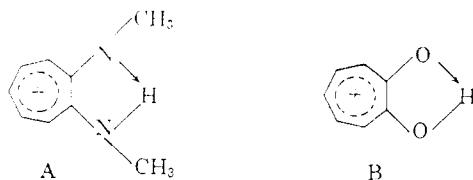
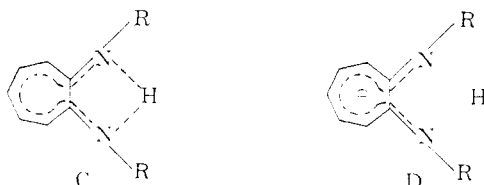


a form such as A, as has been done in the case of tropolone (B). In view of the predicted<sup>9</sup> and later demonstrated<sup>10,11</sup> resonance stabilization associated



with a conjugated 10- $\pi$  electron system in a carbocyclic system, it is attractive to assume that a 10- $\pi$  electron system around the periphery of the molecule is achieved in these compounds through hybridization of the  $\pi$ -electrons of the four formal double bonds with the pair of non-bonding electrons on nitrogen of the NHR substituent. Thus, the aminoimines are most nearly represented by C with possible contribution from D.



In confirmation of their more electronegative character, the aminoimines are more susceptible than tropolone to attack by electrophilic reagents.

**Acknowledgments.**—The author expresses his thanks to Drs. W. R. Brasen, H. E. Holmquist, and W. D. Phillips for helpful discussions.

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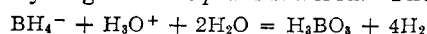
R. E. BENSON

RECEIVED OCTOBER 5, 1960

# GENERAL ACID CATALYSIS OF THE HYDROLYSIS OF SODIUM BOROHYDRIDE<sup>1,2</sup>

Sir:

Alkali borohydrides, widely used as reducing agents,<sup>3</sup> are stable in basic aqueous solution but liberate hydrogen as the  $pH$  is lowered. The rate of



hydrolysis is known from the work of Jensen,<sup>3,4</sup> Kilpatrick,<sup>5</sup> Pecsok<sup>6</sup> and J. B. Brown<sup>9,10</sup> to involve

(1) Supported in part by a postdoctoral fellowship to R. E. D. from the National Science Foundation, M.I.T., 1958–1959, and research grants from the National Science Foundation at M.I.T. and the Research Corporation at Purdue.

(2) Cf. R. E. Davis, C. L. Kibby and C. G. Swain, *This Journal*, **82**, 5950 (1960).

(3) "Sodium Borohydride and Potassium Borohydride, a Manual of Techniques," Metal Hydrides, Inc., Beverly, Mass., 1958.

(4) E. H. Jensen, "A Study on Sodium Borohydride with Special Reference to its Analytical Application in Organic Chemistry," Nyt Fordisk Forlag, Arnold Busch, Copenhagen, 1954.

(5) M. Kilpatrick and C. D. McKinney, Jr., *This Journal*, **72**, 5474 (1950). The rate measured seems to be the rate of evolution of hydrogen from a supersaturated solution and not the rate of decomposition of borohydride, since their rate constant is lower than Pecsok's by a factor of  $3 \times 10^5$ . The Setchenow equation<sup>6,7</sup> can be expanded into a power series to explain the apparent first-order dependence of

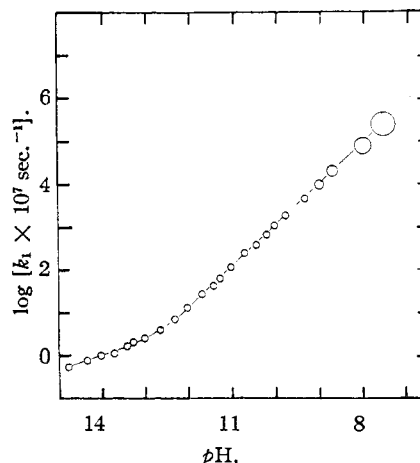


Fig. 1.—Hydrolysis of sodium borohydride in aqueous solution at 25.00°; plot of  $\log k_1 \times 10^7 \text{ sec.}^{-1}$  vs.  $pH$ , where  $-d[BH_4^-]/dt = k_1[BH_4^-]$ .

acid catalysis. The rate expression in dilute buffer solution is first order in hydronium ion over the  $pH$  range of 7.7 to 10.1, but at very high  $pH$  (12 to 14) the rate is less sensitive to hydronium ion concentration. The apparent order<sup>4,9,10</sup> decreases to about 0.4. Furthermore, the rate has been reported to depend upon the ionic strength and upon the anion component of the buffer solution. Freund<sup>11</sup> concluded that the rate-determining step for reduction of ferricyanide ion is the same as that for hydrolysis.

We consequently have searched for and found general acid catalysis. The studies of the hydrolysis as a function of  $pH$  were repeated and agree with the earlier work as shown in Fig. 1. In the present investigation the rate of hydrolysis of sodium borohydride was measured from  $pH$  7.6 to 14.8 at 25° under nitrogen. The borohydride concentration was measured volumetrically by the iodate method.<sup>12</sup> The buffers of Fig. 1 had 0.10  $M$  ionic strength from  $pH$  7.6 to 12.4 but higher above  $pH$  12.4 from the high concentration of NaOH. The  $pH$  range was covered by these buffers:  $KH_2PO_4$ -NaOH (7.6–8.1);  $H_3BO_3$ -NaOH (7.8–10.0);  $NaBO_2$ -HCl (9.0–10.0);  $NaBO_2$ - $Na_2CO_3$  (9.2–11.0);  $NaBO_2$ -NaOH (9.2–12.4),  $NaHPO_4$ -NaOH (11–12), and NaOH (>12). We attribute the change in slope above  $pH$  to general acid catalysis.<sup>13</sup> Thus the rate expression is

$$\frac{-d(BH_4^-)}{dt} = (BH_4^-) \sum_i \sum_j k_{ij}(HA_i)$$

where  $HA_i$  is a general acid. The value of  $K_{H_3O^+}$  rate of evolution on hydronium ion concentration over a small range of concentration.

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(9) J. B. Brown and M. Svensson, *ibid.*, **79**, 4241, 6581 (1957).

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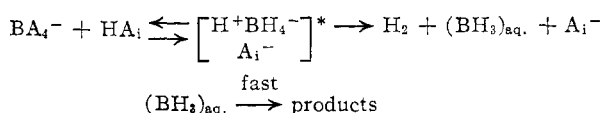
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(12) D. A. Lytle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

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is estimated from the straight line<sup>14</sup> from pH 7.6 to 12 as  $1.00 \pm 0.04 \times 10^6 M^{-1} \text{ sec.}^{-1}$  at  $\mu = 0.10$  and pH 10.0. It decreases with increasing ionic strength as predicted by the Brønsted-Christian-sen-Scatchard equation ( $z_A z_B = -1$ ). The value of  $k_{H_2O}$  is estimated as  $2 \pm 1 \times 10^{-9} M^{-1} \text{ sec.}^{-1}$ . The fact that the rate does not become completely independent of pH is ascribed to a small negative salt effect on the borohydride-water reaction. At a constant pH with 0.09 and 1.09 M sodium hydroxide solutions, where the water reaction predominates, the addition of sodium and potassium salts steadily decreases the rate. Lithium chloride gives a small acceleration. Variation of the buffer strengths at constant ionic strength permits assignment of  $k_{H_2PO_4^-}$  as  $1 \pm 4 \times 10^{-2} M^{-1} \text{ sec.}^{-1}$ ,  $k_{H_2BO_3}$  as  $1 \pm 5 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$  and  $k_{HCO_3^-}$  as  $9 \pm 4 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$ . Thus the Brønsted  $\alpha$  is about 0.8. The fact that  $\alpha$  is near unity and  $k_{H_2O}$  is so large means that general acid catalysis is difficult to observe.<sup>15</sup>

The hydrolysis in heavy water gives HD. Thus no exchange occurs between the hydride and the solvent, and an electronically unlikely  $BH_3$  intermediate of high symmetry is excluded. A mechanism consistent with the data is



Diborane can be prepared from borohydrides in concentrated sulfuric acid.<sup>16</sup> The borane also can be trapped as the trimethylamine adduct when lithium borohydride is treated with trimethylamine hydrochloride in anhydrous ether.<sup>17</sup>

(14) The best line through the points gives an order of  $0.92 \pm 0.03$  in hydronium ion.

(15) Thus at pH 9.24 in a borate buffer solution (0.05 M borax), 99% of the reaction is with  $H_3O^+$  and about 1% with the  $H_2BO_3$  present.

(16) H. G. Weiss and I. Shapiro, *THIS JOURNAL*, **81**, 6167 (1959).

(17) G. W. Schaeffer and E. R. Anderson, *ibid.*, **71**, 2143 (1949).

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RECEIVED SEPTEMBER 7, 1960

# AN INVERSE HYDROGEN ISOTOPE EFFECT IN THE HYDROLYSIS OF SODIUM BOROHYDRIDE<sup>1,2</sup>

Sir:

Kinetic study of the hydrolysis of sodium borohydride in aqueous buffers<sup>2</sup> suggested that cleavage of a B-H bond is the first step and the rate-determining step. In a further study,  $NaBD_4$  of 99% purity was prepared from  $B_2D_6$  and  $NaB(OCH_3)_4$  on a vacuum line with recrystallization from diglyme.<sup>3</sup> Its rate of decomposition was measured as before<sup>2</sup> in borate buffers under nitrogen. The results are reported in Table I.

(1) Supported in part by a research grant and a fellowship to C. K. from the Research Corporation. Mr. W. J. Wallace aided this study by material assistance in the synthesis of the deuterium compound.

(2) Cf. R. E. Davis and C. G. Swain, *THIS JOURNAL*, **82**, 5949 (1960).

(3) H. C. Brown, E. J. Mead and P. A. Tierney, *ibid.*, **79**, 5400 (1957).

TABLE I

HYDROLYSIS IN AQUEOUS BORATE BUFFERS AT  $25.00 \pm 0.01^\circ$

pH $\pm 0.02$	$\mu, M$	$NaBH_4$ $10^4 k_1, \text{ sec.}^{-1}^a$	$NaBD_4$ $10^4 k_1, \text{ sec.}^{-1}$	$k_H/k_D$
9.70	0.10	$1.74 \pm 0.02$	$2.62 \pm 0.02$	$0.67 \pm 0.02$
9.96	.05	$1.02 \pm .02$	$1.33 \pm .03$	$.77 \pm .03$
10.20	.10	$0.587 \pm .008$	$0.835 \pm .007$	$.70 \pm .03$
10.20 <sup>b</sup>	.10	$0.59 \pm .01$	$0.84 \pm .01$	$.70 \pm .03$

<sup>a</sup> Rate =  $k_1[BH_4^-]$  where  $k_1 = k_2[H_3O^+]$ . Limits given are standard deviations. Rate constants during a given run were constant to 85-90% reaction. <sup>b</sup> Experiments where infinite solutions were used again and isotopes crossed.

The purity of each material was tested kinetically for trace metal contamination.<sup>4</sup> The remaining solution after a borodeuteride run was used as the initial solution for a borohydride run. The other combination was also tried. The pH remained constant and the inverse isotope effect was identical; thus the borodeuteride is free from catalytic impurities.

The tritium isotope effects for alcoholyses of lithium borohydride and lithium aluminum hydride were reported by Kaplan and Wilzbach as  $k_H/k_T = 0.8-1.2$ .<sup>5</sup> Apparently experimental problems prevented their estimating the direction of the effect.

We ascribe the inverse isotope effect to a secondary isotope effect of the other hydrogen or deuterium atoms not undergoing the protonolysis reaction in the rate-determining step. There is a greater reluctance of HB- bonds to change to HB (uncharged) in aquated borane than that of DB- bonds to change to DB. The effect is analogous to the greater basicity and nucleophilicity of  $DO^-$  compared to  $HO^-$ .<sup>6</sup> Thus borodeuteride should be a stronger base than borohydride. The non-reacting hydrogen or deuterium atoms have more zero-point vibrational energy in the transition state than in the ground state.

As the tetrahedral borohydride forms a transition state which resembles one-half of the diborane molecule,<sup>2</sup> the normal B-H stretching vibrations ( $A_1(\nu_1)$ ) at  $2264 \text{ cm.}^{-1}$  become more like the B-H stretching frequencies of diborane which occur at  $2524 \text{ cm.}^{-1}$  ( $A_g(\nu_1)$ ).<sup>7,8,9</sup> Thus in loose terminology, the non-reacting B-H bonds stiffen in the transition state.

Some data on the isotope effect of boranes would seem to support this conclusion. The isotope effect of the hydrolysis of trimethylamine borane in 1.40 M hydrochloric acid at  $25^\circ$  is  $k_H/k_D = 1.05 \pm 0.02$ . Several reactions with diborane have isotope effects very close to unity. Apparently, it is the placing of the fourth deuterium atom on the boron which leads to an inverse isotope effect. The order of magnitude (0.7) is very comparable to the effect found in the hydroxide ions (0.6-0.7).

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