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MASS SPECTRA OF FLUOROXY AND RELATED COMPOUNDS

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SUMMARY

Mass spectra have been obtained for CF_3OF, $CF_2(OF)_2$, CF_3OOF, CF_3OOCF_3 and CF_3OOOCF_3. Examples are given of the utility of mass spectrometry for preparation, identification, purification and use of such reactive reagents.

INTRODUCTION

CF_3OF was prepared first by Kellogg and Cady [1] in 1948. In recent years considerable use has been made of this substance as an agent for fluorination of organic compounds. Compared to fluorine it is relatively mild and selective and is now commercially available. Somewhat less frequent use is being made of the related compounds $CF_2(OF)_2$, CF_3OOF, CF_3OOCF_3 and CF_3OOOCF_3.

Very little use has been made of mass spectrometry by those working with these substances. This may be due in part to a statement by Porter and Cady [2] that "mass spectra were not very helpful in establishing the purity of CF_3OF because the mass spectrum of CF_3OF was strikingly like that of COF_2. The most prominent mass numbers were 47 and 66, due respectively to COF^+ and COF_2^+." Because it seemed unlikely that the mass spectrum of CF_3OF should not contain a prominent peak at m/e = 69 (CF_3^+) we determined its mass spectrum using an unreactive inlet system of Kel-F, similar to that used for the discovery of hypofluorous acid [3], and did indeed observe m/e = 69 as the base peak for CF_3OF along with other peaks to be expected in the mass spectrum of this compound. Presumably the sample of CF_3OF used by Porter and Cady was reduced to COF_2 on its way through the inlet system of their mass spectrometer. We believe that use of appropriate inlet systems allows greater use to be made of mass spectrometry for study of reactive substances. While we used a Kel-F inlet system for this work we have in the past used metal systems which could be fluorinated with ClF_3 and have obtained mass spectra of such highly reactive compounds as XeF_6 and KrF_2. When ClF_3 is used to fluorinate an inlet system its own appearance in the mass spectrometer, signaled by ClF_2^+, shows that the system has been sufficiently conditioned to pass highly reactive fluorine compounds.

We believe that while mass spectrometry has become a commonplace analytical technique its utility for monitoring the progress of reactions, purifications, etc., is still not as well appreciated as it could be. Its ability to analyze very small volatile samples withdrawn from reaction vessels makes it an essentially non-destructive tool for such uses.

Carbon, oxygen and fluorine are involved in these reversible gas-phase equilibria:

$$CF_4 + CO_2 \rightleftarrows 2COF_2$$

$$COF_2 + F_2 \rightleftarrows CF_3OF$$

$$CF_3OF + COF_2 \rightleftarrows CF_3OOCF_3$$

While attempting to develop a technique for elemental analysis of coal by burning it in fluorine followed by mass spectrometric analysis of the resulting combustion products we have observed the formation of at least the five carbon compounds involved in these three equilibria. Mass spectra are known for CO_2, CF_4, and COF_2. We have determined the mass spectra of CF_3OF and CF_3OOCF_3 along with those of the similar compounds $CF_2(OF)_2$, CF_3OOF and CF_3OOOCF_3, and have investigated the reactions of these compounds with mercury and with water. These reactions can be used to simplify the gaseous mixtures to be used for the elemental analysis of coal.

RESULTS AND DISCUSSION

CF_3OF, fluoroxytrifluoromethane (trifluoromethyl hypofluorite)

The mass spectrum of CF_3OF is given in Figure 1 and Table 1. For comparison Table 1 also gives the mass spectrum of COF_2, obtained with the same inlet system and the same mass spectrometer. The spectrum of CF_3OF is quite characteristic of the compound, the molecular ion and all possible fragment ions being observed except OF^+, m/e = 35. The fragmentation can be represented as

$$\begin{tikzcd}
CF_3OF \arrow[r] & CF_3OF^+ \arrow[r] & CF_3O^+ \arrow[r] \arrow[d] & CF_2O^+ \arrow[r] \arrow[d] & CFO^+ \arrow[r] \arrow[d] & CO^+ \\
 & & CF_3^+ \arrow[r] & CF_2^+ \arrow[r] & CF^+ &
\end{tikzcd}$$

The spectrum is most obviously distinguished from that of COF_2, the material from which it is most commonly made, by the presence of substantial peaks at m/e = 69 (CF_3^+) and m/e = 85 (CF_3O^+). Otherwise the two spectra are qualitatively similar but quantitatively different.

The mass spectrum of CF_3OF was obtained from a commercial product (PCR, Gainesville, Florida) which contained CO_2 impurity The gas was stated by the manufacturer to be 97% pure. If the remaining 3% is CO_2 the theoretical molecular weight of 104.0 is reduced to 102.2 which is just what was obtained by a gas density measurement. The presence of a small amount of CF_3OOCF_3 in this material was suggested by a tiny parent peak at m/e = 170 and a peak at m/e = 151 ($CF_3OOCF_2^+$).

$CF_2(OF)_2$, bis(fluoroxy)difluoromethane

The mass spectrum of $CF_2(OF)_2$ is given in Figure 2 and in Table 2. All possible fragment ions are observed except the molecular ion, $CF_2(OF)_2^+$. The fragmentation can be represented, not uniquely, as:

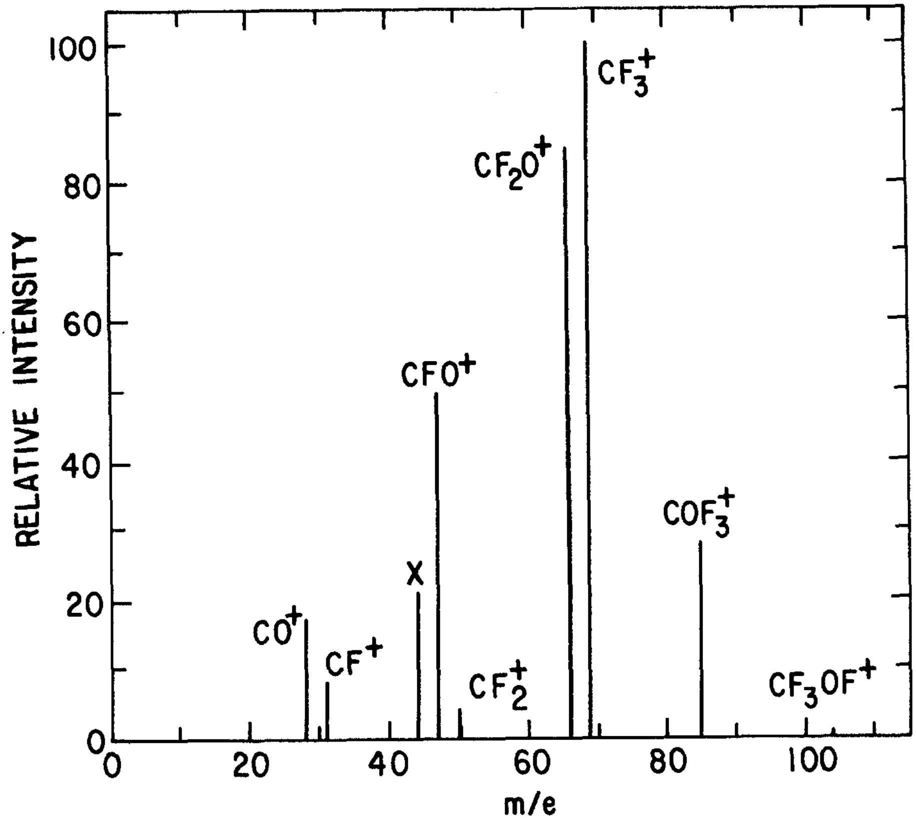

Fig. 1. Mass spectrum of CF_3OF.

TABLE 1

Mass spectra of CF_3OF (top) and COF_2

m/e	Ion	Relative Intensity	m/e	Ion	Relative Intensity
28	CO^+	16.5	66	CF_2O^+	84.8
31	CF^+	7.6	69	CF_3^+	100
44	CO_2^+	21.5(x)	85	CF_3O^+	28.2
47	CFO^+	49.8	104	CF_3OF	0.2
50	CF_2^+	4.2			
28	CO^+	24.0	50	CF_2^+	3.2
31	CF^+	5.2	66	CF_2O^+	100
47	CFO^+	89.0			

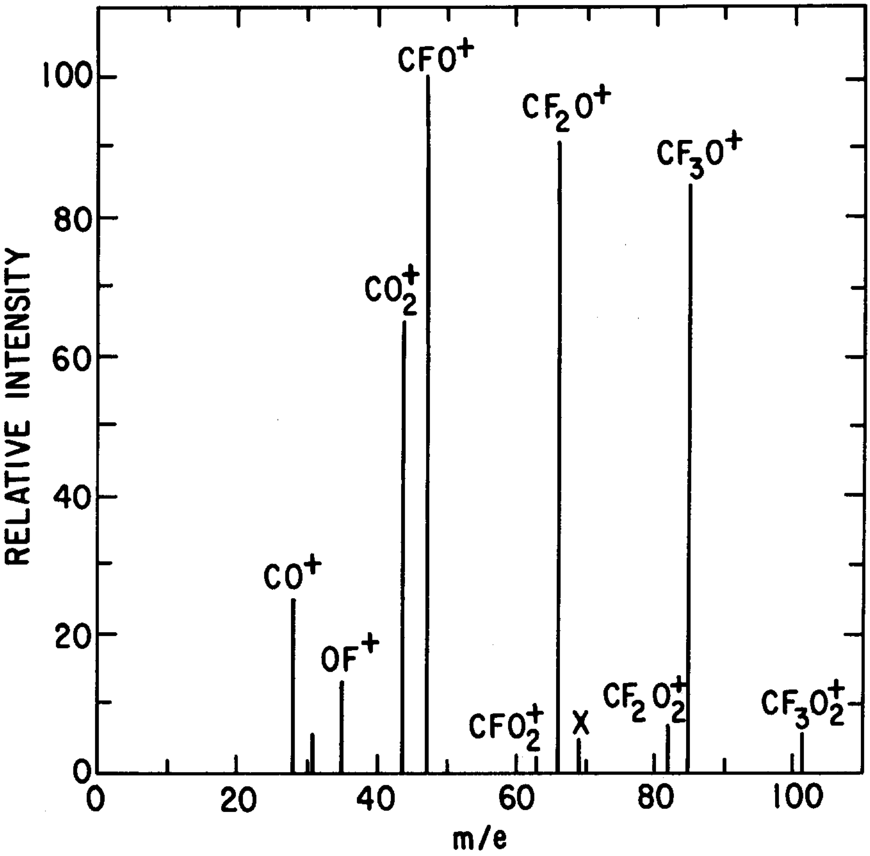

Fig. 2. Mass spectrum of $CF_2(OF)_2$.

TABLE 2

Mass spectrum of $CF_2(OF)_2$

m/e	Ion	Relative Intensity	m/e	Ion	Relative Intensity
28	CO^+	25.3	63	CFO_2^+	2.6
31	CF^+	5.7	66	CF_2O^+	90.8
35	OF^+	13.2	69	CF_3^+	5.2
44	CO_2^+	64.8	82	$CF_2O_2^+$	7.3
47	CFO^+	100	85	CF_3O^+	85.2
50	CF_2^+	4.4	101	$CF_3O_2^+$	6.1

$$\begin{tikzcd}
CF_2(OF)_2 \arrow[r] \arrow[d] & CF_3O_2^+ \arrow[r] \arrow[d] & CF_2O_2^+ \arrow[r] \arrow[d] & CFO_2^+ \arrow[r] \arrow[d] & CO_2^+ \arrow[r] \arrow[d] & CO^+ \\
OF^+ & CF_3O^+ \arrow[r] & CF_2O^+ \arrow[r] \arrow[d] & CFO^+ \arrow[r] & CF^+ & \\
 & & CF_2^+ & & &
\end{tikzcd}$$

The spectrum is distinguished from that of CF_3OF most conspicuously by the presence of fragments containing two oxygen atoms and by the absence of any large peak at m/e = 69 (CF_3^+). The small peak observed at m/e = 69 persists when the compound has been completely destroyed by reaction with mercury and so is due at least in part to impurities.

The mass spectrum was obtained from a sample whose gas density molecular weight of 120.2 agreed with the theoretical value of 120.0 within experimental error.

CF_3OOF, fluoroperoxytrifluoromethane

The mass spectrum of CF_3OOF is given in Figure 3 and Table 3. It is generally similar to the spectrum of CF_3OF, but distinguished by small fragments containing two oxygen atoms at m/e = 82 and 101. It is most obviously different from the spectrum of the isomeric $CF_2(OF)_2$ in its base peak m/e = 69 (CF_3^+). The spectrum was obtained from a small sample with a gas density molecular weight of 116 (theor. 120); variability in the intensity of m/e = 44 relative to the rest of the spectrum indicated the presence of carbon dioxide impurity. CF_3OF impurity also may have been present. The fragmentation can be represented as

$$\begin{tikzcd}
CF_3OOF \arrow[r] \arrow[dd] & CF_3O_2^+ \arrow[r] \arrow[dd] & CF_2O_2^+ \arrow[r] \arrow[d] & CO_2^+ \arrow[r] \arrow[d] & CO^+ \\
 & & CF_2O^+ \arrow[r] \arrow[d] & CFO^+ \arrow[d] & \\
OF^+ & CF_3^+ \arrow[r] & CF_2^+ \arrow[r] & CF^+ &
\end{tikzcd}$$

CF_3OOCF_3, bis(trifluoromethyl) peroxide

The mass spectrum of CF_3OOCF_3 is given in Figure 4 and in Table 4. Quantitatively it is dominated by the intense base peak at m/e = 69 (CF_3^+) to a greater extent than are the spectra

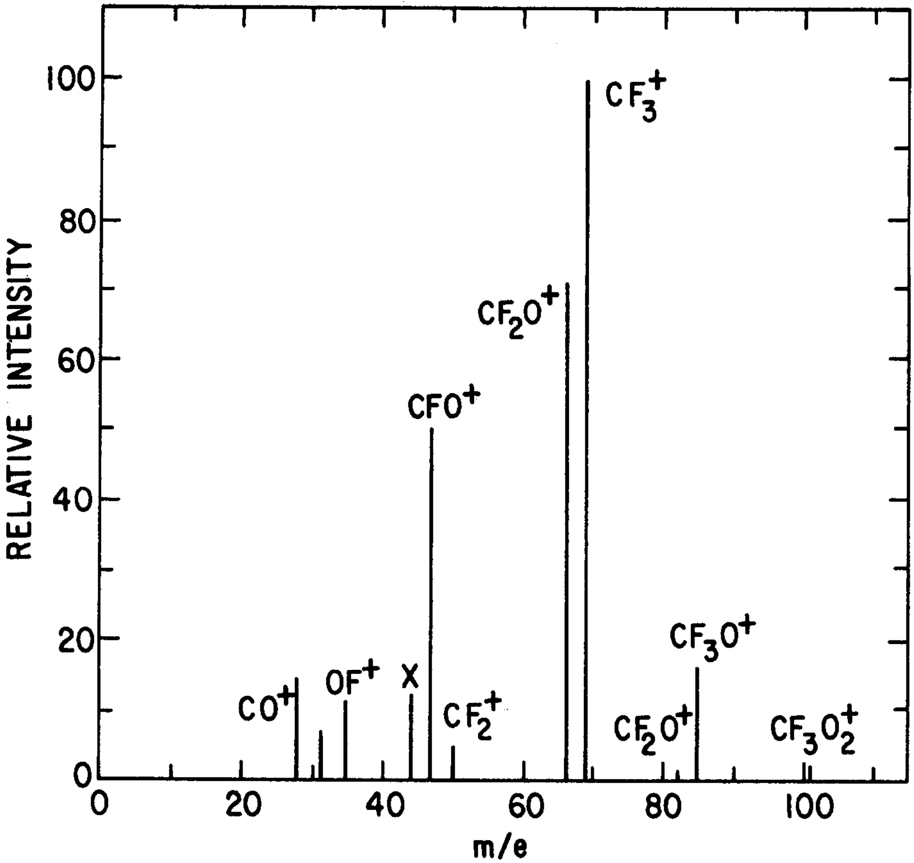

Fig. 3. Mass spectrum of CF_3OOF

TABLE 3

Mass spectrum of CF_3OOF

m/e	Ion	Relative Intensity	m/e	Ion	Relative Intensity
28	CO^+	14.4	66	CF_2O^+	71.0
31	CF^+	6.8	69	CF_3^+	100
35	OF^+	10.2	82	$CF_2O_2^+$	1.6
44	CO_2^+	12.1	85	CF_3O^+	16.5
47	CFO^+	49.9	101	$CF_3O_2^+$	2.0
50	CF_2^+	5.3			

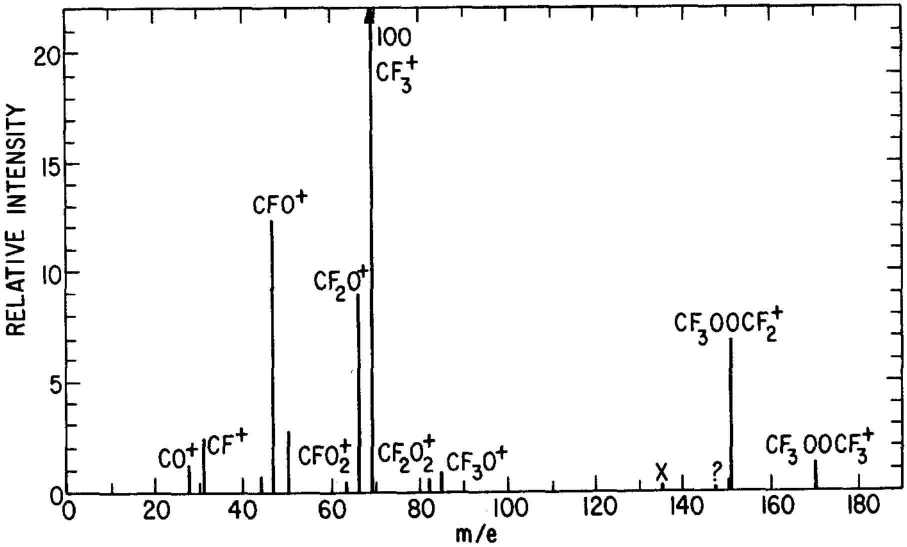

Fig. 4. Mass spectrum of CF_3OOCF_3

TABLE 4

Mass Spectrum of CF_3OOCF_3

m/e	Ion	Relative Intensity	m/e	Ion	Relative Intensity
28	CO^+	1.2	69	CF_3^+	100
31	CF^+	2.6	82	$CF_2O_2^+$	0.6
44	CO_2^+	0.8	85	CF_3O^+	1.0
50	CF_2^+	2.8	151	$C_2F_5O_2^+$	6.9
63	CFO_2^+	0.6	170	$C_2F_6O_2^+$	1.4
66	CF_2O^+				

of CF_3OF and CF_3OOF, but the molecular ion $CF_3OOCF_3^+$ is readily detected and the spectrum shows all expected fragments except $CF_3O_2^+$. The peaks most obviously characteristic of the compound are those at m/e = 170 ($CF_3OOCF_3^+$) and m/e = 151 ($CF_3OOCF_2^+$). These peaks permit easy identification of the presence of this compound as an impurity in any of the other compounds whose mass spectra are reported in this paper. The fragmentation can be represented as:

$$\begin{tikzcd}
CF_3OOCF_3^+ \arrow[r] \arrow[d] & CF_3OOCF_2^+ \arrow[r] \arrow[d] & CF_2O_2^+ \arrow[r] \arrow[d] & CFO_2^+ \arrow[r] \arrow[d] & CO_2^+ \arrow[r] & CO^+ \\
CF_3^+ & CF_3O^+ \arrow[l] \arrow[r] & CF_2^+ \arrow[r] & CF^+ & &
\end{tikzcd}$$

This mass spectrum was obtained from a sample with a gas density molecular weight of 170.0, in exact agreement with the theoretical value. A very small peak at m/e = 135 corresponds to $CF_3OCF_2^+$ and may indicate the presence of a small amount of $(CF_3)_2O$ impurity.

The mass spectrum of CF_3OOCF_3 was mentioned by Porter and Cady [2] but no data were given.

CF_3OOOCF_3, bis(trifluoromethyltrioxide)

The mass spectrum of CF_3OOOCF_3 is given in Figure 5 and in Table 5. This spectrum is the least characteristic of these five compounds, showing no fragment in which the skeleton of carbon and oxygen is maintained. Apart from this it is generally similar to the spectrum of CF_3OOCF_3. The fragment with the largest value of m/e is $CF_3O_2^+$, which, incidentally, is absent from the spectrum of CF_3OOCF_3. This fragment shows no enhancement of intensity relative to the rest of the spectrum when the sample is cooled to -140° as would be expected if it were due to an impurity more volatile than CF_3OOOCF_3, such as CF_3OOF or $CF_2(OF)_2$. Therefore it probably is a part of the mass spectrum of CF_3OOOCF_3. The fragmentation can be represented as:

$$\begin{tikzcd}
CF_3OOOCF_3 \arrow[r] & CF_3O_2^+ \arrow[r] \arrow[d] & CF_2O^+ \arrow[r] \arrow[d] & CFO^+ \arrow[r] & CF^+ \\
 & CO_2^+ \arrow[d] & CF_2^+ & & \\
 & CO^+ & & &
\end{tikzcd}$$

This spectrum was obtained from a sample with a gas density molecular weight of 186.1 (theor. 186.0).

The mass spectrum of CF_3OOOCF_3 has been reported by Thompson [4] and by Anderson and Fox [5]. Thompson reported no peaks at m/e > 82 ($CF_2O_2^+$). Anderson and Fox reported peaks at m/e = 85 (CF_3O^+) and m/e = 101 $(CF_3O_2)^+$ as do we. They also

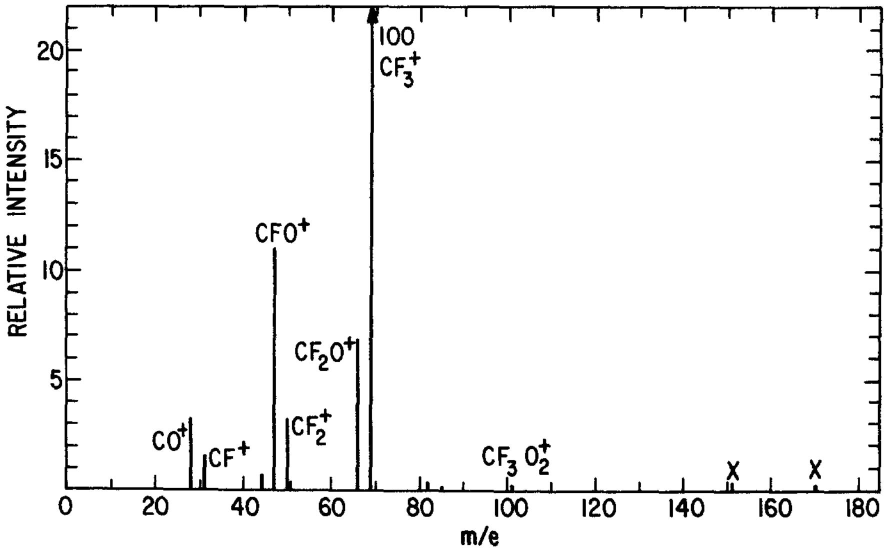

Fig. 5. Mass spectrum of CF_3OOOCF_3.

TABLE 5

Mass spectrum of CF_3OOOCF_3

m/e	Ion	Relative Intensity	m/e	Ion	Relative Intensity
28	CO^+	3.4	66	CF_2O^+	6.9
31	CF^+	1.8	69	CF_3^+	100
32	O_2^+	2.4	82	$CF_2O_2^+$	0.5
44	CO_2^+	0.7	85	CF_3O^+	0.2
50	CF_2^+	3.4	101	$CF_3O_2^+$	0.3

reported a peak at m/e = 151 ($CF_3OOCF_2^+$) which is accompanied in our spectrum by $CF_3OOCF_3^+$ and which we suspect is due to CF_3OOCF_3 impurity in CF_3OOOCF_3. Otherwise, our spectrum is generally similar to those previously reported.

EXPERIMENTAL

All samples subjected to mass spectrometric analysis were introduced to the source of a Bendix time-of-flight mass spectrometer by an inlet system of Kel-F valves and Kel-F tubing.

Preparation of $CF_2(OF)_2$

$CF_2(OF)_2$ was prepared by the method of Hohorst and Shreeve [6]. Mass spectrometric examination of the product after removal of excess fluorine showed the presence of a small amount of oxygen difluoride which was removed by pumping with the sample at -195°.

Preparation of CF_3OOF

CF_3OOF was prepared by the method of Solomon et al. [7], using six moles of oxygen difluoride for each mole of carbonyl fluoride absorbed by cesium fluoride. In spite of the use of excess oxygen difluoride most of the carbonyl fluoride was converted to CF_3OOOCF_3 which was retained in a trap at -160° and only a small sample of CF_3OOF was obtained. Initially this had a gas density molecular weight of 98 and mass spectrometric examination showed the presence of residual oxygen difluoride. Pumping on the sample at -184° removed the oxygen difluoride and raised the apparent molecular weight to 116 (theor. 120). The low value was due to carbon dioxide contamination which could not be removed easily from this small sample.

Preparation of CF_3OOCF_3

CF_3OOCF_3 was prepared by heating carbonyl fluoride and fluorine (2:1 ratio) to 400° in a nickel can which was then allowed to cool to ambient temperature. Mass spectrometric examination of the resulting mixture showed the presence of CF_3OF, COF_2, and CO_2. Pumping on the mixture from a trap at -130° gradually removed these impurities to give a product with an apparent molecular weight of 165. Mass spectrometric examination of the gases then being removed from the sample showed the presence of HF: storage of the sample with sodium fluoride pellets raised the apparent molecular weight to 170.0 in exact agreement with the theoretical value.

Preparation of CF_3OOOCF_3

CF_3OOOCF_3 was prepared by the method of Anderson et al. [8].

Reactions with mercury

CF_3OF, $CF_2(OF)_2$, CF_3OOF, CF_3OOCF_3 and CF_3OOOCF_3 were each admitted to a Kel-F tube containing clean mercury. In each case immediate darkening of the mercury surface occurred. The tube was shaken briefly and the gaseous contents examined by mass spectrometry. CF_3OF and CF_3OOCF_3 were reduced to COF_2; $CF_2(OF)_2$ was reduced to CO_2; CF_3OOF and CF_3OOOCF_3 were reduced to mixtures of CO_2 and COF_2. In the latter case the product mixture was analyzed and found to be equimolar within experimental error (5%). This reaction then can be represented as:

$$CF_3OOOCF_3 + Hg \rightarrow HgF_x + CO_2 + COF_2 \quad .$$

In each case all of the compound admitted to the Kel-F tube was destroyed by the mercury.

This observation appears to conflict with the statement by Anderson et al. [8] that CF_3OOOCF_3 "is not destroyed rapidly by mercury although the mercury darkens." Possibly the discrepancy is due to differences in effectiveness of interphase contact.

Reduction of CF_3OF to COF_2 by mercury has been reported previously [2].

Reactions with water

Kellogg and Cady [1] observed that the reaction of CF_3OF with water was sufficiently slow so that COF_2 impurity could be removed from CF_3OF by hydrolysis. We find that $CF_2(OF)_2$, CF_3OOF, CF_3OOCF_3 and CF_3OOOCF_3 also react slowly with water, each showing incomplete reaction after eighteen hours. Of the four compounds CF_3OOCF_3 seems to be the least reactive; showing only a few percent conversion to CO_2 and O_2 in two days.

Attempted formation of FC(O)OF, fluorocarbonyl hypofluorite

FC(O)OF has been made photochemically [9]. We have used mass spectrometry to look for its intermediate formation during the cesium fluoride catalyzed reaction of fluorine and carbon dioxide (to give $CF_2(OF)_2$) at -78° and during reduction of

$CF_2(OF)_2$ by mercury and by solid sodium chloride. No evidence for formation of any FC(O)OF was observed. Also we have investigated the pyrolysis of $CF_2(OF)_2$ in a fluorinated nickel can, withdrawing small samples for mass spectrometric analysis, to look for possible decomposition $CF_2(OF)_2 \rightarrow FC(O)OF + F_2$, similar to the reversible decomposition of CF_3OF to give carbonyl fluoride and fluorine. The $CF_2(OF)_2$ showed no change up to 225°; above that temperature mass spectral fragments containing two oxygen atoms disappeared and species appeared corresponding to the formation of CF_3OF, COF_2 and O_2 with elemental fluorine being formed above 300°, presumably by decomposition of CF_3OF. No evidence was obtained for formation of FC(O)OF.

USES OF REAGENTS

CF_3OF is being used as a relatively mild and selective agent for fluorination of organic compounds: It has been reacted with olefinic linkages [10] to give products bearing fluorine linked to the carbon constituting the more electrophilic terminus of the olefinic substrate and for electrophilic addition to aromatic rings [11]. For example, it reacts with hexafluorobenzene to add F and CF_3O 1,2 and 1,4 [12]. It has been used to substitute fluorine for one hydrogen of uracil [13] and uracil nucleotides [14] to produce compounds of biological significance thereby avoiding complicated synthetic procedures. It reacts with adamantane [15] to give 1-fluoroadamantane without disturbing the rest of the molecule. Such reactions usually are conducted in solvents and at low temperature: it would appear that mass spectrometry can be a useful tool to monitor uptake of CF_3OF reagent.

$CF_2(OF)_2$ has been used for purposes similar to those of CF_3OF [16] but not as commonly. The two fluoroxy groups attached to one carbon allows it to be used as a reagent in the preparation of poly(fluorodiethers). For example, tetrafluoroethylene reacts to give perfluorodiethoxymethane [17].

$$CF_2(OF)_2 + 2\ F_2C = CF_2 \rightarrow CF_2(OC_2F_5)_2$$

CF_3OOF has had some use as a reagent. For example, it has been used for synthesis of fluorocarbon peroxides by addition of CF_3OO and F to alkene substrates [18].

The first step in the pyrolytic decomposition of CF_3OOCF_3 is symmetrical cleavage of the central oxygen-oxygen bond to give $CF_3O\cdot$radicals [19,20] and it has been used as a thermal and photochemical polymerization catalyst [21].

CF_3OOOCF_3 has been used in much the same way as CF_3OOF, as a source of compounds containing CF_3O and CF_3OO groups [22].

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