

532. Diboron Tetrafluoride. Part I. Its Decomposition, and its Reactions with Oxygen and Nitric Oxide.

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Diboron tetrafluoride decomposes slowly at room temperature, giving boron trifluoride and a solid polymer $(BF)_n$, and attacks glass slightly to give silicon tetrafluoride and oxygen difluoride; it dissolves in boric oxide and is then stabilised. Reaction with oxygen yields boron trifluoride and a stable solid $(B_2O_3F)_n$; nitric oxide reacts in a mainly 2 : 1 ratio, giving nitrous oxide, nitrogen, and boron trifluoride.

PREVIOUS studies^{1,2} of diboron tetrafluoride have shown it to be more stable than the tetrachloride, but like the latter it readily adds simple donor molecules (*e.g.*, trimethylamine) in a 2 : 1 ratio; unsaturated hydrocarbons similarly add to it in, generally, a 1 : 1 ratio, although more slowly than to the tetrachloride. We report here some observations on the stability of diboron tetrafluoride and its reactions with oxygen and nitric oxide, both of which react readily with the tetrachloride.^{3,4}

Experimental.—Diboron tetrafluoride was prepared by reaction of the tetrachloride with antimony trifluoride;¹ the product after fractionation had v. p. 18.5 mm. at -78° and molecular weight 98.4, and 1.00 mmole reacted with 0.96 mmole of ethylene. Other starting materials were prepared, and the reactions studied, by methods similar to those previously described;^{4,5} quantities used were usually of the order of 1 mmole in each reaction. Analyses for boron and fluorine in residues were made as previously described,⁶ by prolonged alkaline hydrolysis in presence of calcium chloride.

RESULTS AND DISCUSSION

Silicon tetrafluoride appeared as a minor volatile product whenever diboron tetrafluoride was prepared, kept, or allowed to react in glass vessels. Another fraction, volatile at -120° , was often formed in very small amounts under the same conditions; a little of this also appeared when boron trifluoride was heated with boron monoxide in an unsuccessful attempt to prepare diboron tetrafluoride, and similar small amounts almost invariably appeared in the tetrafluoride–nitric oxide reactions. Qualitative analysis of the fraction indicated presence of fluorine and some boron, but quantitative analysis by hydrolysis gave unsatisfactory results with the small amounts available. In the infrared spectrum two broad bands, centred at 930 and 826 cm^{-1} , and a sharp peak at 1268 cm^{-1} were always observed; an absorption at $\sim 1103 \text{ cm}^{-1}$ varied considerably in intensity and breadth from sample to sample. The 930 and 826 cm^{-1} bands were very similar to those observed for oxygen difluoride;⁷ the weak band at 1740 cm^{-1} expected for this substance would not be detectable at the pressure attainable with the samples in our work. Oxygen difluoride is volatile at -120° and molecular-weight determinations on four samples gave values 50, 50, 52, and 41 ($OF_2 = 54$) which suggested the presence of this substance as a major constituent of the fraction. The presence of boron and the additional bands in the spectrum could not be explained by postulating the presence of known boron–fluorine (–oxygen) compounds of high volatility and reasonably low molecular weight, *e.g.*, boron trifluoride or trifluoroboroxine; but a substance of “BOF” type might well be formed in the reaction of BF radicals (see below) with oxygen-containing substances.⁸

¹ Finch and Schlesinger, *J. Amer. Chem. Soc.*, 1958, **80**, 3573.

² Ceron, Finch, Frey, Kerrigan, Parsons, Urry, and Schlesinger, *J. Amer. Chem. Soc.*, 1959, **81**, 6368.

³ Apple and Wartik, *J. Amer. Chem. Soc.*, 1958, **80**, 6153.

⁴ Holliday and Massey, *J. Inorg. Nuclear Chem.*, 1961, **18**, 108.

⁵ Holliday and Massey, *J.*, 1960, 43.

⁶ Grimley and Holliday, *J.*, 1954, 1215.

⁷ Jones, Kirby-Smith, Woltz, and Nielsen, *J. Chem. Phys.*, 1951, **19**, 337.

⁸ Cf. Fisher, Lehmann, and Shapiro, *J. Phys. Chem.*, 1961, **65**, 1166.

The reactions of diboron tetrafluoride with oxygen and nitric oxide were carried out at or below room temperature, because the rate of decomposition of the tetrafluoride is appreciable at higher temperatures (see below). Both reactions produced boric oxide, and this was found to retain considerable amounts of apparently unreactive diboron tetrafluoride at the low temperatures used. In an experiment to determine the extent of retention, the tetrafluoride was allowed to remain in contact with boric oxide, prepared by controlled, rigorous dehydration of boric acid, for 5 days at room temperature. 52% of the tetrafluoride was recovered as volatile material, with boron trifluoride produced by decomposition of the tetrafluoride and equivalent to 10% of the latter. Hence 38% of the tetrafluoride was retained, and the 10% decomposition in 5 days was much less than for the tetrafluoride alone. Hydrolysis of the residue produced a vigorous evolution of hydrogen, but the amounts of this, and of fluoride ion in the hydrolysate, were much less than expected.

The decomposition of diboron tetrafluoride is reported¹ to be slow at ordinary temperatures, and to give boron trifluoride and a non-volatile solid. We have confirmed these observations; the amount of decomposition at room temperatures to give the trifluoride was 8.2% after 27 hr. and 21% after 96 hr. Complete decomposition was found after 96 hr. at 140°, with a 99% yield of boron trifluoride as required by the equation $n\text{B}_2\text{F}_4 \rightarrow n\text{BF}_3 + (\text{BF})_n$. The solid residue consisted of a small amount of white solid deposited over the cooler part of the reaction vessel, and a brown solid at the bottom; the white solid was sparingly soluble in benzene, the brown solid insoluble. Further heating of the solid residue to 230° gave some silicon tetrafluoride and a small amount of the oxygen difluoride fraction. The $(\text{BF})_n$ residue did not react with oxygen at ordinary temperatures. Even after prolonged alkaline hydrolysis, the yield of hydrogen was only 10% of the theoretical, and fluoride recovery was low and variable.

Reaction with Oxygen.—We have confirmed the observation⁹ that diboron tetrafluoride reacts explosively with oxygen at ordinary temperatures. After mixing at -196° , warming to above -140° produced immediate inflammation, and only by keeping the reaction mixture at -140° for some time, and then slowly warming, could inflammation be avoided. With or without inflammation, the reaction deposited a mixture of brown and white solids and boron trifluoride was the only major volatile product. The results are shown in Table 1 (units are mmoles).

TABLE 1.

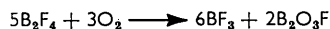
Expt.	B_2F_4 reacted	O_2		BF_3 produced	Reaction ratios	
		added	reacted		$\text{B}_2\text{F}_4/\text{O}_2$	$\text{BF}_3/\text{B}_2\text{F}_4$
1 *	1.03	1.59	0.63	1.25	1.64	1.21
2	1.46	1.75	0.85	1.67	1.72	1.14
3 *	1.30	1.22	0.76	1.62	1.71	1.24
4	1.67	2.67	0.96	2.01	1.74	1.20
5 *	2.30	1.43	1.43	2.76	1.61	1.20
6 *	2.90	2.46	1.45	2.85	2.00	0.95
7 *	3.98	2.77	1.55	4.01	2.56	1.00

* Reaction mixture inflamed.

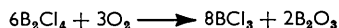
In the reactions involving inflammation, the residues yielded no hydrogen on hydrolysis and the volatile products contained small amounts of the oxygen difluoride fraction; the non-inflaming reactions gave no oxygen difluoride and the residues yielded a trace of hydrogen on hydrolysis. This suggests that, on inflammation, a small amount of $(\text{BF})_n$ (or B_2F_4) may have reacted with the residue or with the glass to form the oxygen difluoride. In experiments 6 and 7, where larger amounts of the tetrafluoride and relatively small amounts of oxygen were mixed, it is possible that some diboron tetrafluoride escaped reaction, being retained in the residue in unreactive form. But in the other experiments the material balance shows that the residues contained a relatively large amount of fluorine;

⁹ Trefonas and Lipscomb, *J. Chem. Phys.*, 1958, **28**, 54.

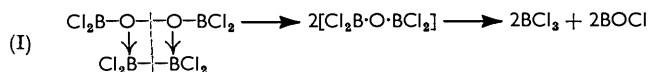
alkaline hydrolysis gave 90% recovery of this as fluoride and quantitative recovery of the boron. The very low or zero hydrogen evolution on hydrolysis, and this ready recovery of fluorine, seem to preclude presence of unchanged tetrafluoride or of $(BF)_n$ in amounts sufficient to account for all the fluorine. Experiments to ascertain the form in which the bulk of the fluorine was retained were not conclusive; in one, the residue was heated to 90° but yielded no volatile products, which seemed to preclude the presence of boron trifluoride. In another, the residue was heated at 145° with boron for 10 hr., but yielded very small amounts of silicon tetrafluoride, oxygen difluoride, and boron trifluoride—insufficient to account for all the fluorine present. Heating with white phosphorus gave only a trace of phosphorus trifluoride. The composition of the residue in experiments 1–5 corresponded closely to B_2O_3F , and the reaction ratios of Table 1 suggest the reaction



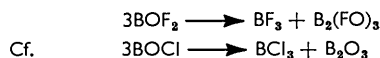
This can be compared with the corresponding reaction for the tetrachloride, *viz.*:



In this reaction, the 2 : 1 reaction ratio has been explained⁴ in terms of addition of oxygen across the boron–boron bond followed by co-ordination of another molecule of the tetrachloride and fission of the O–O bond (I). If, with the tetrafluoride, this second molecule



did not add on, the OB_2F_2 moiety produced by O–O bond fission might decompose in an analogous manner to $BOCl$ thus:



and the overall reaction would then be



The solid product " B_2O_3F " shows a considerable resemblance to the white solid $B_2(NO)_3$, produced ultimately by the diboron tetrachloride–nitric oxide reaction;⁴ the nitrogen in this solid was as intractable as the fluorine in " B_2O_3F " and no way could be found of removing it from the solid in volatile form. If " B_2O_3F " is in fact a mixture of boric oxide and $B_2(FO)_3$, then the observed $5B_2F_4 : 3O_2$ reaction ratio may be due to two reactions, a 2 : 1 reaction, analogous to the diboron tetrachloride case, predominating, and a minor 1 : 1 reaction producing some $B_2(FO)_3$. Until some method of studying solids of this $B_2O_3X_n$ type can be devised, the above explanation must remain largely speculative.

Reaction with Nitric Oxide.—As with oxygen, mixing of the tetrafluoride and nitric oxide at -196° was quiet, but warming produced inflammation in most cases, and again boron trifluoride was a major volatile product. An excess of nitric oxide was usually present and this formed the unstable red adduct $BF_3 \cdot NO$;¹⁰ it was therefore necessary to warm the mixture to -78° to release nitric oxide retained in this form, and $B_2F_4 : NO$ reaction ratios could not be determined at very low temperatures. When the reaction mixture was formed at -196° , the colour was red, changing to pink on warming and then to green if inflammation did not occur, and finally to white, as solid. These colour changes are similar to those observed for the reaction of diboron tetrachloride and nitric oxide, where boron trichloride was the only volatile product; but, here, nitrous oxide was formed as well as boron trifluoride, and from mixtures which inflamed some nitrogen was also produced. The results of twelve experiments are shown in Table 2 (units are mmoles).

The wide range of reaction times and temperatures (used in attempts to discover optimum non-inflaming conditions) did not greatly affect the course of the reaction as the

¹⁰ Findley, *J. Chem. Educ.*, 1947, **24**, 149.

Table shows, but the absence of gaseous nitrogen in the non-inflaming runs is to be noted. An excess of nitric oxide was avoided in experiments 9 and 10 and these mixtures did not inflame or produce any nitrogen. Each BF_3 value in Table 2 represents the amount

TABLE 2.

Expt.	Reaction		B_2F_4 added	NO used	Products				Effective reaction ratios (B_2F_4) = 1			
	time	temp.			N_2	N_2O	BF_3	NO	B_2O_3	BF_3	$\text{N}_2\text{O} + \text{N}_2$	
1	7 days,	-78°	1.08	1.50	0.00	0.59	1.13	1.75	0.35	0.81	0.87	
2*	5 mins.,	20°	1.18	0.92	0.14	0.33	1.32	1.64	0.37	1.25	0.84	
3*	45 mins.,	-78°										
	+15 mins.,	20°	1.18	1.17	0.13	0.31	1.32	1.65	0.41	1.14	0.82	
4*	7 days,	-78°										
	+24 hr.,	-33°	1.05	1.24	0.12	0.49	1.33	1.59	0.32	1.36	0.79	
5*	5 days,	-78°										
	+24 hr.,	-33°	1.04	1.21	0.04	0.49	1.16	1.95	0.40	1.20	0.97	
6*	5 sec.,	-78°	1.12	1.06	0.15	0.30	1.31	1.54	0.36	1.28	0.75	
7*	8 days,	-78°	1.00	1.07	0.07	0.39	1.21	1.81	0.42	1.36	0.81	
8	1 day,	-78°										
	+2 hr.,	20°	1.04	1.26	0.00	0.46	0.60	2.20	0.47	1.05	1.11	
9	7 days,	-78°	1.37	0.73	0.00	0.19	1.53	0.77	0.19	1.61	0.39	
10	7 days,	-78°	1.12	0.59	0.00	0.17	1.02	0.91	0.22	1.57	0.40	
11*	6 days,	-78°	3.25	3.65	0.17	1.41	3.83	2.60	0.29	1.42	1.30	
Mean reaction ratios (excluding 9 and 10)								1.88	0.37	1.21	0.91	
$3\text{B}_2\text{F}_4 + 6\text{NO} \longrightarrow 4\text{BF}_3 + 3\text{N}_2\text{O} + \text{B}_2\text{O}_3$								2.00	0.33	1.33	1.00	
$6\text{B}_2\text{F}_4 + 6\text{NO} \longrightarrow 8\text{BF}_3 + 3\text{N}_2 + 2\text{B}_2\text{O}_3$								1.00	0.33	1.33	0.50	

* Reaction mixture inflamed.

recovered immediately after reaction together with that obtained on subsequent warming to room temperature in those experiments where the reaction temperature was below 20° . Recovery of nitrogen as nitrous oxide or nitrogen gas was about 80% for the non-inflaming, and about 90% for the inflaming, reactions; but the material balance indicated retention of considerable amounts of fluorine in the residues. Analysis of these, after removal of boron trifluoride at room temperature, gave reasonable results for boron but (in contrast to the oxygen reaction residues) fluoride recovery was very low. The small amount of residual nitrogen was not detectable as nitrate or nitrite, and reduction of the hydrolysate gave only a trace of ammonia. Tests for presence of the adduct $\text{BF}_3 \cdot \text{N}_2\text{O}_4$ in the residue were negative. In experiment 8, the residue was heated to 170° ; slow release of boron trifluoride occurred, with no other volatile products. These facts and the data of Table 2 suggest that the residue was mostly boric oxide, in which was retained some nitrogen [possibly as $\text{B}_2(\text{NO})_3$] and some unchanged diboron tetrafluoride in the non-inflaming runs, and that on inflammation most of the nitrogen was released as N_2 and the diboron tetrafluoride decomposed to give boron trifluoride and residual $(\text{BF})_n$. In the few non-inflaming reactions, the composition of the residues was rather variable, but corresponded on the average to $\text{B}_2\text{O}_3 + x\text{B}_2\text{O}_3 + y\text{N}_2$, with $x = \sim 2$ and $y \leq 0.5$. From the inflaming mixtures the composition was less variable, and corresponded to $\text{B}_2\text{O}_3 + 2\text{BF} + y\text{N}_2$ ($y \leq 0.1$). These compositions indicate substantial amounts of unchanged tetrafluoride, and so effective reaction ratios were calculated by (1) subtracting from " B_2F_4 used" a value for unchanged B_2F_4 calculated in each case from the residual fluorine (as B_2F_4 in the non-inflaming runs and as BF in the inflaming runs), (2) assuming the remaining residual boron to be present as boric oxide, and (3) correcting the BF_3 values for the inflaming mixtures by subtracting the amount of trifluoride formed from the residual tetrafluoride. These effective reaction ratios, relative to $\text{B}_2\text{F}_4 = 1$, are given on the right of Table 2. The mean effective reaction ratios for reactions involving an excess of nitric oxide are also given in the Table, and these can be accounted for in terms of the two reactions shown at the foot of Table 2; the predominant reaction is clearly the 2 : 1, producing nitrous oxide, and the 1 : 1 reaction to give nitrogen is of minor importance. The products of the latter

reaction could equally be written as $8\text{BF}_3 + 2\text{B}_2(\text{NO})_3$ to account for retained nitrogen; this reaction then corresponds to the diboron tetrachloride-nitric oxide reaction. It is possible that the inflammation in these reactions, which could not be avoided in most experiments, was initiated by a strongly exothermic change of the kind observed in the B_2Cl_4 -NO reactions, but occurring here at a much lower temperature.

The predominating 2:1 addition of nitric oxide to diboron tetrafluoride, with no evidence of intermediate adduct formation, is in contrast to the strictly 1:1 addition to diboron tetrachloride, where an unstable adduct could be observed. It suggests that "π-donation" ⁴ to the tetrafluoride is less easy than ordinary donation of two nitric oxide molecules, one to each boron, although the resulting 2:1 adduct is too unstable to be detectable. This weaker acceptor behaviour towards π-donation may be correlated with the less ready addition of olefins to the tetrafluoride than to the tetrachloride. In the oxygen reactions, the tetrachloride can readily act as acceptor to the $\text{Cl}_2\text{B-O-O-BCl}_2$ intermediate and so give an overall $\text{B}_2\text{Cl}_4 : \text{O}_2$ reaction ratio of 2:1; the lower ratio in the case of the tetrafluoride may be due to less effective acceptance of the intermediate $\text{F}_2\text{B-O-O-BF}_2$ by a second B_2F_4 molecule.

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