Chloroxyfluoroxydifluoromethane

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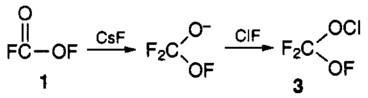
Introduction

Fluorocarbonyl hypofluorite, FC(O)OF (**1**),[1] was previously described as a low-yield, unstable product of the UV irradiation of a mixture of F_2 and bis(fluoroformyl) peroxide, $[FC(O)O]_2$ (**2**),[2] prepared by flowing CO, O_2, and F_2 through a Pyrex glass vessel. Other than the few reactions described by Cauble and Cady in 1967,[1] there were no further reports on the chemistry of this unusual hypofluorite until the recent synthesis of difluorodioxirane, CF_2OO (**3**).[3]

We have found that the reaction of **1** with chlorine monofluoride in the presence of cesium fluoride doped with H_2O results in the formation of the new and interesting compound $CF_2(OCl)OF$ (**4**). Chloroxyfluoroxydifluoromethane is the first example of a compound containing both of these reactive functional groups.

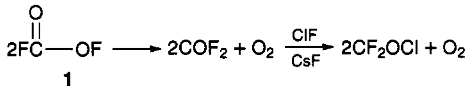
Results and Discussion

A potential route to **4** was envisioned by us to be the oxidation of the anion $FOCF_2O^-$ by ClF. This anion could be generated in principle by the nucleophilic attack of fluoride ion on the unstable molecule FC(O)OF (**1**) (eq 1). This plan was reinforced by the fact that **1** is converted to $CF_2(OF)_2$ by reaction with elemental fluorine in the presence of CsF.[1] However, we have found that when dry CsF was used, this reaction was not successful and led mainly to the formation of CF_3OCl and O_2. Depending on the CsF and the reaction conditions, CF_3OOCl was also observed as a reaction product.

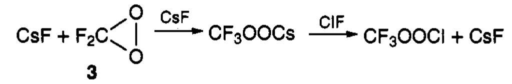


$$FC(O)OF \xrightarrow{CsF} F_2C(O^-)(OF) \xrightarrow{ClF} F_2C(OCl)(OF) \qquad (1)$$

The formation of CF_3OCl arises from the known CsF-catalyzed oxidation of COF_2 by chlorine monofluoride[4] and/or the decomposition of CF_3OOCl.[5] Carbonyl fluoride may be formed by decomposition of **1** (eq 2). The formation of CF_3OOCl probably occurs via the difluorodioxirane which is the major product when the reaction is carried out in a flow system (eq 3).[3] This reaction is consistent with the known synthesis of CF_3OOCl starting with $CF_3OOC(O)F$ (eq 4, 5).[5] We have previously argued that eq 5 was the reaction path to CF_3OOCl and the related SF_5OOCl from $SF_5OOC(O)F$.[5,6] On the basis of considerable experience since this earlier research, we now favor the intermediary of the peroxy anion in these reactions.



$$2FC(O)OF \longrightarrow 2COF_2 + O_2 \xrightarrow[CsF]{ClF} 2CF_2OCl + O_2 \qquad (2)$$



$$CsF + F_2COO \xrightarrow{CsF} CF_3OOCs \xrightarrow{ClF} CF_3OOCl + CsF \qquad (3)$$

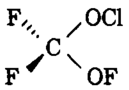
$$CF_3OOC(O)F \xrightarrow[-78\ ^\circ C]{CsF} CF_3OOCs + COF_2 \xrightarrow[-CsF]{ClF} CF_3OOCl + COF_2 \qquad (4)$$

$$CF_3OOC(O)F \xrightarrow[-78\ ^\circ C]{CsF/ClF} [CF_3OOCF_2OCl] \rightarrow CF_3OOCl + COF_2 \qquad (5)$$

When "wet" CsF was used in place of dry CsF, $CF_2(OCl)OF$ (**4**) was obtained in 40−70% yield (see the Experimental Section for details). Although the presence of water has been shown to be essential in this synthesis, the mechanism of its action has not yet been determined. Other products with water-doped CsF are CF_3OCl, O_2 and CO_2, with the latter forming via hydrolysis of COF_2.

Chloroxyfluoroxydifluoromethane when frozen is a pale yellow solid which melts at −128 ± 2 °C, with an estimated bp of −20 °C. The calculation of the normal boiling point from vapor pressure data was not possible because of the mild explosive decomposition that the compound undergoes when the pressure approaches ~40 Torr. A strong dependence of the stability on partial pressure has been observed for other hypochlorites and hypofluorites.[7,8] The stability of the compound when stored at low temperature is high. In the gas phase at 22 °C and 4−5 Torr, the compound slowly decomposes to COF_2, ClF, and O_2. This probably occurs by the initial loss of ClF which is a common mode of decomposition for R_fOCl in general. Loss of ClF should give rise to FC(O)OF, which may then decompose to COF_2 and O_2, but this intermediate was not observed.

The IR data are consistent with the structure:



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While the bands from 820 to 1280 cm^{-1} are consistent with the expected C−F, C−O, and O−X stretches, they cannot be readily assigned. It is likely that $CF_2(OF)OCl$ exists as a mixture of conformational isomers as was found for $CF_2(OF)_2$, which has at least two conformers in the gas and liquid phase.[9] This fact has made a detailed vibrational assignment of $CF_2(OF)_2$ difficult. The ^{19}F NMR gives the expected δOF at +155.6 ppm and $\delta(CF_2)$ at −79.9 ppm with $^3J_{FF} = 32.2$ Hz. Further support for $CF_2(OF)OCl$ was obtained by vapor density molecular weight (136.4, calcd 136.46) and oxidizing equivalents (3.9, calcd 4.0).

The reaction chemistry of $CF_2(OF)OCl$ has not yet been investigated. From preliminary work it is clear that it does not behave like $CF_2(OF)_2$ on addition to fluorinated alkenes.[10] In

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addition, our original hypothesis that $CF_2(OF)OCl$ would be a source of difluorodioxirane has not been substantiated.

Experimental Section

General Procedures. Volatile compounds were handled in a Pyrex glass or stainless steel vacuum system equipped with a MKS-BARATRON Type 223 B pressure transducer. Amounts of gaseous reactants and products were measured assuming ideal gas behavior. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR using a 10 cm gas cell fitted with AgCl windows. NMR spectra were recorded at 188 MHz using an IBM NR 200 AF FT-NMR. Carbon tetrachloride was used as a solvent with $CFCl_3$ as a reference. Lock was via acetone-d_6 contained in a sealed capillary tube.

Reagents. Fluorine, carbon monoxide, oxygen, CsF, and chlorine were obtained from commercial sources. Chlorine monofluoride was prepared by heating equimolar amounts of Cl_2 and F_2 (90 mmol) at 230 °C in a 150 mL Monel cylinder for 18 h. (*Caution!* Contained explosions are observed under these conditions as the temperature approaches ~100 °C.) The ClF was taken out of the bomb at −111 °C to prevent contamination by ClF_3.

Caution! Although no serious explosions occurred during this work, fluorinated peroxides, hypofluorites, and hypochlorites under certain conditions are capable of an energetic explosive decomposition. Appropriate precautions should be taken when handling these compounds.

Bis(fluoroformyl) Peroxide (2), [FC(O)O]$_2$.[2] **2** was prepared by reaction of F_2 (2), CO (1), and O_2 (6) in a flow system at 22 °C. The O_2 and F_2 were premixed and contacted the CO in a 1 L glass vessel. The total flow rate was approximately 200 std cm^3/min. The product was collected in a −78 °C trap and used without further purification. Ten grams could safely be prepared in a period of 10−12 h.

Caution! The preparation of **2** is potentially hazardous depending on how the CO is mixed with O_2 and F_2. We had no incidents as long as the flow of gases was started in the order O_2, F_2, and CO with a 2 min delay between each. Shutdown was in the order CO, F_2, and O_2. Gas flow in the order O_2, CO, and F_2 results in a violent explosion.

Fluorocarbonyl Hypofluorite (1), FC(O)OF. **1** was prepared by reaction of F_2 and **2** under UV irradiation as previously described.[1] We nevertheless found that by using a 12 W low-pressure UV lamp in place of a 350 W medium-pressure Hg lamp, as reported in the literature, both the conversion and the yield were greatly improved. In a typical reaction, 7 mmol of **2** and 14 mmol of F_2 were added to a 500 mL Pyrex glass vessel by vacuum transfer and irradiated for 5 h via a quartz immersion well. The conversion of the peroxide into other products was 98%. Vacuum fractional condensation of the reaction mixture through -110, −125, −140, and −196 °C traps gave essentially pure hypofluorite in the −140 °C trap in an average yield of 40%. The purity of the compound was checked by IR and ^{19}F NMR spectroscopy. We found the stability of the hypofluorite to be much higher than that originally reported.[1] Decomposition during routine manipulation in the vacuum line was slight at pressures below 10−15 Torr.

Synthesis of Chloroxyfluoroxydifluoromethane (4), F$_2$C(OCl)OF. In a typical reaction FC(O)OF (1 mmol) and ClF (1.1 mmol) were condensed at −196 °F in a 75 mL Teflon reactor previously charged with 5 g of CsF. The catalyst was doped with water by keeping it in an open vessel until water (1−3 mmol) was absorbed from the air. The Teflon reactor was then allowed to warm to room temperature over 30 min. The reaction products were then separated by vacuum fractional condensation through −125 and −196 °C traps. **4** was collected in the −125 °C trap in an average yield of 40%. In the −196 °C trap were collected CF_3OCl, COF_2, and CO_2. Yields of $CF_2(OCl)OF$ ranged from 20 to 70%.

4: mp = -128 ± 2°C, bp ≃ −20°C; MW = 136.4, calcd 136.46; IR (gas, 10 Torr) 1280 (sh), 1245 (vs), 1202 (vs), 1172 (vs), 1143 (sh), 1039 (vw), 941 (w), 924 (vw), 878 (w), 820 (w), 667 (w, complex), 607 (vw) cm^{-1}; ^{19}F NMR (CCl_4) −79.9 (2F, d), 155.6 (1F, t), $^3J_{FF}$ = 32.2 Hz.

Iodimetry. The oxidizing equivalents of **3** were determined by reaction of a weighed sample with acidified aqueous potassium iodide. The liberated iodine was titrated with standard $Na_2S_2O_3$. The sample gave a value of 3.9 equivs/mol compared to the expected value of 4 based on the following equation.

$$6I^- + CF_2(OCl)OF \rightarrow 2I_3^- + 3F^- + Cl^- + CO_2$$

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