due to the differing purities of the materials. The occurrence of lanthanum hydride in these samples (as indicated both by X-ray diffraction and from the method of preparation of the metal) suggested that the lower transition temperature of the Cooper 2 sample might be due to the presence of hydrogen, since it has been shown that lanthanum hydride ($LaH_{2.45}$) is not a superconductor down to 1.8°K.[29] However, heat treatment of La 7 in high vacuum for four days at 700° resulted in no marked change in the superconducting transition temperature or the width of the transition, although this treatment has been found adequate to convert lanthanum hydride to lanthanum metal.[30]

Acknowledgments.—The authors wish to express their appreciation to Dr. F. H. Spedding for making available two of the lanthanum samples, to Dr. W. M. Spicer for making the spectrographic analyses, and to R. B. Belser for the evaporation of the protective aluminum films used in the X-ray studies. They wish to acknowledge the assistance of J. B. Downs, Jr., and F. H. Lafond in carrying out the chemical analyses, of J. O. Blomeke and J. T. Roberts, Jr., in making the low temperature measurements, and of George Cook and J. M. Ziegler in the construction of the apparatus.

ATLANTA, GEORGIA

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[29] W. T. Ziegler and R. A. Young, Proc. Int. Conf. on Low Temperature Physics, Oxford, England, August, 1951, p. 124.

[30] Unpublished work in this Laboratory.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

Mechanism of the Hydrolysis of Diborane in the Vapor Phase[1]

BY H. G. WEISS[1a] AND I. SHAPIRO[1a]

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The order of the hydrolysis of diborane at 50.5° in the vapor phase was found to be 3/2; *i.e.*, first order with respect to water concentration and half-order with respect to diborane concentration. A plausible mechanism to fit the data is the dissociation of diborane into borine followed by the stepwise substitution of hydroxyl groups for hydrogen in borine. Evidence for the formation of the intermediate products is presented. The stoichiometric ratio of water to diborane is *ca.* 5.5:1. Variations in the composition of the condensed end-products as a function of the relative concentration of reactants are given.

The hydrolysis of diborane as expressed by the equation

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2 \qquad (1)$$

has been used as the basis for the quantitative analysis of diborane,[2a,b] although very little is known about the mechanism of the hydrolysis. Stock, Wiberg and collaborators have assumed that the hydrolysis occurs in a stepwise fashion with the general replacement of H with OH groups directly in the diborane molecule. Their proposed 10-step mechanism[3] for the hydrolysis appears to be hypothetical since there is no experimental support. Nekrasov[4] has speculated that the initial step in the hydrolytic process is the reaction of diborane either with one molecule of water in the case of excess diborane, or with two molecules of water in the case of excess water. Such an interpretation implies a second or third order reaction and is contradictory to the experimental data obtained in this Laboratory.

The mechanism of the hydrolysis presented here is consistent with the results of a detailed study of the order of reaction under conditions of widely varying concentrations of reactants. The over-all order was found to be 3/2; *i.e.*, first order with respect to water and 1/2 order with respect to diborane.

Experimental

1. **Reagents.** Diborane.—The preparation of diborane used in these experiments has been described in detail in a previous publication.[5] Immediately before use the diborane was purified (v.p. 225 mm. at −111.8°) by the usual high vacuum techniques.

Water.—Distilled water was freed of dissolved gases by repeated distillation in the vacuum apparatus prior to use.

Boric Acid.—J. T. Baker analyzed boric acid was used without further purification. The boric acid was dried *in vacuo* at 50°.

2. **Apparatus.**—A two-liter round bottom flask served as the reaction chamber. Mixing of the gases was accomplished by means of a glass-encased induction-type stirrer. A diborane storage and injection tube was inserted into one neck of the flask. Two concentric stopcocks at the top of the injection tube were constructed so that the relative positions of the openings could be set for either storage of the diborane or injection of the diborane into the reaction chamber by displacement with mercury. The assembly could be removed from the flask and attached directly to the vacuum line for filling with diborane. A three-way stopcock was used either to admit water vapor into the reaction chamber or to connect the reaction chamber with the vacuum system. The pressure of the system was measured with a cathetometer on a single column mercury manometer. The entire system was maintained at 50.5 ± 0.2° in an oil-bath.

3. **Procedure.**—A measured quantity of diborane was placed in the storage tube in the reaction flask. Then the reaction flask was evacuated and brought to the temperature of the bath. The stirring motor was turned on and water vapor from a reservoir tube was admitted slowly into the reaction chamber until a predetermined pressure was reached. This pressure always was lower than the vapor pressure of water at 50°. Next, the diborane was injected into the reaction chamber and the total pressure of the system was followed as a function of time. At the end of the experiment the reaction was "quenched" by condensing the remaining diborane and water in liquid nitrogen traps and then the hydrogen was pumped into a gas buret and measured. The diborane remaining was measured after separation from water.

Results and Discussion

The order of the reaction is obtained by comparison of the rates of hydrolysis under conditions

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[1] Presented before the Pacific Southwest Regional Meeting, American Chemical Society, San Diego, California, May 10, 1952.

[1a] Mathieson Chemical Corporation, Pasadena, California.

[2] (a) A. Stock and C. Massenez, *Ber.*, **45**, 3529 (1912); (b) A. Stock and K. Friederici, *ibid.*, **46**, 1959 (1913).

[3] E. Wiberg, *ibid.*, **69B**, 2816 (1936).

[4] B. V. Nekrasov, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1156 (1940).

[5] I. Shapiro, H. G. Weiss, M. Schmich, Sol Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

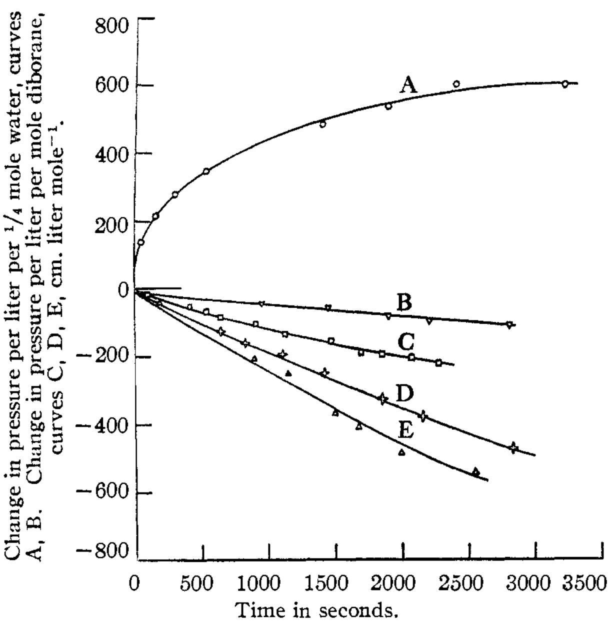

Fig. 1.—Effect of relative initial concentration of reactants upon rate of change of pressure of system at 50.5°. Water to diborane ratio: A, 0.192; B, 1.27; C, 5.46; D, 6.26; E, 11.6.

of varying molar concentrations of reactants. From eq. 1 it would appear that the rate of reaction of diborane with water (vapor) is related directly with the rate of change of total pressure of the system; however, the curves in Fig. 1 indicate that the change in pressure of the system is a function of the relative concentration of reactants. At high ratios of water to diborane concentration the decrease in pressure approaches that expected of eq. 1; at low ratios the pressure of the system actually increases. Thus, to determine the rate of reaction, it becomes necessary to supplement the data on the rate of pressure change with the measurement of the amount of diborane consumed (or hydrogen generated) in a given time. In this way one is able to extrapolate the total change in pressure of the system for complete reaction.

The End Products.—Variations from the expected pressure change of the system can be explained by the formation of metaboric acid[6] and/or boron oxide in the condensed end-products, *viz.*

$$B_2H_6 + 4H_2O \longrightarrow 2HBO_2 + 6H_2 \qquad (2)$$

$$B_2H_6 + 3H_2O \longrightarrow B_2O_3 + 6H_2 \qquad (3)$$

There is no change in the non-condensable end product since it has been found experimentally that the ratio of hydrogen to diborane consumed always is 6 to 1 (within 1% experimental error), as expected from eq. 1, 2 and 3. This constancy in ratio provides a check on the accuracy of the experimental data.

In the case of excess diborane the pressure rise of the system (curve A, Fig. 1) approached, but did not exceed, that expected from eq. 2, thus it is very probable that in all reactions reported here the main products in the condensed phase are mixtures of orthoboric and metaboric acids. In this connection it is pointed out that the true stoichiometric ratio is not 6:1 as indicated by eq. 1, but is found to be *ca.* 5.5:1.

Homogeneity of Reaction.—The degree of homogeneity of the reaction was determined by measuring the rate of reaction under conditions in which the surface to volume ratio of the reactor was varied by a factor of 10. Glass wool was used as the packing material. Since boric acid is a product of the reaction, the effect of boric acid coated[8] surfaces also was examined. Table I shows the values of k (liter$^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$) at the stoichiometric ratio for a packed and unpacked reactor. Since the increase in the value of k is small in comparison with the change in surface, the reaction is considered homogeneous. The effect of boric acid coated surfaces also is negligible. Presumably the boric acid formed during the reaction coats the walls of the reactor.

Table I

Temp., °C.	Condition of reactor	k (liter$^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$)
50.5	Unpacked reactor	4.8×10^{-3}
50.5	Unpacked reactor	4.6×10^{-3}
50.5	Packed reactor	6.9×10^{-3}
50.5	Packed-boric acid coated	7.0×10^{-3}

Order of the Reaction.—As will be shown below the data for the rate of pressure change of the system at the stoichiometric ratio can be represented by a reaction which is first order with respect to water and $^1/_2$ order with respect to diborane. Under steady state conditions the rate of hydrogen formation is given by

$$\mathrm{d}[H_2]/\mathrm{d}t = k[B_2H_6]^{1/2}[H_2O] \qquad (4)$$

Equation 4 can be generalized conveniently in terms of pressure change of the system since the ratio of hydrogen formed to diborane consumed always is 6, and the volume of the condensed products can be neglected, thus

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{\Delta k}{6P^{*}_{B_2H_6}(RT)^{1/2}}\left(P^{0}_{B_2H_6} - P^{*}_{B_2H_6}\frac{x}{\Delta}\right)^{1/2}\left(P^{0}_{H_2O} - (\Delta + 5P^{*}_{B_2H_6})\frac{x}{\Delta}\right) \qquad (5)$$

where x is the change in pressure of the system at time t, Δ is the total decrease in pressure for complete reaction, and k is the rate constant expressed in the same units as in eq. 4. $P^{*}_{B_2H_6}$ represents the amount of diborane that is consumed for complete reaction, and $P^{0}_{B_2H_6}$ and $P^{0}_{H_2O}$ are the initial partial pressures of diborane and water, respectively. In the case of excess water or at the stoichiometric point, $P^{*}_{B_2H_6} = P^{0}_{B_2H_6}$. Δ is obtained by determining the per cent. reaction at the end of an experiment and then by extrapolating the observed pressure change to that of complete reaction. As indicated from Fig. 1 the value of Δ varies with the relative concentrations of reactants.

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(6) Upon prolonged exposure of diborane to orthoboric acid at 50.5° there was no evidence of reaction so the formation of metaboric acid presumably results directly from the intermediate products. However, at 65° a slight reaction was observed between orthoboric acid and diborane, and at 75° a definite increase in the amount of hydrogen generated was noted. Since at these temperatures orthoboric acid decomposes giving off free water,[7] the reactions at the higher temperatures can be attributed to the hydrolysis of diborane by the free water.

(7) C. Duval, *Anal. Chim. Acta*, **4**, 55 (1950).

(8) C. K. McLane, *J. Chem. Phys.*, **17**, 379 (1949).

At the true stoichiometric ratio, where $P^0_{H_2O} = 5.5\ P^0_{B_2H_6}$ and $2\Delta = P^0_{B_2H_6}$, eq. 5 is reduced to an easily integrated function of x

$$\frac{dx}{dt} = \frac{11\sqrt{2}k}{12(RT)^{1/2}}(\Delta - x)^{3/2} \qquad (6)$$

which by rearrangement and integration gives

$$\frac{1}{(\Delta - x)^{1/2}} = \frac{11k}{12(2RT)^{1/2}}t + \frac{1}{\Delta^{1/2}} \qquad (7)$$

A curve of the three-halves order expression (eq. 7) is given in Fig. 2. From this curve the rate constant is calculated to be 4.8 × 10^{-3} liter$^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$.

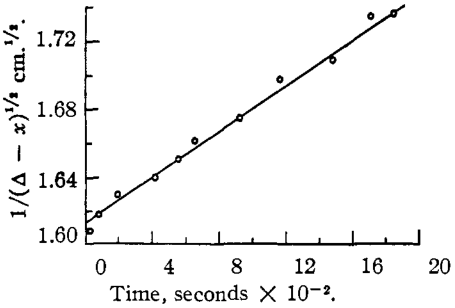

Fig. 2.—Three-halves order curve at stoichiometric ratio.

To determine the order of reaction with respect to diborane experiments were made using a large excess of water. Under this condition the value of $P^0_{B_2H_6}/\Delta$ approaches unity and the term $(\Delta + 5P^0_{B_2H_6})/\Delta$ can be neglected in comparison to $P^0_{H_2O}$ thus eq. 5 becomes

$$\frac{dx}{dt} = \frac{k}{6(RT)^{1/2}}P^0_{H_2O}(\Delta - x)^{1/2} \qquad (8)$$

Integration gives the half-order equation

$$(\Delta - x)^{1/2} = \frac{-k}{12(RT)^{1/2}}P^0_{H_2O}\,t + \Delta^{1/2} \qquad (9)$$

the curve of which is shown in Fig. 3. From the slope of the curve in Fig. 3 the value of k in eq. 9 was calculated to be 4.8 × 10^{-3} liter$^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$. This value is in good agreement with the value of k obtained at the stoichiometric ratio.

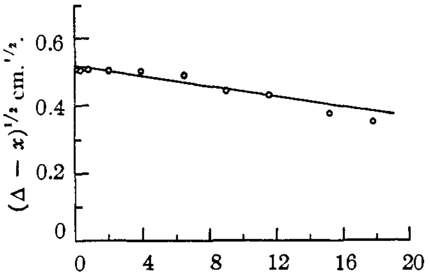

Fig. 3.—Half-order curve for experiment with excess water.

The value of Δ in eq. 9 also can be obtained directly from the rate of change of pressure of the system[9] and thus serve as a check on the extrapolation procedure. Setting $k_1 = kP^0_{H_2O}/12(RT)^{1/2}$ and squaring both sides of eq. 9, one can obtain the equation

$$\frac{x}{t} = 2k_1\Delta^{1/2} - k_1{}^2t \qquad (10)$$

The value of Δ from the slope of eq. 10 was found to be 0.277 which agrees well with the extrapolated experimental value of Δ, 0.274.

Hydrolysis with Excess Diborane.—In the experiments in which diborane was in large excess, it was found that the reaction was first order with respect to the concentration of water. In this case substitution of $P^*_{B_2H_6} = (P^0_{H_2O} - \Delta)/5$ in eq. 5 leads to the equation

$$\frac{dx}{dt} = \frac{5P^0_{H_2O}k}{6(P^0_{H_2O} - \Delta)(RT)^{1/2}}(P^0_{B_2H_6})^{1/2}(\Delta - x) \qquad (11)$$

which on integration becomes

$$\ln\left(\frac{\Delta}{\Delta - x}\right) = \frac{5P^0_{H_2O}k}{6(P^0_{H_2O} - \Delta)(RT)^{1/2}}(P^0_{B_2H_6})^{1/2}t \qquad (12)$$

In order to show in terms of actual pressure change that the order of the over-all reaction is 3/2 rather than, say, second order, the value of k obtained from previous experiments (case of stoichiometric and excess water) was substituted in eq. 12, and then using the extrapolated value (0.30) for Δ eq. 12 was plotted as x *vs.* t (solid curve, Fig. 4). The experimentally determined values are given by the circles. Since previous investigators[3,4] appear to have favored a second-order reaction for the hydrolysis, the experimental data also were analyzed in terms of a second-order reaction. The values of k based on second-order reaction for the condition of stoichiometric reaction and excess water differed widely from each other. Even using the "best" value of k based on a second-order reaction, the theoretical curve for excess water (dotted line in Fig. 4) differs considerably from the experimentally determined values. The agreement of the theoretical curve for a 3/2 order reaction with the experimental values is a good indication that this order is the correct one.

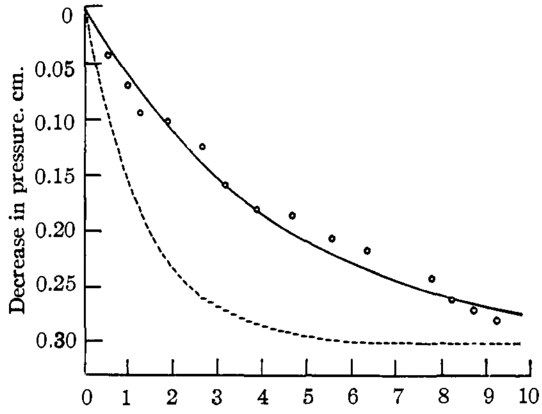

Fig. 4.—Rate of change of pressure for case of excess diborane: O, experimental; —, first-order curve based on a 3/2 order reaction; - - -, first-order curve based on a second-order reaction.

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[9] We thank Dr. D. S. Villars for kindly pointing this out. *Cf.* Villars, "Statistical Design and Analyses of Experiments for Development Research," Wm. C. Brown, Dubuque, Iowa, 1951, paragraph 12;8, page 285 ff. See also paragraph 12;9, page 290.

Mechanism of the Reaction.—A plausible mechanism to fit the data, especially in the case of excess water is

$$B_2H_6 \rightleftarrows 2BH_3 \qquad (13)$$

$$BH_3 + H_2O \longrightarrow [BH_3 \cdot H_2O]^* \longrightarrow BH_2OH + H_2 \qquad (14)$$

$$BH_2OH + H_2O \longrightarrow [BH_2OH \cdot H_2O]^* \longrightarrow BH(OH)_2 + H_2 \qquad (15)$$

$$BH(OH)_2 + H_2O \longrightarrow [BH(OH)_2 \cdot H_2O]^* \longrightarrow B(OH)_3 + H_2 \qquad (16)$$

In the case of excess diborane it may be possible for borine to react with the intermediates to give rise to other boric acid products, *e.g.*, metaboric acid. Because of the relatively low concentrations of the partially hydrolyzed intermediates it is unlikely that any disproportionation reaction occurs in the mechanism.

Intermediate Products of the Reaction.—The mechanism postulated for the hydrolysis of diborane involves various intermediates which could not be isolated in the vapor phase reaction. Evidence of the existence of these intermediates has been obtained from the reaction of diborane with ice and with the "bound water" in silica gel.[10]

Diborane reacts with ice at −80° to give a 4:1 ratio of hydrogen to diborane consumed. This reaction presumably is a surface reaction in which each boron atom is attached to two hydroxyl groups in the surface of the ice crystal. An active hydrogen atom remains attached to each boron atom. At −23° there evidently is sufficient mobility of the molecules within the ice crystal to permit this active hydrogen atom to react. The final hydrogen to diborane ratio approaches 6:1. It appears that these experiments give the closest approach to direct evidence for the formation of a $BH(OH)_2$ molecule.

When diborane is exposed to the "bound" water in silica gel (the gel being heated previously to 150° to ensure complete removal of adsorbed water) at a low temperature (−23°), hydrolysis occurs with the hydrogen to diborane consumed ratio being *ca.* 2:1.[10] The state of hydrolysis at this point corresponds to the formation of BH_2OSi– which is analogous to the formation of BH_2OH (eq. 14). In the case of silica gel, however, the silicon atoms serve as anchor points to prevent the migration of the partially hydrolyzed borine and, consequently, limit its degree of hydrolysis.[10]

Acknowledgment.—The authors are grateful to Dr. G. B. L. Smith for reviewing the manuscript.

PASADENA, CALIF.

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[10] I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **57**, 219 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Aqueous Solubility Relations of Potassium Molybdate, and Aqueous Ternary Isotherms at 25° with KOH, KNO_3 and KIO_3

BY JOHN E. RICCI AND FRANK J. LOPREST

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The system K_2MoO_4–H_2O, with a eutectic at −38° and a boiling point of 119° for the saturated solution, involves anhydrous K_2MoO_4 throughout. Over the range directly studied, −18° to 119°, the solubility of the salt, in weight percentage, varies very little and practically linearly with the temperature: $S = 63.82 + 0.0300t$. The anhydrous nature of the solid phase was further confirmed through solubility measurements in presence of KOH. The ternary systems with KNO_3 and with KIO_3, studied at 25°, involve only the separate salts as solid phases.

Despite Amadori's work[1] on the ternary systems K_2MoO_4–K_2SO_4–H_2O and K_2MoO_4–K_2CrO_4–H_2O, involving continuous solid solutions of the salts, and in which the salt K_2MoO_4 appeared definitely to be anhydrous as the saturating phase at room temperature, there seemed still to be some uncertainty regarding the hydration of this salt. The uncertainty may have continued because of old reports of various improbable hydrates cited in Gmelin and in Mellor; and the formula $K_2MoO_4 \cdot 5H_2O$ is still listed in a current handbook. In fact, commercially supplied C.P. potassium molybdate was received with the label of a pentahydrate in 1950, although the contents of the various 5-lb. bottles was strictly anhydrous. The binary system K_2MoO_4–H_2O was therefore investigated over a wide range and further information was sought through the study of the ternary system K_2MoO_4–KOH–H_2O at 25°. The systems K_2MoO_4–KNO_3–H_2O and K_2MoO_4–KIO_3–H_2O were also investigated at 25°, for comparison with the corresponding systems involving the sodium salts.[2,3] In all the work no hydrate of K_2MoO_4 was observed.

The general experimental procedure of equilibration, sampling, analysis, proof of equilibrium, etc., used for the solubility determinations, both binary and ternary, was the same as that used in the investigation of similar systems involving Na_2MoO_4[2,3] and $MgMoO_4$.[4] The K_2MoO_4 used was about 99.9% pure, on the basis of the volumetric determination of molybdate with standard $AgNO_3$ and standard KCNS, in an adaptation of the Volhard method.[2] One batch of the salt was found to form a slight white deposit from moderately concentrated solutions, and was therefore recrystallized before analysis and use.

System K_2MoO_4–H_2O.—The solubility curve from 9 to 90° was determined by direct analysis of the filtered solution, in some cases by evaporation

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[1] M. Amadori, *Atti R. accad. Lincei*, [5] **21**, I, 667 (1912).

[2] For Na_2MoO_4–$NaNO_3$–H_2O: J. E. Ricci and L. Doppelt, THIS JOURNAL, **66**, 1985 (1944).

[3] For Na_2MoO_4–$NaIO_3$–H_2O: J. E. Ricci and W. F. Linke, *ibid.*, **69**, 1080 (1947).

[4] J. E. Ricci and W. F. Linke, *ibid.*, **73**, 3603 (1951).