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Two Fluorinated, Fluorosulfonyl-Containing Hypochlorites and Their Alkali-Metal Precursors

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The relatively stable hypochlorites $ClOCF_2CF_2SO_2F$ and $ClOCF_2CF(CF_3)SO_2F$ were synthesized either by chlorofluorination of the corresponding acid fluorides or by reaction of their potassium or cesium analogues with chlorine monofluoride or chlorine fluorosulfate. The thermolysis of the hypochlorites yields ClF and the acid fluorides $FC(O)CFXSO_2F$, while photolysis yields COF_2 and $ClCFXSO_2F$ ($X = F, CF_3$). They readily insert CO into the ClO bond but not SO_2. The latter catalyzes decomposition, giving the same products as observed from the photolysis. The precursor salt $KOCF_2CF(CF_3)SO_2F$ and $FC(O)CF(CF_3)SO_2F$ were investigated for their thermal stability in aprotic polar solvents. The complex decomposition leads to a number of products, viz. $C_2F_5C(O)F$, SO_2F_2, KSO_2F, CF_3CHFSO_2F, $CF_3CHFC(O)F$, and a remarkable complex formed from KF and $O{=}C{=}C(CF_3)C(O)C_2F_5$.

Introduction

Several methods are known for the synthesis of hypochlorites.[1] The formation of covalent highly fluorinated organic and inorganic hypochlorites requires positive chlorine-containing reagents[2] which are normally the readily available chlorine monofluoride and chlorine fluorosulfate. Polyfluorinated alcohols,[3,4] carboxylic acids,[5–8] and sulfonic acids[5–9] are converted to their corresponding chlorine derivatives by ClF and/or $ClOSO_2F$. In some cases, product HF and HSO_3F are difficult to separate and the yields of the pure hypochlorites are low.

In the course of the well-known chlorofluorination of fluorinated ketones,[10] an alkali-metal fluoride functions as a catalyst, forming the presumed intermediate $R_fR_fFC{-}O^-M^+$, which reacts with ClF to give hypochlorites and metal fluoride. Formation of the latter salt is an important part of the driving force of these reactions. Since the first synthesis of relatively stable fully fluorinated alkali-metal alkoxides,[11] this class of compounds has also been used to prepare hypochlorites by reaction with ClF or $ClOSO_2F$.[1,4,6–8,12,13]

In this paper we report further applications of these methods to the synthesis of novel fluorosulfonyl-containing compounds. The synthesis and properties of the precursor salts are described, followed by their reactions with ClF and $ClOSO_2F$ to form the hypochlorites; then the fluoride catalyzed chlorofluorination pathway is described, followed by a discussion of the stability of the hypochlorites and their reactivity with carbon monoxide and sulfur dioxide.

Experimental Section

General Methods. Gases and volatile liquids were transferred through either stainless-steel or glass vacuum systems, fitted with Teflon-packed stainless-steel valves or with glass–Teflon valves, respectively. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Amounts of reactants and products were determined by direct weighing or by *PVT* measurements, assuming ideal gas behavior. Reactions were carried out in 50-, 100-, or 250-mL Pyrex vessels fitted with glass–Teflon valves. Before use, they were dried in high vacuum at 200–400 °C.

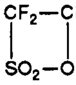
IR spectra were recorded on a Perkin-Elmer 1430 spectrometer with a Model 1500 Data System employing KCl or AgCl plates for 10-cm gas cells or for Nujol–solids mulls. ^1H and ^{19}F NMR spectra were measured on a JEOL FX-90Q or an IBM NR200AF spectrometer using generally C_6D_6, $CDCl_3$ and CD_3CN solutions of 1–2 mmol/L concentrations. The chemical shift values are relative to $CFCl_3$, as the internal standard for ^{19}F spectra.

Mass spectra were recorded with a Hewlett-Packard 5985-B spectrometer at 70 eV and a 200 °C source temperature for CI (CH_4) and EI, with samples introduced by gas injection or direct insertion.

Reagents. The starting materials F_2, Cl_2, SO_3, C_2F_4, C_3F_6, CO, SO_2, KF, and CsF were obtained from commercial sources. Active KF and CsF were prepared by fusion in a Pt dish followed by pulverization under very dry nitrogen in a porcelain mortar and then to a fine powder in a porcelain ball mill over a period of 8 h. Dry solid materials were handled inside an efficient drybox. Chlorine monofluoride[14] and chlorine fluorosulfate[15] (here at a scale of 160 mmol) were prepared by literature methods. Acetonitrile was distilled twice over P_4O_{10} and stored over molecular sieves. Dimethylformamide and diglyme were dried according to standard procedures.

Preparation of the Sultones. Sultones **1** and **2** were prepared according to literature methods.[16]

3,3,4,4-Tetrafluoro-1,2-oxathietane 2,2-Dioxide (1) and 5,5,6,6-Tetrafluoro-1,3,2,4-dioxadithiane 2,2,4,4-Tetraoxide (2). A Parr bottle (450 mL) was connected to a stainless-steel vacuum line. Several batches (between 0.2 and 1.0 mol) were run with partially solid SO_3; the optimum reaction conditions were found to be 60–70 °C and ~50 psi of C_2F_4 pressure. The pure sultone was obtained by trap to trap fractionation in which the sultone was trapped at −110 °C after passing through at −30 °C trap. ^{19}F NMR of **1**: $\delta(OCF_2)$ −90.3, $\delta(CF_2S)$ −100.0.



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When a big excess of SO_3 was applied (0.96 mol of SO_3; ~0.6 mol of C_2F_4) a different result was obtained. The mixture of solid SO_3 and sultone **1** was kept at room temperature for 1 week; after that time, no further C_2F_4 was absorbed by the liquid product. Fractional distillation gave sultone **1** (59 g, 0.33 mol, 34.4%) at −110 °C and pyrosultone **2**[16,17] (60 g, 0.23 mol, 47.9%) at −30 °C: mol wt 260.14 (calcd), 253.7 (found).

$\overline{\mathbf{CF_2{}^ACF_2{}^BSO_2OSO_2O}}$ **(2).** IR (10 Torr): 1495 (vs), 1468 (vs), 1370

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(m), 1313 (vs), 1242 (vs), 1170 (vs), 1102 (vs), 986 (vs), 932 (m), 885 (vs), 803 (vs), 763 (vs), 706 (m), 665 (m), 634 (m), 584 (s), 511 (vs) cm^{-1}. ^{19}F NMR: δ(A) −83.9 (t), δ(B) −117.7 (t); J_{AB} = 6.1 Hz.

3,3,4-Trifluoro-4-(trifluoromethyl)-1,2-oxathietane 2,2-Dioxide[16] **(3).** Sulfur trioxide (3.3 g, 41.2 mmol) and hexafluoropropene (50.8 mmol) were condensed into a thick-walled glass bomb (60 mL) at −196 °C. The reactor was sealed under vacuum and heated to 100 °C for 3 days. The clear liquid product was purified by trap to trap fractionation in vacuo; at −100 °C, pure sultone $CF_3\overline{CFCF_2OSO_2}$ (**3**) (9.3 g, 98%) was collected after passing through a −30 °C trap. IR and NMR data were in substantial agreement with literature values.

(Fluorosulfonyl)difluoroacetyl Fluoride[16] **(4).** A glass reactor (250 mL) was loaded with pulverized sodium fluoride (3.4 g), and sultone **1** (14.7 g, 82 mmol) was condensed in at −196 °C. The suspension was warmed up to 40–50 °C and stirred for 15 h, followed by fractional distillation, which gave the compound $FSO_2CF_2C(O)F$ (**4**) (14.7 g, 100%). IR and NMR data were in good agreement with literature values.

2,3,3,3-Tetrafluoro-2-(fluorosulfonyl)propanoyl Fluoride[16] **(5).** A glass reactor (250 mL) was loaded with sultone **3** (12.1 g, 52.6 mmol) and triethylamine (0.5 mmol) at −196 °C; when the reactor was slowly warmed up, a violent isomerization reaction occurred; the reaction mixture was allowed to stir at room temperature for an hour, followed by fractional distillation, which gave pure $FSO_2CF(CF_3)C(O)F$ (**5**) (11.7 g, 96.7%) at −110 °C. IR and NMR data agreed well with literature values.

[2-(Fluorosulfonyl)tetrafluoroethoxy]potassium (6). Method A. Into a glass reactor (250 mL), containing activated potassium fluoride (4.8 g, 83 mmol), sultone **1** (15 g, 83 mmol) was condensed at −196 °C. After warming up to room temperature, the suspension was stirred at 40 °C for 24 h; a white solid was formed after that time. Extraction with acetonitrile followed by drying gave the pure potassium salt **6** (19.5 g, 81.9 mmol, 98.6%). A reaction on a larger scale (0.4 mol of **1**) with an equimolar amount of KF in CH_3CN (30 mL) was carried out by warming the mixture slowly to 22 °C and then heating at 50 °C for 2 h. Washing the solid with CH_3CN and filtering gave **6** in 66.3% yield.

IR (KBr disk): 2096 (m, b), 1700 (s), 1512 (vs, br), 1430 (vs), 1383 (m), 1250 (s), 1221 (vs), 1176 (vs), 1076 (s), 933 (s), 870 (s), 795 (vs), 727 (m), 649 (s), 607 (vs), 543 (w), 487 (m) cm^{-1}. ^{19}F NMR for $KOCF_2{}^{A}CF_2{}^{B}SO_2F^{C}$: δ(A) −29.8 (br s), δ(B) −105.1 (br d), δ(C) 39.6 (br s).

Method B. A glass reactor (100 mL) was charged with potassium fluoride (2.6 g, 50.7 mmol), followed by **4** (7.6 g, 42.2 mmol) and acetonitrile (1.1 g) at −196 °C in vacuo. The mixture was warmed up slowly to room temperature and stirred for 24 h. The suspension was filtered off and the solvent removed in vacuum, and the solid remaining was pulverized and dried under vacuum. The yield of pure **6** was 6.5 g (65%).

Method C. A two-necked flask (250 mL), fitted with a reflux condenser with a T connection to a dry nitrogen stream on the top and a septum seal, was loaded with activated KF (15 g, 0.258 mol), acetonitrile (2 mL), and $CFCl_3$ (50 mL). The stirred mixture was cooled to −10 °C; using a syringe, pyrosultone **2** (30 g, 0.115 mol) was slowly dropped in. The $CFCl_3$ slightly boiled under reflux. When addition was complete, the cooling bath was removed and stirring was continued overnight at room temperature to evaporate the $CFCl_3$. To the remaining light yellow solid product was added acetonitrile (100 mL), and the resulting mixture was stirred until a fine suspension was formed. The filtration and washing was filtered under a dry nitrogen atmosphere and after evaporation of the solvent, pulverization and drying yielded the light yellow potassium salt **6** (10.2 g, 37%). The insoluble white precipitate (21 g) consisted of potassium fluorosulfate (^{19}F NMR, δ +37.1 in D_2O)[1] and unreacted potassium fluoride.

[2-(Fluorosulfonyl)tetrafluoroethoxy]cesium (7). The procedure followed was as reported for method A using CH_3CN solvent (3 mL) and a reaction time of 50 h. **1** (4.0 g, 22.4 mmol) gave pure cesium salt **7** (7.1 g, 95%). ^{19}F NMR for $CsOCF_2{}^{A}CF_2{}^{B}SO_2F^{C}$: δ(A) −27.9 (br s), δ(B) −104.7 (br s), δ(C) 39.8 (br s).

[1,1,2,3,3,3-Hexafluoro-2-(fluorosulfonyl)-1-propoxy]potassium (8). The procedure followed was the same as for **7**. Sultone **3** (6.0 g, 3 mmol) gave pure potassium salt **8** (6.3 g, 21.9 mmol, 84%) over a 12 h reaction time at 22 °C. ^{19}F NMR for $KOCF_2{}^{A}CF^{B}(CF_3{}^{C})SO_2F^{D}$: δ(A) −19.7 (d, pent), δ(B) −115.6 (d, t, q), δ(C) −71.3 (d, d, t), δ(D) 50.1 (sextet); J_{AB} = 18.8, J_{AC} = 6.7, J_{AC} = 11.0, J_{AD} = 12.0, J_{BC} = 2.5, J_{CD} = 12.0 Hz.

[1,1,2,3,3,3-Hexafluoro-2-(fluorosulfonyl)-1-propoxy]cesium (9). The same method as described for the preparation of **8** was used. Sultone **3** (4.0 g, 17.4 mmol) gave pure white cesium salt **9** (4.4 g, 11.5 mmol, 66%). ^{19}F NMR for $CsOCF_2{}^{A}CF^{B}(CF_3{}^{C})SO_2F^{D}$: δ(A) −20.0 (br s), δ(B) −155.7 (d, t, q), δ(C) −71.4 (d, d, t), δ(C) 50.1 (sextet); J_{AB} = 18.8, J_{BC} = 6.8, J_{AC} = 11.2, J_{AD} = 12.4, J_{BD} = 1.7, J_{CD} = 11.7 Hz.

Decomposition of [(2-Fluorosulfonyl)hexafluoropropoxy]potassium (8) in Acetonitrile. A glass reactor (250 mL), fitted with a Teflon valve, was loaded with potassium salt **8** (6.3 g, 22 mmol), and acetonitrile (1.2 g, 29 mmol) was added under vacuum at −196 °C. After warming to room temperature, the suspension was stirred for 2 h; then stirring was continued at 45 °C for an hour. The suspension turned orange after some minutes at elevated temperature. Volatile products were fractionated through traps cooled to −60, −110, and −196 °C. At −196 °C, a mixture of SO_2F_2, COF_2, and $C_2F_5C(O)F$[18] (2.0 g, 14.5 mmol) was condensed. At −110 °C a mixture of **5**, $C_2F_5C(O)F$, $CF_3CHFC(O)F$,[19] CF_3CHFSO_2F,[20] and CH_3CN (2.0 g) was found, and at −60 °C CH_3CN and a small amount of fluorocarbon compounds (1.0 g) were trapped. A pink solid (2.5 g) remained in the reactor. Both the IR and ^{19}F NMR spectra of the −196 °C fraction indicated SO_2F_2 and $C_2F_5C(O)F$ as major products and COF_2 as the minor part. All three compounds could not be separated by further fractionation in high vacuum, at 600 Torr or by gas chromatography for quantitative estimation. Assuming only a small amount of carbonyl fluoride, a molecular weight determination (gas density) resulted in an estimated ratio of a 1:1 mixture of SO_2F_2 and pentafluoropropionyl fluoride (7 mmol, 32% each). The compounds trapped at −110 °C were refractionated, giving $C_2F_5C(O)F$ (0.11 mmol, 0.5%) at −196 °C, CH_3CN (0.2 g) at −60 °C, and a mixture of the remaining compounds (1.8 g) at −115 °C. The latter was separated by GC to yield $CF_3CHFC(O)F$ (0.26 g, 1.8 mmol, 8.2%), CF_3CHFSO_2F (0.6 g, 3.3 mmol, 15%), and **5** (0.75 g, 3.3 mmol, 15%). The solid products, remaining in the reactor, were extracted with diethyl ether, yielding an orange powder **10** (1.5 g, ∼4.8 mmol) after the solvent was evaporated the residue dried under vacuum overnight. The insoluble solid salt (1.0 g) was also dried and then heated to a temperature >200 °C giving sulfur dioxide (0.5 g, 8 mmol) and potassium fluoride (0.5 g, 8.6 mmol); also the orange solid was heated to >150 °C in vacuo to yield light yellow (perfluoromethyl)propionylketene $O{=}C{=}CCF_3C(O)CF_2CF_3$ (**11**)[21] (0.7 g, 2.7 mmol). **11** was identified by MS, IR, and NMR data and a comparison with literature values.

$\mathbf{CF_3{}^{A}CH^{B}F^{C}C(O)F^{D}}$. ^{1}H NMR: δ(B) 5.34 (d–d–q). ^{19}F NMR: δ(D) 33.2 (d–d–q), δ(A) −75.8 (d–d–d), δ(C) −204.7 (d–d–q); J_{BC} = 45.5, J_{CD} = 30.5, J_{AD} = 8.3, J_{BC} = 6.1, J_{BC} = 2.7, J_{AC} = 12.5 Hz.

$\mathbf{K^+[OCF^{D}C(CF_3{}^{A})C(O)CF_2{}^{B}CF_3{}^{C}]^-}$ **(10).** Anal. Calcd for $C_6F_9KO_2$ (fw 314.15): C, 22.94; F, 54.43. Found: C, 22.44; F, 53.85; H, 0.57. IR (Nujol): 2045 (m), 1830 (m), 1725–1376 (m–vs, br), 1329 (s), 1235 (vs, br), 1044 (m), 916 (w), 750 (m), 649 (w) cm^{-1}. ^{19}F NMR ($(CD_3)_2CO$, 188.313 MHz): δ(D) 21.97 (t–q–q) (1 F), δ(A) −52.52 (d–t) (3 F), δ(B) −116.64 (d–q) (2 F), δ(C) −80.09 (s, br) (3 F); J_{AD} = 18.8, J_{BD} = 17.5, J_{AB} = 8.5, J_{CD} = 1.4 Hz.

Test Experiment for the Formation of 10. To a tube (5 mL) fitted with a Teflon stopcock were added potassium fluoride (0.5 g, 8.6 mmol) and ketene **11** (0.3 g, 1.0 mmol) by vacuum transfer at −196 °C; then the tube was warmed to 50–100 °C for 5 min. After cooling down, extracting with diethyl ether, and drying, the adduct **10** (≃0.25 g, ≃0.8 mmol, ≃80%) was isolated as a viscous orange liquid.

Reaction of 5 with Potassium Fluoride in Acetonitrile. In a glass reactor (250 mL), fitted with a Teflon stopcock, **5** (3.11 g, 13.5 mmol), active KF (1.33 g, 22.9 mmol), and acetonitrile (2.4 g) were combined at −196 °C; the reaction mixture was warmed to room temperature and stirred overnight. The volatile products were separated by fractionation. At −196 °C a mixture (12.7 mmol) of SO_2F_2 and $C_2F_5C(O)F$ and at −110 °C a mixture of CH_3CN, $CF_3CHFC(O)F$, and some unidentified fluorocarbon material (2.8 g) were trapped. The remaining orange solid was extracted with diethyl ether, yielding the potassium complex **10** (1.0 g, ≃3.2 mmol, ≃47%) and an insoluble residue of KSO_2F and KF (1.3 g). Potassium fluorosulfite was identified by heating the latter mixture to >200 °C, giving sulfur dioxide (10 mmol, 74%). In this reaction no COF_2 or CF_3CHFSO_2F was formed.

Reaction of 5 with Potassium Fluoride in Diglyme. The reactants, **5** (3.37 g, 14.6 mmol), KF (0.8 g, 13.8 mmol), and diglyme (1.1 g), were transferred to a glass reactor (250 mL) at −196 °C, and the reaction mixture was stirred for 22 h at room temperature followed by trap fractionation, which gave SO_2F_2 (major) and $C_2F_2C(O)F$ (11.8 mmol) at −196 °C and a mixture of products which were refractionated giving $C_2F_5C(O)F$, SO_2F_2, and $CF_3CHFC(O)F$ (major), $C_2F_5C(O)F$, and **5** (0.7 mmol) at −110 °C; at −60 °C some solvent and unidentified fluo-

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rocarbon material were trapped. The remaining orange liquid–solid suspension was dried in vacuo at room temperature overnight, giving a viscous orange liquid. This was extracted with CH_3CN to remove KSO_2F/KF (0.9 g), and the remaining orange liquid (2.1 g) was dissolved in ether. Removal of the ether under dynamic vacuum gave a solid foam, which could be pulverized to a powder after continued evacuation for 12 h at 22 °C.

Reaction of 5 with Potassium Fluoride in DMF. A glass reactor (250 mL) was loaded with KF (0.65 g, 11.2 mmol), dimethylformamide (1.73 g, 23.7 mmol), and **5** (2.44 g, 10.6 mmol) at −196 °C. The reaction mixture was warmed to room temperature and was stirred for 1 h followed by heating it to 100 °C for 10 min; the suspension turned orange. Volatile products were pumped through traps cooled to −20, −70, −110, and −196 °C. DMF was trapped mainly at −20 and −70 °C together with $(CH_3)_2NCH{=}CFCF_3$[22] (**12**) and some $CF_3CHFC(O)F$ (1.76 g). At −110 °C $CF_3CHFC(O)F$ (0.3 mmol) was recovered; at −196 °C a mixture of mainly SO_2F_2 and smaller amounts of CO_2 and a trace of COF_2 (10 mmol) were trapped. An orange syrup (1.8 g) stayed in the reactor, and the ^{19}F NMR spectrum indicated the K complex **10** and fluorocarbon oil.

2,3,3,3-Tetrafluoro-*N*,*N*-dimethyl-1-propen-1-amine (12), $(CH_3^X)_2NCH^Y{=}CF^ACF_3^B$. MS (EI): *m/e* 157 [$M^+$, 29.1], 156 [$(M - H)^+$, 14.8], 141 [$(M - CH_4)^+$, 6.7], 140 [$(M - CH_4 + H)^+$, 5.5], 101 [$C_2HF_4^+$, 16.7], 88 [$(M - CF_3)^+$, 20.8], 82 [$C_2HF_3^+$, 70.7], 69 [$CF_3^+$, 67.0], 51 [$CHF_2^+$, 22.4], 44 [$C_2H_6N^+$, 100] 42 [$C_2H_4N^+$, 26.7]. IR (5 Torr): 2935 (m), 2847 (m), 1720 (vs), 1334 (s), 1229 (s), 1187 (s), 1145 (s), 1109 (s), 1046 (s), 865 (w), 723 (w) cm^{-1}. NMR: $\delta(Y)$ 5.95 (d), $\delta(X)$ 2.89 (s), $\delta(B)$ −68.7 (d), $\delta(A)$ −181.1 (d–m–q); $J_{AB} = 16.1$, $J_{AZ} \simeq 1.8$, $J_{AY} = 28.9$ Hz.

Decomposition of 5 with a Catalytic Amount of KF in DMF. A solution of **5** (1.06 g, 4.6 mmol) in DMF (0.32 g, 4.4 mmol) containing KF (0.1 g, 1.7 mmol) was stirred for 3 h at 24 °C and 2 h at 50–60 °C. Fractionation gave a mixture of DMF, **12**, and CF_3CHFSO_2F (0.6 g) at −60 °C, a mixture of mainly $CF_3CHFC(O)F$ and traces of **5** and CF_3CHFSO_2F (1.05 mmol) at −110 °C, and SO_2F_2 (major) and small amounts of CO_2 and COF_2 (4.7 mmol) at −196 °C.

1-Chloroxy-2-(fluorosulfonyl)tetrafluoroethane (13). Method A. A stainless-steel cylinder (75 mL) was charged with **6** (1.07 g, 4.5 mmol) and chlorine monofluoride (4.5 mmol) at −196 °C. The reactor was warmed to −60 °C from −110 °C in a $CFCl_3$ bath during 1 h and was left for another 1 h at this temperature. Fractional distillation gave the yellowish hypochlorite **13** (1.7 mmol, 38%) at −60 °C and **4** (0.3 mmol) at −110 °C as well as COF_2 (1.7 mmol) at −196 °C. The solid remaining (0.63 g) was comprised of unreacted **6** and potassium fluoride. Under similar conditions, using the cesium salt **7** and warming from −110 to −20 °C over 6 h gave **13** in a 34% yield.

$ClOCF_2CF_2SO_2F$ (13). Vapor pressure: 100 Torr, 23 °C; MS: *m/e* (CI) 199 [$M - Cl)^+$, 1.4], 181 [$(M - ClF + H)^+$, 100], 161 [$(M - 2F - Cl)^+$, 12.4], 133 [$CF_3O_2S^+$, 6.8], 97 [$C_2F_3O^+$, 25.5], 95 [$C_3HF_2O_2^+$, 15.4], 87 [F_2HOS^+, 24.2], 69–67 [$CHClF^+$, SOF^+, 13.9–78.8], 65 [HO_2S^+, 37.7]; (EI) 85 [$C_2F_4^+$, 100]. IR (10 Torr): 1468 (vs), 1302 (m), 1247 (vs), 1196 (vs), 1139 (vs), 990 (s), 821 (s), 795 (Cl–O, s), 651 (m), 609 (s), 538 (w) cm^{-1}. ^{19}F NMR for $ClOCF_2^ACF_2^BSO_2F^C$: $\delta(A)$ −84.0 (d, t), $\delta(B)$ −109.4 (d, t), $\delta(C)$ 44.5 (pent); $J_{AB} = 2.8$, $J_{AC} = 6.6$, $J_{BC} = 5.5$ Hz.

Method B. A glass reactor (100 mL) was charged with potassium salt **6** (1.9 g, 8.0 mmol), and chlorine fluorosulfate (1.12 g, 8.3 mmol) was condensed in at −196 °C. The bulb was warmed up in a $CFCl_3$ bath from −110 °C to room temperature during the course of 12 h. Fractional distillation gave hypochlorite **13** (1.4 g, 6 mmol, 74.5%) at −60 °C beside some **4** and COF_2 at −110 and −196 °C respectively. The remaining white solid (1.3 g) consisted mainly of potassium fluorosulfate (^{19}F NMR: δ + 37.1 ppm).

Method C. Into a stainless-steel cylinder (75 mL) dry, unactivated potassium fluoride (8 g) was added, and **4** (0.5 g, 2.8 mmol) was condensed on the upper wall of the container at −196 °C in vacuo; then chlorine monofluoride (3.1 mmol) was added by vacuum transfer. The cylinder was allowed to warm up to room temperature in a cold empty dewar over 4 h. Dynamic fractionation gave pure hypochlorite **13** (0.5 g, 2.1 mmol, 76%) at −60 °C, **4** (<1 mmol) at −110 °C, and some ClF together with COF_2 at −196 °C.

1-Chloroxy-2-(fluorosulfonyl)hexafluoropropane (14). Method A. A glass reactor (250 mL) was loaded with the cesium salt **9** (3.7 g, 9.7 mol), and chlorine fluorosulfate (1.4 g, 10.4 mmol) was added by vacuum transfer at −196 °C in vacuo; then chlorine monofluoride (3.1 mmol) was added by vacuum transfer. The cylinder was allowed to warm to room temperature in a cold empty dewar over 4 h. Dynamic fractionation gave pure hypochlorite **14** (0.5 g, 2.1 mmol, 76%) at −60 °C, **4** (<1 mmol) at −110 °C, and some ClF together with COF_2 at −196 °C. Using only $ClOSO_2F$ and warming from −110 to +22 °C over 36 h gave 13 in only 44% yield. Using the potassium salt **8** with $ClOSO_2F$ and warming from −110 to −25 °C (7 h) followed by warming from 0.5 h each at −10 and 0 °C, gave **14** in 80% yield.

$ClOCF_2CF(CF_3)SO_2F$ (14). Vapor pressure: 40 Torr at 22 °C. MS: *m/e* (CI) 231 [$(M - ClO)^+$, 11.2], 211 [$(M - Cl - 2F)^+$, 100]; (EI) 147 [$C_3F_5O^+$, 12.1], 137–135 [$C_2ClF_4^+$, 4.6–11.6], 128 [$C_3F_4O^+$, 14.7], 119 [$C_2F_5^+$, 100], 100 [$C_2F_4^+$, 15.5], 85 [CF_3O^+, 43.4], 83 [SO_2F^+, 11.1] 69 [CF_3^+, 87.8], 67 [SOF^+, 49.4]. IR (5 Torr): 1472 (vs), 1249 (vs), 1177 (s), 1149 (s), 973 (s), 821 (s), 789 (Cl–O, m), 758–736–713 (w), 618 (s), 538 (w) cm^{-1}. ^{19}F NMR for $ClOCF_2^ACF^B(CF_3^C)SO_2F^D$: $\delta(A)$ −77.2 (d, d, q), $\delta(B)$ −163.4 (m), $\delta(C)$ −71.7 (d, d, t), $\delta(D)$ 55.0 (d, m); $J_{AB} = 11.3$, $J_{BC} = 7.8$, $J_{AC} = 9.0$, $J_{BD} = 4.1$, $J_{AD} = 10.5$, $J_{CD} = 10.8$ Hz.

Method B. The same procedure according to method C for **13** was used. The starting materials were **5** (1.2 g, 5.2 mmol), ClF (5.4 mmol), and unactivated KF (7 g, 120 mmol). The fractionation gave hypochlorite **14** (0.35 g, 1.2 mmol, 24%) at −60 °C, **5** (1.0 mmol, 19.2%) at −120 °C and an orange mixture of ClF, CO_2, and another substance (?) (2.7 mmol) at −196 °C. When active KF was used under the same conditions a lower yield of **14** (10.5%) was observed.

Reaction of Hypochlorite 13 with Carbon Monoxide. 1,1,2,2-Tetrafluoro-2-(fluorosulfonyl)ethyl Chloroformate (15). In a glass bulb (100 mL) CO (12 mmol) was added onto **13** (2.65 g, 11.3 mmol) at −196 °C. With stirring, the reaction mixture was warmed from −100 °C in an alcohol bath to room temperature during the course of 2 h and kept for several hours. Fractionation gave **15** (2.6 g, 9.9 mmol, 88%) at −60 °C as a colorless liquid and some **4** at −110 °C. **$ClC(O)OCF_2CF_2SO_2F$ (15).** Vapor pressure: 20 Torr at 24 °C. MS: *m/e* (CI) 283/281 [$(M + F)^+$, 4.6/13.1], 265/263 [$(M + H)^+$, 18.5/46.3], 183 [$C_2F_4SO_2F^+$, 6.4], 181/179 [$(M - SO_2F)^+$, 36.0/100]; (EI) 137/135 [$C_2ClF_4^+$, 7.3/23.4], 133 [$CF_2SO_2F^+$, 21.7], 119 [$C_2F_5^+$, 40.3], 100 [$C_2F_4^+$, 27.0], 85 [CF_3O^+, 10.6], 83 [SO_2F^+, 7.5], 69 [CF_3^+, 25.3], 67 [SOF^+, 100], 65/63 [$COCl^+$, 39.4/97.9], 50 [CF_2^+, 13.5]. IR (10 Torr): 1911 (w), 1837 (C=O, vs), 1811 (m), 1467 (vs), 1324 (s), 1247 (vs), 1212 (vs), 1180 (vs), 1147 (vs), 1065 (vs), 993 (s), 855 (m), 814 (vs), 757 (vs), 731 (m), 662 (s), 645 (s), 612 vs), 556 (w), 528 (w) cm^{-1}. ^{19}F NMR for $ClC(O)OCF_2^ACF_2^BSO_2F^C$: $\delta(A)$ −85.1 (d, t), $\delta(B)$ −112.2 (d, t), $\delta(C)$ 44.5 (pent); $J_{AB} = 2.8$, $J_{AC} = 6.6$, $J_{BC} = 5.5$ Hz.

Reaction of Hypochlorite 14 with Carbon Monoxide. 1,1,2,3,3,3-Hexafluoro-2-(fluorosulfonyl)propyl Chloroformate (16). The reaction was done as reported for **15**. The reactants, hypochlorite **14** (1.0 g, 3.5 mmol) and CO (4.0 mmol) were warmed to room temperature within 24 h and allowed to stand for 2 days. Fractionation gave **16** (0.4 g, 1.3 mmol, 36.6%) as a colorless liquid at −60 °C, **5** (1.9 mmol, 54.3%) at −110 °C, and a mixture of COFCl and SiF_4 (0.4 mmol) at −196 °C.

$ClC(O)OCF_2CF(CF_3)SO_2F$ (16). Vapor pressure: 18 Torr at 24 °C. MS (CI) 315/313 [$(M + H)^+$, 1.0/2.7], 295 [$(M - F + 2H)^+$, 7.4], 233 [$(M - CO_2Cl)^+$, 100], 231/229 [$(M - SO_2F)^+$, 4.9/15.9], 169 [$C_3F_7^+$, 29.4]; (EI) 150 [$C_3F_6^+$, 6.5], 135 [$C_2F_5^+$, 5.5], 119 [$C_2F_5^+$, 6.0], 199 [$C_2F_4^+$, 21.9], 85 [CF_3O^+, 10.5], 83 [SO_2F^+, 12.4], 69 [CF_3^+, 68.4], 67 [SOF^+, 100], 65/63 [$COCl^+$, 42.9/87.8], 50 [CF_2^+, 7.4], 49/47 [CCl^+, 1/3/10.6], 44 [CO_2^+, 8.4]. IR (9 Torr): 1892–1836–1776 (C=O, w–vs–w), 1472 (vs) 1289 (s), 1253 (vs), 1154 (s), 1061 (vs), 1027 (s), 975 (s), 852 (w), 819 (s), 759 (m), 722 (m), 702 (m), 674 (w), 616 (s) cm^{-1}. ^{19}F NMR for $ClC(O)OCF_2^ACF^B(CF_3^C)SO_2F^D$: $\delta(A)$ −78.0 (sextet) $\delta(B)$ −165.9 (m), $\delta(C)$ −71.6 (d, q), $\delta(D)$ 55.2 (d, sextet); $J_{AB} = 9.3$, $J_{AC} = 9.3$, $J_{BC} = 8.8$, $J_{AD} = 9.3$, $J_{BD} = 3.7$, $J_{CD} = 10.0$ Hz.

Reaction of Hypochlorite 13 with Sulfur Dioxide. A glass reactor (100 mL) was charged with **13** (3.0 mmol) and SO_2 (2.8 mmol) at −196 °C. The stirred mixture was warmed to room temperature from −110 °C in a $CFCl_3$ bath during a 17-h period. Fractionation gave $ClCF_2SO_2F$[23] (0.1 mmol) at −50 °C, a mixture of SO_2 and $ClCF_2SO_2F$ (4.9 mmol) at −110 °C and COF_2 (3.0 mmol) at −196 °C.

Reaction of Hypochlorite 14 with Sulfur Dioxide. The reaction mixture of **14** (0.65 g, 2.3 mmol) and SO_2 (2.3 mmol) was placed in a glass reactor (100 mL), which was warmed up to room temperature from −196 °C in a cold empty dewar over the course of 3 h, and stirred for 17 h in the dark. Fractionation gave a mixture of COF_2 and traces of SO_2 and SiF_4 (2.1 mmol) at −196 °C and a mixture of **5**, SO_2, SO_2ClF (trace), and $CF_3CFClSO_2F$[24] at −110 °C.

Results and Discussion

Potassium and Cesium Alkoxides. Previously, properties of the potassium salt **6** were reported,[25,26] but no accurate claim has been

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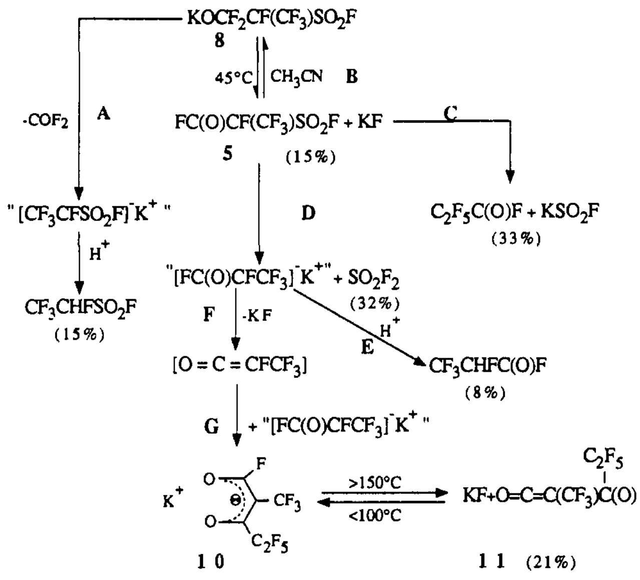
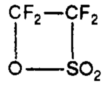
Scheme I. Decomposition of $KOCF_2CF(CF_3)SO_2F$ (**8**)



made regarding its synthesis. It has been shown[25] that $KOCF_2CF_2SO_2F$ (**6**) decomposes in diglyme at 40–50 °C, releasing carbonyl fluoride.

In the course of our work using acetonitrile as the solvent, such decomposition was not observed. The direct preparation from sultone **1** without solvent led quantitatively to **6** (eq 1). When



$$+\ \mathrm{KF} \xrightarrow[100\%]{40\ ^\circ\mathrm{C},\ 24\ \mathrm{h}} \underset{\mathbf{6}}{\mathrm{KOCF_2CF_2SO_2F}} \qquad (1)$$

1

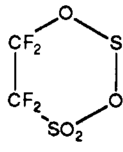
acetonitrile was used, the reaction was found to be incomplete, giving also compound **4** (eq 2). Compound **4** arises from the

$$\mathbf{1} + \mathrm{KF} \xrightarrow[\mathrm{CH_3CN}]{\text{room temperature to 50 °C/2 h}} \mathbf{6} + \underset{\mathbf{4}\ (66\%)}{\mathrm{FC(O)CF_2SO_2F}} \qquad (2)$$

fluoride-catalyzed isomerization of sultone **1**, and while **4** reacts with excess KF to give **6**, the yields are never as high as the direct reaction of **1** with KF without solvent (eq 3). The formation of

$$\mathbf{4} + \mathrm{KF} \xrightarrow[\mathrm{CH_3CN}]{\text{room temperature, 24 h}} \underset{(65\%)}{\mathbf{6}} + \mathbf{4} \qquad (3)$$

6 from the pyrosultone **2** has not been reported before (eq 4). In



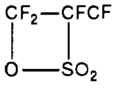
$$+\ \mathrm{KF} \xrightarrow[\mathrm{CH_3CN/CFCl_3}]{0\text{–}24\ ^\circ\mathrm{C}} \mathbf{6} + \underset{(37\%)}{\mathrm{KSO_3F}} \qquad (4)$$

2

all cases no byproduct COF_2 was detected even from reaction 2 at 50 °C. The formation of the corresponding cesium salt **7** requires higher temperature and longer reaction time, giving the alkoxide in quantitative yield (eq 5). The lower reactivity of CsF

$$\mathbf{1} + \mathrm{CsF} \xrightarrow[\mathrm{CH_3CN}]{50\ ^\circ\mathrm{C}/50\ \mathrm{h}} \underset{\mathbf{7}\ (100\%)}{\mathrm{CsOCF_2CF_2SO_2F}} \qquad (5)$$

is surprising, since one normally expects CsF to be more active than KF under similar reaction conditions, but the result was reproducible. The white salts **6** and **7** are stable at room temperature in the solid state in dry nitrogen atmosphere over a period of several months. The solutions in acetonitrile are similarly stable for several weeks. In contrast, the alkoxides **8** and **9** are much less stable. While no reaction occurs between KF or CsF and sultone **3** at room temperature, only small amounts of acetonitrile are necessary to complete the reaction at room temperature in 20 h. This reaction includes the intermediate isomerization to $FC(O)CF(CF_3)SO_2F$ (**5**)[16] although the direct formation of **8** and **9** from **3** cannot be ruled out (eqs 6 and 7). In the solid state



$$+\ \mathrm{MF} \xrightarrow{\mathrm{CH_3CN}} \underset{\mathbf{5}}{\mathrm{FC(O)CF(CF_3)SO_2F}} \qquad (6)$$

3

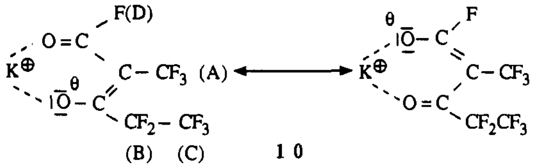
$$\mathbf{5} + \mathrm{MF} \xrightarrow[\mathrm{CH_3CN}]{\text{room temperature, 20 h}} \underset{\substack{\mathbf{8}\ (\mathrm{M} = \mathrm{K})\\ \mathbf{9}\ (\mathrm{M} = \mathrm{Cs})}}{\mathrm{MOCF_2CF(CF_3)SO_2F}} \qquad (7)$$

they decompose at room temperature in the dark in a sealed tube completely within several days according to eq 8. In acetonitrile

$$\underset{\substack{\mathbf{8}\ (\mathrm{M} = \mathrm{K})\\ \mathbf{9}\ (\mathrm{M} = \mathrm{Cs})}}{\mathrm{MOCF_2CF(CF_3)SO_2F}} \xrightarrow{24\ ^\circ\mathrm{C}/7\ \mathrm{days}} \mathbf{5} + \mathrm{MF} \qquad (8)$$

solution the potassium salt **8** is stable at room temperature for several hours. At 40–50 °C, however, it decomposes in a complicated manner, involving the solvent as a proton supplier, as shown in Scheme I. The percentages indicate the yield of the compounds identified with respect to the starting potassium salt **8**. This decomposes in two different ways, A and B; the formation of CF_3CHFSO_2F as a minor product can be explained by the loss of COF_2 via A, forming an intermediate $[CF_3CFSO_2F]^-K^+$,[25] which abstracts a proton from the solvent. The second path is given by equilibrium B, forming the acid fluoride **5**, which is found in 15% yield in the product mixture. The origin of the major products $C_2F_5C(O)F$, KSO_2F, and SO_2F_2 are the reactions C and D between **5** and KF.

These products were identified by their IR and ^{19}F NMR spectra, respectively; KSO_2F was identified by its decomposition products[27] at 200 °C. When SO_2F_2 is formed, an intermediate $[FC(O)CFCF_3]^-K^+$ provides a rationale for the observed products. Via reaction E, tetrafluoropropionyl fluoride is formed. The loss of KF via path F gives fluoro(trifluoromethyl)ketene, which is unstable,[22] probably reacting with its precursor $[FC(O)CFCF_3]^-K^+$ via G to give an orange potassium complex with the proposed structure **10**. Since this material is difficult to purify and to crystallize, its crystal structure could not be determined. The elemental analysis indicates the predicted composition. The structure appears to be a planar system formed by a conjugated π-system:



10

This conclusion is derived from its ^{19}F NMR spectrum, which contains signals with chemical shift values typical for groups as formulated in the structure of **10**. The signal at +21.97 ppm is due to a fluorine bonded to a carbonyl group, and the one at −52.52 ppm indicates a CF_3 group bonded to an olefinic carbon atom. The C_2F_5 group shows signals in the expected region at δ −80.09 (CF_3) and −116.64 (CF_2). Large long-range coupling constants are found as $^4J(AD)$ = 18.8 Hz, $^5J(BD)$ = 17.5 Hz, $^5J(AB)$ = 8.5 Hz, and $^6J(CD)$ = 1.4 Hz. These results argue for a planar structure. The orange powder does not melt, and it decomposes slowly at temperatures between 100 and 150 °C. Above 150 °C the pyrolysis products are KF and the ketene **11**, O=C=C(C-

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$F_3)C(O)C_2F_5$.[21] A test experiment shows that the K complex **10** is formed from **11** and KF below 100 °C. The IR and ^{19}F NMR spectra of **10** and **11** show a close relationship of these complexes to each other. The long-range coupling constants observed for complex **10** are absent in the ^{19}F NMR spectrum of ketene **11**, which does not have a rigid structure. The typical strong stretching vibrations for $O{=}C{=}C$ and $C{=}O$ at 2178 and 1731 cm^{-1}, respectively, in the infrared spectrum of **11** are still found in the spectrum of **10** as broad bands at 2045 ($O{=}C{=}C$) and 1830 cm^{-1} ($C{=}O$).

The intermediacy of **5** in Scheme I (step B) was proven by test reactions of **5** with KF in different solvents (eqs 9–12), showing

$$5 + KF \xrightarrow[CH_3CN]{\text{room temperature, 20 h}} SO_2F_2,\ C_2F_5C(O)F,\ KSO_2F,\ CF_3CHFC(O)F,\ \text{K complex } \mathbf{10} \tag{9}$$

$$5 + KF \xrightarrow[\text{diglyme}]{\text{room temperature, 22 h}} SO_2F_2,\ C_2F_5C(O)F,\ KSO_2F,\ CF_3CHFC(O)F,\ \text{K complex } \mathbf{10} \tag{10}$$

$$5 + KF \xrightarrow[DMF]{100\ °C/22\ h} SO_2F_2,\ CF_3CHFC(O)F,\ \underset{\mathbf{12}}{(CH_3)_2NCH{=}CFCF_3},\ CO_2\ (COF_2),\ \text{K complex } \mathbf{10} \tag{11}$$

$$5 + KF \xrightarrow[DMF]{50\text{–}60\ °C,\ 3\ h} SO_2F_2,\ CF_3CHFC(O)F,\ \underset{\mathbf{12}}{(CH_3)_2NCH{=}CFCF_3},\ CO_2(CF_3CHFSO_2F,\ COF_2) \tag{12}$$

similar product mixtures as found for the decomposition of salt **8**. (In all reactions (eqs 9–12) no CF_3CHFSO_2F and COF_2 (or only traces of them) was found, which accounts for their formation from **8** via pathway A in Scheme I.) (Reaction C takes place also in eqs 9 and 10 but not in eqs 11 and 12.) The major reaction in the latter cases is step D (Scheme I), followed by steps E and F. The product based on step G (K complex **10**) is not found in eq 12. Instead of this, 2,3,3,3-tetrafluoro-*N*,*N*-dimethyl-1-propen-1-amine, **12** is formed according to eq 13 as reported in

$$(CH_3)_2NC(O)H + O{=}C{=}CFCF_3 \xrightarrow[-CO_2]{} \underset{\mathbf{12}}{(CH_3)_2NCH{=}CFCF_3} \tag{13}$$

the literature.[22] The spectroscopic data for **12** are consistent with those previously reported. Product **12** indicates the intermediate existence of fluoro(trifluoromethyl)ketene, which is trapped by DMF before it rearranges to $FC(O)CF{=}CF_2$, from which the reaction product with DMF is not observed.[22]

The Hypochlorites. Several methods were applied to synthesize the hypochlorites $ClOCF_2CF_2SO_2F$ (**13**) and $ClOCF_2CF(CF_3)SO_2F$ (**14**). In the case of **13** the fluoride-catalyzed chlorofluorination[1] of the acetyl fluoride **4** led to a very satisfactory result, whereas **14** was obtained in a low yield (eq 14). It is important

$$\underset{\substack{\mathbf{4}\ (X = F)\\ \mathbf{5}\ (X = CF_3)}}{FC(O)CFXSO_2F} + ClF \xrightarrow{(KF)} \underset{\substack{\mathbf{13}\ (76\%)\\ \mathbf{14}\ (24\%)}}{ClOCF_2CFXSO_2F} \tag{14}$$

in this synthesis to use dry, but not too active, potassium fluoride as a catalyst. If highly active KF (fused and ground to a fine powder) is applied, the yield of **14** is only 10.5%.

Hypochlorite **13** is formed in a much lower yield from the corresponding salts **6** and **7** reacting with chlorine monofluoride (eq 15). This result is in contrast to the quantitative yield reported for $(CF_3)_3COCl$ from $(CF_3)_3CONa$ and ClF.[4]

$$\underset{\mathbf{6,\ 7}}{MOCF_2CF_2SO_2F} + ClF \xrightarrow[-MF]{} \underset{\mathbf{13}\ (38\%,\ 34\%)}{ClOCF_2CF_2SO_2F} \tag{15}$$

More controlled reactions with higher yields occur when the salts are allowed to react with chlorine fluorosulfate as a source of positive chlorine (eqs 16 and 17). Both hypochlorites are pale yellow liquids at room temperature, stable enough to record MS, IR, and NMR spectra. The molecular ion is not found, but [M − Cl]$^+$ for **13** and [M − ClO]$^+$ for **14** were observed, and other characteristic fragmentations support the existence of the compounds. The IR spectra contain the typical stretching vibrations as $\nu_{as}(SO_2)$ = 1468 (**13**) and 1472 cm^{-1} (**14**), ν(CF) and $\nu_s(SO_2)$ in the region ~1200–1100 cm^{-1}, and ν(ClO) = 795 (**13**) and 789 cm^{-1} (**14**).

$$\underset{\mathbf{6}}{KOCF_2CF_2SO_2F} + ClOSO_2F \rightarrow \underset{(74.5\%)}{\mathbf{13}} + KSO_3F \tag{16}$$

$$\underset{\substack{\mathbf{8}\ (M = K)\\ \mathbf{9}\ (M = Cs)}}{MOCF_2CF(CF_3)SO_2F} + ClOSO_2F \rightarrow \underset{\substack{(80.2\%)\\ (44.2\%)}}{\mathbf{14}} + MSO_3F \tag{17}$$

The ^{19}F NMR spectrum of **13** is quite different from that of the salts **6** and **7**. While the chemical shift values for the SO_2F and CF_2S groups are similar, the OCF_2 signal of **13** is shifted upfield by 34 ppm and that of **14** by 57 ppm, compared to that of **6** and **8**, respectively. Different electronegativities, the mesomeric + effect of the chlorine atom in **13** and **14**, and the ionic charge at the oxygen in **6** and **8** are responsible for the differences. The spectrum of **13** shows all the expected F–F spin couplings which are not observed with **6** and **7**. This result also confirms the fast equilibrium[26] (eq 18). No significant difference in the

$$\underset{\mathbf{6,\ 7}}{MOCF_2CF_2SOF} \rightleftarrows MF + \underset{\mathbf{4}}{FC(O)CF_2SO_2F} \tag{18}$$

splitting patterns of corresponding signals due to **14** compared to **8** and **9** was observed, which argues for the lack of an equilibrium or the existence of a slow equilibrium similar to that of eq 18.

The hypochlorites **13** and **14** were tested for their thermal and photolytic stability. In the gaseous state (10 Torr in IR cell with AgCl windows), **13** decomposes completely in the dark at 40 °C after 90 min and **14** incompletely after 3 h, both giving the products indicated in eq 19, analogous to reported results.[1] The

$$\underset{\mathbf{13,\ 14}}{ClOCF_2CFXSO_2F} \xrightarrow{\Delta} \underset{\mathbf{4,\ 5}}{FC(O)CFXSO_2FR} + ClF \tag{19}$$

progress of these reactions was monitored by observing the increase of intensity of $\nu(C{=}O)$ = 1885 (**4**) and 1884 cm^{-1} (**5**) and the disappearance of $\nu(Cl{-}O)$ = 795 (**13**) and 789 cm^{-1} (**14**).

The same result was obtained from an NMR experiment with $CDCl_3$ solutions, although small amounts of COF_2 and $ClCFXSO_2F$ were also observed. The latter were the main products formed during photolysis (eq 20). The photolytic investigations were done at 10 Torr in an IR gas cell fitted with AgCl windows using Pyrex-filtered UV radiation. The reactions were fast according to eq 20; they were complete for **13** after $^1/_2$ min and for **14** after 5 min.

$$\underset{\mathbf{13,\ 14}}{ClOCF_2CFXSO_2F} \xrightarrow{h\nu} ClCFXSO_2F + COF_2 \tag{20}$$

The general result of these experiments is the greater stability of **14**. This stands in contrast to the reported tendency[1] of generally decreasing stability of fluorinated hypochlorites with an increase in the number of carbon atoms increases and with increased carbon branching. No spontaneous decomposition or an explosion was observed when the liquids were allowed to develop their equilibrium vapor pressures of 100 (**13**) and 40 Torr (**14**) at 22 °C. In comparison, C_2F_5OCl explodes at room temperature and >100 Torr vapor pressure. It appears that the fluorosulfonyl group is stabilizing.

Reaction of 13 and 14 with CO and SO_2. Many fluorinated hypochlorites are reported to insert carbon monoxide[1,2,4,8,12] and sulfur dioxide[1,2,4,8] into the ClO bond, giving chloroformates and chloro sulfates, respectively, in high yields.

In the case of the hypochlorites **13** and **14**, carbon monoxide inserts readily (eq 21), yielding the expected chloroformate esters

$$\underset{\mathbf{13,\ 14}}{ClOCF_2CFXSO_2F} + CO \rightarrow \underset{\mathbf{15,\ 16}}{ClC(O)OCF_2CFXSO_2F} \tag{21}$$

15 (88%) and **16** (54.3%): The mass, infrared, and ^{19}F NMR spectra confirm the compounds. The C=O stretching vibration, 1837 (**15**) and 1836 cm^{-1} (**16**), is found in the typical region for fluorinated chloroformates. The ^{19}F NMR spectra of **15** and **13** as well as **16** and **14** are almost identical in shift values and coupling constants.

The reaction with sulfur dioxide, however, does not yield the expected chlorosulfates (eq 22). In both cases **13** and **14** are

$$\underset{\mathbf{13,\ 14}}{ClOCF_2CFXSO_2F} + SO_2 \nrightarrow ClSO_2OCF_2CFXSO_2F \tag{22}$$

catalytically decomposed by SO_2 according to (eq 23). This result is thus identical to that of the photolysis reactions.

$$\underset{\mathbf{13,\ 14}}{ClOCF_2CFXSO_2F} \xrightarrow{(SO_2)} ClCFXSO_2F + COF_2 \tag{23}$$

Summary

Improved methods for preparing the known salts $MOCF_2CF(X)SO_2F$ (X = F, CF_3) have been developed. The instability of the salt $MOCF_2CF(CF_3)SO_2F$ in the presence of fluoride ion in polar solvents was demonstrated, and the complex reactions leading to formation of stabilized complex of KF with $O{=}C{=}C(CF_3)C(O)C_2F_5$ were fully characterized. The new hypochlorites $ClOCF_2CF(X)SO_2F$ were prepared by reactions of ClF or $ClOSO_2F$ with the respective metal salts and fully characterized. Unexpected thermal stability of $ClOCF_2CF(CF_3)SO_2F$ compared to previously known hypochlorites of related structure was found, and the stabilizing effect of the $-SO_2F$ group in both hypochlorites was evident. The reactivity of the O–Cl bonds with CO to form chloroformates was as expected, but reactions with SO_2 led to a catalytic decomposition with loss of COF_2.

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Registry No. 1, 697-18-7; **2**, 1858-59-9; **3**, 773-15-9; **4**, 677-67-8; **5**, 754-41-6; **6**, 81439-24-9; **7**, 136490-29-4; **8**, 136490-30-7; **9**, 136490-31-8; **10**, 94560-03-9; **11**, 53352-88-8; **12**, 41874-82-2; **13**, 136490-32-9; **14**, 136490-33-0; **15**, 136490-34-1; **16**, 136490-35-2; $ClCF_2SO_2F$, 64544-26-9; $CF_3CF{=}CF_2$, 116-15-4; SO_3, 7446-11-9; $C_2F_5C(O)F$, 422-61-7; $CF_3CHFC(O)F$, 6065-84-5; CF_3CHFSO_2F, 2127-74-4; $CF_3CF(Cl)SO_2F$, 25221-40-3.

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Alkyl Radical Colligation and Release by a Chromium Macrocycle

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Alkyl radicals, generated from the photohomolysis of organocobalt complexes, were allowed to react in aqueous solution with $(H_2O)_2CrL^{2+}$ (L = 1,4,8,12-tetraazacyclopentadecane or [15]aneN_4). The reaction rates were evaluated by laser flash photolysis, using the known reaction between R• and the methyl viologen radical cation as a kinetic probe. Data were obtained for reactions of 13 radicals. The rate constants span a narrow range, (6–19) × 10^7 L mol^{-1} s^{-1} at 25 °C. The decomposition of $CH_3CH(OH)CrL(H_2O)^{2+}$ takes place by concurrent homolysis and β-elimination. At 25 °C the overall rate constant has a value (1.60 ± 0.15) × 10^{-4} s^{-1} independent of [H^+]. The complexes with R = CH_2OH and CH_2OCH_3 undergo decomposition too slowly for detection. Equilibrium constants for radical binding calculated from forward and reverse rate constants are $\log K_{298} = 11.23$ ($CH(CH_3)_2$) and 12.19 ($CH_2C_6H_5$). The kinetic and equilibrium data are discussed in terms of a reaction model featuring concurrent Cr–C and Cr–OH_2 bond making and bond breaking. Results for analogous reactions are compared.

Introduction

Colligation[1] reactions between free radicals and certain transition-metal complexes lead to the formation of stable metal–carbon bonds: $ML_{n+1} + R^{\bullet} \rightarrow L_nMR + L$. The resulting complexes are stable with respect to the reverse reaction, dissociation of a free radical, unless forced to completion by the addition of a radical trap. Isolated cases of colligation reactions of alkyl radicals have been investigated.[2-6] These often involve $^{\bullet}CH_3$, because it is easily generated pulse radiolytically by the reaction of $HO^{\bullet}$ with $(CH_3)_2SO$. More recently, systematic investigations of the kinetics of colligation reactions have been reported. Data are now available[7-10] for $Cr(H_2O)_6^{2+}$, Vitamin B_{12r}, cobalt(II) complexes of N_4 macrocycles such as [14]aneN_4 (=1,4,8,11-tetraazacyclotetradecane), and the nickel(II) complexes *RRSS*-Ni([14]aneN_4)$^{2+}$ and *RRRR*-Ni([14]aneN_4)$^{2+}$. The reactions of this group of complexes have been examined for quite a range of primary and secondary alkyl and substituted alkyl radicals. This work has been facilitated because alkyl radicals can be produced by the laser flash photolysis of organocobalt complexes. Kinetic probes have been used to monitor the reaction progress, since the attendant absorbance changes are otherwise too small for observation.

We turn our attention here to reactions of the chromium complex of the macrocycle [15]aneN_4, or 1,4,8,12-tetraazacyclopentadecane = L. The organometallic complexes RCr([15]aneN_4)$(H_2O)^{2+}$ were originally prepared[11] by reduction of alkyl halides by the chromium(II) macrocycle (eq 1 and 2). The structure of one compound was recently determined crystallographically for R = 4-$BrC_6H_4CH_2$.[12]

$$(H_2O)_2CrL^{2+} + RX \rightarrow XCrL(H_2O)^{2+} + R^{\bullet} + H_2O \tag{1}$$

$$(H_2O)_2CrL^{2+} + R^{\bullet} \rightarrow RCrL(H_2O)^{2+} + H_2O \tag{2}$$

In this sequence, eq 1 is rate controlling. Study of the much faster second reaction requires the sudden generation of the radical in a solution containing $(H_2O)_2CrL^{2+}$. Pulse radiolysis was used[13]

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(1) "The process of forming a covalent bond by means of one electron of each of the combining units will be called *colligation*. ...It is to be distinguished from co-ordination ... the distinction is in the process by which the bond is formed, not in the bond itself." Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; p 5.

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