while in the case of ethylgermane these two effects reinforce one another.

All of our measurements have been carried out using sodium salts of the acids. Streitwieser, *et al.*, have noted[25] that the counterion affects the acidity of certain compounds in cyclohexylamine solution. Burley and coworkers[26] have used nmr methods to obtain information about ion pairing in solution of alkali metal salts. Table III presents some nmr data which we have obtained for solutions of germane and its alkali metal salts. The chemical shifts are reported relative to the solvent ammonia, and one notes that while the shift of the germane peak is constant, that for the germyl ion is dependent upon the cation. The lithium, sodium, and potassium salts have the same shift relative to germane whereas the cesium salt has a chemical shift to lower field. We conclude that this is because $Cs^+GeH_3^-$ exists as a contact ion pair in ammonia solution but that the other salts exist as solvent-separated ion pairs. By analogy to Streitwieser's systems[25] we expect that the use of the cesium instead of the sodium salt would cause the acidity of the germanes, in which the anions have a localized charge, to increase relative to the hydrocarbons. However we would not expect to change the acidity of the germanes relative to each other.

TABLE III[a]

Alkali metal cation	$\delta(GeH_3^-)$, ppm	$\delta(GeH_4)$, ppm	Alkali metal cation	$\delta(GeH_3^-)$, ppm	$\delta(GeH_4)$, ppm
Li^+	−0.38	−2.40	K^+	−0.42	−2.43
Na^+	−0.42	−2.43	Cs^+	−0.50	−2.40

[a] Values ±0.02 ppm relative to center peak of NH_3 triplet. Solutions ~0.4 *M* in both GeH_4 and salt.

Acknowledgments.—The National Research Council of Canada is thanked for financial support.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA 46556

Reactions of Borane (BH_3). IV. The Absolute Rate of Reaction with Acetone

BY T. P. FEHLNER

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The reaction of free borane (BH_3) with acetone to produce an adduct having a mass corresponding to BC_3H_9O has been shown to occur in the gas phase. At 450°K, 4.6 Torr total pressure of helium, and low partial pressures of reagents, the absolute bimolecular rate constant for this reaction is 3×10^8 l./mol sec. It is likely that the observed product of the reaction between BH_3 and acetone is a Lewis acid–base adduct rather than an alkoxyborane.

It has been suggested that the reactivity of tricoordinate boron compounds is controlled by two factors: the acceptor strength of the boron species and the ease of ligand displacement or rearrangement.[1] These principles follow if the reactions expected for a tricoordinate boron species, BX_3, may be written in general as

$$X_3B + :YL_p \longrightarrow X_3B:YL_p \tag{1}$$

$$X_3B:YL_p \longrightarrow X_2BYL_{p-1} + XL \tag{2}$$

$$X_3B:YL_p \longrightarrow X_2BYXL_p \tag{3}$$

where boron is attached to three, not necessarily identical, ligands X and where Y is a central atom attached to p, not necessarily identical, ligands L. Reaction 1 is a Lewis acid–base addition reaction; (2) is an elimination reaction which may occur when Y is saturated and at least one ligand L is hydrogen; and (3) is a rearrangement reaction which may occur when Y is unsaturated and at least one ligand X is hydrogen. These postulates certainly allow the rationalization of many of the reactions of tricoordinate boron compounds. However, to understand the factors that control the reactivity of these compounds it is necessary to probe in detail the reactions of carefully selected systems containing tricoordinate boron. We are engaged in a program of examining the reactions of the simplest tricoordinate boron species, borane (BH_3). By identifying the reactions of this species and measuring the rates, we hope more fully to document the concepts of reactivity presented above.

Our methods for producing kinetically useful quantities of BH_3 and for examining the reactions of BH_3 in the gas phase have been reported previously.[2–6] Thus far we have examined the reactions of BH_3 with BH_3,[3] PF_3,[4] $N(CH_3)_3$,[4] C_2H_4,[5] B_2H_6,[6] and B_5H_9.[6] In this report, an examination of the reaction of BH_3 with acetone, $(CH_3)_2CO$, is presented. This molecule possesses both a basic site and unsaturation. Consequently, we wished to contrast the identity and absolute rate of its reaction or reactions with BH_3 with those of the other species mentioned above.

The uses of boron hydrides in the reduction of various organic functional groups has been extensively discussed by Brown.[7] Although the reaction of BH_3

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(1) E. L. Muetterties in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, Chapter 1.

(2) G. W. Mappes and T. P. Fehlner, *J. Amer. Chem. Soc.*, **92**, 1562 (1970).

(3) G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, *J. Phys. Chem.*, **74**, 3307 (1970).

(4) S. A. Fridmann and T. P. Fehlner, *ibid.*, **75**, 2711 (1971).

(5) T. P. Fehlner, *J. Amer. Chem. Soc.*, **93**, 6366 (1971).

(6) S. A. Fridmann and T. P. Fehlner, *ibid.*, **93**, 2824 (1971).

(7) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, Chapter 17.

with acetone may not actually be an elementary reaction in the overall reduction of a ketone, it is hoped that this study will provide a more detailed basis for understanding the role of boron hydrides in these complex reductions.

Experimental Section

Technique.—The apparatus used in this study consists of a fast-flow, gas-phase, tubular reactor directly coupled to a mass spectrometric analysis system. This apparatus and the procedures involved in utilizing it in this type of study have been described in detail previously.[2,3,8,9] Briefly, our procedure is as follows. Helium containing a few per cent of a weakly bound adduct of BH_3 flows through a tubular reactor at *ca.* 10^4 cm/sec. A hot zone of sufficiently high temperature and length serves to decompose better than 95% of the borane adduct. We have shown previously[2] that the major boron hydride present in the flow immediately downstream of the hot decomposition zone is free borane, BH_3. In a later study[4] we added a movable injection probe to the apparatus so that a third gas may be added to the flow at any desired position downstream of the hot zone. With this system we can examine the reactions of BH_3 as a function of reaction time, temperature, and partial pressures of reactants.

The composition of the gas in the reactor is determined by sampling the flow with a small thin-edged orifice into a mass spectrometer system utilizing modulated molecular beam sampling. The efflux of the sampling orifice is collimated into a molecular beam using a three-stage differentially pumped system. The molecular beam is crossed with an electron beam and the resulting ions are accelerated, mass analyzed, and detected. The molecular beam is mechanically modulated and the signal from the electron multiplier is fed either to a narrow-band amplifier which is locked into the frequency and phase of the modulation device or to a modulated counting system. This type of mass spectrometric technique not only provides unambiguous sampling but also provides a convenient means for the identification of the neutral species in the molecular beam.[8-11] The phase shift between the reference signal and the ion signal is related to the average flight time in the molecular beam of the neutral molecule that gives rise to the ion signal. Consequently, the relative phase of a given ion signal yields the apparent molecular weight of the neutral progenitor of a given ion signal.

In the present experiments a single temperature profile similar to that shown at the top of Figure 1 in ref 3 with a decomposition zone temperature of 630°K and length of 2.8 cm was used in each rate constant measurement. Measurement of the rate constant involved changing the position of the gas probe alone. The movement of the probe defines a reaction zone consisting of the last 2 cm of the flow reactor. These measurements were made at a mean reaction zone temperature of 450°K with a high value of 460°K. BH_3PF_3 was used as a source of BH_3 in this work. The total pressure in the reactor was 4.6 Torr and the flow velocity was 10^4 cm/sec. Calibrations were carried out as described previously.

Materials.—BH_3PF_3 was prepared by the method of Parry and Bissot[12] and was purified by trap to trap fractionation. The major impurities were PF_3 and B_2H_6 present at levels of less than 5 mol %. Diborane was prepared by the method of Jeffers[13] and was also purified by trap to trap fractionation. Acetone (J. T. Baker, Reagent) was degassed by several freeze–thaw cycles and used without further purification. PF_3 (Peninsular Chemresearch) was used without further purification. Diisopropoxyborane was prepared by condensing a 20-fold excess of B_2H_6 with acetone in a glass bulb, warming the mixture quickly to room temperature (total pressure *ca.* 50 cm), and then quenching with liquid nitrogen after 10 min. After removing the excess B_2H_6 the product disproportionated rapidly at room temperature to form trialkoxyborane and diborane. The spectrum reported below was obtained by direct introduction of the sample into the source immediately after warming to 0°.

Results

Product Identification.—The initial experiments were oriented toward the identification of the products of the reaction of acetone with BH_3. $(CH_3)_2CO$ was injected immediately downstream of the BH_3 preparation zone at a partial pressure of *ca.* 300 mTorr such that the interval between the point of injection and the sampling orifice corresponded to a time of 0.5 msec. Products were sought at mean BH_3 levels of up to 15 mTorr. The mass spectrum was searched only at *m/e* values greater than that of the parent ion of $(CH_3)_2CO$ (*m/e* 58). Ions were observed from *m/e* 68 through 73 and the relative intensities of these ions are displayed in Table I. The *m/e* values of these ions correspond to those expected for the addition product of BH_3 and acetone. The intensity of *m/e* 71 was approximately 100 times less intense than *m/e* 58 from acetone. The intensities of all of the ions observed depended on the partial pressures of both BH_3 and $(CH_3)_2CO$. Ions corresponding to the dialkoxy derivative of borane and the dimer of the monoalkoxy derivative of borane were sought but were not found. Although it is not known whether the dialkoxydiborane exists the diisopropoxyborane was prepared and its mass spectrum is illustrated in Figure 1. Ions corresponding to both of these species were not present at levels greater than 0.01 of the *m/e* 71 ion intensity.

TABLE I[a]

MASS SPECTRA OF THE ADDUCT OF BH_3 with $(CH_3)_2CO$, BC_3H_9O

Ion[b]	*m/e*	Rel intens	Ion[b]	*m/e*	Rel intens
P + 1	73	0.5	P − 2	70	30
P	72	5	P − 3	69	*c*
P − 1	71	100	P − 4	68	3

[a] Normal abundance of boron isotopes. [b] P refers to parent. [c] Obscured by *m/e* 69 from PF_3.

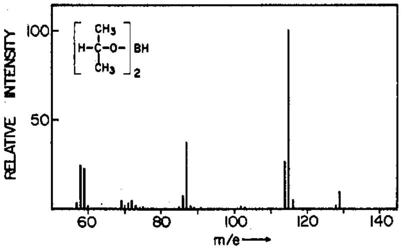

Figure 1.—The mass spectrum of diisopropoxyborane at 70 eV.

To confirm that the ions observed in the *m/e* 70 region correspond to a real addition product, the relative phase of the *m/e* 71 ion peak was measured with respect to *m/e* 58 from *n*-butane and *m/e* 69 from PF_3 under the reaction conditions. The results of these measurements are shown in Figure 2 which is a plot of the difference of the signal at phase angle ϕ and the signal at phase angle $\phi + 180°$ *vs.* the phase angle ϕ. The straight lines are least-squares fits of the data. The apparent molecular weight of the neutral progenitor of the *m/e* 71 ion calculated from this data is 70 ± 10. The uncertainty is unfortunately large but the measurements do lend confirmation to the identification of the formation of an addition product.

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(8) T. P. Fehlner, *J. Amer. Chem. Soc.*, **90**, 4817 (1968).

(9) S. N. Foner, "Advances in Atomic and Molecular Physics," Vol. 2, D. R. Bates and I. Estermann, Ed., Academic Press, New York, N. Y., 1966, p 385.

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(12) R. W. Parry and T. C. Bissot, *J. Amer. Chem. Soc.*, **78**, 1524 (1956).

(13) W. Jeffers, *Chem. Ind.* (*London*), 431 (1961).

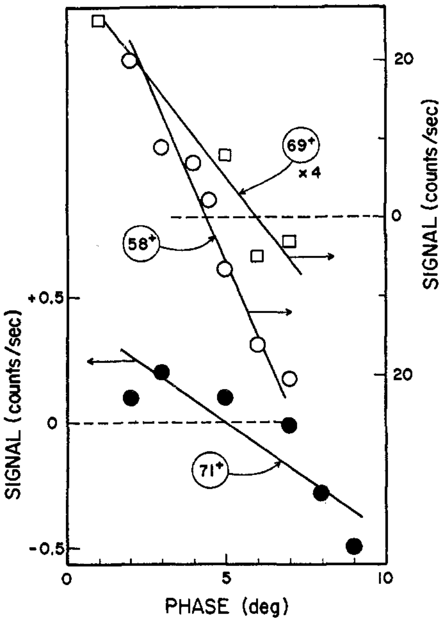

Figure 2.—Determination of the relative phase of the *m/e* 71 ion signal produced from the reaction of BH_3 with acetone. *m/e* 58 is derived from *n*-butane and *m/e* 69 is derived from PF_3. Counting times of 100 sec were used.

Apparently, the only additional reaction taking place on adding $(CH_3)_2CO$ to the flow at relatively high levels is the reaction of BH_3 with acetone to produce a species which has a mass corresponding to the sum of BH_3 and $(CH_3)_2CO$. It must be kept in mind that the dimerization of BH_3 to form B_2H_6 is a competing reaction and one which has been examined previously. In the reaction zone then two major reactions are taking place

$$BH_3 + (CH_3)_2CO \longrightarrow BC_3H_9O \qquad (4)$$

$$2BH_3 \longrightarrow B_2H_6 \qquad (5)$$

Sensitivity.—In order to analyze conveniently the kinetics and to obtain an absolute rate constant for reaction 4 it is necessary to know the extent of (4) compared to (5). The most straightforward way to do this is to obtain a sensitivity for the addition product, BC_3H_9O, and thus quantify the measurements of this species. As it is impossible to obtain such a species in a pure state such a sensitivity must be obtained indirectly. Previously,[5] we obtained the sensitivity of $C_2H_5BH_2$ produced from the reaction of BH_3 with C_2H_4 by "titrating" the BH_3 with C_2H_4. The same type of procedure was attempted with the reaction of BH_3 with acetone. In the former study it was quite easy to swamp out reaction 5 with excess ethylene as the rate constants for the two processes are roughly equal under our conditions. In the case of acetone, however, it is clear from the much lower relative ion intensities observed that the rate constant for (4) is considerably less than that for (5). Consequently, one must work at as low a BH_3 level as possible and must check the quantitativeness of the "titration" after the fact. Figure 3 gives an example of a "titration" experiment plotted in the empirical form that best appeared to linearize the data at high titrating reagent levels for the reaction of BH_3 with C_2H_4. The ion intensity of the *m/e* 71 peak at infinite acetone partial pressure is taken to represent a partial pressure of BC_3H_9O equal to the partial pressure of BH_3 at the injection probe position in the absence of acetone. The latter value is obtained from spot measurements made in this study along with the extensive measurements reported previously.[3] It was found that the sensitivity of *m/e* 71 from BC_3H_9O is 1.7 times the sensitivity of *m/e* 13 from BH_3 and 0.9 times the sensitivity of *m/e* 58 from acetone. From the rate constant for reaction 4 calculated below one may show that, in the region where Figure 2 appears to be linear, reaction 4 accounts for roughly 90% of the consumption of BH_3. Therefore, it is felt that the relative sensitivity obtained for BC_3H_9O, although crude, is essentially correct.

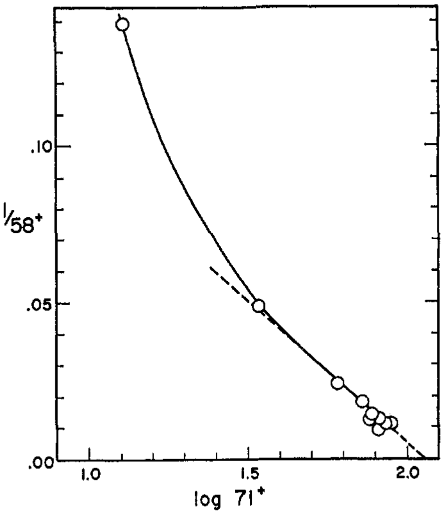

Figure 3.—"Titration" of BH_3 with acetone. The "titration" was carried out at probe position 38 at which the BH_3 partial pressure in the absence of acetone was 4.8 mTorr. The graph is a plot of the inverse of the *m/e* 58 ion intensity from acetone *vs.* the log of the *m/e* 71 ion intensity from the acetone–borane adduct.

Rate Constant.—Using the *m/e* 71 ion peak as a monitor of adduct formation, the amount of adduct formed as a function of probe position (time) at various fixed acetone partial pressures and two initial BH_3 partial pressures was measured and is reported in Table II. The relationship between the probe position and the sampling orifice is shown in Figure 4. The values of $(BH_3)_0$ given in the table are the values of the BH_3 partial pressure at the probe position in the absence of acetone. These were calculated from the measured partial pressures of BH_3 for the temperature profile used here and the decay of BH_3 reported previously.[3] Data were not taken between probe positions 60 and 80 as between these positions one is sam-

TABLE II

PARTIAL PRESSURES OF THE PRODUCT OF THE REACTION OF BH_3 AND $(CH_3)_2CO$ IN MTORR AT 450°K AND A TOTAL PRESSURE OF 4.6 TORR

Probe position	$(BH_3)_0$, mTorr	$((CH_3)_2CO)$, mTorr 7.1	24	58	147	212	284
38	4.8	0.064	0.430	1.16	1.80	2.40	2.74
58	3.9	0.058	0.212	0.502	0.945	1.12	1.12
48	4.4	0.107	0.365	0.880	1.52	1.72	1.72
38	4.8	0.172	0.451	0.988	1.98	2.32	2.49
38	19.9	0.258	0.558	1.44	3.01		
58	12.2	0.116	0.327	0.713	1.35		
48	15.6	0.172	0.344	1.16	2.19		
38	19.9	0.258	0.451	1.42	2.84		

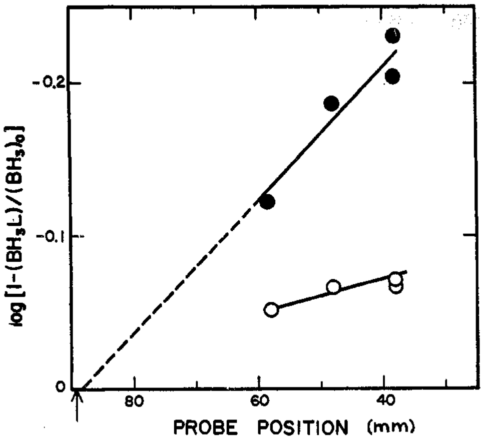

Figure 4.—A plot of log [1 − $(BH_3 \cdot L)/(BH_3)_0$] *vs.* probe position at an acetone partial pressure of 147 mTorr. $BH_3 \cdot L$ refers to the acetone–borane adduct and $(BH_3)_0$ refers to the partial pressure of BH_3 at a given probe position in the absence of acetone. The arrow indicates the position of the sampling orifice. The closed circles refer to data at the lower partial pressures of BH_3 in Table II while the open circles refer to the data at the higher BH_3 pressures.

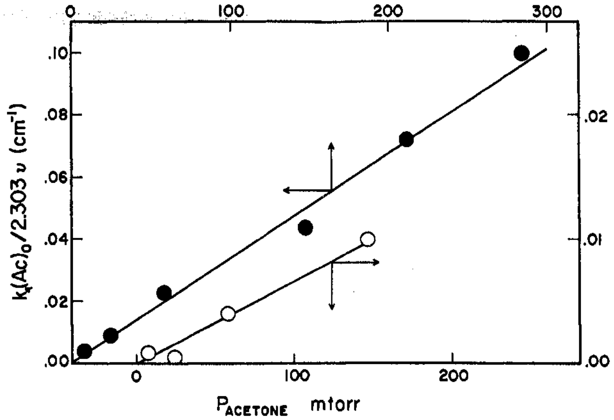

Figure 5.—A plot of $k_4(Ac)_0/2.303$ *vs.* $(Ac)_0$ at 450°K and a total pressure of 4.6 Torr. The closed circles refer to data at the lower partial pressures of BH_3 in Table II while the open circles refer to the data at the higher BH_3 pressures.

pling the mixing zone.[4] In order to extract a rate constant for reaction 4 the competing reaction 5 was initially ignored. In addition it was assumed that the acetone partial pressure was independent of the extent of reaction. The latter assumption is fairly good, particularly at the higher acetone partial pressures, while the former is only valid at high acetone partial pressures and low BH_3 partial pressures. With these assumptions the integrated kinetic equation that is applicable is

$$\log [1 - (BC_3H_9O)/(BH_3)_0] = -k_4(Ac)_0t/2.303 \quad (6)$$

where $(BH_3)_0$ is the partial pressure of BH_3 at the particular probe position in the absence of acetone, (BC_3H_9O) is the partial pressure of acetone–borane adduct, k_4 is the bimolecular rate constant for reaction 4, $(Ac)_0$ is the initial acetone partial pressure, and t is the reaction time. A plot of the left-hand side of (6) *vs.* probe position (*i.e.*, time) should yield a straight line with a slope of $-k_4(Ac)_0/2.303$. Figure 4 illustrates a plot of some of the data in Table II at a single acetone level for two initial BH_3 levels. The intercept of the data at the lowest BH_3 level is close to the known sampling orifice position (*i.e.*, zero time). The slopes of all such plots from the data in Table II are plotted *vs.* the acetone partial pressure in Figure 5. The slopes of the plots in Figure 4 yield values for k_4. For the mean $(BH_3)_0$ = 4.4 mTorr, $k_4 = 2.1 \times 10^8$ l./mol sec, while for the mean $(BH_3)_0$ = 15.6 mTorr, $k_4 = 0.41 \times 10^8$ l./mol sec.

The apparent dependence of the rate constant on $(BH_3)_0$ is due to the assumption that (4) is the only reaction leading to the consumption of BH_3. The simplest way to correct the k_4 for the error introduced by this assumption is to extrapolate the k_4 to $(BH_3)_0 = 0$. Doing so yields a $k_4 = 2.9 \times 10^8$ l./mol sec which is equal within experimental error to the value of k_4 measured at the lower $(BH_3)_0$. The correction may be carried out more rigorously by examining the integrated rate expression for reactions 4 and 5 occurring concurrently.[14] For $(Ac)_0 \gg (BH_3)_0$ and $(Ac) \approx (Ac)_0$ the appropriate expression is

$$\ln [(BH_3)_0/(BH_3)]\{[2k_5(BH_3) + k_4(Ac)_0]/[2k_5(BH_3)_0 + k_4(Ac)_0]\} = k_4(Ac)_0t \quad (7)$$

where the term in braces may be viewed as a correction on the argument of the logarithm in eq 6. Using the value of k_5 reported previously and the value of k_4 at the lower $(BH_3)_0$ one may correct the data at the higher $(BH_3)_0$ and $(Ac)_0$ = 147 mTorr such that k_4 is independent of $(BH_3)_0$ provided that at the higher $(BH_3)_0$ roughly 40% of the BH_3 reacts *via* (4) and 60% *via* (5). This is quite reasonable as, at the higher $(BH_3)_0$, $k_4(Ac)_0$ is *ca.* 40% of $[k_4(Ac)_0 + 2k_5(BH_3)_0]$. Therefore the best value for k_4 is 3×10^8 l./mol sec at a total pressure of 4.6 Torr and a temperature of 450°K. The various other errors in our procedures have been discussed previously in some detail.[3,4] We estimate that this value of k_4 is good to a factor of 2 or 3.

Discussion

We have shown that BH_3 reacts with acetone to produce a product with a mass corresponding to BC_3H_9O and have measured the rate constant for this simple reaction. An important question, which has been avoided up to this point, concerns the structure of the adduct. Are we observing the product of a reaction similar to (1), a Lewis acid–base adduct, or the product of reactions similar to (1) plus (3), an alkoxyborane? Our experiments provide no direct information on the structure of BC_3H_9O; however, the probable structure is indicated by several indirect observations.

First no dialkoxyborane or dialkoxydiborane was observed (see above). The Lewis acid–base adduct is not expected to undergo additional reaction with acetone whereas the alkoxyborane is expected to react further and apparently does so rapidly.[7] Therefore, the nonobservation of a dialkoxyborane or dialkoxydiborane means either that the product is the acid–base adduct or that the rate constants for

$$ROBH_2 + (CH_3)_2CO \longrightarrow (RO)_2BH \quad (8)$$

and

$$ROBH_2 + ROBH_2 \longrightarrow (ROBH_2)_2 \quad (9)$$

are $k_8 \leq 1 \times 10^6$ and $k_9 \leq 2 \times 10^8$ l./mol sec.[15] It is

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[14] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 31.

[15] These upper limits were calculated from the upper limit on the signal for the dialkoxyborane (*m/e* 127–129) and the dialkoxydiborane (*m/e* 83–85). It was assumed that the sensitivities for both the dialkoxyborane and dialkoxydiborane were equal to that for acetone and that $k_8 = \Delta[(RO)_2BH]/\Delta t \cdot (ROBH_2)(Ac)$ and $k_9 = \Delta[(ROBH_2)_2]/\Delta t(ROBH_2)^2$.

possible that k_8 is $\leq 10^6$ l./mol sec but then it becomes difficult to explain why the monoalkoxyborane has not been observed.[16] In addition, with ethylborane, where we did observe the dimer and diadduct, we found that the partial pressure of the diadduct did not go to zero as the probe closely approached the sampling orifice. The nonzero intensity at zero time was attributed to the fact that, in the vicinity of the probe where mixing is incomplete, there are high local concentrations of the added reagent gas and thus enhanced diadduct formation. Thus the limits on k_8 and k_9 should be lower. We feel then that the observation of no dialkoxyborane at all suggests that BC_3H_9O is $(CH_3)_2COBH_3$. If this conclusion is correct, the reaction we are observing is of the same type as reaction 1.

Acknowledgments.—This research was supported by the National Science Foundation under Grant No. GP 10199. The aid of G. W. Mappes and S. A. Fridmann in setting up the apparatus is gratefully acknowledged.

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[16] H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Amer. Chem. Soc.*, **61**, 673 (1939).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA 85721

The Reaction of Diborane with Trimethylamine–Alane and Dimethylaminoalane

BY PHILIP C. KELLER

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Diborane adds to trimethylamine–alane in toluene or diethyl ether to produce $(CH_3)_3N\cdot Al(BH_4)_3$. The action of excess diborane in toluene establishes an equilibrium competition between aluminum borohydride and diborane for trimethylamine. Reaction of trimethylamine–borane with aluminum borohydride in toluene produces the same equilibrium mixture. In diethyl ether diborane and $(CH_3)_3N\cdot Al(BH_4)_3$ form trimethylamine–borane and $(C_2H_5)_2O\cdot Al(BH_4)_3$. Diborane adds to solutions of dimethylaminoalane in diethyl ether or toluene to form $(CH_3)_2NAl(BH_4)_2$. Excess diborane slowly causes formation of μ-dimethylaminodiborane and aluminum borohydride. In tetrahydrofuran dimethylaminoalane and borane form $(CH_3)_2NAl(BH_4)_2$ which reacts with excess borane to produce μ-dimethylaminodiborane and n-$C_4H_9OAl(BH_4)_2$.

Introduction

A number of workers have shown that diborane adds to aluminum–hydrogen bonds to produce aluminum borohydride derivatives.[1-3] Neither the utility of this reaction for the synthesis of aluminum borohydride derivatives nor the behavior of these products in the presence of excess diborane has been explored. This paper describes the preparation of the known compounds $(CH_3)_3NAl(BH_4)_3$ and $(CH_3)_2NAl(BH_4)_2$[4] by the addition of diborane to trimethylamine–alane and dimethylaminoalane, respectively, and details the reactions of these materials with excess diborane.

Experimental Section

General Data.—All manipulations involving air- or moisture-sensitive materials were carried out using standard inert-atmosphere and high-vacuum techniques. Boron-11 nmr spectra were obtained with a Varian HA-100 spectrometer equipped with a 32.1-MHz probe; boron chemical shifts are in ppm relative to diethyl ether–boron trifluoride. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers.

Nmr studies were performed using reaction vessels of the type shown in Figure 1. The overall dimensions of the vessel are such that it may be inserted in and removed from the nmr instrument without disturbing the probe.

Trimethylamine–alane and dimethylaminoalane were prepared by the method of Ruff and Hawthorne.[5] Aluminum borohydride was generated by the reaction of aluminum chloride with sodium borohydride.[6] Trimethylamine–borane was prepared by the method of Schaeffer and Anderson.[7] Diborane was formed by treating sodium borohydride with warm polyphosphoric acid. The pure solvents diethyl ether, toluene, and tetrahydrofuran (THF) were stored in evacuated bulbs over lithium aluminum hydride and were vacuum transferred directly into reaction vessels when used.

Reaction of Trimethylamine–Alane with Diborane in Toluene. A solution of 0.175 g (1.96 mmol) of trimethylamine–alane in 5 ml of toluene was stirred magnetically in the presence of 4.20 mmol of diborane in a 250-ml bulb for 1 hr at room temperature. Fractionating the volatile products through −126° resulted in the recovery of 1.14 mmol of diborane, implying a consumption of 3.06 mmol (calcd for $(CH_3)_3NAl(BH_4)_3$, 2.94 mmol). The colorless solid residue in the reaction bulb was sublimed to a −78° cold finger by gentle warming with an infrared heat lamp. The sublimate was identified as $(CH_3)_3NAl(BH_4)_3$ by its melting point of 79–81° (lit.[8] mp 79°) and its known infrared spectrum (Nujol).[4] This experiment produced 0.133 g (1.02 mmol, 52%) of sublimed product.

In experiments with longer reaction times, more diborane was consumed and work-up of volatile products produced some trimethylamine–borane (identified by ir spectrum). Further attempts at separation resulted in the appearance of more diborane and an easily sublimed colorless solid, identified as $(CH_3)_3N\cdot Al(BH_4)_3$, strongly suggesting a reversible reaction.

Boron-11 Nmr Study of the Diborane–Trimethylamine–Alane–Toluene System.—A solution of 0.123 g (1.38 mmol) of trimethylamine–alane in 1 ml of toluene was prepared in an nmr reaction vessel. Diborane was added in approximately 0.7-mmol increments and the boron-11 nmr spectrum of the solution was recorded after each addition. The first two spectra consisted only of a single quintet at 37.4 ppm with $J = 85$ Hz. No signal characteristic of diborane was detected. After the third

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