Hydrogen Adducts of Cobalt and Nickel Boride

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Summary Interaction of sodium borohydride with salts of cobalt(II) or nickel(II) produces metal borides that have been found to contain hydrogen; stoicheiometries Co_2B and Ni_2B as have been suggested previously are inadequate in explaining the physical and chemical properties of these substances, and the formulations $(Co_2B)_5{\cdot}H_3$ and $(Ni_2B)_2{\cdot}H_3$ have been tentatively assigned.

IN the course of his work on borohydrides, Schlesinger observed that although a number of salts (silver, mercury, bismuth salts, *etc.*) were reduced to the metallic state when treated with alkali borohydrides, they gave only the corresponding borides with cobalt and nickel salts.

We have now prepared borides‡ of cobalt and nickel which contain hydrogen, by interaction of 1 M ethanolic solutions of the halides of the metals with a 4 fold molar excess of ethanolic $NaBH_4$ under N_2.

Elemental analysis carried out on freshly precipitated samples indicate a metal:boron ratio of *ca.* 2:1 in agreement with previous findings,[1] although this only accounts for about 95% of the sample weight. The borides(H) when dry are ferromagnetic, pyrophoric in air, and are very soluble in dilute mineral acids liberating H_2, but are almost insoluble in alkali. It should be noted that the authentic borides Co_2B and Ni_2B[2] obtained by fusion of the elements at high temperatures melt at 1265 and 1230 ° respectively, whereas samples obtained by the above procedure slowly decompose at 100 ° liberating H_2.

Although the crystal structure of authentic Co_2B has been investigated and is shown to have the $CuAl_2$ type lattice, we have found by *X*-ray diffraction analysis that these borides(H) are amorphous, with B.E.T. surface areas varying from 5·3 to 57·8 m^2/g.

ESCA examination shows that cobalt boride(H) is contaminated with sodium chloride, this being precipitated during the preparation in ethanol. From the peak areas for Cl(2*p*) and B(1*s*) there appears to be almost twice as much chlorine as boron exposed on the amorphous surface. Since more than 95% of the sample weight may be accounted for in terms of cobalt and boron, this discrepancy which has been noted by other workers[1] must be explained in terms of salt adsorption on to large aggregates of amorphous material.

On heating a dry (freshly precipitated) sample of either cobalt or nickel boride(H) *in vacuo*, evolution of hydrogen (as evidenced by mass spectrometric analysis of the gas) occurs at 100 ° and continues as the temperature is raised to 800 ° or more, and a grey metallic mass of approximate composition M_2B (where M is metal) is left. A little water (presumably tightly bound) is detected also at temperatures as high as 300°. From experiments of this type, molar ratios for H_2/Co_2B of 0·3 and H_2/Ni_2B of 0·75 were obtained

‡ We shall refer to these compounds as borides(H) for convenience.

in agreement with the stoicheiometries $(Co_2B)_5{\cdot}H_3$ and $(Ni_2B)_2{\cdot}H_3$. For cobalt boride(H); H(found), 4·65, 4·28, and $4{\cdot}58 \times 10^{-3}\%$. H(calc.) for $(Co_2B)_5{\cdot}H_3$, $4{\cdot}64 \times 10^{-3}\%$. For nickel boride(H); H(found), 1·22, 1·13, and $1{\cdot}71 \times 10^{-2}\%$. H(calc.) for $(Ni_2B)_2{\cdot}H_3$, $1{\cdot}16 \times 10^{-2}\%$.

The evidence that hydrogen does not arise from reaction between residual water and the boride itself is shown by the fact that dry samples have been found to contain less than 0·1 mol H_2O per M_2B unit, this not being sufficient to provide the necessary H_2 evolved upon thermal decomposition.

The cobalt boride(H) on treatment with pure methanesulphonic acid *in vacuo* liberates H_2 and a small amount of a gaseous mixture comprised of *ca.* 65% H_2S, 30% CH_4, and traces of SO_2 (as evidenced from mass spectrometric analysis). The absence of diborane suggests the lack of any residual borohydride and probably the lack of terminal BH bonds, implying that the borides are acting as clathrates containing molecular hydrogen trapped in the lattice.

A suspension of freshly precipitated cobalt boride(H) in water slowly liberates hydrogen with the formation of boric acid. Elemental analysis for boron[3] carried out on samples that have been exhaustively washed with large quantities of water show that almost 60% of their B-content has been lost as H_3BO_3 in the washings. Thermal quantitative analysis for H_2 on such washed samples show only the presence of about 30% of the expected hydrogen and a grey residue of approximate composition Co_5B remains. This is consistent with the interaction of $(Co_2B)_5H_3$ with water to form a lower metal boride $(Co_5B)_2{\cdot}H$, which may be decomposed on heating, *i.e.*

$$2(Co_2B)_5H_3 + 18\,H_2O \longrightarrow 2(Co_5B)_2{\cdot}H + 6H_3BO_3 + 11H_2$$

$$2(Co_5B)_2{\cdot}H \longrightarrow 4Co_5B + H_2$$

Cobalt and nickel boride(H) contain hydrogen, and this fact alone renders them potential hydrogenation catalysts not only in liquid phase,[4] but also in gas-phase reactions involving unsaturated substrates. We shall subsequently show how the catalytic activity (for gas-phase hydrogenation and hydrogenolysis reactions of olefins and also the methanation of carbon monoxide) of these compounds is paralleled by the amount of hydrogen bound into the boride lattice.

We have indicated here only two examples of probably a whole family of related boride(H) compounds. Further studies are required to establish the nature of these compounds and whether other representatives occur.

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