and washed several times with ether. The orange-colored crystals gave: Co, 6.82; water, 5.36 (calcd.: Co. 6.88; water, 5.25). Another preparation has been made by stirring 10 g. of the hexahydrate with three times the weight of pyridine, cooling and filtering. Ether was then stirred into the clear red filtrate until solid precipitated. The solid was filtered on a sintered surface, and rinsed with ether. The analysis, Co, 6.96; water, 5.69, corresponds to the formula $Co(ClO_4)_2 \cdot 6.84Py \cdot 2.68H_2O$, and indicates that under the precipitation procedure used water replaced a small portion of the pyridine in the crystals.

**$Co(ClO_4)_2 \cdot 9Py \cdot 2.5H_2O$.**—Crystalline $Co(ClO_4)_2 \cdot 7Py \cdot 2.5H_2O$ was dissolved in several volumes of pyridine diluted with benzene and additional benzene added to bring the concentration of pyridine down to 50%. Evaporation was allowed to proceed in a draft until a jelly-like mass had formed. More benzene–pyridine mixture (1:1) was added just sufficient to dissolve the solid, and then ether was slowly added until two liquid phases separated, a colorless supernatant and a cobalt-bearing lower phase. After separation, the lower liquid was set aside to evaporate. Solid which formed was separated on a sintered disk, as flaky light-orange crystals. An ether wash darkened their color to a salmon-orange. *Anal.* Calcd.: Co, 5.81; water, 4.44. Found: Co, 5.68; water, 4.55. On standing the crystals "sweated" pyridine. Another preparation in which the starting solid was dissolved in a smaller volume of pyridine–benzene mixture, so that phase separation occurred without the aid of ether, gave crystals which analyzed: Co, 5.76; water, 4.73. When the preparation is attempted by dissolving the starting solid in pyridine (without added benzene) and evaporating, a gelatinous solid slowly separates. Filtering on a sintered disk gives a wet, gummy preparation, which bleeds pyridine on standing. *Anal.* Co, 5.73; water, 5.02. Apparently from the undiluted pyridine the leaf-like crystals formed pack down so as to retain the mother liquor strongly.

**$Co(ClO_4)_2 \cdot 6Py \cdot 2H_2O$** (?).—When crystals of the 9-pyridine-$2.5H_2O$ compound that have bled pyridine were thoroughly dried by pressing between sheets of filter paper, the residual orange-pink colored solid showed Co, 7.74; water, 4.75. This corresponds to a formula $Co(ClO_4)_2 \cdot 5.91Py \cdot 2.01H_2O$. This may be fortuitous approximation to the hexapyridine–dihydrate formula, although the analogous $Co(NO_3)_2 \cdot 6NH_3 \cdot 2H_2O$ has been reported.[2]

**$Co(ClO_4)_2 \cdot 4Py \cdot 2H_2O$.**—Crystalline $Co(ClO_4)_2 \cdot 7Py \cdot 2.5H_2O$ was washed twice with chloroform, which partially dissolves the starting material and changes its appearance. The remaining orange-pink solid analyzed: Co, 9.62; water, 6.25. After the initial wash, the figures had been essentially the same. Theory for $Co(ClO_4)_2 \cdot 4Py \cdot 2H_2O$: Co, 9.66; water, 5.90. The product was then washed a number of times with alternate portions of chloroform and ether-absolute alcohol, and the light-pink solid showed Co, 10.00; water, 5.97. It therefore seems certain that the compound is as formulated, that the water is not present only because of mechanical entrapment and that the deviation of the analyses from theory is probably due to replacement of part of the pyridine by water in the reagents.

## Summary

1. Preparations of pyridinates and mixed pyridinate–hydrates of cobalt chloride, nitrate and perchlorate are described, and the relationships to the hydrates and ammoniates are discussed.

2. New compounds reported, or questionable compounds confirmed, include the hexa-, tetra-, tri- and dipyridinate, and the dihydrate–dipyridinate of cobaltous nitrate; hexa- and tetrapyridinate, and the tetrapyridine–dihydrate of cobaltous perchlorate, and crystalline cobaltous perchlorates containing, respectively, six pyridines–four water; seven pyridines–2.5 water; nine pyridines–2.5 water; and a possible six pyridine–two water solvate.

CHICAGO 80, ILL. RECEIVED MAY 10, 1950

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

# Kinetics of the Reaction of Lithium Borohydride in Aqueous Acid Solution[1,2]

BY MARTIN KILPATRICK AND C. DANA MCKINNEY, JR.

During a study of the kinetics of fast reactions evolving gases, some data were obtained on the relatively slow reaction between lithium borohydride and acidified water. As pointed out by Schlesinger,[3] when lithium borohydride is dissolved in water only a portion of the available gas is liberated and the solution becomes strongly alkaline. In acid solution the reaction is qualitatively much faster, and Davis, Mason and Stegeman[4] in their study of the heat of formation give the equation for the reaction as

$$LiBH_4 + HCl + 3H_2O \longrightarrow LiCl + H_3BO_3 + 4H_2 \quad (1)$$

Preliminary experiments with an apparatus similar to that used earlier[5] but equipped with a magnetic stirrer indicated that in some cases the volume change of the gas on adding lithium borohydride to water was negative. This effect was attributed to reaction with oxygen and was eliminated by carrying out experiments in an atmosphere of nitrogen. Upon adding lithium borohydride to a solution three normal in acid, the sudden surge of gas last two or three seconds. This is followed by a low increase in volume of gas. This was interpreted to mean that the first reaction produces diborane

$$LiBH_4 + HCl \longrightarrow LiCl + {}^1/_2B_2H_6 + H_2 \quad (2)$$

and the second is the slower hydrolysis of the diborane

$${}^1/_2B_2H_6 + 3H_2O \longrightarrow H_3BO_3 + 3H_2 \quad (3)$$

with the over-all reaction corresponding to equation (1).

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[1] Based upon a part of the thesis submitted by C. Dana McKinney, Jr. to the Graduate School of Illinois Institute of Technology in June, 1950, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This research was sponsored by the Office of Naval Research.

[3] Schlesinger and Brown, THIS JOURNAL, **62**, 3429 (1940).

[4] Davis, Mason and Stegeman, *ibid.*, **71**, 2775 (1949).

[5] Kilpatrick, *ibid.*, **48**, 2091 (1926).

The rate studies reported below are for reaction (2) using sulfuric instead of hydrochloric acid.

## Experimental Method

The bomb reactor, which will be described in detail elsewhere,[6] employs a mixer similar to that used in earlier studies in the senior author's laboratory,[7] based on the method of Hartridge and Roughton.[8]

The apparatus is shown in cross section in Fig. 1. Essentially it consists of two cylinders F and J whose floating pistons can be driven downward by gas pressure released from above. The reactants flow out at high speed (in 16 milliseconds) in two opposing jets, contacting and mixing at M. The bomb is equipped with a strain gage, the output of which is amplified and impressed on the vertical plates of a cathode-ray oscilloscope. The horizontal axis of the oscilloscope is a time base and the amplitude of the resulting trace which is photographed yields the change in pressure with time.

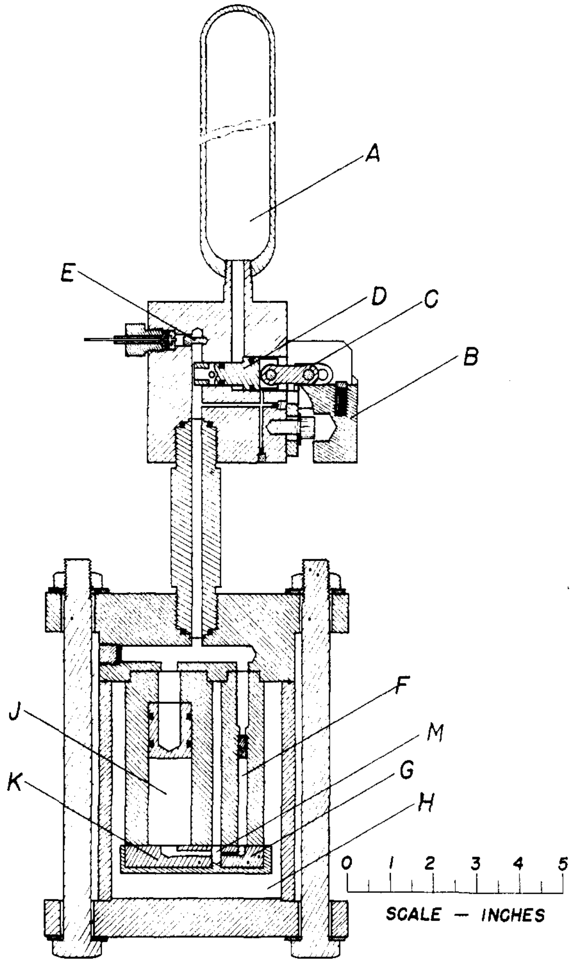

Fig. 1.—Cross sectional assembly drawing of pneumatic injector and bomb reactor: A, storage reservoir for driving gas; B, cocking block; C, valve toggle; D, rapid-acting valve; E, pressure-actuated contacts; F, small reactant cylinder; G, small injection plate; H, reaction bomb; J, large reactant cylinder; K, large injection plate; M, mixing zone.

It was found that an alkaline solution of lithium borohydride is quite stable and that 1 ml. of a solution 5 molar in lithium borohydride gave a convenient pressure rise when reacting with 25 ml. of sulfuric acid of different normalities, 1.24 to 3.10. The pressure rise corresponded to equation (2). The reactions were run at room temperature which ranged from 24 to 28°. It would have been preferable to use a strong monobasic acid but as the apparatus was constructed of stainless steel and as the use of perchloric acid was not considered advisable, sulfuric acid was used.

## Experimental Results

Figure 2 shows a plot on a logarithmic scale of the amplitude of the trace at complete reaction minus the amplitude at various times *vs.* time. This corresponds to the equation

$$k = \frac{1}{t} \ln \frac{\text{amp}_\infty}{\text{amp}_\infty - \text{amp}_t} = \frac{1}{t} \ln \frac{P_\infty}{P_\infty - P_t} \quad (4)$$

The linearity, along with the constancy of the slopes with varying concentration of borohydride, shows the reaction to be first order in borohydride in the presence of considerable excess of acid.

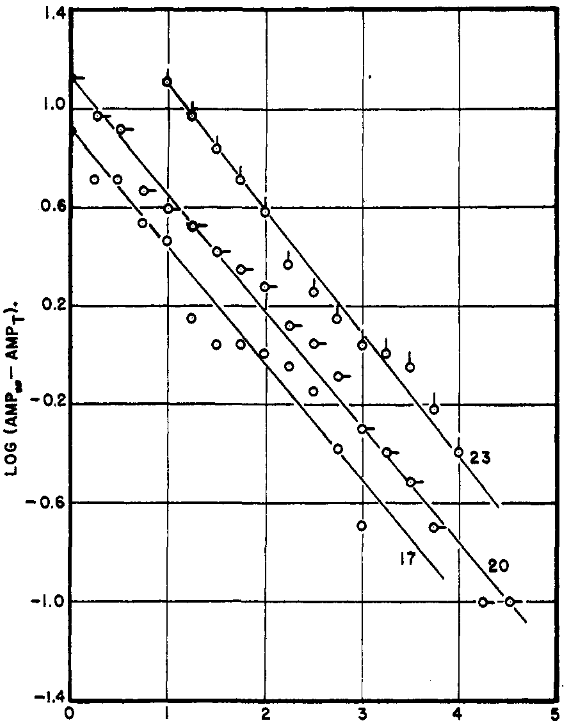

Fig. 2.—Velocity constant of lithium borohydride reaction. For the sake of clarity, the time axis for Run 23 has been shifted by one second.

The velocity constants can be calculated from the slopes of the lines in Fig. 2; however, such a method places undue emphasis on the evaluation of the amplitude of the trace at complete reaction. The method of Guggenheim[9] does not

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(6) McKinney and Kilpatrick, submitted to *J. Franklin Institute.*

(7) Chance, *J. Franklin Inst.*, **229**, 455 (1940); **229**, 613 (1940); **229**, 737 (1940).

(8) Hartridge and Roughton, *Proc. Roy. Soc.* (*London*), **A104**, 376 (1923).

(9) Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

require a knowledge of the value at completion of the reaction, and the velocity constants were computed by this method. The slopes were determined both graphically and by the method of least squares. The data are given in Table I.

TABLE I

VELOCITY CONSTANTS AT VARIOUS ACID CONCENTRATIONS

| $H_2SO_4$, $N$ | Graphical method $k_{obsd.}$, sec.$^{-1}$ | Least squares method $k_{obsd.}$, sec.$^{-1}$ | $t_{1/2}$, sec. |
|---|---|---|---|
| 1.24 | 0.61 | 0.55 | 1.26 |
| | .51[a] | .63[a] | 1.10 |
| | .82 | .72 | 0.98 |
| | .82[a] | .56[a] | 1.24 |
| | .46 | .43 | 1.61 |
| | .73[a] | .45[a] | 1.54 |
| | .61 | .56 | 1.21 |
| | .47 | .43 | 1.61 |
| | 0.59 ± 0.10 | 0.54 ± 0.09 | |
| 1.59 | 0.82[a] | 0.52[a] | 1.33 |
| | 0.64[a] | .46[a] | 1.51 |
| | 1.04[a] | .50[a] | 1.39 |
| | 0.84 | .88 | 0.79 |
| | .57 | .58 | 1.20 |
| | .69 | .64 | 1.08 |
| | .73 | .76 | 0.91 |
| | .77 | .80 | 0.87 |
| | 0.72 ± 0.07 | 0.73 ± 0.10 | |
| 2.59 | 1.29 | 1.28 | 0.53 |
| | 1.08 | 1.00 | .69 |
| | 1.21[a] | 0.86[a] | .81 |
| | 1.08 | 1.10 | .63 |
| | 1.27 | 1.24 | .56 |
| | 1.53[a] | 1.25[a] | .55 |
| | 1.24[a] | 0.80[a] | .87 |
| | 1.09 | 1.09 | .69 |
| | 1.16 ± 0.09 | 1.12 ± 0.11 | |
| 3.10 | 1.81 | 1.98 | 0.35 |
| | 2.26[a] | 3.03[a] | .23 |
| | 1.35 | 1.52 | .46 |
| | 1.88 | 1.87 | .37 |
| | 1.23 | 1.14 | .61 |
| | 1.32 | 1.44 | .48 |
| | 1.52 ± 0.22 | 1.59 ± 0.27 | |

[a] Results of this run rejected before computing average.

For the runs in which the Guggenheim method gives good linearity, the values for the slope of the line obtained graphically and by least squares are in good agreement. However, if the points are scattered about the line or the line curves, the slopes given by the two methods may differ considerably. The least squares method without a weighting factor weighs all points equally and the results by this method may be less accurate than those given by the graphical method. In all experiments where the results by the two methods differ by more than 15%, the values have been excluded from the average.

From the data given in Table I it can be seen that the observed velocity constant varies with the concentration of the sulfuric acid. If the reaction is first order with respect to both borohydride and hydrogen ion, equation (5) should hold

$$k_{obsd.} = k_2 C_{H_3O^+} \qquad (5)$$

where $k_2$ is the second order constant.

To test this equation the hydrogen ion concentrations were calculated using the values of the second dissociation constant from the data of Maranville[10] who measured the concentrations of the various species in sulfuric acid solutions by Raman spectra. The sulfuric acid concentrations were corrected for the amount of neutralization by the sodium hydroxide, and lithium borohydride was assumed to be completely dissociated in the calculation of the ionic strength. The data are summarized in Table II, and show that equation (5) is valid.

TABLE II

SUMMARY OF THE DATA

| $H_2SO_4$ $N$ | $H_3O^+$ $M$ | Graphical method $k_{obsd.}$ sec.$^{-1}$ | Graphical method $k_2$ l. mole$^{-1}$ sec.$^{-1}$ | Least squares method $k_{obsd.}$ sec.$^{-1}$ | Least squares method $k_2$ l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|---|
| 1.24 | 0.74 | 0.59 | 0.80 | 0.54 | 0.72 |
| 1.59 | 0.96 | 0.72 | .75 | 0.73 | .76 |
| 2.59 | 1.57 | 1.16 | .74 | 1.12 | .71 |
| 3.10 | 1.78 | 1.52 | .85 | 1.59 | .89 |
| | | | 0.79 ± 0.04 | | 0.77 ± 0.06 |

Lithium borohydride must have a water reaction but a plot of $k_{obsd.}$ *vs.* $C_{H_3O^+}$ for the series of experiments reported in Table II shows the intercept to be small. There is the possibility of reaction with the acid $HSO_4^-$ but the data cannot be of sufficient accuracy to test this point. The reaction measured went to completion in ten seconds, the heat of reaction amounting to 125 cal., which would mean a temperature rise of 5° in the liquid phase if no heat were transferred to the reactor, but the reaction is slow enough to permit some transfer of heat.

## Summary

The reaction of alkaline solutions of lithium borohydride with sulfuric acid solutions was studied.

The reaction was found to occur in two steps, the first involving the formation of diborane which was hydrolyzed in the second step.

The rate measured was that of the first step and the reaction was first order with respect to lithium borohydride and hydrogen ion.

CHICAGO 16, ILLINOIS RECEIVED JUNE 28, 1950

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(10) Maranville, Ph.D. Dissertation, University of Chicago, 1949.