$$CF_3OOC(O)CF_3\ (0.60) + H_2O\ (0.60) \xrightarrow{1\ \text{day}} CF_3CO_2H\ (0.60) + CF_3OOH\ (0.60)$$

$$[CF_3OOC(O)CF_2]_2CF_2\ (0.37) + H_2O\ (0.76) \xrightarrow{1\ \text{day}} [HOC(O)CF_2]_2CF_2\ (0.35) + 2CF_3OOH\ (0.78)$$

$$CF_3OOC(O)CH_3\ (0.42) + H_2O\ (0.44) \xrightarrow{5\ \text{weeks}} CH_3CO_2H\ (0.38) + CF_3OOH\ (0.39)$$

Traces of O_2 and SiF_4 were observed in each case, and a small amount of unreacted $CF_3OOC(O)CH_3$ was present even after 5 weeks.

The cesium fluoride catalyzed reaction of $CF_3OOC(O)CF_3$ with fluorine was carried out to see if the corresponding fluoroxy compound could be obtained. When the reaction was run for 3 hr from −111 to −78° with stoichiometric quantities of fluorine, a 35% yield of the new fluoroxy compound $CF_3OOCF(OF)CF_3$ was obtained. The other product present in significant amounts was C_2F_5OF. No attempts were made to prepare fluoroxy derivatives of the other RC (O)OOCF$_3$ compounds, but it is likely that the corresponding RCF(OF)OOCF$_3$ derivatives can be prepared.

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Preparation and Properties of Chloroperoxytrifluoromethane[1]

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Abstract: The interaction of chlorine monofluoride with trifluoromethyl hydroperoxide at −111° produces chloroperoxytrifluoromethane, CF_3OOCl. This material, a stable yellow gas at room temperature, is the first stable compound containing an OOCl linkage. Characterization and physical properties of CF_3OOCl are consistent with the peroxide structure.

Compounds of the type R_fOOX (X = halogen) are very rare, the only previously reported examples being CF_3OOF[2a] and a few higher perfluoroalkyl homologs, R_fOOF.[2b] No analogous peroxides containing the OOCl function have hitherto been observed.

The conversion of fluorinated alkoxide salts and fluorinated alcohols to the corresponding hypochlorites by reaction with chlorine momofluoride has recently been noted[3-7]

$$R_fOM + ClF \longrightarrow R_fOCl + MF$$

$$R_fOH + ClF \longrightarrow R_fOCl + HF$$

and we have now extended this technique to the preparation of the first stable compound containing an OOCl grouping, chloroperoxytrifluoromethane. The

$$CF_3OOH + ClF \longrightarrow CF_3OOCl + HF$$

existence of a stable OOCl compound is of particular interest in light of recent studies involving detection of the short-lived ClOO· radical.[8]

Despite the presence of an additional reactive site—the peroxide linkage—trifluoromethyl hydroperoxide reacts cleanly with chlorine monofluoride at the O–H bond to produce CF_3OOCl exclusively; no O–O scission to produce CF_3OCl is discernible. Whether the driving force for this reaction is the production of HF or whether this reflects an unusually strong O–O bond in CF_3OOH cannot be ascertained from our experiments, though it is likely that the thermodynamic stability of HF is a major factor.

The possibility exists that the new material, with empirical formula CF_3O_2Cl, may exist in either of the isomeric forms $CF_3OCl{=}O$ or CF_3OOCl, but only the latter structure is consistent with the observed data. The presence of CF_3OO^+ and CF_2OO^+ in the mass spectrum of the material, as well as the similarity between its infrared spectrum and that of CF_3OOH[9] and CF$_3$-

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OOF,[2a] are indicative of the CF_3OOCl form. Further, no infrared absorption in the Cl=O region (~1100 cm^{-1} [10]) is observed, though $CF_3Cl{=}O$ would be expected to absorb strongly in this region.

Although we have conducted no detailed thermal stability tests, CF_3OOCl is stable at 25° for prolonged periods, indicating both reasonably strong O–O and O–Cl bonds. There is perhaps a parallel between CF_3OOCl and CF_3OOF in that both are reasonably stable molecules (as are CF_3OCl and CF_3OF), though the matrix-isolated OOCl[11] and OOF[12] radicals exhibit extremely weak oxygen–halogen bonds.

Although the reaction chemistry of CF_3OOCl has not been extensively explored as yet, the molecule does not seem to exhibit properties similar to those of the perfluoroalkyl hypochlorites.[13] Thus CF_3OCl readily adds CO, SO_2, or C_2F_4 to yield $CF_3OC(O)Cl$, CF_3OSO_2Cl, and $CF_3OC_2F_4Cl$, respectively,[13,14] while CF_3OOCl does not yield the corresponding addition products under similar reaction conditions. This may imply a stronger Cl–O linkage in CF_3OOCl. The compound may exhibit primarily peroxidic properties inasmuch as it initiates extremely vigorous polymerization of tetrafluoroethylene at relatively low temperatures; further, the products obtained from photolysis of CF_3OOCl can be readily explained by primary cleavage of the O–O bond.

$$CF_3OOCl \xrightarrow{uv} CF_3O\cdot + \cdot OCl$$

$$2CF_3O\cdot \longrightarrow CF_3OOCF_3$$

$$ClO\cdot \longrightarrow [ClOOCl] \longrightarrow ClO_2 + Cl\cdot$$

The production of some oxygen in the mixture may indicate the cleavage of the O–Cl bond and subsequent coupling of the resultant $CF_3OO\cdot$ radicals to yield an unstable tetroxide which could then decompose to $CF_3OOCF_3 + O_2$.

The existence of a stable compound containing the OOCl grouping suggests that chemical "trapping" of the OOCl radical in the form of CF_3OOCl should be explored as a possible alternative to the currently available methods for detecting the OOCl radical by either low-temperature matrix isolation (~4°K)[11] or elaborate spectroscopic techniques.[8]

Experimental Section

Preparation of CF_3OOCl. Chlorine monofluoride was obtained from the Ozark-Mahoning Co. Trifluoromethyl hydroperoxide, CF_3OOH, was prepared by oxidation of hexafluoroacetone with hydrogen peroxide[15] and was purified by trap-to-trap fractionation. The product, collected at −111°, was shown by its infrared spectrum and physical properties to be identical with the CF_3OOH prepared by Talbott.[9]

Preparation and characterization procedures were carried out under vacuum conditions in a nickel–Monel line equipped with Kel-F traps. Reaction vessels were fabricated from $^3/_8$-in. Kel-F tubing and attached to metal Hoke valves with Swagelok fittings.

In a typical reaction CF_3OOH (1.0 mmol) and ClF (1.1 mmol) were condensed at −196° into a 5-ml Kel-F reaction vessel and allowed to warm to −111° for 1 hr. A light yellow product was observed which contained a second clear immiscible layer. Separation of the products was conveniently carried out by condensing the mixture onto dry NaF. The by-product, HF, was effectively removed at room temperature by this technique without decomposing the CF_3OOCl. Final purification for physical measurements required the removal of trace quantities of ClO_2. This was accomplished by passing the mixture through a −111° trap, which retained the impurity, and collecting CF_3OOCl at −196°. Samples were checked for purity by gas chromatography with a 20% Kel-F No. 10 on Teflon 6 column. Yield of the reaction was generally above 95% with 100% conversion of the CF_3OOH.

Anal. Calcd for CF_3OOCl: C, 8.79; F, 41.76; Cl, 26.00. Found: C, 8.40; F, 40.00; Cl, 28.30.

Properties of CF_3OOCl. Chloroperoxytrifluoromethane is a pale yellow liquid which is stable at room temperature and can be stored without decomposition in glass or Kel-F containers. The compound is not readily hydrolyzed by atmospheric moisture and can be easily handled *in vacuo* after removal of the by-product HF. Thermal decomposition of CF_3OOCl in a glass tube at 100° was complete in 5 min; COF_2, SiF_4, CO_2, and ClO_2F were the main decomposition products observed by infrared spectroscopy.

Vapor Pressure, Boiling Point, and Melting Point. The vapor pressure of CF_3OOCl was measured in a Monel vacuum system with a Model F-145 Wallace & Tiernan gauge; temperatures were determined with a chromel–alumel thermocouple attached externally to the sample tube. The vapor pressure over the range −110 to 23° is represented by the equation

$$\log P\ (\text{mm}) = 7.742 - (1.221 \times 10^3)/T\ (^\circ\text{K})$$

as calculated from the following data [temperature, °K (pressures, mm)]: 253.1 (794.5), 253.0 (770.0), 252.4 (746.5), 251.6 (727.5), 251.0 (705.0), 248.0 (648.0), 247.5 (620.5), 244.8 (568.9), 244.4 (549.0), 241.4 (470.5), 238.6 (417.5), 235.8 (363.5), 233.1 (317.5), 230.5 (275.5), 227.4 (237.0), 225.4 (211.5), 221.8 (175.0), 217.6 (134.0), 212.4 (98.5), 206.1 (64.5), 202.8 (51.7), 197.4 (32.5), 191.5 (22.5), 188.1 (16.7), 186.1 (14.5), 183.1 (11.0).

The boiling point calculated from the above equation is −22° the latent heat of vaporization is 5573 cal/mol, and the Trouton constant is 22.2.

Chloroperoxytrifluoromethane freezes to a yellow solid but tends to form a glass when not totally pure. The melting point was determined to be approximately −132°.

Infrared Spectrum. The infrared spectrum of CF_3OOCl was recorded on a Perkin-Elmer Model 521 spectrophotometer from 4000 to 450 cm^{-1}. The spectrum contained three strong bands at 1275, 1235, and 1207 cm^{-1} which can be assigned to C–F asymmetric and symmetric stretching frequencies. The band at 891 (m) can be assigned to C–O stretch while the band at 813 (m) is in the region assigned by others to the O–O stretching mode.[16,17] The three bands at 655 (m), 600 (w), and 570 (m) are in the region expected for OCl stretch as well as CF_3 deformation, but cannot definitely be assigned.[16,18,19]

Nmr and Mass Spectra. The F-19 nmr spectrum was recorded at room temperature on a Varian A56-60 nmr spectrometer. A single resonance was observed at +69.9 ppm relative to $CFCl_3$ internal standard.

The mass spectrum was determined with a Consolidated Electrodynamics Corp. Model 21-103 spectrometer operating at an ionizing potential of 70 eV. It was necessary to "condition" the inlet chamber with purified samples of CF_3OOCl before a reproducible cracking pattern could be obtained. Characteristic peaks observed in the cracking pattern are listed below [*m/e* (abundance, including isotopic contribution), assignment]: 136 (7.2) CF_3OOCl (m^+); 104 (1.0) CF_3Cl^+; 101 (0.2) CF_3OO^+; 82 (5.9) CF_2OO^+; 69 (100) CF_3^+; 66 (39.2) CF_2O^+; 53 (36.2) ClO^+.

Reactions of CF_3OOCl. With C_2F_4. The interaction of CF_3OOCl (2 mmol) with C_2F_4 (2.2 mmol) was carried out by condensing the two reactants into an evacuated 3-ml Kel-F reactor at −196°.

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As the vessel was warming slowly from −196°, an explosion occurred at about −110°. Products of the reaction were not contained.

With SO_2. An equimolar mixture of SO_2 and CF_3OOCl (2 mmol) was observed to react slowly at −24°. The product mixture showed mainly COF_2 and starting materials. Minor products were identified as CF_3OOH, SiF_4, and SO_2ClF.

With CO. A 2-mmol sample of CF_3OOCl was allowed to react with excess CO in a 75-ml of stainless steel Hoke vessel for 24 hr. The product mixture contained COF_2, COFCl, CF_3OOH, and one unidentified product. Spectra of the latter were consistent with spectroscopic data for $CF_3OOC(O)F$, but the material was not fully characterized.

Photolysis. A 2-mmol sample of CF_3OOCl was condensed into an evacuated 200-ml glass reaction vessel equipped with a concentric quartz well and irradiated at −78° for 30 min with a 20-W uv lamp. After warming to room temperature, the major products were identified as CF_3OOCF_3, ClO_2, and a noncondensable gas (O_2). No other fluorocarbons were detected in photolysis reactions under the above conditions or at higher temperature. Higher oxygen-containing species may exist as intermediates in the reaction, but were not isolated under these conditions.

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