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1,1,2,2-Tetrafluoro-2-(polyfluoroalkoxy)ethanesulfonyl Fluorides

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Several new 1,1,2,2-tetrafluoro-2-(polyfluoroalkoxy)ethanesulfonyl fluorides, $R_fOCF_2CF_2SO_2F$ (R_f = CF_3CH_2, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$, CH_3CH_2, $C(CF_3)_2H$, $CF_3CH(CF_3)$, $CH_3C(CF_3)_2$, $CH_2CF_2CF_2CF_2CH_2$, and $C(CH_2O)_4$), were prepared in good yield by fluorinating their corresponding esters with SF_4 in anhydrous hydrogen fluoride. Under the conditions used, cleavage of the acyl–oxygen bond or the carbon–sulfur bond was negligible. In addition, $CF_3CH_2OCF_2CF_2SO_2OCH_2CF_3$ and $CF_3CH_2OCF_2CF_2SO_2N(CH_3)_2$ were formed when $CF_3CH_2OCF_2CF_2SO_2F$ was reacted with CF_3CH_2OH and $(CH_3)_2NH$.

Introduction

Sulfur tetrafluoride has been demonstrated to be an extremely useful and versatile fluorinating reagent, particularly with molecules that contain one or more of a variety of organic functional groups, such as –C(O)OH, –C(O)H, –C(O)–, –OH, or –C≡N, or with inorganic compounds, e.g., $SeO_2 \rightarrow SeOF_2 \rightarrow SeF_4$. Apropos of the work reported here, earlier workers utilized sulfur tetrafluoride for the fluorination of the carbonyl functionality of esters to form difluoroethers,[1-4] e.g.

$$XArOC(O)Y \xrightarrow{SF_4/HF} XArOCF_2Y$$

X = H, NO_2; Y = F, CF_3

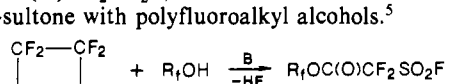
$$R_fC(O)OR \xrightarrow{SF_4/HF} R_fCF_2OR$$

R_f = C_7F_{15}, $C_2F_5O(CF_2CF_2O)_2CF_2$;
R = $C_2F_5CH_2$, $(CF_3)_2CH$, $(CF_3)_3C$

$$ROC(O)R_fC(O)OR \xrightarrow{SF_4/HF} ROCF_2R_fCF_2OR$$

R_f = $CF_2CF_2CF_2$; R = $(CF_3)_2CH$

Recently, we reported the high-yield, straightforward preparation of polyfluoroalkyl esters of difluoro(fluorosulfonyl)acetic acid, $R_fOC(O)CF_2SO_2F$, from the reactions of tetrafluoroethane-β-sultone with polyfluoroalkyl alcohols.[5]



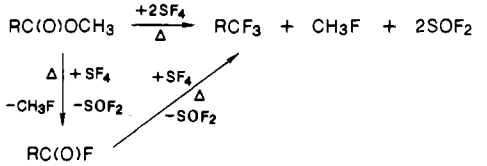
R_f = CF_3CH_2, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$, $(CF_3)_2CCH_3$, $CF_3CH(CH_3)$, $(CF_3)_2CH$, $C_7F_{15}CH_2$, $CH_2(CF_2)_3CH_2OC(O)CF_2SO_2F$

When alkanediols, -triols, and -tetraols were used, $RCH_n(CH_2OC(O)CF_2SO_2F)_{3-n}$ (R = CH_3, n = 0; R = O_2N, n = 0; $OC(O)CF_2SO_2F$, n = 2; R = $CH_2OC(O)CF_2SO_2F$, n = 0) were formed.[5] In (polyfluoroalkyl)difluoro(fluorosulfonyl)acetates, there are reaction centers at carbonyl and fluorosulfonyl that are available to react with (polyfluoroalkyl)-alcohols to produce alkanesulfonates.[5] Our interest was the fluorination of the carbonyl functionality in the (polyfluoroalkyl)difluoro(fluorosulfonyl)-acetates with the sulfur tetrafluoride to form corresponding α,-α-difluoro ethers. This has led to a general and direct synthesis of tetrafluoro(polyfluoroalkoxy)ethanesulfonyl fluorides, $R_fOCF_2CF_2SO_2F$.

$$R_fOC(O)CF_2SO_2F \xrightarrow[\Delta]{SF_4/HF} R_fOCF_2CF_2SO_2F$$

Results and Discussion

Uncatalyzed fluorination of carboxylic esters with sulfur tetrafluoride required vigorous conditions. Because of the easy scission of the carbon–oxygen single bond in esters, trifluoromethyl-containing compounds often were formed.[6]

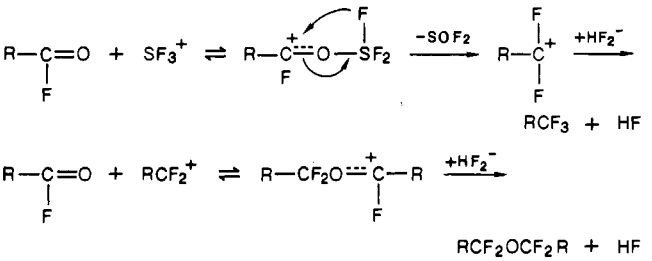


However, when anhydrous hydrogen fluoride (AHF) was used in large excess (10–15 times) with sulfur tetrafluoride, moderate yields of ethers were obtained under less rigorous temperature conditions. However, to obtain good product yields, a considerably larger excess of AHF was required per mole of ester functionality when R_f was bulky, e.g., $(CF_3)_2CCH_3$ or $(CF_3)_2CH$, or with $C[CH_2OC(O)CF_2SO_2F]_4$.

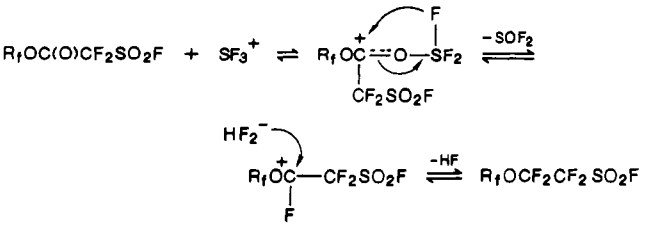
It is interesting to speculate on the role of AHF in these fluorination reactions with SF_4. Does the catalytic behavior result from activation of the carbonyl group or of the sulfur tetrafluoride molecule? Results from two independent studies[7,8] on the effect of AHF concentration on the rate of reaction of SF_4 with RC(O)F and ROH indicated that, in contrast to the view held previously, coordination of AHF to a carbonyl group inhibited its reaction with SF_4. Therefore, it is possible that the catalytic activity arises from activation of SF_4 by forming a strongly polar HF–SF_4 complex.

$$HF + SF_4 \rightleftharpoons SF_4{\cdot}HF \rightleftharpoons SF_3^+ + HF_2^-$$

Spectral and conductometric measurements by Gillespie[9] showed the existence of the ionic species SF_3^+ and HF_2^- in the SF_4–HF system.



In our work, the proposed mechanism for the reaction of acid fluorides with SF_4 seems consistent with our experience in utilizing SF_4/AHF to fluorinate the esters in this study.



This mechanism involves electrophilic attack by SF_3^+ on the

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carbonyl oxygen to form a mesomeric cation that eliminates SOF_2 to form a carbonium ion. The latter is attacked by the hydrogen difluoride ion to form the product. These new ethers are all colorless, slightly volatile or nonvolatile liquids at 25 °C. They are stable toward water and are thermally stable to at least 170 °C when pure.

Experimental Section

Materials. $CF_3CH_2OC(O)CF_2SO_2F$, $CF_3CF_2CH_2OC(O)CF_2SO_2F$, $CF_3CF_2CF_2CH_2OC(O)CF_2SO_2F$, $CH_3CH_2OC(O)CF_2SO_2F$, $(CF_3)_2CHOC(O)CF_2SO_2F$, $CF_3CH(CH_3)OC(O)CF_2SO_2F$, $CH_3C(CF_3)_2OC(O)CF_2SO_2F$, $CF_2(CF_2CH_2OC(O)CF_2SO_2F)_2$, and $C[CH_2OC(O)CF_2SO_2F]_4$ were prepared according to literature methods.[4] SF_4 and HF were obtained from Air Products and Chemicals, Inc., and were used as received.

General Procedures. A conventional Pyrex glass vacuum line equipped with Heise Bourdon tube and Televac pressure gauges was used to manipulate the volatile starting materials and to free products from impurities. Volatile compounds were measured quantitatively by using *PVT* techniques. Infrared spectra were recorded as liquid films between KBr disks with a Perkin-Elmer 599 spectrometer. ^{19}F NMR spectra were obtained on a JEOL FX-90Q Fourier transform spectrometer operating at 84.26 MHz. $CDCl_3$ was used as the solvent with $CFCl_3$ as an external reference. Chemical shifts upfield from $CFCl_3$ were assigned negative values. ^1H NMR spectra were obtained at an operating frequency of 89.94 MHz. Mass spectra were recorded by using a VG 7070 HS mass spectrometer with an ionization potential of 17 or 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of 1,1,2,2-Tetrafluoro-2-(2,2,2-trifluoroethoxy)ethanesulfonyl Fluoride, $CF_3CH_2OCF_2CF_2SO_2F$. Sulfur tetrafluoride (40 mmol) and hydrogen fluoride (40 mmol) were condensed into a Hoke stainless-steel vessel charged with $CF_3CH_2OC(O)CF_2SO_2F$ (4 mmol) at −196 °C and then warmed slowly to 25 °C. After 8 h of shaking, the vessel was heated at 70–80 °C for 85–90 h. The reaction mixture was transferred into a stainless-steel vessel charged with dry NaF (about 55 mmol). After the HF was absorbed, the reaction mixture was distilled by using trap-to-trap fractionation. The product was held in a trap at −70 °C. Both unreacted SF_4 and SOF_2 were collected in a trap at −196 °C. The yield was 90%.

The infrared spectrum of $CF_3{}^ACH_2{}^BOCF_2{}^CCF_2{}^DSO_2F^E$ is as follows: 2981 w, 1463 vs, 1422 m, 1337 s, 1302 s, 1248–1138 vs, br, 1079 w, 1044 m, 972 m, 812 s, 795 m, 738 w, 665 w, 649 w, 612 s, 543 w cm^{-1}. The ^1H NMR spectrum shows a quartet at δ 4.41 (J_{A-B} = 7.57 Hz). The ^{19}F NMR spectrum has overlapping triplets at ϕ 44.65 (E) ($J_{D-E} \sim J_{C-E}$ = 5.73 Hz), a triplet of triplets at ϕ −74.59 (A) (J_{A-C} = 2.5 Hz), a multiplet at ϕ −84.61 (C), and a doublet of triplets at ϕ −111.73 (D) (J_{C-D} = 4.15 Hz). The mass spectrum (CI^+) is as follows (*m/e*, species, %): 281, M − 1^+, 0.2; 263, M − F^+, 1.5; 199, $CF_3CH_2OCF_2CF_2^+$, 9.5; 149, $CF_3CH_2OCF_2^+$, 27.1; 83, SO_2F^+, 100; 69, CF_3^+, 16.1; 67, SOF^+, 41.1. Anal. Calcd for $C_4H_2F_8O_3S$: C, 17.02; H, 0.71; F, 53.90. Found: C, 17.15; H, 0.70; F. 54.1.

Several compounds were prepared in a similar manner from $R_fOC(O)CF_2SO_2F$ and SF_4/HF. Yields were based on the amount of $R_fOC(O)CF_2SO_2F$ used. The materials are colorless liquids at room temperature.

$CF_3{}^ACF_2{}^BCH_2{}^COCF_2{}^DCF_2{}^ESO_2{}^GF$ (Yield 76%). IR: 2978 w, 1466 vs, 1330 m, 1320 m, 1300 m, 1298 vs, 1210 vs, 1150 s, 1110 m, 1095 m, 1040 w, 1020 w, 975 w, 805 s, 737 m, 614 m cm^{-1}. ^1H NMR: δ 4.44 (C, tr) (J_{B-C} = 11.47 Hz). ^{19}F NMR: ϕ 44.36 (G, complex overlapping triplets), −84.15 (A, br s), −85.37 (D, mult), −111.78 (E, d of tr), −124.29 (B, tr of tr); J_{D-E} = 4.27 Hz, J_{E-G} = 5.61 Hz, J_{B-D} = 2.44 Hz. MS (CI^+) (*m/e*, species, %): 313, M − F^+, 4.7; 249, M − SO_2F^+, 12.0; 199, $CF_3CF_2CH_2OCF_2^+$, 12.0; 133, $CF_2SO_2F^+$, 100; 119, CF_3CF^{2+}, 24.1; 83, SO_2F^+, 15.7; 69, CF_3^+, 59.9; 67, SOF^+, 59.2; 64, SO_2^+, 8.3. Anal. Calcd for $C_5H_2F_{10}O_3S$: C, 18.07; H, 0.60; F, 57.23. Found: C, 18.09; H, 0.60; F, 57.3.

$CF_3{}^ACF_2{}^BCF_2{}^CCH_2{}^DOCF_2{}^ECF_2{}^GSO_2F^H$ (Yield 85%). IR: 2984 w, 1462 s, 1419 m, 1337 s, 1305 s, 1240 s, 1132 s, 1075 w, 1041 m, 1018 m, 979 m, 925 w, 909 m, 804 s, 760 w, 728 m, 681 w, 662 w, 611 s, 539 m, 512 w, 489 w, 465 w, 419 w cm^{-1}. ^1H NMR: δ 4.51 (tr). ^{19}F NMR: ϕ 44.54 (H, tr of tr), −81.20 (A, tr), −85.13 (E, tr), −111.6 (G, d or tr), −121.2 (B, mult), −127.7 (C, tr); J_{C-D} = 12.21 Hz, J_{E-G} = 9.15 Hz, J_{G-H} = 5.37 Hz. MS (EI^+) (*m/e*, species, %): 299, M − SO_2F^+, 3.92; 183, $CF_2CF_2SO_2F^+$, 10.9; 133, $CF_2SO_2F^+$, 5.85; 119, $CF_3CF_2^+$, 67.4; 83, SO_2F^+, 19.3; 69, CF_3^+, 59.9; 67, SOF^+, 100; 50, CF_2^+, 72.5. Anal. Calcd for $C_6H_2F_{12}O_3S$: C, 18.80; H, 0.52; F, 59.69. Found: C, 19.14; H, 0.65; F, 60.0.

$CF_3CH(CH_3)OCF_2CF_2SO_2F$ (Yield 81.6%). IR: 3000 w, 1453 s, 1382 w, 1325 w, 1288 m, 1231 s, 1200 s, 1170 s, 1150–1130 s, br, 1078 m, 1019 w, 981 w, 804–792 s, br, 649 w, 610 m cm^{-1}. ^1H NMR: δ 4.79 (CH, complex), 4.80 (*CH, complex), 1.53 (CH_3, d), 1.57 (*CH_3, d). ^{19}F NMR: ϕ 44.31 (SF, tr of tr), −79.72 (CF_3, tr), −79.66 (CF_3*, tr), −83.85 (OCF_2, mult), −111.66 (CF_2S, d of tr); J_{CH_3-CH} = 6.59 Hz, $J_{CF_3-OCF_2}$ = 3.42 Hz, J_{SF-OCF_2} = 5.99 Hz, J_{SF-CF_2S} = 5.61 Hz, $J_{CF_2-CF_2}$ = 4.52 Hz. MS (EI^+) (*m/e*, species, %): 227, M − CF_3^+, 12.5; 163, $CF_3CH(CH_3)OCF_2^+$, 11.1; 133, $FSO_2CF_2^+$, 4.5; 97, $CF_3CH(CH_3)^+$, 65.7; 93, $CF_2CO(CH_3)^+$, 5.1; 83, SO_2F^+, 3.9; 77, $CH_3CCF_2^+$, 100; 69, CF_3^+, 33.0; 67, SOF^+, 79.6. Anal. Calcd for $C_5H_4F_8O_3S$: C, 20.27; H, 1.35; F, 51.35. Found: C, 20.43; H, 1.36; F, 51.6.

$(CF_3)_2CHOCF_2CF_2SO_2F$ (Yield 75%). IR: 2998 w, 1470 s, 1368 m, 1332 w, 1309 m, 1260 vs, 1222 vs, 1197 m, 1160 s, 1118 m, 1071 w, 988 w, 908 w, 820 m, 800 m, 733 w, 696 m, 665 w, 643 w, 612 m cm^{-1}. ^1H NMR: δ 4.75 (CH, sept). ^{19}F NMR: ϕ 45.00 (SF, pentet), −73.90 (CF_3, d), −83.22 (OCF_2, mult), −111.95 (CF_2S, d of tr); J_{CF_3-CH} = 5.01 Hz, $J_{CF_2S-OCF_2}$ = 3.66 Hz, $J_{CF_2S-SF} \sim J_{CF_2O-SF}$ = 5.86 Hz. MS (CI^+) (*m/e*, species, %): 351, M + 1^+, 0.1; 331, M − F^+, 1.0; 267, M − SO_2F^+, 40.3; 217, $(CF_3)_2CHOCF_2^+$, 13.4; 151, $(CF_3)_2CH^+$, 73.0; 83, SO_2F^+, 1.1; 69, CF_3^+, 100; 67, SOF^+, 75.4 Anal. Calcd for $C_5HF_{11}O_3S$: C, 17.14; H, 0.29; F, 59.71. Found: C, 17.32; H, 0.27; F, 59.6.

$CH_3C(CF_3)_2OCF_2CF_2SO_2F$ (Yield 85%). IR: 2990 w, 1464 vs, 1303 vs, 1250 vs, 1210 vs, 1166–1150 vs, br, 1092 m, 1027 s, 997 w, 819 m, 798 s, 760 w, 740 w, 706 w, 646 w, 611 m cm^{-1}. ^1H NMR: δ 2.01 (CH_3, sept). ^{19}F NMR: ϕ 44.89 (SF, overlapping triplets), −76.79 (OCF_2, mult), −78 (CF_3, mult), −111.90 (CF_2S, d of tr); $J_{CF_3-CH_3}$ = 0.98 Hz, $J_{CF_3-CF_2S}$ = 4.27 Hz, $J_{OCF_2-CF_2S}$ = 4.03 Hz, J_{SF-CF_2O} = 5.61 Hz, J_{SF-CF_2S} = 5.98 Hz. MS (EI^+) (*m/e*, species, %): 295, M − CF_3^+, 0.8; 275, $CF_2C(CH_2^+)OCF_2CF_2SO_2F$, 5.0; 165, $CH_3C(CF_3)_2^+$, 6.6; 145, $CF_2C(CF_3)CH_2^+$, 57.7; 133, $FSO_2CF_2^+$, 6.1; 117, $FSOCF_2^+$, 6.0; 95, $(CF_3CCH_2)^+$, 10.1; 83, SO_2F, 1.5; 77, $CF_2C(CH_3)^+$, 31.7; 69, CF_3^+, 59.4; 67, SOF^+, 100. Anal. Calcd for $C_6H_3F_{11}O_3S$: C, 19.78; H, 0.82; F, 57.42. Found: C, 19.89; H, 0.86; F, 56.9.

$CH_3CH_2OCF_2CF_2SO_2F$ (Yield 69%). IR: 2999 s, 2950 m, 2931 m, 1467 vs, 1383 m, 1338 vs, 1245 vs, 1207 s, 1153 s, 1127 s, 1053 m, 1029 s, 985 m, 879 w, 852 w, 797 s, 759 m, 746 m, 656 m, 613 s, 548 m, 530 w, 513 w, 491 m, 466 w, 432 w cm^{-1}. ^1H NMR: δ 4.25 (CH_2, *q*), 1.37 (CH_3, tr); $J_{CH_3-CH_2}$ = 7.08 Hz. ^{19}F NMR: ϕ 42.92 (SF, tr of tr), −84.15 (OCF_2, tr of d), −111.8 (CF_2S, d of tr); J_{CF_2S-SF} = 5.30 Hz, $J_{OCF_2-CF_2S}$ = 5.00 Hz. MS (EI^+) (*m/e*, species, %): 227, M −1^+, 2.02; 145, $C_2H_5OCF_2CF_2^+$, 1.93; 95, $C_2H_5OCF_2^+$, 58.7; 83, SO_2F^+, 2.71; 67, SOF^+, 100; 64, SO_2^+, 72.6; 51, CF_2H^+, 17.8; 45, $C_2H_5O^+$, 6.21. Anal. Calcd for $C_4H_5F_5O_3S$: C, 21.05; H, 2.19; F, 41.67. Found: C, 21.25; H, 2.11; F 41.1.

Preparation of $CF_3CH_2OCF_2CF_2SO_2OCH_2CF_3$ and $CF_3CH_2OCF_2CF_2SO_2N(CH_3)_2$. Each of these compounds was prepared in a similar manner. To 2 mmol of $LiOCH_2CF_3$ (or 4 mmol of $HN(CH_3)_2$) in a 50-mL Pyrex glass vessel was added 2 mmol of $CF_3CH_2OCF_2CF_2SO_2F$. After 1 h at 0 °C and several hours at 25 °C, the product was removed under vacuum and purified by trap-to-trap distillation.

$CF_3CH_2OCF_2CF_2SO_2OCH_2CF_3$ (Yield 65%). IR: 2990 w, 1425 s, 1335 m, 1304–1286 s, br, 1225 s, 1179 s, 1148–1129 s, br, 1080 w, 1050 m, 1029 s, 969 s, 860 m, 820 m, 790 m, 745 w, 670 m, 650 w, 613 m, 565 w, 544 w, 442 w cm^{-1}. ^1H NMR: δ 4.68 (CH_2OSO_2, q), 4.38 ($CH_2OC(O)$, q). ^{19}F NMR: ϕ −74.77 (CF_3, tr), −84.84 (OCF_2, mult), −113.23 (CF_2SO_2, mult); $J_{CF_3-CH_2}$ = 7.57 Hz. MS (CI^+) (*m/e*, species, %): 343, M − F^+, 1.4; 279, $CF_3CH_2OCF_2CF_2SO_2O^+$, 8.4; 199, $CF_3CH_2OCF_2CF_2^+$, 8.2; 149, $CF_3CH_2OCF_2^+$, 13.8; 147, $CF_3CH_2OSO^+$, 30.6; 83, $CF_3CH_2^+$, 100; 69, CF_3^+, 8.0. Anal. Calcd for $C_6H_4F_{10}O_4S$: C, 19.89; H, 1.10; F, 52.49. Found: C, 20.02; H, 1.20; F, 52.4.

$CF_3CH_2OCF_2CF_2SO_2N(CH_3)_2$ (Yield 62%). IR: 2940 w, br, 1455 w, 1420 m, 1375 s, 1325 m, 1290 s, 1215–1170–1110 s, br, 1040 w, 975 s, 965 s, 955 s, 740 m, 720 s, 660 w, 640 w, 598 s, 590 s, 552 w, 540 w, 490 m cm^{-1}. ^1H NMR: δ 4.36 (CH_2, q), 3.07 (CH_3, mult). ^{19}F NMR: ϕ −74.25 (CF_3, tr of tr), −85.08 (OCF_2, mult), −114.9 (CF_2SO_2, mult); $J_{CF_3-CH_2}$ = 7.81 Hz, $J_{CF_3-OCF_2}$ = 2.38 Hz. MS (EI^+) (*m/e*, species, %): 307, M^+, 1.7; 208, $C_2F_4SO_2N(CH_3)_2^+$, 3.2; 155, $CF_2SO_2NC_2H_3^+$, 6.0; 149, $CF_3CH_2OCF_2^+$, 3.9; 111, $C_3H_2F_3O$, 3.1; 108, $SO_2N(CH_3)_2^+$, 100; 100, $C_2F_4^+$, 3.4; 83, $CF_3CH_2^+$, 35.1; 69, CF_3, 3.5; 44, $N(CH_3)_2^+$, 30.4. Anal. Calcd for $C_6H_8F_7NO_3S$: C, 23.45; H, 2.60, F, 43.32. Found: C, 23.43; H, 2.60; F, 43.0.

Preparation of $C(CH_2OCF_2CF_2SO_2F)_4$. SF_4 (100 mmol) and anhydrous HF (150 mmol) were condensed into a 75-mL stainless-steel vessel charged with $C(CH_2OC(O)CF_2SO_2F)_4$ (2.5 mmol) at −196 °C and then warmed slowly to room temperature. Shaking was continued for 8 h. The vessel was heated at 75–80 °C for 85–90 h. Volatile materials (SF_4, SOF_2, HF) were pumped out (HF must be absorbed by NaF). A liquid product and solid sulfur were left in the vessel. The colorless liquid was separated by filtration and then distillation. The yield was 50%. The infrared spectrum of $C(CH_2OCF_2CF_2SO_2F)_4$ is as follows: 2980 w, 1455 vs, 1412 w, 1337 s, 1215 vs, br, 1150 s, br, 1053 w, 1011 m, 967 w, 800

s, br, 662 m, 620 s, 544 m, 490 w, 464 w cm^{-1}. The ^1H NMR spectrum was a singlet at δ 4.11. The ^{19}F NMR spectrum showed a multiplet at ϕ 43.26 (SF), a multiplet at ϕ -86.18 (OCF_2), and overlapping triplets at ϕ -111.84 (CF_2S); $J_{CF_2S-OCF_2}$ = 5.96 Hz, J_{CF_2S-SF} = 5.86 Hz. MS (EI^+) (*m/e*, species, %): 664, $CHC(CH_2OCF_2CF_2SO_2F)_3^+$, 0.8; 464, $[C_3H_2(CH_2OCF_2CF_2SO_2F)_2]^+$, 22.2; 451, $[CHC(CH_2OCF_2CF_2SO_2F)_2]^+$, 11.6; 285, $[C_3H_4O_2(CH_2OCF_2CF_2SO_2F)]^+$, 8.7; 265, $[C_4H_4(CH_2OCF_2CF_2SO_2F)]^+$, 27.4; 213, $FSO_2CF_2CF_2OCH_2^+$, 30.3; 199, $FSO_2CF_2CF_2O^+$, 3.9; 183, $FSO_2CF_2CF_2^+$, 2.8; 133, $FSO_2CF_2^+$, 4.1; 85, $C_4H_5O_2^+$, 88.9; 83, SO_2F^+, 2.6; 67, SOF^+, 100. Anal. Calcd for $C_{13}H_8F_{20}O_{12}S_4$: C, 18.06; H, 0.93; F, 43.98. Found: C, 18.31; H, 1.02; F, 43.0.

Preparation of $F^GSO_2CF_2^ECF_2^DOCH_2^CCF_2^BCF_2^ACF_2^BCH_2^COCF_2^DCF_2^ESO_2F^G$. This compound was prepared in a similar manner from $FSO_2CF_2C(O)OCH_2CF_2CF_2CF_2CH_2OC(O)CF_2SO_2F$ and SF_4/HF. Tye yield was 59.5%. It is a colorless liquid. IR: 2978 w, 1455 s, 1410 w, 1327 s, 1240 s, 1198 s, 1170-1125 s, br, 1067 w, 1032 m, 1017 w, 970 m, 891 w, 800 s, 747 w, 723 w, 658 w, 610 s, 532 w cm^{-1}. ^1H NMR: δ 4.51 (CH_2, tr). ^{19}F NMR: ϕ 44.59 (G, tr of tr), -85.02 (D, mult), -111.49 (E, d of tr), -120.33 (B, mult), -125.16 (A, mult); J_{B-C} = 12.94 Hz, J_{E-G} = 5.74 Hz, J_{D-G} = 5.49 Hz, J_{D-E} = 5.01 Hz. MS (CI^+): 557, M - F^+, 6.3; 473, $CF_2CF_2OCHCFCF_2CF_2CH_2OCF_2CF_2SO_2F^+$, 13.3; 377, $CH_2CF_2CF_2CF_2CH_2OCF_2CF_2SO_2F^+$, 16.4; 357, $CHCFCF_2CF_2CH_2OCF_2CF_2SO_2F^+$, 15.3; 213, $CH_2OCF_2CF_2SO_2F^+$, 8.4; 183, $CF_2CF_2SO_2F^+$, 5.7; 167, $CF_2CF_2SOF^+$, 13.9; 133, $CF_2SO_2F^+$, 13.3; 83, SO_2F^+, 20.7; 67, SOF^+, 100. Anal. Calcd for $C_9H_4F_{16}O_6S_2$: C, 18.75; H, 0.69; F, 52.78. Found: C, 18.99; H, 0.80; F, 52.4.

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Registry No. $CF_3CH_2O(CF_2)_2SO_2F$, 109012-55-7; $CF_3CF_2CH_2O(CF_2)_2SO_2F$, 109012-56-8; $CF_3(CF_2)_2CH_2O(CF_2)_2SO_2F$, 109012-57-9; $CF_3CH(CH_3)O(CF_2)_2SO_2F$, 109012-58-0; $(CF_3)_2CHO(CF_2)_2SO_2F$, 109012-59-1; $CH_3C(CF_2)_2O(CF_2)_2SO_2F$, 109012-60-4; $EtO(CF_2)_2SO_2F$, 84506-53-6; $CF_3CH_2O(CF_2)_2SO_2OCH_2CF_3$, 109012-61-5; $CF_3CH_2O(CF_2)_2SO_2NMe_2$, 109012-62-6; $C(CH_2O(CF_2)_2SO_2F)_4$, 109012-63-7; $FSO_2(CF_2)_2OCH_2(CF_2)_3O(CF_2)_2SO_2F$, 109012-64-8; SF_4, 7783-60-0; HF, 7664-39-3; $CF_3CH_2O_2CCF_2SO_2F$, 108344-43-0; $CF_3CF_2CH_2O_2CCF_2SO_2F$, 108795-92-2; $CF_3(CF_2)_2CH_2O_2CCF_2SO_2F$, 108795-93-3; $EtO_2CCF_2SO_2F$, 756-21-8; $(CF_3)_2CHO_2CCF_2SO_2F$, 108795-89-7; $CF_3CH(CH_3)O_2CCF_2SO_2F$, 108795-90-0; $MeC(CF_3)_2O_2CCF_2SO_2F$, 108795-91-1; $CF_2(CF_2CH_2O_2CCF_2SO_2F)_2$, 108815-93-6; $C(CH_2O_2CF_2SO_2F)_4$, 108795-95-5; $LiOCH_2CF_3$, 69163-14-0.

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Equilibrium and Kinetic Studies of the Peroxo Complex of Molybdenum(VI) in Acidic Perchlorate Solution

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The principal equilibrium between molybdenum(VI) and hydrogen peroxide in acidic perchlorate solution is $HMoO_3^+ + 2H_2O_2 = MoO(O_2)_2 + H^+ + 2H_2O$. The value of the formation constant is $(9.4 \pm 0.6) \times 10^6$ M^{-1} at 25 °C over the range $[HClO_4]$ = 0.10-1.00 M at I = 1.00 M ($LiClO_4$); $\Delta H_f^\circ = -12 \pm 1$ kcal/mol and $\Delta S_f^\circ = -9 \pm 3$ cal/(K mol). Oxodiperoxomolybdenum(VI) shows an absorption maximum at 328 nm with an extinction coefficient of 1040 M^{-1} cm^{-1}. On the basis of spectral variations at $[HClO_4] \leq 0.10$ M, oxodiperoxomolybdenum(VI) is proposed to hydrolyze according to $MoO(O_2)_2 + H_2O = MoO(OH)(O_2)_2^- + H^+$, with K_a = 0.014 M at 25 °C. The rapid formation of $MoO(O_2)_2$ was studied by stopped-flow procedures. The rate expression was determined to be $d[MoO(O_2)_2]/dt = k_{forward}[HMoO_3^+][H_2O_2]^2 - k_{reverse}[MoO(O_2)_2][H^+]$. At 25 °C and I = 1.0 M, $k_{forward} = (2.3 \pm 0.4) \times 10^6$ M^{-2} s^{-1} + $((1.0 \pm 0.1) \times 10^6$ M^{-1} $s^{-1})/[H^+]$. The dissociation rates for $MoO(O_2)_2$ were measured in the presence of sulfur(IV), a very rapid reductant toward H_2O_2. The rate expression is proposed to be $-d[MoO(O_2)_2]/dt = k_{reverse}[MoO(O_2)_2][H^+] + k_{S(IV)}[MoO(O_2)_2][S(IV)]$; at 25 °C and I = 1.00 M, $k_{reverse} = 0.31 \pm 0.02$ M^{-1} s^{-1} + $(0.15 \pm 0.01$ $s^{-1})/[H^+]$. A reaction scheme is proposed in which entry and loss of the second peroxide ligand is rate-determining. The results of concentration-jump experiments are in accord with the reaction scheme. The results are compared with those obtained by other investigators for oxodiperoxochromium(VI). Diperoxo complexes of d^0 transition-metal ions appear to be much more reactive toward substrates than the monoperoxo complexes. Results of preliminary studies of the peroxo complex(es) of tungsten(VI) are presented.

Introduction

Molybdate is commonly used as a catalyst in the iodometric determination of hydrogen peroxide. A detailed kinetic study of this system in acidic solution has been reported.[1] It was proposed that a diperoxo complex of molybdenum(VI) was the reactive species toward iodide. Peroxo complexes of molybdenum(VI) have been used as oxidants for organic substrates[2] and are implicated as intermediates in the catalyzed epoxidation of olefins by alkyl hydroperoxides.[3-8] A number of crystal structures of peroxomolybdenum(VI) complexes have been reported,[9] and solution studies of the complexes have been reviewed.[10]

We have studied the redox chemistry of peroxo complexes of several d^0 transition-metal ions and compared the results to the corresponding reactions of hydrogen peroxide.[11-16] An important objective of this work is to increase our understanding of how metal ions modify the reactivity of peroxide. The advantage in using d^0 transition-metal ions is their ability to rapidly form peroxo complexes with large formation constants. We have recently turned our attention to molybdenum(VI) and are finding that its peroxo complex is markedly more reactive than hydrogen peroxide

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