Table VI. Interpretation of "Thermal" Parameters in Terms of Static Displacements Arising from Substitutional Disorder

Atoms averaged	Apparent rms radial thermal displacement, Å	Postulated rms radial static displacement, Å	Resultant rms radial thermal displacement, Å	Equiv thermal B, Å^2
Pt(1), Pt(2)	0.488	0.388	0.100	0.79
Cl(1), Cl(2), Cl(3)	0.570	0.388	0.182	2.62
All C, N, O except O(1)	0.687	0.388	0.299	7.06
O(1)	1.078	0.388 + 0.391	0.299	7.06

the resultant rms radial thermal displacements run 0.1, 0.18, and ~0.3 Å for Pt atoms, Cl ligands, and iminol ligands, respectively, and the equivalent thermal B values are reasonable, as summarized in Table VI.

The Original Platinblau

In order to circumvent the problem of silver contamination, an attempt was made to prepare Platinblau by the solid reaction of $PtCl_2(CH_3CN)_2$ and acetamide, as described in the Experimental Section. Although the resulting deep blue powder appears, visually, to be very similar to Platinblau, it is clear from the analysis that it is in fact a chloride complex, $PtCl_2(CH_3CONH)_2$, analogous to the blue trimethylacetamide complex III described above. This similarity is confirmed by integration of the nmr spectrum, which indicates the presence of acetamido anions, and, consequently, the existence of a Pt^{IV} complex.

With this clue, we return to the analysis of the chloride-free Platinblau. Virtually perfect agreement for all elements can be obtained for the analysis of Platinblau if it is written as the tetravalent complex, $Pt^{IV}(CH_3CONH)_2(OH)_2$ [Calcd: Pt, 56.51; C, 13.92; N, 8.12; O, 18.54; and H, 2.92], and this is our new formulation for the complex. Consistent with this formulation, the mass spectrum of Platinblau shows mass peaks beyond those of the parent ion of $Pt(CH_3CONH)_2 \cdot H_2O$ (329), but none higher than that of the parent ion of $Pt(CH_3CONH)_2(OH)_2$ (345). Moreover, the divalent hydrate formulation of Platinblau would lead to a band in the 1600–1640-cm^{-1} region of the infrared spectrum due to the H_2O bending vibration, and, in fact, Kutzelnigg and Mecke[10] have assigned a band at 1658 cm^{-1} in Platinblau to this mode. However, contrary to this, we find that the material recovered from dissolution of Platinblau in D_2O, followed by evaporation of the solvent, has an infrared spectrum in the 1600–1700-cm^{-1} region which is identical with that of the material before deuteration.

By analogy to the other blue complexes, Platinblau must be a Pt^{IV} complex, containing two anionic ligands in addition to the two acetamido anions, and the analytical, mass spectral, and infrared evidence obtained here indicate that the correct formulation is as the tetravalent hydroxide complex.

The electronic spectra of the three blue materials studied here are, as expected, very similar. In each case the most prominent feature is an extremely broad absorption centered at 15,100 cm^{-1} in $PtCl_2[(CH_3)_3CCONH]_2$, at 16,700 cm^{-1} in $PtCl_2(CH_3CONH)_2$, and at 14,500 cm^{-1} in $Pt(OH)_2(CH_3CONH)_2$. Although the intensities of these bands are somewhat concentration dependent, most likely indicating some polymerization, the molar extinction coefficients of the visible band for all three compounds are approximately 4000. The most probable origin of the visible band in Platinblau is an amide-to-metal charge transfer, about which we hope to say more in the future.

Acknowledgments. It is our pleasure to acknowledge the assistance given us by Mr. J. J. Ryan, Dr. J. D. E. McIntyre, and Miss Shirley Vincent in the experimental work, and discussions with Dr. F. A. Bovey.

Chloroxyperfluoroalkanes

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Abstract: The preparation, identification, and characterization of the new class of compounds, the chloroxyperfluoroalkanes, are described. Chloroxytrifluoromethane, chloroxypentafluoroethane, and 2-chloroxyheptafluoropropane are discussed. Derivatives of chloroxytrifluoromethane, including CF_3OOCF_3, CF_3ONF_2, and CF_3OCClO, were prepared in high yield.

The preparation of fluoroxyperfluoroalkyl compounds has been the subject of several recent papers.[1–3] The best synthesis for compounds of this type is that of Lustig, Pitochelli, and Ruff[3] which involves an alkali metal fluoride catalyzed addition of fluorine across the

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(1) J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, **87**, 230 (1965).

(2) J. H. Prager, *J. Org. Chem.*, **31**, 392 (1966).

(3) M. Lustig, A. R. Pitochelli, and J. K. Ruff, *J. Am. Chem. Soc.*, **89**, 2841 (1967).

carbon–oxygen double bond of a perfluorocarbonyl compound. We wish to report that a similar metal fluoride catalyzed addition to the carbonyl double bond using ClF in place of F_2 results in the formation of the previously unknown chloroxyperfluoroalkanes.

$$(R_f)_2C{=}O + ClF \xrightarrow{MF} (R_f)_2CFOCl$$

$$R_f = CF_3 \text{ or } F;\quad M = K, Rb, Cs$$

These reactions occur in high yield (90+ %) in a few hours. The chloroxy compounds prepared in this manner were CF_3OCl, C_2F_5OCl, and $(CF_3)_2CFOCl$. The materials were purified using a stainless steel–Teflon vacuum line and identified by vapor density, infrared spectra, and ^{19}F nmr and mass spectra. The thermal stability of the chloroxy compounds is in the order $CF_3OCl > C_2F_5OCl > (CF_3)_2CFOCl$. The methyl derivative was successfully utilized in high-yield syntheses of the known compounds, CF_3OOCF_3[4] and CF_3ONF_2,[5] as well as the new chloroformate, CF_3OCClO.

Experimental Section

Apparatus. Synthetic reactions were conducted in stainless steel cylinders and the products were separated and purified using a stainless steel Teflon vacuum line. Pressures were measured by means of a Heise, bourdon tube type, pressure gauge. Infrared spectra were taken on Perkin-Elmer Infracords 137 and 337 using 5-cm path length stainless steel or Kel-F cells fitted with AgCl windows. The ^{19}F nmr spectra were obtained at −40° using a Varian Associates high-resolution nmr spectrometer operating at 56.4 Mc. Samples were sealed in Pyrex tubes, and $CFCl_3$ was employed as the internal standard. Mass spectral data was obtained with a CEC 21-103 C mass spectrometer.

Materials. Chlorine monofluoride was prepared by heating an equimolar mixture of chlorine and fluorine to 150° for several hours in a stainless steel cylinder. Carbonyl fluoride was prepared from phosgene and sodium fluoride in acetonitrile,[6] and trifluoroacetyl fluoride was prepared by the reaction of trifluoroacetic anhydride and cesium fluoride. Perfluoroacetone was purchased from Allied Chemical Corp., and the N_2F_4 was obtained from Air Products Co. The alkali metal fluorides were fused and then powdered in a drybox prior to use. Gaseous reactants were purified by fractional condensation.

Preparation of CF_3OCl. Method A. In a typical reaction CsF powder (4.80 g, 30.2 mmol) was loaded into a 30-ml prepassivated cylinder in the drybox. After evacuation, COF_2 (263 cm^3, 11.7 mmol) and ClF (277 cm^3, 12.4 mmol) were separately condensed into the reactor at −196°. The cold bath was changed to −78° for 15 min before allowing the temperature to rise to room temperature. After standing overnight the reactor was opened, and the products were separated by fractional condensation at −142 and −196°. The trap cooled at −142° contained the colorless liquid CF_3OCl (262 cm^3, 11.7 mmol), and the trap cooled at −196° contained 16 cm^3 (0.71 mmol) which was shown to be ClF with traces of SF_6 (impurity in the ClF) and COF_2 by its infrared spectrum. The yield of CF_3OCl was 99+ %. A reaction on this scale when stopped after 1 hr by cooling to −196° and fractionating was found to be approximately 60 % complete.

Method B. A sample of $KOCF_3$–KF, prepared according to Redwood and Willis,[7] was loaded in a prepassivated 10-ml bomb in the drybox. After evacuation, ClF (154 cm^3, 6.87 mmol) was condensed in the bomb at −196°. The reactor was kept at −78° for several days. Subsequent fractionation through traps cooled to −142 and −196° yielded CF_3OCl (55 cm^3, 2.46 mmol) and unreacted ClF (97 cm^3, 4.33 mmol).

Properties of CF_3OCl. Chloroxytrifluoromethane is a colorless material and is stable at room temperature in clean and dry stainless steel, perhalogenated plastics, or glass apparatus, *Anal.* Calcd for CF_3OCl: Cl, 29.5. Found: Cl, 28.6.

Molecular Weight. The molecular weight of CF_3OCl as determined by gas density, assuming ideal gas behavior, was 117 (calculated 120).

Vapor Pressure and Boiling Point. The vapor pressures of CF_3OCl over the temperature range −112 to −47° are [given as T (°K), P (mm)]: 160.6 7; 178.1, 34; 194.4, 114; 207.8, 261; 225.7, 699. The vapor pressure–temperature relationship is described by the equation $\log P_{mm} = 7.7719 - 1112.0/T(°K)$. The normal boiling point calculated from the equation is −45.8°, with a heat of vaporization of 5.09 kcal/mole and a Trouton constant of 22.4. The sample was tensiometrically homogeneous.

Melting Point. A melting point was not determined for CF_3OCl, but it was noted that samples were liquid down to −142°.

Reactions of CF_3OCl. Photolysis. A sample of CF_3OCl (45.5 cm^3, 2.03 mmol) was condensed at −196° into a Pyrex ampoule fitted with a stopcock lubricated with halocarbon grease. The ampoule was allowed to warm to room temperature and was irradiated overnight (Hanovia 100-W utility lamp, Catalog No 30620). Products of the photolysis were partially separated by fractional condensation in traps cooled to −126, −142, and −196°. Identification and additional quantitative measurements were obtained from the infrared spectra and gas chromatograms of the fractions. No unreacted CF_3OCl was observed. The products were CF_3OOCF_3 (20.8 cm^3, 0.93 mmol), COF_2 (4.0 cm^3, 0.18 mmol), Cl_2 (24.2 cm^3, 1.08 mmol), and a small amount of SiF_4. The yield of peroxide was 91 %.

Reaction with N_2F_4. A sample of CF_3OCl (49.2 cm^3, 2.19 mmol) was condensed into a Pyrex ampoule at −196° together with N_2F_4 (56.7 cm^3, 2.56 mmol). Upon warming to ambient temperature the ampoule was irradiated for 20 min. The contents of the ampoule were then vacuum fractionated through traps cooled to −142, −156, and −196°. The −156° fraction contained CF_3ONF_2 and COF_2, the warmer trap contained Cl_2, and the −196° fraction consisted of a small amount of unreacted N_2F_4. The mixture of CF_3ONF_2 and COF_2 was purified by a wash with dilute NaOH, and after drying afforded pure CF_3ONF_2 (35 cm^3, 1.56 mmol) in 71 % yield. The CF_3ONF_2 was characterized by both its infrared[5a] and ^{19}F nmr spectra,[5b] which were identical with those published.

Reaction with CO. A sample of CF_3OCl (53 cm^3, 2.37 mmol) was condensed into a Pyrex ampoule cooled to −196° and CO added (60 cm^3, 2.68 mmol). Irradiation with uv for 35 min was carried out after warming to ambient temperature. The products were vacuum fractionated through traps cooled to −142 and −196°. The −142° trap contained pure CF_3OCClO (52 cm^3, 2.32 mmol) in 98 % yield. The infrared spectrum and ^{19}F nmr spectrum were consistent with the proposed structure.

Properties of CF_3OCClO. Molecular Weight. The molecular weight of CF_3OCClO was determined from its vapor density as 149 (calculated 148.5).

Vapor Pressure and Boiling Point. The vapor pressures of CF_3OCClO over the temperature range −78 to 0° are [given as T(°K), P(mm)]: 195.2, 7; 210.0, 21; 227.3, 66; 242.8, 155; 273.2, 584. The vapor pressure–temperature relationship is described by the equation $\log P_{mm} = 7.6083 - 1318.6/T(°K)$. The normal boiling point calculated from the equation is 5.7°, with a heat of vaporization of 6.03 kcal/mole and a Trouton constant of 21.6.

Preparation of C_2F_5OCl and $(CF_3)_2CFOCl$. Chloroxypentafluoroethane and 2-chloroxyheptafluoropropane were prepared from CF_3CFO and $(CF_3)_2C{=}O$, according to method A outlined above for CF_3OCl. However, for these compounds the reaction temperature was maintained at −78° to prevent loss of the products through irreversible decomposition. Fractional condensation was suitable for purification of the compounds which are retained in traps cooled at −126 and −95°, respectively. The products were obtained in 99 % (C_2F_5OCl) and 91 % [($(CF_3)_2CFOCl$)] yields. Reaction of ClF and $CsOC_2F_5$[8] at −78° was also used as a route to C_2F_5OCl.

Properties of C_2F_5OCl and $(CF_3)_2CFOCl$. Both materials are pale yellow liquids in the condensed phase. The stability of these materials at ambient temperature appears to be marginal. Extensive decomposition was observed at temperatures much in excess of −78° until the container became well conditioned to the

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(4) R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 5628 (1957).

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(6) F. A. Fawcett, C. W. Tullock, and D. D. Coffmann, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

(7) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

(8) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **45**, 389 (1967).

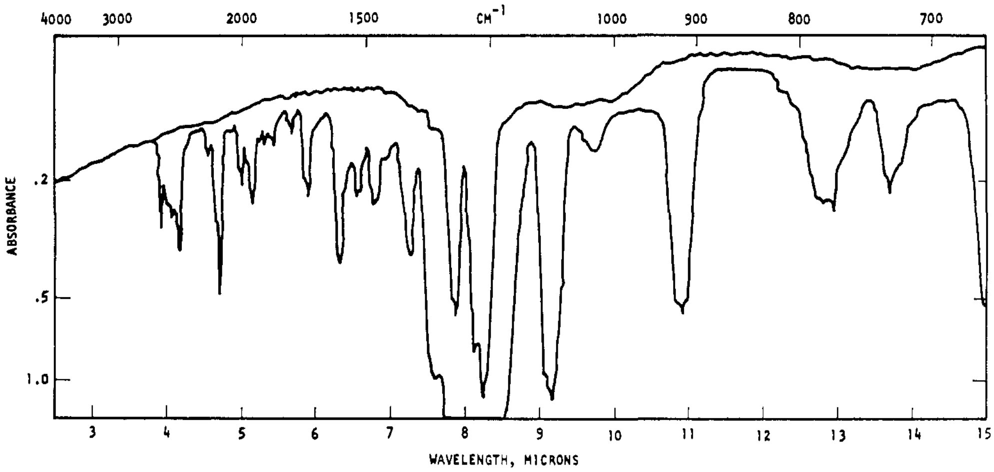

Figure 1. Infrared spectrum of CF_3OCl at 330 and 4.2 mm.

compounds. Even then, some slow degradation usually occurred.

Molecular Weight. Gas density measurements gave a molecular weight of 164 for C_2F_5OCl (calculated 170) and 216 for $(CF_3)_2CFOCl$ (calculated 220).

Vapor Pressure and Boiling Point. The measured vapor pressures of C_2F_5OCl over the temperature range -80 to $-25°$ are [given as T (°K), P (mm)]: 193.6, 11; 209.0, 37; 227.2, 120; 241.9, 272; 248.3, 365. The vapor pressure–temperature relationship derived from the data is represented by the equation $\log P_{mm} = 7.9643 - 1338.4/T(°K)$. The calculated normal boiling point is $-9.9°$ and the heat of vaporization is 6.13 kcal/mole giving a Trouton constant of 23.3. For $(CF_3)_2CFOCl$ the vapor pressures over the temperature range -79 to 0° are [given as T (°K), P (mm)]: 194.6, 6; 208.8, 17; 226.5, 47; 245.7, 125; 273.2, 380. The equation relating these vapor pressure–temperature data is $\log P_{mm} = 7.0374 - 1215.5/T(°K)$. The calculated normal boiling point is 19.2°, and the heat of vaporization is 5.56 kcal/mole corresponding to a Trouton constant of 19.

Decomposition of C_2F_5OCl. Degradation of C_2F_5OCl at ambient temperature was observed to follow two paths. In incompletely passivated metal, reaction occurred to give CF_3CFO and Cl_2. This is essentially a reversal of the synthetic reaction with the Cl_2 arising through the metal–ClF interaction. Under ultraviolet photolytic conditions (Hanovia 100-W utility lamp) in a Pyrex container a sample of C_2F_5OCl (33.9 cm^2, 1.51 mmol) was observed to be completely decomposed after 1 hr. The products (68.7 cm^3, 3.07 mmol) as identified by infrared and mass spectra consisted of a 1:1 mixture of COF_2 and CF_3Cl together with barely detectable traces of CF_3CFO, Cl_2, and SiF_4.

Decomposition of $(CF_3)_2CFOCl$. While the decomposition of C_2F_5OCl was smooth and gradual, that of 2-chloroxyheptafluoropropane was sometimes instantaneous. For example, on expanding a sample of the liquid in a Teflon trap, as ambient temperature was approached, the material suddenly and completely vaporized, driving the Heise gauge to its maximum stop. The sample was cooled to $-196°$ and fractionated through traps cooled to -95, -142, $-196°$. No noncondensable gases were observed and the products, as determined by infrared spectra and gas chromatography, were CF_3CFO (128 cm^3, 5.71 mmol), CF_3Cl (131 cm^3, 5.85 mmol), Cl_2 (6 cm^3, 0.27 mmol), CF_3CF_3 (7.1 cm^3, 0.32 mmol), and undecomposed $(CF_3)_2CFOCl$ (3.6 cm^3, 0.16 mmol). No $(CF_3)_2CO$ was noted. The original sample had not been measured accurately but was known to be 145–150 cm^3. These same decomposition products were found when the material did not decompose instantly with the exception that CF_3CF_3 was not formed and some $(CF_3)_2CO$ was.

Discussion

The new class of compounds, chloroxyperfluoroalkanes, have been prepared in high yield by the alkali metal fluoride catalyzed chlorofluorination of the carbonyl bond in perfluorocarbonyl compounds. Evidence obtained from material balances in the synthetic reactions, molecular weight data, derivative formation, and decomposition products supports the assigned compositions. Confirmation of the structure of the compounds was obtained from infrared, ^{19}F nmr, and mass spectra.

The parent compound of this series, chloroxytrifluoromethane, has the infrared spectrum shown in Figure 1. The three strong bands at 1270, 1230, and 1212 cm^{-1} are attributable to the CF stretching modes of the CF_3O group and are quite comparable to similar absorptions in CF_3OF[9,10] which occur at 1294, 1262, and 1223 cm^{-1}. The band at 915 cm^{-1} is probably due to the CO stretch which appears at 882 cm^{-1} in CF_3OF. Bands at 660, 605, and 550 cm^{-1} are assigned to CF_3 deformation modes by analogy with these assigned absorptions in CF_3OF: 679, 608, and 584 cm^{-1}. Whereas CF_3OF has no strong bands in the 700–800-cm^{-1} region, CF_3OCl has two bands (789 and 730 cm^{-1}); the higher frequency one is probably ascribable to the ClO stretching vibration. This band appears at 809 cm^{-1} in $ClONO_2$.[11] The bands at 1095 and 730 cm^{-1} are unassigned.

The infrared spectrum of C_2F_5OCl[12] is shown in Figure 2 and is comparable to that of C_2F_5OF[1] for absorptions related to the C_2F_5O group. The absence of the OF stretching mode at 900 cm^{-1} is apparent while a new band is present at 760 cm^{-1} which is attributed to the ClO stretching vibration. Figure 3 shows the infrared spectrum of $(CF_3)_2CFOCl$.[12] Comparison with the corresponding fluoroxy compound[1] reveals the same good correlation observed for the other chloroxy–fluoroxy analogs. The OF stretching vibration at 883 cm^{-1} is absent and has been replaced by a band at 752 cm^{-1} assignable to the ClO stretching vibration.

The ^{19}F nmr spectra of the chloroxy compounds were quite simple, and the observed values are given in Table I along with the values reported[1] for the related fluoroxy compounds. The single resonance observed for

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[9] R. T. Lagemann, E. A. Jones, and P. J. H. Woltz, *J. Chem. Phys.*, 20, 1768 (1952).

[10] P. M. Wilt and E. A. Jones, *J. Inorg. Nucl. Chem.*, 29, 2108 (1967).

[11] R. H. Miller, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta*, 23, 223 (1967).

[12] Absorptions were found for (a) C_2F_5OCl at 1380 (m), 1240 (s), 1185 (s), 1100 (s), 1045 (w), 760 (w), 730 (m), and 530 cm^{-1} (w); (b) for $(CF_3)_2CFOCl$ at 1315 (s), 1255 (s), 1215 (w), 1195 (m), 1155 (s), 1118 (s), 1009 (s), 790 (w), 752 (m), 727 (m), 670 (w), and 540 cm^{-1} (w).

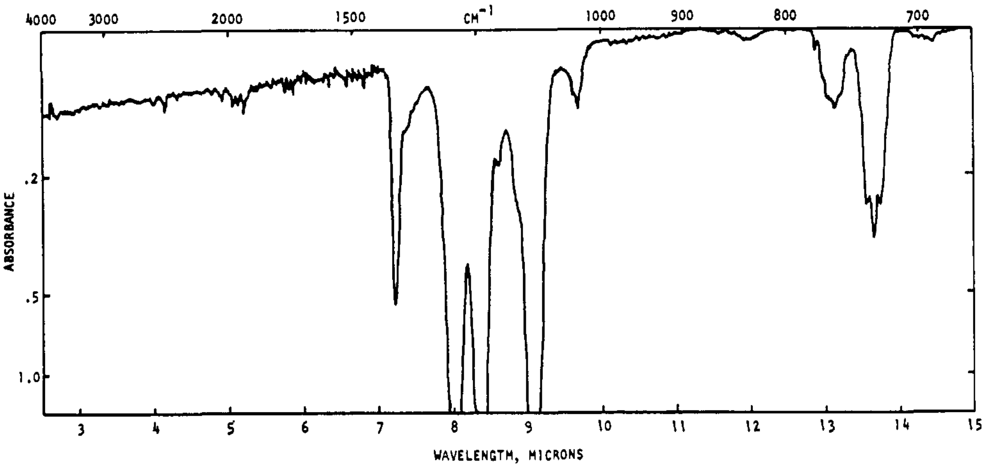


Figure 2. Infrared spectrum of C_2F_5OCl at 25 mm.

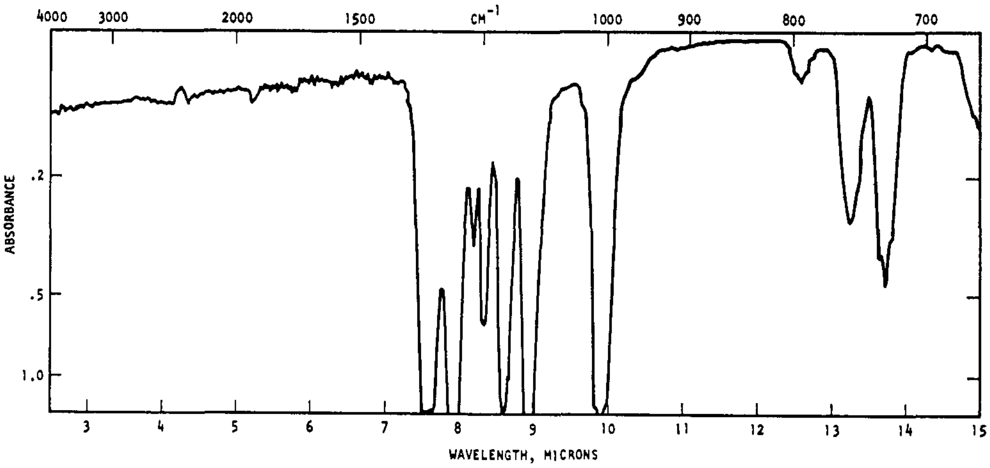


Figure 3. Infrared spectrum of $(CF_3)_2CFOCl$ at 20 mm.

CF_3OCl indicates the equivalence of all three fluorine atoms. By using measured quantites of CF_3OCl and the reference, $CFCl_3$, and measuring the areas under the respective absorptions, it was demonstrated that the number of fluorine atoms in the two compounds were in the expected 3:1 ratio. The peaks of the other chloroxy compounds were slightly broadened singlets and not resolvable owing to small coupling constants (the resolution limit was approximately 1 cps). The expected area ratios for the two different fluorine groups in CF_3CF_2OCl (3:2) and $(CF_3)_2CFOCl$ (6:1) were observed.

Table I. ^{19}F Nmr Spectra Data[a]

Group	CF_3OCl	C_2F_5OCl	$(CF_3)_2CFOCl$
CF_3	64 (72.3)[b]	83 (82)	76.5 (75.6)
CF_2		90 (97.9)	
CF			136 (137.4)

[a] Chemical shift in ppm relative to internal $CFCl_3$. [b] Values in parentheses are the corresponding chemical shifts reported[1] for the related fluoroxy compound.

A reproducible mass cracking pattern for CF_3OCl was obtained and is presented in Table II. Some conditioning of the inlet system of the spectrometer with the compound itself was carried out to avoid decomposition of the sample prior to determination of the spectral pattern. The numerous, intense ion fragments recorded, including the parent ions, serve amply to verify and support the assigned structure of CF_3OCl.

Table II. Mass Spectrum of CF_3OCl

m/e	Ion	Rel intensity	m/e	Ion	Rel intensity
12	C^+	50.2	51	$^{35}ClO^+$	42.1
16	O^+	25.6	53	$^{37}ClO^+$	13.7
19	F^+	16.2	66	CF_2O^+	52.6
28	CO^+	63.7	69	CF_3^+	100.0
31	CF^+	21.0	85	CF_3O^+	73.7
35	$^{35}Cl^+$	82.1	101	$CF_2O^{35}Cl^+$	13.7
37	$^{37}Cl^+$	26.3	103	$CF_2O^{37}Cl^+$	4.4
47	CFO^+	96.0	120	$CF_3O^{35}Cl^+$	23.0
50	CF_2^+	7.4	122	$CF_3O^{37}Cl^+$	7.4

Because of the difficulties experienced in handling and transferring C_2F_5OCl, a stable mass cracking pattern was not obtained. However, the ions most relevant in terms of structural implications were observed. Thus *m/e* values corresponding to the following ions were found: $C_2F_5O^+$, CF_3^+, $^{37}ClO^+$, and $^{35}ClO^+$. No attempt was made to obtain the mass spectrum of $(CF_3)_2CFOCl$.

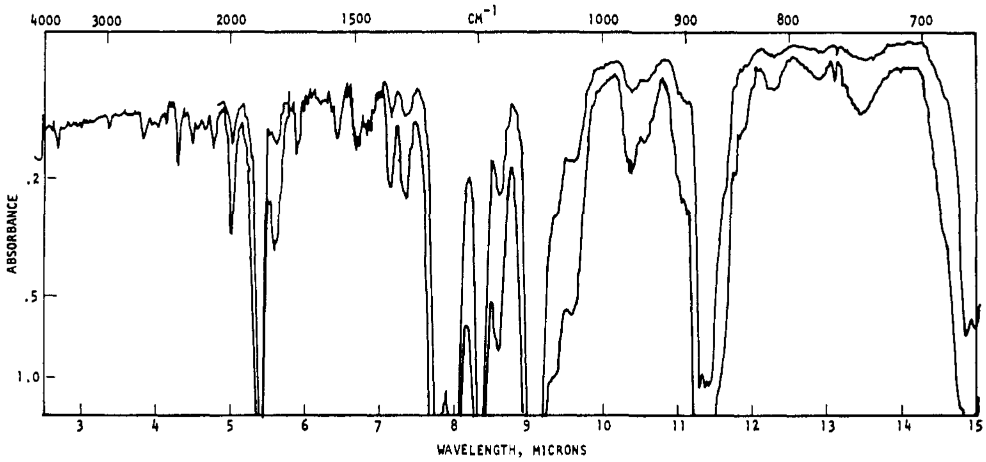
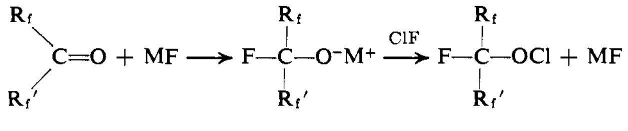


Figure 4. Infrared spectrum of CF_3OCClO at 62 and 16 mm.

All the spectral results for the chloroxy compounds prepared are in agreement with the structural formulation R_fOCl. No evidence was obtained to indicate the presence of any isomeric species such as $ClCF_2OF$, $CF_3C(Cl)FOF$, or $(CF_3)_2CClOF$. The failure to find other isomeric products in these reactions emphasizes the strong polar or ionic nature of the effective intermediates. The presumed reaction sequence is



$$R_fR_f'C{=}O + MF \longrightarrow F{-}C(R_f)(R_f'){-}O^-M^+ \xrightarrow{ClF} F{-}C(R_f)(R_f'){-}OCl + MF$$

The high electronegativity of fluorine results in a pronounced bond polarization in ClF and ensures that its reaction with the methoxide ion proceeds by one path only. Reaction of preformed $R_fO^-M^+$ and ClF to give R_fOCl supports the intermediacy of such an ionic species. Also, the perfluorocarbonyl-ClF systems were experimentally shown to be unreactive under these conditions in the absence of alkali metal fluorides.

The thermal stability of the chloroxy compounds in the series decreases rapidly with increasing number of carbon atoms. Chloroxytrifluoromethane is stable at room temperature under scrupulously dry, inert conditions. Samples heated in stainless steel containers to 65° overnight were recovered unchanged for the most part. Even at 165° for this period some CF_3OCl could be recovered. The decomposition products found are consistent with a twofold reaction path involving the CF_3O radical.

$$CF_3OCl \longrightarrow CF_3O\cdot + Cl\cdot$$
$$2CF_3O\cdot \longrightarrow CF_3OOCF_3$$
$$CF_3O\cdot \longrightarrow COF_2 + F\cdot$$

Elemental Cl_2 was found and may have resulted from the coupling of two Cl atoms or the abstraction of chlorine from CF_3OCl by a Cl atom. Photolytic decomposition of CF_3OCl at ambient temperature is quite rapid and gives the same products as the thermal process. However, the yield of trifluoromethyl peroxide (91%) is quite high and constitutes a convenient laboratory synthesis of the compound.

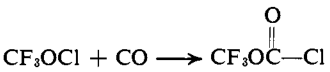
Fluorine and CF_3OCl did not react at room temperature in metal containers. At higher temperatures, 65°, some CF_3OCl was decomposed but no appreciable yield of CF_3OF resulted.

Molecules known to readily undergo free-radical reactions were very effective in forming derivatives of CF_3OCl in which the CF_3O group is retained. Tetrafluorohydrazine is an excellent source of NF_2 and its reaction with CF_3OCl led to the formation of CF_3ONF_2.

$$CF_3OCl + {}^1/_2N_2F_4 \longrightarrow CF_3ONF_2 + {}^1/_2Cl_2$$

The yield of CF_3ONF_2 (71%) is as good or better than that achieved from CF_3OF and N_2F_4.[5] Chlorodifluoramine, $ClNF_2$, a possible by-product of the reaction was not observed; instead, the other products of the reaction were Cl_2, COF_2, and a trace of SiF_4.

Insertion of carbon monoxide into the OF group of CF_3OF has been established[13] as a facile high-yield reaction yielding trifluoromethyl fluoroformate. A similar insertion reaction employing CF_3OCl as a substrate was carried out and found to give a nearly quantitative yield of trifluoromethyl chloroformate.



$$CF_3OCl + CO \longrightarrow CF_3O\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl$$

This new compound was identified by its molecular weight and infrared, ^{19}F nmr, and mass spectra. An important feature of the infrared spectrum[14] (Figure 4) is the C=O stretching band at 1835 cm^{-1} shifted to a lower frequency from that of CF_3OCFO[13] (1906 cm^{-1}) as expected.[15]

Trifluoromethyl chloroformate exhibits a single ^{19}F nmr resonance at 61 ppm relative to $CFCl_3$. Using carefully measured quantities of CF_3OCClO and $CFCl_3$, the observed area ratio for the resonances of the two compounds was employed to determine the relative number of fluorine atoms in each molecule. These were found to be in the expected 3:1 ratio. Table III shows the mass spectrum of CF_3OCClO. The recorded ions corroborate the proposed structure. The parent ions are weak, as is often the case for highly fluorinated compounds. Similar ion fragments have been reported[16] for CF_3OCFO. Trifluoromethyl chloroformate is a colorless liquid, stable at ambient tem-

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(13) P. J. Aymonino, *Chem. Commun.*, 241 (1965).

(14) Absorptions for CF_3OCClO were found at 1835 (vs), 1285 (vs), 1255 (vs), 1200 (s), 1105 (vs), 1070 (sh), 1042 (sh), 962 (w), 880 (s), 740 (w), and 670 cm^{-1} (m).

(15) D. G. Weiblen in "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press, New York, N. Y., 1954, p 457.

(16) T. Johnson, J. Heicklein, and W. Stuckey, *Can. J. Chem.*, 46, 332 (1968).

Table III. Mass Spectrum of CF_3OCClO

m/e	Ion	Rel intensity	m/e	Ion	Rel intensity
12	C^+	1.7	50	CF_2^+	2.7
16	O^+	1.4	63	$CO_2{}^{35}Cl^+$	31.6
19	F^+	0.4	65	$CO_2{}^{37}Cl^+$	10.3
28	CO^+	10.7	69	CF_3^+	100.0
31	CF^+	3.0	85	CF_3O^+	0.23
35	$^{35}Cl^+$	8.8	113	$CF_3CO_2^+$	4.2
37	$^{37}Cl^+$	2.7	148	$CF_3CO_2{}^{35}Cl^+$	0.16
44	CO_2^+	2.5	150	$CF_3CO_2{}^{37}Cl^+$	0.05
47	COF^+	1.9			

perature for days, and easily handled in Pyrex or metal equipment without decomposition.

$$CF_3CF_2OCl \longrightarrow CF_3CF_2O + Cl\cdot$$

$$CF_3CF_2O\cdot \longrightarrow CF_3CFO + F\cdot$$

$$CF_3CF_2O\cdot \longrightarrow COF_2 + CF_3\cdot$$

$$CF_3\cdot + Cl\cdot \longrightarrow CF_3Cl$$

Chloroxypentafluoroethane decomposes readily with either thermal or photolytic initiation. Both conditions give products which are readily accounted for in terms of the intermediacy of the C_2F_5O radical. The thermal decomposition gives predominantly CF_3CFO, ClF, and Cl_2, the latter arising, in part perhaps, through reaction of ClF with the metal walls. Decomposition in this manner is essentially a reversal of the synthetic reaction. Photodecomposition yields COF_2 and CF_3Cl almost exclusively, presumably because of the pronounced instability of the C_2F_5O radical under such conditions. Analogous products (CF_4 and COF_2) are obtained from C_2F_5OF[1] by thermal or radical initiation of decomposition. The instability of the C_2F_5O radical is indicated also by the failure to form $C_2F_5ONF_2$ through reactions with N_2F_4. Irradiation of a mixture of C_2F_5OCl and N_2F_4 gave a mixture of COF_2, CF_3CFO, CF_3Cl, CF_3NF_2, and Cl_2 but no $-ONF_2$ species.

Gradual, but sometimes instantaneous, decomposition of $(CF_3)_2CFOCl$ occurs at room temperature and below. The products found were CF_3CFO, CF_3Cl, CF_3CF_3, and Cl_2; the products can be rationalized through radical fragmentation and recombination.

$$(CF_3)_2CFOCl \longrightarrow (CF_3)_2CFO\cdot + Cl\cdot$$

$$(CF_3)_2CFO\cdot \longrightarrow CF_3CFO + CF_3\cdot$$

$$CF_3\cdot + Cl\cdot \longrightarrow CF_3Cl$$

$$2CF_3\cdot \longrightarrow CF_3CF_3$$

Similarly, $(CF_3)_2CFOF$[1] and reducing agents gave CF_3CFO, CF_4, and $(CF_3)_2C{=}O$. When decomposition of the $(CF_3)_2CFOCl$ was gradual, minor amounts of $(CF_3)_2C{=}O$ were obtained along with CF_3CFO and CF_3Cl.

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Chloroxysulfur Pentafluoride

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Abstract: The preparation, identification, and characterization of chloroxysulfur pentafluoride are reported. Reactions of SF_5OCl leading to SF_5OOSF_5, SF_5ONF_2, and the new compound SF_5OCClO are described.

The reaction of thionyl tetrafluoride or fluorocarbonyls with fluorine in the presence of alkali metal fluorides has been shown[1,2] to be an excellent method for the synthesis of the corresponding fluoroxy compounds, SF_5OF or R_fOF. The previous part of this work[3] reports a similar reaction of fluorocarbonyls with chlorine monofluoride in place of fluorine that results in the formation of chloroxyperfluoroalkanes. This paper describes an extension of the ClF addition reaction to thionyl tetrafluoride which resulted in the new compound, chloroxysulfur pentafluoride, SF_5OCl. Derivatives prepared from SF_5OCl include SF_5OOSF_5,[4] SF_5ONF_2,[5] and the previously unknown chloroformate, SF_5OCClO.

Experimental Section

Apparatus. Synthetic reactions were conducted in stainless steel cylinders, and the products were separated and purified using a stainless steel–Teflon vacuum line. Pressures were measured by means of a Heise, bourdon tube type, pressure gauge. Infrared spectra were taken on Perkin-Elmer Infracords 137 and 337 using 5-cm path length stainless steel or Kel-F cells fitted with AgCl windows. The ^{19}F nmr spectra were obtained at −40° using a Varian Associates high-resolution nmr spectrometer operating at 56.4 Mc. Samples were sealed in Pyrex tubes with $CFCl_3$ as the internal standard. Mass spectral data were obtained with a CEC 21-103 C mass spectrometer modified with a metal inlet system, CEC Part No. 285400.

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