

Synthesis and reaction chemistry of fluoroxydifluoromethyl fluoroformyl peroxide

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Abstract

The reaction of bis(fluoroformyl) peroxide **1** with F₂ in the presence of CsHF₂ or KHF₂ produces FOCF₂OOC(O)F **2** in 60% yield. The previously known FOCF₂OOCF₂OF is also obtained as a byproduct along with small amounts of the new compounds FOCF₂OOC(O)OOC(O)F **3** and FOCF₂OOC(O)OOCF₂OF **4**. Hydrolysis of **2** affords either FOCF₂OOC(O)OOCF₂OF **4** or FOCF₂OOH **5** in low yield, depending on the reaction conditions. Fluorination of peroxides **3–5** provides the corresponding fluoroxy compounds in high yields and provides further proof of structure. © 2001 Published by Elsevier Science B.V.

Keywords: Fluoroxy compounds; Peroxygen compounds; Cesium bifluoride; Novel structures

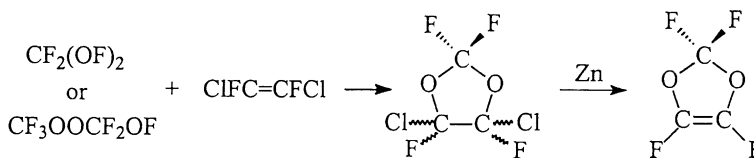
1. Introduction

Hypofluorites are a class of high-energy oxidizers which are among the most reactive compounds in chemistry [1–3]. The relatively weak O–F bond, coupled with high bond energies of oxygen and fluorine to many elements, accounts for their reactivity. Hypofluorites can be used for selective electrophilic fluorination [4–7] and for the preparation of fluorinated vinyl ethers in a process developed by Ausimont [8,9]. The commercial use of CF₃OF and other hypofluorites was based in part on early research that showed that CF₃OF could be added to a variety of alkenes [10].



method for a variety of geminal bis(fluoroxy) compounds by reaction of fluorinated carboxylic acids with fluorine in the presence of cesium fluoride which gave the corresponding 1,1-bis(fluoroxy)perhaloalkanes in high yield [16]. Recently, Zedda and DesMarteau reported a new preparative method for 2,2-bis(fluoroxy)perfluoropropane based on the fluorination of (CF₃)₂C(OH)₂ in the presence of CsF or KF [17].

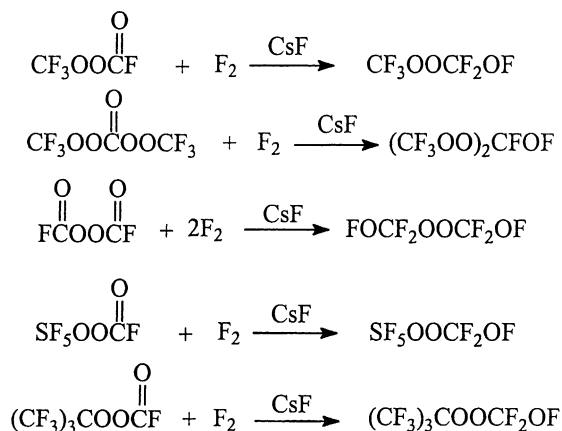
Since, the commercial developments in late 1980s, the reactions of perfluoroalkyl hypohalites with olefins have been extensively studied. The recent discovery of reactions of CF₂(OF)₂ or CF₃OOCF₂OF to prepare novel dioxoles [18–20], increased interest in the synthesis and reactivity of geminal bis(fluoroxy) compounds and geminal fluoroxy peroxy compounds.



The first fluorocarbon bis(fluoroxy) compound, CF₂(OF)₂ was reported by several groups in 1967 [11–14]. Other geminal compounds including CF₃CF(OH)₂ and (CF₃)₂C(OH)₂ were synthesized in the same year but in low yields [15]. Sekiya and DesMarteau developed a better preparative

The work presented in this paper was part of a study of the chemistry of bis(fluoroformyl) peroxide. Previously, only five compounds containing both the peroxy and the fluoroxy functional groups on the same carbon had been reported. They are CF₃OOCF₂OF, (CF₃OO)₂CFOF, FOCF₂OOCF₂OF, SF₅OOCF₂OF and (CF₃)₃COOCF₂OF and were first prepared by the following reactions [21–24].

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Recent research on the chemistry of difluorodioxirane and bis(fluoroformyl) peroxide has led to several additional analogous compounds, including $\text{CF}_3\text{OOCF}_2\text{OOCF}_2\text{OF}$, $\text{CF}_3\text{O}(\text{OCF}_2\text{O})_n\text{OCF}_2\text{OF}$, $\text{FOCF}_2\text{OOCF}_2\text{OOCF}_2\text{OF}$ and 1-fluoroxy-1,4,4-trifluoro-2,3,5,6-tetraoxacylohexane [25,26].

This paper describes the synthesis and chemistry of fluoroxydifluoromethyl fluoroformyl peroxide $\text{FOCF}_2\text{OO-C(O)F}$, the first example of a compound having the peroxy, fluoroformyl and hypo fluorite function in one molecule. The synthesis of $\text{FOCF}_2\text{OOC(O)F}$ was based in part on the research work of DesMarteau and Anderson [27] who showed that monohypofluorites $\text{FOCF}_2(\text{CF}_2)_n\text{C(O)F}$ could be obtained by CsHF_2 or KHF_2 catalyzed addition of F_2 to one carbonyl group of the diacyl fluorides [27].

2. 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.

Volatile compounds were handled in a Pyrex vacuum system equipped with glass-Teflon valves. Pressures were measured on an MKS Baratron Type 223B Pressure Transducer and Type PDR-D-1 Digital Readout. Quantities of reactants and products were measured by direct weighing and by PVT measurements. Temperatures were measured with a Fluke 51 K/J thermometer. Molecular weights were obtained by gas density measurements. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 with a 7500 data station using a 10 cm glass cell fitted with AgCl windows. NMR spectra were recorded on an IBM NR-200 AF instrument (^{19}F , 188 MHz) using CCl_4 as solvent, CFCl_3 as an internal reference and D_2O as external lock.

Fluorine was purchased from Air Products and Chemicals and was passed through an NaF scrubber to remove HF before use. Cesium fluoride was fused in a platinum dish and then ground to fine powder and stored in the dry box. Cesium bifluoride was prepared by using a modified literature procedure [28,29]. Bis(fluoroformyl) peroxide was prepared by reaction of CO, F_2 and O_2 at room temperature in a flow

system as described in the literature [30]. The bifluorides CsHF_2 and KHF_2 were activated before use by exposure to 1 atm F_2 at 22 °C. After several hours, the fluorine was pumped out by vacuum through a soda lime column. The remaining CsHF_2 or KHF_2 was then kept under vacuum until use.

2.1. Preparation of $\text{FOCF}_2\text{OOC(O)F}$ 2

The reaction of peroxide **1** with fluorine in the presence of metal fluorides was carried out under a variety of conditions in attempting to optimize the yield of **2**. The procedure used involved condensing **1** into a 150 ml stainless steel reactor containing 5 g of dry metal fluoride at -196 °C, and then adding the desired amount of F_2 . The vessel was then warmed to the desired reaction temperature by placing it in a CFCl_3 or ethanol cold bath. After reaction had proceeded for the appropriate time, the vessel was cooled to 196 °C and F_2 and O_2 were removed. The remaining material was then transferred to the glass vacuum line and separated by vacuum fractional condensation through traps at -70 , -95 , -110 , and -196 °C as the sample warmed from -196 °C in an empty dewar initially at 22 °C. The -70 °C trap retained a small quantity of $\text{FOCF}_2\text{OOC(O)OOCF}_2\text{OF}$ **4** and $\text{FC(O)OOC(O)OOCF}_2\text{OF}$ **3**. Unreacted **1** was retained in the -95 °C trap. The $\text{FOCF}_2\text{OOC(O)F}$ **2** and $\text{FOCF}_2\text{OOCF}_2\text{OF}$ were retained in the -110 °C trap and other low boiling products such as COF_2 , CF_3OF were collected in the -196 °C trap. The data for several representative reactions are summarized in Table 1.

$\text{F}^a\text{OC}^a\text{F}_2^b\text{OOC}^b(\text{O})\text{F}^c$ **2** (94% pure, with small amounts of **1** and $\text{FOCF}_2\text{OOCF}_2\text{OF}$): IR (3 Torr): 1920.3 (s, C=O), 1294.6 (m), 1255.9 (s), 1196.7 (vs), 1162.8 (vs), 1001.6 (w), 933.0 (vw), 748.9 (vw), 598.5 (vw) cm^{-1} ; ^{19}F NMR, $\delta_a = 160.1$ (t, 1F, $^3J_{a-b} = 36.0$ Hz), $\delta_b = -80.8$ (d-d, 2F, $^5J_{b-c} = 2.1$ Hz), $\delta_c = -31.6$ (s, 1F) ppm; ^{13}C NMR (CCl_4 solvent & reference, external D_2O lock, 75.5 MHz) $\delta_A = 125.9$ (t, d, $^1J_{A-b} = 275.4$ Hz, $^2J_{A-a} = 6.1$ Hz), $\delta_B = 141.1$ (d, $^2J_{B-c} = 303.7$ Hz) ppm.

$\text{F}^a\text{OCF}_2^b\text{OOC}^b(\text{O})\text{OOC}^b(\text{O})\text{F}^c$ **3** (from the mixture of **3** and **4**): ^{19}F NMR $\delta_a = 161.1$ (t, 1F, $^3J_{a-b} = 36.3$ Hz), $\delta_b = -80.6$ (d, 2F), $\delta_c = -31.4$ (s, 1F) ppm.

2.2. Preparation of $(\text{FOCF}_2\text{OO})_2\text{CFOF}$ 6

The mixture of **3** and **4** (0.3 mmol) was condensed onto activated CsF (1.0 g) held at -196 °C, and then F_2 (1.0 mmol) was added. The mixture was allowed to warm to -20 °C and remained at -20 °C for 16 h. Excess F_2 was pumped out at -196 °C and destroyed. The products were transferred to vacuum line for measurement. Compound **6** (0.27 mmol, 90%) was obtained pure ($\text{F}^a\text{OCF}_2^b\text{OO})_2\text{CF}^c\text{-OF}^d$: mp. $-86.5 \sim -89.0$ °C; IR (3 Torr): 1257.4 (s), 1195.4 (s), 1155.9 (s), 1120.2 (vs), 944.2 (vw) cm^{-1} . ^{19}F NMR: $\delta_a = 158.8$ (t-d, 2F, $^3J_{a-b} = 36.7$ Hz, $^6J_{a-c} = 2.4$ Hz), $\delta_b = -80.0$ (d-d, 4F, $^5J_{b-c} = 4.2$ Hz), $\delta_c = -89.9$ (d-m, 1F, $^3J_{c-d} = 22.6$ Hz), $\delta_d = 170.7$ (d, 1F) ppm.

Table 1
Reactions of FC(O)OOC(O)F with F₂

	Reactants (mmol)		Conditions			Products (mmol)
	FC(O)OOC(O)F	F ₂	Time (h)	Temperature (°C)	Catalyst	
1	0.5	1.11	10	−50	CsHF ₂	FOCF ₂ OOC(O)F (0.19) FOCF ₂ OOCF ₂ OF (0.28)
2	0.5	0.5	24	−50	CsHF ₂	FOCF ₂ OOC(O)F (0.31) FOCF ₂ OOCF ₂ OF (0.06) FC(O)OOC(O)F (0.08)
3	1.0	0.5	5	−40	CsHF ₂	FOCF ₂ OOC(O)F (0.19) FOCF ₂ OOCF ₂ OF (0.007) FC(O)OOC(O)F (0.17)
4	2	4.5	12	−15	KHF ₂	FOCF ₂ OOC(O)F (0.62) FOCF ₂ OOCF ₂ OF (1.07)
5	0.5	0.5	16	−40	KHF ₂	FOCF ₂ OOC(O)F (0.25) FOCF ₂ OOCF ₂ OF (0.15) FC(O)OOC(O)F (0.12)
6	2	0.5	12	−30	KHF ₂	FOCF ₂ OOC(O)F (0.2) FOCF ₂ OOCF ₂ OF (0.004) FC(O)OOC(O)F (0.14) Other peroxides (0.2)

2.3. Preparation of FOCF₂OOC(O)OOCF₂OF 4

Compound **4** can be obtained by reaction of **2** with water. The mixture of **2** (0.2 mmol) and FOCF₂OOCF₂OF (0.1 mmol) was condensed into a 50 ml flask and then H₂O (0.3 mmol) was added. The mixture was allowed to warm to 22 °C in 4 h and remained at 22 °C for another 4 h. The products were separated by vacuum fractional condensation through traps at −50, −85 and −196 °C. Compound **4** (0.08 mmol, yield 40%) was obtained pure in −85 °C trap. The −196 °C trap contained SiF₄, CO₂ and unreacted FOCF₂OOCF₂OF. Water was retained in −50 °C trap.

F^aOCF₂^bOOC(O)OOCF₂^bOF^a: IR (2 Torr): 1925.3 (m, C=O), 1297.6 (w), 1246.9 (s), 1214.6 (m), 1189.9 (m), 1112.0 (s), 945.9 (vw), 861.9 (vw), 774.0 (vw) cm^{−1}; ¹⁹F NMR δ_a = 160.6 (t, 2F, ³J_{a−b} = 36.5 Hz), δ_b = −80.6 (d, 4F) ppm.

2.4. Preparation of FOCF₂OOH 5

The hydroperoxide **5** can be obtained by reaction of **2** with water in flow system. The mixture of **2** (0.54 mmol) and FOCF₂OOCF₂OF (0.36 mmol) was passed through a 20 ft × 1/4 in. stainless steel column packed with Chromosorb P 80/100 over 40 min at room temperature.

Compound **2** was hydrolyzed by the water which was absorbed on the Chromosorb. The products were collected in a −196 °C trap and separated by vacuum fractional condensation through traps at −90, −115 and −196 °C. The −90 °C trap contained **5** (0.11 mmol, yield 20%) along with a trace of **4**. The −115 °C trap contained 0.26 mmol of a mixture of **2**, FOCF₂OOCF₂OF, and **5**. Low boiling compounds SiF₄, COF₂ and CO₂ were collected at −196 °C.

F^aOCF₂^bOOH: IR (3 Torr): 3568 (m, OH), 1386.0 (m), 1229.8 (vs), 1168.4 (s), 1112.3 (w) cm^{−1}; ¹⁹F NMR δ_a = 141.2 (t, 1F, ³J_{a−b} = 30.9 Hz), δ_b = −81.1 (d, 2F) ppm; ¹H NMR (200.1 MHz): δ_H = 9.52 (s) ppm.

2.5. The reaction of 5 with F₂ in the presence of KHF₂

The reaction was carried out in order to probe the possibility of the synthesis of difluorotrioxirane, a potentially interesting but unknown compound. The hydroperoxide **5** (0.3 mmol) and F₂ (0.3 mmol) were condensed into a 10 ml stainless steel cylinder which contained 1 g dry KHF₂ at −196 °C. The mixture was allowed to warm to −78 °C over 2 h and remained at −78 °C for another 4 h. Excess F₂ was pumped out at −196 °C and destroyed. The products were then transferred to vacuum line and 0.18 mmol of material was obtained in the −196 °C trap. ¹⁹F NMR showed the latter to be a mixture of FOCF₂OOF, CF₂(OF)₂, CF₃OF and FOCF₂OOCF₂OF, easily identified from each other by ¹⁹F NMR.

F^aOCF₂^bOOF^c (mixture): ¹⁹F NMR: δ_a = 160.9 (t, d, 1F, ³J_{a−b} = 36.3 Hz, ⁵J_{a−c} = 3.2 Hz), δ_b = −80.2 (d-d, 2F, ⁴J_{b−c} = 3.8 Hz), δ_c = 293.5 (q, 1F) ppm.

2.6. The reaction of 2 with ClF in the presence of CsF

The mixture (0.5 mmol) of **2** (60%) and FOCF₂OOCF₂OF (40%) was condensed into a 10 ml stainless steel cylinder which contained 3 g dry CsF at 196 °C. Chlorine monofluoride (0.5 mmol) was added and the mixture was then allowed to warm to −78 °C and remained at that temperature for 15 h. The products were separated by vacuum fractional condensation through traps at −107, −120, −133 and −196 °C. The products were COF₂, CF₃OOCF₂OF,

FOCF₂OCl and unreacted FOCF₂OOCF₂OF by IR and ¹⁹F NMR.

3. Results and discussion

Perfluoroalkoxy anions are postulated as intermediates in the metal fluoride catalyzed reactions leading to the fluoroxy compounds from acid fluorides. Generally, organic fluoroxy derivatives can be prepared from acid fluorides by the action of metal fluorides and elemental fluorine [31].



α,ω -diacylfluorides can also be fluorinated to the bis(fluoroxy) derivatives catalyzed by active CsF or KF and the bis(fluoroxy) product is always the only product observed. No monohypofluorites of the type FC(O)R_fF₂OF had been isolated in these syntheses in spite of considerable efforts to do so. Recently, DesMarteau and Anderson developed a new process and successfully obtained these potentially important compounds by using less active metal fluorides KHF₂ or CsHF₂ as catalysts in the fluorination of perfluorodiacyl fluorides FC(O)R_f(O)F₂ [27]. For example perfluorosuccinyl fluoride underwent reaction with F₂ in the presence of CsHF₂ producing FC(O)CF₂CF₂CF₂OF in 80.6% yield.

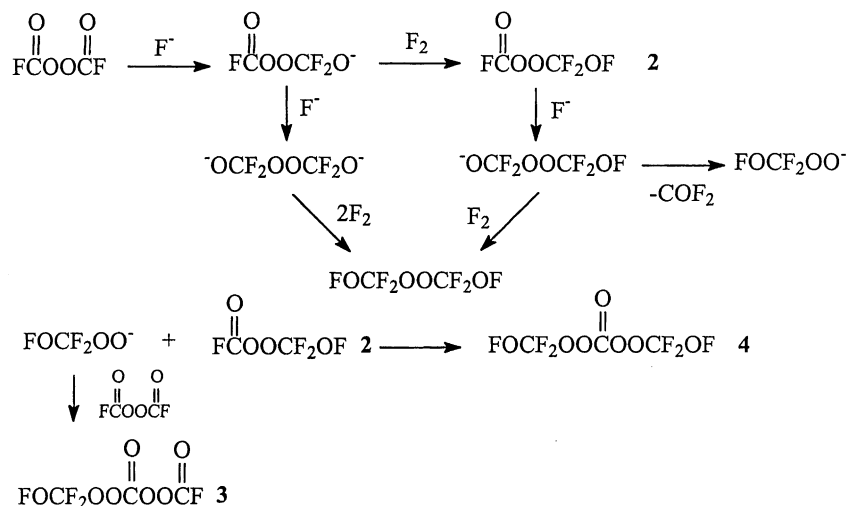


Compound **2** can be obtained in yields as high as 60% from the reaction of FC(O)OOC(O)F with F₂ in the presence of MHF₂ (M = Cs, K). The data summarized in Table 1 clearly show that CsHF₂ or KHF₂ is necessary for the formation of the monofluoroxy derivative. Substitution of CsF for MHF₂ (M = Cs, K) yields FOCF₂OOCF₂OF as the only product, whereas the absence of alkali metal fluorides results in essentially no reaction at low temperature. Both KHF₂

and CsHF₂ gave similar results. The KHF₂ is preferred because it is inexpensive and commercially available. The quality of KHF₂ is essential for a good yield. The KHF₂ must be powdered and dried by pumping under vacuum at 22 °C for at least 6 h before using. The ratio of starting material is also an important factor. Excess F₂ will increase the quantity of the bis(fluoroxy) derivative which is very difficult to be separate from **2**. Although, excess **1** can limit the amount of FOCF₂OOCF₂OF, this results in the generation of 3,3 difluoro-2,4,5, trioxacyclopentanone and a large quantity of unreacted FC(O)OOC(O)F which are also difficult to separate from the desired product. A 1:1 ratio of F₂ to FC(O)OOC(O)F gave the best result, limiting the FOCF₂OOCF₂OF to 20–30%, while giving a yield of **2** up to 50–60%. The separation of **2** from FOCF₂OOCF₂OF was not successful by fractional condensation. The two compounds always collected in the same traps during trap to trap distillation. As mentioned above, a 1 to 1 ratio of **1** to F₂ gave the best yield of **2**. But the resulting product always contained 30–40% FOCF₂OOCF₂OF impurity. Increasing the ratio of **1** to F₂ will decrease the quantity of FOCF₂OOCF₂OF. In an extreme situation, when the ratio of **1** to F₂ is 4–1, the resulting **2** can be purified up to 94%.

Compound **2** is easily identified by its ¹⁹F NMR with characteristic chemical shifts for the OF (160.9), OCF₂OO (–80.8) and C(O)F (–31.6) in the expected 1:2:1 intensities, and ³J_{FF} and ⁵J_{FF} coupling constants of 36 and 2.1 Hz, respectively. Similarly, the ¹³C NMR showed the two expected carbon signals with characteristic large ¹J_{13C-F} coupling constants (275.4 and 303.7 Hz) and a small ²J_{13C-F} = 6.1 Hz.

All of the observed products can be explained by Scheme 1, based on the known chemistry of CF₃OOC(O)F and the behavior of carbonyl compounds in the presence of CsF and F₂ [32]. The thermal stability of **1** is quite good and the compound (mixture of 60% FOCF₂OOC(O)F and 40%

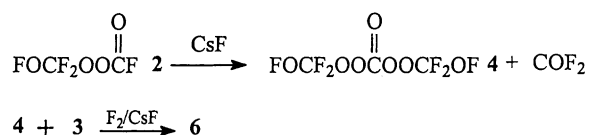


Scheme 1.

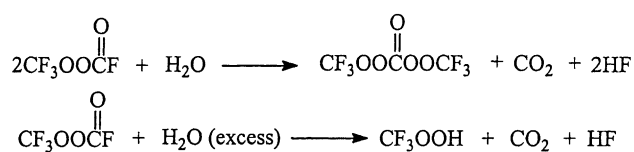
of $\text{FOCF}_2\text{OOCF}_2\text{OF}$ has shown no tendency to undergo explosive decomposition in the vapor (1 atm, 22 °C) or in the condensed state during routine handling.

The formation of a small quantity of **4** and **3** is interesting. Compound **2** was expected to decompose to FOCF_2OO^- and COF_2 in the presence of CsF. The resulting anion FOCF_2OO^- may react with **2** or **1** to give **4** or **3**. The formation of **4** was also observed in the reaction of **3** with CsF. Higher yields (40%) of $\text{FOCF}_2\text{OOC(O)OOCF}_2\text{OF}$ could be obtained by the reaction of **3** with H_2O . The structures of **4** and **3** were further confirmed by reacting the mixture with F_2 and CsF which gave a rare example of a tris(fluoroxy) derivative $(\text{FOCF}_2\text{OO})_2\text{CFOF}$ **6** [33].

Compounds **3** and **4** exhibit characteristic $\nu(\text{C}=\text{O})$ near 1920 cm^{-1} and the ^{19}F NMR contains the appropriate resonances for the OF, OCF_2OO and C(O)F functions with the expected intensities and large $^3J_{\text{FF}}$ coupling constants (36 Hz) for the FOCF_2- groups. For compound **6**, the $\nu(\text{C}=\text{O})$ is absent and the unique $-\text{CF}(\text{OF})-$ function is easily identified by $\delta_{\text{CF}} = -89.9$ and $\delta_{\text{OF}} = 170.7$ with the expected coupling constants and intensities, as well as the signals for the two FOCF_2OO groups.



The chemistry of $\text{FOCF}_2\text{OOC(O)F}$ bears some analogy to $\text{CF}_3\text{OOC(O)F}$. It is well known that hydrolysis of trifluoromethyl peroxy ester $\text{CF}_3\text{OOC(O)F}$ forms two interesting peroxides, trifluoromethyl hydroperoxide CF_3OOH and bis(trifluoromethyl) peroxy carbonate $(\text{CF}_3\text{OO})_2\text{C}=\text{O}$ [21,34,35].



The hydrolysis of **2** also gives a mixture of two new hypofluorites, fluoroxy difluoromethyl hydroperoxide FOCF_2OOH **5** and bis(fluoroxydifluoromethyl) peroxy carbonate $(\text{FOCF}_2\text{OO})_2\text{C}=\text{O}$ **6**, but in low yield. This is probably a result of the lower stability of **5** compared to CF_3OOH and the decomposition of **5** is catalyzed by H_2O and metal fluorides. When a trace of water was used, the major product was **4**. Unlike CF_3OOH which can be obtained in high yield by the reaction of $\text{CF}_3\text{OOC(O)F}$ with water in a glass flask, **2** can not be prepared in the similar static system, because the resulting FOCF_2OOH is sensitive to water and will decompose to COF_2 , O_2 and HF. Pure **5** was prepared in flow system and ^1H NMR of **5** shows a low-field signal assigned to the OOH group (δ : 9.52) which is very close to that of other similar hydroperoxides [21,36,37]. Compound **5** is the

first example of a molecule containing both the OF and OH functions.

The reaction of **5** with F_2 in the presence of KHF_2 gave a mixture of FOCF_2OOF **7**, $\text{CF}_2(\text{OF})_2$, CF_3OF and $\text{FOCF}_2\text{OOCF}_2\text{OF}$. This mixture was not separated but the four products were easily identified in the mixture by ^{19}F NMR. The ^{19}F NMR of the mixture shows a high-field doublet-doublet assigned to the OCF_2OO group of **7** and two low-field signals assigned to the OOF group and the OF group of **7**. The OOF shift is very characteristic, because it is shifted about 150 ppm downfield from a typical OF signal [38–42]. Compound **7** is the first example of a molecule contain both OF and OOF functions.

4. Summary

The selective monofluorination of FC(O)OOC(O)F provides the first example of a trifunctional compound containing the fluoroformyl, peroxide and fluoroxy function in the same molecule. A number of other unusual peroxides were also identified further illustrating the remarkable diversity of simple fluorocarbon peroxygen compounds that can be synthesized.

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