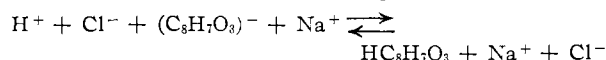


tinues up to the addition of 2.3 moles of sodium mandelate due to the reversible nature of the equilibrium.



The correctness of this interpretation was demonstrated by the titration of an equivalent amount of hydrochloric acid with sodium mandelate (curve 2, Fig. 6); a maximum in the curve occurs in the same region (2.4 moles of sodium mandelate).

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LUCKNOW, INDIA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## Diboron Tetrafluoride

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The preparation and properties of the new compound, diboron tetrafluoride,  $\text{B}_2\text{F}_4$ , are described.

The preparation of diboron tetrachloride,  $\text{B}_2\text{Cl}_4$ , was accomplished by passing boron trichloride through an electric discharge between mercury electrodes.<sup>1,2</sup> The corresponding treatment of boron trifluoride leaves the latter unchanged. We have, however, succeeded in preparing the tetrafluoride in excellent yield and purity by treating diboron tetrachloride with antimony trifluoride, as will be described below.

In contrast to diboron tetrachloride, which undergoes partial slow decomposition at  $0^\circ$ , the corresponding tetrafluoride suffers very little if any change at room temperature. A sample of it heated at  $100^\circ$  for 20 minutes liberated a trace of what appeared to be boron trifluoride but underwent no other noticeable change; even at  $200^\circ$  only about 40% of the compound was lost by decomposition in several hours. The products were boron trifluoride and a yellow, non-volatile solid not further investigated. The tetrafluoride is considerably more volatile than the tetrachloride, but its melting point is higher.

The chemical behavior of the tetrafluoride closely resembles that of the tetrachloride, as is illustrated in the experimental part by its hydrolysis and by its reactions with diethyl ether and with trimethylamine. Its reactions with ethylene, with butene-2 and with acetylene also follow the pattern of the reactions of tetrachloride; description of this aspect of its behavior will be included in a subsequent paper covering the behavior of both the tetrachloride and the tetrafluoride in this respect. It is of interest in this connection to mention that the tetrafluoride exerts a more decided catalytic effect on the polymerization of the unsaturated compounds than does the tetrachloride.

### Experimental

**Materials and Procedure.**—The preparation and purification of diboron tetrachloride were as described in the earlier paper<sup>2</sup> already referred to, which also described the methods employed for the purification of the diethyl ether and trimethylamine. Antimony trifluoride was a commercial sample sublimed into the reaction vessel by electrically

heating an evacuated tube containing the sample. Standard type vacuum lines<sup>3</sup> equipped with mercury float valves were used throughout.

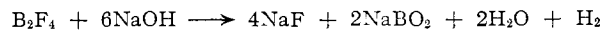
**Preparation of Diboron Tetrafluoride.**—Diboron tetrachloride was transferred by distillation into a reaction vessel containing freshly sublimed antimony trifluoride. After the mixture had stood overnight at  $-80^\circ$ , the volatile portion of the mixture was transferred to a storage bulb (or U-tube) attached to the line. The reaction vessel, which was designed to make this possible without exposure to air, was then charged with a fresh supply of antimony trifluoride, and the volatile material previously removed from the reaction vessel was returned to it. After the mixture had once more stood at  $-80^\circ$  for several hours, the volatile material was once more removed and was fractionated. By this procedure 2.23 mmoles of the tetrafluoride was obtained from 2.86 mmoles of the tetrachloride, a yield of 78%. The purity of the product is shown by the sharpness of its melting point, by its molecular weight and by its analysis as is described below.

Although good yields were obtained at  $-80^\circ$ , the preparation may be accelerated by raising the temperature to  $-45^\circ$  after the mixture had stood for some length of time at  $-80^\circ$ . On the other hand, when the second treatment of the volatile material with antimony trifluoride was omitted, the yield was poor and the purity unsatisfactory.

**Physical Properties and Analysis of Diboron Tetrafluoride.**—Three determinations of the melting point gave the values:  $-55.4$ ,  $-56.2$  and  $-56.4$ , average  $-56.0$ . Temperatures were measured with a liquid ammonia vapor tension thermometer.<sup>3</sup> A Stock melting point apparatus was used.<sup>3</sup>

A 0.1004-g. sample of the compound exerted a pressure of 304.7 mm. at  $27.5^\circ$  in a volume of 63.7 cc. The corresponding molecular weight is 97.0 (calcd. for  $\text{B}_2\text{F}_4$  is 97.6).

For the analysis, a 0.894 mmole sample of the compound was heated with an excess of chloride-free sodium hydroxide solution (15%) for two hours at from  $60$  to  $80^\circ$  in the vacuum line, producing 538.1 cc. of hydrogen at  $24^\circ$  and 30.7 mm. This quantity represents 0.891 mmole, in excellent agreement with the 0.894 mmole demanded by the equation



A fluorine determination by the thorium nitrate method showed that the 0.894 mmole sample contained 3.55 mmoles of fluoride and an only insignificant amount of chloride. The theoretical fluorine content for 0.894 mmole of  $\text{B}_2\text{F}_4$  is 3.57 mmoles.

The following data were obtained for the vapor tensions of the solid and of the liquid diboron tetrafluoride. The values in the last row were calculated from the equation  $\log_{10} p_{(\text{mm.})} = 10.82 - 1856/T$ . For the calculated values of the vapor tension of the liquid the equation  $\log_{10} p_{(\text{mm.})} = 9.009 - 1466/T$  was used. The equation leads to the values

(3) See, for example, R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(1) Thomas Wartik, R. E. Moore and H. I. Schlesinger, THIS JOURNAL, **71**, 3265 (1949).

(2) Grant Urry, Thomas Wartik, R. E. Moore and H. I. Schlesinger, *ibid.*, **76**, 5293 (1954).

TABLE I

VAPOR TENSIONS OF SOLID DIBORON TETRAFLUORIDE						
<i>t</i> , °C.	-95.3	-80.6	-80.1	-74.8	-70.3	-63.7
<i>p</i> obsd. (mm.)	2.5	14.6	15.0	30.0	49.0	87.5
<i>p</i> calcd. (mm.)	2.45	15.3	16.2	29.2	47.1	91.3

TABLE II

VAPOR TENSIONS OF LIQUID DIBORON TETRAFLUORIDE					
<i>t</i> , °C.	-54.8	-50.5	-48.9	-39.4	-35.0
<i>p</i> obsd. (mm.)	196.7	271.0	299.7	547.0	715.4
<i>p</i> calcd. (mm.)	198.1	266.7	297.3	549.4	715.5

of  $-34^\circ$  for the normal boiling point, of about 6700 cal./mole for the heat of evaporation and to about 28 for the Trouton constant. The high value for the constant and the small liquid range ( $-56$  to  $-34^\circ$ ) are not unusual for fluorine compounds.

Attention is called to the fact that when a sample of the compound was allowed to stand at  $-80^\circ$  its vapor tension rose from 15 to 18 mm. in 30 minutes and to 20 mm. in another half hour. However, no detectable weight loss accompanied the increase in vapor tension. Leaving the sample at  $110^\circ$  for 20 minutes again raised the vapor tension from 15 to 18 mm. The more volatile material formed was boron trifluoride as shown by its vapor tension at  $-126^\circ$  (66 instead of 67.6 mm.). The small rise in vapor tension may have been due to slow escape of adsorbed boron trifluoride.

**The Reaction of Diboron Tetrafluoride with Diethyl Ether.**—A mixture of 0.413 mmole of diboron tetrafluoride and 1.422 mmoles of diethyl ether was allowed to warm from  $-80^\circ$  to room temperature. After about 12 hours material volatile at  $-45^\circ$  was removed and shown to consist of 0.61 mmoles of ether (identified by its 186 mm. vapor tension at  $0^\circ$ ). Hence the residue contained 0.81 mmole of ether and 0.414 mmole of the tetrafluoride, *i.e.*, had the composition of a dietherate. It appeared to be stable at  $-23^\circ$ , but at  $0^\circ$  an additional 0.41 mmole of ether was removed by pumping. The molar ratio  $\text{Et}_2\text{O}/\text{B}_2\text{F}_4$  of the remainder thus was 0.40/0.41. This mono-etherate is a crystalline, non-volatile solid at  $0^\circ$ . On standing overnight at this temperature it gave off a volatile product having a vapor tension of 52.2 mm., at  $-78^\circ$ , at which temperature ethyl fluoride has a vapor tension of 53.3 mm.;<sup>4</sup> the identity of the volatile material was further confirmed by a rough vapor density determination carried out with a very small sample. The value thus found for the molecular weight was 50 (calculated for ethyl fluoride is 48).

It is thus seen that the behavior of diboron tetrafluoride toward diethyl ether is identical with that of diboron tetrachloride.

**The Compound  $[\text{B}_2\text{F}_4 \cdot 2\text{N}(\text{CH}_3)_3]_4$ .**—A mixture of 4.53 mmoles of trimethylamine and 0.91 mole of  $\text{B}_2\text{F}_4$  was allowed to warm from  $-80^\circ$  to room temperature over a period of 8 hours. The only volatile material remaining was 2.71 mmoles of unchanged trimethylamine; hence 1.82 mmoles of the latter had reacted with 0.92 mmole of the tetrafluoride, a molar ratio  $\text{B}_2\text{F}_4/\text{N}(\text{CH}_3)_3 = 1.98$ . In a second experiment the value 1.96 was obtained for the ratio. The dark grey product sublimes at about  $-80^\circ$  to form white crystals.

(4) Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(According to the equation given below, the vapor tension of the compound at this temperature is about 2 mm.)

For the boron analysis a tube containing 0.2120 g. of a sublimed sample of the solid was broken under the surface of an aqueous solution of sodium hydroxide in a silver dish. In the resulting solution boron was determined in the usual way. For the fluorine determination another sample (0.1977 g.) was hydrolyzed in a Pyrex flask. Hydrogen was evolved but not measured, the fluorine content was determined by the thorium nitrate method. Percentages of boron and of fluorine found were 10.4 and 34.9, respectively; the values corresponding to the formula  $[\text{B}_2\text{F}_4 \cdot 2\text{N}(\text{CH}_3)_3]_z$  are 9.6 and 35.3%.

The solid compound gave these vapor tension data:

TABLE III

VAPOR TENSIONS OF $[\text{B}_2\text{F}_4 \cdot 2\text{N}(\text{CH}_3)_3]_4$							
<i>t</i> , °C.	108.3	111.9	117.9	126.1	104.2*	97.8*	93.4*
<i>p</i> obsd. (mm.)	9.85	11.90	15.50	24.50	7.96	5.51	4.27
<i>p</i> calcd. (mm.)	9.84	12.02	16.46	24.72	7.85	5.56	4.29

The data marked by an asterisk were obtained as the temperature fell. The calculated values are derived from the equation  $\log_{10} p(\text{mm.}) = 9.915 - 3400/T$ , according to which the heat of sublimation is 15,550 cal./mole.

Two experiments were carried out to determine the molecular weight of the compound by the vapor tension lowering method. In one of these a hexane solution containing 0.3983 g. of the compound in 2.9877 g. of solvent gave the data

<i>t</i> , °C.	26.9	28.2	30.0
V.t. of solvent (mm.)	166.38	176.61	190.81
V.t. lowering (mm.)	2.18	2.21	2.21
Mol. wt. (calcd.)	854	893	891 (av. 879)

In the second experiment a benzene solution containing 0.0171 g. of the compound in 0.0886 g. of solvent was used with the results

<i>t</i> , °C.	31.3	39.7	45.1
V.t. of solvent	128.7	183.8	228.4
V.t. lowering	2.32	3.0	3.78
Mol. wt. (calcd.)	805	886	879 (av. 857)

The average of all 6 values is 868 corresponding closely to the theoretical value (863) and a tetramer  $[\text{B}_2\text{F}_4 \cdot 2\text{N}(\text{CH}_3)_3]_4$ .<sup>5</sup> It will be recalled that the corresponding adduct of diboron tetrachloride and trimethylamine also is a tetramer.<sup>5</sup>

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(5) Since we have no explanation of the fact that in each experiment the first value is lower than the second and third, we have used all the values in calculating the average. In this connection it should be mentioned that in another determination a very concentrated benzene solution was used to secure as large a vapor tension lowering as possible. In this case the calculated molecular weight was close to that of the trimer. We have not included this result because we assume it to have been due to deviations from the laws of perfect solutions.