

PREPARATION OF FLUORINE PEROXIDES AND DIOXYGEN TETRAFLUOROBORATE
BY LOW TEMPERATURE RADIOLYSIS

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Introduction

More than three decades have elapsed since it was shown that oxygen and fluorine could be combined by passage through an electrical discharge. The product, condensed on a very cold surface, was dioxygen difluoride, O_2F_2 .¹⁾ More recently, higher oxides of fluorine have been similarly prepared; these have been claimed to be O_3F_2 ,²⁾ O_4F_2 ,³⁾ O_5F_2 and O_6F_2 .⁴⁾ The existence of O_4F_2 appears to be well established; however, there has been some controversy concerning the existence of O_3F_2 as a molecular species.⁵⁾

Although O_2F_2 and O_4F_2 are stable only at very low temperatures, considerable evidence has been acquired concerning their physical⁶⁻¹⁰⁾ and chemical¹¹⁻¹⁶⁾ properties. With all these studies the method of preparation of the oxygen fluorides has remained the same. No work has been reported on the radiation-induced reaction of oxygen and fluorine in a condensed phase.

The present study describes the reaction of these materials in the liquid phase at 77°K. Reactions were induced by high intensity 3 Mev bremsstrahlung.

Procedure

Except for certain cases, ca 1.0 ml samples (28 mmoles) were irradiated in vacuo in stainless steel or sapphire vessels at 77°K for 1-2 hr at dose rates up to 100 megarads/hr of 3 Mev bremsstrahlung. The high-intensity 3 Mev bremsstrahlung was generated by directing the 3 Mev, 1 ma unscanned electron beam from a Van de Graaff accelerator onto a water-cooled gold target.¹⁷⁾ Following the irradiation the reaction vessel was attached to a vacuum line with provisions for expanding into a predetermined volume, measuring the pressure and analyzing with a mass spectrometer.¹⁸⁾ With this equipment the total volume and composition of gases from decompositions of products could be measured.

In experiments where BF_3 was added to the irradiated sample, the BF_3 was condensed in the top of the irradiated sample tube. The dewar of liquid nitrogen surrounding the tube was then slowly lowered to distill the BF_3 to the bottom of the tube. By this method any material deposited on the walls of the reaction vessel could react with the BF_3 . The excess oxygen and fluorine were removed at 77°K; the sample tube was warmed to 195°K and the unreacted BF_3 was pumped off.

Results and Discussion

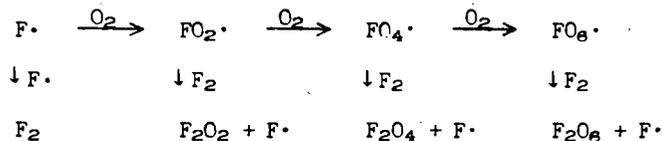
The initial mixtures of F_2 and O_2 had a yellow color; after irradiation a reddish-brown solid was observed on the walls of the sapphire tube. The solid is presumed to be a mixture of F_2O_2 and F_2O_4 with possibly other oxides of fluorine. In each of the experiments described below (Table 1), excess F_2 and O_2 were removed at 77°K, first by evaporation into the calibrated

volume and then by pumping to a few microns pressure; this treatment would also remove F_2O . The sample was then warmed cautiously to decompose the F_2O_4 to F_2O_2 ; the O_2 released was measured gasometrically. This operation was carried out most successfully by removing the liquid nitrogen bath until a small increase in pressure was observed, replacing the liquid nitrogen, and repeating the process until the F_2O_2 could be melted ($113^\circ K$) without further oxygen evolution. The oxygen thus evolved was mass spectrometrically free of F_2 (however, this was not a very sensitive test because the mass spectrometer inlet system was somewhat reactive with small quantities of fluorine). The blood-red liquid F_2O_2 was then frozen at $77^\circ K$ (orange solid) and the residual O_2 was pumped away. Subsequent remelting at $113^\circ K$ resulted in no further release of O_2 . The sample was then warmed slowly to room temperature to decompose the F_2O_2 and measure the $F_2 + O_2$.

This procedure was occasionally unsuccessful in cases with the initial mole ratio F_2/O_2 of 1.0 or 3.0, because a minor explosion ("pop") would be heard during the decomposition of F_2O_4 , accompanied by a sudden rise in pressure. The gasometric data indicated that in these cases some of the F_2O_2 was decomposed during the sudden decomposition of F_2O_4 . Because of this, the apparent yields of F_2O_4 and F_2O_2 reported in Table 1 are taken only from experiments in which there was no audible evidence of explosion. Nevertheless, the reported yields of F_2O_4 may be slightly too high in some cases because of some decomposition of F_2O_2 during the decomposition of F_2O_4 .

The data reported in Table 1 show several unusual features. First, in the mixtures containing only F_2 and O_2 , the number of millimoles of oxygen converted to F_2O_2 and F_2O_4 remain nearly constant despite a large variation in the initial ratio of F_2 to O_2 , even when the major part of the oxygen was consumed. The G-value for products also remained constant at a value that is several-fold higher than the values that are usually found for non-chain reactions.⁸ These observations suggest that the formation of F_2O_2 under these conditions involves a short chain process that is initiated with approximately equal efficiency whether the initial absorption of energy is done by oxygen or by fluorine.

Another observation is that the ratio of F_2O_4 to F_2O_2 in the products displays no obvious trend with the initial ratio of F_2/O_2 . The possible chain



would not lead to these results in a homogeneous system, but the kinetics are probably complicated by the fact that the products precipitate as solids.

The experiments in which the reactants were diluted with argon show that the presence of argon had a small positive effect on the total conversion of oxygen, whereas dilution with nitrogen does not appear to effect the yield. Some energy transfer from argon seems indicated.

a) G for ion pair formation is expected to be about 4; for radicals it often ranges from 6-10.

One experiment was done with a large excess of oxygen ($F_2/O_2 = 1/6$). The unreacted F_2 and O_2 (21.6 mmoles out of an initial 28) were removed and the reaction tube evacuated to $< 5 \mu$. The color of the solid remaining in the sapphire tube was very dark brown. When the liquid nitrogen bath was momentarily removed and the sample was illuminated briefly with a flashlight, the product detonated violently and shattered the sapphire tube. Whether the detonation was due to the presence of a large amount of F_2O_4 or to F_2O_8 is not known. It is unlikely that the detonation was due to O_3 since its vapor pressure is well above 5μ at $77^\circ K$ and should have been pumped off. The very unstable F_2O_8 (dark brown in color) has been reported to explode on illumination or sudden warming. It is claimed to decompose thermally about $90^\circ K$.

In the experiments listed in Table 1, some F_2O was formed in addition to F_2O_2 and F_2O_4 ; the amount was relatively small and was not studied systematically. The presence of F_2O was detected by mass spectrometric analysis.

Experiments With Added BF_3

It has been shown by others¹⁵⁾ that BF_3 reacts with F_2O_2 at low temperatures to form the ionic compound $O_2^+BF_4^-$. We therefore added BF_3 to irradiated mixtures of O_2 and F_2 in order to explore the radiation route to $O_2^+BF_4^-$ and possibly to $O_4^+BF_4^-$.

Boron trifluoride (3.5 mmoles) was condensed in the top of the irradiation tube containing the formed fluorine peroxides (ca 1.7-2.0 millimoles) suspended in the excess fluorine and oxygen. The BF_3 was distilled to the bottom of the tube and the contents mixed by alternately vaporizing and condensing a portion of the excess fluorine and oxygen. In this manner the BF_3 was better able to contact the reddish-brown peroxide. The excess fluorine and oxygen were then removed under vacuum at $77^\circ K$. When the contents were warmed to $113^\circ K$, a rapid reaction occurred, and the color changed to orange. This suggests that much of the F_2O_4 decomposed without reacting with BF_3 . The orange color changed to white when the temperature was raised to $143^\circ K$; this corresponds to the conversion of the F_2O_2 to $O_2^+BF_4^-$. Further warming to $240^\circ K$ led to slight decomposition; the remaining solid was relatively stable, decomposing only very slowly at room temperature and atmospheric pressure. The decomposition is much more rapid under reduced pressure, indicating a reversible step with a gaseous product in the decomposition. The yield was measured by recovering the solid in a dry box and weighing it.

The gases evolved upon warming to $240^\circ K$ consisted of O_2 , F_2 , and BF_3 . Irradiation of various fluorine-oxygen mixtures followed by addition of BF_3 gave gases for this low-temperature decomposition in the ratio of $(O_2 + F_2)/BF_3$ of $1.9 \pm .35$. There is a systematic tendency for this ratio to be higher when the total volume of gas liberated is low. These findings correspond to decomposition of an oxygen-rich compound, probably $O_4^+BF_4^-$, with simultaneous induced decomposition of some of the $O_2^+BF_4^-$. (Evidence for the formation of $O_4^+BF_4^-$ from F_2O_4 has also been obtained in an independent investigation by Soloman and his colleagues.)¹⁹⁾

The more stable product (presumed to be $O_2^+BF_4^-$) decomposed rapidly above $300^\circ K$ to give O_2 , F_2 , and BF_3 . The elemental analysis of the solid was F, 62.6%; B, 8.6%; theory, F, 63.7%; B, 9.2%). The infrared spectrum of the powder between silver chloride plates exhibits the characteristic absorption frequencies²⁰⁾ of the BF_4^- ion. No absorption band attributable to O_2^+ was observed, but this ion should have no dipole moment.

The x-ray powder pattern (Table 2) is very similar to that of the likely isomorphous NO^+BF_4^- compound. (The nitrosyl and dioxygenyl cations are similar in size.)²¹⁾ A comparable correlation¹⁴⁾ was found for $\text{NO}^+\text{AsF}_6^-$ and $\text{O}_2^+\text{AsF}_6^-$.

The EPR spectrum of the solid at 77°K was a broad signal with a G-value of 1.9⁴ and a peak-to-peak separation in the derivative mode of about 382 gauss. Kirshenbaum and Grosse²²⁾ found similar results in HF solution. Solomon, et al¹⁵⁾²³⁾ reported similar results for the solid.

The yields of $\text{O}_2^+\text{BF}_4^-$ recovered from various experiments are listed in Table 3. Comparison of the yields after 1 hr irradiation time in the experiments listed in Tables 1 and 3 indicates that a little less than two moles of F_2O_2 are required to produce one mole of $\text{O}_2^+\text{BF}_4^-$. Either some decomposition of F_2O_2 occurred during the process of warming to the temperature of reaction with BF_3 , or the formation of $\text{O}_2^+\text{BF}_4^-$ is accompanied by a side reaction that decomposes part of the F_2O_2 . It will also be noted that in the single experiment with a large excess of oxygen present during irradiation ($\text{F}_2/\text{O}_2 = 1/6$), the excess F_2 and O_2 were successfully removed without detonation after BF_3 was added. The yield of $\text{O}_2^+\text{BF}_4^-$ was relatively small, but there was evidence for the formation of larger amounts of a less stable compound. One other observation of interest is that when BF_3 is present during the irradiation, the yield of $\text{O}_2^+\text{BF}_4^-$ finally recovered is relatively small.

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Table 1. YIELDS OF F_2O_2 AND F_2O_4 FROM IRRADIATION^{a)} OF FLUORINE/OXYGEN MIXTURES

Mole Ratio, F_2/O_2	Amount Irradiated, millimoles				Yield, ^{b)} millimoles		Ratio, F_2O_4/F_2O_2	Oxygen Consumed		G-Value (c)
	F_2	O_2	Ar	N_2	F_2O_2	F_2O_4		mmole	%	
1	14.0	14.0	-	-	1.50	0.13	0.087 ± 0.02	1.72	12.3	17.5
3	21.0	7.0	-	-	1.72	0.085	0.05 ± 0.02	1.89	27.0	18.5
5	22.8	4.6	-	-	1.93	0.105	0.055 ± 0.02	2.14	46.6	21.2
7	24.5	3.5	-	-	1.86	0.14	0.075 ± 0.015	2.14	61.2	20.6
1	10.5	10.5	-	7.0		(d)	n.d.	1.26	12.0	13.5
1	10.5	10.5	7.0	-		(d)	n.d.	1.73	16.5	17.1
1	10.5	10.5	7.0	-	1.65	0.07	0.042 ± 0.02	1.79	17.1	17.6
3	15.7	5.3	7.0	-	1.62	0.14	0.09 ± 0.02	1.90	35.9	18.2
5	17.5	3.5	7.0	-	1.62	0.105	0.065 ± 0.02	1.83	52.3	17.3
7	18.4	2.6	7.0	-	1.62	0.09	0.055 ± 0.02	1.79	68.9	16.8

a) 77°K, 100 megarads, 1 hr.

b) Yield data accurate to ca ± 0.03 mmole.

c) Molecules of product formed per 100 ev absorbed energy.

d) Amount of F_2O_4 not reliably determined because of a slight detonation on warming the system to decompose F_2O_4 .Table 2. DIFFRACTION PATTERNS OF $NO^+BF_4^-$ AND $O_2^+BF_4^-$

$NO^+BF_4^-$		$O_2^+BF_4^-$		
Interplanar Spacing A	Intensity of Reflection	Interplanar Spacing A	Intensity of Reflection	hkl
5.50	24	5.50	16	110
4.41	40	4.33	34	101
3.96	8	3.91	5	111
3.76	12	3.74	9	120
3.51	100	3.47	100	021
3.25	12	3.27	16	210
3.13	80	3.10	88	121
2.82	60	2.82	75	211
2.75	12	2.74	12	220
2.52	40	2.49	44	112
2.40	3	2.43	7	131
2.39	8	2.35	7	022
2.26	60	2.24	63	122

Table 3. PREPARATION OF $O_2^+BF_4^-$ ^{a)}

Irradiation Time, min ^{b)}	Ratio $F_2:O_2$ Irradiated ^{c)}	$O_2^+BF_4^-$ Produced, mg	% $O_2^+BF_4^-$ Based on Oxygen	G-Value Total ^{g)}
15	1:1	27	1.6	8.9
30	1:1	53	3	8.8
60	1:1	96	6	7.9
60	2:1	129	12	11.0
60	3:1	134	16	10.6
60	5:1	127	24	10.5
60	7:1	113	27	8.8
60	1:6	44 ^{d)}	1.5	4.1
60 ^{e)}	1:1	45	2.7	14.9
120	3:1	216	26	8.6
180	1:1	231	14	6.3
180	5:1	248	47	6.9
120 ^{f)}	3:1	21	2.6	0.2

- a) 14 mmoles of BF_3 was added after irradiation.
b) Dose rate of 100 megarads/hour.
c) Millimoles of oxygen used with $F_2:O_2$ ratios was:
1:1 = 14 mmoles; 2:1 = 8.75 mmoles; 3:1 = 7.0 mmoles;
5:1 = 4.4 mmoles; 7:1 = 3.5 mmoles; 1:6 = 21.9 mmoles.
d) A second compound was formed which decomposed at 133°K yielding about 3 mmoles of noncondensable gases.
e) Dose rate of 25 megarads/hour.
f) 10.5 mmoles of BF_3 added to the reaction tube before irradiation.
g) Molecules of product formed per 100 ev absorbed energy.

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