# The Catalytic Addition of Fluorine to a Carbonyl Group. Preparation of Fluoroxy Compounds[1]

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**Abstract:** The low-temperature metal fluoride catalytic fluorination of carbonyl halides and fluoroalkyl acid fluorides provides a simple method for the preparation of fluoroxyfluoroalkanes in high yields. In addition to some known fluoroxy derivatives the new compounds, 1-fluoroxy-1,1,2,2-tetrafluoroethane, $FOCF_2CF_2H$, octafluoro-1,4-bis(fluoroxy)butane, $FO(CF_2)_4OF$, decafluoro-1,5-bis(fluoroxy)pentane, $FO(CF_2)_5OF$, 1-fluoroxy-2-difluoraminotetrafluoroethane, $CF_2(NF_2)CF_2OF$, and 1-fluoroxy-2-difluoraminohexafluoropropane, $CF_3CF(NF_2)CF_2OF$, are also prepared by this method. Some chemical and physical properties of the new compounds are given.

Although the first example of a fluoroxyalkane has been known for 19 years,[2] it was not until recently that other members of this class of compounds have been prepared.[3,4] The techniques of fluorination employed in these preparations have varied from the high-temperature, catalyzed, flow fluorination of $CH_3OH$, CO, or $COF_2$ to produce $CF_3OF$ to the lower temperature fluorination of alcohols.[3,4] A new low-temperature fluorination procedure has been developed which, in the presence of a suitable catalyst, permits the controlled addition of fluorine across a carbon–oxygen double bond. Fluoroxyfluoroalkanes can be prepared by this method in high yields.

## Experimental Section

**Materials.** The perfluoroalkyl acid fluorides were prepared from the corresponding chlorides by reaction with KF in 3-methylsulfolane. Hexafluoroacetone was obtained from General Chemical Division, Allied Chemical Corp., and used without further purification. The difluoramino acid fluoride derivatives were available from another study.[5]

*Caution. Explosions have been encountered on occasion upon handling the new bis- and α-difluoraminohypofluorites. Workers should be properly shielded.*

**General Preparative Procedure.** A 10-g sample of cesium fluoride, which had been dried overnight at 175–200° under vacuum and then ground in a nitrogen-filled drybox, was loaded into a 150-ml Monel Hoke cylinder containing approximately 30 $^3/_8$-in. diameter stainless steel balls. The cylinder was then shaken for several hours to ensure fine grinding of the cesium fluoride. A 1.72-mmole sample of $COF_2$ was condensed into the reactor at $-196°$, and then fluorine (1.73 mmoles) was allowed to expand into the reactor at this temperature. The reactor was then placed in a $-78°$ bath and allowed to stand for 4 hr. After cooling the reactor to $-196°$, any unreacted fluorine was pumped out through a trap containing KOH. The condensable product was then removed for further purification. This procedure was employed for all the substrates at the same temperature and for the same time interval indicated above except for $HCF_2C(O)F$ (*cf.* Discussion), which was allowed to react with fluorine at 0°. A summary of the experimental data is given in Table I.

**General Purification Procedure.** Reaction mixtures containing the known compounds $CF_3OF$, $C_2F_5OF$, $C_3F_7OF$, and $(CF_3)_2CFOF$ were prepared for analysis first by subjecting them to vapor phase chromatography using the column recommended in the literature.[3] The $^{19}F$ nmr and infrared spectra of the pure components were then compared with those published.[3] Purification of the bis(fluoroxy)fluoroalkyl compounds was performed by vacuum-line fractionation. The butane derivative was retained in a trap set at $-126°$ while the pentane was held in a $-95°$ trap. Any unreacted acyl fluoride was removed by allowing the mixture to stand over water at room temperature for no longer than 0.5 hr. The purification of $CF_3CF(NF_2)CF_2OF$ was accomplished by vacuum-line fractionation through a trap set at $-126°$ in which it was retained. No purification of $NF_2CF_2CF_2OF$ was necessary since it was obtained in quantitative yield.

**Analyses.** Although some analyses are given, they were generally difficult to obtain because several of the samples exploded during handling. For the fluorine analysis, samples were reduced with lithium in *n*-propylamine within high-pressure Pyrex tubes containing Fischer–Porter Teflon valves. Conventional techniques were then employed. The Dumas method was used to determine nitrogen in gaseous samples; carbon was determined by the conventional Pregl combustion method using fresh MgO mixed with the catalyst in the combustion tube (see Table I for some results).

**Molecular Weights.** Molecular weights were obtained by vapor density measurements (refer to Table I).

**Melting Points.** The melting points of $FO(CF_2)_4OF$ and $FO(CF_2)_5OF$ were measured by immersing samples contained in 5-mm o.d. Pyrex tubes into a 1:1 v/v pentane–isopentane cold bath which warmed at a rate of *ca.* 0.5°/min (see Table I).

**Infrared Spectra.** The infrared spectra of the new materials were obtained using gaseous samples in cells having a 10-cm path length employing a Perkin-Elmer Model 21 spectrometer. The following are the frequencies in $cm^{-1}$ (relative intensities) for $FO(CF_2)_4OF$: 1333 (m), 1284 (s), 1250 (sh), 1227 (vs), 1203 (sh), 1176 (m), 1136 (s), 1096 (w), 1061 (w), 962 (m), 917 (m), 886 (s), 862 (m), 821 (w), 803 (m), 782 (s), 763 (s), 738 (w), 717 (w), 680 (w); for $FO(CF_2)_5OF$: 1348 (sh), 1332 (m), 1258 (sh), 1227 (vs, complex), 1174 (s), 1148 (s), 1110 (m), 1036 (w), 1014 (w), 897 (wm), 877 (wm), 855 (wm), 820 (w), 793 (wm), 778 (wm), 752 (s), 727 (ms), 705 (w), 694 (w); for $CF_2(NF_2)CF_2OF$: 1333 (ms), 1253 (vs), 1218 (vs), 1176 (sh), 1159 (s), 8018 (ms), 977 (s), 936 (s), 893 (wm), 881 (w), 781 (m); and for $CF_3CF(NF_2)CF_2OF$: 1311 (ms), 1277 (s), 1252 (vs), 1183 (m), 1136 (wm), 1099 (w, complex), 1011 (m), 968 (sh), 963 (m), 932 (m), 984 (wm, complex), 813 (wm), 766 (w), 741 (wm).

The infrared spectra of all the new compounds exhibit multiple bands in the region (1400–1000 $cm^{-1}$) which are assigned to C–F stretching vibrations. They also show several weak-to-medium intensity absorptions in the O–F[3] and C–O[6] domain (917–855 $cm^{-1}$). The difluoramino derivatives have absorptions between 1020 and 925 $cm^{-1}$, and some of these may be assigned to the N–F stretching motions.

**$^{19}F$ Nmr Spectra.** The $^{19}F$ nmr spectra were obtained on $CCl_3F$ solutions of the fluoroxy derivatives at room temperature employing a Varian Model V4310 spectrometer operating at 40 Mc at room temperature. Resonances for $FO(CF_2)_4OF$ are located at $\phi$ $-146.7$, 92.5, 122.7 having an area ratio of 1.0:2.0:2.1, respectively, while the spectrum of $FO(CF_2)_5OF$ shows absorptions at $\phi$ $-146.9$, 92.9, and 124.0 having the respective area ratio, 1.0:2.1:3.1. 1-Fluoroxy-2-difluoraminotetrafluoroethane has resonances at $\phi$ $-147.0$, $-17.3$, 92.5, and 115.2; the area ratio was measured to be 1.0:1.8:1.9:1.9, respectively, and $CF_3CF(NF_2)CF_2OF$ has

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[1] For a preliminary report on this method of preparation, see J. K. Ruff, A. R. Pitochelli, and M. Lustig, *J. Am. Chem. Soc.*, **88**, 4531 (1966).

[2] G. H. Cady and K. B. Kellogg, *ibid.*, **70**, 3986 (1948).

[3] J. H. Prager and P. G. Thompson, *ibid.*, **87**, 230 (1965).

[4] J. H. Prager, *J. Org. Chem.*, 31, 392 (1966).

[5] M. Lustig and J. K. Ruff, *Inorg. Chem.*, **4**, 1441 (1965).

[6] R. T. Lagemann, E. A. Jones, and J. H. Woltz, *J. Chem. Phys.*, **20**, 1768 (1952).

**Table I.** Preparation of Fluoroxy Compounds

| Substrate (mmoles) | Fluorine, mmoles | Product(s) (mmoles) | Vapor density mol wt Calcd | Vapor density mol wt Found | Additional data |
|---|---|---|---|---|---|
| $COF_2$ (1.72) | 1.73 | $CF_3OF$ (1.67) | 104 | 105 | Trace of $CF_4$ present |
| $CF_3C(O)F$ (1.59) | 1.61 | $C_2F_5OF$ (1.53) | 154 | 151 | Traces of $CF_4$ and $C_2F_6$ |
| $C_2F_5C(O)F$ (1.82) | 1.83 | $C_3F_7OF$ (1.77) | 204 | 202 | |
| $(CF_3)_2CO$ (1.05) | 1.07 | $(CF_3)_2CFOF$ (1.03) | 204 | 205 | Trace of $CF_4$ |
| $F(O)C(CF_2)_2C(O)F$ (1.38) | 2.76 | $FO(CF_2)_4OF$ (1.13) | 270 | 273 | *Anal.* Calcd for $C_4F_{10}O_2$: C, 18.07; F, 70.3. Found: C, 17.78; F, 66.5.<br>Mp $-119 \pm 0.6°$ |
| $F(O)C(CF_2)_3C(O)F$ (0.427) | 0.854 | $FO(CF_2)_5OF$ (0.425) | 320 | 316 | Mp $-102.9 \pm 0.3°$ |
| $NF_2CF_2C(O)F$ (0.22) | 0.25 | $NF_2CF_2CF_2OF$ (0.22) | 187 | 184 | |
| $CF_3CF(NF_2)C(O)F$ (1.80) | 2.01 | $CF_3CF(NF_2)CF_2OF$ (1.71) | 237 | 239 | *Anal.* Calcd for $C_3F_9NO$: C, 15.19; N, 5.91. Found: C, 15.47; N, 6.21. |
| $FCONF_2$ (0.756) | 0.970 | $NF_3$ $COF_2$ $CF_3OF$<br>(0.753) (0.551) (0.200) | | | |
| $FCONF_2$ (0.872) | 10.5 | $NF_3$ $CF_3OF$<br>(0.871) (0.872) | | | |
| $COCl_2$ (1.13) | 1.15 | $COCl_2$ $Cl_2$ $CF_3OF$<br>(0.55) (0.54) (0.57) | | | |
| $CO_2$ (1.47) | 3.40 | $CF_2(OF)_2$ (1.44) | 120 | 118 | Trace of $CO_2$ |

bands at $\phi$ $-150.7$, $-24.3$, 72.8, 86.1, and 167.2 (area ratio 1.0:1.8:3.1:2.01:1.0, respectively).

The nmr spectra of these compounds are rather diagnostic. They all have resonances near $\phi$ $-150$ which are assigned to the fluoroxy fluorine atoms. Both $CF_2(NF_2)CF_2OF$ and $CF_3CF(NF_2)CF_2OF$ have an absorption assigned to the $NF_2$ group fluorine atoms at $-17.3$ and $-24.3$, respectively. The $NF_2$ group fluorine resonance lies at higher field when the group is bound to a $CF_2$ than when it is attached to a CF. The positions of these N-F fluorine absorptions are close to those found in the respective $\alpha$-difluoraminoacyl fluorides.[5] Other resonances for $FO(CF_2)_4$ are located at $\phi$ 92.5 (terminal $CF_2$) and 122.9 (central $CF_2$); for $FO(CF_2)_5OF$ at 92.9 (terminal $CF_2$ groups) and 124.0 (three central $CF_2$ groups); for $CF_2(NF_2)CF_2OF$ at 92.5 ($CF_2$ group adjacent to OF) and 115.2 ($CF_2$ adjacent to $NF_2$); and for $CF_3CF(NF_2)CF_2OF$ at 72.8 ($CF_3$), 86.1 ($CF_2$), and 167.2 (CF). These tentative assignments are based on field positions, area ratios, and comparison of the spectra of these new compounds with each other as well as with published information.[3,5]

**Alkaline Hydrolysis.** Both $FO(CF_2)_4OF$ (52.2 mg) and $FO(CF_2)_5OF$ (80.0 mg) were admitted into bulbs containing 50 ml of 0.996 *N* NaOH solution and allowed to stand at room temperature for 3 hr. The aqueous phases were titrated to determine the amount of hydroxide consumed as well as analyzed for fluoride. The vapor phases were measured by their pressure-volume-temperature relationships and subjected to mass spectral analysis. The analytical results are summarized in Table II.

**Table II.** Alkaline Hydrolysis

| Products, moles/mole of reactant | $FO(CF_2)_4OF$ | $FO(CF_2)_5OF$ | Theory |
|---|---|---|---|
| $F^-$ | 5.9 | 5.7 | 6.0 |
| $O_2$ | 0.9 | 0.9 | 1.0 |
| $OH^-$ (consumed) | 8.7 | 8.5 | 8.0 |

The alkaline hydrolysis of both $FO(CF_2)_4OF$ and $FO(CF_2)_5OF$ followed the general equation

$$FO(CF_2)_xOF + 8OH^- \longrightarrow {}^-OOC(CF_2)_{x-2}COO^- + 6F^- + 4H_2O + O_2$$

The presence of trace quantities of perfluorocarbons and the larger than theoretical quantities of $OH^-$ consumed is explained by the known decarboxylation of perfluorinated acids in alkaline solution.

## Results and Discussion

Cesium fluoride has been shown to catalyze the addition of fluorine across the sulfur-oxygen double bond of thionyl fluoride.[7] It was postulated that the active intermediate in the fluorination was the $SF_5O^-$ ion. Since cesium fluoride was reported to react with carbonyl fluoride to form $CsOCF_3$,[8] an attempt was made to determine whether cesium fluoride would catalyze the addition of fluorine across the C=O bond of several fluorocarbon derivatives. This was found to occur readily and high yields of the corresponding fluoroxy compounds could be obtained when the reactions were allowed to progress at $-78°$ in a static system. The following conversions to known compounds were easily accomplished: $COF_2 \rightarrow CF_3OF$, 97% yield; $CF_3COF \rightarrow C_2F_5OF$, 96% yield; $C_2F_5COF \rightarrow C_3F_7OF$, 97% yield; and $(CF_3)_2CO \rightarrow (CF_3)_2CFOF$, 98% yield.[1] When the technique was extended to include the two diacyl fluorides derived from perfluorosuccinic and perfluoroglutaric acids, the corresponding bis(fluoroxy) compounds were produced. These reactions were carried out using close to stoichiometric amounts of fluorine in order to eliminate C–C bond cleavage that is commonplace with fluorinations carried out at elevated temperatures. The advantage of this catalyzed method of fluorination becomes obvious in comparing the yield in the preparation of the only other known example of a bis(fluoroxy) compound, $FO(CF_2)_3OF$ (approximately 2%),[4] with the yields obtained in this study. The yields of the monofluoroxy derivatives are also much higher than those previously reported, and essentially no purification of the compounds is necessary for most purposes.

$$F(O)C(CF_2)_2C(O)F + 2F_2 \xrightarrow[-78°]{CsF} FO(CF_2)_4OF$$

$$F(O)C(CF_2)_3C(O)F + 2F_2 \xrightarrow[-78°]{CsF} FO(CF_2)_5OF$$

The high-temperature fluorination of carbon dioxide has been reported to produce only the known fluoroxy compound, $CF_3OF$.[9] However, in the presence of cesium fluoride the catalytic addition of fluorine occurs, and $CF_2(OF)_2$ is obtained in nearly quantitative yield. Some variation in the conversion was noted, and this

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(7) J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

(8) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

(9) J. W. Dale, International Symposium on Fluorine Chemistry, Birmingham England, 1959.

seems to depend on the history of the cesium fluoride employed. Better results were obtained with a catalyst that had been previously used to convert the acid fluoride derivatives to fluoroxy compounds. Identification of $CF_2(OF)_2$ was achieved by vapor density molecular weight and by a comparison of its infrared and $F^{19}$ nmr spectra with those previously obtained.[10]

This method of fluorination could not be extended to compounds containing an atom or group other than fluorine or a perfluoroalkyl group bonded to the carbonyl carbon. Displacement occurred and only the fluoroxy compound derived from the related acid fluoride was observed upon fluorination. For example, treatment of $COCl_2$ with 1 equiv of fluorine at $-78°$ in the presence of CsF produced only $CF_3OF$ and chlorine in equal amounts. Unreacted $COCl_2$ was also recovered. Fluorination of $FCONF_2$ with excess fluorine at $-78°$ yielded $NF_3$ and $CF_3OF$ as the major products. However, the catalyzed fluorination of the $\alpha$-substituted difluoraminoacyl fluorides, $NF_2CF_2C(O)F$ and $CF_3CF(NF_2)C(O)F$, produced the corresponding fluoroxy derivatives in high yield. Both products are stable in the gas phase in Pyrex at room temperature.

$$NF_2CF_2C(O)F + F_2 \xrightarrow[-78°]{CsF} NF_2CF_2CF_2OF$$

$$CF_3CF(NF_2)C(O)F + F_2 \xrightarrow[-78°]{CsF} CF_3CF(NF_2)CF_2OF$$

The fluorination of $HCF_2COF$ at 0° produced an unstable material which was contaminated with small amounts of $COF_2$, $HCF_3$, and $CF_4$. Purification of this product by either vacuum-line fractionation or gas chromatography resulted in spontaneous and often violent decomposition. The main products in this decomposition were $COF_2$ and $HCF_3$. The $^{19}F$ nmr spectrum of the crude product consisted of an unresolved broad singlet at $\phi$ $-131$ (OF), an unresolved singlet at $\phi$ 99.9 (C–F), and a doublet at $\phi$ 136.4 (C–F) ($J_{HF}$ = 56 cps). The relative area ratio of the peaks is 1.0:2.1:1.9. This spectrum is consistent with the formulation of the compound as $HCF_2CF_2OF$. The infrared spectrum of the crude material showed no absorptions attributable to a carbonyl group but exhibited a weak band in the fluoroxy region which was not observed in the starting material. The instability of this hydrogen-containing fluoroxy compound is in agreement with previous observations.[3,4]

The presence of a metal fluoride is necessary in these reactions although its role is not known with certainty. For example, when either $CF_3COF$ or $(CF_3)_2C{=}O$ was allowed to stand with 1 equiv of fluorine at $-78°$ in a Pyrex reactor, no reaction was observed and the carbonyl derivatives were quantitatively recovered. However, in the presence of an alkali metal fluoride the formation of the corresponding fluoroxy compound was complete in 1 hr (on the 1–2-mmole scale). It is probable that the metal fluoride either reacts directly with or polarizes the carbon–oxygen double bond to such an extent that a polar intermediate is formed, which is the active species in the fluorination. Support for this assumption was obtained by fluorination of $CsOCF_3$ at $-78°$ in a static system. Fluoroxytrifluoromethane was formed in quantitative yield. Furthermore, when $(CF_3)_2C{=}O$ was allowed to react with an excess of CsF, it was completely absorbed and could not be removed *in vacuo* at ambient temperature. Fluorination of the preabsorbed $(CF_3)C{=}O$ under similar conditions also produced $(CF_3)_2CFOF$.

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(10) P. G. Thompson, private communication.