

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

## Reactions of Borane (BH<sub>3</sub>). VI.<sup>1</sup> Reactions with Alcohols

T. P. FEHLNER

Received August 8, 1972

The reaction of borane with methanol and 2-propanol to produce the acid-base adduct ROH·BH<sub>3</sub>, the alkoxyborane ROBH<sub>2</sub>, the dialkoxyborane (RO)<sub>2</sub>BH, and H<sub>2</sub> has been shown to take place. These results establish that the product of the reaction of BH<sub>3</sub> and acetone is a simple donor-acceptor adduct. The results with fluorinated acetone and 2-propanol suggest that in the reaction of BH<sub>3</sub> with ketones and alcohols the formation of the donor-acceptor adduct precedes further reaction. An estimated bimolecular rate constant for the reaction of BH<sub>3</sub> with 2-propanol is also reported.

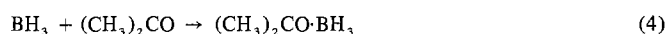
The reactions of boranes with oxygen-containing compounds are of interest for a number of reasons. Boron has a high affinity for oxygen, and many interesting compounds containing boron and oxygen exist.<sup>2</sup> The reaction of diborane with various organic functional groups containing oxygen is competitive with the chemically useful hydroboration reaction.<sup>3</sup> More directly, there are two major reasons for the direct examination of the reaction of BH<sub>3</sub> with alcohols. First, this author wished to investigate a reaction of BH<sub>3</sub> in which a tricoordinate borane may be formed by molecular elimination, *e.g.*, H<sub>2</sub>. In addition it was hoped that this system would provide a test of the two detailed mechanisms possible for the formation of the tricoordinate borane, namely



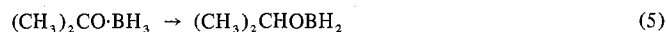
or



Second, this author wished to test the deductions made previously concerning the nature of the product of the reaction of BH<sub>3</sub> and acetone.<sup>4</sup> In this case the reaction product was tentatively identified as the donor-acceptor adduct of BH<sub>3</sub> and acetone. Thus the reaction observed was thought to be



the further reaction corresponding to



presumably being slow. It will be noted that the product of reaction 2 or 3 for 2-propanol is the same as the product of reaction 5. As the product of reaction 2 or 3 can be proved by H<sub>2</sub> production, the behavior of the two products can be compared and, consequently, the conclusions reached previously can be checked.

### Experimental Section

The apparatus has been described in detail previously.<sup>5-7</sup> It consists of a fast-flow, gas-phase, tubular reactor directly coupled with modulated molecular beam sampling to a mass spectrometric analysis system. This system provides for variation in reactant partial pressures and reaction time. Reaction temperature

and total pressure are not easily varied. Product identification was carried out both by conventional analysis of the mass spectra and by analysis of the relative phases of selected ions.<sup>7-10</sup>

The present experiments were carried out under the following conditions. BH<sub>3</sub> was prepared by the thermal decomposition of F<sub>3</sub>P·BH<sub>3</sub> in a hot zone similar to that shown at the top of Figure 1 in ref 6. Two separate, but identical, flow reactors were used for this work. One was heavily coated with boron deposits while the other was relatively clean, having only been conditioned by F<sub>3</sub>P·BH<sub>3</sub> pyrolysis until reproducible production of BH<sub>3</sub> was achieved. The deposits in the original reactor were evidently somewhat porous and adsorbed or trapped alcohols. This showed up clearly when samples of alcohols were placed in the reactor under *static* conditions.<sup>5</sup> Measurable amounts of alkoxyboranes were observed and, in the case of the deuterated alcohols, some H-D exchange was also observed. These annoying effects were just barely visible in the flow experiments. In order that the results of the flow experiments not be compromised, a new reactor was installed. In the clean reactor these effects were not observed either in the static or in the flow modes. The observations reported below were independent of the reactor used. Rate measurements were carried out by changing the position of the gas probe only.<sup>11</sup> The movement of this probe defines a reaction zone consisting of the last 2 cm of the reactor. In the original flow reactor, the gas probe had a diameter of 3 mm while in the new reactor it was 2 mm. Neither the probe size nor the newness of the reactor had any significant effect on the rate constant measurements for the alcohols or for acetone.<sup>4</sup> The temperature of the reaction zone was 450 ± 10°K. The total pressure of the reactor was 4.5 Torr and the flow velocity was *ca.* 10<sup>5</sup> cm/sec. Calibrations of stable materials were carried out as described previously.<sup>6</sup>

Trifluorophosphine-borane and diborane were prepared and purified as described previously.<sup>11</sup> The alcohols (Fisher, Reagent) were degassed by several freeze-thaw cycles and used without further purifications. 2-Propanol-*d*<sub>4</sub>, 2-propanol-*O-d*, and acetone-*d*<sub>6</sub> were obtained from Merck Sharp and Dohme. Hexafluoro-2-propanol and hexafluoroacetone were both obtained from PCR and were used without further purification.

### Results

**Mass Spectra.** Products were sought using a total reaction time of *ca.* 0.5 msec, BH<sub>3</sub> partial pressures of up to 12 mTorr, and alcohol partial pressures up to 50 mTorr. Most attention was paid to the mass region above the parent ion mass of the alcohol as the interesting parts of the lower mass region were obscured by fragment ions from species known to be present, *i.e.*, F<sub>3</sub>P·BH<sub>3</sub>, PF<sub>3</sub>, BH<sub>3</sub>, B<sub>2</sub>H<sub>6</sub>, and ROH. The most prominent product ions observed were in the mass range *m/e* 70-73. This range corresponds to that expected for a product formed by the addition of BH<sub>3</sub> to 2-propanol. The relative intensities of these ions for 2-propanol are shown in Figure 1. The intensities of these ions exhibited the dependence on the partial pressure of BH<sub>3</sub> and the

(1) Part V: S. A. Fridmann and T. P. Fehlner, *Inorg. Chem.*, **11**, 936 (1972).

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966.

(3) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y. 1962; *Chem. Brit.*, **7**, 458 (1971).

(4) T. P. Fehlner, *Inorg. Chem.*, **11**, 252 (1972).

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

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

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

(8) S. N. Foner, *Advan. At. Mol. Phys.*, **2**, 385 (1966).

(9) R. M. Yealland, R. L. LeRoy, and J. M. Deckers, *Can. J. Chem.*, **45**, 2651 (1967).

(10) M. H. Boyer, E. Murad, H. Inami, and D. L. Hildenbrand, *Rev. Sci. Instrum.*, **39**, 26 (1968).

(11) S. A. Fridmann and T. P. Fehlner, *J. Phys. Chem.*, **75**, 2711 (1971).

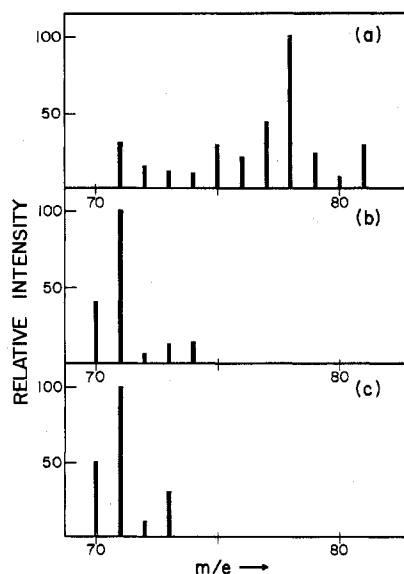


Figure 1. The mass spectra of the parent ion regions of the products of the reaction of  $\text{BH}_3$  and (a)  $(\text{CD}_3)_2\text{CDOD}$ , (b)  $(\text{CH}_3)_2\text{CHOD}$ , and (c)  $(\text{CH}_3)_2\text{CHOH}$ .

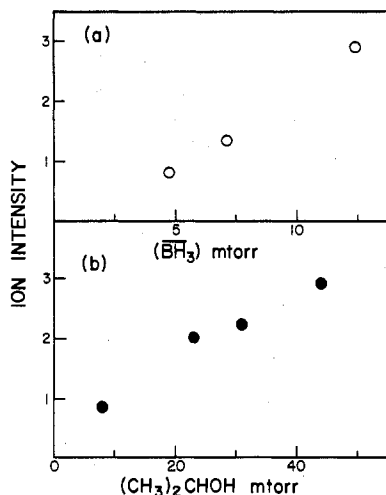


Figure 2. The variation in the intensity of  $m/e$  71 (a) with mean borane partial pressure,  $(\text{BH}_3)$ , at constant 2-propanol partial pressure of 44 mTorr and a probe position of 38.0 and (b) with 2-propanol partial pressure at a constant mean borane partial pressure of 12 mTorr and a probe position of 38.0.

partial pressure of 2-propanol expected for a product of the reaction of these two species. This behavior is illustrated in Figure 2. These ion intensities also depended upon reaction time—the intensities decreasing with decreasing time as shown in Figure 3. However, the time behaviors of the ion intensities were not identical as is also illustrated in Figure 3 by the change in the ratio of  $m/e$  73 to  $m/e$  71 with reaction time. This is a clear indication that these ions are due to more than one species. The reaction of  $\text{BH}_3$  with  $\text{CH}_3\text{OH}$  yielded a spectrum qualitatively similar to that in Figure 1 except in the mass region  $m/e$  42–45. The signal to noise was much worse, however, because of the large background noise in this region. The intensities of the major product ions were *ca.* 100 times less intense than the base peaks of the alcohols. This is a qualitative indication of a fairly low rate constant for the reaction.

Ions at still lower levels were observed at  $m/e$  values greater than 73 in the case of 2-propanol and greater than 45 in the case of methanol. These ions also depended on the presence of both  $\text{BH}_3$  and the alcohol. In the case of

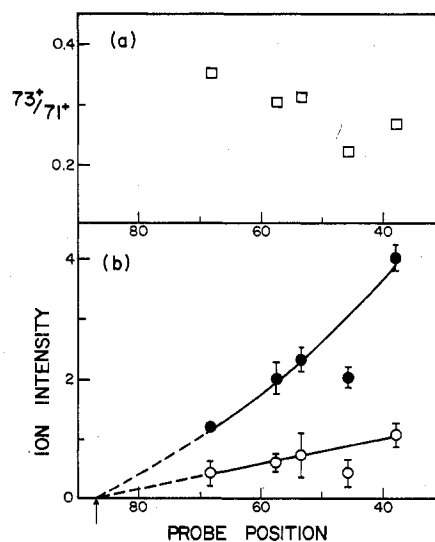


Figure 3. The variation in (a) the ratio of the ion intensities at  $m/e$  73 and 71 and (b) the ion intensity at  $m/e$  73 (open circles) and 71 (closed circles) as a function of probe position (reaction time) at a mean borane partial pressure of 6 mTorr and a 2-propanol partial pressure of 36 mTorr. The arrow indicates the relative position of the sampling orifice.

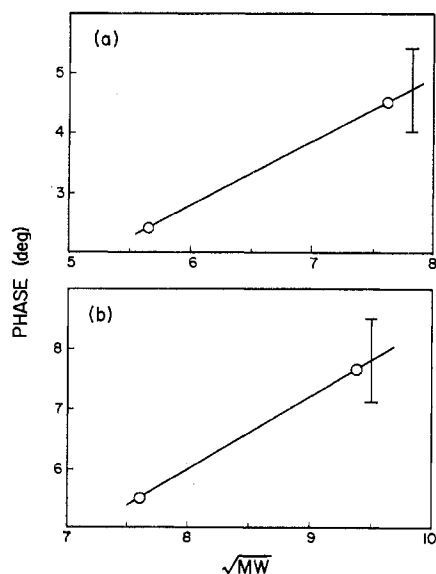
Table I. Partial Fragmentation Pattern of Diisopropoxyborane and Selected Ion Intensities from the Spectrum of Products

$m/e$	$[(\text{CH}_3)_2\text{CHO}]_2\text{BH}^a$	Products <sup>b</sup>
115	100	100
114	27	$10 \pm 10$
87	37	$50 \pm 20$
86	7	$10 \pm 5$
73	22	120
71	3	290

<sup>a</sup> Ref 4. <sup>b</sup> This work.

2-propanol one of the high-mass species was identified. The major ions of diisopropoxyborane and their relative abundances are given in Table I.<sup>4</sup> The relative intensities of like ions in the product mass spectrum are also shown in this table. Clearly one of the products is diisopropoxyborane. It should also be noted from this table that the fragmentation of diisopropoxyborane cannot account for the intensity of either  $m/e$  73 or 71. Other weaker ions were observed at other mass numbers but their molecular progenitors could not be identified.

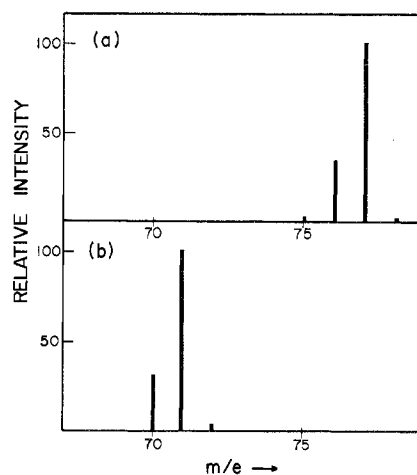
**Phase Spectra.** The relative phase angle of selected ion signals was measured in order to measure directly the apparent molecular weights of the neutral progenitors of the ions selected.<sup>9,10</sup> The relative phase angles of ions of both known and unknown molecular sources were obtained from plots of the signal at phase angle  $\phi$  minus the signal at phase angle  $\phi + 180^\circ$  vs. the phase angle  $\phi$ . The intercept at zero signal intensity was taken as the relative phase angle.<sup>7</sup> The results for  $m/e$  71 from the reaction of  $\text{BH}_3$  and 2-propanol and for  $m/e$  43 from the reaction of  $\text{BH}_3$  and methanol are shown in Figure 4. The apparent molecular weight of the former is  $91 \pm 10$  and that of the latter is  $60 \pm 10$ . As the relative phase angle of a given ion signal, *i.e.*, the apparent molecular weight, depends on the molecular weights and mole fractions of all species that contribute to the ion signal,<sup>7–10</sup> these results clearly indicate the presence of both the simple addition product of  $\text{BH}_3$  and the alcohol and higher mass products. If one assumes that only the alkoxyborane and the dialkoxyborane contribute to these ion signals, the measured phases set



**Figure 4.** Plot of relative phase angle vs. the square root of the molecular weight of the neutral progenitor of the ion. Calibration points: (a)  $m/e$  31 from  $\text{CH}_3\text{OH}$  and  $m/e$  43 from  $n$ -butane; (b)  $m/e$  58 from  $n$ -butane and  $m/e$  69 from  $\text{PF}_3$ . All calibrations were carried out under operating conditions of temperature, pressure, and flow. The relative phase of the  $m/e$  43 ion from the borane-methanol product is shown by the hash mark in (a) and the relative phase of the  $m/e$  71 ion from the borane-2-propanol product is shown by the hash mark in (b). The calculated apparent molecular weights are  $60 \pm 10$  in (a) and  $91 \pm 10$  in (b).

the mole fractions of alkoxyborane as 0.67 and 0.47 for 2-propanol and methanol, respectively. This calculation is an oversimplification as the product composition is more complex as will be shown below.

**Isotopic Substitution.** Complete unraveling of the stoichiometric nature of the major products was achieved by treating  $\text{BH}_3$  with 2-propanol- $d_8$  and 2-propanol- $O-d$ . One objective of deuterium labeling was to facilitate the search for the production of  $\text{H}_2$ . Examination of  $m/e$  2 with the protonated reactants gave a negative result; however, the result was not significant because of the very large background noise at  $m/e$  2. Much less noise is encountered at  $m/e$  3; thus the reactions of  $(\text{CD}_3)_2\text{CDOD}$  and  $(\text{CH}_3)_2\text{-CHOD}$  with  $\text{BH}_3$  were examined for the production of HD. In both cases the production of HD was easily observed ( $S/N = 3$ ) by the increase in the  $m/e$  3 ion intensity. This increase was also dependent on the presence of both  $\text{BH}_3$  and the alcohol. The amount of HD produced was the same for both D-substituted alcohols. The observation of the production of HD from  $(\text{CH}_3)_2\text{-CHOD}$  and  $\text{BH}_3$  is clear proof that one hydrogen atom was originally bound to boron and the other to oxygen. It is also good evidence for the occurrence of either reaction 2 or 3 and, thus, indirectly for the production of  $(\text{CH}_3)_2\text{-CHOBH}_2$ . As the ion at  $m/e$  73 can only be due to the adduct  $(\text{CH}_3)_2\text{CHOH}\cdot\text{BH}_3$ , the spectrum in Figure 1(c) must be due to both species. That such is really the case comes from an analysis of the parent ion region for reaction of  $\text{BH}_3$  with the deuterated alcohols (Figure 1(a) and (b)). If the spectrum in Figure 1(c) is due only to the addition product  $(\text{CH}_3)_2\text{CHOH}\cdot\text{BH}_3$ , one would expect the total spectrum to shift up 1 mass unit for  $(\text{CH}_3)_2\text{CHOD}\cdot\text{BH}_3$  and 8 mass units for  $(\text{CD}_3)_2\text{CDOD}\cdot\text{BH}_3$  as clearly happens for the reaction of  $\text{BH}_3$  with acetone (Figure 5). If, however, the spectrum in Figure 1(c) is due to both  $(\text{CH}_3)_2\text{CHOH}\cdot\text{BH}_3$  and  $(\text{CH}_3)_2\text{CHOBH}_2$ , for  $(\text{CH}_3)_2\text{CHOD}$  one would expect



**Figure 5.** The mass spectra of the parent ion regions of the products of the reaction of  $\text{BH}_3$  with (a)  $(\text{CD}_3)_2\text{CO}$  and (b)  $(\text{CH}_3)_2\text{CO}$ . In (b)  $m/e$  69 is obscured by fragmentation of  $\text{PF}_3$ .

the contribution due to  $(\text{CH}_3)_2\text{CHOD}\cdot\text{BH}_3$  to shift up 1 mass unit and the contribution due to  $(\text{CH}_3)_2\text{CHOBH}_2$  to remain unshifted. This is what the data indicate in Figure 1(b). On the other hand, for  $(\text{CD}_3)_2\text{CDOD}$  one expects the contribution due to  $(\text{CD}_3)_2\text{CDOD}\cdot\text{BH}_3$  to shift up 8 mass units and the contribution due to  $(\text{CD}_3)_2\text{CDO}\cdot\text{BH}_3$  to shift up 7 mass units. Once again this is what is indicated by the data (Figure 1(a)). Therefore, both the products of reaction 1 and 2 or 3 are present.

**Fluorine Substitution.** In an attempt to test the likelihood of reaction 2 vs. reaction 3 (see discussion below) the reactions of  $\text{BH}_3$  with hexafluoro-2-propanol,  $(\text{CF}_3)_2\text{CHOH}$ , and hexafluoroacetone,  $(\text{CF}_3)_2\text{CO}$ , were examined. In both cases no evidence for an addition product or any other product was obtained. Both  $(\text{CH}_3)_2\text{CHOH}$  and  $(\text{CH}_3)_2\text{CO}$  were run simultaneously with the fluorinated derivatives and products were observed in normal abundances. This work establishes a lower limit on the rate constant for the reaction of  $\text{BH}_3$  with  $(\text{CF}_3)_2\text{CHOH}$  of  $6 \times 10^6$  l./mol sec and a lower limit for  $(\text{CF}_3)_2\text{CO}$  of  $3 \times 10^6$  l./mol sec. In both cases a product sensitivity equal to that for the fluorinated compound was assumed.

**Rate Constant Measurements.** The results presented thus far indicate that more than one elementary reaction of  $\text{BH}_3$  is being observed. In addition, the relatively low product ion intensities indicate that the rate of the reaction of  $\text{BH}_3$  with alcohols is fairly slow compared to the dimerization of  $\text{BH}_3$  to yield  $\text{B}_2\text{H}_6$ . Both of these factors make it difficult to apply the titration technique used previously to obtain product ion sensitivities.<sup>12</sup> Therefore, the sensitivities for both  $(\text{CH}_3)_2\text{CHOH}\cdot\text{BH}_3$  and  $(\text{CH}_3)_2\text{CHOBH}_2$  were estimated to be the same as the product of the reaction of  $\text{BH}_3$  and acetone.<sup>4</sup> The sum of the ion intensities at  $m/e$  73 and 71 was then taken as a measure of the total amount of reaction of  $\text{BH}_3$  with 2-propanol. The essential correctness of this assumption is confirmed by the fact that the partial pressure of HD produced in the experiments with the deuterated alcohols is only 40% greater than the sum of the partial pressures of products calculated in this fashion. The amount of HD is expected to be high as the production of  $[(\text{CH}_3)_2\text{-CHO}]_2\text{BH}$  involves the formation of 1 mol of hydrogen also. In calculating the rate constant the association of  $\text{BH}_3$  to produce  $\text{B}_2\text{H}_6$  was ignored as was subsequent reaction to yield diisopropoxyborane. In addition, the 2-propanol

partial pressure was assumed to be independent of the extent of reaction. A rate constant was then obtained from the time dependence of the product ion intensities such as that shown in Figure 3. The bimolecular rate constant obtained is  $10^8$  l./mol sec at  $450^\circ\text{K}$  and a total pressure of 4.5 Torr. This rate constant refers to the reaction



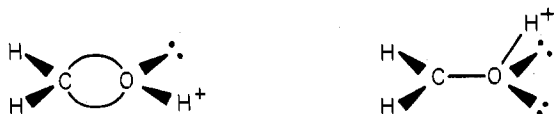
and must be considered as only an order of magnitude estimate. However, it is interesting to note that the value obtained is equal within experimental error to that for the reaction of  $\text{BH}_3$  with acetone.

### Discussion

**Nature of the Products.** In the reaction of  $\text{BH}_3$  with 2-propanol four products are clearly identified with empirical formulas:  $\text{BC}_3\text{H}_{11}\text{O}$ ,  $\text{BC}_3\text{H}_9\text{O}$ ,  $\text{H}_2$ , and  $\text{BC}_6\text{H}_{15}\text{O}_2$ . As has been implicitly assumed above, the only chemically reasonable structures for these products are the donor-acceptor adduct  $(\text{CH}_3)_2\text{CHOH}\cdot\text{BH}_3$ , isopropoxyborane  $(\text{CH}_3)_2\text{CHOBH}_2$ , molecular hydrogen  $\text{H}_2$ , and diisopropoxyborane  $[(\text{CH}_3)_2\text{CHO}]_2\text{BH}$ . The observation of the first three products is direct evidence for the existence of reaction 1 and either reaction 2 or 3 or both. The observation of diisopropoxyborane is most easily explained by the subsequent reaction of isopropoxyborane with 2-propanol in one or two steps.

The products observed in this study also serve clearly to identify the initial product of the reaction of  $\text{BH}_3$  with acetone.<sup>4</sup> It was previously shown that  $\text{BH}_3$  adds to acetone to yield a single product of empirical formula  $\text{BC}_3\text{H}_9\text{O}$  which may be either the donor-acceptor adduct or isopropoxyborane.<sup>4</sup> However, if isopropoxyborane were being formed, it should behave as the  $(\text{CH}_3)_2\text{CHOBH}_2$  produced in the reaction of  $\text{BH}_3$  with 2-propanol does, as the product ion intensities observed correspond to similar partial pressures. Thus, if  $(\text{CH}_3)_2\text{CHOBH}_2$  were produced in the reaction of acetone with  $\text{BH}_3$ ,  $\text{BC}_6\text{H}_{15}\text{O}_2$  should have been observable also. It was not and, therefore, the product of the reaction of acetone with  $\text{BH}_3$  must be the donor-acceptor adduct. This implies that reaction 5 must be slow under our conditions. A reasonable frequency factor of  $10^{12}$   $\text{sec}^{-1}$  for the rearrangement reaction 5 along with the known reaction conditions and estimated sensitivities yields a minimum activation energy for reaction 5 of 17 kcal/mol.

The results of a theoretical treatment of carbonyl donors show that this activation energy is quite reasonable.<sup>13</sup> This localized-orbital study considered three structures for the proton adduct of formaldehyde. The two pertinent ones here are bent (I) and the out-of-plane (II) structures. In I

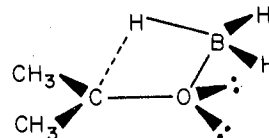


the OH  $\sigma$  orbital "may be thought of as the strongly polarized CO  $\pi$  orbital."<sup>13</sup> The bent structure is found to be more stable than the out-of-plane structure by 26 kcal/mol. As many Lewis adducts of the carbonyl group are known to exhibit the bent structure,<sup>14</sup> it is reasonable to

expect the bent structure to be the stable one for the acetone-borane adduct, *i.e.*



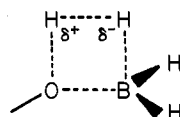
The out-of-plane structure corresponds to the interaction of  $\text{BH}_3$  with the CO  $\pi$  orbital and is probably a good picture of the activated complex for reaction 5, *i.e.*



Considering the interaction of  $\text{H}^+$  and  $\text{BH}_3$  with the carbonyl group as analogous, it is quite reasonable that the activated complex for reaction 5 is more than 17 kcal/mol above  $(\text{CH}_3)_2\text{CO}\cdot\text{BH}_3$  in the bent form.

**Detailed Mechanism.** An important question regarding the mode of reaction of  $\text{BH}_3$  concerns whether reaction 1 plus 2 or reaction 1 plus 3 best represents the mechanism. In other words is the addition product of reaction 1 a dead-end complex or does the interaction of  $\text{BH}_3$  with the donor molecule facilitate further reaction which in this case is elimination of  $\text{H}_2$ ? The same question may be asked concerning the reaction of  $\text{BH}_3$  with acetone or, for that matter, any reaction of  $\text{BH}_3$ .

An attempt to answer this question in the cases of acetone and 2-propanol was made as follows. The major barrier to the formation of the out-of-plane structure of the proton adduct of  $\text{H}_2\text{CO}$  is caused by electron repulsions.<sup>13</sup> By analogy, a major factor contributing to the energy for the activated complex of reaction 5 (which may also be considered the activated complex for the direct reaction of  $\text{BH}_3$  with acetone to yield isopropoxyborane) will be that caused by electron repulsions. Photoelectron spectra show that in hexafluoroacetone the nonbonding molecular orbital on oxygen in  $(\text{CH}_3)_2\text{CO}$  is partially delocalized over the fluorine atoms.<sup>15</sup> This would tend to reduce the energy of the activated complex for reaction 5 and thus enhance the probability of both reaction 5 and the direct reaction. On the other hand fluorine substitution would reduce the donor strength of  $(\text{CF}_3)_2\text{CO}$  *vis-a-vis*  $(\text{CH}_3)_2\text{CO}$  thereby reducing the formation of the donor-acceptor adduct *via* reaction 4. The fact that we see no reaction with  $(\text{CF}_3)_2\text{CO}$  and  $\text{BH}_3$  suggests that the donor-acceptor adduct is prerequisite to formation of the alkoxyborane. A similar argument can be made for 2-propanol. The OH hydrogen on  $\text{ROH}\cdot\text{BH}_3$  will have more protonic character than that on  $\text{ROH}$  itself. In addition, the BH hydrogen on  $\text{ROH}\cdot\text{BH}_3$  is hydridic and so the activated complex for the elimination of  $\text{H}_2$  might well be represented in general as



where the dashed line indicates a bond that exists in reaction 2 and a bond that is being formed in reaction 3. This model would predict that the greater the protonic character of the OH hydrogen and the greater the hydridic character of the BH hydrogen the faster will be  $\text{H}_2$  elimination. The

(13) K. F. Purcell and T. G. M. Dolph, *J. Amer. Chem. Soc.*, **94**, 2693 (1972); K. F. Purcell and J. M. Collins, *ibid.*, **92**, 465 (1970).

(14) I. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds," Springer-Verlag, Berlin, 1963.

(15) C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, **94**, 1451 (1972).

basic reasonableness of this crude model is supported by the fact that both the ratio of the  $p-1$  to  $p-3$  intensities<sup>16</sup> and the relative phase measurements suggest that  $H_2$  elimination is faster in the case of methanol than in the case of propanol.<sup>17</sup> Thus, fluorine substitution would be expected to enhance the production of  $H_2$  in either reaction 2 or 3. On the other hand, as  $(CF_3)_2CHOH$  is a poorer Bronsted base than is  $(CH_3)_2CHOH$  and if  $BH_3$  acts like a proton, fluorine substitution would reduce the formation of the adduct in reaction 1. Therefore, the fact that we see no reaction with  $(CF_3)_2CHOH$  again suggests that the donor-acceptor adduct is prerequisite to  $H_2$  elimination and that reactions 1 and 2 constitute the proper detailed mechanism.

These results are in accord with ideas based upon the chemistry of more complex reaction systems.<sup>3,18</sup> Although this agreement is pleasing and shows that the previous ideas are more than formal rationalizations, these results have

(16) Here  $p$  represents the parent ion mass.

(17) In this argument the  $CH_3$  group is taken to exhibit an electron-donor character with respect to H.<sup>13</sup>

added significance. They suggest that the initial rapid reactions of a species containing an unused valence orbital consist solely of forming donor-acceptor adducts. Once formed, such adducts react by a variety of paths and rates all of which depend upon the details of how the electronic structures of the two species are modified in the donor-acceptor interaction. Therefore, the key to an understanding of the reactivity of these species is the donor-acceptor interaction itself.

**Registry No.**  $BH_3$ , 13283-31-3;  $(CD_3)_2CDOD$ , 22739-76-0;  $(CH_3)_2CHOD$ , 3979-51-9;  $(CH_3)_2CHOH$ , 67-63-0;  $CH_3OH$ , 67-56-1;  $(CD_3)_2CO$ , 666-52-4;  $(CH_3)_2CO$ , 67-64-1;  $(CF_3)_2CHOH$ , 920-66-1;  $(CF_3)_2CO$ , 684-16-2.

**Acknowledgments.** The support of the National Science Foundation under Grant No. GP 28320 is gratefully acknowledged.

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

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306

## Donor Properties of Positively Charged Ligands. Metal Complexes of the *N*-Chloromethyl-Dabconium Ligand

L. M. VALLARINO\*, V. L. GOEDKEN, and J. V. QUAGLIANO

Received May 11, 1972

In a series of positively charged ligands obtained from the ditertiary amine Dabco,  $N(CH_2CH_2)_3N$ , by monoquaternization, the *N*-chloromethyl-Dabconium cation,  $[N(CH_2CH_2)_3N^+CH_2Cl]$  (abbreviated  $L^+CH_2Cl$ ), appears to be unique in its ability to form a variety of complexes with nickel(II) chloride. The complexes  $[NiCl_3(L^+CH_2Cl)]$  (four-coordinate, pseudotetrahedral monomer),  $[Ni_2Cl_4(L^+CH_2Cl)_2]$  (chloro-bridged, five-coordinate dimer),  $[NiCl_3(L^+CH_2Cl)_2]X$  (with  $X^- = Cl^-, ClO_4^-$ ) (five-coordinate, trigonal-bipyramidal cation),  $[NiCl_3(L^+CH_2Cl)_2][NiCl_4]$  (five-coordinate, trigonal-bipyramidal cation, tetrahedral anion), and  $[NiCl_3(H_2O)(L^+CH_2Cl)] \cdot (L^+CH_2Cl)Cl$  (five-coordinate, trigonal bipyramidal) were obtained in the crystalline state and were identified by analyses, magnetic properties, and spectra (d-d electronic, vibrational, and X-ray powder diffraction). In solution, the complexes of Ni(II) with the *N*-chloromethyl-Dabconium ligand give rise to unusual equilibria involving four-, five-, and six-coordinate species, with the five-coordinate species being the most stable in a well-defined temperature interval.

### Introduction

Previous investigations of the donor properties of the monoquaternized ditertiary amine 1,4-diazabicyclo[2.2.2]octane (Dabco) showed that monoquaternization reduced the basicity of the remaining lone pair by a factor of  $10^6$ , but the resulting cationic amine  $L^+$  (Figure 1a) could still function as a ligand.<sup>1-4</sup> In the presence of an excess of metal halides, the four-coordinate pseudotetrahedral complexes of the type  $[MX_3(L^+)]$  were generally formed,<sup>1</sup> but these had a tendency to take on a fifth ligand (water, ammonia, or an additional *N*-alkyl-Dabconium cation) to form unusual five-coordinate complexes. It was also found that minor variations in the quaternizing group of the Dabconium cation markedly affected the type of complex

formed. For example, nickel(II) chloride reacted in anhydrous ethanol solution with an excess of protonated Dabconium chloride to yield the deep pink, five-coordinate<sup>4</sup> cation  $[NiCl_3(L^+H)_2]^+$ . Under similar experimental conditions, the *N*-methyl-Dabconium chloride formed the four-coordinate complex  $[NiCl_3(L^+CH_3)]$ , having a pseudotetrahedral stereochemistry with  $C_{3v}$  symmetry.<sup>2</sup> However, if an excess of perchlorate ions (as  $LiClO_4$ ) was added and the reaction mixture was diluted with nitromethane to prevent precipitation of the *N*-methyl-Dabconium perchlorate (insoluble in either pure ethanol or pure nitromethane, but moderately soluble in 1:1 ethanol-nitromethane mixture), then the deep pink, five-coordinate complex  $[NiCl_3(L^+CH_3)_2]ClO_4$  separated readily from solution. It thus appeared appropriate to explore systematically the metal complexes of Dabconium cation ligands containing different quaternizing groups, chosen to provide a variety of electronic and steric effects.

### Results and Discussion

Monoquaternization of Dabco can be accomplished

(1) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, **8**, 2331 (1969).

(2) J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Amer. Chem. Soc.*, **92**, 482 (1970).

(3) B. B. Garrett, V. L. Goedken, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **92**, 489 (1970).

(4) L. M. Vallarino, V. L. Goedken, and J. V. Quagliano, *Inorg. Chem.*, **11**, 1466 (1972).