CXXX.—*The Parachor and Chemical Constitution. Part IX. Boron Compounds.*

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MOST of the atomic parachors so far studied are those of elements in Groups IV to VII of the periodic table. The parachor of boron is therefore of special interest since its value will show whether atomic parachors, like atomic volumes in the solid state, pass through a minimum value at carbon. For this reason we have measured the surface tension and density of methyl and ethyl borates; the parachors obtained from these data are recorded in Table I together with that of boron trichloride calculated from the recent measurements of Mills and Robinson (J., 1927, 1823). The column headed $\Sigma[P]$ gives the sum of the atomic constants except

TABLE I.

	[*P*] obs.	Σ [*P*].	Boron.
Methyl borate	243·7	228·3	15·4
Ethyl borate	363·1	345·3	17·8
Boron trichloride	178·8	162·9	15·9
		Mean	16·4

that of boron, which is obtained by subtracting Σ[*P*] from [*P*] obs. The three values obtained are in satisfactory agreement in view of the fact that they are found from the difference of two much larger quantities, any errors of measurement being magnified considerably.

The mean value, 16·4, shows clearly that atomic parachors pass through a sharp minimum at carbon. An approximate value for lithium is given by the measurements of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1), and it is hoped shortly to complete this series by measurements on compounds of beryllium.

Li.	Be.	B.	C.	O.	F.
ca. 50	—	16·4	4·8	20·0	25·7

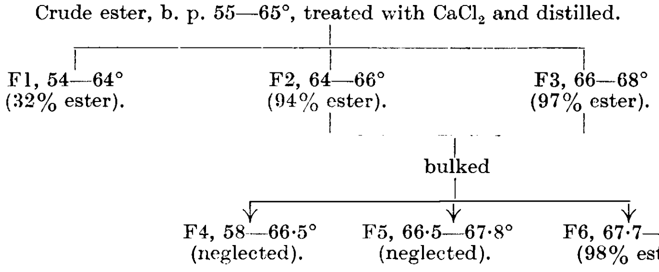
In the course of this work it was found that methyl alcohol and methyl borate form a mixture of maximum vapour pressure which boils at 55° and contains 30% of the ester.

EXPERIMENTAL.

The chief methods which have been employed for the preparation of boric esters are : (i) the action of boron trichloride on the alcohol (Ebelman and Bouquet, *Annalen*, 1846, **60**, 251); (ii) the action of boric anhydride on the alcohol under pressure (Schiff, *Annalen*, 1867, Suppl. 5, 158; Copaux, *Compt. rend.*, 1898, **127**, 719); (iii) the distillation of anhydrous borax with the alkyl potassium sulphate (Rose, J., 1856, 574; Frankland, *Annalen*, 1862, **124**, 132); (iv) the action of the alcohol on the mixed anhydride of boric and acetic acids (Pictet and Geleznov, *Ber.*, 1900, **33**, 2221). The fourth method is recommended by Beilstein, but we made several unsuccessful attempts to prepare the esters in this way. The crude product of the action of methyl alcohol on the mixed anhydride was found to be a ternary mixture of methyl alcohol, b. p. 65°, methyl borate, b. p. 69°, and methyl acetate, b. p. 57°, from which we were unable to obtain the pure ester by repeated fractionation. The separation was complicated by the occurrence of the constant-boiling mixture of methyl alcohol and methyl borate described below. The method is also of little value for the preparation of the ethyl ester, b. p. 117°, which cannot be separated by distillation from the acetic acid, b. p. 118°, set free when the ester is formed. Pictet and Geleznov do not mention these difficulties and it is probable that the methyl and ethyl esters which they describe were not pure substances.

The method by which the pure esters were finally obtained was a modification of that of Schiff and Copaux (*locc. cit.*). At first excess of boric anhydride was used, but this appeared to give a product (probably metaboric ester) which decomposed during distillation.

Methyl borate. 70 G. (1 mol.) of boric anhydride and 100 g. (3 mols. + 5%) of methyl alcohol, dried over aluminium amalgam, were placed in a pressure bottle which was closed and shaken vigorously to prevent caking of the anhydride. The bottle was heated at 120° in an oil-bath for 12 hours, and the contents on distillation gave a 68% yield of crude ester, b. p. 55—65°. The crude product was then fractionated and the fractions were analysed by decomposing a weighed amount with water and titrating the liberated boric acid with alkali in the presence of glycerol, bromophenol-blue being used as indicator. The crude ester contained 70% of Me_3BO_3; it was placed over freshly ignited calcium chloride for 24 hours to remove some methyl alcohol and then fractionated through a 2-foot column filled with glass beads. It soon became evident that methyl alcohol and the borate form a mixture of constant boiling point and maximum vapour pressure. This was isolated and found to contain only 30% of the ester and to boil at 55°. Small amounts of the alcohol can therefore be separated from the ester by distillation. The course of the separation is shown by the scheme below.



Further fractionation with separation of small fractions of lower boiling point gave the following figures: F7, b. p. 68·2—68·7°, 99% ester: F8, b. p. 68·5—68·7°, 99·4% ester; F9, b. p. 68·6—68·7°, 99·6% ester; and F10, b. p. 68·7°/765 mm., 99·9% ester. The physical constants given in the literature for this ester vary considerably:

Boiling point.	Density at 0°.
72° (Ebelman).	0·940 (Schiff).
65° (Schiff).	0·919 (Gasselin).
55—56° (Gasselin).	0·955 (Ebelman).
68·7°/765 mm. (present authors).	0·9547 (present authors).

It is evident that Gasselin's product was the constant-boiling mixture and not the pure ester.

Ethyl borate. This substance was prepared in a similar manner and was more easily purified. The crude ester was obtained in 76% yield, and fractionated after treatment with calcium chloride. A constant-boiling mixture was not observed, and a few distillations gave a product, b. p. 117·2°/740 mm., which was found to contain 99·9% ester. The constants quoted in the literature for this ester are in much better agreement:

Boiling point.	Density at 0°.
120° (Schiff).	0·887 (Schiff).
119·5° (Copaux).	0·886 (Ghira).
117·2°/740 mm. (present authors).	0·8864 (present authors).

The surface tensions of these esters were measured by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). As the esters are very readily hydrolysed, a long tube coated internally with phosphoric oxide was used to dry the air entering the bubbler. The density of the liquid, D, was determined in sealed tubes by means of carefully calibrated floats. The vapour density, d, was calculated by the method described in an earlier paper (J., 1925, **127**, 1540). The parachor was obtained by the formula $P = M\gamma^{1/4}/(D - d)$, where M is the molecular weight and γ the surface tension in dynes/cm.

Methyl borate, $C_3H_9O_3B$, $M = 104{\cdot}0$. Densities determined: $D_{4^\circ}^{24{\cdot}3^\circ}$ 0·9205; $D_{4^\circ}^{40{\cdot}2^\circ}$ 0·8981; whence $D_{4^\circ}^{t^\circ} = 0{\cdot}9547—0{\cdot}00141t$.

t	15°	33·5°	52°	
γ	22·66	20·50	18·00	
$D - d$	0·9330	0·9062	0·8792	
Parachor	243·2	244·2	243·6	Mean 243·7

Ethyl borate, $C_6H_{15}O_3B$, $M = 146{\cdot}0$. Densities determined: $D_{4^\circ}^{10^\circ}$ 0·8746; $D_{4^\circ}^{28^\circ}$ 0·8546; $D_{4^\circ}^{52^\circ}$ 0·8264; whence $D_{4^\circ}^{t^\circ} = 0{\cdot}8864 - 0{\cdot}00115t$.

t	15°	35·5°	50°	64°	
γ	21·80	19·52	18·02	16·60	
$D - d$	0·8691	0·8452	0·8282	0·8118	
Parachor	363·1	363·0	363·2	363·1	Mean 363·1

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