20.5 tr (J_{P-F} = 88.0 Hz) and −9.2 tr (J_{P-F} = 92.4 Hz) appeared.

Reaction of $(CF_3)_3PO$ with CH_3NH_2. One millimole of CH_3NH_2 was condensed into a 50-mL Pyrex flask that contained 3 mmol of $(CF_3)_3PO$. The mixture was allowed to warm overnight from −78 °C to room temperature. After volatile CF_3H (~1 mmol) and CH_3NH_2 were removed, a light yellow solid, $(CF_3)_2P(O)NHCH_3$, remained. ^1H NMR: δ 7.67 s; br (NH), 2.43 s (CH_3). ^{19}F NMR: ϕ −73.35 d (CF_3, J_{P-F} = 102.5 Hz). $^{31}P\{^1H\}$ NMR: δ −2.67 septet. IR: 3050 s, br, 2900 w, 2800 w, 2610 w, 2510 w, 1658 w, 1645 w, 1550 w, br, 1475 w, 1395 w, 1295 s, 1252 m, 1212 s, 1140 s, 1105 s, 1070 m, 980 m, 755 m, 585 vs, 510 s cm^{-1}. MS (EI) (*m/e* (species), %): 218 ($(CF_3)_2PONH_3CH_3^+$), 7.36; 198 ($(CF_3)_2PNCH_3^+$), 1.72; 157 ($C_2F_3PONCH_3^+$), 5.24; 146 ($CF_3PONCH_4^+$), 1.1; 133 (CF_3PONH^+), 4.25; 119 (CF_4P^+), 11.0; 100 (CF_3P^+), 6.59; 81 (CF_2P^+), 3.53; 78 ($P(O)NCH_5^+$), 3.7; 69 (CF_3^+), 100.

Reaction of $(CF_3)_3PO$ with Excess CH_3NH_2. Six millimoles of CH_3NH_2 as condensed into a 50-mL Pyrex flask that contained 2 mmol of $(CF_3)_3PO$. The mixture was allowed to warm overnight from −78 °C to room temperature. After volatile CF_3H (3.45 mmol) and CH_3NH_2 were removed, 0.34 g of a light yellow viscous liquid, $CF_3P(O)[NHCH_3]_2$, remained. ^1H NMR: δ 5.52 s, br (NH), 2.69 dd (CH_3, J_{CH_3-P} = 11.7 Hz, J_{CH_3-NH} = 4.4 Hz). ^{19}F NMR: ϕ −72.41 d (CF_3, J_{P-F} = 107.4 Hz); $^{31}P\{^1H\}$ NMR: 10.56 q. IR: 3250 m, br, 2940 w, 1390 s, br ($\nu_{P=O}$), 1293 m, 1235 s, 1210 s, 1110 s, br, 975 w, 890 m, 825 w, 810 m, 585 m, 565 m, 510 m cm^{-1}. MS (EI) (*m/e* (species), %): 175 ($M^+ - 1$), 1.43; 125 ($FPON_2HC_2H_6^+$), 1.42; 107 ($PON_2H_2C_2H_6^+$), 100; 96 (CF_2PNH^+), 8.48; 93 ($PON_2H_3CH_3^+$), 3.29; 78 ($PONH_2CH_3^+$), 35.71; 69 (CF_3^+), 7.06.

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Registry No. CF_3I, 2314-97-8; CF_3PI_2, 421-59-0; $(CF_3)_2PI$, 359-64-8; $(CF_3)_3P$, 432-04-2; $(CF_3)_3PO$, 423-01-8; CF_3H, 75-46-7; $(CF_3)_3P(NH_2)_2$, 115421-79-9; SF_4, 7783-60-0; $(C_4F_9)_2P(O)OH$, 52299-25-9; $(C_4F_9)_2PF_3$, 115421-80-2; $(Me_3Si)_2O$, 107-46-0; $(C_4F_9)_2PF_2(OSiMe_3)$, 115421-81-3; $(C_4F_9)_2P(O)F$, 115421-82-4; Me_3SiF, 420-56-4; $(C_4F_9)_3PF_2$, 91543-34-9; $(C_4F_9)_3PO$, 58431-34-8; $(CF_3)_2P(O)Cl$, 115421-83-5; $[(CF_3)_2P(O)]_3NH^+Cl^-{\cdot}N(Et)_3$, 115436-91-4; C_4F_9H, 375-17-7; $(C_4F_9)_2P(O)NH^-NH_4^+$, 115421-84-6; NH_4F, 12125-01-8; $C_4F_9P(O)(NHCH_3)_2$, 115421-85-7; $C_4F_9P(O)(N(CH_3)_2)$, 115421-86-8; $(C_4F_9)_2P(O)N(CH_3)_2$, 115421-87-9; $(C_4F_9)_3P[N(CH_3)_2]_2$, 115421-88-0; $(C_4F_9)_3P(OH)[N(CH_3)_2]$, 115421-89-1; $(C_4F_9)_2P(OH)[N(CH_3)_2]_2$, 115436-92-5; $C_4F_9P(O)[N(CH_3)_2]_2$, 115421-90-4; $C_4F_9P(OH)[N(CH_3)_2]_3$, 115436-93-6; $(CF_3)_2P(O)NHCH_3$, 31411-29-7; $CF_3P(O)[NHCH_3]_2$, 115421-91-5; $C_4F_9P(O)(NH_2)_2$, 115421-92-6.

Contribution from the Department of Chemistry,
Portland State University, Portland, Oregon 97207

A New Pentafluorothio (SF_5) Sultone: Rearrangement and Pathway to $SF_5CH_2SO_3H$. New Pentafluorothio Fluoro Esters

Robin J. Terjeson, Javid Mohtasham, and Gary L. Gard*

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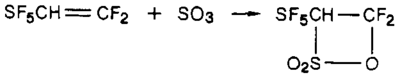
The new fluorosultone $SF_5\overline{CHCF_2OS}O_2$ has been prepared along with its rearranged isomer ($SF_5CH(SO_2F)COF$) and hydrolysis product ($SF_5CH_2SO_2F$); further reaction of $SF_5CH_2SO_2F$ with base and acid affords the corresponding sulfonic acid and salt: $SF_5CH_2SO_3H{\cdot}H_2O$ and $Ca(SF_5CH_2SO_3)_2$. New pentafluorothio (SF_5) esters, $SF_5CX(SO_2F)C(O)OR_f$ (R_f = CF_3CH_2, $(CF_3)_2CH$; X = H, F), have been synthesized by using the fluorosultones $SF_5\overline{CFCF_2OS}O_2$ and $SF_5\overline{CHCF_2OS}O_2$ with appropriate polyfluoro alcohols in the presence of sodium fluoride. In a like manner, the diester $[SF_5CF(SO_2F)C(O)OCH_2CF_2]_2CF_2$ was prepared from $HOCH_2(CF_2)_3CH_2OH$ and $SF_5\overline{CFCF_2OS}O_2$. These new esters, unlike fluorinated esters with fluorine at the alkoxy α-carbon atoms, are stable in the presence of fluoride ion at 25 °C or higher temperature. The new compounds are characterized by their IR, NMR (^1H, ^{19}F, ^{13}C), and mass spectra.

Introduction

Fluorinated sultones are occupying an ever-increasing importance in the synthesis of new sulfonyl fluorides (RSO_2F, R = hydrocarbon or fluorocarbon moieties). The incorporation of the sulfonyl fluoride group into molecular systems can lead to compounds useful as ion-exchange resins, surface-active agents, and thermally stable and strong sulfonic acids.[1-5] Since fluorinated sultones lead to new RSO_2F systems, it is of considerable interest that new sultones with unique structural features be prepared. While there are a number of fluorocarbon sultones, only one sultone with the unique pentafluorothio group (SF_5) exists.[3] We wish to present our success in preparing the second SF_5-containing sultone and its rearrangement, hydrolysis, and reaction chemistry leading to $SF_5CH_2SO_3H$; in addition, results obtained by using both SF_5-containing sultones in preparing new SF_5-containing fluorosulfonyl fluoro esters will be reported.

Results and Discussion

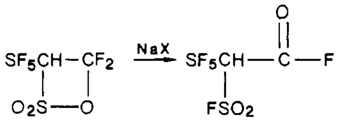
The new pentafluorothio β-sultone 2-hydroxy-1-(pentafluoro-λ^6-sulfanyl)-2,2-difluoroethanesulfonic acid sultone, $SF_5\overline{CHCF_2OS}O_2$, was prepared via the reaction of $SF_5CH{=}CF_2$ with monomeric sulfur trioxide in a Carius tube under autogeneous pressure at 100 °C:



$$SF_5CH{=}CF_2 + SO_3 \longrightarrow \begin{array}{c} SF_5CH{-}CF_2 \\ |\quad\;\; | \\ O_2S{-}O \end{array} \qquad (1)$$

The $SF_5\overline{CHCF_2OS}O_2$ product is a stable crystalline solid with a vapor pressure of 9 Torr at 22 °C; it melts at 47–48 °C.

The SF_5 sultone undergoes rearrangement in the presence of NaX (X = I, F), giving the isomeric bifunctional fluoride 2-(fluorosulfonyl)-2-(pentafluoro-λ^6-sulfanyl)acetyl fluoride:



$$\begin{array}{c} SF_5CH{-}CF_2 \\ |\quad\;\; | \\ O_2S{-}O \end{array} \xrightarrow{NaX} \begin{array}{c} \\ SF_5CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}F \\ | \\ FSO_2 \end{array} \qquad (2)$$

In the presence of water, $SF_5\overline{CHCF_2OS}O_2$ undergoes rearrangement, followed by a concerted hydrolysis–decarboxylation reaction:

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(1) Haszeldine, R. N.; Kidd, J. M. *J. Chem. Soc.* **1954**, 4228.
(2) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, 2640.
(3) Canich, J. M.; Ludvig, M. M.; Gard, G. L.; Shreeve, J. M. *Inorg. Chem.* **1984**, *23*, 4403.
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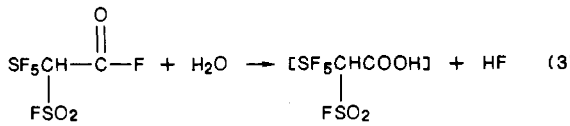
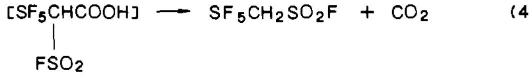
0020-1669/88/1327-2916$01.50/0



$$\mathrm{SF_5CH(FSO_2){-}C({=}O){-}F + H_2O \longrightarrow [SF_5CH(FSO_2)COOH] + HF} \tag{3}$$



$$\mathrm{[SF_5CH(FSO_2)COOH] \longrightarrow SF_5CH_2SO_2F + CO_2} \tag{4}$$

Attempts to isolate the acid intermediate prior to decomposition failed. The final SF_5-containing product, $SF_5CH_2SO_2F$ (hydryl(pentafluoro-λ^6-sulfanyl)methanesulfonyl fluoride), is a stable, colorless liquid that boils at 110–111 °C. Treatment of the SF_5 sulfonyl fluoride compound with an aqueous sodium hydroxide solution gives in solution the corresponding sodium sulfonate salt, which, when treated with gaseous hydrogen chloride, produces the desired SF_5 sulfonic acid:

$$SF_5CH_2SO_2F + 2NaOH(aq) \rightarrow [SF_5CH_2SO_3Na] + NaF + H_2O \tag{5}$$

$$[SF_5CH_2SO_3Na] + HCl(g) \rightarrow SF_5CH_2SO_3H(aq) + NaCl(s) \tag{6}$$

The new SF_5-containing acid hydryl(pentafluoro-λ^6-sulfanyl)methanesulfonic acid hydrate is isolated from solution and purified by sublimation; it is a white solid that melts at 97 ± 1 °C. The corresponding salt of this acid can be prepared by reacting the sultone with an appropriate base:

$$2SF_5CHCF_2OSO_2 + 5Ca(OH)_2(aq) \rightarrow Ca(SF_5CH_2SO_3)_2 + 2CaCO_3 + 2CaF_2 + 4H_2O \tag{7}$$

In addition to preparing the SF_5-containing sultone, its rearranged product, and eventually a new SF_5 sulfonic acid, we have found that interaction of SF_5-containing sultones, $SF_5CXCF_2OSO_2$ (X = F, H), with fluoroalcohols produces new SF_5-containing sulfonyl fluoride esters:

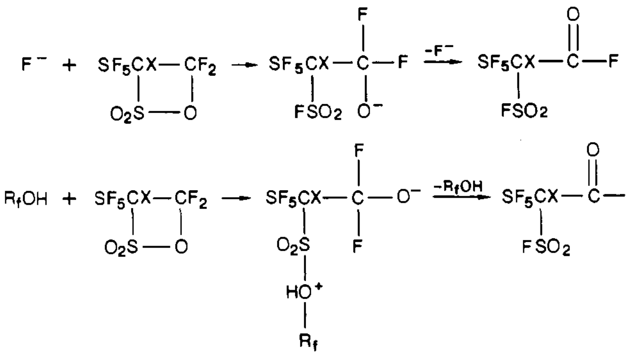
$$SF_5CXCF_2OSO_2 + R_fOH + NaF \rightarrow SF_5CX(SO_2F)C(O)OR_f + NaHF_2 \tag{8}$$

$$R_f = CF_3CH_2, (CF_3)_2CH; X = H, F$$

With a fluorinated dialcohol the following diester is produced:

$$2SF_5CFCF_2OSO_2 + HOCH_2(CF_2)_3CH_2OH + 2NaF \rightarrow [SF_5CF(SO_2F)C(O)OCH_2CF_2]_2CF_2 + 2NaHF_2 \tag{9}$$

The new SF_5-containing sulfonyl fluoride esters are clear, colorless liquids that are stable upon heating. Mechanistically, in ester formation, the sodium fluoride and/or the alcohol serves as a catalyst for the rearrangement of the sultone:[6,7]



The resulting acid fluoride reacts with alcohols, in the presence of NaF, forming the corresponding ester and $NaHF_2$. These routes to the stable ester products are strongly supported by the isomerization of β-sultones with different nucleophiles to the acyclic isomer:[3-7]

$$XCFCF_2OSO_2 \xrightarrow{A} FSO_2CFXC(O)F \tag{10}$$

$$A = F^-, Et_3N, H_2O, \text{dioxane}; X = F, CF_3$$

Additional support for the rearrangement mechanism is found by examining reaction mixtures prior to final workup. In these reaction mixtures, it was found via infrared spectral studies that the sultone had rearranged during the course of the reaction to $SF_5CX(SO_2F)C(O)F$ (X = H, F).

The infrared spectra for all new compounds have in common the characteristic absorption bands of the SF_5 group. Cross and co-workers[8] reported that the most intense band for compounds containing the SF_5 grouping should appear in the region 850–920 cm^{-1} (SF stretching modes) and in the region of 600 cm^{-1} (S–F deformation modes). For the new compounds reported in this paper, absorption bands in the 816–930-cm^{-1} region are found with the new SF_5 esters having absorptions in the higher part of this range. The SF_5 deformation modes are located in the 597–620-cm^{-1} range.

For compounds containing CF and CF_3 groups, the C–F stretching vibration is usually located in the 1000–1100-cm^{-1} region[9] while marked absorption in the range 1360–1300 cm^{-1} can be correlated with the CF_3 group.[9] In the compound SF_5CFHCF_3, the C–F stretching vibration was assigned to the 1161-cm^{-1} absorption band.[10] For the new esters, the stretching vibration for the CF group appears to be located in the 1100–1200-cm^{-1} region while the CF_3 group is located in the 1230–1390-cm^{-1} region. The CF_3 deformation band is located in the 737–760-cm^{-1} region.[9]

Compounds containing the $-SO_2-$ functional group exhibit a strong asymmetric stretching band in the 1419–1469-cm^{-1} region and a strong symmetric stretching band in the 1200–1259-cm^{-1} range. This assignment is complicated in some cases by the appearance of strong carbon–fluorine absorption bands in the 1110-1300-cm^{-1} region, but in any case, the above assignment agrees closely with that found for CF_3SO_2F and other fluorosulfonyl derivatives.[11] For the sulfonyl fluoride group, the strong S–F absorption band is located near 786 cm^{-1} and is in the region found for other sulfonyl fluorides.[12] This band disappears when the acid/salts are formed from $SF_5CH_2SO_2F$. The asymmetric and symmetric SO_3 stretching bands for the sulfonic acid hydrate $SF_5CH_2SO_3H{\cdot}H_2O$ and calcium salt are found in the 1223–1244- and 1033–1064-cm^{-1} regions, respectively; for salts containing the $CF_3SO_3^-$ group the respective regions are 1266–1279 and 1025–1042 cm^{-1}.[11] The carbonyl stretching frequency is characteristically found in the 1790–1834-cm^{-1} range for esters prepared from $SF_5CFCF_2OSO_2$ and in the 1750–1820-cm^{-1} range for the esters prepared from $SF_5CHCF_2OSO_2$; the carbonyl frequencies for the esters prepared from the perfluorinated sultone are significantly higher and are in line with the expected inductive effect. The C–H absorption bands are located near 3000 cm^{-1} (for SF_5CFHCF_3 the C–H stretching frequency was found at 3007 cm^{-1}).[10] The acid $SF_5CH_2SO_3H{\cdot}H_2O$ gave a broad O–H absorption band centered at 3308 cm^{-1}.

The major mass spectral peaks for these compounds are listed in the Experimental Section. The molecular ion peaks were not observed for any of the compounds listed; however, many did show M – X peaks such as $(M - F)^+$, $(M - HF)^+$, and $(M - H_2O)^+$. For the sultone I the $(M - H)^-$ peak was found. Prominent peaks (*m*/*e*) at 89 (SF_3^+) and 127 (SF_5^+) were observed for all compounds, and a peak at 69 (CF_3^+) occurred in all esters except

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[7] Huang, T. J.; Dong, Z. X.; Shreeve, J. M. *Inorg. Chem.* **1987**, *26*, 2304.

[8] Cross, L. H.; Cushing, G.; Roberts, H. L. *Spectrochim. Acta* **1961**, *17*, 344.

[9] Brown, J. K.; Morgan, K. J. *Adv. Fluorine Chem.* **1965**, *4*, 256.

[10] Efner, H. F.; Kirk, R.; Noftle, R. E.; Uhrig, M. *Polyhedron* **1982**, *1*, 723.

[11] Robinson, E. A. *Can. J. Chem.* **1961**, *39*, 247.

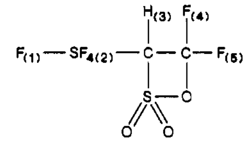
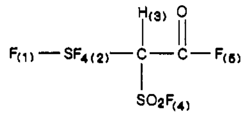
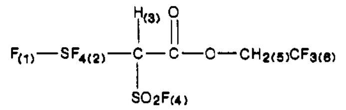
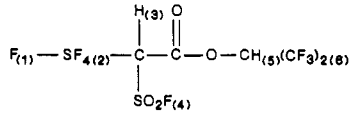
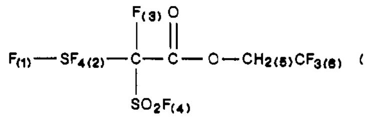
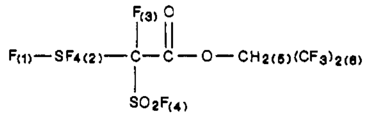
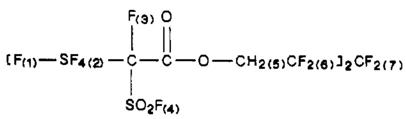
[12] Ham, N. S.; Hambly, A. N.; Laby, R. H. *Aust. J. Chem.* **1960**, *13*, 443.

Table I. NMR Chemical Shifts[a,c]

compd	SF_{ax}	$S(F_{eq})_4$	CF_3	CF_2	CF	SO_2F	CH	CH_2
$SF_5\overline{CHCF_2OSO_2}$ (I)[g]	69.4 (m)			−72.8 (d) −79.7 (d)			6.58 (m)	
$SF_5CH(SO_2F)COF$ (II)[b]	66 (9-line)	72.2 (d)				58.4	6.18 (d, p)	
$SF_5CH_2SO_2F$ (III)	71.4 (m)					58.5 (m)[d]		5.33 (m)
$(SF_5CH_2SO_3)_2Ca$ (IV)	76.7 (9-line)	64.3 (d)						5.0 (p)
$SF_5CH_2SO_3H{\cdot}H_2O$ (V)[f,h]	81.4 (9-line)	68.1 (d)						5.13 (p)[e]
$SF_5CH(SO_2F)COOCH_2CF_3$ (VI)	70.0 (m)		−76.4 (t)			57.0 (p)	6.23 (p, d)	4.83 (br q)
$SF_5CH(SO_2F)COOCH(CF_3)_2$ (VII)	70.5 (m)		−75.4 (d)			58.5 (p)	6.20 (p) 6.07 (sept)	
$SF_5CF(SO_2F)COOCH_2CF_3$ (VIII)	62.3 (9-line)	56.5 (d)	−76.2 (t)		−123.5 (d, p)	48.9 (p)		4.97 (q)
$SF_5CF(SO_2F)COOCH(CF_3)_2$ (IX)	61.5 (9-line)	57.2 (d)	−75.2 (d)		−119.0 (d, p)	49.6 (p)	6.25 (sept)	
$[SF_5CF(SO_2F)COOCH_2CF_2]_2CF_2$ (X)	62.6 (9-line)	56.7 (d)		−121.3 (br t) −127 (br s)	−123.4 (br p)	49.1 (br p)		5.22 (br t)

[a] Fluorine chemical shifts in ppm from $CFCl_3$ and proton chemical shifts in ppm downfield from TMS. [b] Chemical shift for the COF fluorine is 46.5 ppm (m); it is found at 30.4 ppm in $SF_5CF(SO_2F)COF$.[3] [c] Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septet, br = broadened, m = multiplet. [d] For SF_5CHFSO_2F and $CF_3CH_2SO_2F$ the chemical shifts are ϕ +51.3 and +64.45, respectively.[3,17] [e] δ values:[3,17] SF_5CHFSO_2F, 6.31; $CF_3CH_2SO_2F$, 4.10. [f] The chemical shift for the proton on $-SO_3H$ is 10.22 ppm. [g] In Freon-11. [h] In CD_3CN.

Table II. ^1H and ^{19}F NMR Coupling Constants

compd	coupling const, Hz	
 (I)	$J_{1,2} \approx 130$ $J_{4,5} = 103$	$J_{2,3} = 4.6$
 $F_{(1)}{-}SF_{4(2)}{-}C(H_{(3)})(SO_2F_{(4)}){-}C(=O){-}F_{(5)}$ (II)	$J_{1,2} = 148.9$ $J_{2,3} = 3.0$ $J_{2,4} = 12.0$ $J_{2,5} = 8.7$	$J_{3,5} = 4.9$ $J_{4,5} = 12$
$F_{(1)}{-}SF_{4(2)}{-}CH_{2(3)}SO_2F_{(4)}$ (III)		
$(F_{(1)}{-}SF_{4(2)}{-}CH_{2(3)}SO_3)_2Ca$ (IV)	$J_{1,2} = 141.1$ $J_{2,3} = 7.5$	
$F_{(1)}{-}SF_{4(2)}{-}CH_{2(3)}SO_3H{\cdot}H_2O$ (V)	$J_{1,2} = 141.1$ $J_{2,3} = 7.5$	
 $F_{(1)}{-}SF_{4(2)}{-}C(H_{(3)})(SO_2F_{(4)}){-}C(=O){-}O{-}CH_{2(5)}CF_{3(6)}$ (VI)	$J_{1,2} \approx 100$ $J_{1,3} = 2.3$ $J_{2,3} = 4.5$	$J_{2,4} = 12.8$ $J_{5,6} = 7.8$
 $F_{(1)}{-}SF_{4(2)}{-}C(H_{(3)})(SO_2F_{(4)}){-}C(=O){-}O{-}CH_{(5)}(CF_3)_{2(6)}$ (VII)	$J_{1,2} \approx 122$ $J_{2,3} = 4.5$	$J_{2,4} = 11.8$ $J_{5,6} = 5.4$
 $F_{(1)}{-}SF_{4(2)}{-}C(F_{(3)})(SO_2F_{(4)}){-}C(=O){-}O{-}CH_{2(5)}CF_{3(6)}$ (VIII)	$J_{1,2} = 141$ $J_{1,3} = 3.0$ $J_{2,3} = 3.0$	$J_{2,4} = 9.4$ $J_{5,6} = 7.4$
 $F_{(1)}{-}SF_{4(2)}{-}C(F_{(3)})(SO_2F_{(4)}){-}C(=O){-}O{-}CH_{2(5)}(CF_3)_{2(6)}$ (IX)	$J_{1,2} = 136$ $J_{1,3} = 3.0$ $J_{2,3} = 3.0$	$J_{2,4} = 10.1$ $J_{5,6} = 5.6$
 $[F_{(1)}{-}SF_{4(2)}{-}C(F_{(3)})(SO_2F_{(4)}){-}C(=O){-}O{-}CH_{2(5)}CF_{2(6)}]_2CF_{2(7)}$ (X)	$J_{1,2} = 136$ $J_{1,3} = 3.0$ $J_{2,3} = 3.0$	$J_{2,4} = 9.2$ $J_{5,6} = 12$

$[SF_5CF(SO_2F)COOCH_2CF_2]_2CF_2$. Appropriate fragments were found for cleavages at the $-C(O)O-$ functional group in the esters.

The NMR spectra generally consist of complex multiplets (see Table I for chemical shift values). Some of the first-order coupling constants were determined and are reported in Table II. In most cases the SF_5 fluorine resonances consist of the AB_4 multiplet with B_4 equatorial fluorine split into a doublet and the A part into a nine-line pattern. In compounds I, III, VI, and VII the AB_4 pattern is overlapping; therefore, the chemical shifts and/or coupling constants could only be approximated. The AB_4 pattern in $SF_5CH(SO_2F)COF$ is reversed with the A axial fluorine pattern occurring upfield from the B_4 doublet. Compounds I, VI, and VII also show overlap and reversal of the AB_4 pattern compared to that for other SF_5 systems. This reversal of the AB_4 pattern has also been noted for SF_5NCO and $SF_5C{\equiv}CH$.[13,14] The

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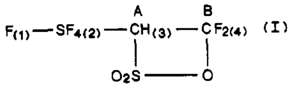
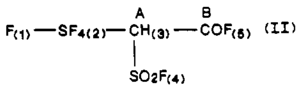
Table III. ^{13}C NMR Spectra[a]

 (I)	δ_A = 99.6 (d, p, m) $J_{A,2}$ = 23	δ_B = 112.0 (br p) $J_{B,2}$ = 3.8 $J_{B,4}$ = 293
 (II)	δ_A = 88.5 (d, d, p, d) $J_{A,2}$ = 21.6	δ_B = 146.8 (d, p) $J_{B,2}$ = 2.9 $J_{B,5}$ = 363.5
$F_{(1)}SF_{4(2)}\overset{A}{C}H_{2(3)}SO_2F_{(4)}$ (III)	δ_A = 77.6 (m)	
$F_{(1)}SF_{4(2)}—\overset{A}{C}H_{2(3)}—SO_3H\cdot H_2O$ (V)	δ_A = 82.8 (br s)	

[a] Solvent $CDCl_3$; chemical shifts in ppm relative to TMS and coupling constants in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, p = pentet, br = broadened, m = multiplet.

chemical shift values for the SF_5 group in all compounds fall within the expected range.[15,16] It is interesting to note that the collapse and reversal of the SF_5 pattern occurs only for derivatives of sultone I and not for derivatives of $SF_5\overline{CFCF_2OSO_2}$. The acid SF_5CFHSO_3H gives SF_{ax} at 72.3 ppm and $S(F_{eq})_4$ at 53.5 ppm,[3] while compound V gives SF_{ax} at 81.4 ppm and $S(F_{eq})_4$ at 68.1 ppm. The axial and equatorial fluorine chemical shifts of the SF_5 group in SF_5CH_2CHFBr are 79.9 and 66.4 ppm, respectively.[16]

The ^{19}F NMR resonance for the fluorosulfonyl group is found in the range 48.9–58.5 ppm. The splitting pattern of the CF_2 group for the new sultone I consists of a doublet of doublets exhibiting the weak–strong–strong–weak pattern reported for other fluorinated sultones.[3,4,17] The ^{1}H NMR spectra for all compounds were self-consistent with respect to the expected chemical shifts for CH and CH_2 groups.

In general, we find that replacing a hydrogen with fluorine on carbon adjacent to an SF_5 group results in greater shielding (shift to high field) for all fluoro groups present; for example, in going from $SF_5CH_2SO_2F$ to SF_5CHFSO_2F the SF_{ax}, $S(F_{eq})_4$, and SO_2F groups are more shielded by 6, 16, and 7 ppm, respectively. Also, as one goes from $SF_5CH(SO_2F)R$ to $SF_5CF(SO_2F)R$, where R = C(O)F, C(O)OR′, greater shielding for the SF_{ax}, $S(F_{eq})_4$, SO_2F, and C(O)F groups is found. While it is impossible to rule out anisotropic effects produced upon replacing a hydrogen with fluorine, it is suggested that, inductively, replacement by fluorine allows for electron donation from that fluorine to other fluoro groups, thereby causing a general increase in shielding. Correspondingly, the CF resonance is deshielded in molecular systems in which SF_5, SO_2F, C(O)F, and C(O)OR groups are present.

Coupling constants for the SF_{ax} to $S(F_{eq})_4$ fluorines in the new compounds vary from approximately 100 to 149 Hz. The coupling constants for $J_{1,2}$ could not be determined for compound III. It is interesting to note that the lower values for $J_{1,2}$ occur in compounds derived from sultone I and go as low as 100 Hz in ester IV. The sultone $SF_5\overline{CFCF_2OSO_2}$ and its derivatives have an AB_4 coupling in the range J = 141–157 Hz; one exception is found for $SF_5CF(SO_2F)COF$ with $J_{1,2}$ = 100.1 Hz.[4] Esters derived from this sultone and reported here have coupling constants $J_{1,2}$ in the 136–141-Hz range; by comparison, the ester $SF_5CF(CF_3)COOCH_3$ has $J_{1,2}$ = 144 Hz.[16] The compounds containing the sulfonyl fluoride grouping vicinal to $S(F_{eq})_4$ have values in the range $J_{2,4}$ = 9.2–12.8 Hz.

The new sulfonyl fluoride esters contain fluorine–fluorine and fluorine–proton coupling constants that are self-consistent. In esters VIII, IX, and X the $J_{1,2}$ and $J_{2,3}$ values are the same, 3.0 Hz. The coupling constant $J_{4,5}$ = 103 Hz in β-sultone I is approximately the same as in $SF_5\overline{CFCF_2OSO_2}$, where $J_{4,5}$ = 104 Hz. The coupling $J_{2,3}$ values in compounds I, II, and V vary considerably; 4.8, 3.0, and 7.5 Hz, respectively. These values reflect the differences in structure with different group attachments to the SF_5CH moiety. Due to the complexity of the spectrum, no coupling constants could be determined for compound III.

The ^{13}C NMR spectral data for compounds I, II, III, and V are given in Table III. Chemical shift values for the carbon next to an SF_5 group, C(A), range from 77.6 to 99.6 ppm; for C(B) in I and II the values are 112.0 and 146.8 ppm, respectively. Compound V has only a broadened singlet at 77.6 ppm while III has a band center of a complex multiplet at 82.8 ppm. The coupling constant for I ($J_{B,4}$) is in good agreement with values reported for other cyclic systems; for c-C_4F_8 and c-$C_4F_4Cl_4$ the J_{CF} values are 298 and 300 Hz, respectively.[18] The large J_{CF} coupling ($J_{B,5}$) value of 363.5 Hz for II is in good agreement with that of other acyl fluorides.

Experimental Section

Materials. The compounds used in this work were obtained from commercial sources: SO_3 (MCB); NaF (Baker); $(CF_3)_2CHOH$ (Eastman); CF_3CH_2OH (PCR); HCl (Matheson); NaOH (Baker); $Ca(OH)_2$ (Baker); $MgSO_4$ (Mallinckrodt). $HOCH_2(CF_2)_3CH_2OH$ was obtained from 3M and sublimed prior to use. All other reagents were used without further purification. $SF_5CH{=}CF_2$ and $SF_5CF{=}CF_2$ were synthesized by literature methods.[16,19]

General Procedure. Gases were manipulated in a conventional Pyrex-glass vacuum apparatus equipped with a Heise-Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained with use of a Pyrex-glass gas cell equipped with KBr windows or as liquids or solids between KBr or KRS-5 disks on a Nicolet 20DX spectrometer. The NMR spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine resonances or on a Bruker AM400 spectrometer operating at 400.1 MHz for proton, 376.5 MHz for fluorine, and 100.6 MHz for carbon resonances. TMS, $CFCl_3$, and $CDCl_3$ were used as external/internal standards. The mass spectra were recorded with a VG 7070 HS mass spectrometer with an ionization potential of 70 eV. Perfluorokerosene was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, West Germany.

$SF_5CH{=}CF_2$ with SO_3. Into a 130-mL Pyrex-glass Carius tube equipped with a Kontes Teflon valve were placed 52.3 mmol of SO_3 and 57.05 mmol of $SF_5CH{=}CF_2$. The mixture was heated for 24 h at 95 ± 5 °C. Distillation gave 30.33 mmol of a white solid, $SF_5\overline{CHCF_2OSO_2}$, in 58% yield: bp 108–111 °C (600 mm); mp 47–48 °C.

The infrared spectrum had the following bands (cm^{-1}): 3002 (wm), 1419 (s), 1315 (s), 1271 (s), 1203 (vs), 1106 (s), 1078 (s), 965 (m), 916 (vw), 878, 845, 819 (vs, b), 750 (vs), 684 (s), 669 (w), 656 (ms), 612 (ms), 575 (m, sh at 565), 525 (s), 444 (m), 403 (m).

The ^{19}F NMR spectrum (ϕ) gave the following relative peak areas: SF_5 (4.94), CF_2 (1 ÷ 1). Negative ion (Cl)$^-$ mass spectrum (m/e, species, %): 269, $(M - H)^-$, 11.1; 142, $C_2F_2SO_3^-$, 13.5; 138, $SC_2SO_3H_2^-$, 17.1; 136, $SC_2SO_3^-$, 21.2; 127, SF_5^- or $FSCSO_2^-$, 100; 123, $C_2FSO_3^-$, 9.5; 83, SF_2CH^- or SO_2F^-, 34.5; 81, SO_3H^-, 30.7; 79, $CHCF_2O^-$, 29.6.

Anal. Calcd. for $C_2HF_8O_3S_2$: C, 8.89; H, 0.37; S, 23.74; F, 49.2. Found: C, 9.05; H, 0.51; S, 23.63; F, 48.9.

$SF_5\overline{CHCF_2OSO_2}$ with NaF. Into a 50-mL Pyrex-glass round-bottom flask equipped with a Teflon stirring bar were placed 29 mmol of dried NaF and 12.4 mmol of $SF_5\overline{CHCF_2OSO_2}$. The reaction vessel was connected to a reflux condenser and dry-ice trap, which was attached to a drying tube. The mixture was heated at 60 °C with stirring (4 days). Distillation gave a clear liquid in 58% yield; bp 115–117 °C.

The infrared spectrum had the following absorption bands (cm^{-1}): 3037 (vw), 2980 (w), 1856 (m), 1448 (ms), 1387 (vw), 1291 (wm), 1222 (m), 1181 (w), 1116 (w), 1078 (vw), 872 (vs, b, sh at 850, 834, 816, 803), 772 (wm), 681 (w), 656 (w), 609 (wm), 578 (m), 572 (m), 559 (ms), 487 (w), 450 (w), 419 (w), 413 (w).

The ^{19}F NMR spectrum gave the following relative peak areas: SF (1.1); SF_4 (4.8); SO_2F (1.1); COF (1.0).

$SF_5\overline{CHCF_2SO_2}$ with H_2O. Into a 40-mL Kel-F vessel equipped with a Teflon stirring bar was placed 17.74 mmol of $SF_5\overline{CHCF_2OSO_2}$. The reaction vessel was cooled to 0 °C, and 88 mmol of H_2O was added slowly with stirring over a period of 4 h. The mixture was allowed to

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stand at room temperature overnight, after which the lower layer was separated, washed with water, and dried over $MgSO_4$. Distillation gave 9.03 mmol of $SF_5CH_2SO_2F$ in 51% yield; bp 110–111 °C.

The infrared spectrum had the following bands (cm^{-1}): 3037 (m), 2980 (m), 1478 (w), 1441 (s), 1384 (m), 1356 (w), 1291 (ms), 1222 (s), 1181 (m), 1150 (w), 1075 (w), 1028 (w), 894, 872 (vs, b), 847 (s), 831 (s, sh at 816), 791 (m), 769 (m), 709 (wm), 656 (ms), 613 (m), 578 (s), 559 (s), 487 (m), 450 (m), 406 (m).

The ^{19}F NMR spectrum gave the following relative peak areas: SF_5 (5.0) and SO_2F (1.0). EI^+ mass spectrum (*m/e*, species, %): 204, $(M - F)^+$, 2.23; 129, $FSCH_2SO_2^+$, 6.92; 127, SF_5^+ or $FSCSO_2^+$, 100; 97, $CH_2SO_2F^+$ or $FSCH_2S^+$, 25.71; 89, SF_3^+, 42.59; 78, $CHSO_2^+$ or SCF_2S^+, 8.25; 67, SOF^+, 53.44.

Anal. Calcd for $CH_2F_6O_2S_2$: C, 5.36; H, 0.90; S, 28.61; F, 50.9. Found: C, 5.48; H, 0.90; S, 28.59; F, 50.8.

$SF_5CH_2SO_2F/SF_5CH_2SO_3Na$ with HCl. Into a 50-mL Pyrex-glass round-bottom flask equipped with a Kontes Teflon valve and a Teflon stirring bar were placed 20 mL (1389 mmol) of H_2O and 78.5 mmol of NaOH. To this solution, cooled to 0 °C, was slowly added 27.8 mmol of $SF_5CH_2SO_2F$ (2 days). The mixture was heated to 50 °C (42 h) under reflux. Hydrogen chloride was slowly bubbled into this solution at room temperature for 1 h. The mixture was filtered; excess water was evaporated away. The crude product, $SF_5CH_2SO_3H{\cdot}H_2O$, was purified by sublimation: 6 mmol of $SF_5CH_2SO_3H{\cdot}H_2O$, yield 22%; mp 97 ± 1 °C.

The infrared spectrum had the following bands (cm^{-1}): 3308 (s, b), 3051 (w), 2987 (w), 1718 (m, b), 1400 (vw), 1242 (vs), 1223 (vs), 1177 (m), 1064 (m), 1029 (m), 900 (m), 892 (m), 876 (ms), 862 (m), 829 (m), 821 (ms), 810 (s), 772 (w), 695 (w), 649 (w), 624 (wm), 589 (ms), 564 (wm), 528 (m, sh at 517), 438 (vw).

The ^{19}F NMR spectrum (ϕ) gave the following relative peak areas: SF (1.0) and SF_4 (3.8). EI^+ mass spectrum (*m/e*, species, %): 223, $(M + H - H_2O)^+$, 0.73; 202, $SF_4CH_2SO_3^+$, 32.05; 149, $SF_2CH_2SO_2H^+$, 8.06; 127, SF_5^+ or $FSCSO_2^+$, 25.46; 122, SF_4CH^+, 71.88; 97, SCH_3S^+, 12.27; 95, $CH_2SO_3H^+$, 36.24; 89, SF_3^+, 100; 81, SO_3H^+, 15.57; 80, SO_3^+, 4.77; 70, SF_2^+, 9.48; 67, SOF^+, 15.37; 65, $FSCH_2^+$, 54.5; 64, $FSCH^+$ or SO_2^+, 18.55; 48, SO^+, 17.03; 44, CS^+, 8.22.

Anal. Calcd for $CH_5F_5O_4S$: C, 5.00; H, 2.10; S, 26.70; F, 39.5. Found: C, 5.30; H, 1.93; S, 26.55; F, 39.1.

$SF_5\overline{CHCF_2OS}O_2$ with CaO. Into a Pyrex-glass round-bottom flask was placed 11.6 mmol of $SF_5\overline{CHCF_2OS}O_2$, 26.8 mmol of CaO, and 14.7 g of H_2O. The mixture was heated at 50 ± 5 °C for a period of 1.1 days. CO_2 gas was bubbled vigorously through the mixture (15 min). It was then filtered and the salt dried under vacuum, giving 3.15 mmol of $Ca(SF_5CH_2SO_3)_2$ in 54.3% yield; dec 340 °C.

The infrared spectrum had the following bands (cm^{-1}): 3051 (vw), 2987 (vw), 1391 (w), 1286 (m), 1244 (s), 1223 (s), 1173 (ms), 1103 (m, sh at 1082), 1033 (m), 885 (ms), 871 (ms), 815 (ms), 779 (m), 702 (w), 653 (m), 618 (w), 597 (m), 562 (wm), 534 (w), 512 (m).

The ^{19}F NMR spectrum gave the following relative peak areas: SF (1.0) and SF_4 (4.0).

$SF_5\overline{CHCF_2OS}O_2$ with CF_3CH_2OH. Into a 100-mL Pyrex-glass reaction vessel equipped with a Teflon stirring bar and a kontes Teflon valve were placed 60 mmol of dried NaF, 19.05 mmol of $SF_5\overline{CHCF_2OS}O_2$, and 20.6 mmol of CF_3CH_2OH. The mixture was heated with stirring at 60 °C (4 days). Distillation under vacuum gave 13.38 mmol of $SF_5CH(SO_2F)C(O)OCH_2CF_3$ in 70% yield; bp 103 °C (100 mm).

The infrared spectrum of $SF_5CH(SO_2F)C(O)OCH_2CF_3$ had the following bands (cm^{-1}): 2987 (wm), 1785 (s), 1448 (s), 1412 (m), 1315 (s), 1293 (s), 1272 (s), 1223 (s), 1187 (s), 1147 (s), 1050 (w), 1033 (vw), 984 (ms), 875 (vs, b, sh at 920), 803 (ms), 775 (wm), 750 (wm), 694 (wm), 666 (wm), 644 (wm), 612 (m), 569 (s), 553 (m), 491 (m), 459 (w), 444 (w), 434 (w), 419 (w), 403 (w).

The ^{19}F NMR spectrum gave the following relative peak areas: SF_5 (5.3), SO_2F (1.0), and CF_3 (3.0). The ^1H NMR spectrum gave the following relative peak areas: CH (1.0) and CH_2 (2.2). EI^+ mass spectrum (*m/e*, species, %): 331, $(M - F)^+$, 0.93; 330, $(M - HF)^+$, 5.06; 251, $SF_5CHSO_2FCO^+$, 30.54; 231, $SF_5CSO_2CO^+$, 20.62; 209, $SF_3C_2SO_4^+$, 9.06; 127, SF_5^+ or $CF_3CH_2O^+$ or $FSCSO_2^+$, 44.79; 105, $CHSO_2CO^+$, 6.26; 89, SF_3^+, 67.29; 83, $CH_2CF_3^+$ or SO_2F^+, 100 + 3.08; 69, CF_3^+, 9.90; 67, SOF^+, 26.2; 51, SF^+, 4.07; 44, CS^+, 6.19.

Anal. Calcd for $C_4H_4F_{10}O_4S_2$: C, 13.72; H, 0.8635; S, 18.31; F, 48.8. Found: C, 13.86; H, 0.85; S, 18.24; F, 48.5.

$SF_5\overline{CHCF_2OS}O_2$ with $(CF_3)_2CHOH$. Into a 100-mL Pyrex-glass reaction vessel equipped with a Teflon stirring bar and a Kontes Teflon valve were placed 75.5 mmol of dried NaF, 17.73 mmol of $SF_5\overline{CHCF_2OS}O_2$, and 17.92 mmol of $(CF_3)_2CHOH$. The mixture was heated with stirring (7 days) at 45 ± 5 °C. Distillation under vacuum gave 14.18 mmol of liquid $SF_5CH(SO_2F)C(O)OCH(CF_3)_2$ in 80% yield; bp 98–100 °C (100 mm).

The infrared spectrum had the following bands (cm^{-1}): 2987 (wm), 1799 (ms), 1453 (ms), 1384 (ms), 1366 (ms), 1287 (ms, sh at 1303), 1269 (ms), 1237 (s), 1212 (s), 1118 (s), 1081 (wm), 1066 (wm), 969 (wm), 956 (wm), 897 (s), 875 (vs), 806 (wm), 784 (wm), 775 (wm), 756 (wm), 722 (wm), 691 (ms), 647 (w), 613 (ms, sh at 603), 569 (ms), 525 (w), 491 (w), 469 (w), 456 (wm), 419 (vw), 409 (w).

The ^{19}F NMR spectrum (ϕ) gave the following relative peak areas: SF_5 (5.3), SO_2F (1.0), and CF_3 (5.4). EI^+ mass spectrum (*m/e*, species, %): 401, $(M - H_2O)^+$, 0.28; 400, $(M - F)^+$, 0.77; 399, $(M - HF)^+$, 4.32; 398, $(M - H_2F)^+$, 6.65; 251, $SF_5CSO_2FCO^+$, 61.95; 231, $SF_5CSO_2CO^+$, 25.72; 195, $CO_2CH(CF_3)_2^+$, 44.12; 151, $CH(CF_3)_2^+$, 37.38; 143, $F_2SCHSCO^+$, 8.31; 127, SF_5^+ or $FSCSO_2^+$, 79.96; 105, $HCSO_2CO^+$, 8.54; 89, SF_3^+, 88.64; 83, SO_2F^+, 6.31; 69, CF_3^+, 100; 67, SOF^+, 40.57; 51, SF^+, 16.68; 48, SO^+, 5.6; 44, CO_2^+ or CS^+, 3.58.

Anal. Calcd for $C_5H_3F_{13}O_4S_2$: C, 14.36; H, 0.48; S, 15.34; F, 54.5. Found: C, 14.45; H, 0.53; S, 15.36; F, 54.2.

$SF_5\overline{CFCF_2OS}O_2$ with CF_3CH_2OH. Into a 100-mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were placed 116.7 mmol of dried NaF, 13.9 mmol of CF_3CH_2OH, and 13.5 mmol of $SF_5\overline{CFCF_2OS}O_2$. The mixture was stirred at 40–50 °C (5 days). Distillation of the mixture gave 10.35 mmol of the ester $SF_5CF(SO_2F)COOCH_2CF_3$ in 76.45% yield; bp 88 °C (101 mm).

The infrared spectrum had the following bands (cm^{-1}): 3051 (vw), 2995 (vw), 1806 (s), 1455 (s), 1413 (m), 1321 (s), 1293 (s), 1259 (s), 1230 (s), 1195 (vs), 1166 (vs), 1054 (m), 1026 (w), 991 (m), 977 (m), 955 (m), 927 (s), 913 (vs), 892 (vs), 871 (vs), 850 (s), 808 (ms), 787 (s), 681 (m), 667 (m), 653 (m), 646 (m), 639 (m), 611 (ms), 597 (s), 576 (s), 534 (w), 520 (vw), 491 (wm), 477 (w), 438 (wm).

The ^{19}F NMR spectrum (ϕ) gave the following relative peak areas: SF (0.9), SF_4 (4.0), SO_2F (1.1), CF (1.0), and CF_3 (3.0). CI^+ mass spectrum (*m/e*, species, %): 369, $(M + H)^+$, 0.4; 349, $(M - F)^+$, 1.2; 127, SF_5^+ or $FSCSO_2^+$ or $OCH_2CF_3^+$, 46.1; 89, SF_3^+, 61.6; 83, SO_2F^+ or $CF_3CH_2^+$, 100; 69, CF_3^+, 7.3; 67, SOF^+, 51.3; 64, SO_2^+, 5.8; 63, CFS^+, 4.7.

Anal. Calcd for $C_4F_{10}H_2S_2O_4$: C, 13.04; H, 0.54; F, 51.6; S, 17.39. Found: C, 13.09; H, 0.55; F, 52.3; S, 17.14.

$SF_5\overline{CFCF_2OS}O_2$ with $HOCH_2(CF_2)_3CH_2OH$. Into the same reaction vessel described previously were placed 115.2 mmol of dried NaF, 9.25 mmol of $HOCH_2(CF_2)_3CH_2OH$, and 23.8 mmol of $SF_5\overline{CFCF_2OS}O_2$. The mixture was stirred at 40–50 °C (4 days) and 60–70 °C (5 days). Distillation of the mixture gave 7.29 mmol of $(SF_5CF(SO_2F)COOCH_2CF_2)_2CF_2$ in 78.9% yield; bp 152 °C (15 mm).

The infrared spectrum had the following bands (cm^{-1}): 3044 (w), 2988 (w), 1806 (vs), 1785 (vs), 1462 (vs), 1406 (m), 1286 (vs), 1272 (vs), 1237 (vs), 1216 (vs), 1202 (s), 1181 (s), 1159 (s), 1124 (s), 1103 (m), 1082 (w), 1054 (m), 1019 (w), 977 (ms), 963 (ms), 934 (vs), 899 (vs), 878 (vs), 865 (vs), 850 (vs), 815 (vs), 801 (vs), 779 (vs), 766 (s), 738 (w), 731 (w), 716 (w), 709 (vw), 695 (m), 681 (m), 674 (m), 667 (m), 646 (w), 618 (s), 597 (s), 582 (s), 569 (s), 550 (w), 541 (m), 527 (w), 513 (vw), 491 (m), 470 (w), 456 (w), 435 (w), 414 (w).

The ^{19}F NMR spectrum (ϕ) gave the following relative peak areas: SF (0.9), SF_4 (4.0), SO_2F (1.0), CF (1.0), and CF_2 (2.1 for CF_2 external and 1.0 for CF_2 internal). CI^+ mass spectrum (*m/e*, species, %): 621, $(M - SF_5)^+$, 0.14; 269, $SF_5CF(SO_2F)C^+$, 15.05; 143, $C_3COOCFS^+$, 8.55; 175, $CH(CF_2)_3C^+$, 11.07; 127, SF_5^+, 13.03; 113, SF_2CFC^+, 6.21; 95, CSO_2F^+, 6.73; 89, SF_3^+, 100; 83, SO_2F^+, 3.08; 69, $COOCHC^+$, 6.30; 67, SOF^+, 43.67; 65, C_4HO^+, 14.77; 64, SO_2^+, 4.93; 51, SF^+, 7.74; 48, SO^+, 6.85; 41, $COCH^+$, 66.29.

Anal. Calcd for $C_9F_{20}H_4S_4O_8$: C, 14.44; H, 0.54; F, 50.7; S, 17.14. Found: C, 14.67; H, 0.46; F, 50.6; S, 15.90.

$SF_5\overline{CFCF_2OS}O_2$ with $(CF_3)_2CHOH$. Into a 100-mL Pyrex-glass reaction vessel containing a Teflon-coated stirring bar and 102.1 mmol of dry NaF were placed 138.2 mmol of $SF_5\overline{CFCF_2OS}O_2$ and 140.5 mmol of $(CF_3)_2CHOH$. The mixture was heated at 40–50 °C (24 days). Distillation of the mixture gave 107.6 mmol of $SF_5CF(SO_2F)COOCH(CF_3)_2$ in 77.5% yield; bp 124 ± 2 °C (455 mm).

The infrared spectrum had the following bands (cm^{-1}): 2988 (w), 1813 (s), 1469 (s), 1462 (s), 1384 (s), 1363 (ms), 1300 (s), 1258 (vs), 1237 (vs), 1209 (vs), 1166 (s), 1117 (vs), 1082 (m), 1061 (wm), 998 (w), 997 (mw), 948 (m), 906–892 (vs, b), 857 (s), 822 (m), 787 (s), 730 (m), 688 (s), 660 (w), 625 (mw), 583 (s), 576 (s), 548 (w), 527 (w), 512 (w), 491 (w), 470 (w), 428 (w).

CI^+ mass spectrum (*m/e*, species, %): 290, $S_2F_6C_4O_4^+$, 1.21; 225, $SF_5CF(SOF)^+$, 17.69; 195, $FSO_2CFCOOCHC_2^+$, 35.25; 151, CH-

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$(CF_3)_2^+$ or $SF_5C_2^+$, 79.44; 131, $C_2O_2CHC_2F_4^+$, 6.67; 89, SF_3^+, 100; 79, $CFSO^+$, 5.53; 78 $OC_2F_2^+$, 5.59; 70, SF_2^+, 10.30; 69, CF_3^+, 100; 67, SOF^+, 87.85; 65, SO_2H^+, 7.25; 64, SO_2^+, 9.18; 51, SF^+, 29.41; 50, CF_2^+, 9.67; 48, SO^+, 13.75.

Anal. Calcd for $C_5H_2F_{14}O_4S_2$: C, 13.70; H, 0.23; F, 56.6; S, 17.42. Found: C, 13.90; H, 0.34; F, 57.2; S, 17.14.

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Registry No. I, 113591-65-4; II, 115339-97-4; III, 115339-98-5; IV, 115340-05-1; V, 115339-99-6; VI, 115340-00-6; VII, 115340-01-7; VIII, 115340-02-8; IX, 115340-03-9; X, 115340-04-0; $F_5SCH{=}CF_2$, 58636-78-5; F_3CCH_2OH, 75-89-8; $(F_3C)_2CHOH$, 920-66-1; $HOCH_2(CF_2)_3CH_2OH$, 376-90-9; 4,4-difluoro-3-(pentafluorothio)-1,2-oxathietane 2,2-dioxide, 93474-29-4.

Contribution from the Laboratorium für Anorganische Chemie,
ETH Zürich, CH-8092 Zürich, Switzerland

Coordination Chemistry of Gold(I) with Cyanide and 1-Methylpyridine-2-thione. Kinetics and Thermodynamics of Ligand Exchange at Gold(I) in Aqueous Solution

Peter N. Dickson, Alex Wehrli, and Gerhard Geier*

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The equilibrium constants for the stepwise cyanide substitution at $Au(CN)_2^-$ by 1-methylpyridine-2-thione (mpt) were determined in acidic solution by UV spectroscopy. The kinetics of the forward and reverse reaction of $Au(CN)_2^-$ with mpt were studied by means of the stopped-flow method. Surprisingly, the rate constant in the exergonic direction is significantly below the diffusion-controlled limit. This reveals a lower reactivity of the Au(I) center compared with the metal center of similar Hg(II) and Ag(I) complexes. The reactivity of CN^- toward Au(CN)(mpt) is at least 7 orders of magnitude greater than that of HCN. This is indicative of an associative mechanism.

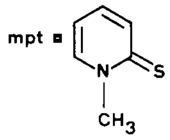
Introduction

The importance of gold(I) compounds in the treatment of rheumatoid arthritis has recently increased the interest in gold(I) coordination chemistry. Although structural aspects are well documented,[1] quantitative investigations of the thermodynamics of individual ligand-exchange reactions in aqueous solution are scarce, and knowledge about their kinetics is generally limited to the observation that Au(I) complexes are labile. Isad and Sadler[2] have estimated the rate constants and activation parameters for thiol exchange in gold-bound thiolates in solutions that contain predominantly polynuclear Au(I) species. In a very recent study by Boles Bryan, Mikuriya, Hempel, Mellinger, Hashim, and Pasternack,[3] the rate and equilibrium constants for the substitution of tetraacetylthioglucose by chloride in auranofin were measured in aqueous acid solutions. The dearth of information about the dynamics of ligand exchange is surprising in the light of the important role such processes are likely to play in the biological chemistry of Au(I).[4]

Many possibilities exist for facile reactions of Au(I)-containing antiarthritis drugs with S-containing molecules in the human body.[2] Indeed, some hypotheses suggest that Au(I) is the active moiety in these drugs and that sequential ligand-exchange processes alter the pharmacokinetics and intracellular distribution of the gold.[5] Evaluation of this and other hypotheses concerning the efficacy of gold therapy will require detailed understanding of all facets of the ligand-exchange process. In this paper we report a stopped-flow kinetic study on a ligand-exchange process at a mononuclear Au(I) in aqueous solution. In addition, new equilibrium information is presented.

In this and several other studies, the stable linear $Au(CN)_2^-$ was used as starting material. Protonation of the cyanide released upon ligand exchange facilitates the use of ligands with very different affinities in the studies of the kinetics and equilibria of ligand substitution reactions of $Au(CN)_2^-$. Cyanide can be displaced by various soft ligands without causing the disproportionation to Au(0) and Au(III). It was shown by Raman and ^{13}C NMR spectroscopy that thiolates (RS^-) form mixed-ligand complexes, $RSAuCN^-$, which undergo ligand redistribution to form $Au(CN)_2^-$ and $Au(SR)_2^-$.[6] The complex $Au(CN)(S_2O_3)^{2-}$ can be formed by dissolving AuCN in aqueous thiosulfate solution.[7] The stepwise substitution of CN^- on $Au(CN)_2^-$ by I^- could be studied spectrophotometrically.[8]

The present study utilizes the S-donor ligand 1-methylpyridine-2-thione (mpt). The reactions can be monitored directly



because the UV spectrum of mpt changes upon coordination with Au(I). Some years ago we used mpt in the investigation of rate-equilibria relationships for ligand-exchange reactions at CH_3Hg^{II}.[9] Starting with $Au(CN)_2^-$, eq 1, or with $Au(mpt)_2^+$, eq 2, it was possible to investigate the stepwise substitution reactions of mpt with $Au(CN)_2^-$. Similar thione complexes were shown to form linear complexes (with coordination through the S) by X-ray structure determination of chloro(1-propyl-1,3-imidazolidine-2-thione)gold(I)[10] and of bis(1-propyl-1,3-

$$Au(CN)_2^- + mpt + H^+ \rightleftharpoons Au(CN)(mpt) + HCN \quad (1)$$

$$Au(mpt)_2^+ + HCN \rightleftharpoons Au(CN)(mpt) + mpt + H^+ \quad (2)$$

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