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Difluorodioxirane, a Possible Intermediate in the Reaction of Bis(fluoroxy)difluoromethane with Cesium Trifluoromethoxide

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Introduction

Bis(fluoroxy)difluoromethane, $CF_2(OF)_2$, is a highly reactive but easily prepared compound.[1,2] Most reports on the chemistry of this unusual compound appeared prior to 1980.[3−5] However, the recent development by Ausimount of the synthesis of the 2,2-difluoro-1,3-dioxolanes via cycloaddition of $CF_2(OF)_2$ with alkenes has rekindled interest in this compound.[6]

One of the more interesting early reactions of $CF_2(OF)_2$ was the synthesis of perfluoroperoxy ester, $CF_3OOC(O)F$, by reaction with cesium trifluoromethoxide in the presence of cesium fluoride and excess carbonyl fluoride:[3]

$$\mathrm{FOCF_2OF + CsOCF_3 + COF_2 \xrightarrow[-22\ ^\circ C,\ 16\ h]{CsF} CF_3OF + \underset{70\%}{CF_3OOC(O)F}} \quad (1)$$

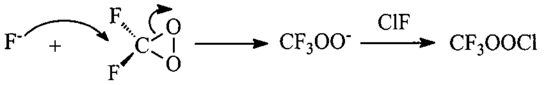
The mechanism originally proposed for reaction 1 involved an intermediate, trifluoromethylperoxy anion CF_3OO^-, but how this anion was formed was unknown (see Scheme 1).

Scheme 1

$$\mathrm{FOCF_2OF + CsOCF_3 \rightarrow CF_3OF + [CsOCF_2OF] \rightarrow CsOOCF_3}$$

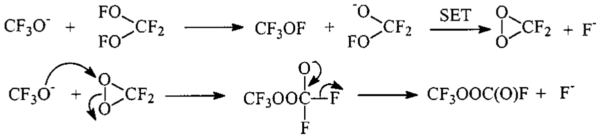
$$\mathrm{CsOOCF_3 + 2COF_2 \rightarrow CF_3OOC(O)F + CsOCF_3}$$

The discovery of difluorodioxirane[7] in 1993 provided a potential alternative route to CF_3OO^- (reaction 2) based on the observation of a significant amount of CF_3OOCl in the formation of the dioxirane from the reaction of fluorocarbonyl hypofluorite with ClF in the presence of CsF.[8]

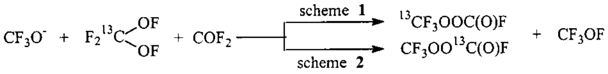


(2)

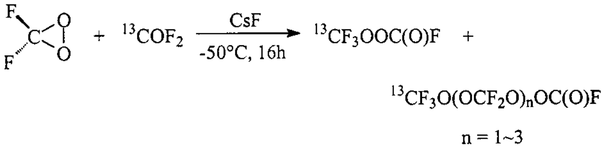
Scheme 2



Scheme 3



However, this proposal is not consistent with our recent ^{13}C labeling studies. These studies of difluorodioxirane chemistry have shown that the O−O bond of difluorodioxirane is the preferred site of attack by nucleophiles:[9]



(3)

When we run reaction 1 by using ^{13}C-labeled COF_2, we found that the ratio of ^{13}C in the CF_3 group was higher than the ratio of ^{13}C in the C(O)F group. If CF_3OO^- was an intermediate as proposed in Scheme 1, the opposite would have been observed. From the results of reaction 3, we now propose a more reasonable mechanism for the formation of $CF_3OOC(O)F$ as in reaction 1, involving difluorodioxirane as an intermediate in the reaction (Scheme 2).

The proposed reactions in Schemes 1 and 2 are in theory distinguishable by the different origins of the carbonyl and the trifluoromethyl carbon atoms. For example, the reaction of labeled $^{13}CF_2(OF)_2$ with cesium trifluoromethoxide in the presence of cesium fluoride and excess carbonyl fluoride in Scheme 1 would lead to $^{13}CF_3OOC(O)F$ and in Scheme 2 it would give $CF_3OO^{13}C(O)F$ (see Scheme 3).

In this paper, the results of a series of ^{13}C-labeling experiments, which provide mechanistic insight for the formation of $CF_3OOC(O)F$, are reported.

Experimental Section

Caution! The chemicals employed in this work are hazardous and should only be used by experienced personnel familiar with the safe handling of toxic strong oxidizers.

$^{13}COF_2$ was obtained according to literature method.[9] ^{13}CO and $^{13}CO_2$ (>99% ^{13}C) were obtained from Cambridge Isotopes. Cesium fluoride was dried at high temperature in a Pt crucible and then ground to a powder in a drybox. IR spectra were recorded on a Perkin-Elmer 2000 FT/IR using a 10 cm glass cell fitted with AgCl windows. NMR spectra were recorded on Brucker FT-NMR instruments at 188.3 MHz for ^{19}F and 75.4 MHz for ^{13}C. Carbon tetrachloride was used as a solvent with an external D_2O lock.

$^{13}CF_2(OF)_2$ was prepared by reacting $^{13}CO_2$ with F_2 in the presence of CsF at 25 °C for 24 h. $^{13}CF_2(OF)_2$. ν_{max} (cm^{-1}): 1260, 1212, 1173, 1152, 922, 688, 649. δ_c (CCl_4) (ppm): 126.6 (t−t), $^1J_{C-F} = 275.5$, $^2J_{C-F} = 6.0$ Hz. δ_F ($CFCl_3$): −83.8 (d−t, CF_2), 159.6 (t−d, OF), $^3J_{F-F} = 39.4$ Hz.

Reaction of $CF_2(OF)_2$ with CF_3O^-. In a typical reaction, bis(fluoroxy)difluoromethane (0.2 mmol) and COF_2 (0.8 mmol) were condensed onto dry CsF (2 g) in a 75 mL stainless steel reactor cooled to −196 °C. The reactor was then warmed to −20 °C and held at this temperature for several hours. Oxygen was then removed at −196 °C,

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Table 1

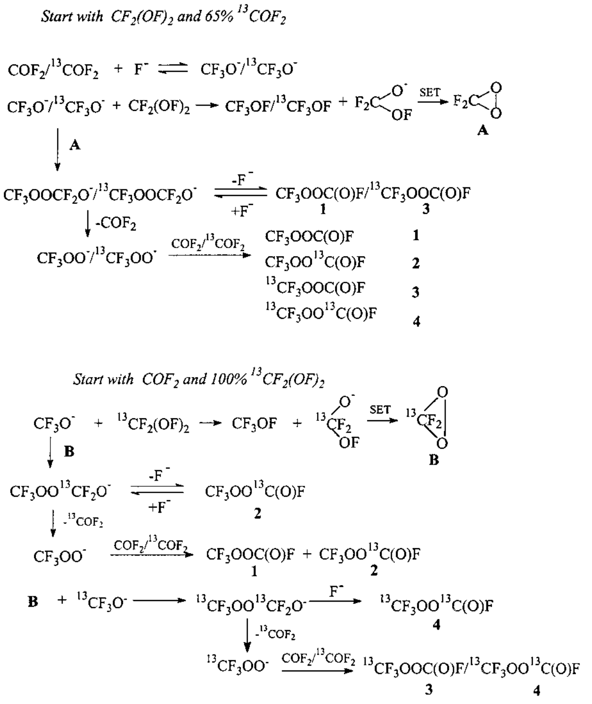
	COF_2	$CF_2(OF)_2$	reaction condition	% ^{13}C in $CF_3OOC(O)F$	
				$-CF_3$	$-C(O)F$
1	70% ^{13}C	99% ^{12}C	−20 °C, 16 h	68	64
2	65% ^{13}C	99% ^{12}C	−20 °C, 5 h	63	10
3	99% ^{12}C	100% ^{13}C	−20 °C, 16 h	3	12
4	99% ^{12}C	100% ^{13}C	−20 °C, 8 h	6	45

Scheme 4

$$CF_3OOC(O)F \underset{-F^-}{\overset{+F^-}{\rightleftharpoons}} CF_3OO^- + COF_2$$

$$CF_3OO^- + {}^{13}COF_2 \underset{-F^-}{\overset{+F^-}{\rightleftharpoons}} CF_3OO{}^{13}C(O)F$$

Scheme 5



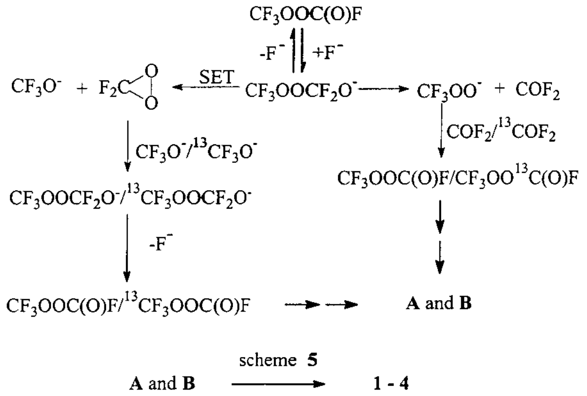
and the remaining volatile substances were fractionated through traps held at −125 and −196 °C. The yield of CF_3OF in the −196 °C trap was quantitative, but the yield of $CF_3OOC(O)F$ varied from 10 to 40% based on $CF_2(OF)_2$. The yield of $CF_3OOC(O)F$ is very dependent on reactant ratios, pressure, temperature, and time. The ^{13}C ratio in $CF_3OOC(O)F$ was checked by ^{19}F NMR. The results are summarized in Table 1.

^{13}C Exchange in the $CF_3OOC(O)F/^{13}COF_2/CsF$ System. $CF_3OOC(O)F$ (0.3 mmol, 98.9% ^{12}C) and COF_2 (1 mmol, 100% ^{13}C) were condensed onto dry CsF (2 g) as above. The reactor was then warmed to −20 °C and held at this temperature for 24 h. Oxygen was then removed at −196 °C, and the remaining volatile substances were fractionated through traps held at −125 and −196 °C. The −196 °C trap contained 1.3 mmol of COF_2 (71% ^{13}C). The −125 °C trap contained 0.15 mmol of $CF_3OOC(O)F$ (CF_3, 27% ^{13}C; C(O)F, 69% ^{13}C).

Results and Discussion

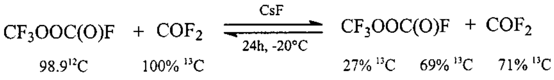
The use of ^{13}C labels in fluorocarbon chemistry is a powerful tool for providing mechanistic insight into complex reactions. The large isotopic shifts for fluorine bound to ^{13}C and the characteristic large $^1J_{^{13}C-F}$ coupling constant allows the use of ^{19}F NMR to determine the isotopic distribution in all compounds containing C−F bonds. In this study the facile syntheses of the ^{13}C-labeled COF_2 and $CF_2(OF)_2$ were instrumental in our decision to undertake these studies.

Scheme 6



Our earlier work on the reaction of nucleophiles with difluorodioxirane did not provide a source of CF_3OO^- anion as initially envisioned and offered little support for the proposal that $CF_3OOC(O)F$ arises from CF_3OO^- attack on COF_2 in the reaction of $CF_2(OF)_2$ with COF_2/CsF. Using ^{13}C-labeled COF_2 and $CF_2(OF)_2$ was then an attractive route toward a better understanding of this reaction. The results in Table 1 show two striking features: With $^{13}COF_2$ and $CF_2(OF)_2$ (runs 1 and 2) the product $CF_3OOC(O)F$ contains a majority of ^{13}C in the CF_3 group, depending on reaction conditions. With $^{13}CF_2(OF)_2$ and COF_2 (runs 3 and 4) the majority of ^{13}C is in the carbonyl group, again depending on reaction conditions. The isotopic distribution in the CF_3OF is essentially the same as the starting COF_2.[10] These results are consistent with Scheme 2, but clearly the reactions taking place are more complex.

Initially we were puzzled by these results, but earlier work on the use of $CF_3OOC(O)F$ as a source of CF_3OO^- provided direction. Since $CF_3OOC(O)F$ appears to react with CsF to form CF_3OO^-,[11,12] we reasoned that this could provide a route for carbonyl exchange (Scheme 4). In the presence of excess $^{13}COF_2$ and COF_2, this would lead to the introduction of ^{13}C in the carbonyl group in runs 1 and 2. This was confirmed by the reaction of $CF_3OOC(O)F$ with $^{13}COF_2$:



$$\underset{98.9\%\ ^{12}C}{CF_3OOC(O)F} + \underset{100\%\ ^{13}C}{COF_2} \xrightleftharpoons[24h,\ -20°C]{CsF} \underset{27\%\ ^{13}C\quad 69\%\ ^{13}C}{CF_3OOC(O)F} + \underset{71\%\ ^{13}C}{COF_2} \qquad (4)$$

However, this reaction also gave 27% ^{13}C in the CF_3 group. This result and the appearance of ^{13}C in the CF_3 group in runs 3 and 4 clearly indicated that any mechanistic proposal must also provide a means for carbon exchange in the CF_3 group of $CF_3OOC(O)F$.

In Scheme 5 a simplified mechanistic route is proposed that explains the observed products for runs 1−4. In our opinion it is necessary to invoke the CF_3OO^- anion to obtain the observed isotopomers.[13] However, Scheme 5 will not account for the

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(10) In a control experiment, ^{13}C exchange between CF_3OF and a 70% ^{13}C mixture of COF_2 gave the following results: 0% exchange of ^{13}C after 10 h at −20 °C; 9% ^{13}C exchange after 10 h at 22 °C. At higher temperatures we would anticipate a larger exchange, but this experiment was not carried out.

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(12) We cannot identify the amounts of the individual isotopomers **1**−**4**. From the ^{19}F NMR data one can conclusively state that at least two must be present. However, since the ^{19}F integrations for fluorine bound to ^{13}C and for fluorine bound to ^{12}C are not in the ratios of 3:1 (CF_3/C(O)F), we have a high degree of confidence that all four possible isotopomers are present.

observed isotopomers in the reaction of $CF_3OOC(O)F$ with $COF_2/^{13}COF_2$ in the presence of CsF. No reasonable reaction other than invoking the dioxirane as an intermediate can explain the formation of the products. In Scheme 6 this route is outlined. Clearly, if this proposal is correct, then this pathway must also be included in Scheme 5.

In both Schemes 5 and 6 not all possible reactions and interconnects are shown for the sake of clarity. However, the indicated reactions can account for all the observed isotopomers. Obviously in this complex system the extent of the different reactions depends critically on the experimental conditions. Also, we do not know the origin of the single electron-transfer reactions, but we are confident that they occur; otherwise, the difluorodioxirane cannot form from the required intermediate radicals $FOCF_2O^{\bullet}$ and $CF_3OOCF_2O^{\bullet}$.[14] Without the dioxirane, a rationale for the observed products could not be found.

In conclusion, the use of ^{13}C labeling has provided good insight for a plausible mechanism for a reaction first discovered in 1970. Like much of chemistry, the closer one looks, the more complex seemingly simple reactions become.

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(14) The radicals $FOCF_2O^{\bullet}$ and $CF_3OOCF_2O^{\bullet}$ are involved in reactions of $CF_2(OF)_2$ and CF_3OOCF_2OF, respectively, with halogenated alkenes. In these cases, the difluorodioxirane is not observed as a product because the intermediate radicals are trapped by the excess alkene. See ref 6 and the following. Russo, A.; Montanari, V.; Navarrini, W.; DesMarteau, D. D. *J. Fluorine Chem.* **1995**, *74*, 83.