BOROHYDRATES, PART II.

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In a previous communication (Borohydrates, Part I.), in conjunction with Mr. N. M. Gupta, we have shown that the action of water on magnesium boride results in the formation of a compound which appears to be the magnesium salt of a borohydrate of the formula $B_m(O\ H_2)_n$, together with free magnesium oxide. This substance, when the reaction which results in its formation is complete, does not appear to react further with water; and even the prolonged action of either hot or cold water does not give rise to any further quantity of the borohydrates described in the previous paper.

With a view to isolating the borohydrate $B_m(OH_2)_n$ as an ammonium salt, a quantity of the spent boride was treated with strong ammonia solution in an atmosphere of hydrogen. At first a small quantity of hydrogen was evolved; but on treatment of the spent boride with successive quantities of ammonia solution, though the reaction which resulted in the formation of the borohydrate, which we shall presently describe, proceeded with undiminished rapidity, the rate of evolution of the hydrogen slackened, and finally ceased altogether. It appears the reaction between the spent boride and ammonia solution really proceeds without the formation of hydrogen. It was also noticed that however long the ammonia solution was allowed to remain in contact with the spent boride, the ultimate concentration of the borohydrate in the solution appeared never to exceed a certain limiting value. This point will be discussed later.

The ammoniacal solution was generally allowed to remain in contact with the spent boride for two or three days, but sometimes for a much longer period. After filtering, it was found to contain, besides ammonia and some carbon dioxide, a substance which, in some respects, resembled the compounds described in the previous paper. On addition of acids, hydrogen, together with carbon dioxide was evolved, and the acid solution absorbed iodine. The solution contained a trace of magnesium. The solutions appeared to be extremely stable, no hydrogen being evolved from them when they were allowed to remain for several days in sealed tubes, and only slight oxidation taking place on exposure to the air. On evaporating the solution to dryness *in vacuo* in the cold, a white crystalline residue was left, which contained, besides boron, hydrogen, and oxygen, the elements of ammonia, and which evolved hydrogen slowly on standing. On heating the residue hydrogen was given off, and a substance was left which, as we shall show presently, appears to be the oxide B_4O_5.

The hydrogen and iodine equivalents the magnesium in the original solution, the boron in the residue obtained by evaporating the solution to dryness, and the ammonia in the solution which had been evaporated to small bulk, were determined in the manner already described. The following are the results of the experiments, which, as usual, are expressed in gram-atoms or gram-molecules per 100 ccs. of the solution:—

		I	II	III	IV	V
H. Equivalent	...	0.007:3	0.0090	0.0069	0.0060	0.0077
I. Equivalent	...	0.0035	0.0042	0.0032	0.0028	0.0037
NH_3	...	0.0034	0.0037	0.0029	0.0028	0.0033
B.	...	0.0068	0.0080	0.0064	0.0056	0.0072
Mg.	...	0.0003	0.0001	0.0002	0.0001	0.0001

The results show that the following relationship holds good:—

$$\text{H. Equiv.} : \text{I. Equiv.} : (NH_3 + Mg) : B :: 2 : 1 : 1 : 2$$

As in the former experiments the nature of the residue was carefully investigated, and as the results obtained in these experiments differed considerably from those obtained in the former, several determinations of the value of the ratio

$$(B_2O_3 \text{ from residue.})/(\text{Weight of residue less } MgO).$$

were made. The following are the results of the seven determinations which were carried out:—

1.13, 1.18, 1.12, 1.10, 1.13, 1.16, 1.14.

Where the residue consists of the oxide B_2O_2 the value of the ratio should be 1.295, but in the case of the present experiments the ratio corresponds very closely to 1.129, the value for the oxide B_4O_5. As we shall show later there is no doubt that that formula properly represents the composition of the residue, which consists mainly of an hitherto unknown oxide.

With a view to determining the molecular weights of the substance in the original solution a procedure was adopted which was identical with that employed in the case of the ammonium salt of hydrate $H_6B_2O_2, H_2O$ (Borohydrates, Part I). Where x, y, and z are the quantities of boron, ammonium, and magnesium in the solution, expressed in gram-atoms or gram-molecules per 100 ccs., A is the depression of the freezing point, and n is the number of boron atoms in the molecule of the substance present in the solution ; supposing that the substance is a salt which is completely dissociated into its ions, the value of n can bo calculated by means of the equation.

$$A = 18\cdot$$

The following are the results of the experiments :—

		I	II
ss	...	0.0064	0.0056
y	...	0.0029	0.0026
z	...	0.0002	0.0001
A	...	0.085	0.075
n	...	4.38	3.82

The 'correction' which is applied on account of the presence of the ammonium and magnesium is a large one, and very accurate results cannot be looked for. However, taking these results in conjunction with the analyses, we are justified in assuming that the compound contains four atoms of boron in the molecule.

As has already been stated, on heating the residue obtained by evaporating the original solutions in the cold, hydrogen is given off. In certain experiments the hydrogen was collected and measured, and the quantity compared with the sum of the hydrogen and iodine equivalents.

		I	II	III
a.	H. Equiv. + i. Equiv.	0.0073	0.00575	0.0072
b.	Gas on heating	0.0135	0.01015	0.0129
c.	Ratio a/b	6/11·1	6/10·4	6/10·8

The experimental values of the ratio a/b cannot be determined with so high a degree of accuracy as to make it possible to arrive at a definite conclusion as to whether the value should be 6/10 or 6/12. However, since water vapour and an oxidisable substance B_4O_5 are produced when the gas is given off, it is probable that the experimental value for the quantity of hydrogen evolved on heating would be too high rather than too low. If the value 6/10 is accepted as correct the formula for the borohydrate in the solution may be written $H_{12}B_4O_6$, $2NH_3$, or $B_m(OH_2)_n$ with the addition of the elements of ammonia. If this formula is correct the following facts may be explained : —

(a) That the borohydrate is formed from the spent boride without the evolution of hydrogen.

(b) That, as will appear later, only two hydrogen atoms are removed by iodine in the presence of acid.

The results of these experiments can now he explained as follows. The borohydrate which exists in the original solution as an ammonium salt may be represented by the formula,

$$BH_2(OH)_2 \,.\, BH(OH) : BH(OH) \,.\, BH_2(OH_2).$$

On addition of acid to the solution it may he assumed that a change takes place similar to that which appears to take place in the case of the borohydrates containing two boron atoms, atoms of hydrogen being simultaneously removed from adjacent boron atoms, thus,

$$BH_2(OH)_2 \,.\, BH(OH) : BH(OH) \,.\, BH_2(OH)_2 = 2\,H_2 + BH(OH)_2 : B(OE) : B(OH) : BH(OH)_2.$$

On addition of iodine to the acid solution the removal of the two atoms of hydrogen can be represented thus,

$$BH(OH)_2 : B(OH) : B(OH) : BE(OH), \quad + \quad 2\,I = 2\,HI \quad + \quad B(OH)_2 \,.\, B(OH).B(OH).B(OH)_2$$

The action of heat on the residue obtained by evaporating the original solution *in vacuo* may be represented by the equation,

$$BH_2(OH)_2 \,.\, BH(OH) : BH(OH) \,.\, BH_2(OH)_2 + (2\,NH_3) = BO : BO \,.\, BO : BO + 5\,H, + H_2O + (2\,NH_3).$$

It must be pointed out that if the actual value of the ratio (H. Equiv. + I. Equiv.) /(Gas on heating.) is 0/12, the formula for the soluble borohydrate, and the evolution of hydrogen on the addition of acid will probably have to be represented as follows,

$$BH_2(OH)_2 \,.\, BH_2(OH) \,.\, BH_2(OH) \,.\, BH_2(OH)_2 = BH(OH)_2 : BH(OH) \,.\, BH(OH) : BH(OH)_2 + 2\,H_2.$$

If this formula were correct, following the analogy of the compound $(H_2 : BOH)_2$, the compound should lose not four, but eight atoms of hydrogen in presence of acid, or if the change proceeds in the manner indicated above, four atoms of hydrogen should be removed on addition of iodine to the acid solution. It appears therefore that if the value of the ratio is 6/12 it becomes practically impossible to explain the experimental results, which is a simple matter if the ratio is 6/10.

We have now to consider the nature of the residue. It is generally of a pale brown colour, and appears to be infusible at the softening point of Jena glass. When allowed to remain in contact with water *in vacuo* it slowly dissolves, without evolution of gas, forming a golden yellow solution, and leaving a small amount of a flocculent residue, which is insoluble in acids, and which appears to resemble the compound to which the formula $B_4O_3, 2H_2O$ was assigned (Borohydrates, Part II.) The freezing point of the solution was determined, and also the quantity of boron and magnesium in the solution, and from the results of the experiments the number of boron atoms *n* in the molecule of the substance in solution was calculated by means of the formula previously employed.

	I	II	III
x	0·0190	0·0102	0·0129
z	0 0009	0·0003	0·0008
A	0-1(59	0-OS2	0·110
n		2 51	2·43

The close agreement between the analytical results makes it quite clear that the residue has the composition corresponding to the formula B_4O_5. It appeared however possible that it might consist of an equimolecular mixture of the oxides B_2O_2 and B_2O_3, though from the high melting point this appeared to be improbable, or it might, on passing into solution, break up into a mixture of those oxides. In order to determine whether such change actually took place, a quantity of the solution was shaken for two days with excess of light magnesium oxide in an exhausted vessel, when, if the hydrates of the two oxides were present, the greater part of the boric acid would be converted into the insoluble metaborate, and the solution would consist largely of borite. The following are the results of the experiment.

x	0·0012
z	0·00195
A	0·099
n	1·23

The solution contained but a small quantity of the metaborate, as is proved by the fact that the value of *n* is only just over unity, and that the atomic proportions of the boron and the magnesium in the solution are 2/1.

It is possible to write an equation for the hydrolysis of one molecule of the oxide B_4O_5 into two molecules of a hydrate HB_2O_3, but as such a hydrate cannot be represented graphically, the boron atoms being trivalent or pentavalent, it is hardly likely that it can exist.

It has already been pointed out that when the residue is dissolved in water a substance is left undissolved, which resembles the oxide B_4O_3 described in the previous paper. If this substance is formed according to the equation.

$$3\,B_4O_5 = B_4O_3 + 4\,B_2O_3$$

the change will take place without effecting the composition of the residue, and as eight molecules of boric acid are formed, the conversion of 25 per cent of the residue into B_4O_3 and B_2O_3, will give rise to a solution containing equimolecular quantities of hydrated B_4O_5 and $B(OH)_3$. Such a mixture would give a value of 2·5 for *n* in the equation. It must be expected therefore that the value of *n* for the original solutions will be low.

It was also observed that the hydrated B_4O_5 oxidised rapidly when exposed to the air.

An attempt was made to separate the constituents of the solution by fractional crystallisation. About 0 1 gram of the residue was obtained, and the aqueous solution was evaporated *in vacuo* to very small bulk and then cooled for an hour in ice. The liquid was drained off through a very small filter plate, and both the liquid and the crystals were made up to 15 ccs. of solution for the molecular weight determination. The following are the results of the experiment :—

Crystals.

x	...	...	0·00735
z	...	...	0·0002
A	...	...	0·005°
n	...	...	1·67

Liquid.

x	...	...	0·0284
*	...	...	0·0009
A	...	...	0·205°
n	...	...	2·79

By this process a slight increase in the concentration of the substance of higher molecular weight had been effected, but as it did no seem possible to separate it from the substance of lower molecular weight, we decided to attempt to obtain the latter in a pure state. A quantity of the solution of the residue was therefore evaporated almost to dryness, and the crystals were redissolved in water. The solution was then again evaporated, the crystals drained off and freed from liquid by means of filter paper. The molecular weight was then determined, the following being the results of the experiment :—

ss	0·00405
z	0·00005
A	0·079°
•*n*	0·94

The value of *n* being almost exactly equal to unity, it follows that the substance in solution must be boric acid.

If the liquid in the first of the two experiments contained the two compounds boric acid and hydrated B_4O_5 they should be present in the proportion of 40 molecules of the former to 60 molecules of the latter or in other words the residue from the solution would contain only 16 per cent of boric acid, reckoned as B_2O_3. Stating the case in this way the difficulty of separating the two substances, particularly as one of them tends to change by oxidation into the other becomes very apparent. However, though it is not outside the bounds of possibility that the compound having the higher molecular weight may contain three or five atoms of boron in the molecule, taking all the facts into consideration this appears to be extremely unlikely. We therefore conclude that the residue consists mainly of the oxide B_4O_5, and that the hydrate of this oxide is formed when the residue is dissolved in water.

The following is a summary of the known oxides and hydrates of boron :—

Oxide,	*Hydrate.*
B_2O_3	$B(OH)_3$, $BO(OH)$,&c.
B_4O_5	?
B_2O_2	?
B_4O_3	$H_4B_4O_5$

Finally we have a few remarks to make with regard to the action of ammonia on the spent boride. Referring back to the previous paper it will be seen that when the spent boride was dissolved in acid the quantity of hydrogen evolved was slightly in excess of three atoms for every atom of boron passing into solution. When the spent boride is treated with ammonia hydrogen is at first evolved, but after a short time gas ceases to be given off. The total quantity of hydrogen collected was about equivalent to 1/12 atom for every atom of boron passing into solution. That this hydrogen is given off may be accounted for by the fact that, as was indicated in the previous paper, it takes a very long time for the reaction of the original boride and water to become complete.

The change in the composition of the spent boride which takes place on addition of ammonia to it is therefore negligible; and as the soluble borohydrate continues to be formed after the evolution in hydrogen has ceased altogether, it may be considered to be formed by a process which involves only polymerisation, and the addition or removal of the elements of water.

However, we have now to show that the spent boride is changed by the action of ammonia, for when it is dissolved in acid only two atoms of hydrogen are evolved for every atom of boron which passes into solution. Further, the solution does not contain boric acid, but a substance which appears to have an acidic character, but which we have not been able to isolate. This reaction will be made the subject of a special investigation, but for the moment it will suffice to point out that while the relationship between the boron, oxygen, and hydrogen in the spent boride, which has been treated with ammonia, and in the soluble borohydrate which is described in this paper, may be represented by the formula $B_m (OH_2)_n$, three different borohydrates appear to exist. The fact that the borohydrate in the solution appears to attain a limiting concentration remains unexplained. The main facts may be summed up as follows.

(a) The spent boride dissolves in acids according to the equation,

$$B(OH_2)_3 \qquad 2\,B(OH)_3 \qquad H.$$

(b) The spent boride, after treatment with ammonia, when treated with acids yields two atoms of hydrogen for each atom of boron which passes into solution, and an acidic boron compound, which is not boric acid, but which has not been isolated.

(c) The soluble borohydrate described in this paper on treatment with acid yields one atom of hydrogen for each atom of boron in solution.

We have reason to believe that the boride Mg_3B_2, and the product of the action of water upon it, contain single boron atoms, united only to magnesium or to oxygen atoms, that the spent boride after treatment with ammonia contains the group B-B, and as the soluble borohydrate contains the group—B-B-B-B-, and if this proved to be correct it may be possible to account for the formation of the diborons described in the last paper, and of the gaseous hydroborons described by Stock and his collaboraters.

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