(38) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Am. Chem. Soc.*, **95**, 6629 (1973).
(39) D. F. Gaines, S. Hildebrandt, and J. A. Ulman, *Inorg. Chem.*, **13**, 1217 (1974).
(40) S. G. Shore, M. M. Magion, and J. D. Ragaini, Paper 13, 9th Central Regional Meeting of the American Chemical Society, Charleston, WV, Oct 12, 1977.
(41) R. Weiss, J. R. Bowser, and R. N. Grimes, *Inorg. Chem.*, **17**, 1522 (1978).

Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas 66506

Chlorine(I) Derivatives of Fluorinated Carboxylic Acids. Synthesis and Properties of CF_3CO_2Cl, $C_2F_5CO_2Cl$, $C_3F_7CO_2Cl$, $ClCF_2CO_2Cl$, HCF_2CO_2Cl, and $CF_2(CF_2CO_2Cl)_2$

ISAO TARI and DARRYL D. DESMARTEAU*[1,2]

Received May 30, 1979

The syntheses of the chlorine(I) derivatives of six fluorinated carboxylic acids are described. Low-temperature reaction of the sodium salts of the acids with ClF is the preferred method of preparation. The new compounds CF_3CO_2Cl, $C_2F_5CO_2Cl$, $C_3F_7CO_2Cl$, HCF_2CO_2Cl, and $ClCF_2CO_2Cl$ have been characterized by IR, NMR, and Raman spectroscopy as well as by their decomposition products. $CF_2(CF_2CO_2Cl)_2$ could not be completely characterized due to its low volatility and explosiveness above −10 °C. All the compounds are thermally unstable at 22 °C and are explosive, especially in the gas phase at pressures greater than 20–50 torr. Reactions of CF_3CO_2Cl and $C_3F_7CO_2Cl$ with SO_2 and CO are also discussed.

Introduction

Halogen(I) derivatives of strong oxy acids and acid alcohols (hypohalites) provide a variety of reactive reagents for synthetic chemistry.[3,4] The majority of these compounds are chlorine derivatives, with the bromine(I) and iodine(I) analogues, in general, having much lower thermal stabilities. In nearly every case where the chlorine(I) compound is known, the fluoro derivative is also known. Historically, the fluoro derivatives preceded the chlorine compounds in most instances. The fluorine derivatives are not strictly analogous to the halogen(I) derivatives because the concept of a formal +1 oxidation state for fluorine has no validity. As a qualitative indicator, however, the existence of the fluoro derivative implies the chlorine(I) compound can be prepared and vice versa.

Methods for the synthesis of chlorine(I) derivatives have normally involved reactions of ClF with the acids or cesium salts of the acids.

$$HOA + ClF \rightarrow HF + ClOA$$
$$CsOA + ClF \rightarrow CsF + ClOA$$

Mercury and potassium salts have been utilized in some cases and $ClOSO_2F$ has been shown to be an effective replacement of ClF in several reactions. The use of metal salts has allowed the preparation of some chlorine(I) compounds where the parent acid or alcohol is not known, as is the case for several fluorocarbon derivatives of the type R_fOCl. In some cases for R_fOCl, the isolated metal salt is not used and the apparent addition of the elements of ClF across the carbon–oxygen double bond in ketones (or OSF_4) is accomplished by carrying out the reaction in the presence of KF or CsF.

As part of ongoing effort in the synthesis and properties of compounds containing halogen–oxygen single bonds, we decided to explore the synthesis of the chlorine(I) derivatives of fluorinated carboxylic acids. The fluoro derivatives of CF_3CO_2H, $C_2F_5CO_2H$, and $C_3F_7CO_2H$, while explosive and not well studied, were known.[5-7] This implied that the chlorine(I) compounds could be obtained. In addition, indirect evidence for the existence of $CF_3C(O)OX$ (X = I, Br) was available via the Hunsdiecker reaction applied to the synthesis of perfluoroalkyl iodides and bromides.[8] In this paper, the syntheses of CF_3CO_2Cl, $C_2F_5CO_2Cl$, $C_3F_7CO_2Cl$, HCF_2CO_2Cl, and $ClCF_2CO_2Cl$ by reaction of the corresponding acids or their sodium salts with ClF are described.[9] Evidence is also presented for the existence of $CF_2(CF_2CO_2Cl)_2$. The compounds have been characterized by NMR, IR, and Raman spectroscopy and by their thermal decomposition. Reactions of CF_3CO_2Cl and $C_3F_7CO_2Cl$ with CO and SO_2 are also discussed. During the course of this work an independent synthesis of CF_3CO_2Cl and $ClCF_2CO_2Cl$, different from that described here, was reported.[10]

Experimental Section

General Procedures. Volatile compounds were handled in a glass and stainless steel vacuum system equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gage, Series 1500. All reactions were carried out in 4HS75 Hoke cylinders or ~10-mL Kel-F tubes fitted with stainless steel valves. Separation of volatile products was by trap-to-trap distillation and GLC with columns packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P.

Infrared spectra were recorded on Perkin-Elmer Model 180 or 337 spectrophotometers using a 10-cm glass cell fitted with AgCl windows. Raman spectra were recorded at low temperatures by using a Spex 14018 double monochromator with photon counting detection. A low-temperature cell similar to that described by Brown et al. was employed.[11] Excitation was by the ~600-nm line of a CW dye laser pumped by an argon ion laser. NMR spectra were recorded at ca. −40 °C with a Varian XL-100-15 spectrometer using ~15 mol % solutions in $CFCl_3$. Chemical shifts are reported as ϕ^* values (δ relative to internal $CFCl_3$ not at infinite dilution).

Reagents. Fluorine, chlorine, CF_3COOH, $CClF_2COOH$, CF_2HCOOH, C_2F_5COOH, C_3F_7COOH, CO, SO_2, and NaOH were obtained from commercial sources. Sodium salts of the acids were prepared by reactions between acids and NaOH and then drying under vacuum. ClF was prepared by a reaction between equimolar amounts of fluorine and chlorine (90 mmol) in a 150 mL Monel vessel (5000 psi) at 250 °C for 12 h. (**Caution!** Contained explosions are observed under these conditions as the temperature approaches ~100 °C.) ClF for reaction was removed at −112 °C from the storage vessel to eliminate contamination by any ClF_3 present.

Preparation of Hypochlorites. Method A. The initial method of synthesis was via reaction of the acids with ClF. In a typical reaction, 3.0 mmol of the acid was condensed into a Kel-F reactor and allowed to liquefy in the bottom of the reaction tube. The reactor was then cooled to −195 °C and 3.3 mmol of ClF was condensed in the upper walls of the reactor. The vessel was then placed in ~500 mL of a $CFCl_3$ slush at −112 °C containing solid CO_2. Over a period of about 6 h, the reaction temperature increased slowly to −78 °C. After a total reaction time of 14–18 h, the reactor was cooled to −112 °C and pumped on. This removed unreacted ClF and CO_2 and R_fCl from decomposition of the hypochlorite.

The remaining mixture of R_fCO_2Cl and HF was then transferred slowly through a short connection onto ~25 g of NaF in a 75-mL stainless steel cylinder at −195 °C. This was most readily accomplished by allowing the reactor to warm from −195 °C in an empty Dewar. The vessel was then warmed to −70 °C and allowed to stand for a few minutes with gentle shaking. The hypochlorite was then collected

0020-1669/79/1318-3205$01.00/0

by pumping, as the reactor warmed in the air, through a trap which would stop any unreacted acid and into a trap cold enough to stop the hypochlorite but not the decomposition products, CO_2 and R_fCl. Yields of pure hypochlorite via this method varied greatly. With CF_3CO_2H, 70–80% yields could usually be obtained. With HCF_2CO_2H, 15–20% was average.

In a modification of the above procedure, the reaction of the acid was carried out in the presence of NaF. In a ~20 mL Kel-F reactor, the acid was condensed onto 5 g of NaF followed by the ClF. The reaction was then carried out as before. The hypochlorite was then collected directly in the appropriately cooled trap. This procedure produced somewhat better yields, but HF removal was not always complete. This led to frequent contamination by acid in trying to handle the hypochlorite in a glass system.

For the preparation of $CF_2[CF_2CO_2Cl]_2$, the solid acid, $CF_2(CF_2CO_2H)_2$, was placed in a Kel-F reactor and the reaction carried out as above with only ClF. The resulting solid product was then purified by pumping on it at −40 °C. Warming the solid above −15 to −10 °C always resulted in explosive decomposition.

Method B. After considerable frustration with the above procedure, a method of synthesis not involving HF was found. In a typical reaction, 10 mmol of sodium salt of the acid was placed in a 75-mL stainless steel reactor. The reactor was cooled to −195 °C and 3 mmol of ClF was added. It was then placed in ~500 mL of $CFCl_3$ at −112 °C containing solid CO_2. The reactor warmed slowly over a few hours to −78 °C and was kept at this temperature for 24 h. The volatile material was then pumped into a trap at −195 °C as the reactor warmed in the air. This material was then pumped through traps cooled to appropriate temperatures as the mixture warmed in the air from −195 °C. Yields of pure hypochlorite from this method were normally 80–90% based on the amount of ClF used.

Caution! *All the hypochlorites described in this work are explosive. If samples are warmed in a closed system so that the partial pressure of the hypochlorite exceeds 20–50 torr, they explode without fail. Adequate shielding must be used at all times and we recommend a maximum sample size of 3–4 mmol.*

CF_3CO_2Cl: mp −87.1 °C; NMR ϕ*(CF_3) 70.9 (s); IR 1837 (s), 1306 (m), 1238 (s), 1207 (vs), 1090 (vs), 849 (w), 770 (m), 713 (m), 575 (w) cm^{-1}; Raman (liquid) 1833 (m, br), 1386 (m)?, 1313 (m), 1241 (w, br), 1195 (w, br), 1100 (w, br), 856 (s), 815 (m), 771 (s), 716 (vs), 574 (w, br), 548 (w, br), 475 (w)?, 444 (w)?, 416 (m), 398 (w)?, 338 (s), 278 (vs), 171 (m), 117 (m) cm^{-1}, all bands polarized; collected at −111 °C after passing through a −78 °C trap; Raman ($CF_3CO_2H(l)$) 1738 (m, br), 1452 (m), 1312 (w), 1177 (w, br), 813 (vs), 790 (w, sh), 697 (w), 596 (w), 439 (m), 411 (m), 370 (w, sh), 262 (m), 235 (w) cm^{-1}.

$C_2F_5CO_2Cl$: mp −81.5 °C; NMR ($CF_3{}^ACF_2{}^BCO_2Cl$) ϕ_A* 83.6 (t), ϕ_B* 118.6 (q); IR 1830 (vs), 1605 (w), 1337 (s), 1225 (vs), 1200 (m), 1126 (vs), 1004 (vs), 823 (m), 758 (m), 712 (m), 673 (m), 592 (w), 535 (w) cm^{-1}; Raman (liquid) 1362 (m, dp), 1196 (w, ?), 1126 (w, ?), 1005 (w, ?), 827 (s, p), 765 (m, dp), 754 (s, p), 712 (s, p), 590 (w, ?), 539 (w, ?), 412 (w, ?), 373 (w, ?), 360 (m, ?), 327 (w, ?), 272 (s, p), 193 (w, ?), 163 (w, ?), 127 (w, ?) cm^{-1}; collected at −111 °C after passing through a −65 °C trap; Raman ($C_2F_5CO_2H(l)$) 1738 (s, br, p), 1453 (w, p), 1351 (m, p), 1254 (w, p) 1227 (vw, p?), 1130 (m, p), 1094 (w, sh, dp?), 930 (vs, p), 763 (s, p), 574 (m, p), 470 (w, sh, dp?), 432 (w, br, p), 337 (w, p), 266 (w, dp) cm^{-1}.

$C_3F_7CO_2Cl$: mp −58.0 °C; NMR ($CF_3{}^ACF_2{}^BCF_2{}^CCO_2Cl$) ϕ_A* 94.1 (t-t), ϕ_B* 127.4 (m), ϕ_C* 116.1 (q-t) ($J_{AC} = 9.0$, $J_{BC} \simeq J_{AB} \simeq 0.2$ Hz); IR 1832 (vs), 1354 (s), 1282 (m), 1240 (vs), 1235 (w), 1200 (w), 1137 (vs), 1095 (m), 1062 (s), 956 (s), 920 (s), 874 (w), 814 (m), 753 (m), 706 (w), 663 (w), 530 (w) cm^{-1}; Raman (liquid) 1366 (m, p), 1295 (w, p), 1280 (w, p), 1235 (w, br, p), 1200 (w, br, dp), 1140 (w, p), 1103 (w, dp), 1066 (vw, dp), 924 (vw, dp), 821 (s, p), 761 (vs, p), 707 (s, p), 649 (w, p), 606 (w, dp), 585 (m, p), 378 (m, p), 367 (w, p), 351 (w, sh, ?), 339 (w, dp), 323 (w, dp), 294 (w, p), 279 (vs, p), 205 (m, p), 160 (m, p) cm^{-1}; collected at −78 °C after passing through a −35 °C trap; Raman ($C_3F_7CO_2H(l)$) 1841 (w), 1817 (w, br), 1438 (w), 1410 (w), 1317 (w), 1256 (w, br), 1214 (w, br), 1125 (w), 1090 (w), 932 (w), 738 (m), 723 (s), 665 (w, br), 616 (w), 563 (w), 550 (w), 504 (w, br), 414 (w), 371 (w), 350 (m), 308 (m), 284 (m), 257 (m), 230 (w), 162 (w) cm^{-1}.

$ClCF_2CO_2Cl$: mp −103 °C; NMR ϕ* ($ClCF_2$) 60.4 (s); IR 1835 (vs), 1235 (m), 1183 (s), 1097 (vs), 1028 (w), 970 (s), 913 (w), 845 (s), 815 (m), 668 (w), 620 (w), 462 (w) cm^{-1}; Raman (liquid) 1173 (m, p), 1103 (w, dp), 1027 (w, dp), 900 (w, p), 747 (s, p), 688 (s, p), 635 (m, p), 552 (s, p), 417 (w, dp), 362 (s, p), 294 (m, p), 247 (m, p), 208 (vs, p), 160 (m, p) cm^{-1}; collected at −78 °C after passing through a 0 °C trap; Raman ($ClCF_2CO_2H(l)$) 1440 (m, dp), 1281 (w, p), 1171 (w, dp), 1139 (m, p), 972 (m, dp), 780 (s, p), 695 (s, p), 621 (s, p), 525 (m, dp), 437 (vs, p), 400 (m, dp), 378 (m, p), 340 (m, dp), 262 (w, dp), 204 (m, dp) cm^{-1}.

HCF_2CO_2Cl: mp −111 °C; NMR ϕ*(CF_2) 123.7 (d) ($J_{HF} = 52.9$ Hz); IR 3000 (w), 1820 (s), 1350 (w), 1222 (w), 1125 (m), 1107 (vs), 915 (w), 888 (w), 662 (m) cm^{-1}; Raman (liquid) 3004 (m, ?), 1810 (m, ?), 1382 (w, p), 1351 (w, dp), 1227 (w, dp), 1173 (w, dp), 1128 (w, dp), 1092 (m, p), 1029 (m, p), 804 (m, p), 747 (vs, p), 622 (w, p), 580 (m, p), 559 (m, p), 413 (w, dp), 365 (w, dp), 333 (m, p), 276 (vs, p), 180 (m, dp), 131 (w, dp?) cm^{-1}; collected at −78 °C after passing though 0 °C trap; Raman ($HCF_2CO_2H(l)$) 1440 (m, dp), 1369 (m, dp), 1284 (w, p), 1220 (w, br, p), 1197 (w, dp?), 1032 (w, dp), 780 (vs, p), 598 (w, dp), 609 (w, dp), 583 (m, p), 537 (m, dp), 411 (s, p), 379 (s, p), 357 (s, p), 292 (m, p), 260 (w, dp), 167 (w, br, dp) cm^{-1}.

Reactions of CF_3CO_2Cl and $C_3F_7CO_2Cl$. Reactions with SO_2 and CO were carried out in 100-mL Pyrex reactors fitted with a glass–Teflon valve. The hypochlorite was condensed into the bulb at −195 °C through a short connection followed by SO_2 or, in the case of CO, the appropriate pressure of gas. In a typical reaction, 2 mmol of R_fCO_2Cl and 6 mmol of SO_2 or CO were allowed to warm from −111 to −15 °C over 18–20 h in a Dewar filled with $CFCl_3$. The products were then separated by trap to trap distillation. In the reaction of $C_3F_7CO_2Cl$ with SO_2, only decomposition products, C_3F_7Cl and CO_2, along with unreacted SO_2 were found. In the other reactions, colorless liquids were isolated and partially characterized as $CF_3C(O)OSO_2Cl$, $CF_3C(O)OC(O)Cl$, and $C_3F_7C(O)OC(O)Cl$. The CO adducts were unstable at 22 °C. The SO_2 adduct was contaminated with CF_3CO_2H and a small amount of two other CF_3 products having NMR shifts at ϕ* 74.7 and 74.5.

$CF_3C(O)OSO_2Cl$: IR 1880 (m), 1855 (m), 1490 (w), 1475 (m), 1340 (w), 1320 (w), 1300 (w), 1250 (vs), 1205 (vs), 1040 (vs), 840 (m), 788 (sh), 765 (s), 745 (sh), 710 (sh), 665 (m), 605 (s), 538 (w), 510 (m) cm^{-1}; NMR ϕ*(CF_3) 75.9 (s); collected in a −78 °C trap.

$CF_3C(O)OC(O)Cl$: IR 1845 (m), 1788 (m), 1250 (vs), 1200 (vs), 1070 (m), 1050 (m), 1030 (vs), 870 (w), 795 (w), 745 (w), 700 (m), 660 (w), 580 (w) cm^{-1}; NMR ϕ*(CF_3) 75.4 (s); collected in a −78 °C trap.

$C_3F_7C(O)OC(O)Cl$: IR 1850 (w), 1800 (s), 1285 (w), 1250 (vs), 1225 (m), 1205 (m), 1143 (vs), 1058 (m), 1025 (vs), 990 (sh), 960 (w), 915 (m), 850 (m), 745 (m), 705 (m), 530 (w) cm^{-1}; NMR ($CF_3CF_2{}^BCF_2C(O)OC(O)Cl$) ϕ_A* 94.1 (t), ϕ_B* 126.9 (s), ϕ_C* 119.21 (q) ($J_{AB} = 9.0$, $J_{BC} \leq 0.5$ Hz); collected in a −78 °C trap.

Results and Discussion

The reaction off fluorinated carboxylic acids or their sodium salts with ClF produces the chlorine(I) derivatives of the acids.

$$R_fCO_2M + ClF \xrightarrow{-111\text{ to }-78\ ^\circ C} R_fCO_2Cl + MF$$
$$R_f = CF_3, C_2F_5, C_3F_7, HCF_2, ClCF_2;\ M = H, Na$$

The reaction of dicarboxylic acids also succeeds although only one example was tried.

$$CF_2(CF_2CO_2H) + 2ClF \xrightarrow{-111\text{ to }-78\ ^\circ C} CF_2(CF_2CO_2Cl)_2 + 2HF$$

The synthesis of these new acyl hypochlorites from the acids is complicated by the need to remove HF. Sodium fluoride was effective but this necessitated additional handling of the unstable hypochlorites. Addition of NaF prior to the reaction eliminated the additional transfer after reaction, but HF removal was often incomplete. This latter method would probably be effective if a method were available to stir or otherwise renew the surface of the NaF. This could not be effectively accomplished in the small volume Kel-F reactors that were used in this work.

The use of the sodium salts of the acids surmounts the HF problem and provides the best method of synthesis. The reaction of ClF with the salts is slow at −78 °C, but this is the most effective temperature. Higher temperatures result in an increase of the hypochlorite in the vapor phase, resulting in greater decomposition and diminished yields. The hypochlorites prepared in this way were of the highest purity and also exhibited the best thermal stability. The compounds were essentially colorless liquids or solids when prepared in this manner and seemed less prone to explosive decomposition. Via the acids, the hypochlorites were frequently yellow when handled in glass, presumably due to contamination by HF resulting in the presence of chlorine oxides.

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$
$$H_2O + R_fCOCl \rightarrow R_fCO_2H + HOCl$$
$$2HOCl \rightarrow H_2O + Cl_2O$$

The thermal stability of the acyl hypochlorites is relatively low. At low pressure (<10 torr) in glass, their complete decomposition often required several hours at 22 °C. At higher pressures, the materials showed a pronounced tendency to explode. The relative order of stability at 22 °C was $CF_3CO_2Cl > C_2F_5CO_2Cl > C_3F_7CO_2Cl > ClCF_2CO_2Cl > HCF_2CO_2Cl >> CF(CF_2CO_2Cl)_2$. Explosive decompositions were not especially energetic, certainly not as damaging as explosive oxygen–fluorine derivatives under similar conditions. However, this generalization is clearly very qualitative and all these compounds must be handled with great care. Their tendency to explode in the condensed phase as liquids or solids did not seem high, excepting $CF_2(CF_2CO_2Cl)_2$, which always exploded near −10 °C as a solid. In one instance, however, an 8-mmol sample of $C_2F_5CO_2Cl$ prepared from the acid exploded at ca. −100 °C as it was being warmed for transfer onto NaF. This explosion was the most energetic observed over 2 years of work with these materials and serves to emphasize the unpredictability of the compounds.

The controlled thermal decomposition of the materials provides a good method of analysis. The decompositions were essentially quantitative to form CO_2 and the chloride

$$R_fCO_2Cl \rightarrow R_fCl + CO_2$$

Minor amounts of other products are probably formed and HCF_2CO_2Cl always showed a few percent of $HCF_2C(O)Cl$. In the case of $CF_2(CF_2CO_2Cl)_2$, the decomposition products $ClCF_2CF_2CF_2Cl$ and CO_2, in nearly the expected amounts, are the main evidence for the existence of the compound. The explosive decomposition products were only analyzed for CF_3CO_2Cl and $C_3F_7CO_2Cl$. For CF_3CO_2Cl, the products were (ca. >95%) CF_3Cl and CO_2. For $C_3F_7CO_2Cl$, the major products were CF_3Cl and CO_2 with smaller amounts of COF_2, CF_2Cl_2, and other unidentified compounds. The decomposition of CF_3CO_2Cl seems to parallel closely that of CF_3CO_2F ($CF_3CO_2F \rightarrow CF_4 + CO_2$) with their thermal stabilities being about equal. The decomposition of CF_3CO_2F was found to obey second-order kinetics with respect to CF_3CO_2F at low pressures.[12] Most probably, CF_3CO_2Cl is similar since the decomposition was markedly faster at higher pressures. This was easily observed in an IR cell by following the appearance of CF_3Cl at varying pressures from 1 to 10 torr.

In addition to the thermal decomposition as proof of structure, the compounds were also characterized by vibrational spectroscopy and by ^{19}F NMR. The latter exhibited the expected spectrum in every case and also provided easy identification of R_fCl. Initial spectra run at −40 °C always contained minor amounts of R_fCl. Warming the sample to 22 °C for a short period and rerunning the spectrum at −40 °C showed a marked increase in the impurity and a decrease in resonances attributable to R_fCO_2Cl. The IR spectra were difficult to obtain for the compounds but the bands listed for each compound are probably real. Weaker absorptions in the IR are undoubtedly missing, since the spectra could only be run at <5 torr. The spectra exhibit characteristic $\nu(C{=}O)$ frequencies near 1830 cm^{-1} and are in each case considerably different from that of the respective acids.

The low-temperature Raman spectra of the liquids are very characteristic for each compound. The spectra of the acids are given for comparison in the experimental section and it is clear by inspection that the hypochlorite spectra are very different from the acids, especially below 1000 cm^{-1}. In each case, there is a characteristic, strong polarized band(s) near 700 cm^{-1}, one of which can probably be assigned to $\nu(OCl)$.[13] $ClCF_2CO_2Cl$ appeared to undergo photolysis of CF_2Cl_2 and CO_2 in the laser beam, whereas the other compounds showed no rapid change with time. For CF_3CO_2Cl, the absence of any depolarized bands suggests C_1 symmetry and we plan to assign the spectrum and compare it to those of CF_3CO_2H and CF_3CO_2F if the Raman spectrum of CF_3CO_2F can be obtained.

The chemical reactivity of these new hypochlorites is of interest and we have examined several of their reactions. Their reactions with olefins to form a variety of esters and the stereochemistry of these reactions will be reported separately. Here, the reactions with SO_2 an CO are discussed and the reaction with water was mentioned earlier. When the first perfluoroalkyl hypochlorites were obtained, characteristic reactions of these compounds were the insertion of SO_2 and CO to form chlorosulfates and chloroformates.[14–16]

$$R_fOCl + CO \rightarrow R_fOC(O)Cl$$
$$R_fOCl + SO_2 \rightarrow R_fOSO_2Cl$$

We have examined the similar reactions with CF_3CO_2Cl and $C_3F_7CO_2Cl$ and found that the acyl hypochlorites are similar in reactivity to the alkyl hypochlorites. With SO_2 the following reactions were observed.

$$CF_3CO_2Cl + SO_2 \xrightarrow{-111 \text{ to } -15\ °C} CF_3C(O)OSO_2Cl + \text{other}$$
$$C_3F_7CO_2Cl + SO_2 \xrightarrow{-111 \text{ to } -15\ °C} C_3F_7Cl + CO_2 + SO_2$$

The failure to isolate the addition product with $C_3F_7CO_2Cl$ and the low yield with CF_3CO_2Cl reflect the lower stability for these compounds compared to R_fOCl and an apparent low stability of acyl chlorosulfates.

With CO, both CF_3CO_2Cl and $C_3F_7CO_2Cl$ formed the acyl chloroformates

$$CF_3CO_2Cl + CO \xrightarrow{-111 \text{ to } -75\ °C} CF_3C(O)OC(O)Cl$$
$$C_3F_7CO_2Cl + CO \xrightarrow{-111 \text{ to } -75\ °C} C_3F_7C(O)OC(O)Cl$$

These novel compounds are unstable at 22 °C, forming CO_2 and the acyl chloride quantitatively. At low pressure in the gas phase, the rate of decomposition

$$R_fC(O)OC(O)Cl \xrightarrow{22\ °C} R_fC(O)Cl + CO_2$$

is slow and some of the acyl chloroformate is present even after 1 day. In principle these compounds could decarboxylate in two ways, losing either the central or terminal CO_2 group. This could be easily checked by using $C^{18}O$ to prepare the compounds, but we have not carried out the experiment.

In summary, a general synthesis of R_fCO_2Cl has been found and the existence of acyl hypohalites in the Hunsdiecker reaction for fluorinated systems has been further substantiated. Although the thermal stability of these compounds is low, their reactivity can be exploited and it is probable that their stability in appropriate solvents would be higher. The utility of CF_3CO_2Cl in electrophilic chlorination of organic and organometallic compounds should be of interest.

Acknowledgment. The financial support of this research by the National Science Foundation is gratefully acknowledged.

Registry No. CF_3CO_2Cl, 65597-25-3; $C_2F_5CO_2Cl$, 71359-61-0; $C_3F_7CO_2Cl$, 71359-62-1; $ClCF_2CO_2Cl$, 68674-44-2; HCF_2CO_2Cl,

71359-63-2; $CF_2(CF_2CO_2Cl)_2$, 71359-64-3; $CF_3C(O)OSO_2Cl$, 71359-65-4; $CF_3C(O)OC(O)Cl$, 71359-66-5; $C_3F_7C(O)OC(O)Cl$, 71359-67-6; CF_3COOH, 76-05-1; $CClF_2COOH$, 76-04-0; CF_2HCOOH, 381-73-7; C_2F_5COOH, 422-64-0; C_3F_7COOH, 375-22-4; $CF_2(CF_2CO_2H)_2$, 376-73-8; ClF, 7790-89-8.

References and Notes

(1) To whom all correspondence should be addressed.
(2) Alfred P. Sloan Foundation Fellow, 1975–1977.
(3) Aubke, F.; DesMarteau, D. D. *Fluorine Chem. Rev.* **1977**, *8*, 73.
(4) Schack, C. J.; Christe, K. O. *Isr. J. Chem.* **1978**, *17*, 20.
(5) Cady, G. H.; Kellogg, K. B. *J. Am. Chem. Soc.* **1953**, *75*, 2501.
(6) Menefee, A; Cady, G. H. *J. Am. Chem. Soc.* **1954**, *76*, 2020.
(7) Lustig, M.; Shreeve, J. M. *Adv. Fluorine Chem.* **1973**, *7*, 175.
(8) Haszeldine, R. N.; Sharpe, A. G. *J. Chem. Soc.* **1952**, 993.
(9) For a preliminary report of this work see: DesMarteau, D. D. *J. Am. Chem. Soc.* **1978**, *100*, 340.
(10) Schack, C. J.; Christe, K. O. *J. Fluorine Chem.* **1978**, *12*, 325.
(11) Brown, C. W.; Hopkins, A. G.; Daily, F. P. *Appl. Spectrosc.* **1974**, *28*, 194.
(12) Stewart, R. D.; Cady, G. H. *J. Am. Chem. Soc.* **1955**, *77*, 6110.
(13) For reference to ν(OCl) in various compounds see: Christe, K. O.; Schack, C. J.; Curtis, E. C. *Spectrochim. Acta., Part A* **1970**, *26a*, 2367. DesMarteau, D. D.; Hammaker, R. M. *Isr. J. Chem.*, **1978**, *17*, 103.
(14) Gould, D. E.; Anderson, L. R.; Young, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1310.
(15) Schack, C. J.; Maya, W. *J. Am. Chem. Soc.* **1969**, *91*, 2902.
(16) Young, D. E.; Anderson, L. R.; Gould, D. E.; Fox, W. B. *Tetrahedron Lett.* **1969**, 723; *J. Am. Chem. Soc.* **1970**, *92*, 2313.

Contribution from the Anorganisch-Chemisches Institut der Universität Heidelberg,
D-6900 Heidelberg, West Germany

Raman and Infrared Spectra, Normal-Coordinate Analysis, and Thermodynamic Properties of (Methylene-h_2)sulfur Tetrafluoride and (Methylene-d_2)sulfur Tetrafluoride

S. SUNDER,* H. H. EYSEL, G. KLEEMANN, and K. SEPPELT

Received April 4, 1979

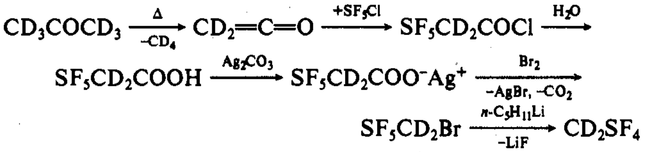
Infrared spectra of gaseous and Raman spectra of liquid (methylene-h_2)sulfur and (methylene-d_2)sulfur tetrafluorides have been recorded and assigned. A normal-coordinate analysis is presented to check the compatibility of the assignment of the two molecules and to determine the nature of the bonding. The molecule has a totally rigid structure and the CS bond shows a strong double-bond character. The average methylene stretching frequency in this molecule is higher than for any other methylene compound.

Introduction

The first published synthesis of methylenesulfur tetrafluoride, CH_2SF_4, was reported recently.[1] The molecule is of special interest because of its relationship to sulfur and phosphorus ylides. Electron diffraction[2] and NMR[1] studies indicate that the structure of CH_2SF_4 is an almost regular trigonal bipyramid. The C atom is occupying one of the equatorial positions, and the hydrogen atoms are located in the axial plane.[2] In order to gain further insight into the structure of this novel molecule, we have studied its vibrational spectra. Room-temperature infrared spectra of gaseous and Raman spectra of liquid CH_2SF_4 and CD_2SF_4 are presented here along with a normal-coordinate analysis for the fundamental vibrations. The results are discussed in relation to the structure.

Experimental Section

(a) Material. (Methylene-h_2)sulfur tetrafluoride was prepared by metalation of SF_5CH_2Br and subsequent LiF elimination as described earlier.[1] (Methylene-d_2)sulfur tetrafluoride was prepared according to the reaction scheme



$$CD_3COCD_3 \xrightarrow[-CD_4]{\Delta} CD_2{=}C{=}O \xrightarrow{+SF_5Cl} SF_5CD_2COCl \xrightarrow{H_2O}$$
$$SF_5CD_2COOH \xrightarrow{Ag_2CO_3} SF_5CD_2COO^-Ag^+ \xrightarrow[-AgBr,\ -CO_2]{Br_2}$$
$$SF_5CD_2Br \xrightarrow[-LiF]{n\text{-}C_5H_{11}Li} CD_2SF_4$$

Chemically this synthesis is identical with the reported synthesis of CH_2SF_4. The isotopic purity of CD_2SF_4 is estimated to be better than 98%, as indicated by proton NMR and infrared spectra.

(b) Spectra. Raman spectra were recorded by using the 6328-Å radiation of a He–Ne laser (OIP, Gent), ~120 mW, and two different monochromators: a modified Cary 81 and a Coderg PH 1. Both spectrometers are equipped with an RCA-C 31034 photomultiplier, Servogor-5 strip chart recorders, and necessary electronics. Spectra were obtained by using a DC amplification system, and the resolution used was about 2 cm^{-1}. The liquid samples were sealed in a 5-mm o.d. NMR glass tube, and a 90° scattering geometry was used. Infrared spectra were recorded on a PE 283 spectrophotometer. Gaseous samples were contained in a 10 cm long gas cell with CsBr windows. At a later stage of this work a PE-180 spectrophotometer became available and the spectrum of CH_2SF_4 was rerecorded in a

Table I. Infrared and Raman Spectra of (Methylene-h_2)sulfur Tetrafluoride at Room Temperature

IR (gas) ν,[a] cm^{-1}	Raman (liq) $\Delta\nu$,[a] cm^{-1}	Raman (liq) polarizn[b]	assignt[c]
3210 mw	3216 w	dp	ν_{10} (B_1)
3092 mw	3092 s	p	ν_1 (A_1)
1630 vw			$2\nu_{12}$
1550 vw			$\nu_4 + \nu_{12}$
1426 mw			ν_2 (A_1)
1307 m			ν_{11} (B_1)
	1210 vw	p	$2\nu_{17}$
1157 s	1149 s	p	ν_3 (A_1)
1124 m	1124 mw	p	$2\nu_{14}$
1018 s	1014 vw	dp	ν_{15} (B_2)
890 w			$2\nu_{18}$
818 vs			ν_{12} (B_1)
	797 vw, br		$\nu_6 + \nu_7$
760 s			ν_{16} (B_1)
	739 vs	p	ν_4 (A_1)
	693 vw	p	$2\nu_9 + \nu_7$
676 ms	684 vw	dp	ν_{13} (B_1)
647 w	656 w	p	ν_5 (A_1)
604 w	590 m	dp	ν_{17} (B_2)
565 ms	566 w	dp	ν_{14} (B_1)
509 mw	502 vw	pp[d]	ν_6 (A_1)
457 mw	449 ms	dp	ν_{18} (B_2)
	430 vw, sh	dp	ν_8 (A_2)
298 w	298 w	p	ν_7 (A_1)
	207 s	dp	ν_9 (A_2)
206 vvw			$\nu_6 - \nu_7$

[a] s, m, w, v, sh, and br stand for strong, medium, weak, very, shoulder, and broad, respectively. [b] p, dp, and pp stand for polarized, depolarized, and partially polarized, respectively. [c] See Table V for the description of the normal modes and Table III for a listing of the internal and symmetry coordinates used. [d] Part of the observed depolarized intensity in this feature may be due to the combination $\nu_7 + \nu_9$.

---

* To whom correspondence should be addressed at the Research Chemistry Branch, Whiteshell Nuclear Research Est., AECL, Pinawa, Manitoba, Canada.

0020-1669/79/1318-3208$01.00/0