Summary

1. The upper and lower limits of the low pressure thermal explosion of hydrogen–oxygen mixtures were measured between 480 and 540° in a potassium chloride-coated Pyrex vessel over the range 0.04–0.9 mole fraction of hydrogen.

2. The effect of nitrogen on the explosion limits was investigated.

3. A kinetic expression (equation 6) represents our experimental results for both limits. It requires that: (a) branching of reaction chains involves a collision of a chain carrier, x_1, with an oxygen molecule: $x_1 + O_2 \longrightarrow x_2 + x_3 + \ldots$; $E = 24{,}200$ calories. (b) Breaking of reaction chains at the wall depends upon a diffusion of the chains to the wall. Apparent $E = 13{,}500$ calories. (c) Breaking of reaction chains in the gas phase occurs by a triple collision: $x + O_2 + M$, the products of which are incapable of continuing the chain. $E < 4000$ calories.

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Preparation and Purification of Methyl Borate and Ethyl Borate[1]

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Schiff[2] prepared ethyl borate by digesting boric oxide with absolute alcohol for twenty-four hours in a copper digestor at a temperature slightly below 120°.

Etridge and Sugden,[3] after testing various methods that had been described in the literature for the preparation of these borates, selected as the most suitable procedure the heating of boric oxide with the proper alcohol, methyl or ethyl, in a pressure bottle at 120° for twelve hours.

Experimental

Since the methods used for preparing and purifying these two compounds were quite similar, only that for methyl borate will be described in detail.

Methyl Borate.—When boric oxide is added to anhydrous methyl alcohol and the flask is gently shaken, a violent reaction takes place in a few seconds.

The following procedure makes possible the control of the speed of the reaction and avoids the use of a pressure bottle or digestor such as were employed in the two methods cited above. It has the further advantage of shortening the time of preparation and increasing the yield.

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[2] Schiff, *Ann.*, Suppl., **5**, 158 (1867).

[3] Etridge and Sugden, *J. Chem. Soc.*, 989 (1928).

Boric acid, spectroscopically free from impurities, except minute traces of magnesium and sodium, was fused in platinum and the resulting boric oxide was quickly cooled and powdered and was then kept in a desiccator over phosphorus pentoxide until used.

A three-necked flask, Fig. 1, the necks of which terminate in normal, ground, slip-joints, is equipped as follows. A rubber stopper inserted in A carries a glass reservoir R, for the boric oxide. The lower end of the reservoir is flared and ground and can be closed by drawing the glass ball-valve up against it. The aluminum wire stirrer E is used to break up any lumps that may form near the exit from the reservoir.

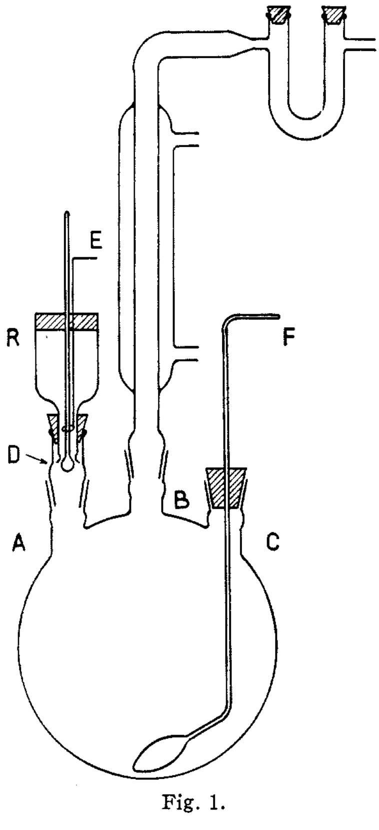

Fig. 1.

In the neck B is inserted a condenser to the upper end of which is fused a U-tube filled with calcium chloride. A rubber stopper inserted into C carries a bent glass rod by means of which the contents of the flask can be stirred.

In the preparation of methyl borate, 75 g. of finely powdered boric oxide is placed in R, the ball-valve being of course closed; 320 cc. of absolute methyl alcohol is run into the large flask through B, and the condenser is inserted. By slightly lowering the ball-valve D from time to time, boric oxide can be dropped into the alcohol at any desired rate, and the progress of the exothermic reaction can readily be controlled. As the boric oxide is added, the alcohol is stirred by turning the rod F forward and backward.

The boric oxide should be added rapidly enough to keep the mixture hot, but not so fast that the liquid is caused to boil.

The addition of the 75 g. of the oxide takes about ten minutes. The reaction mixture is allowed to cool, whereupon white snow-like crystals of boric acid separate.

The cloudy liquid is decanted off and is distilled with a Johnson column.[4] The above amounts yielded 175 cc. of an azeotropic mixture of methyl borate and methyl alcohol. This was freed from the alcohol by treatment of the liquid with cold, concentrated sulfuric acid.[5] The bottom layer was discarded, and the treatment with sulfuric acid was twice repeated. The methyl borate was then fractionally distilled with the Johnson column[4] and by further fractionation in the vacuum distillation chain[6] there was finally obtained a homogeneous sample with the use of which the vapor tension of methyl borate at temperatures from -27 and $+70°$ was determined by the differential manometer method of Laubengayer and Corey.[6] The results are expressed by the equation $\log P = -1785.3 \times 1/T + 8.1073$. The boiling point calculated from this equation is 68.5°, which differs only 0.25° from the value, 68.75°, obtained by distillation of the liquid.

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(4) Dennis and Johnson, THIS JOURNAL, **45**, 1380 (1923).

(5) Schiff, *Ann.*, Suppl., **5**, 160 (1867); Seaman and Johnson, THIS JOURNAL, **53**, 713 (1931).

(6) Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

The melting point of methyl borate, determined by the "drop-ring" method,[7] was found to be −29.3 ± 0.1°, a result that differs appreciably from the only value[8] given in the literature, −34°.

The yield of pure methyl borate by this method was 42% of the theoretical.

Ethyl Borate.—In general the same procedure as was used in the preparation of methyl borate was employed for the production of ethyl borate from absolute ethyl alcohol and boric oxide. The boiling point of the ethyl compound is, however, so high (about 120°) that the fractionation column was shortened and the jacket-tube around the Hempel column was exhausted of air.

After the resulting liquid was shaken with cold concentrated sulfuric acid, it was fractionally distilled. The fourth fraction came over at 117–118° and this, on further fractionation, yielded ethyl borate of b. p. 118.3–118.4° at 740.5 mm. After this fourth fraction had passed over, the temperature rose suddenly to 150°, the liquid turning dark brown. To carry on the distillation satisfactorily, it was necessary to heat the glycerin bath to from 125 to 150°, and this elevated temperature doubtless accelerated the decomposition of the product. Another factor that caused loss of ethyl borate is its appreciable solubility in sulfuric acid. The yield of ethyl borate under the above conditions was 31% of the theoretical.

The relation between the vapor tension and the temperature for ethyl borate up to about 65° is that expressed by the equation (1) $\log P = -2298.0 \times 1/T + 8.8553$. The boiling point at 760 mm. calculated from this equation is 111.8°. Above 65°, deviations due to decomposition occur, which account for the higher boiling points reported by other investigators. Since the material that has once been heated much above 65° will subsequently show a greater vapor tension at temperatures below 65°, it is evident that decomposition occurs during distillation at atmospheric pressure and that it is impossible in this manner to obtain the material in a state of high purity. By further fractionation in the chain, however, the impurities can be removed and the original vapor tension can again be obtained. Repeated distillations at low pressures of this purified material were carried out in the fractionation chain and complete distillation occurred in every case, thus showing that no appreciable decomposition occurs at room temperature.

Duplicate determinations by the drop ring method gave identical results of −84.8° as the melting point of ethyl borate.

Summary

Methods for the preparation and purification of methyl borate and ethyl borate are here described, and redeterminations of the melting points and boiling points of the two compounds are given. It is shown that ethyl borate undergoes partial decomposition when heated above 65°, and that for the preparation of this substance in highly pure condition, it is necessary to fractionate it at low pressures and at temperatures well below 65°.

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[7] Dennis, Corey and Moore, THIS JOURNAL, **46**, 666 (1924).

[8] Timmermans and Mattaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).