_2O_5 at 200–250° while product distilled at 90–95°. The distillate was filtered and re-distilled to give 72.6 g

(77%) of ω-*H*-dodecafluoroheptanenitrile (nc), b.p. 102°. IR (CCl_4): 3.38 (weak satd. CH) and 4.43 μ (C≡N). NMR: ^1H at δ 6.01 ppm (triplet, *J*(HF) = 52 Hz, into triplets, *J*(HF) = 5 Hz, $CF_2CF_2\underline{H}$); ^{19}F at −106 (triplet, *J*(FF) = 11 Hz, into multiplets, 1F, $C\underline{F}_2CN$), −122 (multiplet, 1F, $C\underline{F}_2$), −123 (multiplet, 1F, $C\underline{F}_2$), −124 (multiplet, 1F, $C\underline{F}_2$), −130 (multiplet, 1F, $C\underline{F}_2$) and −138 ppm (doublet, *J*(HF) = 52 Hz, into multiplets, 1F, $C\underline{F}_2H$).

Peroxydisulfuryl difluoride (7.9 g, 0.04 mole) was stirred magnetically in a 40° bath while 16.4 g (0.05 mole) of the nitrile was added drop-wise in 50 min. The temperature rose to about 50° during the addition and was kept there for 1 h after the addition was complete, then at 75° for 2.5 h. Distillation afforded 9.0 g of fuming liquid, b.p. 85–87° (100 mmHg). Re-distillation gave 5.8 g, b.p. mainly 80–82° (100 mmHg) and still fuming. Distillate washed with a small amount of distilled water, dried and filtered gave 3.7 g (22%) of ω-fluorosulfatododecafluoroheptanenitrile (nc). The yield would be improved with a better work-up. IR: 4.43 (C≡N) and 6.68 μ (S=O). NMR: ^1H none; ^{19}F at 50.7 (triplet, *J*(FF) = 8.5 Hz, 1F, $\underline{F}SO_2$), −83.6 (multiplet, 2F, $OC\underline{F}_2$), −106 (triplet, *J*(FF) = 11 Hz, into multiplets, 2F, $C\underline{F}_2CN$), −121 (broad, 2F, $C\underline{F}_2$), −122 (multiplet, 4F, $C\underline{F}_2C\underline{F}_2$) and −125 ppm (multiplet, 2F, $C\underline{F}_2$). (Calcd. for $C_7F_{13}NO_3S$: C, 19.78; F, 58.10; N, 3.30; S, 7.54%. Found: C, 19.85; F, 58.76; N, 3.26; S, 7.67%.)

Crosslinking and substitution into hexafluoropropylene/vinylidene fluoride copolymer

Hexafluoropropylene/vinylidene fluoride copolymer (uncured Viton® fluoroelastomer) was pressed at 200° and 12 000 psi between sheets of Teflon® fluorocarbon resin. (Viton and Teflon are Du Pont registered trademarks.) One such film, 1.02 g, was supported on a screen of Teflon® and treated at 50° with vapors from 0.5 g of $F_2S_2O_6$ for 5 h. The irregularly darkened film was rinsed with 4 × 200 ml water (last two rinses neutral) and dried to give 1.33 g of yellow, stiffened film. This film was swollen in acetone, but no longer soluble; extraction with acetone-d_6 gave only traces of fluorine-containing solubles by NMR spectroscopy. Analysis of the polymer showed 7.21% S present.

A sample of the fluorosulfated, crosslinked polymer, 0.10 g, was treated with pyridine/water for 1 day at 25°, rinsed with water and then with pyridine/water for 4 h at 100°. The resulting polymer was washed well with water and dried to give 0.09 g of more limp material which was swollen by CH_3CN, but still not soluble. Analysis showed that 0.86% S was now present.

1,2-Bis(fluorosulfato)hexafluoropropane and mixed 2:1 adducts of hexafluoropropylene and peroxydisulfuryl difluoride

While 30.7 g (0.155 mole) of $F_2S_2O_6$ was stirred in a flask fitted with a −80° condenser and cooled in a water bath, excess hexafluoropropylene (26 ml at −80°) was passed into the vapor phase during a 2 h period. The reaction temperature just over the liquid phase was kept at 60–70° by adjusting the rate of olefin addition.

At the end of the addition the temperature of the reaction mixture had dropped to 15° and the peroxide was all consumed. Distillation gave 33.9 g (63%) of 1,2-bis-(fluorosulfato)hexafluoropropane, b.p. 74° (200 mmHg). IR: identical with literature spectrum[8]. NMR: ^{19}F at 50.8 (triplet, $J = 8$ Hz, 1F, $CF_2OSO_2\underline{F}$), 50.7 (doublet, $J = 9.5$ Hz, into quartets, $J = 3$ Hz, into overlapping doublets, $J = 3$ Hz, 1F, $CFOSO_2\underline{F}$), −79.3 (triplet, $J = 9$ Hz, into doublets, $J = 3$ Hz, into overlapping doublets, $J = 2$ Hz, 3F, $C\underline{F}_3$), −82.7 (multiplet, 2F, $C\underline{F}_2$) and −141 ppm (doublet, $J = 9.5$ Hz, into quartets, $J = 2$ Hz, 1F, $C\underline{F}$).

A higher boiling mixture of 2:1 adducts, 16.9 g (22%), was also obtained, b.p. 84–85° (50 mmHg). IR: 6.71 μ (S–O stretch). NMR: ^{19}F at 50.7 (multiplet, 1F, $SO_2\underline{F}$), −69.8, −71.8, −73.6, −75.3, −77.1 and −78.2 (multiplets, 4.6F, $C\underline{F}_3 + O\underline{C}F_2$), −112 (multiplet, 0.4F, $C\underline{F}_2$), −120 and −136 (multiplets, 0.4F, $O\underline{C}F$) and −176 and −184 ppm (multiplets, 0.6F, $C\underline{F}$). (Calcd. for $C_6F_{14}O_6S_2$: C, 14.46; F, 53.39; S, 12.87%. Found: C, 15.05; F, 53.29; S, 13.03%.)

Oligomer of trifluoropyruvic acid hydrate

A mixture of 7.0 g (0.02 mole) of 1,2-bis(fluorosulfato)hexafluoropropane and 1 g of KF was stirred and heated at reflux (*ca.* 110°). After 2 h the liquid phase was nearly gone, and volatiles had collected in a −80° trap. The residue was evacuated at 1 mmHg and 25° to give a total of 2.8 g of condensable gas, shown by IR to be SO_2F_2. At 110° (1 mmHg), 0.4 g (6%) of white solid sublimed out of the reaction flask. Re-sublimation at 80° (1 mmHg) gave a very hygroscopic solid, m.p. 118–119° (subl.), insoluble in CCl_4, soluble in acetone. IR: 3.02 (OH), 5.72 (C=O) and 8–9.5 μ (C–F and C–O). NMR ($(CD_3)_2CO$): ^1H present and exchanged with $(CD_3)_2CO$; ^{19}F at −82.6 ppm (singlet, $C\underline{F}_3$). Mass spectroscopy indicated a highly associated or covalently bridged compound with highest observed mass *m/e* 337. (Calc. for $(C_3H_3F_3O_4)_x$: C, 22.51; H, 1.89; F, 35.61%. Found: C, 22.98; H, 2.00; F, 35.54%.)

cis- *and* trans-*1,2-Dichloro-1,2-bis(fluorosulfato)hexafluorocyclopentane*

Reaction proceeds very slowly below room temperature, but near 15° and over becomes very rapid and exothermic, as shown by the following experiments.

A flask containing 0.10 mole of 1,2-dichlorohexafluorocyclopentene was cooled in a −80° bath (contents at *ca.* −30°) and stirred while 0.088 mole of $F_2S_2O_6$ was added drop-wise. The clear, colorless solution was allowed to come near room temperature, after which it suddenly detonated.

1,2-Dichlorohexafluorocyclopentene (24.5 g, 0.10 mole) was stirred and heated at 50° in a flask topped by a condenser. Through the condenser was added drop-wise 9.9 g (0.05 mole) of $F_2S_2O_6$ at a rate sufficient to maintain the temperature at 55–60° (45 min). After the exothermic reaction was over and the mixture had cooled to 25°, KI paper indicated the peroxide had been consumed. Conc. H_2SO_4 (100 ml) was added to the reaction mixture, the product heated to boiling and the final crude distillate collected, b.p. 90–130°. Apparently no hydrolysis of fluorosulfonyl groups occurred; the distillate was re-distilled from P_2O_5 to give 15.7 g (71%) of 1,2-dichloro-1,2-bis(fluorosulfato)hexafluorocyclopentane as a mixture of isomers, b.p. 79–80 (10 mmHg). An analytical sample was prepared by re-distillation, b.p. 65° (5 mmHg). IR: 6.73 (SO stretch), 7.5–9 (S=O and C–F), 13.05 μ (C–Cl). NMR: ^{19}F at 51.8 (multiplet, 2F (both isomers), $SO_2\underline{F}$), −6012, −6253, −6679 and −6919 Hz (2F (isomer A), AB with unresolved fine structure, $C\underline{F}_2CCl$), −114 (pentet, J = 3.5 Hz, 2 F (isomer B), $C\underline{F}_2CCl$), −121 (quartet, J = 3.5 Hz, 1F (isomer B), $C\underline{F}_2$) and −121.5 ppm (pentet, J = 2 Hz, 1F (isomer A), $C\underline{F}_2$). (Calcd. for $C_5Cl_2F_8O_6S_2$: C, 13.56; Cl, 16.01; F, 34.30%. Found: C, 13.55; Cl, 15.89; F, 34.58%.)

Pyrolysis of fluorosulfato derivatives

Adducts of $F_2S_2O_6$ to hexafluoropropene and to dichlorohexafluorocyclopentene were pyrolyzed over nickel gauze and the products determined by a combination of GLC and mass spectroscopy.

Pyrolysis of 1,2-bis(fluorosulfato)hexafluoropropane required rather high temperatures. At 450°, pyrolysis proceeded well to give substantial amounts of two early peaks using a 10% fluoroalkyl pyromellitate column. Product from a preparative scale run collected on a similar column and examined by mass spectroscopy showed a large amount of SO_2F_2 to have been formed. The other product, presumed to be 2-fluorosulfatotetrafluoropropionyl fluoride, may have hydrolyzed on the column on standing and thus was not seen. This pyrolysis route may be a result of fluoride-catalyzed elimination, since such a reaction is known and active fluoride may be formed on the nickel gauze at such a high temperature.

Pyrolysis of the 1,2-dichloro-1,2-bis(fluorosulfato)hexafluorocyclopentane isomers occurred readily at 250° and gave three major products. Products, analyzed by mass spectroscopy in order of elution from the GLPC column, gave parent peaks and fragmentation patterns suggestive of 1,2-dichlorohexafluorocyclopentene, 2-chloropentafluorocyclopentenone-3 and 1-chloro-2-fluorosulfatohexafluorocyclopentene. Comparison of the mass spectrum of the first-eluted compound with that of authentic 1,2-dichlorohexafluorocyclopentene confirmed the structure. Correlating with a radical mechanism for this pyrolysis is the mass spectrum of the starting material, 1,2-dichloro-1,2-bis(fluorosulfato)hexafluorocyclopentane; no parent was observed, but major peaks appeared at m/e 407 (M^+—Cl), 359 (M^+—SO_2F) and 343 (M^+—OSO_2F).

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