# The Vapor Phase Reaction of Diborane with Acetone

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**Abstract:** The kinetics of the gas-phase reaction, $B_2H_6 + 4(CH_3)_2C{=}O \rightarrow 2(i\text{-}PrO)_2BH$, was studied. The reaction was found to be homogeneous, first order in diborane, and first order in acetone. The second-order rate constant is given by the equation $k = 5 \times 10^7 e^{-14,800/RT}$ l. mol$^{-1}$ sec$^{-1}$. The reaction is catalyzed by ethyl ether and tetrahydrofuran. The THF-catalyzed reaction is first order in ligand, first order in diborane, and zero order in acetone. Its second-order rate constant is given by the equation $k = 3 \times 10^{10} e^{-16,500/RT}$ l. mol$^{-1}$ sec$^{-1}$. The data suggest that diborane and the ligand react reversibly to form a 1:1 complex in which both bridged B–H bonds remain intact. The complex then rearranges slowly in a rate-determining step to form a second complex in which one of the bridged B–H bonds is broken. The second complex reacts with acetone in a series of rapid steps to form diisopropoxyborane. Consistent with this hypothesis is the observation that cyclobutanone is reduced by diborane in the uncatalyzed reaction at a slower rate than acetone and in the catalyzed reaction at the same rate as acetone.

The reaction between diborane and acetone to yield diisopropoxyborane was first reported by Brown, Schlessinger, and Burg.[1] Since then a great deal of work has been done on the reaction of diborane and borohydride salts with various oxidizing agents. However, except for the work of Lehmann, *et al.*, who studied the infrared spectrum of dialkoxyboranes in the vapor phase[2] and who, in the course of their work, made some observations on the reactivity of alcohols and diborane,[3] all of the work is concerned with reactions in solution. When we observed that the reaction between diborane and acetone goes cleanly and at a convenient rate in the vapor phase we decided to study the kinetics of the reaction and to compare it with the kinetics of the reaction of acetone with sodium borohydride which was carried out in the liquid phase.[4,5]

## Experimental Section

The reactions were carried out in a thermostated infrared cell. The rate of disappearance of reactants was followed by measuring the intensity of the bridge B–H band or of the carbonyl band, each in the 6-$\mu$ region, as a function of time.

**Apparatus.** A Perkin-Elmer Model 137 infracord equipped with the Perkin-Elmer expanded scale kit and a 10-MV potentiometric recorder was used in this investigation.

An oven was constructed within the sample chamber of the spectrophotometer. The exterior and interior walls of the oven were stainless steel with firebrick sandwiched between them to furnish insulation. Fiberglass covered heating tapes attached to the interior walls were the source of heat. Energy transmission was achieved using Irtran-2 windows fitted into each of four apertures—two for the sample beam and two for the reference beam—cut in the walls of the oven. Three openings in the top of the oven accommodated the shaft of a blower, the projecting stopcock of the reaction cell, and a differential thermometer.

The heart of the temperature control system was a Thermo-Watch controller. The oscillator head of the Thermo-Watch controller was clipped to the differential thermometer which rested in the top of the oven. As mercury in the thermometer rose and fell, the Thermo-Watch controller switched on and off, actuating the electrical relay which in turn controlled two Variacs. At any moment one Variac was furnishing power to the heating tapes. The Variac operating in the "off" position of the controller furnished 50% of the power produced by the Variac operating in the "on" position. In this way, sharp temperature fluctuations were avoided.

The reaction cells were constructed of 3.5-cm diameter glass tubing with path lengths of 7.0 and 3.7 cm. Irtran-2 windows were sealed to the ends of the tubing using Dow Corning Silastic RTV731. Glass tubing was attached to each cell and was of a length just adequate to extend from the cell through the top of the oven where a stopcock was affixed. The stopcock was attached *via* a glass ball joint to a vacuum system. The reaction cells were enclosed by a metal block to ensure a minimum in temperature variation. Four iron constantan thermocouples inserted through holes in the metal block and resting against the sides of the reaction cell provided the temperature readings. The average of the four temperature readings was used as the reaction temperature. The four readings agreed to within ±0.2°.

**Reagents.** The diborane was obtained from the Callery Chemical Co. and was purified by distillation on the vacuum system. It was kept frozen in liquid nitrogen until used. The acetone, tetrahydrofuran, and diethyl ether were Fisher "Certified Reagents." They were used without further treatment. The cyclobutanone was obtained from the Columbia Organic Chemicals Co. and was determined by gas chromatographic analysis to be greater than 99% pure.

**Procedure.** In a typical run the reactants were mixed in a 1-l. bulb, pressurized with helium to 600 Torr, and then expanded into the heated reaction cell. Pressurization with helium was necessary to eliminate pressure broadening effects. The changes in diborane and acetone were followed by locking the spectrophotometer on the B–H bridge band (6.15 $\mu$) and the carbonyl band (5.75 $\mu$), respectively. Beer's law plots were made of diborane and acetone at the above wavelengths. The data obtained on the recorder from reaction runs were in the form of per cent transmittance *vs.* time. Conversion of these data to absorbance and then to concentration using the Beer's law plots produced a continuous record of concentration *vs.* time.

## Results

The reaction between diborane and acetone was found to be catalyzed by Lewis bases such as tetrahydrofuran and ethyl ether. Both the catalyzed and the uncatalyzed reactions were studied and will be reported separately.

**The Uncatalyzed Reaction.** The determination of the products, of the stoichiometry, and the order of the reaction between diborane and acetone was undertaken at 141°. Mixtures in which the pressure of diborane was 10 Torr and the pressure of acetone varied from 20 to 100 Torr were placed in the reaction cell. Infrared spectra in the 2–15-$\mu$ range were obtained immediately after expansion of the gases into the reaction cell and at later intervals. The spectra indicated that only with

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[1] H. Brown, H. Schlessinger, and A. Burg, *J. Amer. Chem. Soc.*, **61**, 673 (1939).

[2] W. J. V. Lehmann, H. G. Weiss, and I. Shapiro, *J. Chem. Phys.*, **30**, 1226 (1959).

[3] W. J. V. Lehmann, H. G. Weiss, and I. Shapiro, *ibid.*, **30**, 1222 (1959).

[4] H. C. Brown, O. H. Wheeler, and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957).

[5] H. C. Brown and K. Ichikawa, *ibid.*, **1**, 221 (1957).

pressures of 10 Torr diborane and 40 Torr acetone did both the B–H bridge band (6.15 $\mu$) and the carbonyl band (5.75 $\mu$) disappear. All other ratios of reactants resulted in the incomplete reaction of diborane or the incomplete reaction of acetone. The spectrum of the gases in the reaction cell following disappearance of both the B–H bridge band and the carbonyl band agreed with the published spectrum of diisopropoxyborane.[2] The spectra indicated that diisopropoxyborane was the sole product in all of the reactions and that 4 mol of acetone reacted with 1 mol of diborane. Low pressures of acetone (20 Torr) produced spectra at early stages of reaction containing only those absorption bands which could be ascribed to diisopropoxyborane. Prolonged heating of reaction mixtures containing a large excess of acetone (100 Torr) produced spectra which indicated only diisopropoxyborane and unreacted acetone. There was never evidence in any of the spectra to indicate the presence of monoisopropoxyborane or triisopropoxyborane.

In order to show that the stoichiometry is constant throughout the reaction, duplicate experiments were performed using reaction mixtures in which the pressures of diborane and acetone were 10 and 40 Torr, respectively. In one run the decrease in the carbonyl band was followed. Using the previously mentioned Beer's law plots, the change in concentration of both diborane and acetone *vs.* time was obtained. Typical results are given in Table I. The overall reaction between diborane and acetone under these experimental conditions is represented by the following equation.

$$B_2H_6 + 4Me_2CO \longrightarrow 2(Me_2CHO)_2BH$$

**Table I.** Determination of the Stoichiometry of the Diborane–Acetone Reaction[a]

| Time, sec | $B_2H_6$ reacted, Torr | $Me_2CO$ reacted, Torr | $Me_2CO$ reacted/$B_2H_6$ reacted |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 60 | 0.9 | 4.4 | 4.9 |
| 120 | 1.8 | 7.3 | 4.0 |
| 180 | 2.5 | 10.0 | 4.0 |
| 240 | 3.1 | 12.1 | 3.9 |
| 300 | 3.6 | 13.9 | 3.9 |
| 360 | 4.0 | 15.5 | 3.9 |
| 420 | 4.5 | 17.1 | 3.8 |
| 480 | 4.8 | 18.5 | 3.9 |
| 540 | 5.1 | 19.9 | 3.9 |

[a] At 141.0°; $B_0$ = 10.0 Torr, $(Me_2CO)_0$ = 40.0 Torr.

Initially, two series of experiments were performed to determine the order of the reaction. In one series, the initial concentration of diborane was varied while the initial concentration of acetone was held constant. A linear relationship is evident between the initial rate of diborane decrease and the initial concentrations of diborane. In the other series of experiments, the initial concentration of diborane was held constant while the initial concentration of acetone was varied. In this case, a linear relationship is evident between the initial rate of diborane decrease and the initial concentrations of acetone. The results of these experiments are summarized in Table II. To further substantiate the apparent second-order character of the reaction, runs were made using 1:4 ratios of diborane and acetone at different initial concentrations. Under these experimental conditions, the second-order expression $1/B = 4kt + 1/B_0$, where $k$ is the rate constant and $t$ is time, should apply. Plots of the reciprocal of diborane concentration *vs.* time produced straight lines whose slopes were constant as indicated in Table III; thus, the reaction is second order under these conditions.

**Table II.** Determination of the Order in Diborane and Acetone at 114.0°

| Initial pressures, Torr | | Initial rate, Torr $sec^{-1}$ | Initial rate/ $(concn)_0$ |
|---|---|---|---|
| $B_2H_6$ | $Me_2CO$ | | |
| 6.0 | 20.0 | $0.50 \times 10^{-3}$ | $8.3 \times 10^{-4}$ |
| 8.0 | 20.0 | 0.63 | 7.9 |
| 10.0 | 20.0 | 0.83 | 8.3 |
| 12.0 | 20.0 | 1.00 | 8.3 |
| 16.0 | 20.0 | 1.28 | 8.0 |
| 10.0 | 10.0 | 0.33 | 3.3 |
| 10.0 | 20.0 | 0.80 | 4.0 |
| 10.0 | 40.0 | 1.50 | 3.7 |
| 10.0 | 60.0 | 2.21 | 3.7 |
| 10.0 | 100.0 | 3.33 | 3.3 |

**Table III.** Results of Second-Order Plot at 118.0°

| Initial pressures, Torr | | |
|---|---|---|
| $B_2H_6$ | $Me_2CO$ | $k$, l. $mol^{-1}$ $sec^{-1}$ |
| 5.0 | 20.0 | $3.2 \times 10^{-1}$ |
| 7.6 | 30.0 | 3.4 |
| 10.0 | 40.0 | 3.2 |
| 13.0 | 50.0 | 3.4 |
| 18.0 | 72.0 | 3.0 |

The effect of temperature upon the rate of reaction was determined through the exponential factor of the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Reaction mixtures with initial pressures of 10 Torr diborane and 40 Torr acetone were studied over the temperature range 118.0–151.0°. Plots were made of the reciprocal of diborane concentration *vs.* time at each of four temperatures. Using the above second-order equation, rate constants were obtained at each temperature. The activation energy and frequency factor were determined from a plot of log $k$ *vs.* $1/T$ (Figure 1). The Arrhenius equation for the reaction may be expressed as

$$k = 5.0 \times 10^7 e^{-14,800/RT} \text{ l. mol}^{-1} \text{ sec}^{-1}$$

**The Catalyzed Reaction.** The effect of tetrahydrofuran upon the reaction of diborane and acetone was initially studied at 118.0°. Experiments were performed using reaction mixtures containing initial pressures of 10 Torr diborane, 20 Torr tetrahydrofuran, and 40 Torr acetone. Examination of the infrared spectra obtained during these reactions indicated that diisopropoxyborane was the only product. There was no evidence of a change in the tetrahydrofuran but its influence upon the rate of reaction was quite impressive. The addition of 20 Torr tetrahydrofuran to a mixture containing 10 Torr diborane and 40 Torr acetone pro-

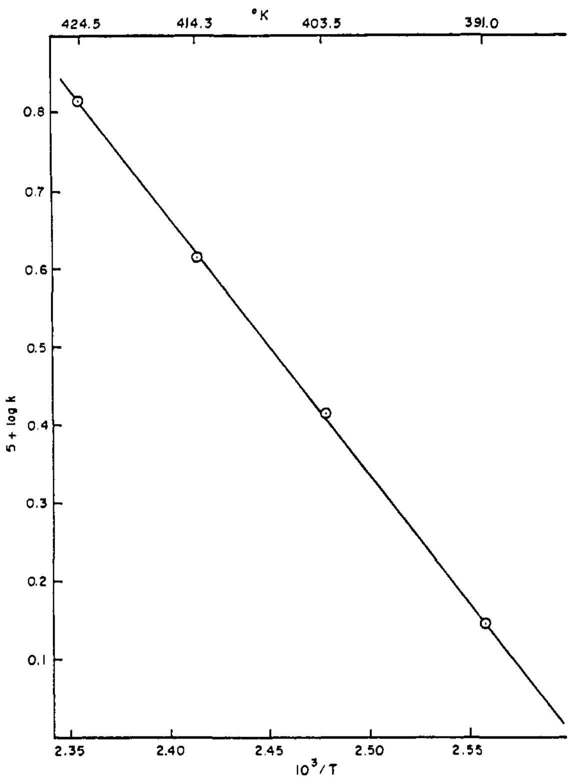


Figure 1. Arrhenius plot of the reaction between diborane and acetone.

duced a 30-fold increase in the reaction rate at 118.0°. There was evidence of a very slow reaction at room temperature; however, rapid mixing of the gases and immediate expansion into the reaction cell produced consistent rate data.

The infrared spectra indicated the same stoichiometry as that found for the reaction of diborane and acetone without tetrahydrofuran. Confirmation of the implied stoichiometry was achieved using the same procedure as previously described. In this case, reaction mixtures containing pressures of 10 Torr diborane, 20 Torr tetrahydrofuran, and 40 Torr acetone were studied in duplicate experiments. The results agreed with those previously presented in Table I. Tetrahydrofuran does not alter the stoichiometry of the reaction between diborane and acetone.

As before, the order of the reaction was determined by varying the initial concentration of each reactant in turn, while maintaining the initial concentrations of the other reactants constant. The relationship between the initial rate of diborane decrease and the initial concentrations of reactants is given in Table IV. The results indicate a reaction which is first order in diborane, first order in tetrahydrofuran, and zero order in acetone. Since the reaction is zero order in acetone and the tetrahydrofuran is unchanged, a plot of log diborane concentration *vs.* time should be linear. The results presented in Figure 2 support this hypothesis.

The increased rate of reaction required temperature dependence studies to be made over the temperature range 84.7–118.0°. Only mixtures with pressures of 10 Torr diborane, 20 Torr tetrahydrofuran, and 40 Torr acetone were used in these runs. Plots of log diborane concentration *vs.* time were made at each of four temperatures. Reaction rate constants were calculated at each temperature using the following expression, where $L_0$ is the concentration of tetrahydrofuran.

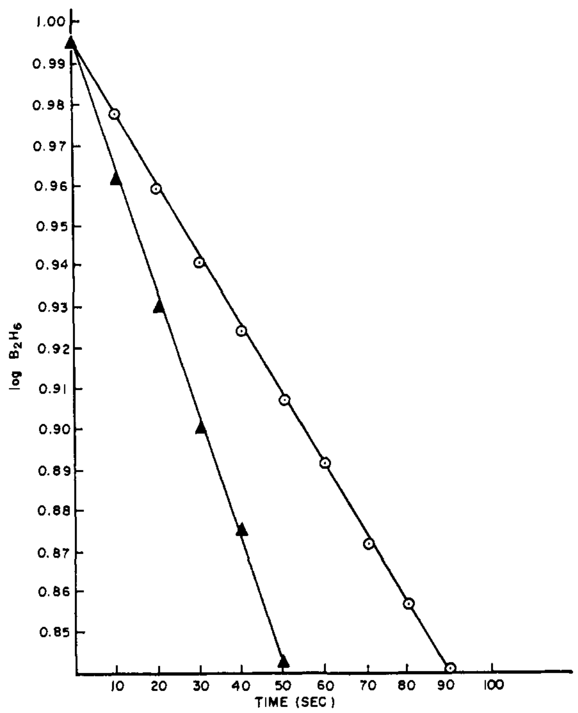


Figure 2. First-order plot of $B_2H_6$ concentration *vs.* time at 118.0°: ▲, 10 Torr $B_2H_6$, 20 Torr THF, 40 Torr $Me_2CO$; ⊙, 10 Torr $B_2H_6$, 10 Torr THF, 40 Torr $Me_2CO$.

$$\log B = \frac{kLt}{2.303} + \log B_0$$

The activation energy and frequency factor were evaluated in the usual way from a plot of log *k vs.* 1/*T* (Figure 3). The resulting Arrhenius equation is expressed as

$$k = 3.0 \times 10^{10}\, e^{-16{,}500/RT}\ \text{l. mol}^{-1}\ \text{sec}^{-1}$$

Table IV. Determination of the Orders in THF-Catalyzed Reactions at 118.0°

| Initial pressures, Torr $B_2H_6$ | $Me_2CO$ | THF | Initial rate, Torr sec$^{-1}$ | Initial rate/$P_0$ |
|---|---|---|---|---|
| 10.0 | 40.0 | 5 | $2.0 \times 10^{-2}$ | $4.0 \times 10^{-3}$ |
| 10.0 | 40.0 | 10.0 | 4.0 | 4.0 |
| 10.0 | 40.0 | 20.0 | 8.0 | 4.0 |
| 10.0 | 40.0 | 40.0 | 17.0 | 4.2 |
| 10.0 | 10.0 | 20.0 | 7.1 | |
| 10.0 | 20.0 | 20.0 | 7.0 | |
| 10.0 | 40.0 | 20.0 | 7.7 | |
| 4.7 | 40.0 | 20.0 | 3.9 | $8.2 \times 10^{-3}$ |
| 10.0 | 40.0 | 20.0 | 7.7 | 7.7 |
| 14.3 | 40.0 | 20.0 | 10.7 | 7.5 |

**Additional Experiments.** Several experiments were performed to determine the rate of the reaction between diborane and cyclobutanone. The effect of tetrahydrofuran upon this reaction was also studied. Another group of experiments were made to determine the effect of diethyl ether upon the reaction of diborane and acetone. A comparison of these significant results with

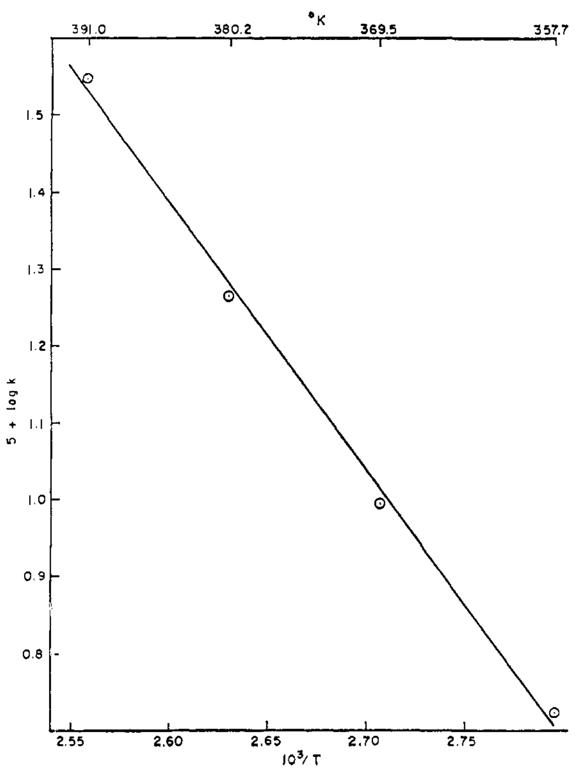


Figure 3. Arrhenius plot of the reaction between diborane and acetone catalyzed by THF.

those previously obtained for the reaction of diborane and acetone is presented in Table V.

Table V. Initial Rates with Various Reactants at 118.0°

| Initial pressures, Torr sec⁻¹ | | | | | |
|---|---|---|---|---|---|
| $B_2H_6$ | $Me_2CO$ | Cyclobutanone | THF | $Et_2O$ | Initial rate, Torr sec⁻¹ |
| 10.0 | 20.0 | | | | $2.5 \times 10^{-3}$ |
| 10.0 | 20.0 | | 20.0 | | $7.6 \times 10^{-2}$ |
| 10.0 | | 20.0 | | | $1.6 \times 10^{-3}$ |
| 10.0 | | 20.0 | 20.0 | | $7.0 \times 10^{-2}$ |
| 10.0 | 20.0 | | | 20.0 | $1.0 \times 10^{-2}$ |

The effect of an increase in surface area upon the rate of reaction was determined by placing quartz chips in the reaction cell. An increase in surface area of 100% was possible without interfering with energy transmission through the cell. The rate of reaction between diborane and acetone, with and without tetrahydrofuran, is unchanged under these conditions.

## Discussion

The mechanism of the reaction between diborane and acetone must be consistent with the following experimental findings: (1) in the absence of catalyst the reaction is first order in acetone and first order in diborane; (2) the reaction is catalyzed by Lewis bases such as ethyl ether and tetrahydrofuran, the latter being more active than the former; (3) the catalyzed reaction is first order in catalyst and first order in diborane but zero order in acetone; and (4) the reaction has a rather low activation energy and a low frequency factor. A frequency factor of $10^{11}$–$10^{12}$ l. mol⁻¹ sec⁻¹ is typical for a second-order reaction.[6] The experimental findings rule out any mechanism involving the breaking of the diborane molecule into two $BH_3$ molecules in a rate-determining step such as

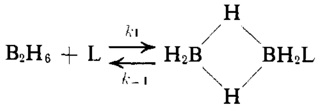
$$B_2H_6 \overset{\text{slow}}{\rightleftarrows} 2BH_3$$

$$BH_3 + O{=}CMe_2 \xrightarrow{\text{fast}} H_2BOCHMe_2$$

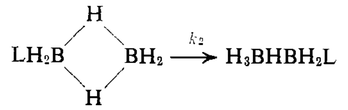
$$H_2BOCHMe_2 + O{=}CMe_2 \xrightarrow{\text{fast}} \text{products}$$

Such a mechanism would be first order in diborane and zero in acetone. The alternate possibility of having the first step fast and the second step slow and rate determining is also ruled out because it would require a reaction which is half order in diborane and first order in acetone.

A mechanism which has the correct order and would also have a low-frequency factor and activation energy is as follows (eq 1 and 2), where L is a ligand—an ether or a ketone.



(1)



(2)

$$H_3BHBH_2L + O{=}CMe_2 \xrightarrow{\text{fast}} \text{product}$$

The rate of this reaction is given by the equation

$$-d[B]/dt = k_1[B][L] - k_{-1}[C]$$

where [C] is the concentration of the complex formed in eq 1, [C′] is the concentration of the complex formed in eq 2, and [B] is the concentration of diborane. Making the steady-state assumption for C we find that

$$[C] = \frac{k_1[B][L]}{k_{-1} + k_2}$$

Substituting this in the rate equation gives

$$\frac{-d[B]}{dt} = k_1[B][L] - \frac{k_{-1}k_1[B][L]}{k_{-1} + k_2} = k_1[B][L]\left[1 - \frac{k_{-1}}{k_{-1} + k_2}\right] = k_1[B][L]\frac{k_2}{k_{-1} + k_2}$$

If we assume that $k_{-1} \gg k_2$, then the rate equation becomes

$$-d[B]/dt = K_e k_2[B][L]$$

The low activation energy and frequency factor is explained by the fact that the equilibrium constant, $K_e$, decreases with increase in temperature. The second step has an activation energy because it involves the breaking of a B–H bond. In the absence of added ethers the acetone acts as the ligand as well as the oxidizing agent. The equilibrium constant, $K_e$, for the formation of the first complex must by very small. The addition of THF (200 Torr) to diborane (10 Torr) had

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(6) A. Frost and R. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 75.

no significant effect upon the spectrum of the diborane nor did any new bands appear except those of THF. The structure of a 1:1 complex between diborane and THF is not known. The structure of such a complex between diborane and amines in solution has been studied and is the subject of some controversy.

Shore and Hall[7] contend that the initial adduct formed in the reaction of ammonia with diborane in solution at low temperature has a structure like our complex C′ with a single hydrogen bridge between the two boron atoms. Eastham,[8] on the other hand, contends that the diborane moiety remains intact in the formation of the adduct. Our kinetic data are most consistent with the idea that an Eastham type complex forms first followed by a Shore type complex which then reacts rapidly with acetone in a series of steps to yield diisopropoxyborane. Two plausible mechanisms for these fast steps are shown in Chart I, where R = isopropyl, and Chart II. In the first mechanism the single-bridged hydrogen structure is maintained and the hydrogen transfer occurs *via* a six-membered ring transition state. Such hydrogen transfers are known to occur with great ease. In the second mechanism the bridged B–H bond is broken and the hydrogen transfer occurs *via* a four-membered ring transition state.

**Chart I**

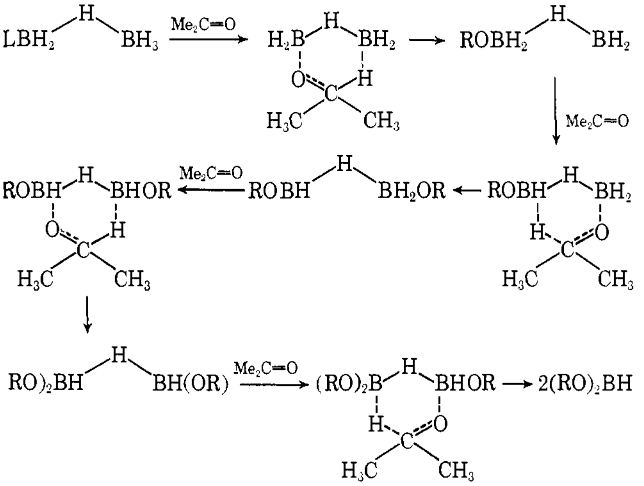
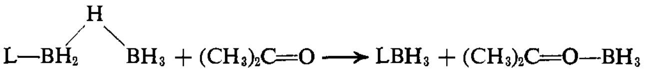


**Chart II**



$$L{-}BH_2\overset{H}{\frown}BH_3 + (CH_3)_2C{=}O \longrightarrow LBH_3 + (CH_3)_2C{=}O{-}BH_3$$

$$LBH_3 + (CH_3)_2C{=}O \longrightarrow (CH_3)_2C{=}O{-}BH_3 + L$$

$$(CH_3)_2C{=}O{-}BH_3 \longrightarrow ROBH_2$$

$$ROBH_2 + (CH_3)_2C{=}O \longrightarrow (CH_3)_2C{=}O{-}BH_2OR$$

$$(CH_3)_2C{=}O{-}BH_2OR \longrightarrow HB(OR)_2$$

Since the rate-determining step is the formation of the diborane–ligand complex the reaction is first order in diborane and first order in ligand. When the reaction is carried out in the absence of catalyst, acetone acts as the ligand and so under these circumstances the reaction is first order in acetone. The rate of the reaction in the presence of three different ligands increases in the order acetone < ethyl ether < tetrahydrofuran. This is the order of increasing basicity[9] and is consistent with the premise that the complex formation is rate determining.

It is of interest to compare our results with the liquid-phase reaction between acetone and sodium borohydride which has been carefully studied by Brown and coworkers.[4,5] This reaction is first order in borohydride and first order in ketone. The rate-determining step in this reaction is the transfer of the hydrogen, probably as the hydride ion, from boron to carbon. The rate of this reaction therefore depends upon the ketone that is being reduced. Thus cyclobutanone, whose reduction is accompanied by relief of steric strain, is reduced at a rate 40 times greater than acetone. Since the rate of reduction of ketones by diborane in the vapor phase depends upon the rate of complex formation and not upon the hydrogen transfer from boron to carbon, one would not expect to see an enhancement in rate in going from acetone to cyclobutanone. This expectation is confirmed by experiment which shows that diborane reduces cyclobutanone at a rate which is slower than the rate of reduction of acetone. The slower rate is due to the fact that cyclobutanone is a weaker base[7] than acetone. The tetrahydrofuran-catalyzed reaction between cyclobutanone and diborane was found to occur at the same rate as the tetrahydrofuran-catalyzed reaction between acetone and diborane. This is consistent with our hypothesis that the rate-determining step is the formation of the diborane–tetrahydrofuran complex which is followed by a rapid reaction with ketone. We are indebted to the referee for calling our attention to a related paper[10] in which it was necessary to postulate the formation of a 1:1 $B_2H_6$–ligand complex in the vapor-phase diborane–trimethylamine reaction.

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(7) S. Shore and G. Hall, *J. Amer. Chem. Soc.*, **88**, 5346 (1966); **89**, 3947 (1967).

(8) J. Eastham, *ibid.*, **89**, 2237 (1967).

(9) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(10) S. Bauer, J. Martinez, D. Prince, and W. Jones, *Advan. Chem. Ser.*, No. **42**, 35 (1964).