Hydrogen Generation by Hydrolysis of Sodium Tetrahydroborate: Effects of Acids and Transition Metals and their Salts

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A study was undertaken in order to investigate the potential of $NaBH_4$ as a precursor fuel source for a hydrogen–oxygen (air) fuel cell. At appropriate initial acid concentration, hydrolysis of $NaBH_4$ is nearly 80% complete in 2.5 min, and nearly 90% complete in 10 min at 21.7 °C. Transition metals and their salts also accelerate hydrolysis of $NaBH_4$. The effect of transition metals is characterized by zero-order kinetics.

As a combustible fuel, hydrogen produces more energy per kg (12.24×10^4 kJ) when compared to the common fossil fuels coal, petroleum, and natural gas. In addition, hydrogen as a fuel has a number of advantages including: (*i*) minimal environmental pollution, (*ii*) mass transportability comparable to petroleum and natural gas, (*iii*) combustibility in internal combustion engines (Carnot-cycle devices) and in rocket engines, and (*iv*) feasibility of electrochemical combination with an oxidant in fuel cells (free-energy devices).

It is anticipated that precursor chemicals will play an important role in hydrogen-based energy systems, *e.g.* various types of hydrides including the interstitial hydrides. Among the hydrides, sodium tetrahydroborate has a number of advantages over all other hydrides. It is a compound of known composition which can be made to liberate a stoicheiometric amount of hydrogen, is stable under ordinary storage conditions, and does not undergo accidental violent reaction.

Schlesinger *et al.* recognized the potential usefulness of $NaBH_4$ as a hydrogen generator. In the early 1950s they carried out extensive but qualitative investigations of its hydrolysis.[1] Subsequent structural,[2] spectroscopic,[3–5] and polarographic[6] studies indicated that the overall hydrolytic reaction is best represented as in equation (1). In alkaline

$$BH_4^- + 4H_2O \longrightarrow B(OH)_3 + OH^- + 4H_2 \quad (1)$$

solution tetrahydroxoborate is the predominant species [equation (2)]. The overall equilibrium in aqueous solution

$$B(OH)_3 + OH^- \longrightarrow B(OH)_4^- \quad (2)$$

may be represented by[7] equation (3) where $K = 110$ dm^6 mol^{-2}.

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \quad (3)$$

Schlesinger *et al.*[1] observed that at room temperature in an unbuffered medium or in the absence of an acidic accelerator the hydrolysis (1) is extremely restricted, and only a small percentage of the theoretically available hydrogen is liberated. The solution pH was found to be the limiting parameter. They studied qualitatively the accelerating effects of many acids: inorganic protic acids, oxalic acid, succinic acid, phosphorus pentoxide, aluminium chloride, and B_2O_3. Organic polyfunctional acids were found to be efficient accelerators, but the reaction became uncontrollable. They attempted to establish a qualitative correlation between the efficiency of the accelerator and its acid strength. Their choice of accelerator was B_2O_3. However, an amount of this oxide equal to the amount of BH_4^- was required to give a nearly theoretical yield of hydrogen. The objective of our investigation was to quantify this potentially important hydrogen-generating hydrolytic reaction.

In their pioneering studies, Schlesinger *et al.* also studied qualitatively the effects of various transition-metal salts and many typical metal catalysts, primarily the transition metals, on the rate of hydrolysis of $NaBH_4$. Since these initial observations, several other investigators[8–13] have studied the acceleration of BH_4^- hydrolysis by transition-metal salts. However, the results are frequently inconclusive and contradictory. It has been claimed that acceleration of the rate of hydrolysis of $NaBH_4$ is due to metal borides formed *in situ*. The second objective of our study was thus to clarify metal salt-, metal boride-, or metal-induced acceleration of BH_4^- hydrolysis, and to develop a simple model and rate equation as in the case of acid hydrolysis.

Heterogeneous catalysis offered a number of possible advantages over homogeneous acid-catalysed hydrolysis: it was expected that it would be independent of solution pH over a wide range, that hydrolysis would proceed smoothly without any foaming, and that the catalyst would be reusable.

Experimental

Effects of Acids.—There are several important differences between our technique and that employed by Schlesinger *et al.*[1] In our experiments the accelerator and the tetrahydroborate were components of a homogeneous solution. We measured the extent of hydrolysis by an iodometric method[14] which is easier, more reliable, and more reproducible than the gas volumetry used previously.[1]

Distilled, deionized water (50 cm^3) containing a known molar amount of an acid accelerator was added to a sample (189.2 mg, 5.0 mmol) of sodium tetrahydroborate powder in an open Erlenmeyer flask; the mixture was stirred and the reaction allowed to proceed for a specified period of time at 21.7 °C. The kinetic experiments in the carbonate buffer were also carried out in an essentially similar fashion except that they were conducted at three different temperatures: 0, 21, and 35 °C. All reactants, reaction mixtures, and reaction vessels were thermostatted (±0.05 °C).

Hydrolysis was quenched instantaneously by the addition of a known excess of potassium iodate, and unhydrolysed BH_4^- was determined iodometrically[14] according to reactions (4)—(6) using the normal precautions for such determinations.

$$3BH_4^- + 4IO_3^- \longrightarrow 4I^- + 3B(OH)_4^- \quad (4)$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \quad (5)$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^- \quad (6)$$

Table 1. Accelerated hydrolysis of $NaBH_4$ (initial concentration 0.1 mol dm^{-3})

		2.5 min			5.0 min			7.5 min			10.0 min		
Mol % accelerator	$[H^+]$	% Hydrolysis	$pNaBH_4$	pH	% Hydrolysis	$pNaBH_4$	pH	% Hydrolysis	$pNaBH_4$	pH	% Hydrolysis	$pNaBH_4$	pH
(*a*) Perchloric acid, 21.7 °C													
0	0.000	12.9	1.060	10.24	13.6	1.063	10.30	14.3	1.067	10.34	14.8	1.070	10.36
1	0.001	15.2	1.072	9.70	16.5	1.078	9.84	17.6	1.084	9.90	18.3	1.088	9.93
2	0.002	17.6	1.084	9.60	19.0	1.092	9.75	20.4	1.099	9.82	21.5	1.105	9.85
3	0.003	19.9	1.096	9.54	21.6	1.106	9.69	23.1	1.114	9.76	24.6	1.122	9.80
4	0.004	22.2	1.109	9.49	24.3	1.121	9.63	26.0	1.130	9.70	27.5	1.139	9.75
5	0.005	24.5	1.122	9.44	26.6	1.134	9.58	28.4	1.145	9.66	30.1	1.155	9.71
10	0.010	34.7	1.185	9.34	37.4	1.203	9.47	39.9	1.221	9.54	42.1	1.238	9.58
20	0.020	51.0	1.310	9.15	54.5	1.342	9.25	58.0	1.376	9.32	60.5	1.403	9.37
30	0.030	63.2	1.434	9.01	67.0	1.481	9.09	70.6	1.531	9.16	73.0	1.568	9.21
40	0.040	72.4	1.558	8.89	76.0	1.619	8.96	79.3	1.684	9.01	81.4	1.732	9.05
50	0.050	79.2	1.681	8.77	82.4	1.755	8.83	85.4	1.836	8.88	87.2	1.894	8.91
(*b*) Potassium hydrogenphthalate, 21.7 °C													
0	0.000	12.9	1.060	10.24	13.6	1.063	10.30	14.3	1.067	10.34	14.8	1.070	10.36
1	0.001	15.7	1.074	9.55	17.3	1.083	9.72	18.4	1.088	9.80	19.0	1.092	9.89
2	0.002	18.3	1.088	9.49	20.3	1.098	9.66	21.5	1.105	9.74	22.3	1.110	9.82
3	0.003	20.4	1.099	9.43	22.5	1.111	9.60	24.2	1.120	9.69	25.5	1.128	9.75
4	0.004	22.5	1.110	9.40	24.7	1.123	9.56	26.6	1.134	9.65	28.1	1.143	9.71
5	0.005	24.2	1.120	9.38	26.6	1.134	9.52	28.2	1.144	9.61	29.8	1.154	9.67
10	0.010	33.4	1.177	9.27	37.3	1.203	9.39	39.3	1.217	9.48	40.9	1.228	9.57
20	0.020	48.2	1.286	9.10	52.2	1.320	9.24	54.8	1.345	9.31	57.2	1.369	9.37
30	0.030	59.9	1.396	8.98	63.7	1.441	9.12	66.9	1.480	9.18	70.0	1.523	9.23
40	0.040	69.8	1.520	8.87	73.8	1.581	9.00	77.5	1.648	9.05	80.6	1.712	9.09
50	0.050	78.6	1.670	8.76	83.0	1.770	8.88	85.8	1.847	8.92	88.5	1.938	8.96
(*c*) Oxalic acid, 21.7 °C													
0	0.000	12.9	1.060	10.24	13.6	1.063	10.30	14.3	1.067	10.34	14.8	1.070	10.36
1	0.002	18.7	1.090	9.50	20.3	1.098	9.66	21.6	1.106	9.75	22.9	1.113	9.81
2	0.004	23.8	1.112	9.42	26.0	1.130	9.57	27.8	1.142	9.66	29.6	1.152	9.71
3	0.006	28.5	1.146	9.35	30.9	1.160	9.51	32.9	1.173	9.59	34.7	1.185	9.65
4	0.008	32.7	1.172	9.33	35.2	1.188	9.47	37.4	1.204	9.54	39.1	1.216	9.59
5	0.010	36.9	1.200	9.30	39.7	1.219	9.44	42.1	1.238	9.50	44.0	1.251	9.53
10	0.020	54.1	1.338	9.17	57.6	1.373	9.29	60.7	1.406	9.34	62.5	1.425	9.38
20	0.040	75.1	1.604	8.91	78.4	1.665	9.00	81.6	1.735	9.04	82.8	1.766	9.07
30	0.060	86.6	1.872	8.64	89.2	1.964	8.72	91.3	2.062	8.74	92.2	2.110	8.75
(*d*) Oxalic acid													
1 [a]	0.002	19.7	1.095		21.5	1.105		23.2	1.115		24.7	1.123	
2 [a]	0.004	24.8	1.124		27.9	1.142		30.2	1.156		32.3	1.169	
4 [a]	0.008	34.7	1.185		38.0	1.208		41.3	1.231		44.3	1.254	
5 [b]	0.010	24.8	1.124		25.5	1.128		26.3	1.132		26.9	1.136	
10 [b]	0.020	40.8	1.227		42.2	1.238		43.4	1.247		44.3	1.254	
30 [b]	0.060	77.8	1.653		78.9	1.675		80.1	1.702		80.6	1.713	

[a] 35.0 °C. [b] 0.0 °C.

The unreacted amount (mg) of $NaBH_4$ was obtained from (mequiv. KIO_3 − mequiv. $Na_2S_2O_3$) × 4.729, and the percentage hydrolysis from [(189.2 − unreacted $NaBH_4$ in mg)/189.2] × 100.

Effect of Transition Metals and their Salts.—Several sets of experiments were performed. Distilled, deionized water (50 cm^3) containing a known amount of the metal salt MX_2 was added to a sample (189.2 mg, 5.0 mmol) of sodium tetrahydroborate powder in an Erlenmeyer flask. After a measured time, unreacted BH_4^- was determined iodometrically, and the percentage of hydrolysis was calculated.

The metals were prepared by the reduction of the corresponding metal(II) chloride with $NaBH_4$. The black precipitate of the metal was filtered off, repeatedly washed with copious volumes of hot water, and finally dried at 110 °C. The dry metal was ground to a fine powder and stored in a desiccator. Only freshly prepared metals were used in the hydrolysis experiments. Separate analytical studies confirmed that the purity of the metals prepared as described was >99.99%, and the metals did not contain any analytically detectable amount of boron.

So-called nickel and cobalt borides were prepared according to the method of Schlesinger *et al.*[1] However, the boron content of the precipitates was not determined.

Sodium tetrahydroborate (5 mmol) was dissolved in 2 mol dm^{-3} sodium hydroxide (50 cm^3), or a carbonate buffer, and a weighed amount of metal (or metal boride) was immediately added. The mixture was stirred with a magnetic stirrer. The hydrolysis was quenched at a specified time by the addition of an excess of potassium iodate. The black metal was immediately filtered off and washed with a minimum volume of water. The filtrate and washings were immediately neutralized with sulphuric acid, and unreacted BH_4^- determined

Table 2. Values of the constants *A* and *B* of equation (7)

		θ_c/°C		
t/min		0.0	21.7	35.0
2.5	*A*	1.017	1.058	1.064
	B	10.6(0)	12.8(3)	15.2(2)
5.0	*A*	1.019	1.064	1.074
	B	11.0(0)	14.4(3)	16.9(4)
7.5	*A*	1.019	1.067	1.077
	B	11.4(0)	15.8(4)	19.4(2)
10.0	*A*	1.022	1.071	1.081
	B	11.5(0)	16.9(2)	21.8(2)

Numbers in parentheses indicate the uncertainty in the last digit. Uncertainties in *B* terms were computed from non-weighted least-squares calculations.

iodometrically. All reagents, reactants, and reaction mixtures were appropriately thermostatted.

Results and Discussion

Effect of Acids.—The experimental results are summarized in Table 1. The negative logarithm of the amount (mol dm^{-3}) of unreacted sodium tetrahydroborate (p$NaBH_4$) was found to be directly proportional to the mol % of acid initially present in solution at constant reaction time. From plots of p$NaBH_4$ *vs.* mol % acid accelerator, it was found that diprotic oxalic acid was twice as efficient an accelerator as the monoprotic acids. Conversion of the molar accelerator concentration into molar proton concentration yielded nearly congruent (within the range of experimentation) plots for all acid accelerators for constant times. For example, 5 mol % oxalic acid was found to be as efficient an accelerator (within the range of experimentation) as 10 mol % perchloric acid or potassium hydrogenphthalate [*cf.* Table 1(*a*)—(*d*)].

Unbuffered acid-accelerated hydrolysis (at constant time and temperature) of $NaBH_4$ can be described by the simple linear relationship (7). The values of *A* and *B* are given in

$$\mathrm{pNaBH_4} = A + B[\mathrm{H^+}] \tag{7}$$

Table 2; they describe the general acid data as functions of proton concentration at zero time, and represent only a partial solution to a least-squares fit of the data. The parameters *A* and *B* do not account for the large change in pH and the extent of hydrolysis from time zero to 2.5 min.

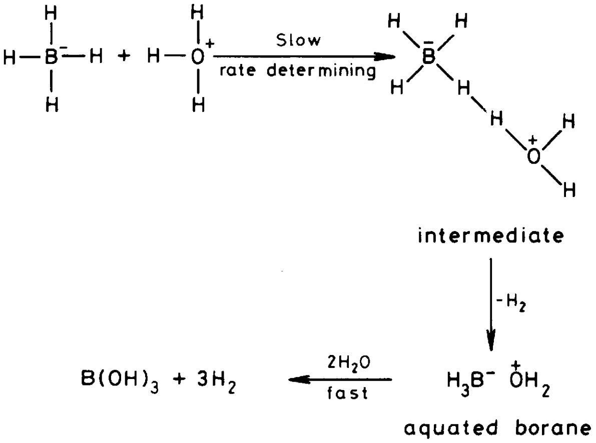
Independent pH measurements showed a rapid initial rise followed by a slower change. Obviously, pH and p$NaBH_4$ are related by a complex set of equilibria, however within the range of our experiments it was possible to express the relationship by a simple empirical equation: pH + p$NaBH_4$ = 10.7 ± 0.2. At constant temperature, the time dependence of factor *B* in equation (7) can be empirically written as in (8).

$$B = C + Dt \tag{8}$$

Within the experimental parameters of this study, a model for acid acceleration in unbuffered media (utilized for fuel-cell work) is generated by combining equations (7) and (8).

$$\mathrm{pNaBH_4} = E + F[\mathrm{H^+}] + G[\mathrm{H^+}]t \tag{9}$$

Linear regression of the entire set of acid data (21.7 °C, non-weighted) yields the values $E = 1.065 \pm 0.003$, $F = 11.3 \pm 0.2$ dm^3 mol^{-1}, and $G = 0.59 \pm 0.03$ dm^3 mol^{-1} min^{-1}.



Scheme 1.

A comparison between average experimental and least-squares fitted calculated hydrolysis data is given in Table 3. A rate law can be generated by mathematical manipulation [equations (10) or (11)]. Differentiating with respect to time

$$-\log_{10}[\mathrm{NaBH_4}] = E + F[\mathrm{H^+}] + G[\mathrm{H^+}]t \tag{10}$$

$$-\ln[\mathrm{NaBH_4}] = \left(\frac{1}{2.303}\right)\{E + F[\mathrm{H^+}] + G[\mathrm{H^+}]t \tag{11}$$

yields expressions (12)—(14). The second-order rate law

$$\frac{-\mathrm{d}(\ln[\mathrm{NaBH_4}])}{\mathrm{d}t} = \left(\frac{1}{2.303}\right)G[\mathrm{H^+}] \tag{12}$$

$$-\left(\frac{1}{[\mathrm{NaBH_4}]}\right)\frac{\mathrm{d}[\mathrm{NaBH_4}]}{\mathrm{d}t} = \left(\frac{G}{2.303}\right)[\mathrm{H^+}] \tag{13}$$

$$\frac{-\mathrm{d}[\mathrm{NaBH_4}]}{\mathrm{d}t} = \left(\frac{G}{2.303}\right)[\mathrm{H^+}][\mathrm{NaBH_4}] \tag{14}$$

is consistent with the bimolecular mechanism proposed by Gardiner and Collat (Scheme 1).[15] Hydrolysis of $NaBH_4$ in a carbonate buffer (*cf.* Table 4) seemed to obey pseudo-first-order kinetics. Table 5 lists the values of rate constants calculated from our experimental data and a selection of values obtained by other investigators in different buffered media. The Arrhenius activation energy calculated from our data was 58 ± 4 kJ mol^{-1}, and those calculated by others ranged from 30 to 96 kJ mol^{-1}. The majority of the reported values are within a few kilojoules of our value.

Effect of Transition Metals and their Salts.—Schlesinger *et al.*[1] provided no explanation for the discrepant catalytic properties of metal salts and metals (or metal borides). We found that the catalytic activity of metal salts was dependent on the cation only (Cu^{2+}, Co^{2+}, or Ni^{2+}), and was independent of the anion (Cl^-, NO_3^-, or $MeCO_2^-$).

Qualitatively, the nickel(II) salts appeared to be the best accelerators of the hydrolysis of $NaBH_4$. On a molar basis, nickel(II) and cobalt(II) salts demonstrated a much greater catalytic efficiency than the monoprotic acids. Our preliminary studies included salts of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II}. However, it appeared that those of Mn^{II} and Fe^{II} have little catalytic effect, and investigations with them were not pursued. Except for the copper(II) salts, plots of p$NaBH_4$ (unreacted) *vs.* initial mol % salt were non-linear (*cf.*, Figures 1—3). Furthermore, these plots could not be transformed into

Table 3. General acid acceleration of hydrolysis of $NaBH_4$ (0.1 mol dm^{-3}) at 21.7 °C: comparison between average experimental and least-squares fit calculated values (in parentheses)

$[H^+]$/mol dm^{-3}	2.5 min		5.0 min		7.5 min		10.0 min	
	pBH_4	% Hydrolysis	pBH_4	% Hydrolysis	pBH_4	% Hydrolysis	pBH_4	% Hydrolysis
0	1.060 (1.065)	12.9 (13.9)	1.063 (1.065)	13.6 (13.9)	1.067 (1.065)	14.3 (13.9)	1.070 (1.065)	14.8 (13.9)
0.001	1.073 (1.078)	15.5 (16.4)	1.080 (1.079)	16.9 (16.7)	1.086 (1.081)	18.0 (17.0)	1.090 (1.082)	18.7 (17.3)
0.002	1.087 (1.091)	18.2 (18.8)	1.096 (1.094)	19.9 (19.4)	1.103 (1.096)	21.2 (19.9)	1.109 (1.100)	22.2 (20.5)
0.003	1.098 (1.103)	20.2 (21.2)	1.108 (1.108)	22.0 (22.0)	1.117 (1.123)	23.6 (22.8)	1.125 (1.117)	25.0 (23.6)
0.004	1.112 (1.116)	22.8 (23.5)	1.125 (1.122)	25.0 (24.5)	1.135 (1.128)	26.8 (25.5)	1.145 (1.134)	28.4 (26.5)
0.005	1.121 (1.128)	24.3 (25.7)	1.134 (1.136)	26.6 (26.9)	1.144 (1.144)	28.3 (28.2)	1.154 (1.151)	30.0 (29.4)
0.006	1.146 (1.142)	28.5 (27.8)	1.161 (1.150)	30.9 (29.3)	1.173 (1.159)	32.9 (30.7)	1.185 (1.168)	34.7 (32.1)
0.008	1.172 (1.167)	32.7 (32.0)	1.188 (1.179)	35.2 (33.8)	1.204 (1.191)	37.4 (35.6)	1.216 (1.203)	39.1 (37.3)
0.010	1.187 (1.193)	35.0 (35.8)	1.208 (1.208)	38.1 (38.0)	1.225 (1.222)	40.4 (40.1)	1.239 (1.237)	42.3 (42.1)
0.02	1.311 (1.320)	51.1 (52.2)	1.345 (1.350)	54.8 (55.3)	1.375 (1.379)	57.8 (58.3)	1.399 (1.409)	60.1 (61.0)
0.03	1.415 (1.448)	61.5 (64.3)	1.460 (1.492)	65.4 (67.8)	1.505 (1.537)	68.7 (70.9)	1.545 (1.581)	71.5 (73.8)
0.04	1.559 (1.576)	72.4 (73.4)	1.620 (1.635)	76.0 (76.8)	1.687 (1.694)	79.5 (79.8)	1.736 (1.753)	81.6 (82.3)
0.05	1.675 (1.703)	78.9 (80.2)	1.762 (1.777)	82.7 (83.3)	1.841 (1.851)	85.6 (85.9)	1.916 (1.925)	87.9 (88.1)
0.06	1.872 (1.831)	86.6 (85.2)	1.964 (1.919)	89.2 (88.0)	2.062 (2.008)	91.3 (90.2)	2.110 (2.097)	92.2 (92.0)

Table 4. Hydrolysis of $NaBH_4$ (0.1 mol dm^{-3}) in carbonate (HCO_3^-–CO_3^{2-}) buffer, pH 10.7 (I = 0.31 mol dm^{-3})

0.0 °C			21.0 °C			35.0 °C		
t/min	$pNaBH_4$	% Hydrolysis	t/min	$pNaBH_4$	% Hydrolysis	t/min	$pNaBH_4$	% Hydrolysis
10	1.008	2.0	2.5	1.009	2.0	1	1.022	5.0
20	1.017	3.8	5.0	1.026	5.7	2	1.032	7.1
30	1.033	7.3	7.5	1.036	7.9	3	1.058	12.5
40	1.038	8.4	10.0	1.044	9.5	4	1.072	15.2
50	1.041	9.0	12.5	1.054	11.8	5	1.085	17.8
60	1.056	12.0	15.0	1.065	13.9	6	1.092	19.2
70	1.061	13.2	17.5	1.069	14.7	7	1.111	22.5
80	1.064	13.7	20.0	1.077	16.2	8	1.127	25.4

Time-dependent equations: 0.0 °C $pNaBH_4 = 1.003 + (8.1 \times 10^{-4})\,t$
21.0 °C $pNaBH_4 = 1.005 + (3.8 \times 10^{-3})\,t$
35.0 °C $pNaBH_4 = 1.008 + (1.48 \times 10^{-2})\,t$

Table 5. Rate constants for the hydrolysis of $NaBH_4$ in buffered media (pseudo-first-order reaction)

Rate constant K/dm^3 mol^{-1} s^{-1}	θ_c/°C	Buffer	Ref.
$(1.4 \pm 0.8) \times 10^{-5}$	0	Carbonate	This study
$(6.3 \pm 0.3) \times 10^{-5}$	22	Carbonate	This study
$(2.5 \pm 0.1) \times 10^{-4}$	35	Carbonate	This study
$(9 \pm 4) \times 10^{-5}$	25	Carbonate	[a]
$(1.5 \pm 0.4) \times 10^{-3}$	25	Ammonia	[b]
$(2.3 \pm 0.2) \times 10^{-4}$	25	Phosphate	[b]

[a] R. E. Davis and C. G. Swain, *J. Am. Chem. Soc.*, 1960, **82**, 5949.
[b] W. H. Stockmeyer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, 1961, **65**, 1076.

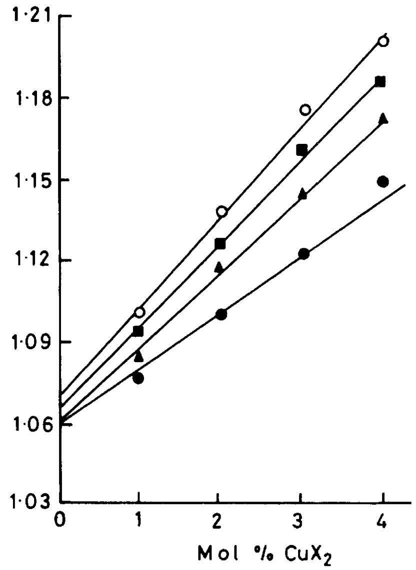


Figure 1. CuX_2-Accelerated hydrolysis of $NaBH_4$ (0.1 mol dm^{-3}) at 21.4 °C. Reaction time: 2.5 (●), 5.0 (▲), 7.5 (■), or 10.0 min (○)

a single composite plot representing general metal salt catalysis as in the case of acid-catalysed hydrolysis. We believe that these anomalous catalytic properties of the metal salts led to much of the confusion in the earlier studies.

Consideration of reaction (15) and the following reactions

$$BH_4^- + 4M^{2+} + 3H_2O \longrightarrow B(OH)_3 + 4M^0 + 7H^+ \quad (15)$$

helps to explain some of the discrepancies of the catalytic activities of the metal salts. First, the speed and the mechanism of reduction of the metal salt is not the same for all the metals (Co, Ni, and Cu). Secondly, there is simultaneous catalysis

$$BH_4^- + H^+ + 3H_2O \longrightarrow B(OH)_3 + 4H_2 \quad (16)$$

[equation (16)] by the protons generated in the reduction reaction. Finally, small but measurable instantaneous hydrolysis of the metal salt itself contributes to the complexity of the overall catalytic property of the metal [equations (17) and

Table 6. Metal-salt acceleration of the hydrolysis of $NaBH_4$ (0.1 mol dm^{-3}) at 21.6 °C

(*a*) CuX_2*

CuX_2		Calculated H^+ production		$pNaBH_4$	
mol %	mol dm^{-3}	mmol	mmol dm^{-3}	Exptl.	Calc.
1	0.001	0.0875	1.75	1.082	1.088
2	0.002	0.1750	3.50	1.104	1.109
3	0.003	0.2625	5.25	1.127	1.132
4	0.004	0.3500	7.00	1.149	1.155

(*b*) Comparison between average experimental and least-squares fit calculated values (in parentheses) of pBH_4

CoX_2					
mol %	mol dm^{-3}	2.5 min	5.0 min	7.5 min	10.0 min
1	0.001	1.078 (1.080)	1.088 (1.092)	1.098 (1.104)	1.106 (1.117)
2	0.002	1.112 (1.112)	1.134 (1.136)	1.156 (1.162)	1.180 (1.189)
3	0.003	1.144 (1.144)	1.178 (1.182)	1.218 (1.223)	1.264 (1.266)
4	0.004	1.176 (1.176)	1.213 (1.229)	1.290 (1.286)	1.374 (1.349)

NiX_2					
mol %	mol dm^{-3}	2.5	5.0	7.5	10.0
1	0.001	1.196 (1.241)	1.237 (1.264)	1.271 (1.287)	1.299 (1.311)
2	0.002	1.360 (1.283)	1.425 (1.331)	1.477 (1.383)	1.570 (1.441)
3	0.003	1.420 (1.326)	1.500 (1.403)	1.570 (1.492)	1.626 (1.600)
4	0.004	1.458 (1.370)	1.546 (1.480)	1.621 (1.620)	1.691 (1.815)

* Reaction time 2.5 min.

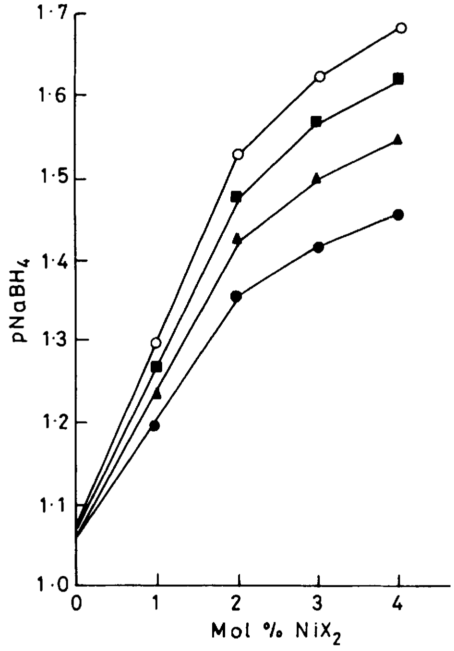


Figure 2. NiX_2-Accelerated hydrolysis of $NaBH_4$. Details as in Figure 1

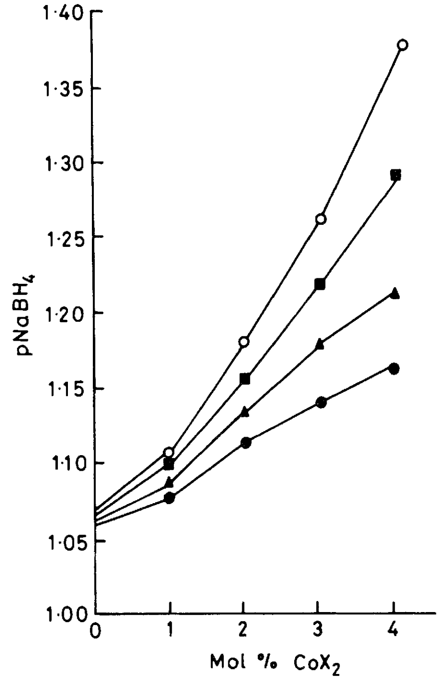


Figure 3. CoX_2-Accelerated hydrolysis of $NaBH_4$. Details as in Figure 1

$$M^{2+} + 2H_2O \longrightarrow M(OH)_2 + 2H^+ \quad (17)$$

$$BH_4^- + 4M(OH)_2 \longrightarrow B(OH)_4^- + 4M^0 + 4H_2O \quad (18)$$

(18)]. However, the effect of the last two processes on the overall catalysis is likely to be insignificant. Both reactions (15) and (16) proceed nearly to completion; therefore, the overall hydrogen generation in the presence of metal salts is simultaneously metal and acid catalysed.

Copper(II) salts behaved like an acid accelerator (*cf.* Figure 1); there seemed to be no metal catalysis. $pNaBH_4$ (unreacted) was calculated using equation (7), assuming that reduction (15) was complete. Excellent agreement [*cf.* Table 6(*a*)] between the calculated and experimental values of $pNaBH_4$ confirmed the lack of catalytic activity of metallic copper. With NiX_2 the rate of hydrolysis showed signs of levelling off after an initial rapid increase in the rate with increasing concentration of NiX_2 (*cf.* Figure 2), whereas with

CoX_2 the rate continued to increase with increasing concentration of CoX_2 (*cf.* Figure 3).

It was possible to calculate the extent of proton-catalysed hydrolysis at 21.7 °C with the help of equation (7) or (9). Subtracting these calculated quantities from the total metal salt-catalysed (experimental) hydrolysis, the percentage of metal-catalysed hydrolysis, and hence $pNaBH_4$ (unreacted) for the metal only, was obtained.

The rate law for metal salt-catalysed hydrolysis of $NaBH_4$ in unbuffered medium can be written as in equation (19).

$$-d[BH_4]/dt = (K_{H^+})[BH_4^-][H_3O^+] + K_M \qquad (19)$$

Therefore, the catalytic effect of the metal salts can be mathematically represented as a combination of two least-squares-fitted equations of the type (20). Substitution of F and

$$pNaBH_4 = E + F[H^+] + G[H^+]t + p\{[BH_4^-]_0 - I[MX_2]t\} - p(NaBH_4)_0 \qquad (20)$$

G with known values, of the calculated proton concentration due to metal reduction, and of other known quantities, finally yields a model equation of the form (21). The constant H is

$$pNaBH_4 = H + 19.775[MX_2] + 1.0325[MX_2]t - \log\{0.1 - It\,[MX_2]\} - 1 \qquad (21)$$

dependent on the pK_a of HX and the concentration of MX_2 in the solution; I is a function of the metal surface area. Linear regression of the entire data set for each metal yielded values of H and I. Since metallic copper exhibits no surface catalysis, $I_{Cu} = 0$, and the model reduces to the equation for acid acceleration. The values of H and I at 21.7 °C are as follows: $H_{Co} = 1.048 \pm 0.004$, $I_{Co} = (8.5 \pm 0.2) \times 10^{-1}$ dm^3 mol^{-1} min^{-1}; $H_{Ni} = 1.20 \pm 0.03$, $I_{Ni} = 1.70 \pm 0.07$ dm^3 mol^{-1} min^{-1}.

A comparison of average experimental and least-squares fitted calculated hydrolysis data is given in Table 6(*b*). The metal (surface)-catalysed hydrolysis of $NaBH_4$ obeys zero-order kinetics [equations (22)].

$$-d[BH_4^-]/dt = K_M \qquad (22)$$

One of the objectives of our investigation was the elucidation of the controversy regarding the actual catalyst, the metal or the metal boride. In our studies we found that nickel and cobalt borides prepared according to the method of Schlesinger *et al.*[1] exhibited the same catalytic activities as the metals prepared by reduction of the metal chlorides with $NaBH_4$. Other investigators have found that the presumed nickel boride has the same catalytic activity as Raney nickel towards several reactions: general hydrogenation,[16] isomerization,[8] desulphurization,[17] methanation of carbon monoxide,[9] decomposition of formates, and oxidation of methanol.[18] Structural studies [8-13] of these borides yielded contradictory data.

From a consideration of solution thermodyanamics (redox potentials), the formation of true metal borides in aqueous solutions seems almost impossible. The theoretical free energies of formation of transition metals by BH_4^- reduction of their salts in aqueous solution range approximately between 800 and 1 200 kJ mol^{-1}, whereas the metal borides are formed under anhydrous conditions at high temperature. However, it is likely that some BH_4^- and H_2 were absorbed by the metal, and were eventually converted into B atoms and inserted in the metal lattice during the drying process. It is interesting to note that unusually high drying temperatures (above 700 °C in some cases) were used in most preparations.

Table 7. Rate constants for metal catalysed hydrolysis of $NaBH_4$ (0.1 mol dm^{-3})

(*a*) Cobalt			
mg	mol %	θ_c/°C	k_{Co}/mol dm^{-3} min^{-1}
15	5.09 [a]	0.0	$(2.5 \pm 0.2) \times 10^{-4}$
20	6.79 [a]	0.0	$(3.2 \pm 0.3) \times 10^{-4}$
25	8.48 [a]	0.0	$(6.0 \pm 0.3) \times 10^{-4}$
	1 [b]	21.6	$(5.3 \pm 0.1) \times 10^{-4}$
	2 [b]	21.6	$(1.19 \pm 0.02) \times 10^{-3}$
	3 [b]	21.6	$(2.00 \pm 0.03) \times 10^{-3}$
	4 [b]	21.6	$(3.05 \pm 0.09) \times 10^{-3}$
15	5.09 [a]	21.8	$(4.3 \pm 0.2) \times 10^{-3}$
20	6.79 [a]	22.1	$(5.8 \pm 0.3) \times 10^{-3}$
25	8.48 [a]	22.0	$(7.7 \pm 0.2) \times 10^{-3}$
15	5.09 [a]	35.0	$(1.05 \pm 0.05) \times 10^{-2}$
20	6.79 [a]	35.0	$(1.6 \pm 0.1) \times 10^{-2}$
25	8.48 [a]	35.0	$(2.02 \pm 0.09) \times 10^{-2}$

(*b*) Raney nickel [a]			
mg	mol %	θ_c/°C	$k_{R\text{-}Ni}$/mol dm^{-3} min^{-1}
20	6.81	0.0	$(2.8 \pm 0.2) \times 10^{-4}$
25	8.52	0.0	$(3.4 \pm 0.3) \times 10^{-4}$
30	10.22	0.0	$(6.9 \pm 0.4) \times 10^{-4}$
20	6.81	21.0	$(1.2 \pm 0.1) \times 10^{-3}$
25	8.52	21.0	$(2.1 \pm 0.1) \times 10^{-3}$
30	10.22	21.0	$(3.9 \pm 0.2) \times 10^{-3}$
20	6.81	35.0	$(4.5 \pm 0.2) \times 10^{-3}$
25	8.52	35.0	$(9.8 \pm 0.5) \times 10^{-3}$
30	10.22	35.0	$(1.95 \pm 0.09) \times 10^{-2}$

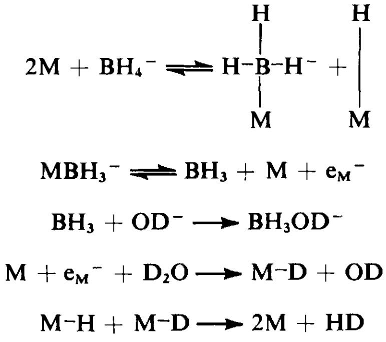
(*c*) Nickel			
mg	mol %	θ_c/°C	k_{Ni}/mol dm^{-3} min^{-1}
15	5.11 [c]	0.0	$(1.21 \pm 0.08) \times 10^{-3}$
	1 [d]	21.5	$(1.7 \pm 0.1) \times 10^{-3}$
	2 [d]	21.5	$(1.59 \pm 0.09) \times 10^{-3}$
	3 [d]	21.5	$(1.5 \pm 0.1) \times 10^{-3}$
	4 [d]	21.5	$(1.39 \pm 0.09) \times 10^{-3}$
15	5.11 [c]	21.6	$(1.41 \pm 0.07) \times 10^{-3}$
15	5.11 [c]	35.0	$(3.6 \pm 0.2) \times 10^{-3}$

[a] Buffer = 2 mol dm^{-3} NaOH. [b] Calculated from CoX_2 data. [c] Calculated from carbonate buffer studies (pH = 10.7, I = 0.31 mol dm^{-3}). [d] Calculated from NiX_2 data.

Zero-order rate constants for Co, Ni, and Raney nickel are compiled in Table 7. Within experimental limits, the rate constants in the case of Co and Raney nickel seem to depend on catalyst surface area, and hence the kinetics may not be truly zero order. The rate constant for Ni as the catalyst seems to be independent of the surface area. Rate constants for the metal-catalysed reactions (Co only) were calculated from MX_2 (CoX_2) data, and they agree well with metal-only catalysed reactions [*cf.* Table 7(*a*)].

The activation energies of metal-catalysed hydrolysis (Co; 75; Ni, 71; Raney Ni, 63 kJ mol^{-1}) seem to be 25—30% higher than that of acid-catalysed homogeneous hydrolysis.

Holbrook and Twist [19] studied the kinetics of solvolysis of $NaBH_4$ catalysed by cobalt–boron and nickel–boron alloys in alkaline deuteriated water. From an analysis of the evolved gas (H_2/D_2), they proposed the mechanism in Scheme 2 for the zero-order kinetics with respect to the metal. This mechanism explains the zero-order kinetics in the presence of metal catalysts, as well as some of the anomalies. Non-elimination of BH_3 from metal sites will give rise to non-zero-order kinetics involving a complicated mechanism. If this mechanism is realistic, some MBH_3^- will be formed during



$$2M + BH_4^- \rightleftharpoons \begin{array}{c} H \\ | \\ H{-}B{-}H^- \\ | \\ M \end{array} + \begin{array}{c} H \\ | \\ | \\ | \\ M \end{array}$$

$$MBH_3^- \rightleftharpoons BH_3 + M + e_M^-$$

$$BH_3 + OD^- \longrightarrow BH_3OD^-$$

$$M + e_M^- + D_2O \longrightarrow M{-}D + OD^-$$

$$M{-}H + M{-}D \longrightarrow 2M + HD$$

Scheme 2.

reduction of a metal. Heat treatment would expel hydrogen leaving the B atoms in the metal lattice. These sites may act differently from the rest of the metal surface.

We note here that we have successfully used hydrogen generated by catalytic hydrolysis of $NaBH_4$ for driving a H_2/air fuel cell. However, the eventual success of this approach will depend upon developing a facile method of converting borate into tetrahydroborate. We are currently investigating this problem.

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