Registry No. BrF_5, 7789-30-2; SbF_5, 7783-70-2; AsF_5, 7784-36-3; $ClF_4^+SbF_6^-$, 25481-31-6; $ClF_5 \cdot xSbF_5$, 41646-49-5; $ClF_4^+AsF_6^-$, 41646-46-2; $BrF_4^+Sb_2F_{11}^-$, 36445-03-1; $IF_4^+SbF_6^-$, 41646-48-4; $BrF_5 \cdot AsF_5$, 41646-50-8; ClF_4^+, 36544-30-6; BrF_4^+, 41646-52-0; IF_4^+, 41646-53-1.

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Hydrogen Abstraction Reactions of Peroxydisulfuryl Difluoride

ROBERT L. KIRCHMEIER and JEAN'NE M. SHREEVE*[1]

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Several new as well as a large number of known fluorosulfate-containing molecules have been synthesized *via* hydrogen radical abstraction with $S_2O_6F_2$. In general, the reactions were moderated sufficiently to permit wide applicability of this synthetic approach by dilution of the reactants and by lowering of the temperature. Amine, alcohol, aromatic, aliphatic, perfluoroalkyl, hydrogen halide, and thiol hydrogens were easily abstracted and in most cases converted to stable fluorosulfate products.

Introduction

Hydrogen abstraction by inorganic radicals has not been studied extensively due in part to the dearth of such radicals and, in some cases, to their extreme reactivity. The inorganic radicals examined most often include the halogen atoms, $NO\cdot$, $NO_2\cdot$, $NF_2\cdot$, $H\cdot$, O_2, a few perfluorinated species ($CF_3\cdot$, $SF_5\cdot$, $(CF_3)_2NO\cdot$), and $\cdot OSO_2F$. Of these, the fluorosulfate radical, which is in equilibrium with the parent dimer, $S_2O_6F_2$, at 25° and below,[2] is the most reactive and has been studied only recently in hydrogen abstraction reactions.[3,4] When the vigor of the reactions between $\cdot OSO_2F(S_2O_6F_2)$ and organic compounds is considered, it is not surprising that more extensive studies of the hydrogen abstraction reactions of this radical have not been undertaken.

The greater reactivity of radicals, such as $CF_3\cdot$ compared to $CH_3\cdot$, has been attributed to the greater electrophilic character of the former.[5] This rationale was used to account for the decreasing difference between reaction rates of $CF_3\cdot$ and $CH_3\cdot$ at a particular site as the site polarity increased; *i.e.*, increased polar repulsions between the electrophilic radical and the more polar reaction site caused a corresponding increase in activation energy and a concomitant decrease in reaction rate.

We note that it is possible to correlate trends in relative reaction rates of $\cdot OSO_2F$ radicals at a particular molecular site with an empirically based description of the polarity of the reaction site. As the site becomes more polar, the reaction rate decreases correspondingly.

Hydrogen abstraction reactions of fluorosulfate radicals occurred with a variety of organic and inorganic molecules, *e.g.*

$$RH + 2\cdot OSO_2F \rightarrow ROSO_2F + HOSO_2F$$

where RH = amines, alcohols, aromatics, aliphatics, perfluoroalkyls, hydrogen halides, and thiols. Stringent moderating conditions (*i.e.*, low temperature, gas phase, dilution with inert liquids or gases) were required to permit the reactions to proceed in a controlled manner to give high yields of some fluorosulfates which had been synthesized earlier and of several new fluorosulfates. In some cases the involatility of the polyhydrogen-containing fluorosulfate product precluded separation from the fluorosulfuric acid formed concomitantly. However, the perfluorinated and a few lighter weight polyhydrogen-containing products were sufficiently volatile to permit separation and purification.

In several reactions which yielded mixtures of fluorosulfate-containing products, the amounts and kinds of products were a direct function of the relative amounts of reactants.

Results and Discussion

Peroxydisulfuryl difluoride has been shown to abstract hydrogen atom(s) successfully from a relatively large number of compounds. These compounds, products, and the conditions required are given in Table I. With alcohols, there was no evidence for peroxide formation, *e.g.*, CF_3CH_2OH and CH_3CH_2OH where CF_3OSO_2F and a nonvolatile, unstable liquid were the major products, respectively. Reaction did occur with the totally fluorinated alcohols, $(CF_3)_3COH$ and $C_2F_5C(CF_3)_2OH$, but again there was no evidence for the symmetric or mixed peroxides, R_fOOSO_2F. The latter have been reported as moderately stable compounds.[6] The $(R_f)_3CO\cdot$ radicals obtained as intermediates in the abstraction reactions probably decomposed in a manner analogous to that observed in the case of $(CH_3)_3CO\cdot$[7] which precluded peroxide formation. This route accounts for the observed products in the alcohol-$S_2O_6F_2$ reactions as indicated for $C_2F_5(CF_3)_2COH$

$$(C_2F_5)C(CF_3)_2OH + \cdot OSO_2F \rightarrow (C_2F_5)C(CF_3)_2O\cdot + HOSO_2F$$

$$(C_2F_5)C(CF_3)_2O\cdot \rightarrow (CF_3)_2CO + C_2F_5\cdot$$

$$(C_2F_5)C(CF_3)_2O\cdot \rightarrow (C_2F_5)CO(CF_3) + CF_3\cdot$$

$$C_2F_5\cdot + S_2O_6F_2 \rightarrow C_2F_5OSO_2F + \cdot OSO_2F$$

$$CF_3\cdot + S_2O_6F_2 \rightarrow CF_3OSO_2F + \cdot OSO_2F, \text{ etc.}$$

The products were unaltered by mixing the reactants in different proportions; *i.e.*, none of the symmetric peroxide R_fOOR_f was observed even in the presence of excess alcohol.

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Similarly with trifluoroacetic acid, hydrogen was abstracted and the products can be rationalized *via* the decomposition of a $CF_3C(O)O\cdot$ intermediate.

In contrast, dimerization of thiol radicals provided an effective route to disulfides. For $CF_3C(O)SH$, the disulfide $[CF_3C(O)S]_2$ was obtained in greater than 99% yield when the reaction was carried out with a twofold molar excess of the thiol. However, when the molar ratio of $CF_3C(O)SH$ to $S_2O_6F_2$ was 1, only a small amount (5%) of the disulfide was obtained and 95% of the trifluoroacetyl group was found as $CF_3C(O)OSO_2F$. Although the unstable $CF_3C(O)SOSO_2F$ cannot be ruled out completely, the disulfide $(CF_3C(O)S)_2$ was the probable intermediate since it was quantitatively (99%) converted to $CF_3C(O)OSO_2F$ by $S_2O_6F_2$ in independent experiments. The reaction between CF_3SH and $S_2O_6F_2$ (1:1) proceeded differently in that CF_3SSCF_3, and no CF_3OSO_2F, was isolated as a product in spite of the fact that CF_3SSCF_3 reacted easily with $S_2O_6F_2$ to form CF_3OSO_2F (58%) when mixed independently. This suggested that in the former reaction an intermediate, such as CF_3SOSO_2F, of sufficient stability must form to allow consumption of the $S_2O_6F_2$, followed by decomposition to CF_3SSCF_3, S, SO_2, and $S_2O_5F_2$. None of this trifluoromethyl thiofluorosulfate was isolated. Some of the $S_2O_6F_2$ could have been consumed in reaction with sulfur to form SO_2 and $S_2O_5F_2$.

In addition to $HOSO_2F$, only $S_2O_5F_2$, SO_2, and S were formed in the reaction of $S_2O_6F_2$ with H_2S. The products evidently resulted from the decomposition of the unstable fluorosulfate $S(OSO_2F)_2$ to give $(SO) \rightarrow S + SO_2$ and $S_2O_5F_2$.

Hydrogen abstraction also occurred with ammonia to form NH_4OSO_2F (from HSO_3F and NH_3) and an unidentified white solid of low solubility in a variety of solvents. Although it seemed likely that the latter solid should be a compound which would consist of $NH_2\cdot$ or N_2H_4 in addition to fluorosulfate units, infrared and elemental analyses were not helpful in establishing the nature of the compound.

The absolute structure of the product from the reaction between toluene and $S_2O_6F_2$ is uncertain. However, it has been determined that substitution of the fluorosulfate group occurred on the ring and not on the methyl group. There are no infrared absorption bands in the 700-cm^{-1} region which indicates that the product is not a monosubstituted ring. There is a strong band at 770 cm^{-1} which implies ortho substitution, although para substitution cannot be excluded. The absorption bands between 1450 and 1600 cm^{-1} confirm that the product is aromatic.[8] The mass spectrum contains a large molecular ion peak at *m/e* 190 which corresponds to an empirical formula $C_7H_7SO_3F$. Lower *m/e* values do not lend support to the structure of either the ring-substituted or the methyl-group-substituted compound. The spectrum was obtained by subtracting the peaks associated with $HOSO_2F$ from the spectrum of the mixture.

Proton nmr data, however, confirm the position of the fluorosulfate group on the ring. The change in chemical shift of the methyl group was only 0.3 Hz (toluene, δ 2.32).[9] When a small amount of water was added to the sample, only the aromatic region of the nmr spectrum was affected. There was little or no change in the resonance in the methyl region. If the fluorosulfate group were bonded directly to the methyl group, a large shift in the methyl resonance downfield from the methyl resonance in toluene would occur. The chemical shift of the methyl group should change only a little with changes in groups bonded to the aromatic ring, *e.g.*, $\delta(CH_3)$ for *m*-cresol, 2.25; *p*-methylthiophenol, 2.30; *p*-trifluoromethyltoluene, 2.38; *p*-xylene, 2.30; *p*-methylanisole, 2.28.[9] Spin density calculations on the benzyl radical do not predict that free-radical substitution will occur on the ring.[10] However, it has been shown that bis(pentafluorosulfur) peroxide reacted with toluene to yield only *p*-pentafluorosulfoxytoluene.[11] Substitution on the alkyl group has been observed in the reaction of bis(trifluoromethyl) nitroxide, $(CF_3)_2NO\cdot$, with $C_6H_5CHR_2$, where R was either H or CH_3.[12] This latter alkyl substitution is the expected position of substitution.

The trends in reactivities of particular X–H sites with $\cdot OSO_2F$ radicals in a variety of molecules correlate very well with an empirical description of the polar character of the reaction site. These calculated sensitivities are reported in Table I and compare satisfactorily with the conditions required in each case for a controlled reaction. *E.g.*, for CH_2Cl_2 (sensitivity parameter 4.7) undiluted at 25°, explosion occurred; but with dilution and at −25°, the reaction proceeded smoothly. For CF_3H (sensitivity parameter 1.8), essentially quantitative abstraction occurred at 80°. The definition of this sensitivity parameter and its application to a wide number of substrates and a variety of radicals will be given in a forthcoming publication.

Experimental Section

Starting Materials. Peroxydisulfuryl difluoride,[13] $(CF_3)_2C{=}NH$,[14] and $(CF_3)_2C{=}NCl$[15] were prepared by literature methods. Photolysis of CF_3SSCF_3 and H_2S in the presence of mercury gave a 96% yield of CF_3SH.[16] All other starting materials were commercially available and were used without further purification.

General Procedures. Conventional vacuum techniques were used for handling of gaseous reactants and products. *PVT* measurements provided quantitative data. Gas-phase reactions were carried out in a Pyrex vessel constructed of two bulbs of 100- and 300-ml capacity joined by a Rotaflo TF 2/13 Teflon stopcock.

Varian A-60 and Varian HA-100 nuclear magnetic resonance spectrometers were used for ^1H and ^{19}F spectra, respectively, with tetramethylsilane and trichlorofluoromethane as internal standards (except in the case of fluorosulfuric acid where external standards were used). Gas-phase infrared spectra were obtained in an 8-cm Pyrex cell equipped with NaCl and KBr windows using a Perkin-Elmer Model 457 infrared spectrometer. Columns constructed of 0.25-in. copper tubing packed with 20% Kel F-3 polymer oil on Chromosorb P were used for gas chromatographic purification of products. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at ionization potentials of 70 and 17 eV. The Kellogg–Cady method was used for vapor pressure studies.[17]

HSO_3F. In most of the reactions, fluorosulfuric acid was identified as an involatile product by ^1H and ^{19}F nmr. The resonances were measured relative to external standards. The ^{19}F resonance was a singlet at −40.6 MHz[18] and the ^1H resonance appeared at δ 9.74.

Included in Table I are the quantities of reactants, reaction conditions, products, and their yields. If the product was a known compound, it was identified by infrared and nmr spectra and the literature

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Table I. Reactants, Conditions, Products, and Calculated Sensitivity

Reactant	Calcd sensitivity	Amt, mmol		Reaction conditions	Products (yields)	Comments
		$S_2O_6F_2$	Reactant			
HCl	1.6	1.0	1.0	25°, 1 hr	Cl_2 (94%), $HOSO_2F$	
CF_3H	1.7	2.0	2.0	80°, 2 hr	CF_3OSO_2F (92-99%), HSO_3F	*a, d*
CF_3SH	1.8	1.0	1.0	$-183 \rightarrow +25°$, 1 hr, gas	CF_3OSO_2F (trace), nonvolatile unstable liquid, plus products below	*c*
CF_3SH	1.8	1.0	1.0	$-183 \rightarrow +25°$	CF_3SSCF_3 (30%), $S_2O_5F_2$, SO_2, S	No CF_3OSO_2F isolated; *m*
CF_3SSCF_3		0.5	1.0	$-183 \rightarrow +25°$	CF_3OSO_2F (58%), SO_2, S, CF_3SSCF_3	*b, m*
CF_3CF_2H	1.9	1.0	1.0	80°, 3 hr	$CF_3CF_2OSO_2F$ (94%), HSO_3F	*a, e*
CF_3CH_2OH	2.2	1.0	1.0	25°	CF_3OSO_2F (64%), $CF_3C(O)H$, $CF_3C(O)F$, $S_2O_5F_2$, COF_2, C_2F_6, HSO_3F	<0.1 mmol of $CF_3C(O)H$, $CF_3C(O)F$ and C_2F_6 combined; *b, c*
CF_3CH_2OH	2.2	2.0	2.0	0°	Same as above	CF_3CH_2OH diluted 2:1 with $CFCl_3$
$CF_3C(O)SH$	2.5	0.5	1.0	25°	$[CF_3C(O)S]_2$ (>99%), HSO_3F	*f, m*
$[CF_3C(O)S]_2$		0.5	0.5	25°	$CF_3C(O)OSO_2F$ (~99%), $S_2O_5F_2$, SO_2, S	*g, m*
NH_3	2.5	3.0	3.0	0°	NH_4OSO_2F (1.3 mmol), white solid, 15.4 mg, excess NH_3 (slight)	*c, l, m*
NH_3	2.5	3.0	1.0	0°	NH_4OSO_2F, white solid, excess $S_2O_6F_2$ (62%)	*c, l, m*
$CF_3C(O)SH$	2.5	2.0	2.0	$-183 \rightarrow +25°$, 6 hr	$CF_3C(O)OSO_2F$ (95%), $[CF_3C(O)S]_2$ (5%), HSO_3F	*m*
$CF_3C(O)OH$	2.7	1.0	1.0	$-183 \rightarrow +25°$	CF_3OSO_2F (80%), CO_2, COF_2, $S_2O_5F_2$, C_2F_6, $HOSO_2F$	
$CF_3C(O)OH$	2.7	0.25	0.5	$-183 \rightarrow +25°$	Same as above	No peroxide isolated; *m*
$C_2F_5C(CF_3)_2OH$	2.8	1.0	1.0	25°, 12 hr	CF_3OSO_2F, $C_2F_5OSO_2F$, $(CF_3)_2CO$, COF_2, $CF_3(C_2F_5)CO$, HSO_3F	$C_2F_5OSO_2F$:CF_3OSO_2F = 2.8; separated by gc (15 ft × 0.25 in. Cu column packed with 20% Kel F No. 3 oil on Chromosorb P); *m*
$C_2F_5C(CF_3)_2OH$	2.8	1.0	2.0	25°, 12 hr	Same as above, plus excess alcohol (51%)	
$(CF_3)_3COH$	2.8	1.0	1.0	0°, 12 hr 60°, 0.5 hr	$(CF_3)_2CO$, CF_3OSO_2F, $HOSO_2F$	
$HCFCl_2$	2.9	1.0	1.0	25°, 1 hr	$FCCl_2OSO_2F$ (>95%), $HOSO_2F$	*a, h*
$(CF_3)_2NOH$	3.0	1.0	1.0	0°, 1 hr	$(CF_3)_2NO\cdot$ (98%), $S_2O_6F_2$ (46%), HSO_3F	
$(CF_3)_2NH$	3.2	1.0	1.0	$-183 \rightarrow +25°$, 0.5 hr	$(CF_3)_2NOSO_2F$ (>99%), HSO_3F	*i*
H_2S	3.4	2.0	1.0	0°, 0.5 hr	$S_2O_5F_2$, SO_2, S, HSO_3F	*m*
$(CF_3)_2C{=}NH$	4.1	2.0	4.0	0°, 1 hr	$(CF_3)_2C{=}NOSO_2F$ (21-58%), $[(CF_3)_2C{=}N]_2$ (5-38%), $[(CF_3)_2C(OSO_2F)N]_2$ (5-25%)	*j*
$(CF_3)_2C{=}NH$	4.1	10.0	10.0	0°, 1 hr	Same as above, only smaller yield dimer and dimer fluorosulfate	*l*
$[(CF_3)_2C{=}N]_2$		1.0	1.0	25°, 2 hr	$[(CF_3)_2C(OSO_2F)N]_2$ (95%)	*k, l*
$HCCl_2OSO_2F$	4.7	1.0	1.0	$-183° \rightarrow$ room temp	$COCl_2$ (73%), $S_2O_5F_2$, $S_2O_6F_2$, HSO_3F	$CCl_2(OSO_2F)_2$ not isolated

Table I. (*Continued*)

Reactant	Calcd sensitivity	Amt, mmol		Reaction conditions	Products (yields)	Comments
		$S_2O_6F_2$	Reactant			
CH_2Cl_2	4.7	1.0	1.0	−183° → room temp, 0.5 hr		Explosion
CH_2Cl_2	4.7	1.0	1.0	−63°, 0.25 hr	$S_2O_6F_2$ (60% recovered; small amounts $COCl_2$ and SO_2)	$CFCl_3$ dilution of CH_2Cl_2 (4:1); $S_2O_6F_2$ titrated slowly
CH_2Cl_2	4.7	2.0	1.0	−20°, 1 hr	$COCl_2$, $S_2O_5F_2$, $HOSO_2F$	$CFCl_3$ dilution of CH_2Cl_2 (2:1); *c*
CH_2Cl_2	4.7	2.0	2.0	−25°, 2 hr	$HCCl_2OSO_2F$ (60%), $COCl_2$, $S_2O_5F_2$, $HOSO_2F$	$CFCl_3$ dilution of CH_2Cl_2 (1:1); *c, l*
CH_3Br	5.7 (C–H) 7.2 (C–Br)	10.0	10.0	25°, 0.4 hr	CH_3OSO_2F, $BrOSO_2F$, Br_2	CH_3OSO_2F distilled from $BrOSO_2F$; Hg removal of Br_2
CH_3OSO_2F	5.3	1.0	1.0	0–25° over 12 hr	$CH_2(OSO_2F)_2$ (75%), $HOSO_2F$	No excess $S_2O_6F_2$ recovered
CH_3CH_2OH	6.5 (CH_3) 6.1 (CH_2) 1.6 (OH)	1.0	1.0	−63°, −25°, 24 hr	$CH_3CH_2OSO_2F$ (<0.1 mmol), SiF_4, unstable, nonvolatile, brown liquid	No CH_3OSO_2F isolated
$C_6H_5CH_3$	7.9 (C_6H_5) 6.1 (CH_3)	1.0	1.0	−63°	$CH_3C_6H_4OSO_2F$, excess $C_6H_5CH_3$, $S_2O_5F_2$, SiF_4, SO_2, nonvolatile, charred product	Toluene diluted 4:1 with $CFCl_3$; $S_2O_6F_2$ titrated in slowly; always good deal of charring; extremely vigorous reaction; *m*

[a] Purified by distillation from 0°. [b] Purified by trap-to-trap distillation. [c] Gas-phase reaction. [d] M. Lustig, *Inorg. Chem.*, 4, 1828 (1965). [e] W. P. Gilbreath and G. H. Cady, *ibid.*, 2, 496 (1963). [f] W. V. Rochat and G. L. Gard, *J. Org. Chem.*, 34, 4173 (1969). [g] J. J. Delfino and J. M. Shreeve, *Inorg. Chem.*, 5, 309 (1966). [h] D. DesMarteau, *ibid.*, 7, 434 (1968). [i] J. A. Lott, D. P. Babb, K. E. Pullen, and J. M. Shreeve, *ibid.*, 7, 2593 (1968). [j] Yields variable and nonreproducible. [k] Work done by Dr. R. F. Swindell. [l] See Experimental Section. [m] See Results and Discussion.

Table II. Mass, ^1H and ^{19}F Nmr, and Infrared Spectra

Compd	Mass spectra	Nmr spectra	Infrared spectra, cm^{-1}
$(CF_3)_2NOSO_2F$	232, $(CF_3)_2NSO_3^+$, 4; 168, $(CF_3)_2NO^+$, 17; 144, $CF_2NSO_3^+$, 3.2; 83, SO_2F^+, 6; 80, SO_3^+, 1.4; 69, CF_3^+, 100; 67, FSO^+, 2.4; 64, SO_2^+, 2.0; 50, CF_2^+, 1.0	^{19}F: ϕ +67.8, −37.4	1510 vs, 1326 vs, 1280 vs, 1257 vs, 1239 vs, 1139 s, 1023 s, 980 s, 862 vs, 821 s, 740 w, 719 m, 635 m
$(CF_3)_2C{=}NSO_3F$	244, $(CF_3)_2C{=}NSO^+$, 1; 180, $(CF_3)_2CNO^+$, 16; 161, $C_2F_5CNO^+$, 4; 92, CF_2CNO^+, 6; 83, SO_2F^+, 13.5; 76, CF_2CN^+, 4; 69, CF_3^+, 100; 67, SOF^+, 4; 64, SO_2^+, 3; 50, CF_2^+, 6; 48, SO^+, 4; 30, NO^+, 14.7	^{19}F: ϕ +67.9, +64.6, −37.3 ($J_{CF_3-CF_3}$ = 6.5 Hz)	1658 w, 1496 s, 1350 m, 1264 w, 1250 s, 1219 s, 1035 m, 915 s, 857 s, 825 w, 779 w, 721 w, 667 w, 577 s
$((CF_3)_2C(OSO_2F)N)_2$	328, $((CF_3)_2CN)_2^+$, 6; 309, $(CF_3)_2CNNC(CF_3)CF_2^+$, 8; 259, $(CF_3)_2CNNCCF_3^+$, 4; 249, $(CF_3)_2COSO_2F^+$, 3; 178, $(CF_3)_2CNN^+$, 3; 166, $(CF_3)_2CO^+$, 2; 159, $CF_3(CF_2)$-CNN^+, 3; 147, $CF_3(CF_2)CO^+$, 25; 131, $CF_3CCF_2^+$, 2; 119, $C_2F_5^+$, 2; 100, $C_2F_4^+$, 6; 97, CF_3CO^+, 22; 83, SO_2F^+, 24; 76, $C_2F_4N^+$, 4; 69, CF_3^+, 100; 67, SOF^+, 3; 64, SO_2^+, 20; 50, CF_2^+, 9; 48, SO^+, 10	^{19}F: ϕ +71.9, −50.9	1487 s, 1290 vs, 1268 vs, 1115 m, 1093 s, 1078 m, 1015 m, 875 m, 842 s, 740 m, 589 s, 530 w
CH_3OSO_2F	114, $CH_3OSO_2F^+$, 4; 113, $CH_2OSO_2F^+$, 29; 96, CH_2OSOF^+, 6; 95, $CH_3OSO_2^+$, 2.3; 94, $CH_2OSO_2^+$, 7; 84, HSO_2F^+, 21; 83, SO_2F^+, 36; 67, FSO^+, 38; 65, HSO_2^+, 13; 64, SO_2^+, 13.5; 48, SO^+, 17; 30, CH_2O^+, 100	^{19}F: ϕ −30.4. ^1H: δ 4.1	1470 s, 1244 s, 1175 w, 1030 s, 847 s, 793 m, 585 w, 529 (PQR) (w)
$CH_2(OSO_2F)_2$	212, $CH_2(SO_3F)_2^+$, 4.0; 113, $CH_2OSO_2F^+$, 100; 96, CH_2OSOF^+, 10.5; 94, CH_2-OSO_2^+, 11.5; 84, HSO_2F^+, 20; 83, SO_2F^+, 75; 81, HSO_3^+, 10; 67, SOF^+, 49; 65, HSO_2^+, 15; 64, SO_2^+, 19	^{19}F: ϕ −43.2 (tr). ^1H: δ 6.0 (J = 14.7 Hz)	1480 s, 1236 s, 1058 w, 982 s, 850 w, 824 m, 772 m, 519 w
$HCCl_2OSO_2F$[a]	147, $HCClOSO_2F^+$, 53; 99, $CHCl_2O^+$, 1.5; 83, $HCCl_2^+$, 71; 82, CCl_2^+, 7.4; 51, SF^+, 1.7; 48, $CHCl^+$, 20; 47, CCl^+, 9.9; 36, HCl^+, 55; 35, Cl^+, 12; 29, HCO^+, 100; 28, CO^+, 99	^{19}F: ϕ −43.1. ^1H: δ 7.5	1477 vs, 1321 w, 1237 vs, 1023 w, 963 vs, 866 vs, 816 s, 762 m, 569 m, 532 m

[a] Correct chlorine isotope ratio observed.

reference is cited in the table. Data for new compounds and new data for known compounds are given below and in Table II.

Reaction of $(CF_3)_2C$=NH with $S_2O_6F_2$. The relative amounts of the products $[(CF_3)_2C$=N$]_2$, $(CF_3)_2C$=$NOSO_2F$, and $(CF_3)_2C(OSO_2F)N$=$N(OSO_2F)C(CF_3)_2$ varied randomly from reaction to reaction. They were purified using gas chromatography and the latter two compounds were characterized.

$(CF_3)_2C$=$NOSO_2F$. Nuclear magnetic resonance, infrared, and mass spectral data are given in Table II. The equation $\log P_{\text{mm}} = 9.22 - 2180/T$ describes the vapor pressure curve over the temperature range from 309 to 339°K from which ΔH_v (9.9 kcal/mol), ΔS_v (28.8 eu), and the boiling point (71°) are obtained.

Anal. Calcd: N, 5.32; S, 12.17; F, 50.6; C, 13.69. Found: N, 5.29; S, 12.37; F, 50.6; C, 13.79.

The compound was also prepared in 94% yield by the reaction of 1.3 mmol of $BrOSO_2F$ with 1.5 mmol of $(CF_3)_2C$=NCl at 0° for 6 hr. The reactants were combined at liquid oxygen temperature and allowed to warm slowly to 0°. The products were separated by a trap-to-trap distillation.

$(CF_3)_2C(OSO_2F)N$=$N(OSO_2F)C(CF_3)_2$. Nuclear magnetic resonance, infrared, and mass spectral data are given in Table II. The equation $\log P_{\text{mm}} = 7.127 - 1850/T$ describes the vapor pressure curve over the temperature range from 342 to 387°K. The compound decomposes in glass at 113° to give SiF_4, $[(CF_3)_2C$=N$]_2$, and others.

Anal. Calcd: C, 13.69; F, 50.6; N, 5.32; S, 12.17. Found: C, 13.75; F, 50.5; N, 5.46; S, 12.13.

The compound was prepared previously in greater than 95% yield by the reaction of $S_2O_6F_2$ with $[(CF_3)_2C$=N$]_2$ at 25° for 2 hr.[19]

Reaction of CH_2Cl_2 with $S_2O_6F_2$. When a mixture of CH_2Cl_2 (1 mmol), diluted 4:1 with Freon 11, and $S_2O_6F_2$ (1 mmol) was held at −25° for 2 hr, $HCCl_2OSO_2F$ (60%), HSO_3F, $COCl_2$, and $S_2O_5F_2$ formed. Decomposition products obtained in the reaction between $HCCl_2OSO_2F$ and $S_2O_6F_2$ are listed in Table I.

$HCCl_2OSO_2F$. Nuclear magnetic resonance, infrared, and mass spectral data are given in Table II. The vapor pressure curve was linear to 87°. Incomplete decomposition in glass of the compound occurred at 25° over a period of 24 hr to give SO_2, SiF_4, and a brown, involatile residue.

Reaction of NH_3 with $S_2O_6F_2$. NH_3 was allowed to react with $S_2O_6F_2$ in a 1:3 molar ratio. In the gas phase at 0°, the reaction yielded a white solid, and excess $S_2O_6F_2$ (62%). The solid was extracted with methanol. Part of the solid was soluble and, upon evaporation of the methanol, was determined to be NH_4OSO_2F by comparison with the infrared spectrum of an authentic sample. The insoluble portion decomposed at 280° and was insoluble in CCl_3F, $(CH_3)_4Si$, CH_2Cl_2, CCl_4, PhCl, $(CF_3)_2CO$, CH_3CN, $(CH_3)_2CO$, C_2H_5OH, $HC(O)N(CH_3)_2$, NH_3(aq), $(CH_3)_2O$, and $(CH_3)_2SO$. It was decomposed by H_2O. Elemental analysis suggests a compound of empirical formula $(NH_3)_5S_3O_9F_2$. The infrared spectrum of the insoluble white solid contained bands at 3120 (s, b), 1410 (s), 1375 (sh), 1260 (s), 1195 (s), 1087 (w), 1023 (m), 863 (m), and 580 (b) cm^{-1}.

Reaction of Toluene with $S_2O_6F_2$. Toluene diluted 4:1 with CCl_3F was allowed to react with $S_2O_6F_2$ in a 1:1 ratio at −63°. The gaseous peroxide was added in small aliquots. Reaction was extremely vigorous and always accompanied by charring. Yields were very low and the fluorosulfate product was not separated from the other involatile products. Volatile materials which resulted from the reaction were identified as excess toluene, CCl_3F, $S_2O_5F_2$, SiF_4, and SO_2.

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Registry No. $S_2O_6F_2$, 13709-32-5; HCl, 7647-01-0; CF_3H, 75-46-7; CF_3SH, 1493-15-8; CF_3SSCF_3, 372-64-5; CF_3CF_2H, 354-33-6; CF_3CH_2OH, 75-89-8; $CF_3C(O)SH$, 2925-25-9; $[CF_3C(O)S]_2$, 21690-87-9; NH_3, 7664-41-7; $C_2F_5C(CF_3)_2OH$, 6188-98-3; $(CF_3)_3COH$, 2378-02-1; $HCFCl_2$, 75-43-4; $(CF_3)_2NOH$, 359-63-7; $(CF_3)_2NH$, 371-77-7; H_2S, 7783-06-4; $(CF_3)_2C$=NH, 1645-75-6; $[(CF_3)_2C$=N$]_2$, 1619-84-7; $HCCl_2OSO_2F$, 42016-50-2; CH_2Cl_2, 75-09-2; CH_3Br, 74-83-9; CH_3OSO_2F, 421-20-5; CH_3CH_2OH, 64-17-5; OCH_3, 108-88-3; $(CF_3)_2NOSO_2F$, 21950-99-2; $(CF_3)_2C$=NSO_3F, 42016-51-3; $((CF_3)_2C(OSO_2F)N)_2$, 42030-68-2; $CH_2(OSO_2F)_2$, 42016-52-4; $BrOSO_2F$, 13997-93-8; $(CF_3)_2C$=NCl, 10181-78-9; $(NH_3)_5S_3O_9F_2$, 39405-86-2; CF_3CO_2H, 76-05-1.

[19] R. F. Swindell, University of Idaho, unpublished results.

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Polar Additions of Chlorine Monofluoride and Chlorine Fluorosulfate to Fluorinated Isocyanates

GEORGE H. SPRENGER, KENNETH J. WRIGHT, and JEAN'NE M. SHREEVE*[1]

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The addition reactions of chlorine monofluoride and chlorine fluorosulfate with various fluorinated isocyanates give a new class of compounds, $R_fN(Cl)C(O)R_f'$. The new chloramines $CF_3N(Cl)C(O)F$, $CF_3C(O)N(Cl)C(O)F$, $FC(O)N(Cl)C(O)F$, $CF_3N(Cl)C(O)OSO_2F$, $CF_3C(O)N(Cl)C(O)OSO_2F$, and $FC(O)N(Cl)C(O)OSO_2F$, as well as the new secondary amines $CF_3C(O)N(H)C(O)F$ and $FC(O)N(H)C(O)F$, have been synthesized and characterized. The previously known compounds $Cl_2NC(O)F$ and $CF_3N(H)C(O)F$ were also prepared.

Chlorine monofluoride is a very versatile reagent which provides a route to the controlled fluorination and/or chlorofluorination of a variety of systems. With fluorinated compounds which contain the -N=S= linkage, *e.g.*, R_fN=S=O[2] and R_fN=SF_2,[3] 2 mol of ClF adds with concomitant severing of the nitrogen-sulfur double bond to form dichloramines, $-NCl_2$, and the respective sulfur(IV)-fluoro compounds. Compounds that result from complete saturation of the carbon-nitrogen multiple bonds in nitriles[4,5] and imines[4,6,7] by ClF are the sole products. Neither carbon-nitrogen bond breaking nor partial saturation of a triple bond is observed. Pursuing our study of the chemistry of ClF and isocyanates,

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