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Hydrolysis of the Borohydride Ion catalysed by Metal-Boron Alloys

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The hydrolysis of the borohydride ion according to the equation (i) is catalysed by nickel-boron and cobalt-boron

 $BH_4^- + 3H_2O \longrightarrow H_2BO_3^- + 4H_2$ (i)

alloys. The metal-catalysed hydrolysis has been studied at 22.0 °C by measurement of the hydrogen gas evolved. Analysis of the gas evolved when the reaction is carried out in deuterium oxide shows that approximately half the hydrogen evolved originates from the borohydride and half from the solvent. The deuterium content of the gas increases with reaction time. In mixtures of H₂O and D₂O, preferential hydrogen evolution occurs and isotope separation factors of 8.5 (for a nickel-boron catalyst) and 9.2 (for a cobalt-boron catalyst) have been derived.

ALTHOUGH numerous studies have been made 1-4 of the solvolysis of the borohydride ion in aqueous solution, the metal-boron alloy-catalysed solvolysis has received relatively little attention.⁵ Both the homogeneous acidcatalysed solvolysis and the heterogeneous alloy-catalysed solvolysis follow the same stoicheiometry expressed by equation (1).

$$BH_4^- + 3H_2O \longrightarrow H_2BO_3^- + 4H_2 \qquad (1)$$

A study of the metal-boron alloy-catalysed solvolysis was undertaken as a part of a wider study concerned with the 'electroless' or autocatalytic deposition of nickel and cobalt films. It is well-known that reaction (1) occurs concurrently with metal deposition when the borohydride ion is employed as reducing agent in such systems.⁶ This work is also relevant to studies ⁷⁻⁹ of the anodic oxidation of the borohydride ion.

EXPERIMENTAL AND RESULTS

Solution Preparation .--- Sodium borohydride (Koch-Light ' Pure') was purified by recrystallisation from diglyme according to the method of Brown, Mead, and Subba Rao.¹⁰ The diglyme was first dried (CaCl₂) and then distilled under nitrogen. The sodium borohydride produced by this method was determined by the method of Lyttle, Jensen, and Struck¹¹ to be 99.6%. Sodium hydroxide solutions were prepared from AnalaR sodium hydroxide and distilled water, and sodium deuteroxide solutions were prepared by dissolving sodium wire in deuterium oxide (99.6%) under nitrogen.

Kinetic Studies.-Apparatus. The apparatus consisted of a three-necked reaction vessel (25 ml) equipped with a nitrogen inlet and a thermometer. The third neck was connected through a water-condenser to a gas-burette to measure the volume of hydrogen evolved at atmospheric pressure. The reaction vessel was immersed in a thermostat bath at (22.0 \pm 0.05) °C and its contents were stirred by a magnetic stirrer.

Catalyst preparation. The following method was developed by which a catalyst was prepared in the reaction vessel before each run and was used for that run alone. A volume (15 ml) of sodium borohydride solution (0.005M, pH 11.0) was placed in the reaction vessel under nitrogen and immediately mixed with a volume (1 ml) of nickel chloride solution (0.0025M). The mixture was stirred continuously with the magnetic stirrer. A black precipitate of a nickelboron alloy was produced which constituted the catalyst to be used in the subsequent run. A standard time (20 min) was allowed from the time of mixing (described above) to the time of addition of the reactant solution so that excess of sodium borohydride decomposed. The nickel catalyst (Ni-16) produced by this method was found to contain about 7.1% by weight of boron as analysed by Kramer's method.¹² A cobalt-boron catalyst (Co-3) was produced from cobaltous chloride solution similarly.

Procedure during a run. The catalyst was prepared in the reaction vessel and left for 20 min with nitrogen bubbling through the solution. A vessel containing the concentrated reactant solution in the same thermostat was allowed to attain the same temperature. A sample (5 ml) of the reactant solution (sodium borohydride in sodium hydroxide) was then withdrawn and added to the contents of the reaction vessel. The nitrogen supply was then interrupted, a stop-watch started, and the hydrogen evolved was collected at atmospheric pressure in the gas burette, the mercury level being read by a cathetometer. The total volume in the reaction vessel after addition of the reactant solution was 21 ml.

Kinetic Results.-The reaction stoicheiometry was confirmed by measuring the total volume of hydrogen evolved for complete reaction for different initial concentrations of sodium borohydride on the nickel-boron catalyst. The results are in Table 1, and confirm the stoicheiometry expressed in equation (1).

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4 R. E. Davis, J. A. Bloomer, D. R. Cooper, and A. Saba, J. Inorg. Chem., 1964, 3, 460.
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⁶ H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hockstra, and E. K. Hyde, J. Amer. Chem. Soc., 1953, 75, 215.

Typical plots of hydrogen evolved as a function of time are shown in Figure 1 for various conditions and for both nickel-boron and cobalt-boron catalysts. From these and from measurements of the initial rates for different concentrations of sodium borohydride and sodium hydroxide

TABLE 1

NaBH /M	HatNTP/ml	H_2 : NaBH ₄ (molar ratio)
NaDII ₄ /M	112 at 19.1.1.1./m	(moiai racio)
0.0226	43.6 0	4 ·10
0.0114	21.98	4 ·09
0.0055	10.45	3.94
0.0027	5.41	3.96
	$[OH^{-}] = 0.095M$	

(Table 2) it can be concluded that the reaction is of zero order in both borohydride and hydroxide ions.



FIGURE 1 Hydrogen evolution as a function of time; $[BH_4^{-}] = 0.011M$; temperature (22.0 ± 0.05) °C

A, Nickel-boron catalyst (Ni-16); B, Cobalt-boron catalyst (Co-3)

Deuterium Tracer Studies.—Apparatus. The apparatus consisted of a small reaction vessel (5 ml) sealed to a watercondenser. Samples of the gas evolved were collected by means of evacuated sample vessels connected to the exit of

TABLE 2

NaOH/M	NaBH₄/м	$[d(H_2)/dt]/ml/min$	No. of runs
0.095	0.0962	0.71 ± 0.11	6
0.092	0.0445	0.69 ± 0.07	6
0.095	0.0226	0.62 ± 0.06	12
0.092	0.0114	0.65 ± 0.04	6
0.092	0.0056	0.68 ± 0.05	6
0.092	0.0027	0.64 ± 0.06	6
0.238	0.0114	0.65 ± 0.06	3
0.513	0.0114	0.63 ± 0.03	3
1.120	0.0114	0.67 ± 0.06	3
1.850	0.0114	0.68 ± 0.05	3
0.238	0.0056	0.66 ± 0.01	3

the condenser. The solution in the reaction vessel was agitated by a magnetic stirrer. The majority of the experiments were done at (22.0 ± 0.05) °C by immersing the re-

action vessel in a water thermostat. Some runs however were done at higher temperatures by immersing the reaction vessel in a vapour jacket and refluxing various liquids.

Catalyst preparation. Nickel-boron (Ni-10) and cobaltboron (Co-5) catalysts were prepared by plating on to platinum gauze from the following plating solutions. Nickel plating solution: NaBH₄ (0.04M), NiCl₂ (0.10M), sodium citrate (0.11M); pH adjusted to 11.2 with ammonia, temperature 22.0 °C. Cobalt plating solution: NaBH₄ (0.05M), CoCl₂ (0.10M), sodium citrate (0.10M); pH adjusted to 11.2 with ammonia; temperature 22.0 °C. The platinum gauze was activated before plating by an immersion (2 min) in aqueous stannous chloride (0.01%, pH 1.9), followed by a distilled water rinse and then an immersion (2 min) in aqueous palladous chloride (0.015%, pH 3.0). The activated platinum gauze was washed with distilled water and then plated for 10 min in one of the above solutions.

Procedure during a run. A sample (2 ml) of reactant solution [sodium borohydride in sodium deuteroxide (or sodium deuteroxide plus sodium hydroxide) solution] was placed in the reaction vessel and allowed to come to a constant temperature. The catalyst-gauze was then immersed in deuterium oxide, dried under vacuum, and then added to the reaction vessel. Samples of the gas evolved were then collected during successive intervals in small evacuated vessels placed over the end of the condenser. Alternatively, if required, the whole of the gas evolved was collected in one large sample vessel. Gas samples were analysed on an MS3 mass spectrometer operating at 50 eV. The percentage of deuterium in the gas was calculated from equation (2), where HD, D₂, and H₂ represent the peak

$$D/\% = \frac{HD/2 + D_2}{H_2 + HD + D_2} \times 100$$
 (2)

heights of these species observed in the mass spectrum. Corrections were made for the background peak heights in the absence of the sample. This was usually a correction of 0.2-1.0% for H₂ and was negligible for HD and D₂. The samples were cooled in liquid air before admission to the mass spectrometer to remove any deuterium oxide vapour.

Results of Tracer Studies.—Deuterium content of the gas for complete reaction. Several experiments were carried out to determine the overall percentage of deuterium (%D) content of the total amount of gas evolved for complete solvolysis in alkaline deuterium oxide on a nickel-boron and a cobalt-boron catalyst. Reaction was carried out with sodium borohydride (0.053M) and sodium deuteroxide (0.10M) at (22.0 ± 0.05) °C. For catalyst (Ni-10) a mean value of the percentage of deuterium for four runs was (48.2 ± 0.10) and for three runs with catalyst (Co-5) was (47.9 ± 0.1) . The molar ratios of $H_2: HD: D_2$ were 1.12: 1.16: 1.00 when the nickel catalyst was used and 1.17: 1.70: 1.00 when the cobalt catalyst was used.

Deuterium content and reactant concentration. For a range of concentrations of sodium borohydride (1.02M-0.05M) and sodium deuteroxide (1.08M-0.1M) the overall percentage of deuterium in the total gas evolved for complete solvolysis varies little as shown by Table 3. Approximately half the gas evolved during complete solvolysis of the borohydride ion originates from the solvent and half from the borohydride ion. This appears to be true over a wide range of conditions both on a nickel-boron and on a cobalt-boron catalyst.

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Effect of reaction products. Three successive reactions were carried out with the same catalyst (Ni-10) and the same reactant solution which was regenerated after complete reaction by the addition of a volume of sodium borohydride stock solution. This enabled the influence of

tions one of which was diluted by a factor of two and both portions were allowed to react to completion on catalyst (Ni-10). In either case the same percentage of deuterium was obtained, indicating that no deuterium oxide was carried

Time/min

300

100

n

TABLE 3 D/% NaBH₄/M NaOD/M Catalyst Ni-10 0.101.020 48.46Ni-10 0.10 0.560**48**·28 Ni-10 0.10 0.110 48.11 Ni-10 0.100.053**48**.16 Ni-10 1.080.05348.21 Ni-10 0.760.05348.13 Ni-10 0.410.05348.00 0.100.983Co-5 48.13Co-5 0.100.636**48**.08 Co-5 0.10 0.11047.88 Co-5 0.10 0.05347.93 Co-5 1.16 0.05348.12 Co-5 0.720.05347.79 Co-5 0.390.05348.04

accumulated borate ion to be examined and little change in the percentage of deuterium in the gas for complete solvolysis was found as shown in Table 4.

TABLE 4

Initial NaBH₄/M	Initial NaBO ₂ /м	Initial NaOD/м	D/%
0.05	0	0.10	48.16
0.02	0.05	0.13	48 ·28
0.02	0.10	0.15	48.12

Deuterium content and reaction time. A considerable and systematic change occurred in the deuterium content of the gas evolved as a function of time or the extent of solvolysis. Reaction was carried out with sodium borohydride (0.1M) and sodium deuteroxide (0.1M) at 22.0 ± 0.05 °C and typical plots of the percentage of deuterium against time for both nickel-boron and cobalt-boron catalysts are shown in Figure 2. Several experiments were carried out in which the catalyst (Ni-10) was successively removed from the solution and then replaced during the same solvolysis. When the deuterium content of the gas is plotted against the catalyst immersion-time (as distinct from the time interval since the reaction started) a smooth curve is obtained as shown in Figure 3.

It appears therefore that the percentage of deuterium in the gas is dependent on the catalyst immersion-time but independent of the time the catalyst is absent from the solution.

Incorporation of deuterium into the borohydride ion. The solvolysis (A) of sodium borohydride in deuterium oxide was carried out in which samples (ca. 0.5 ml) of solution were withdrawn during a run to examine for the presence of any deuterium in the unsolvolysed 'borohydride' or in any intermediate produced during the solvolysis. The extracted samples were evaporated to dryness under vacuum in order to remove the deuterium oxide solvent,¹³ recrystal-lised twice from water (by successive dissolution and vacuum evaporation) and finally dissolved in water (to give a solution S) and hydrolysed (B) to completion on catalyst (Ni-10). The gas was found to contain deuterium and therefore it was concluded that during the solvolysis (A) some intrusion of deuterium into the borohydride had occurred. To check this further, solution S was divided into two por-



FIGURE 2 Percentage deuterium evolved as a function of time
 A, Nickel-boron catalyst (Ni-10) (top and right-hand axes);
 B, Cobalt-boron catalyst (Co-5) (bottom and left-hand axes)



FIGURE 3 Percentage of deuterium evolved as a function of catalyst immersion time Catalyst absence: A, 20 min; B, 11 min; C, 12 h and D, 2 h

over during the recrystallisation procedure. The percentage of deuterium obtained in hydrolysis (B) is shown in column 2 and the catalyst immersion-time in the original solvolysis (A) in column 1 of Table 5. The approximate deuterium content of the 'borohydride' can be calculated by multiplying the percentage of deuterium in the gas by

¹⁸ P. R. Giradot and R. W. Parry, J. Amer. Chem. Soc., 1951, 78, 2368.

two since it has been shown that approximately half the gas evolved comes from the solvent and half from the borohydride ion.

The extent of intrusion of deuterium into the borohydride ion is therefore dependent on the catalyst immersion-

TABLE 5

D/% in gas from hydrolysis (B)
1.83
6.40
6.42
8.23
10.20

time and independent of the time the catalyst is absent from the solution.

Isotope Separation Effects.—When the solvolysis of the borohydride ion on a nickel-boron and a cobalt-boron catalyst was carried out in mixtures of water and deuterium oxide a preferential evolution of hydrogen was found to occur. This is illustrated in Figure 4, in which the overall percentage of deuterium in the gas phase for the complete solvolysis in a particular mixture of water and deuterium oxide is plotted against the percentage of D_2O in that mixture. An isotope-separation factor S has been defined¹⁴ as follows in equation (3). In the metal-boron-catalysed

$$S = \frac{[H/D]_{gas}}{[H/D]_{solution}}$$
(3)

solvolysis of the borohydride ion the term $[H/D]_{gas}$ refers to that portion of the gas which originates from the solvent and as shown above this appears to be approximately half the total gas evolved. Thus if the percentage of deuterium in the gas is *b* the percentage of deuterium from



FIGURE 4 Percentage of deuterium evolved as a function of percentage of D_2O in water. The full curves show the observed separation and the broken line the curve calculated for no isotope separation.

A, Nickel-boron catalyst (Ni-10); B, Cobalt-boron catalyst (Co-5)

the solvent is 2b since only hydrogen originates (directly) from the borohydride ion. If a is the percentage of D_2O in the solvent, equation (3) becomes (4), leading to (5),

¹⁴ J. O'M. Bockris, 'Modern Aspects of Electrochemistry,' Butterworths, London, 1954, pp. 198-213. $S = \frac{\left[\frac{100 - 2b}{2b}\right]}{\left[\frac{100 - a}{a}\right]}$ (4)

$$\left[\frac{50-b}{b}\right] = S\left[\frac{100-a}{a}\right] \tag{5}$$

and if (50 - b)/b is plotted against (100 - a)/a a straight line of slope S should result for a consistent separation fac-



FIGURE 5 Plot of (50 - b)/b against (100 - a)/a [equations (4) and (5)] A, Nickel-boron catalyst (Ni-10); B, Cobalt-boron catalyst (Co-5)

tor. This appears to be true as shown in Figure 5 for both the nickel-boron and cobalt-boron catalysts.

DISCUSSION

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The major features of the metal-boron alloy-catalysed hydrolysis of the borohydride ion which we have observed and must be explained by any suggested mechanism are (a) the overall stoicheometry corresponds to equation (1); (b) the rate of hydrogen evolution is of zero order in borohydride ion on both catalysts; (c) approximately half the gas evolved for the complete solvolysis of the borohydride ion in alkaline deuterium oxide solution comes from the solvent and half from the borohydride ion; (d) during the solvolysis in alkaline deuterium oxide solution, the percentage of deuterium in the gas evolved appears to increase in approximate proportion to the extent of solvolysis; (e) intrusion of deuterium into unsolvolysed borohydride in alkaline deuterium oxide occurs only when the catalyst is present and increases with catalyst immersion time; and (f)large isotope-separation effects are observed for the solvolysis in mixtures of water and deuterium oxide.

A mechanism which will account for these features is given by equations (6)—(10). In this mechanism the

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solvent is assumed to be alkaline deuterium oxide for the sake of clarity, M represents a surface site on the catalyst,

$$2M + BH_4^{-} \rightleftharpoons H - B^{-} - H + H \qquad (6)$$
$$M \qquad M$$

(I)

$$H - \frac{H}{H} - H = BH_3 + M + e_M$$
(7)

$$BH_3 + OD^- \longrightarrow BH_3OD^-$$
(8)

$$M + e_M + D_2 O \longrightarrow M - D + OD^-$$
(9)

$$M - H + M - D \Longrightarrow 2M + HD$$
(10)

and (I) is a negatively charged surface species containing boron. Step (6) represents reversible dissociative chemisorption of the borohydride ion.

Step (7) expresses the tendency of the charge associated with the species MBH_3^- to be associated with the metal and can therefore be regarded as the anodic step of a local cell of which step (9) is the cathodic step and the metal catalyst is the short-circuit between the two. Step (8) is the rapid reaction of borine with deuteroxyl ions to give the relatively stable intermediate BH_3OD^- . If this species is of similar reactivity to the borohydride ion, then it can undergo reaction steps analogous to (6), (7), and (8) to produce $BH_2(OD)_2^-$ which can further react to give $BH(OD)_3^-$ and finally $B(OD)_4^-$ which is equivalent to $D_2BO_3^- + D_2O$. The overall reaction can then be summarised as (11). This immediately

$$BH_4^- + 3D_2O \xrightarrow{M} D_2BO_3^- + 4HD \quad (11)$$

accounts for the observations (a) and (c). A similar stepwise replacement of boron-hydrogen bonds by boron-hydroxyl bonds has been suggested by Mochalov and Gil'manshin² for the homogeneous solvolysis of the borohydride ion.

In order to account for the observation (b) of zeroorder kinetics in borohydride ion concentration, it is necessary to assume that steps (6) and (-6) are relatively fast, producing a high equilibrium concentration of the species MBH_3^- on the catalyst surface. Hydrogen production is then governed by steps (7), (9), and (10). Both steps (9) and (10) have been postulated to occur in the electrochemical evolution of hydrogen on nickel cathodes in aqueous alkaline solution and of these two, step (9) is considered to be the slower rate-controlling step.¹⁵ The reverse of step (9) does not appear to be important under the reaction conditions of borohydride solvolysis.

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The predominance of hydrogen evolution over deuterium in the early stages of the reaction (d) and the appearance of deuterium in the unsolvolvsed borohydride (e) are both accounted for by the participation of M-D in step (-6). To explain (d) it is necessary to assume that M-D undergoes (-6) in preference to step (10). The isotope-separation effects observed (f) can be attributed to the relative difference in rates for step (9) when H_2O and D_2O are involved. Similar large isotope-separation effects are common for the electrochemical evolution of hydrogen on metal cathodes.¹⁴ A possible explanation for the observed value of 48%deuterium in the gas evolved for complete solvolysis in alkaline deuterium oxide compared with the expected 50% could be that the small amount of water present in the deuterium oxide (0.4%) is more reactive than deuterium oxide in step (9). On the basis of an isotope factor of 8.5, the deuterium content of the gas evolved for complete solvolysis can be calculated to be 48%.

The metal-catalysed hydrolysis of the borohydride ion is relevant to studies of the electrochemical oxidation of the borohydride ion.⁷⁻⁹ Indig and Snyder ⁷ have observed that borohydride ion oxidation at a nickel anode approaches a four-electron transfer which may be represented overall by equation (12).

$$BH_4^- + 40H^- = 2H_2 + BO_2^- + 4e^- + 2H_2O$$
 (12)

Such a result can be interpreted on the basis of the mechanism given in steps (6)—(10) which corresponds to open-circuit conditions. As anodic polarisation is imposed, electrons produced in step (7) will pass into the external circuit through the anode. This represents a four-electron transfer for each BH_4^- ion that reacts to BO_2^- [via the intermediates BH_3OH^- , $BH_2(OH)_2^-$, and $BH(OH)_3^-$, each of which contributes one electron]. The hydrogen atoms produced in step (6), *i.e.*, four for each BH_4^- , combined to give $2H_2$ in agreement with the overall stoicheiometry of equation (12).

The mechanism given in steps (6)—(10) can also be extended to cover electroless plating systems, if when suitable metal ions are present (such as Ni^{2+}) they are reduced by the electrons liberated at the catalyst surface *i.e.*, reaction (13). The overall reaction mechanism in

$$Ni^{2+} + 2e_M \xrightarrow{Cat.} Ni$$
 (13)

such systems is undoubtedly complex ⁶ but the participation of surface intermediates containing boron such as $\rm MBH_3^-$ could account for the observation that the deposited metal can contain up to 10% (w/w) of boron.

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¹⁶ S. Srinivasan, H. Wroblowa, and J. O'M. Bockris, *Adv. Catalysis*, 1967, **17**, 394–396.