90–95%. $B_2[N(CH_3)_2]_2(S_2C_2H_4)$ is soluble in most organic solvents.

Anal. Calcd for $C_6H_{16}N_2B_2S_2$: C, 35.68; H, 7.99; N, 13.87; B, 10.71; S, 31.75; mol wt, 201.98. Found: C, 35.34; H, 7.98; N, 13.74; B, 10.50; mol wt, 219 (0.040 *m*) and 236 (0.064 *m*) in benzene. Base hydrolysis gave 0.98 mole of hydrogen per mole of $B_2[N(CH_3)_2]_2(S_2C_2H_4)$.

X-Ray powder diffraction pattern data, *d* (relative intensity): 7.69 (m), 6.68 (vs), 6.05 (m), 5.56 (vs), 5.01 (m), 4.18 (s), 4.00 (m), 3.83 (s), 3.58 (vs), 3.36 (vs), 3.17 (m), 2.468 (vw), 2.404 (vw), 2.292 (vw), 2.161 (vw), 2.113 (vw), 1.965 (vw), 1.920 (vw), 1.823 (w).

Infrared spectrum (KBr, cm^{-1}): 3106 (w), 2907 (s), 2786 (m), 1508 (sh), 1495 (m), 1450 (m), 1449 (m), 1404 (m), 1381 (s), 1284 (s), 1266 (s), 1198 (m), 1136 (m), 1110 (s), 1055 (vw), 1012 (m), 993 (m), 897 (s), 801 (vw), 767 (vw), 676 (m), 571 (vw).

8. **$B_2(S_2C_2H_4)_2[NH(CH_3)_2]_2$.**—$B_2[N(CH_3)_2]_4$ (4.3 mmoles) and $HSCH_2CH_2SH$ (9.2 mmoles) were mixed together in a closed system without solvent. The mixture was agitated and allowed to equilibrate at room temperature. Crystals slowly began to form at the interface of the liquid mixture and the glass walls of the reaction vessel. The reaction mixture was allowed to stand overnight, yielding a pinkish solid plus excess $HSCH_2CH_2SH$. Recrystallization of this solid from a benzene–pentane solution afforded a white crystalline product. It is soluble in common organic solvents and appears to be stable with respect to evolution of $NH(CH_3)_2$.

Anal. Calcd for $C_8H_{22}N_2B_2S_4$: C, 32.44; H, 7.49; N, 9.46; B, 7.31; S, 43.31; mol wt, 296.22. Found: C, 32.26; H, 7.33; B, 7.13; mol wt, 285 (0.012 *m*) in benzene. Base hydrolysis gave 0.86 mole of hydrogen per mole of $B_2(S_2C_2H_4)_2\cdot 2NH(CH_3)_2$.

X-Ray powder diffraction pattern data, *d* (relative intensity): 8.93 (m), 7.53 (s), 6.84 (vs), 5.74 (vs), 5.37 (w), 4.98 (m), 4.28 (s), 3.98 (w), 3.65 (m), 3.39 (vw), 3.18 (w), 3.02 (w), 2.931 (m), 2.849 (w), 2.780 (vw), 2.698 (vw), 2.629 (vw), 2.417 (vw), 2.312 (w).

Infrared spectrum (KBr, cm^{-1}): 2994(m), 2915 (s), 2762 (m), 2421 (w), 1464 (s), 1418 (w), 1266 (s), 1222 (sh), 1132 (s), 1106 (m), 1026 (s), 948 (s), 895 (m), 799 (w), 766 (vw), 693 (w), 684 (w).

9. **$B_2[(NCH_3)_2C_2H_4]_2$.**—B_2Cl_4 (5.38 mmoles) and 25 ml of CH_2Cl_2 were distilled into a reaction vessel containing *sym*-dimethylethylenediamine (21.6 mmoles) at −196°. Reaction was allowed to take place over a temperature range of −78 to 25° for 17 hr, resulting in the formation of a white precipitate. After distilling away the CH_2Cl_2, extraction of the residue with benzene followed by pumping away the benzene afforded a white crystalline solid (mp 45–47°). An identical product (shown by X-ray powder diffraction data) was prepared by the transamination of $B_2[N(CH_3)_2]_4$ with *sym*-dimethylethylenediamine; lit. mp 43–44°, bp 85° (5 mm).[2] This compound is soluble in the common organic solvents.

Anal. Calcd for $C_8H_{20}N_4B_2$: C, 49.55; H, 10.40; N, 28.89; B, 11.16; mol wt, 193.92. Found: C, 49.31; H, 10.22; B, 11.02.

X-Ray powder diffraction pattern data, *d* (relative intensity): 8.46 (vs), 7.25 (s), 6.44 (vs), 4.86 (s), 4.37 (s), 4.22 (s), 4.02 (s), 3.83 (m), 3.75 (m), 3.61 (vs), 3.51 (s), 3.38 (m), 3.21 (vw), 2.641 (vw), 2.468 (w), 2.386 (vw), 2.049 (vw), 1.796 (vw).

Infrared spectrum (KBr, cm^{-1}): 2950 (m), 2849 (s), 2809 (s), 2762 (m), 1486 (m), 1470 (w), 1435 (m), 1426 (m), 1397 (sh), 1387 (s), 1264 (s), 1199 (s), 1059 (s), 971 (w), 648 (w), 638 (m), 624 (w), 543 (w), 526 (w), 519 (w).

10. **$B_2[(NH)_2C_6H_4]_2$.**—This compound was prepared by a procedure reported elsewhere through the transamination of $B_2[N(CH_3)_2]_4$ with phenylenediamine in a 1:2 molar ratio.[7,17] This compound showed good thermal and hydrolytic stability. Its low solubility in common organic solvents precluded molecular weight determinations. Attempts to prepare this compound through the reaction of B_2Cl_4 with *o*-phenylenediamine yielded impure material which could not be successfully purified.

Anal. Calcd for $C_{12}H_{12}N_4B_2$: C, 61.63; H, 5.17; N, 23.95; B, 9.25; mol wt, 233.86. Found: C, 61.39; H, 4.96; B, 9.31.

X-Ray powder diffraction pattern data, *d* (relative intensity): 12.03 (vs), 6.61 (m), 6.05 (m), 4.44 (vs), 3.93 (m), 3.78 (w), 3.63 (s), 3.32 (m), 3.17 (m), 3.07 (s), 3.02 (s), 2.826 (w), 2.637 (w), 1.821 (w), 1.726 (vw).

Infrared spectrum (KBr, cm^{-1}): 3425 (w), 3344 (m), 1608 (w), 1592 (m), 1510 (m), 1495 (sh), 1477 (s), 1399 (w), 1319 (s), 1255 (m), 1200 (vw), 1155 (m), 1044 (vw), 922 (w), 909 (w), 758 (m), 746 (s), 738 (m), 661 (m), 631 (m), 575 (w), 479 (m), 469 (vw), 426 (w).

CONTRIBUTION FROM IIT RESEARCH INSTITUTE
CHICAGO, ILLINOIS, AND ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

The Chemistry and Structure of Dioxygenyl Fluoroborate. Fluorine-18 Tracer Studies and Decomposition Kinetics

BY JAMES N. KEITH, IRVINE J. SOLOMON, IRVING SHEFT, AND HERBERT H. HYMAN

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O_2BF_4 has been prepared from the reaction of BF_3 with O_2F_2 or O_4F_2 at low temperatures. Isotopic tracer studies of the reaction indicate that the compound is dioxygenyl fluoroborate, $O_2{}^+BF_4{}^-$, rather than a coordination compound, $FO_2 \rightarrow BF_3$. It is suggested that O_2F is the intermediate in both the preparation and decomposition of O_2BF_4. The kinetic data for the thermal decomposition are consistent with the rate law $dP/dt = k_1K_{eq}{}^2/P_{BF_3}{}^2$. The data are explained in terms of the equilibrium $O_2BF_4(s) = O_2F(g) + BF_3(g)$ and a bimolecular process for decomposition of O_2F. Values for the product $k_1K_{eq}{}^2$ are presented for the range 0–32°, from which the sum $2\Delta H_s + E_a$ is found to be 40 kcal/mole.

Introduction

The existence of the dioxygenyl ion ($O_2{}^+$) in dioxygenyl hexafluoroplatinate[1] and in the salts of the group V fluorides[2] seems well established. The product of the reaction[3] of O_2F_2 with boron trifluoride (BF_3) is dioxygenyl fluoroborate (O_2BF_4).

$$O_2F_2 + BF_3 \longrightarrow O_2BF_4 + {}^1/_2F_2 \qquad (1)$$

There is no evidence to date, however, that O_2BF_4

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(1) N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 5253 (1962).

(2) A. R. Young, II, T. Hirata, and S. I. Morrow, *J. Am. Chem. Soc.*, **86**, 20 (1964).

(3) I. J. Solomon, R. I. Brabets, R. K. Uenishi, J. N. Keith, and J. M. McDonough, *Inorg. Chem.*, **3**, 457 (1964).

TABLE I

ANALYSIS OF PRODUCTS OF O_2F_2–BF_3 REACTIONS

Ratio	Temp,	Vol, cc						Composition, O_xBF_y		Overall
		Formation			Decomposition					ratio
$O_2:F_2$	°C	BF_3	F_2	O_2	BF_3	F_2	O_2	x	y	$O_2:F_2$
0.94	*a*	...	...	...	...	95.5	96.0	...	...	1.01
0.94	−126	71.0	29.0	0.9	71.0	32.0	70.0	2.0	3.90	1.16
0.94	−126	95.5	37.8	<0.1	91.0	45.5	91.5	2.01	4.00	1.09
1.37	−126	125.7	59.9	19.8	124.5	58.6	119.4	1.92	3.94	1.17
1.37	−138	125.3	31.8	<0.1	121.0	53.7	117.2	1.94	3.89	1.37
1.71	−138	98.5	10.4	0.3	96.0	45.5	95.0	1.98	3.95	1.70
1.96	−138	60.3	6.3	<0.1	59.2	27.4	59.1	2.00	3.93	1.75
1.96	−138	62.9	1.4	2.3	58.8	27.5	58.2	1.98	3.94	2.08
1.96[b]	−138	42.1	2.2	0.4	41.1	19.7	38.7	1.88	3.96	1.78
1.96	*a*	...	...	...	...	29.6	59.0	...	...	1.99
								Av 1.96	3.94	

[a] O_xF_2 sample was decomposed for analysis instead of reaction. [b] An attempt was made to eliminate impurities by preparing O_4F_2, decomposing it, and using the noncondensable part of the product for the next experiment.

is structurally related to the above compounds. The infrared spectrum yielded no significant information other than a single, broad absorption in the B–F region (the O–O stretching frequency would not be infrared active). The epr spectrum[3] consisted of a single, broad line centered at $g = 1.97 + 0.10$, indicating a free electron in the vicinity of oxygen, since otherwise one should expect the line to be split by the fluorine.

Dioxygenyl fluoroborate decomposes at a moderate rate at 0°, to give products which are stable gases that can be conveniently handled in the vacuum line

$$O_2BF_4 \longrightarrow O_2 + {}^1/_2F_2 + BF_3 \qquad (2)$$

The reaction is suited therefore for kinetic and F^{18} tracer studies. The present paper reports such experiments, which can be readily explained by the O_2^+-BF_4^- structure.

Experimental Section

Material and Equipment.—F^{18} tracer studies were performed in a metal vacuum line of the type used for work with reactive fluorine compounds. All other experiments were performed in a Pyrex vacuum line, and the stopcocks were greased with Kel F-90 vacuum grease.

Boron trifluoride was purchased from Harshaw Chemical Co. and used without further purification. Oxygen fluorides were prepared by glow discharge reactions of the elements, which had been previously mixed in the desired proportions.[4]

Reaction of Oxygen Fluorides with BF_3.—Oxygen subfluorides[5] were found to react smoothly with excess BF_3 at the following temperatures: O_2F_2, −126°; O_3F_2, −138°; O_4F_2, −138°. At higher temperatures, oxygen was obtained as a by-product, which signified the decomposition of some of the oxygen fluoride. The procedure consisted of simply condensing BF_3 above the oxygen fluoride in the discharge tube or in the separate reactor to which it had been distilled. The reactor was then brought to the appropriate temperature until the color of the oxygen fluoride had disappeared. Fluorine and excess BF_3 were removed at −80° and analyzed; then the O_2BF_4 was decomposed at room temperature and analyzed. Data for these experiments are presented in Table I.

Analytical Procedure.—Gas mixtures were analyzed by passing them through (1) a series of −196° traps to remove condensable gases, (2) a sodium chloride (NaCl) chamber heated to 200° to convert fluorine to chlorine, (3) −196° traps to remove the chlorine, and (4) an automatic Toepler pump to collect the oxygen. All of the components were measured as gases in calibrated volumes; the chlorine was equated to fluorine in the original mixture. Earlier experiments have shown that the amount of silicon tetrafluoride (SiF_4) obtained was not enough to seriously affect the analytical data. Nevertheless the BF_3 was examined in several cases by infrared spectroscopy, and no significant amount of SiF_4 was detected.

F^{18} Tracer Experiments.—BF_3 was labeled with F^{18} by irradiation with fast neutrons.[6] F^{18} decays by positron emission with a half-life of 110 min, and the radiation detected is the annihilation γ rays that result from collision with electrons in the surrounding material. A sodium iodide scintillation crystal, a photomultiplier, and a single-channel analyzer were used to detect the radiation.[6] The scintillation crystal contained a cylindrical well 3.8 cm deep and 1.6 cm in diameter in which a counting tube containing the sample could be inserted. The counting tubes were nickel, about 4 or 5 cm^3 in internal volume. The O_2BF_4 was prepared in a counting tube or in glass or nickel containers of larger volume, as indicated in Table II. The F^{18} content of the samples was sufficiently small that the change from F^{18} to O^{18} on decay would not measurably alter the chemical analysis of the products.

A typical experiment proceeded as follows. A sample of O_2F_2 (about 5 mmoles) was prepared by glow discharge reaction of a 1:1 $O_2:F_2$ mixture and collected in a small transfer tube connected to the bottom of the discharge tube. After the sample was degassed, it was thawed and distilled into a nickel counting tube, using liquid helium to condense the sample. Distillation of O_2F_2 into a dead-end tube can be performed quite easily by using liquid helium, but it is virtually impossible with liquid nitrogen, due to buildup of noncondensable gases from the decomposition of O_2F_2.

Irradiated BF_3 was then measured out and condensed in the same tube, which was closed and allowed to warm to the reaction temperature. After about 1 hr, the tube, in a −80° bath, was opened and gaseous products were removed by using a liquid oxygen trap to condense excess BF_3 and a liquid helium trap to condense oxygen and fluorine. The BF_3 and O_2–F_2 mixtures were collected separately and counted. At the same time the O_2BF_4 remaining in the original tube was counted. After a satisfactory count was established for the O_2BF_4, the tube was opened, the O_2BF_4 was allowed to decompose by expansion into the vacuum line, and gases were collected as above.

The gaseous products were all subjected to radioassay, and analyses for oxygen, fluorine, and BF_3 were performed by the procedure described. Data on the tracer studies are presented in Table II.

Some inconsistencies appear in the data, largely because of the difficulty of obtaining rapid and complete separation and recovery of the products before counting. It is often necessary to

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[4] A. G. Streng, *Chem. Rev.*, **63**, 607 (1963).

[5] Other work has indicated that the compound reported as O_3F_2 is, in reality, an equimolar mixture of O_2F_2 and O_4F_2: I. J. Solomon, J. K. Raney, A. J. Kacmarek, R. G. Maguire, and G. A. Noble, *J. Am. Chem. Soc.*, **89**, 2015 (1967).

[6] I. Sheft, H. Hyman, R. Adams, and J. Katz, *ibid.*, **83**, 291 (1961).

TABLE II

O_2BF_4 TRACER STUDIES

		Quantity (mmoles) and sp activity[a]					
		Formation			Decomposition		
Conditions	BF_3 taken (mmoles) and sp activity[a]	O_2	F_2	BF_3[b]	O_2	F_2	BF_3
O_2F_2, −80°, 4-cc	3.62	2.95	3.99	0.98	2.66	1.38	2.39
Monel reactor	11,900[c]		3130			8500	8600
O_2F_2, −80°, 4-cc	10.23	3.52	4.87	6.33	3.46	1.64	3.25
Monel reactor	15,700[c]		5960	11,700		11,500	12,500
O_2F_2, −126°, 50-cc	5.25	0.04	0.89	2.39	2.07	0.86	1.68
glass reactor	10,500		7200	10,700		11,900	9500
						9880[d]	
O_4F_2, −138°, 100-cc	5.73	0.03	0.02	1.45	3.82	1.68	3.48
glass reactor	13,100		~25,000	12,300		12,600	9900
						10,700[d]	
O_2F_2, −126°, 130-cc	3.80	0.06	0.80	0.40	2.36	1.13	1.57
Monel reactor	*e*		10,100	27,900		16,400	14,100

[a] Second number given is specific activity of fluorine present in BF_3 or in fluorine in counts/min mmole of fluorine atoms. [b] Excess BF_3. [c] Activity calculated from the counting of the O_2BF_4 sample before decomposition. [d] Since the fluorine value is too low in these samples, the specific activities indicated were calculated from the oxygen analyses. [e] Reference sample lost because of leakage.

sacrifice the material balance in order to obtain the BF_3 fraction free of fluorine and *vice versa*, so that an accurate count can be obtained. In the third and fourth experiments, the fluorine analysis was thought to be too low because of inefficient trapping of the chlorine in this step of the analysis (evidenced by the appearance of scum in the Toepler pump). When these fluorine values were replaced by numbers calculated from the oxygen analyses, the activities obtained were in good agreement with other data.

In a single exploratory experiment, $O_2B^{10}F_4$ was treated in a small counting tube with $BF^{18}{}_3$ at room temperature. Although experimental errors prevented useful comparison of the rates of boron and fluorine exchange, substantial boron exchange did occur, as evidenced by mass spectroscopic analysis.

Kinetic Studies.—O_2BF_4 decomposes at a moderate rate at 0°, and since all of the products are gases, the rate of decomposition is directly proportional to the rate of increase in total pressure, which was conveniently measured with a 0–760-mm Monel Helicoid gauge or a Pyrex sickle gauge (used as a null indicator). The results obtained with the two gauges were in substantial agreement.

O_2BF_4 was prepared in a small reactor, of 50–100-cc volume, attached directly to the pressure gauge. After the excess gases had been removed at −80°, the reactor was thawed to the desired temperature, and pressure readings were taken. When gases were added at the beginning of the reaction, only the end of the tube containing the solid was held at −80° while the gas was admitted to minimize the error in the initial pressure. Upon thawing, the pressure rose rapidly for about 10–15 sec. The initial pressure was taken when this first rapid increase ceased.

Discussion

Since O_2BF_4 had been prepared only from O_2F_2, the reaction of BF_3 with the less stable O_4F_2 was of considerable interest. O_3F_2 was not studied, since nmr data[5] had indicated that the compound reported as O_3F_2 is really a mixture of O_2F_2 and O_4F_2. Mixtures of the oxygen fluorides prepared from intermediate compositions behaved as mixtures of O_2F_2 and O_4F_2.

O_2F_2 and BF_3 reacted smoothly at −126°; about 1 hr was required for completion of the reaction. Mixtures containing O_4F_2 liberated oxygen as well as fluorine at this temperature, but at −138°, little oxygen was produced. The reaction of O_4F_2 with BF_3 at −138° is surprisingly smooth and rapid; it is complete in about 15 min, and the product shows little evidence of decomposition. The data indicate the following stoichiometry for the reactions

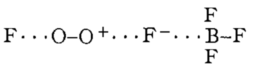
$$O_2F_2 + BF_3 \longrightarrow O_2BF_4 + {}^1/_2F_2 \qquad (1)$$

$$ {}^1/_2O_4F_2 + BF_3 \longrightarrow O_2BF_4 \qquad (3)$$

Two simple explanations for the relative apparent rates of the two reactions can be advanced. Judging by the reported vapor pressures[4] of O_3F_2 and O_2F_2, we think that the vapor pressure of O_4F_2 should be considerably greater than that of O_2F_2, compensating, in part, for the lower BF_3 pressure at −138°. Further, the production of gaseous fluorine as a by-product of the O_2F_2–BF_3 reaction will hinder diffusion in this reaction, but this is not a factor in the reaction with O_4F_2.

However, it is probable that the different rates signify different mechanisms for the two reactions. Thus, the reaction with O_4F_2 probably occurs *via* O_2F, which is known to be present in the liquid phase and may be the major species in the vapor. This simple addition reaction should require very little activation energy.

No such simple mechanism can be proposed for the O_2F_2 reaction; whether the reaction occurs by preliminary dissociation to $O_2F + F$ or by a concerted mechanism *via* an intermediate such as I, the result would probably be a slower reaction than the reaction of O_4F_2.



$$F\cdots O\text{–}O^{+}\cdots F^{-}\cdots \overset{F}{\underset{F}{B}}\text{–}F$$

I

The two most likely structures for O_2BF_4 are the coordination compound II and dioxygenyl fluoroborate (III), which could be distinguished by means of radioactive tracer techniques.

$(O_2F)\rightarrow BF_3$	$O_2{}^+BF_4{}^-$
II	III

Structure II signifies either the oxygen-bonded structure $FOOBF_3$, or the fluorine-bridged structure

$OOFBF_3$, in which one fluorine atom is different from the other three. These structures would be indistinguishable by means of tracer studies, but either would give different results than structure III. Thus, if O_2BF_4 is prepared from BF_3 labeled with F^{18}, the fluorine atoms of structure III would be equivalent but those of structure II would not. If no exchange occurs during formation and decomposition of this compound, the fluorine of decomposition would be found to contain natural fluorine if the structure is II and to contain labeled F^{18} if it is III.

It is conceivable that the fluorine-bridged structure could undergo rearrangement to $O_2^+BF_4^-$ during decomposition, resulting in exchange at this step. It seems far more reasonable, however, to assume that $OOFBF_3$ is an intermediate in the formation and decomposition of $O_2^+BF_4^-$.

The results of the exchange experiments are interpreted in terms of structure III. Thus, when the O_2BF_4 was decomposed for analysis, complete exchange of the F^{18} was found. The partial exchange that occurred with the fluorine in the formation reaction cannot be due to exchange of fluorine molecules with BF_3^*, since this reaction does not occur even at ambient temperatures.

We have found exchange, however, between BF_3^* and fluorine atoms produced by ultraviolet radiation. This exchange would probably not go to completion because of the competition of the recombination reaction and the exchange reaction. Both of these reactions must be very rapid and under the experimental conditions may well have comparable rates. The variation in the extent of this exchange among the different experiments may be due to differences in temperature, partial pressure of BF_3, and the geometry of the containers.

Although the consistency of the individual experiments leaves much to be desired, the data are consistent with the mechanism

$$O_2F_2 \longrightarrow O_2F + F\cdot \tag{4}$$

$$F\cdot + F\cdot \longrightarrow F_2 \tag{5}$$

$$F\cdot + BF_3^* \longrightarrow F\cdot^* + BF_3 \tag{6}$$

$$O_2F + BF_3^* \longrightarrow O_2BF_4^* \tag{7}$$

It should be mentioned that these data are also consistent with a slightly different mechanism involving the initial formation of a coordination compound

$$O_2F_2 + BF_3 \longrightarrow F_2O_2{\rightarrow}BF_3 \tag{8}$$

$$F_2O_2{\rightarrow}BF_3 \longrightarrow O_2BF_4 + F\cdot \tag{9}$$

However, since no evidence has been obtained for the existence of such a coordination compound, the former mechanism seems adequate. The observed exchange might conceivably result from the exchange of fluorine atoms with BF_3 during decomposition by a process such as

$$FO_2{\rightarrow}BF_3^* \longrightarrow O_2F + BF_3^* \tag{10}$$

$$O_2F \longrightarrow O_2 + F\cdot \tag{11}$$

followed by recombination and exchange (eq 5 and 6). However, the fluorine obtained from such a process would have undergone only limited exchange, probably even less than in the formation reaction, since the partial pressure of BF_3 was lower. Since complete exchange was observed in these products, this mechanism is not believed sufficient to account for the results.

One of the first properties of O_2BF_4 that attracted attention was that its rate of decomposition seemed to diminish with time in a closed vessel. Thus, samples that would decompose completely in a matter of a few hours in a dynamic vacuum would be only partially decomposed in a sealed tube after several weeks. It was further noted that BF_3 seemed to suppress decomposition when added in excess. To explore the reason for this behavior and to obtain data on the stability of O_2BF_4, a series of kinetic experiments was undertaken.

O_2BF_4 decomposes smoothly at a moderate rate between 0 and 32°, and a graph of the cube of the total pressure *vs.* time is linear. The data are presented in Table III. In run 4, BF_3 was added to the sample at the beginning of the experiment. The effect of this BF_3 in suppressing the decomposition of O_2BF_4 is shown graphically in Figure 1.

TABLE III

DECOMPOSITION OF O_2BF_4

Run no.	Temp, °C	t, min	P_{obsd}, mm	P_{calcd}, mm
1	0	0	0	0
		1	5	10
		3	10	14
		15	25	25
		30	32	31
		55	38	38
2	0	0	0	0
		5	17	18
		10	23	23
		15	27	26
		45	38	38
3	0	0	0	0
		2	10	11
		5	19	17
		12	23	22
		17	27	25
		30	30	30
		60	36	38
4	0	0	35	34
		40	38	38
		55	40	40
		155	48	49
		240	58	56
5	10.2	0	0	0
		1.0	29	31
		2.0	38	39
		3.0	46	45
		4.0	50	49
		5.0	54	53
		10.0	67	67
6	17.8	0	0	0
		0.5	30	22
		1.0	48	48
		1.5	58	59
		2.0	65	67
		3.0	77	79
		4.0	87	89
		5.0	95	96
		8.0	114	114
		10.0	124	123
7	22.5	0	0	0
		0.5	69	75
		1.0	95	95
		2.0	120	119
		3.0	141	137
		5.0	170	162
		11.0	209	211
8	32.0	0	0	0
		0.5	125	135
		1.5	165	171
		2.5	203	195
		4.0	230	223
		5.0	245	233
		8.0	275	275
		10.0	289	295

By starting with the most obvious inference from the latter experiment, we can easily construct a mechanism for the decomposition by assuming the equilibrium

$$O_2BF_4(s) \rightleftharpoons O_2F(g) + BF_3(g) \tag{12}$$

That such an equilibrium exists has been demonstrated by the boron exchange of $BF^{18}{}_3$ with $O_2B^{10}F_4$ at room temperature. It is also consistent with the ease of formation of O_2BF_4 from O_4F_2 and BF_3. Assuming that undissociated O_2BF_4 is stable under the experimental conditions, decomposition must occur *via* the

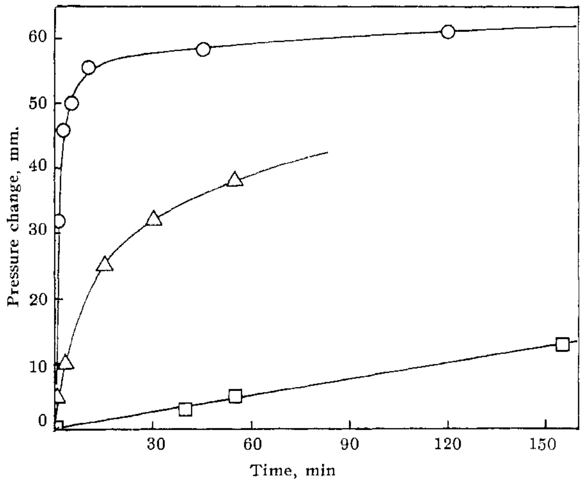


Figure 1.—Decomposition of O_2BF_4 at 0°: ○, O_2BF_4 + O_2, P^0 = 424 mm; △, O_2BF_4, P^0 = 0; □, O_2BF_4 + BF_3, P^0 = 35 mm.

unstable gaseous species O_2F. If $O_2F(g)$ decomposes by a bimolecular process then

$$O_2F + O_2F \xrightarrow{k_1} 2O_2 + F_2 \qquad (13)$$

Since the work is done in a constant-volume apparatus, the rate of disappearance of O_2BF_4 can be represented as

$$\frac{dP_{BF_3}}{dt} = k_1P_{O_2F}{}^2 \qquad (14)$$

P_{O_2F} can be obtained from the equilibrium expression for eq 12. Upon substitution in eq 14

$$\frac{dP_{BF_3}}{dt} = \frac{k_1K_{eq}{}^2}{P_{BF_3}{}^2} \qquad (15)$$

By integrating, we obtain

$$P_{BF_3}{}^3 - P^0{}_{BF_3}{}^3 = 3k_1K_{eq}{}^2t \qquad (16)$$

In terms of the experimental values this becomes

$$\frac{8}{125}\left(P_T + \frac{3}{2}P^0{}_{BF_3}\right)^3 - P^0{}_{BF_3}{}^3 = 3k_1K_{eq}{}^2t \qquad (17)$$

The product of constants, $k_1K_{eq}{}^2$, can be obtained from the slope of the graph of $(P_T + {}^3/_2P^0{}_{BF_3})^3$ *vs.* t. The values for the product obtained in these experiments are listed in Table IV.

Table IV

Kinetic Data for Decomposition of O_2BF_4

Temp, °C	$10^{12}k_1K_{eq}{}^2$, mole³ l.⁻³ sec⁻¹ Obsd	Calcd
0	0.074	0.155
0	0.090	0.155
0	0.067	0.155
0	0.187	0.155
10.2	1.93	1.95
17.8	11.6	11.0
22.5	48	30
32.0	138	220

An Arrhenius plot yields, for the sum of the activation energy and the overall heat of sublimation (actually $E_a + 2\Delta H_s$), a value of 40 kcal/mole.

The effect of O_2 and F_2 was not considered in the above treatment. Although some effect may be observed at high pressures, the success of the proposed mechanism in representing the data indicates that the influence of these gases is not large. The failure of attempts to prepared O_2BF_4 by high-pressure methods[7] would seem to argue against a very pronounced influence in this case. In an exploratory experiment at 0°, oxygen was added to a sample of O_2BF_4 at an initial pressure of 424 mm. The decomposition curve, shown in Figure 1, indicates that there is no strong dependence of the rate on oxygen pressure, aside from small effects such as a slightly greater apparent rate at the beginning of the experiment, and a flattening of the curve after about 10 min. These effects are probably due to initial temperature variation and poor diffusion, respectively.

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(7) J. B. Beal, Jr., and C. Pupp, Seventh Quarterly Technical Summary, Ozark-Mahoning Company, April 1–June 30, 1965, under Contract AF 04-(611) 9556.