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Reaction of Metal Fluorides with $CF_3OOCF_2N(H)CF_3$

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The reactions of $CF_3N(H)CF_2OOCF_3$ with the metal fluorides LiF, NaF, KF, CsF, KHF_2, and PbF_2 have been studied. Lithium and lead fluorides are unreactive whereas the others react to give products related to the fluoride activity KHF_2 < NaF < KF < CsF. The initial product in each case is the oxaziridine $CF_3\overline{NCF_2O}$. A mechanism for the reactions is suggested and two new compounds $CF_3NFC(O)F$ and $CF_3N(OCF_3)C(O)F$ are described.

Introduction

Fluorinated peroxides have considerable potential as synthetic intermediates, as demonstrated by the recent synthesis of the *first* perfluorooxaziridine, $CF_3\overline{NCF_2O}$.[2]

$$CF_3N(H)CF_2OOCF_3 + NaF \rightarrow CF_3\overline{NCF_2O} + COF_2 + NaF{\cdot}HF$$

Both the amine and the oxaziridine are noteworthy for their high thermal stability. The mechanism of the preceding reaction is of interest since there are many similarities to this synthesis and those used to prepare organic oxaziridines.[3] Many oxaziridines can be formed via α-hydroxyperoxyamines or by the action of peroxy acids on Schiff bases, which may involve related intermediates. However, the nucleophilicity of the nitrogen in the fluorinated compound is much lower, and a mechanism involving an internal nucleophilic attack of nitrogen on the peroxide bond, as suggested by some authors or other proposals related to the nucleophilic properties of nitrogen, seems unlikely.[4]

The obvious effect of NaF in the formation of $CF_3\overline{NCF_2O}$ from $CF_3N(H)CF_2OOCF_3$ is simply to remove HF from the amine. If one views $CF_3N(H)CF_2OOCF_3$ as not much different from $(CF_3)_2NH$, then this is very reasonable, since most reactions of the latter are believed to proceed by initial loss of HF.[5,6] In order to gain some insight into the mechanism of the $CF_3N(H)CF_2OOCF_3$/NaF reaction, reactions of $CF_3N(H)CF_2OOCF_3$ with a variety of metal fluorides (LiF, NaF, KF, CsF, KHF_2, PbF_2) have been carried out. In the course of this work, the susceptibility of $CF_3\overline{NCF_2O}$ to nucleophilic attack became apparent and two new compounds, $CF_3NFC(O)F$ and $CF_3N(OCF_3)C(O)F$, were formed with the more active fluorides. The characterization of these compounds is included.

Experimental Section

General Procedures. All volatile compounds were handled in glass and stainless steel vacuum systems as previously described. Characterization of new compounds was carried out in the usual way.[2]

Metal fluorides were obtained from commercial sources. Lithium, potassium, and cesium fluoride were dried by heating, followed by treatment with elemental fluorine at 22 °C. The salts NaF, KHF_2, and PbF_2 were dried under vacuum. The preparation of $CF_3N(H)CF_2OOCF_3$ was by the literature method using equimolar amounts of CF_3OOH and CF_3NCF_2.[2] *Caution*! The peroxides and many of the nitrogen compounds are potentially hazardous. Care must be taken in handling these materials.

Reactions of $CF_3N(H)CF_2OOCF_3$. The reaction with KHF_2 was carried out in Kel-F. All other reactions were carried out in 100-mL glass reactors fitted with glass–Teflon valves. $CF_3N(H)CF_2OOCF_3$ (3 mmol) was condensed onto the metal salt (100 mmol) at −196 °C and warmed to 25 °C. The reactor was maintained at 25 °C for 4.5 h and then cooled to −196 °C. Noncondensable gases were checked for, and the contents were distilled through traps at −111 and −196 °C. If the IR spectrum of the contents of the −111 °C trap showed N–H absorptions, then these contents were refractionated through −78, −111, and −196 °C traps. The −196 °C traps were further separated by GLC at 0 °C using a 10 ft × $^3/_8$ in. stainless steel column packed with 30% Kel-F #10 oil on Chromosorb P. Amounts of volatile products were determined by *PVT* measurements assuming ideal-gas behavior.

Table I. Reactions of $CF_3N(H)CF_2OOCF_3$ with MF

$$\underset{5}{CF_3N(H)CF_2OOCF_3} \xrightarrow[25\ ^\circ C,\ 4.5\ h]{MF} \underset{1}{CF_3\overline{NCF_2O}} + \underset{2}{CF_3NFC(O)F} + \underset{3}{CF_3N(OCF_3)C(O)F} + \underset{4}{COF_2}$$

MF (100 mmol)	% product[a] 1	2	3[b]	4	5[c]
LiF	1				99
NaF	72	16	<1	99	
KF	11	75	14	85	
CsF		17	61	3	
KHF_2	92	<1		98	
PbF_2	1			3	95

[a] Based on 3 mmol of $CF_3N(H)CF_2OOCF_3$. **1**, **2**, and 4 are after separation by GLC. [b] Trapped at −111 °C. [c] Percent recovered after trapping at −78 °C.

Results for all reactions are summarized in Table I. Characterization of the new compounds $CF_2NCF(O)F$ and $CF_3N(OCF_3)C(O)F$ follows: $CF_3N(F)C(O)F$, **2**, bp −16.6 °C; mol wt 151.3, calcd 149.02; log P (torr) = 6.482 −591.2/T − 85362/T^2; ΔH_{vap} = 5.75 kcal/mol; ΔS_{vap} = 22.4 eu; IR 2355 (vw), 2310 (vw), 1904 (s), 1884 (s), 1878 (s), 1464 (vw), 1456 (vw), 1359 (vw), 1345 (vw), 1295 (s), 1248 (vs), 1228 (vs), 1190 (m), 1075 (m), 1012 (vw), 1000 (m), 992 (m), 800 (m), 792 (w), 762 (vw), 689 (m) cm^{-1}; NMR $CF^A{}_3NF^BC(O)F^C$ ϕ_A* 67.9, d-d; ϕ_B* 71.5, br, d; ϕ_C* 7.9, d-q; J_{AB} = 13.2, J_{AC} = 13.2, J_{BC} = 46.3 Hz. $CF_3N(OCF_3)C(O)F$, **3**, bp 18.2 °C; mol wt 215.2, calcd 215.03; log P (torr) = 4.0972 + 638.23/T − 289240/T^2; ΔH_{vap} = 6.16 kcal/mol; ΔS_{vap} = 21.2 eu; IR 2119 (vw), 1900 (s), 1881 (s), 1564 (w), 1440 (vw), 1418 (vw), 1315 (sh), 1302 (vs), 1273 (s), 1255 (s), 1221 (s), 1187 (s), 1143 (sh), 1100 (m), 1020 (w), 981 (m), 812 (w), 763 (w), 717 (w), 634 (m) cm^{-1}; NMR $CF^A{}_3N(OCF^B{}_3)C(O)F^C$ ϕ_A* 64.4, d-q; ϕ_B* 67.2, d-q; ϕ_C* 8.2, q-q; J_{AB} = 4.3, J_{AC} = 14.5, J_{BC} = 5.2 Hz.

Results and Discussion

The reactions of $CF_3N(H)CF_2OOCF_3$ with metal fluorides are summarized in Table I. All reactions were carried out under nearly identical conditions with a large excess of metal fluoride. The latter was necessary to prevent a number of side reactions, which resulted in the formation of SiF_4, O_2, CF_3NO, and CO_2 when only 10 mmol of NaF was employed. The results in Table I clearly indicate that active fluorides capable of complexing HF are reactive with $CF_3N(H)CF_2OOCF_3$. The inactivity of LiF and PbF_2 is in agreement with this, although LiF does form a weak complex with HF.[7,8] For those fluorides that do react, the observed products clearly depend on the effective fluoride ion activity.

Previous work with $CF_3N(H)CF_2OOCF_3$ identified $CF_3\overline{NCF_2O}$ as the only nitrogen-containing product on reaction with NaF.[2] The choice of NaF was a fortunate one, since KF or CsF might well have resulted in a failure to isolate

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the novel oxaziridine. Because $CF_3\overline{NCF_2O}$ is analogous to $CF_3\overline{CFCF_2O}$[9] and because fluorinated epoxides are readily attacked by nucleophiles, the additional products observed with KF and CsF result from nucleophilic attack on the intermediate oxaziridine. The following reactions are consistent with the observed products.

$$\underset{\mathbf{5}}{CF_3N(H)CF_2OOCF_3} + MF \rightarrow \underset{\mathbf{1}}{CF_3\overline{NCF_2O}} + MF\cdot HF + \underset{\mathbf{4}}{COF_2} \quad (1)$$

$$\mathbf{1} \xrightarrow{MF} \underset{\mathbf{2}}{CF_3NFC(O)F} \quad (2)$$

$$\mathbf{1} \xrightarrow{MF} (CF_3NCF_2O)_n \quad (3)$$

$$\mathbf{4} + MF \rightarrow MOCF_3 \quad (4)$$

$$\mathbf{1} + MOCF_3 \rightarrow \underset{\mathbf{3}}{CF_3N(OCF_3)C(O)F} + MF \quad (5)$$

Reaction 1 could proceed by several possible routes as shown in eq 6–11. Of these possibilities, the direct route (11) is the most consistent with our results.

$$\mathbf{5} + MF \rightarrow \underset{\mathbf{6}}{CF_3N{=}CFOOCF_3} + \underset{\mathbf{8}}{MF\cdot HF} \quad (6)$$

$$\mathbf{6} \rightarrow \mathbf{1} + \mathbf{4} \quad (7)$$

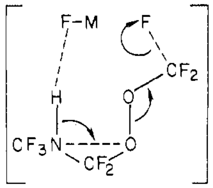
$$\mathbf{5} + 2MF \rightarrow \underset{\mathbf{7}}{(CF_3NCF_2OOCF_3)M} + \mathbf{8} \quad (8)$$

$$\mathbf{7} \rightarrow \mathbf{1} + MOCF_3 \quad (9)$$

$$MOCF_3 \rightleftarrows MF + \mathbf{4} \quad (10)$$

$$\mathbf{5} + MF \rightarrow \mathbf{1} + \mathbf{8} + \mathbf{4} \quad (11)$$

Reactions 6–10 might be reasonable for CsF but not for NaF. Sodium fluoride does not react with $(CF_3)_2NH$ under our conditions and we believe that $(CF_3)_2NH$ and **5** should be similar in acidity and ease of HF elimination. Other alternatives, such as attack by fluoride on the peroxide bond, are unreasonable because bis(perfluoroalkyl) peroxides do not react with alkali metal fluorides at 22 °C. Thus we believe that the fluorides NaF, KF, CsF, and KHF_2 first interact with N–H via an H–F hydrogen bond, followed by elimination of COF_2 and F^-.

$\mathbf{5} + MF \rightarrow$  $\rightarrow \mathbf{1} + \mathbf{8} + \mathbf{4}$ (12)

The observed yields of **1**–**4** are in accord with the relative fluoride ion activity $KHF_2 < NaF < KF < CsF$. All four fluorides will complex HF, but KHF_2 is too inactive to undergo subsequent reaction with **1**. Only KF and CsF will react with COF_2 to form $MOCF_3$,[10,11] with KF < CsF, and the yields of **3** and **4** agree with this.

The polymer indicated in reaction 3 has not been identified. Its formation is likely due to the observed lack of a good material balance with CsF and the observation of an oily material of low volatility with this fluoride. The formation of a polymer with CsF is consistent with its high fluoride activity and with related studies on fluorinated epoxides.[9]

A critical point in the above discussion concerns whether **1** is the intermediate leading to **2**, **3**, and the polymer. This has been proven to our satisfaction by reactions of $CF_3\overline{NCF_2O}$ with KF, CsF, and CsF/COF_2. With some variations in the yields, the results are identical with those observed with reactions of $CF_3N(H)CF_2OOCF_3$ with KF and CsF. The reaction of CsF with **1** in the absence of COF_2 gives exclusively **2** and polymer. An additional important point is that **3** does not arise from **2** and vice versa. **2** and **3** do not react with CsF/COF_2 under these conditions.

The attack of $CF_3\overline{NCF_2O}$ by nucleophiles is completely analogous to reactions of hexafluoropropylene oxide (HFPO).

$$CF_3\overline{CFCF_2O} \xrightarrow{F^-} CF_3CF_2C(O)F \quad (13)$$

$$CF_3\overline{NCF_2O} \xrightarrow{F^-} CF_3N(F)C(O)F \quad (14)$$

$$CF_3\overline{CFCF_2O} + CF_3O^- \rightarrow CF_3CF(OCF_3)C(O)F + F^- \quad (15)$$

$$CF_3\overline{NCF_2O} + CF_3O^- \rightarrow CF_3N(OCF_3)C(O)F + F^- \quad (16)$$

With excess HFPO and CsF, an oligomer $CF_3CF_2CF_2OCF(CF_3)C(O)F$ is formed. The polymer observed in reaction 3 with CsF could by analogy be $CF_3N(F)CF_2ON(CF_3)C(O)F$.

The two new compounds, **2** and **3**, obtained in this work are readily identified by ^{19}F NMR, IR, and molecular weight. The data given in the Experimental Section are in harmony with the proposed structures, and the ^{19}F NMR data are especially convincing. Both **2** and **3** have several structural isomers that have been prepared: $(CF_3)_2NOC(O)F$[12] and $C_3F_7NO_2$[13] in the case of **3**, and C_2F_5NO,[13] $CF_3C(O)NF_2$,[14] $F_2NCF_2C(O)F$,[15] and **1** in the case of **2**. An additional isomer for the latter, $CF_3N(O)CF_2$,[16] has been reported but its characterization is incomplete. Again, by analogy to HFPO which reacts with strong Lewis acids to form a ketone,[9] **1** should react similarly to give the *N*-oxide.

$$CF_3\overline{CFCF_2O} \xrightarrow{SbF_5} (CF_3)_2CO \quad (17)$$

$$CF_3\overline{NCF_2O} \xrightarrow{SbF_5} CF_3N(O)CF_2 \quad (18)$$

This reaction, as well as many other reactions of **1** with nucleophiles, is currently in progress.

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Registry No. **1**, 60247-20-3; **2**, 68986-54-9; **3**, 68986-55-0; **4**, 353-50-4; **5**, 60247-19-0; LiF, 7789-24-4; NaF, 7681-49-4; KF, 7789-23-3; CsF, 13400-13-0; KHF_2, 7789-29-9; PbF_2, 7783-46-2.

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