401. *The Hydrolysis of Magnesium Boride.*

By RAMES C. RAY and PRAFULLA C. SINHA.

IT is well known that when magnesium boride is hydrolysed by dilute acids, small quantities of boron hydrides are evolved together with a large volume of free hydrogen, but when it is hydrolysed by water, scarcely any hydrides are produced. In the latter case, the action takes place with the evolution of a considerable amount of heat and the liberation of hydrogen, but no boric acid or magnesium borate is formed. The aqueous extract, however, contains a small quantity of boron as hydroxy-hydrides.

The present investigation was undertaken in order to find out the mechanism of the hydrolysis under both conditions. It has already been shown (*J. Indian Chem. Soc.*, 1924, **1**, 125) that the main product of aqueous hydrolysis is a substance $Mg_3B_2(OH)_6$. The experiments now described show that the same product is also formed in the hydrolysis by dilute acids at or above 0°, but below $-$ 10° an entirely different *product* is obtained of the composition $H_3B_2(MgOH)_3$.

The magnesium boride for these experiments was prepared by rapidly heating an intimate mixture of 1 part of boron trioxide (finely powdered and passed through a 120-mesh sieve) and 2·2 parts of magnesium powder in a current of hydrogen to red-heat in a crucible lined with magnesia. Careful attention should be paid to temperature, for if this becomes too high, decomposition to crystalline boron and free magnesium occurs; on the other hand, if the temperature is too low, much amorphous boron is produced. Only those preparations which were almost completely soluble in hydrochloric acid and did not contain any free boron, but consisted mainly of magnesium boride and oxide, were employed in these experiments.

The hydrolysis was carried out in the following manner. A wide-mouthed bottle was provided with a tightly fitting rubber stopper, through which passed a mercury-sealed glass stirrer, an outlet tube, and a wide glass tube. The last was connected to a small flask containing the boride. A mixture of 500 c.c. of absolute alcohol and 50 c.c. of hydrochloric acid of the required concentration was introduced into the bottle, which was then fitted with the stopper and immersed in ice, so that the reaction took place at about 0°. Air was removed from the apparatus by a current of hydrogen, freed from oxygen by passage through alkaline pyrogallol, the mixture of acid and alcohol was then vigorously agitated by means of a mechanical stirrer, and the magnesium boride was added slowly and regularly during about 20 mins., scarcely any boron hydrides being evolved. The reaction was allowed to proceed for a further 20 mins., with continuous stirring, otherwise some magnesium boride remained undecomposed. After the reaction was complete, the hydrogen was removed by a rapid stream of carbon dioxide, and the resulting white mass was quickly collected on an Allihn's filter, as far as possible in absence of air, and dried in a vacuum over solid sodium hydroxide.

In all the experiments in which the amount of hydrochloric acid present was in excess of that required to dissolve the whole of the magnesium oxide present with the boride, the product of hydrolysis was of constant composition. It was analysed as follows. A weighed quantity was dissolved in a small amount of concentrated nitric acid, and the solution heated in a sealed bulb for ½ hr. on a water-bath; the contents of the bulb were then washed out and divided into two equal parts. From one part the boric acid was removed by repeated evaporation with a mixture of hydrochloric acid and methyl alcohol, and the remaining magnesium was estimated by precipitation with ammonium phosphate. The other portion was evaporated to dryness in a vacuum at the ordinary temperature, the residue washed into a platinum crucible containing a weighed quantity of lime, and the whole was ignited. The increase in the weight of the lime gave the weight of magnesium oxide and boron trioxide [Found : Mg, 36·5, 35·9, 36·2; B, 10·9, 11·6, 11·3. Calc. for $Mg_3B_2(OH)_6$: Mg, 36·7; B, 11·2%]. It was proved that when an aqueous solution of boric acid, even if acidified, is evaporated slowly at the ordinary temperature in a vacuum desiccator over solid sodium hydroxide, little loss of boric acid takes place.

When the amount of hydrochloric acid in the alcoholic mixture was not sufficient to dissolve all the magnesium oxide in the crude boride, the product which separated was grey, and contained also undecomposed magnesium boride.

The product of hydrolysis was a white powder, completely insoluble in and inactive towards both cold and hot water. It did not possess any reducing property. In a few cases, however, when the temperature of the reaction fell below 0°, the product showed a powerful reducing action, but the reducing substance was not present in sufficient amount to be isolated.

With a view to separate this substance, some experiments were carried out at lower temperatures. If, however, the temperature was in the neighbourhood of — 10°, an identical procedure afforded an entirely different product [Found : Mg, 50·1, 48·9, 49·1; B, 13·9, 14·7, 14·7. $H_3B_2(Mg{\cdot}OH)_3$ requires Mg, 48·65; B, 14·85%]. The *substance* was colourless and very unstable; it reacted with water at the ordinary temperature, being converted into $Mg_3B_2(OH)_6$ with liberation of hydrogen, and it reduced both iodine and permanganate solutions. The reducing power was determined by adding a measured volume of a standard iodine solution to a weighed quantity of the substance in a stoppered bottle, the same volume of iodine solution being kept in a similar stoppered bottle. Both bottles were kept in the dark for 24 hours, with occasional shaking. The iodine contents were then determined, and from the difference the reducing power of the substance was calculated. Similar determinations were also made with a standard potassium permanganate solution acidified with dilute sulphuric acid. The mean results were : 1 g. of substance = 677 c.c. of *N*/10-iodine solution or 828 c.c. of *N*/10-potassium permanganate. If the boron is oxidised to trioxide, then 1 g. of substance should require 822·8 c.c. of *N*/10-iodine or permanganate, but if it is oxidised only to B_2O_2, then 1 g. should reduce 675·7 c.c. of *N*/10-solution. Apparently oxidation was not complete with *N*/10-iodine solution. Travers, Ray, and Gupta (*A.*, **1917**, ii, 308) showed that the boron in certain of its compounds with hydrogen and oxygen is oxidised by iodine only to the B_2O_2 stage; but we found that if the substance was shaken with an excess of *N*-iodine solution in the dark for about 1 week, complete oxidation of boron took place, requiring 838 c.c. of *N*/10-iodine solution per g.

The results of these experiments show that hydrolysis of magnesium boride at the ordinary temperature takes essentially the same course whether it is effected by water or by dilute acids, *viz.*, $Mg_3B_2 + 6H_2O = Mg_3B_2(OH)_6 + 3H_2$. Hydrolysis slightly below — 10°, however, affords $H_3B_2(Mg{\cdot}OH)_3$, which is readily converted by the action of water into $Mg_3B_2(OH)_6$, with liberation of hydrogen, especially when the temperature is slightly increased. The formation and decomposition may be represented by the equations $Mg_3B_2 + 3H_2O = H_3B_2(Mg{\cdot}OH)_3$; $H_3B_2(Mg{\cdot}OH)_3 + 3H_2O = Mg_3B_2(OH)_6 + 3H_2$.

It is found that, contrary to what has been generally supposed, no boric acid or magnesium borate is formed in the hydrolysis of magnesium boride by water or dilute acids.

SCIENCE COLLEGE, PATNA, INDIA.

[*Received, June 3rd*, **1935**.]