Low-Temperature Radiation Chemistry.   I.   Preparation of Oxygen Fluorides and Dioxygenyl Tetrafluoroborate

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Abstract: Radiolysis of liquid mixtures of O_2 and F_2 at 77°K with 3-MeV bremsstrahlung produces a mixture of O_2F_2 and $(O_2F)_n$ with possibly small amounts of higher oxides.   The mixture was converted to pure O_2F_2 at 195°K. Contrary to earlier reports, pure O_2F_2 is yellow, melts sharply at 119°K, and is diamagnetic.   Infrared spectra were obtained of the unpurified product and of O_2F_2.   In the radiolytic synthesis, the G value for generation of F atoms appears to be about 20.   Data support the existence of O_2F_2, O_2F, O_4F_2, and unknown oxides of higher oxygen content.   As previously reported by others, BF_3 reacts with either O_2F_2 or with mixtures of O_2F_2 and superoxygen fluorides to produce O_2BF_4; less stable compounds seem to be produced from the higher superoxides. The infrared and paramagnetic resonance spectra of O_2BF_4 have been obtained; the X-ray powder pattern shows that the crystals are orthorhombic and isomorphous with $NOBF_4$.

It has been more than 30 years 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 purported to be oxygen difluoride or 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]   On the basis of recent evidence[5] it appears likely that the substance reported as O_3F_2 is a mixture of O_2F_2 and $n(\cdot O_2F) \rightleftarrows (O_2F)_n$.

Although these compounds are stable only at very low temperatures, considerable information has been acquired concerning their physical[6-10] and chemical[11-16] properties.   In all of these studies, the method of preparation of the oxygen fluorides has involved gas-phase electric discharge techniques in vessels with cold walls. No work has been reported on the radiation-induced reaction of oxygen and fluorine in a condensed phase. The present paper describes such a reaction at 77°K, induced by high-intensity 3-MeV bremsstrahlung.

Experimental Section

Sample Preparation and Reaction Vessels.   Gaseous mixtures of O_2 and F_2 were prepared in a stainless steel vacuum system equipped with three U-tube traps for low-temperature distillation, calibrated volumes (600 and 110 ml), a stainless-steel Bourdon gauge (0–800 mm), and bellows-type Hoke valves with Teflon seats.   The manifold for connecting reaction vessels to this system was equipped with nitrogen flush arrangements to minimize atmospheric attack on passivated surfaces.   Connections were made by means of Gyroloc fittings with Teflon ferrules or Cajon fittings with flat copper washers.   Waste fluorine was vented or pumped from the system through a 500° chamber packed with carbon.

Reaction vessels were constructed of sapphire or stainless steel. The steel vessel was fabricated from an 8-mm i.d. tube attached to a bellows-type stainless-steel valve, Hoke No. 4112-G4Y, by means of a Gyroloc fitting with Teflon ferrule.   The sapphire vessel[17] comprised a short test tube (24 mm × 8 mm i.d.) made of optical-grade sapphire, silver-soldered to a stainless steel tube,[18] and fitted with a similar valve.   The sapphire made it possible to observe the reaction products visually, since it remained transparent even after exposure to large doses of radiation at low temperature and was inert to attack by fluorine or its oxides.

In most experiments the amount of reaction mixture prepared for irradiation was 28 mmoles; this was condensed at 77°K into a preevacuated reaction vessel, where it occupied a volume of about 1 ml.   The vessel was then transferred to a specially designed stainless steel dewar flask[19] filled with liquid nitrogen.   A small vertical section of the inner wall of this flask was concaved to receive the sample tube; this allowed both more accurate placement and closer proximity (*ca.* 6 mm) to the source of radiation.   During irradiation, the liquid nitrogen in the dewar was replenished by a demand system with thermocouple sensing; this was necessary because the usual dose rate corresponded to absorption of about 240 cal/hr for each gram of material intercepted by the beam at the sample position.

Irradiation.   The sample was exposed to 3-MeV bremsstrahlung of intensity up to 100 Mrads/hr.   The time of irradiation was 1–4 hr. The radiation was generated by directing a horizontal unscanned electron beam (3 MeV, 1 mA) onto a vertical water-cooled gold target;[20] the electron beam was generated in a vertical van de Graaff accelerator and deflected magnetically to the horizontal.[21] Dosimetry was achieved by photoactivation of cadmium;[22] irradiation of a 0.5-ml volume (974 mg) of cadmium metal for 5 min provided sufficient activity for accurate counting (>1.25 MeV photons, half-life 49 min).

Treatment of Products.   After irradiation the reaction vessel, still at 77°K, was transferred to the vacuum system.   Unreacted

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fluorine and oxygen were volatilized at 77°K into the calibrated volume for pressure measurement. Residual excess reactants were pumped away at 77°K. A qaudrupole mass spectrometer[23] was available to analyze these gas mixtures and others generated by subsequent decomposition of products. This instrument, though it was excellent for qualitative identification of species present, was not well suited for reproducible quantitative analysis unless samples of components were available for calibration. It was also insensitive to small amounts of F_2 because of wall reactions in the inlet system and within the spectrometer.

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

Infrared Cell. An infrared cell for obtaining spectra of liquids and solids at temperatures down to 77°K has been designed and constructed.[24] It is specifically for use with materials that must be physically transferred as a liquid or solid at low temperatures.

Basically the cell consists of a hollow metal toroid-shaped cell block. This block is connected to the bottom of a jointed liquid nitrogen reservoir which mates with a vacuum jacket to form a dewar. Two silver chloride cell plates with the sample spread and finely dispersed between them are held in the center of the toroid by a locking ring. The jacket is equipped with cesium iodide windows. The cell is assembled and loaded in a glove box filled with very dry nitrogen.

Melting Point Determination. The apparatus consisted of a bar of aluminum, with a shallow depression in the top to hold the sample, and a thermocouple inserted into a small hole in the aluminum just beneath the bottom of the depression. The block was cooled to 77°K by immersion in liquid nitrogen and allowed to warm slowly as the nitrogen was removed from the dewar. This apparatus also was used in the glove box.

Results and Discussion

Properties of Products of Radiolysis. Irradiation of the pale yellow mixtures of F_2 and O_2 at 77°K produced a reddish brown solid on the walls of the sapphire tube. Traces of OF_2 (order of magnitude 0.05–0.1 mmole) were found mass spectrometrically (mass peaks corresponding to OF^+ and OF_2^+) in the mixture of unreacted F_2 and O_2 after expansion into the vacuum system.

After the unreacted gases were removed the remaining reddish brown solid was warmed cautiously to its melting point at about 86°K where it became a blood-red liquid, subsequently indentified as a mixture of oxygen fluorides. At the same time a small amount of gas was released (ca. 0.1 mmole, Table I) which was measured volumetrically. Mass spectrometric analysis showed it was largely or completely oxygen. The presence of small amounts of fluorine cannot be excluded since the mass spectrometer is not sensitive to small amounts of this substance.

It is not clear whether this evolved gas was the product of decomposition of an unstable compound such as $\cdot O_4F$ (see later discussion) or whether the gas was entrapped by the solids that were formed during reaction and was released on melting. Both effects may have been involved. It has been observed by Malone and McGee[10] that when equimolar gaseous mixtures of O_2 and F_2 were subjected to an electric discharge in a vessel with walls cooled to 77°K, small amounts of O_2, F_2, and OF_2 were trapped in the solid product that condensed on the walls and were released when the solid

melted near 84°K. On the other hand, in our experiments the release of gas at 86°K occasionally occurred explosively indicating the presence of an oxide unstable at that temperature.

In one experiment with a very low mole ratio of fluorine to oxygen (1:6), a dark brown solid remained after irradiation and removal of oxygen and fluorine at 77°K. The brown solid detonated violently, shattering the sapphire tube, when it was illuminated by a flashlight after momentary removal of the liquid nitrogen bath. The detonation could not have been due to ozone since that substance should largely have been removed under high vacuum at 77°K. It may have been due to the presence of a higher oxide, such as $\cdot O_4F$ or O_6F_2. The latter "compound" has been reported[4] to detonate on illumination and sudden warming at temperatures below 77°K.

In "normal" experiments, the blood red liquid remaining after the release of gas on melting could be frozen to an orange-red solid and remelted repeatedly without further release of gas.

Further experiments were performed on the product from radiolysis of a 3:1 mixture of $F_2:O_2$. The melted red liquid could be distilled in dry nitrogen at atmospheric pressure to a nearby cold surface at 80–85°K to give an orange solid with a melting point of 113°K. Heating the original red liquid to 195°K for 3 hr gave pure oxygen[25] and O_2F_2. The latter is a pale yellow solid which melts sharply to a yellow liquid at 119°K. It can be kept for days in vacuo in stainless steel at 195°K, but decomposes below room temperature to oxygen and fluorine. Previous descriptions of O_2F_2 have characterized it as a red liquid freezing to an orange solid melting around 110°K.[1,13,14] The previously described materials apparently contained appreciable amounts of oxygen fluorides other than O_2F_2.

Information on the composition of the red radiolysis product from the 3:1 mixture was obtained from the total yield of oxygen plus fluorine upon decomposition, and by analysis of the product for oxygen content by dilution with a known quantity of nitrogen followed by mass spectrometric analysis. The $F_2:O_2$ ratio was 0.575, corresponding to a mixture of 74 mole % $(O_2F)_n$ and 26 mole % O_2F_2.

Spectroscopic Observations on the Radiolysis Products. The infrared spectrum of the reddish brown solid isolated after irradiation of a 3:1 mole ratio mixture of $F_2:O_2$ was obtained with the special infrared cell. Transfer of the product from the irradiation tube at 77°K to the sample compartment of the cell at a temperature of 80–90°K was accomplished in a nitrogen drybox by means of a narrow spatula that was cooled to 77°K before touching the sample. During this operation the temperature of the sample rose slightly above its melting point of 86°K; this facilitated spreading of the sample over the AgCl or polyethylene window of the sample compartment. The spectrum of the refrozen sample showed strong absorption bands at 376, 586, and 1517–1523 cm⁻¹ (doublet), weaker bands at 368, 462, 612, and 624 cm⁻¹, and a very weak band at 1306 cm⁻¹. The strong bands can all be attributed to $(O_2F)_n$. Arkell[26] observed bands that he attributed to O_4F_2 at

(23) Quad 200 Mass Spectrometer, Electronic Associates, Inc., Palo Alto, Calif.
(24) K. R. Loos, V. A. Campanile, and C. T. Goetschel, submitted for publication.

(25) Established as 98+ % by dilution with a known quantity of nitrogen and quantitative analysis by mass spectrometry.
(26) A. Arkell, J. Am. Chem. Soc., 87, 4057 (1965).

584 and 1519 cm^{-1}, and Spratley, Turner, and Pimentel[27] observed bands at 376, 586, and 1510 cm^{-1} that they attributed to $(O_2F)_n$. The weaker bands can all be assigned to O_2F_2.[26,27] A detailed study and analysis of the spectrum of purified yellow O_2F_2 has been carried out;[28] the bands attributed to $(O_2F)_n$ are absent, and the bands attributed to O_2F_2 in the crude sample are present together with some additional bands that can also be assigned[28] to O_2F_2. The composition of the original reddish brown solid was calculated from the spectrum on the basis of the assumption that the molar extinction coefficients for the O–F stretching vibrations are equal in $(O_2F)_n$ and O_2F_2 (it is worth remarking that the force constants for the OF stretching vibration are very similar in these two compounds); the result was very close to that obtained from gasometric measurements of decomposition products.

To obtain an electron spin resonance spectrum of the product, we irradiated a 3:1 mixture of F_2 and O_2 in a specially constructed sapphire tube, 1.5 mm i.d. and 70 mm long. The differential esr spectrum was recorded at 77°K after removal of the unreacted gases; a very strong signal was obtained with a G value close to 2.0 and a peak-to-peak separation of 10.7 G. No hyperfine structure was observed because the free radical concentration was very high and exchange narrowing occurred.[29] Hyperfine structure has been observed, however, in the esr spectrum of very dilute solutions of $\cdot O_2F$ by Fessenden and Schuler.[30] After the esr spectrum of the crude product was obtained, the sapphire tube was warmed to 195°K for 3 hr to decompose the higher oxides of fluorine. The sample was refrozen, the product oxygen was pumped away, and the remaining yellow solid O_2F_2 was examined in the esr spectrometer; no signal was observed.

On the Nature of O_3F_2 and O_4F_2. Spectroscopic data clearly show that the radiolysis products of a 3:1 F_2–O_2 mixture consist of $(O_2F)_n$ and O_2F_2. Elemental analysis was consistent with this view. Strong evidence has been obtained by Solomon, et al.,[5] that the substance described as O_3F_2 by Kirshenbaum and Grosse[2] is really an equimolar mixture of $(O_2F)_n$ and O_2F_2.

In our view, the substance that we and others have called $(O_2F)_n$ is best described as an equilibrium mixture of $\cdot O_2F$ and O_4F_2. First, the low melting point of the mixtures of O_2F_2 and $(O_2F)_n$ that we and others have made suggests that $(O_2F)_n$ is a relatively small nonpolar aggregate. Second, Kasai and Kirshenbaum[31] have reported on the esr spectra of dilute solutions of "O_4F_2" (ca. 3 vol %) and "O_3F_2" (ca. 0.3 vol %) in solid CF_3Cl at 77°K; they interpreted the observed signal strengths to imply that their O_4F_2 contained about 5 mole % of $\cdot O_2F$ and their O_3F_2, about 5–10 mole %. An alternative interpretation in terms of an equilibrium dissociation of O_4F_2 (assumed to be diamagnetic) at temperatures between 77°K and the freezing point of CF_3Cl

(92°K) leads to estimated equilibrium constants of ca. 2×10^{-5} for the O_4F_2 in "O_3F_2" and 8×10^{-5} for O_4F_2 itself, in mole fraction units. In view of the approximate nature of the measurements, the use of estimated densities in our calculation, and the uncertainty about the temperature at which equilibrium was frozen in during the freezing of the solutions, the agreement is reasonable. An equilibrium constant of this magnitude implies that in pure O_4F_2 near its melting point only a few mole per cent should be present as $\cdot O_2F$. From data for analogous processes (e.g., dimerization of NO_2), we estimate that the standard entropy change for dissociation of O_4F_2 in the liquid state should be about 15 eu. Then an equilibrium constant of 5×10^{-5} for dissociation at 80–90°K implies a standard enthalpy change of about 3 kcal/mole. This value lies between the coupling energies reported for O_4 (0.16 kcal) and N_2O_4 (13.3 kcal/mole).

Fessenden and Schuler[30] observed that $\cdot O_2F$ at 10^{-3} M in CF_4 was predominantly in the monomeric form at temperatures in the range 93–96°K. This implies an equilibrium constant greater than 10^{-4} and possibly of the order of 10^{-3} in our units. This result can be reconciled with those of Kasai and Kirshenbaum[31] if in the latter's experiments the effective temperature for equilibration between monomer and dimer in the solid solutions was close to 77°K. Such an equilibration in the solid would be consistent with the findings of Arkell[26] and of Spratley, Turner, and Pimentel[27] that $\cdot O_2F$ migrates in solid matrices at temperatures well below 77°K to form O_4F_2; an absorption band at 1496 (Arkell) or 1500 cm^{-1} (Spratley, et al.) attributed to the O–O stretch in $\cdot O_2F$ was replaced by a band at, respectively, 1519 or 1510 ± 2 cm^{-1} attributed to $(O_2F)_n$. These small spectral shifts are consistent with the small value estimated above for the energy of dimerization.

Our own infrared observations on the solid products at 77°K disclosed a doublet at 1517–1523 cm^{-1} but no detectable band in the region 1496–1500 cm^{-1}. These observations are consistent with the argument given above that the equilibrium concentration of $\cdot O_2F$ in O_4F_2 near the melting point is small.

In the light of the discussion given above, we have examined the reported data for the visible and near-ultraviolet absorption spectra for solutions of O_2F_2 and "O_3F_2" by Kirshenbaum and Streng[7] and for solutions of O_4F_2 by Streng and Streng.[32] The results are consistent with the presence of a small amount of O_4F_2 in the sample of O_2F_2 that was studied, and are not grossly inconsistent with the concept that the substance described as O_3F_2 is approximately an equimolar mixture of O_2F_2 and O_4F_2. The quantitative comparison is not entirely satisfactory, however, and there are indications that absorbing species other than those postulated may have been present in the O_4F_2. A possible species is $\cdot O_4F$, whose existence at low temperatures has been suggested by Arkell[26] on the basis of matrix spectroscopy. If weak coupling occurs of O_2 with O_2 and of $\cdot O_2F$ with $\cdot O_2F$, a coupling of O_2 with $\cdot O_2F$ would not be surprising. The existence of $\cdot O_4F$ would be consistent with some of our own observations and with the reported formation of substances with empirical compositions corresponding to O_5F_2 and O_6F_2 (mixtures of $\cdot O_2F$, O_4F_2, $\cdot O_4F$, and O_6F_2).

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Table I. Oxygen Conversion to Fluorine Peroxides by Irradiation[a] of F_2-O_2 Mixtures

Mole ratio $F_2:O_2$	Amount irradiated, mmoles				Yield of $O_2 + F_2$[b] from thermal decompn, mmoles		Oxygen consumed[c]		Oxygen consumed, G value[d]
	F_2	O_2	Ar	N_2	86°K	298°K	mmole	%	
1	14	14			0.13	3.26	1.76-2.30	13-16	17-23
3	21	7			0.09	3.62	2.39[a]	34	22
5	22.8	4.6			0.11	4.08	2.15-2.83	47-62	20-27
7	24.5	3.5			0.14	4.00	2.14-2.81	61-80	20-26
1	10.5	10.5		7.0	e	2.52	1.26-1.68	12-16	13-17
1	10.5	10.5	7.0		0.07	3.44	1.79-2.37	17-23	17-22
3	15.7	5.3	7.0		0.14	3.52	1.90-2.49	36-47	17-23
5	17.5	3.5	7.0		0.11	3.46	1.84-2.41	52-69	17-22
7	18.4	2.6	7.0		0.09	3.42	1.80-2.37	69-91	16-21

[a] 77°K, 100 Mrads, 1 hr. [b] Accurate to ±0.03 mmole. [c] Calculated on the assumption that the gases produced upon warming to 298°K are derived from either O_4F_2 or O_2F_2. In the one datum not quoted as a range, the composition ultimately decomposed to F_2 and O_2 was determined to be 85% O_2F_2 and 15% O_4F_2 or a mixture of other peroxides having a corresponding oxygen content. [d] Molecules of oxygen consumed per 100 eV of absorbed energy. [e] Undetermined due to slight "pop"

A further complication in the visible and ultraviolet dilute solution spectra is imposed by the possible presence of $\cdot O_2F$. The increase reported[7] in the absorption coefficient of impure O_2F_2 at 360 nm when the temperature was raised from 77 to 140°K is consistent with increased dissociation of O_4F_2 to form more strongly absorbing $\cdot O_2F$. The inference can also be drawn, since the spectrum was measurable, that the rate of decomposition of O_4F_2 to form O_2F_2 is much slower in dilute than in concentrated solutions.

Radiolytic Yields and Mechanism. Data on the radiation synthesis of oxygen fluorides in liquid phase are summarized in Table I. Interesting findings are (1) the high value of G for oxygen consumed (molecules consumed per 100 eV of energy absorbed by the mixture) and (2) the independence of this G value from the mole fraction of oxygen in the reactant mixtures. The mole fraction varied from 50 mole % at the start of the experiments with 1:1 $F_2:O_2$ to less than 4 mole % at the end of the experiments with 7:1 $F_2:O_2$. This observation suggests that the major end effect of the high-energy radiation absorbed is to generate fluorine atoms and that these are efficiently scavenged by oxygen; the results obtained in the presence of argon suggest also that energy absorbed by the argon is efficiently utilized by energy transfer, while in the presence of nitrogen there is little energy transfer.

The reaction mechanism thus appears to be similar to that proposed by Spratley, Turner, and Pimentel[27] to describe the photolytic reaction in inert matrices at very low temperatures and by Solomon, et al.,[5b] to describe the gas-phase reaction under electric discharge. Schematically, it can be written as

$$F_2 \xrightarrow{\ \ } 2F\cdot$$
$$F\cdot + O_2 \longrightarrow \cdot O_2F \rightleftharpoons O_4F_2$$
$$F\cdot + \cdot O_2F = O_2F_2$$
$$F\cdot + F\cdot = F_2$$
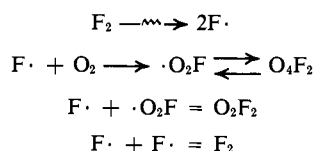
The results of Table I thus imply that the value of G (F·) is about 20; this is several-fold higher than is usually observed for free-radical formation in organic systems, but is comparable to values that have been observed in other halogenated systems such as those containing carbon tetrachloride or chloroform.[33,34] The

(33) A. Chapiro, *J. Phys. Chem.*, **63**, 801 (1959).
(34) M. Magat, L. Bouby, A. Chapiro, and N. Gislon, *Z. Elektrochem.*, **62**, 307 (1958).

proposed mechanism implies that some formation of O_2F_2 will occur in the spurs where the concentration of radicals is momentarily high.

Reactions of Oxygen Fluorides with BF_3. The reaction of BF_3 with O_2F_2 at low temperatures to form O_2^+-BF_4^- was first reported by Solomon, et al.[15,35] The reaction was duplicated in this work with the pure pale yellow O_2F_2. Complete reaction occurred at 147°K in less than 10 min.

The reaction was also studied with the mixture of oxygen fluorides obtained from irradiation of a 3:1 mixture of fluorine and oxygen. Boron trifluoride (3.5 mmoles) was condensed in the top of the sapphire irradiation tube containing the formed oxygen fluorides (ca. 1.7-2.0 mmoles) suspended in the excess fluorine and oxygen. After the boron trifluoride was distilled down to the condensed phase, the contents was further mixed by alternately vaporizing and condensing a portion of the fluorine and oxygen. Then the excess fluorine and oxygen were removed under vacuum at 77°K. When the contents was warmed to 113°K, a small amount of gas was evolved and the color of the oxygen fluorides changed from reddish brown to orange. The gas formed was removed under vacuum. Upon further warming to 143°K, the orange solid changed to a white solid and further slight evolution of gas was observed. Warming this solid to 240°K led to partial decomposition, and the larger quantities of gases evolved (F_2, O_2, and BF_3) were collected and measured. The remaining solid was relatively stable and was identified (see below) as $O_2^+BF_4^-$. Its yield was measured by recovering the solid in a dry nitrogen box and weighing. The yields observed are given in Table II.

According to the mechanism proposed by Keith, Solomon, et al.,[35] and supported by stoichiometric data, the G value for the formation of O_2BF_4 should be equal to that for the conversion of O_2 to a mixture of O_2F_2 and O_4F_2.

$$O_4F_2 \rightleftharpoons 2\cdot O_2F$$
$$BF_3 + \cdot O_2F \longrightarrow O_2BF_4$$
$$BF_3 + O_2F_2 \longrightarrow O_2BF_4 + 0.5F_2$$
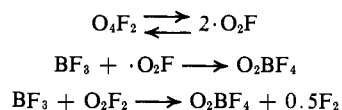
A comparison of the data of Table II with those of Table I (cf. especially experiment no. 6 of Table II) shows that the value of $G(O_2BF_4)$ experimentally ob-

(35) J. N. Keith, I. J. Solomon, I. Sheft, and H. H. Hyman, *Inorg. Chem.*, **7**, 230 (1968).

Table II. Preparation of O_2BF_4[a]

| No.	Mole ratio $F_2:O_2$	Irradiation time, min	mmole (g) liberated at $\sim 240°K$ (± 0.03)	O_2BF_4 produced, mmoles	$G(O_2BF_4)$
1	1.0	15	0.25	0.23	8.9
2	1.0	30	1.11	0.45	8.8
3	1.0	60	0.89	0.81	7.9
4	1.0	180	1.61	1.94	6.3
5	1.0	60[b]	0.57	0.38	14.9
6	2.0	60	0.72	1.09	11.0
7	3.0	60		1.13	10.6
8	3.0	120		1.82	8.6
9	5.0	60		1.07	10.5
10	5.0	180		2.08	6.9
11	7.0	60	1.07	0.95	8.8
12	1/6	60	0.86[c]	0.37	4.1

[a] Total millimoles of $O_2 + F_2$ irradiated, 28 mmoles; 14 mmoles of BF_3 added after irradiation at 100 Mrads/hr unless otherwise stated. [b] Dose rate of 25 Mrads/hr. [c] *Ca.* 3 mmoles of noncondensable gas emitted at *ca.* 133°K. The gas consisted of O_2 and F_2 in a ratio of about 6.

served is only about half that expected. The major reason for this is the loss of active compound by decomposition at 240°K, but the detailed nature of the partial decomposition has not been clarified. Keith, Solomon, *et al.*,[35] observed that some decomposition frequently attended the reaction of BF_3 with O_2F_2 and with O_4F_2, especially if the reaction was not performed at minimum temperature. In our case the BF_3 was mixed with the oxygen fluorides before the reaction, which occurred close to the melting point of BF_3 and 25-30° below its boiling point. The reaction may have been localized close to the surface of the liquid or solid BF_3, and local heating may have been sufficient to decompose some of the O_4F_2. Certainly the reaction with pure O_2F_2 under our conditions was considerably more rapid than that described by Solomon, *et al.*[15,35]

Subject to the uncertainties implied by this apparent partial decomposition, the trends of $G(O_2BF_4)$ shown in Table II imply that the amount of oxygen fluorides formed increases at first linearly with radiation dose but continued irradiation leads to partial decomposition of the oxygen fluorides previously formed (experiments 3 and 4 *vs.* 1 and 2; 8 *vs.* 7; 10 *vs.* 9).

One experiment in which a mixture of 10.5 mmoles of BF_3 (solid), 7 mmoles of O_2, and 21 mmoles of F_2 was irradiated for 120 min in the sapphire reactor led to the recovery of only 0.18 mmole of O_2BF_4, corresponding to a value for $G(O_2BF_4)$ of only 0.8. When the experiment was repeated in a stainless steel stirred reactor, however, in which the fins of the vertically oscillating stirrer were designed to scrape the walls, the yield of O_2BF_4 corresponded to a $G(O_2BF_4)$ of 15 to 20. The reason for the low yield in the unstirred reactor is not known.

The decomposition observed in the solid at 240°K obviously involved at least a small quantity of a less stable compound than O_2BF_4. A reasonable candidate is O_4BF_4, which could conceivably be formed by the reaction

$$\cdot O_4F + BF_3 = O_4{}^+BF_4{}^-$$
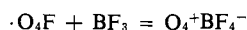
Arguments for the existence of $\cdot O_4F$ were presented above. Also relevant is the evidence[36,37] reported for

the existence of a radical which is believed to be $CF_3O_3\cdot$ but may possibly be $CF_3O_4\cdot$. The decomposition of O_4BF_4 should lead to a ratio of $(O_2 + F_2)/BF_3$ equal to 2.5, whereas that from the decomposition of O_2BF_4 should lead to a ratio of 1.5. This ratio was measured in experiments 1, 2, 4, and 6 and ranged from 2.5 $\pm$ 0.5 to 1.8 $\pm$ 0.1. There was a linear correlation between the value of this ratio and the total volume of gas liberated, the ratio being low when the volume of gas was high. These findings are consistent with the decomposition of an oxygen-rich compound, possibly O_4BF_4, with simultaneous decomposition, induced by the heat of reaction, of neighboring O_2BF_4. The evidence would clearly be more compelling if analyses were available for O_2 and F_2 individually, but we were not prepared to obtain this information at the time the experiments were done.

The decomposition reaction observed in several repeated experiments at 133°K in the solid produced by reaction of BF_3 and the radiolysis product of 1:6 $F_2:O_2$ suggests the existence of a still less stable compound. This decomposition produced noncondensable gases consisting of O_2 and F_2 in a ratio of about 6. We dare to suggest that this may have been $O_6{}^+BF_4{}^-$, produced by the reaction of $\cdot O_6F$ with BF_3; there was presumably simultaneous decomposition of O_4BF_4 and O_2BF_4 induced by the local heat of reaction.

Properties of O_2BF_4. In agreement with the observations reported by Keith, Solomon, *et al.*,[35] and the reaction mechanism suggested by them, we find that O_2BF_4 decomposes only slowly at room temperature in a closed vessel with a dry atmosphere, but decomposes at a measurable rate at 0° under reduced pressure. It hydrolyzes rapidly in moist air to volatile products. We found that it is an extremely active oxidizing agent; small samples (a few milliliters) of benzene or isopropyl alcohol enflamed when a small particle of O_2BF_4 was dropped into the liquid at room temperature. A mixture prepared at 77°K with 0.3 mmole of either methane or ethane detonated when its temperature was raised to 195°K. Surprisingly, on the other hand, when O_2BF_4 was added to liquid cyanogen at 248°K it dissolved with no evidence of reaction; when the solvent was evaporated from the solution a white powder was recovered which appeared to be O_2BF_4 on the basis of thermal decomposition to mass spectrometrically identified O_2, F_2, and BF_3.

The elemental analysis of our preparation of O_2BF_4 was obtained (F and O by neutron activation) as F, 62.6 $\pm$ 1.5 wt %; O, 26.5 $\pm$ 1.5 wt %; B, 8.6 $\pm$ 1.0 wt %; calculated 63.7% F, 26.9% O, 9.2% B. The infrared spectrum of the powder between silver chloride plates exhibits all the characteristic frequencies[38] of the $BF_4{}^-$ ion plus a weak doublet at 1863 and 1865 cm^{-1} which was attributed[24] to the $O_2{}^+$ ion in a site of low symmetry. A strong Raman frequency at 1858-1862 cm^{-1} has been recently observed from O_2AsF_6 and O_2SbF_6 and assigned to $O_2{}^+$ by Shamir, Binenboym, and Claassen.[39] The esr spectrum of the solid is a broad signal centered at $g = 1.94$ with a peak-to-peak separation in the differential mode of about 382 G. Similar

(36) R. W. Fessenden, *J. Chem. Phys.*, **48**, 3725 (1968).
(37) N. Vanderkooi and W. B. Fox, *ibid.*, **47**, 3634 (1967).
(38) N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).
(39) J. Shamir, J. Binenboym, and H. H. Claassen, *J. Am. Chem. Soc.*, **90**, 6223 (1968).

results have been reported by Solomon, *et al.*,[15,35] and attributed to the O_2^+ ion.

As might be expected, the X-ray diffraction pattern of the powder is very similar in both spacings and intensity distribution to that[40] of $NO^+BF_4^-$. We have indexed our pattern on the basis of an orthorhombic unit cell, $8.77 \times 5.58 \times 7.05 \pm 0.01$ Å. Apart from the labeling of the axes, this is similar to the unit cell assigned to $NOBF_4$ by Evans, *et al.*[40] ($8.91 \times 5.68 \times 6.98$ Å). The systematic absences are consistent with the space group P_{nma} which conforms also to the observation of the O_2^+ vibration in infrared absorption. The unit cell and symmetry are very similar to those previously assigned to NH_4BF_4, KBF_4, and other compounds with the $BaSO_4$ structure.[41] Details will be reported elsewhere.

Nomenclature. In this paper we have referred to the compounds O_2F_2 and O_4F_2 as oxygen fluorides, in accordance with the recommendations of one of the referees and with the concurrence of the editor of this

(40) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).
(41) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience Publishers, New York, N. Y., 1965, p 47.

journal. Their recommendations were presumably based on the conviction that, in compounds made up of two elements, the least electronegative element is to be named first. Our originally suggested nomenclature for these two compounds as fluorine peroxide and fluorine superoxide is consistent with the similarity in geometrical structure between H_2O_2 and F_2O_2 and the recent, though controversial, literature suggesting the possible existence of H_2O_3 or H_2O_4 at low temperatures. The fact that the O–O distance in O_2F_2 is close to that prevailing in the cation O_2^+, however, suggests that the accepted name, dioxygenyl difluoride, is appropriate for the compound.

Representative Derivative Chemistry of the 1,6- and 1,10-B₈C₂H₁₀ Carborane System

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Abstract: Basic and acidic hydrolysis degrades $1,6\text{-}B_8C_2H_{10}$ to $B_7C_2H_{12}^-$ ion and boric acid, respectively, but similar conditions do not affect the $1,10\text{-}B_8C_2H_{10}$ isomer. Mono and dilithio derivatives of both isomers have been prepared and subsequent reactions gave C-methyl, C-carboxylic acid, C-amine, and C-halogen derivatives. Chlorination of the $1,10\text{-}B_8C_2H_{10}$ isomer gave perchlorinated products.

The preparation and characterization of the $1,6\text{-}B_8C_2H_{10}$ and $1,10\text{-}B_8C_2H_{10}$ carboranes and their C-monomethyl, C,C'-dimethyl, and C-monophenyl derivatives have been recently reported.[1,2] We now wish to report representative derivative chemistry of these carboranes which illustrates their general reactivities.

Results and Discussion

Of the reactions of 1,6- and $1,10\text{-}B_8C_2H_{10}$ studied to date, few have involved the boron atoms of the carborane cage, but rather the terminal boron and carbon hydrogen atoms. These two known isomers of $B_8C_2H_{10}$ are shown in Figure 1. Two reactions which involve the carborane cage have been described elsewhere.[1] They are the thermal isomerization of $1,6\text{-}B_8C_2H_{10}$ derivatives to their isomeric $1,10\text{-}B_8C_2H_{10}$ counterparts. These rearrangements are nearly quantitative above

(1) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 869 (1968).
(2) P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, in press.

300°. Secondly, the hydroboration of $1,6\text{-}B_8C_2H_{10}$ to $1,7\text{-}B_{10}C_2H_{12}$ (eq 1) has been observed. The third

$$1,6\text{-}B_8C_2H_{10} + B_2H_6 \longrightarrow 1,7\text{-}B_{10}C_2H_{12} \qquad (1)$$
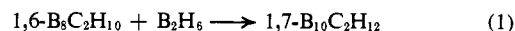
example of cage chemistry is hydrolytic degradation. Hydrolysis of $1,6\text{-}B_8C_2H_{10}$ in basic, aqueous ethanol (eq 2) gives the known[1] $B_7C_2H_{12}^-$ ion in 90% yield.

$$1,6\text{-}B_8C_2H_{10} + OH^- \xrightarrow{H_2O} B_7C_2H_{12}^- + B(OH)_3 \qquad (2)$$
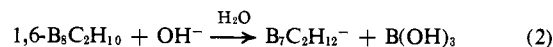
In acidic, aqueous tetrahydrofuran solution $1,6\text{-}B_8C_2H_{10}$ degrades to boric acid. Treatment of $1,6\text{-}B_8C_2H_{10}$ with piperidine in diethyl ether solution at 25° also produces the $B_7C_2H_{12}^-$ ion in 51% isolated yield. However, a large difference between the degradative stabilities of the 1,6- and $1,10\text{-}B_8C_2H_{10}$ isomers exists. Attempted basic and acidic hydrolysis of $1,10\text{-}B_8C_2H_{10}$ under the same conditions employed in the case of the 1,6-isomer degradation afforded recovered starting material in 48 and 70% yields, respectively. Further support of this large difference in the cage stability toward degradation of these two isomers is evidenced by a 53% recovery of starting material when 1,10-