solubility of a gas to the concentration of electrolytes in solution. It is to be expected that the rate of attainment of equilibrium between the gas phase and solution will also obey an expression of this form. This is completely analogous to the quasi-thermodynamics used in the theory of absolute rates. Expanding the Setchenow equation into a power series gives an expression which will predict an apparent first-order dependence of the rate of evolution on the electrolyte concentration over a narrow range.

Jolly[66] has recently investigated the hydrolysis of borohydride in the *p*H region of 7 to 3.5 using a flow apparatus. The rate constant is in agreement with that reported in this paper. At one molar acid, the lower limit of $10^4\ M^{-1}$ sec.$^{-1}$ was placed upon the rate constant.

The present study has been performed at 25°. However, Pecsok[6] reports $E_a = 9.1$; Freund[8] reports $E_a = 7.2$; Stockmayer[24] reports 9 ± 1 and Jolly[66] reports 7.7 kcal./mole for the $k_{H_3O^+}$ term. A best average value would be 8.4 ± 0.9 kcal./mole. From this datum the value of $\Delta H^{\ddagger} = 7.8 \pm 0.9$ kcal./mole and $\Delta S^{\ddagger} = -6 \pm 3$ cal./mole deg. can be calculated. The entropy of activation is abnormally lower than that expected for the uni-opposite charge type as represented in reaction 8.

The thermodynamic functions for reaction 4 have been measured. The heat of reaction,[67] ΔH, is −63.87 kcal. The ΔH^0 at 298°K. is −63.73 kcal.; ΔS^0 is 103.0 e.u.; and ΔF^0 is −94.45 kcal.[68] The half-cell potential, E^0, has been estimated to be +1.24 volts[68] and +1.23 volts.[5] The standard entropy S^0 of aqueous borohydride ion is 25.5 ± 1 e.u.[68]

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[66] R. Mesmer and W. Jolly, Annual A.E.C. Report, private communication, March, 1961.

[67] W. D. Davis, L. S. Mason and G. Stegeman, *J. Am. Chem. Soc.*, **71**, 2775 (1949).

[68] W. H. Stockmayer, D. W. Rice and C. C. Stephenson, *ibid.*, **77**, 1980 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Boron Hydrides. IV. Concerning the Geometry of the Activated Complex in the Hydrolysis of Borohydride Ion by Trimethylammonium Ion

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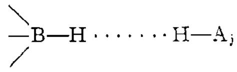
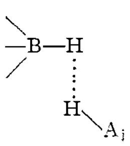
The rate of hydrolysis of sodium borohydride in aqueous solution at constant *p*H and constant ionic strength is increased by trimethylammonium ion. The amount of trimethylamine borane produced is much less than the theoretical amount predicted on a four center activated complex. On this basis the four center complex is rejected. Brief discussion has been made concerning a three center complex. The mean life time of a caged molecular system of borine, hydrogen and trimethylamine is estimated.

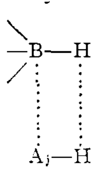
The hydrolysis of sodium borohydride in aqueous solution has been discussed in the preceding paper.[1] Three simple geometric relationships suggest themselves (I–III). The theoretically calculated values[1] of the kinetic isotope effects have been found to be rather *insensitive* to the assumed geometry. The boron–hydrogen isotope effect, k_H/k_D, is in the range of 0.95 to 0.60 for various models. Experimentally the value[1,2] is 0.70.



I



II



III

A simple experimental test can be made between a three center complex (I or II) and a four center complex (III) if the product, $H_3B{-}A_j$, is stable under the conditions of the hydrolysis and if it can be quantitatively determined. In the present report we wish to demonstrate that the four center complex (III) is incorrect when A_j is trimethylamine.

Predictions from the Geometrics of I–III.—The most interesting system would be when A_j is a water molecule. However, aquated borine, H_3BOH_2, is not stable in water[3] nor could one determine that it formed from the hydronium ion or from the water in the solvation sphere of the borohydride ion. When A_j is trimethylamine, the adduct is very stable in aqueous solution and hydrolyzes only slowly in acidic solutions.[4] Trimethylamine borane has a high fugacity and can be determined in aqueous solution by gas chromatography using a sensitive flame ionization detector.

Models I and II predict that a molecule of hydrogen will be formed between the borine and the newly formed trimethylamine molecule.[5] The

[1] R. E. Davis, E. Bromels and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962), Paper III.

[2] R. E. Davis, C. L. Kibby and C. G. Swain, *ibid.*, **82**, 5950 (1960), Paper II.

[3] H. I. Schlesinger, H. C. Brown, *et al.*, *ibid.*, **75**, 186 (1953).

[4] G. E. Ryschkewitsch, *ibid.*, **82**, 3290 (1960).

[5] An analogy can be made with the solvent separated ion-pair[6] and decomposition of azo compounds in which a stable nitrogen[7] molecule is formed between the two radical fragments in the solvent cage.[8]

[6] S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958), and earlier papers.

TABLE I

HYDROLYSIS OF SODIUM BOROHYDRIDE IN AQUEOUS TRIMETHYLAMMONIUM BUFFER SOLUTIONS AT 25.00 ± 0.003°, *p*H = 9.39 ± 0.01 (All experiments were done in triplicate.)

$(CH_3)_3\overset{+}{N}H$, *M*	$(CH_3)_3N$, *M*	$(NaBH_4)_0$, *M*	μ, *M*[a]	10^4k_1, sec.$^{-1}$	A found $(CH_3)_3NBH_3$ 10^3 *M*	B Theory based on model III 10^3 *M*	A/B × 100, %	A/$(NaBH_4)_0$ × 100, %
0	0	....	0.418	1.78[b]	...	..	..	....
0.0568	0.0264	0.0120	.418	1.92	<0.001[c]	0.94	0.1[c]	1×10^{-2}[c]
.0568	.0264	.0209	.418	1.93	.001	1.64	0.08	0.5×10^{-2}
.0999	.0464	.0150	.417	1.97	...	..	..	....
.0999	.0464	.0207	.417	1.95	...	..	..	....
.117	.0545	.0136	.417	2.08	.09	1.96	4.6	0.66
.117	.0545	.0201	.418	2.05	.09	2.68	3.4	0.33
.180	.0837	.0187	.418	2.24	...	..	..	....
.180	.0837	.00987	.418	2.22	...	..	..	....
.284	.132	.0238	.418	2.37	.67	7.86	8.8	2.9
.284	.132	.0114	.418	2.38	.24	3.74	6.5	2.1
.284	.132	.170	.587	2.30	1.4	43.0	3.2	0.8

[a] Ionic strength maintained with sodium chloride. [b] Extrapolated. [c] Calculated on the basis that the amount of amine borane produced was at the limit of detection (10^{-6} *M*).

trimethylamine and water must then compete for the borine. The amount of borine trapped as the amine borane will then depend upon the concentration of *free* trimethylamine in the solution. There should be no direct relationship between the amount of amine borane produced and the catalytic effect of the trimethylammonium ion.

The four center model (III) would predict that the *minimum* amount of amine borane produced would be the *fraction of the borohydride decomposed by the trimethylammonium ion.*

Catalytic Constant for Trimethylammonium Ion.—Variation of the concentration of trimethylammonium ion at a constant ionic strength and a constant *p*H allows a measurement of the catalytic term. The data are presented in Table I. The value of k_j for trimethylammonium ion is about that expected. The value of k_j for ammonium ion[9] is about 1.5×10^{-3} M^{-1} sec.$^{-1}$.

$$\text{Rate} = \frac{-d(BH_4)^-}{dt} = 4.38 \times 10^5 (BH_4^-)(H_3O^+) + 2.28 \times 10^{-4} (BH_4^-) [(CH_3)_3NH^+] \frac{\text{mole}}{\text{l. sec.}} \quad (1)$$

at $\mu = 0.42$ *M*, $T = 25.0°$. A small amount of amine borane could be produced by the reaction of borine[1] with free amine (2b).

$$\begin{tikzcd} & & 3H_2 + H_3BO_3 \quad (2a) \\ BH_3 \arrow[r, dash, "3H_2O", "\text{amine}"'] & {} \arrow[ur] \arrow[dr] & \\ & & (CH_3)_3NBH_3 \quad (2b) \end{tikzcd}$$

Hydrolysis of sodium borohydride in aqueous 3 *M* trimethylamine produced only 1.48 ± 0.09% of the amine borane.[1] Thus the reaction of borine with water (2a) would predominate if the amine concentration is only 0.1 to 0.02 *M* (Table I). The data of Table I show that only 1 to 10% of the amount of amine borane expected on a four center model is produced. *It must be concluded that the nitrogen atom is not close to the boron atom, nor is the nitrogen partially bonded to the boron atom in the activated complex.* The boron–nitrogen bond is strong in the amine–borane. Therefore a partially formed bond satisfying the electron deficiency of the boron should not allow the borine and trimethylamine molecules to separate. In the gas phase trivalent boron compounds react on every collision with trimethylamine.[10] It is therefore concluded that the four-center activated complex is incorrect.

Discussion

The experimental distinction between models I and II at present is difficult. Theoretical calculations[1] in the borohydride system are not sensitive to assumed geometries. The use of isotope effects fails even in a three atom system to distinguish between a linear three center and a triangular system.[11,12]

Lewis[13,14] and Hawthorne[14] favor a triangular complex for hydride transfer reactions. Several analogies can be made. The ion H_3^+ is believed to be triangular on the basis of calculations.[15] Diborane and three atom-two electron bonds[16] are also angular rather than linear. It should be emphasized that both I and II (and III) are represented on the *same adiabatic energy surface* or transition state surface. One system is of lower energy and therefore more probable. But reaction would occur from configurations I and II (and even from III). There appears to be no simple suggestion as to why III represents a system of higher energy than I or II.

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[7] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 70–71, 511–517.

[8] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[9] W. H. Stockmayer, personal communication and W. H. Stockmayer, R. R. Miller and R. J. Zeto, *J. Phys. Chem.*, **65**, 1076 (1961).

[10] D. Garvin and G. B. Kistiakowsky, *J. Chem. Phys.*, **20**, 105 (1952).

[11] The system H–H–Cl was examined in great detail by Bigeleisen[12] who concluded that the data could not favor a linear complex over a triangular complex. These data, however, provide the best experimental test of the current theories of the kinetic isotope effect. The quantum mechanical problem of H–H–Cl has never been accurately solved.

[12] J. Bigeleisen, F. S. Klein, R. E. Weston, Jr., and M. Wolfsberg, *J. Chem. Phys.*, **30**, 1340 (1959).

[13] E. S. Lewis and M. C. R. Symons, *Quart. Rev.*, **12**, 230 (1958).

[14] M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958).

[15] J. O. Hirschfelder, *J. Chem. Phys.*, **6**, 795 (1938).

[16] For a discussion of multicenter bonds, see K. S. Pitzer, "Quantum Chemistry," Prentice–Hall, Inc., New York, N. Y., 1953, pp. 191–194.

Rate of Diffusion of Borine and Trimethylamine.—The foregoing arguments suggest that molecular hydrogen is formed between the borine molecule and the trimethylamine. A rough estimate of the life-time of this solvent caged system can be given. Assuming a hard sphere molecule with a rectangular potential well, the mean life-time of such an assembly can be given by

$$t = \frac{1}{3}\frac{r^2_{\mathrm{AB}}}{D_{\mathrm{AB}}} \exp - \epsilon/kt \qquad (3)$$

where D_{AB} is the sum of the binary diffusion coefficient of the amine and water and that of the borine and water, r_{AB} is the collision radius and ϵ is the energy of separation of the amine and borine in the solvent. A limit can be placed upon the time that it would take for the borine and amine to diffuse together if we take $D_{\mathrm{AB}} = 3 \times 10^{-5}$ cm.²/sec. and $r_{\mathrm{AB}} = 4$ to 5 Å. which are typical values for materials in aqueous solution and $\epsilon = 0$. The value of t is of the order of 10^{-11} sec. which is about ten to one hundred times that of the collision time between two neighboring molecules. Typical vibration times are of the order of 10^{-13} sec. Thus borine collides with water within its primary water solvation sphere at least ten to one hundred times before the amine is able to diffuse in and react. If a water molecule of the primary solvation sphere reacts with the borine within 10^{-13} to 10^{-11} sec., then very little amine borane would be produced. The rate constant for reaction of a hydronium ion with borohydride is about 10^6 M^{-1} sec.$^{-1}$. This means that one collision out of 10^3 to 10^4 is effective in producing reaction. As this step is rate-determining, borine must disappear by steps 2 even faster. Thus two lines of argument would place the rate constant of the reaction of borine with water (or hydronium ion) between 10^9 M^{-1} sec.$^{-1}$ (the theoretical maximum for a diffusion controlled process) and 10^7 M^{-1} sec.$^{-1}$.

Experimental

Materials.—Trimethylamine borane was prepared by the method of Schaeffer and Anderson[17] from trimethylammonium chloride and lithium borohydride in anhydrous ether. The pure material melted at 93.6–94.0° (corr.), reported 94°. The infrared spectrum agreed with the literature.[18] Calcd. for $C_3H_{12}NB$: C, 49.39; H, 16.58; N, 19.20. Found: C, 49.24; H, 16.48; N, 19.07. Available hydrides found 3.01 per molecule; calcd. 3.00.

Kinetics.—The kinetic techniques have been discussed.[1,2] Aliquots then were withdrawn periodically and analyzed. This method measures the total amount of reducing power of the solution. Trimethylamine borane reduced iodate under these conditions.[4]

After twelve half-times the remaining solution was divided into two equal parts. The *p*H of one solution was adjusted to 4.0 with hydrochloric acid and the solution transferred to a vacuum line. The volatile fraction of water and trimethylamine borane was separated quantitatively and condensed in a liquid nitrogen trap. The other solution was transferred to the vacuum line. In this case the volatile fraction contains water, trimethylamine borane and some trimethylamine. In each case the volatile fraction was analyzed for amine borane by vapor phase chromatography.

Analytical.—Trimethylamine borane can be separated from the amine (if present) and quantitatively determined using a F and M Model 609 Flame Ionization Gas Chromatograph. Using a 61-cm. silicone rubber column at 50° with nitrogen gas as a carrier, the amine borane emerged after five minutes. The sensitivity of the instrument placed the lower limit of detection at 10^{-6} M. Pure trimethylamine borane was dissolved in water and dilutions were prepared to obtain a calibration graph. The area under the curve was used as a measure of the amount of trimethylamine borane present. The reproducibility was of the order of 5 to 7% at the lower levels of concentration.

Control Experiments.—Stability of Trimethylamine Borane in Aqueous Solution. A.—The rate of hydrolysis of trimethylamine borane in 0.30 to 1.43 M hydrochloric acid was measured at a constant ionic strength of 1.43 M (maintained with sodium chloride). The hydrolysis slowly produced hydrogen gas, boric acid and trimethylammonium chloride. The rate was studied by the iodate method. The average second order rate constant, k_2, was 2.16×10^{-4} M^{-1} sec.$^{-1}$ at 25°.

$$\frac{-\mathrm{d}[(\mathrm{CH_3})_3\mathrm{NBH_3}]}{\mathrm{d}t} = k_2[(\mathrm{CH_3})_3\mathrm{NBH_3}][\mathrm{H_3O^+}] \qquad (4)$$

B.—Trimethylamine borane was dissolved in the aqueous buffers described in Table I. Aliquots were withdrawn and analyzed. There was no detectable change during several weeks at 25° at *p*H 9.39. No reaction was detected in borate buffer solutions (*p*H = 9.98) after several weeks. Thus the amine borane is stable under the conditions of the hydrolysis of sodium borohydride in the buffer solutions.

Upon several weeks standing in pure water, the amount of trimethylamine borane began to decrease. This was first noticed on the solutions used as standards for the vapor phase chromatography analysis. A peak corresponding to trimethylamine slowly appeared and the peak of the amine borane slowly decreased.

Recovery of Trimethylamine Borane.—Standard solutions of the amine borane were transferred on the vacuum line and then analyzed. In every case 95% or more of the amine borane was recovered at concentrations of 10^{-2} to 10^{-5} M.

Effect of Trimethylamine Borane upon the Rate of Hydrolysis of Sodium Borohydride.—A solution was prepared which contained trimethylamine borane (0.118 M), sodium borohydride (0.002 M) and potassium chloride (0.098 M). The rate of hydrolysis of the borohydride was measured using a "*p*H-Stat" at *p*H = 9.00 at 25°. The first order rate constant was $1.20 \pm 0.09 \times 10^{-3}$ sec.$^{-1}$. Another solution was prepared with 0.002 M borohydride and 0.098 M potassium chloride and the rate measured at *p*H = 9.00. The first order rate constant was $1.35 \pm 0.09 \times 10^{-3}$ sec.$^{-1}$. Thus there is little effect of the amine borane upon the rate of hydrolysis of borohydride.

The "*p*H-Stat" is not capable of the accuracy of a volumetric method. This technique was used in the present control experiments because of the large excess of amine borane which would reduce acidified iodate solutions. Only one mole of acid was required for one mole of sodium borohydride (equations 2 and 3).

Acknowledgment.—This study was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

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[17] G. W. Schaeffer and E. R. Anderson, *J. Am. Chem. Soc.*, **71**, 2143 (1949).

[18] W. C. Price, R. D. B. Frazier, T. S. Robertson and H. C. Longuet-Higgins, *Discussions Faraday Soc.*, **9**, 131 (1950).