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Symmetrical Cleavage of Diborane by Ammonia in Solution

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Received October 18, 1971

The reaction of diborane with ammonia in *n*-hexane and in liquid ammonia yields both unsymmetrical *and* symmetrical cleavage products. Of the two reaction products $H_2B(NH_3)_2BH_4$ and H_3BNH_3, the latter is formed at −83° with only 5% yield. The reaction is independent of ammonia concentration but dependent on reaction temperature: increasing temperature favors the formation of H_3BNH_3 (at −44°, 22% yield). On the basis of relative yields of the reaction products $H_2B(NH_3)_2BH_4$ and H_3BNH_3 it is concluded that the rate of formation of the symmetrical cleavage product is accelerated by ethers. In the solvents diisopropyl ether, diethyl ether, and monoglyme the H_3BNH_3 yield increases with the base strength of the ethers. In ethers the H_3BNH_3 yield is also dependent on the starting material dissolved, much lower yields being obtained if ammonia is dissolved instead of diborane. A mechanism is discussed. H_3BNH_3 formed in these organic solvents is much more stable thermally than described previously and can be sublimed without decomposition. $H_2B(NH_3)_2BH_4$ crystallizes from solution to a varying degree in a new unstable modification.

It is generally accepted that the reaction of diborane with ammonia in the solid state or in liquid ammonia produces exclusively the unsymmetrical cleavage product "diammoniate of diborane."[1,2] No evidence for the symmetrical cleavage product ammonia–borane was found.[2] Only in dimethyl ether and tetrahydrofuran was a mixture of both products obtained.[3,4] However, it was demonstrated that diborane is present in these solvents as an $H_3B \cdot$ether adduct.[5,6] Therefore in these systems ammonia–borane is formed most likely *via* a base displacement reaction and the reactions are not comparable with systems without $H_3B \cdot$ether adduct formation.

In a prior publication it was shown that symmetrical cleavage of diborane by the Lewis bases carbon monoxide and phosphine is accelerated catalytically by ether solvents.[7] The rate of formation of carbon monoxide–borane and of phosphine–borane increased with the base strength of the investigated ethers according to the series diethyl ether < diglyme < monoglyme < dimethyl ether. While dimethyl ether again participates in these reactions probably *via* an $H_3B \cdot O(CH_3)_2$ adduct there is no indication for the formation of such adducts for the other three much less basic ethers. Considering these results it appeared to be worthwhile to reexamine the often examined reaction of diborane with ammonia in organic solvents and to investigate the influence of solvent, temperature, and concentration on the cleavage pattern of diborane by ammonia.

Results

Symmetrical *vs.* Unsymmetrical Cleavage.—Table I contains data on the yield of the symmetrical cleavage product ammonia–borane in various solvents. The unsymmetrical cleavage product $H_2B(NH_3)_2BH_4$ was formed as the only other identifiable reaction product. The reactions were carried out at least twice in each solvent using the following identical conditions. Gaseous ammonia (2.00 mmol) was added quickly to a solution of 1.00 mmol of diborane in 20 ml of solvent at −63°. In *n*-hexane about 10% of the diborane was present in the gas phase; in the other solvents much less. Neglecting these concentrations in the gas phase an approximate B_2H_6 concentration of 0.05 *M* is obtained. For ammonia an approximate concentration of 0.1 *M* can be calculated because the rate of reaction is slow compared with the rate of ammonia dissolution. This was shown by the time dependence of ammonia vapor pressure decrease; whereas the equilibrium vapor pressure above the solvent was reached within seconds, a slow further vapor pressure decrease within a couple of minutes (depending on the solvent) indicated reaction of ammonia in solution. The yield of ammonia–borane depends strongly on the solvent and increases according to *n*-hexane < diisopropyl ether < diethyl ether < monoglyme.

TABLE I
SYMMETRICAL CLEAVAGE OF DIBORANE BY
AMMONIA IN SOLUTION AT −63°

Solvent	Yield of H_3BNH_3, %	Solvent	Yield of H_3BNH_3, %
n-Hexane	15, 18	Diethyl ether	41, 44
Diisopropyl ether	23, 26	Monoglyme	68, 70, 76

Significantly lower ammonia–borane yields are obtained if ammonia is dissolved in ether solvents and gaseous diborane is added. Using the same concentrations as in Table I in diethyl ether corresponding yields of 12% were obtained in two experiments. In monoglyme yields of 32, 50, and 60% were obtained for three different runs. No explanation could be found for these erratic results.

Influence of Temperature and Concentration.—In *n*-hexane the ratio of symmetrical to unsymmetrical cleavage product is strongly dependent on temperature as is shown by the results of Table II. Increasing reaction temperature favors the formation of the symmetrical cleavage product ammonia–borane. No temperature dependence was observed in diethyl ether;

TABLE II
TEMPERATURE DEPENDENCE OF THE
AMMONIA–BORANE YIELD

Solvent	Temp, °C	Yield of H_3BNH_3, %	Solvent	Temp, °C	Yield of H_3BNH_3, %
n-Hexane	−83	5, 6	Diethyl ether	−96	42
n-Hexane	−63	15, 18	Diethyl ether	−63	41, 44
n-Hexane	−44	21, 23	Diethyl ether	−44	45

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(1) R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959).

(2) H. D. Johnson and S. G. Shore "New Results in Boron Chemistry," Vol. 15, Springer-Verlag, New York, N. Y., 1970, pp 94–98.

(3) S. G. Shore and R. W. Parry, *J. Amer. Chem. Soc.*, **80**, 8 (1958).

(4) S. G. Shore and K. W. Boedekker, *Inorg. Chem.*, **3**, 914 (1964).

(5) H. I. Schlesinger and A. B. Burg, *J. Amer. Chem. Soc.*, **60**, 290 (1938).

(6) B. Rice, J. A. Livasy, and G. W. Schaeffer, *ibid.*, **77**, 2750 (1955).

(7) E. Mayer, *Monatsh. Chem.*, **102**, 940 (1971).

the ammonia–borane yields are constant over a wide temperature range within experimental limits.

Changes in ammonia concentration have no influence on the relative yields of symmetrical and unsymmetrical cleavage products. The reaction of 6 mmol of gaseous ammonia (corresponding to an approximately 0.3 *M* ammonia solution) with 1 mmol of diborane dissolved in 20 ml of *n*-hexane produced at −63° 16% of ammonia–borane which is just the average of the two values in Table I. Even in liquid ammonia at −78° ammonia–borane yields of 5.8 and 4% could be obtained in two experiments. These values are very close to the values obtained in *n*-hexane at −83°.

Thermal Stability of Ammonia–Borane.—H_3BNH_3 is reported to be unstable at room temperature and to split off hydrogen slowly in the solid state.[3] On the contrary this compound is much more stable thermally if prepared by the described reaction of diborane with ammonia in organic solvents. H_3BNH_3 does not decompose at room temperature with hydrogen evolution over a period of 2 months. Samples of H_3BNH_3 prepared by above methods have a sharp melting point and can be sublimed in a dynamic vacuum without decomposition.

Among others H_3BNH_3 is prepared by the reaction of ammonium halides with alkali borohydrides.[8] Since the reported instability of H_3BNH_3 could possibly stem from secondary reactions of the compound with one of the starting materials, reactions 1 and 2 were investigated. However, they did not occur

$$H_3BNH_3 + NH_4^+ \nrightarrow H_2B(NH_3)_2^+ + H_2 \qquad (1)$$

$$H_3BNH_3 + BH_4^- \nrightarrow H_2N(BH_3)_2^- + H_2 \qquad (2)$$

neither with ammonium chloride at room temperature in ether solvents and in liquid ammonia nor with sodium borohydride in monoglyme even at 60°. Therefore thermal stability has to be attributed simply to improved purity of the compound as is often the case for boron hydride systems.

Crystalline Modifications of $H_2B(NH_3)_2BH_4$.—$H_2B(NH_3)_2BH_4$ crystallized from organic solvents to a varying degree in a novel modification. By conversion into the modification reported in the literature[4] it was ensured that the new modification is unstable with respect to the one already published. Low temperatures seem to favor the formation of the stable form and *vice versa* which is frequently found. Even in liquid ammonia both types can be obtained by altering the temperature during solvent removal.

Discussion

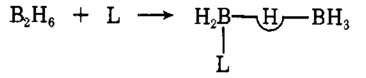
The ammonia–borane yields in Tables I and II show first that with ammonia even in nonethereal solvents such as *n*-hexane or liquid ammonia *both* types of reaction—symmetrical and unsymmetrical diborane cleavage—take place as competitive reactions. Second, in analogy to the reactions of diborane with carbon monoxide and phosphine,[7] respectively, the yield of symmetrical cleavage product increases with the base strength of the ethers, monoglyme producing significantly higher yields than diethyl ether and diisopropyl ether. The same relative ether basicities were obtained from measurements of the equilibrium distribution of trifluoroborane between various ethers[9] and from proton magnetic resonance shifts in chloroform–ether solutions.[10]

Identification of reaction products naturally does not provide definite evidence about reaction mechanism. However, since it was definitely established that the reaction products H_3BNH_3 and $H_2B(NH_3)_2BH_4$ are stable at the conditions used[3,11] it is possible to extrapolate and to draw conclusions from the relative yields of the products to rates of reaction and mechanism.

The yields and therefore the rates of the two reactions leading to H_3BNH_3 and $H_2B(NH_3)_2BH_4$ are very dependent on temperature if *n*-hexane is used as solvent (Table II). This can be interpreted only by differences in activation energy because ammonia concentration has no influence on the relative yields and diborane concentration was kept constant in these reactions. The H_3BNH_3 reaction must have a higher activation energy than the $H_2B(NH_3)_2BH_4$ reaction because the rate of reaction is more influenced by temperature. In diethyl ether no temperature dependence of the relative yields can be found which is indicative of similar activation energies for the two reactions. This clearly demonstrates that diethyl ether acts as a catalyst for the symmetrical cleavage reaction.

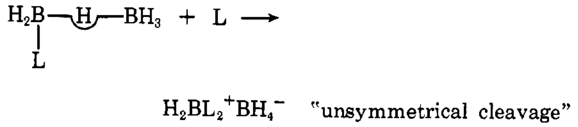
The temperature dependence of the diborane–ammonia reaction gives an explanation as to why in earlier preparations the formation of H_3BNH_3 has been overlooked. The usual procedure is to carry out the reaction at the lowest possible temperature which means that diborane is condensed onto solid ammonia at −140° and allowed to react slowly.[12] Although this reaction in the solid state is not really comparable with above reactions in solution, it appears plausible that here again lower temperature favors unsymmetrical cleavage.

Parry and Shore suggested that the reaction of diborane with a Lewis base occurs stepwise, with the first step involving displacement of hydrogen from the bridge position (L = base)

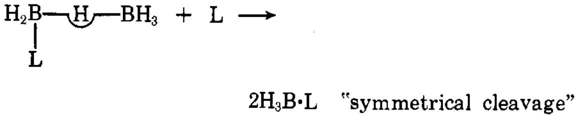


$$B_2H_6 + L \longrightarrow \underset{\displaystyle L}{\underset{|}{H_2B}}\text{—}H\text{—}BH_3 \qquad (3)$$

Good evidence for this proposed intermediate was presented by Shore.[13] The singly bridged intermediate can react further with a base producing either unsymmetrical or symmetrical cleavage products



$$\underset{\displaystyle L}{\underset{|}{H_2B}}\text{—}H\text{—}BH_3 + L \longrightarrow H_2BL_2^+BH_4^- \quad \text{"unsymmetrical cleavage"} \qquad (4)$$



$$\underset{\displaystyle L}{\underset{|}{H_2B}}\text{—}H\text{—}BH_3 + L \longrightarrow 2H_3B{\cdot}L \quad \text{"symmetrical cleavage"} \qquad (5)$$

With ammonia as base the identical product ratios in *n*-hexane and in liquid ammonia imply that the ammonia concentration shows up in both rate equations with the same order, a first-order reaction being most

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[8] S. G. Shore and R. W. Parry, *J. Amer. Chem. Soc.*, **77**, 6084 (1955).

[9] H. E. Wirth and P. I. Slick, *J. Phys. Chem.*, **66**, 2277 (1962).

[10] C. Agami and C. Prevost, *Bull. Soc. Chim. Fr.*, 4467 (1968).

[11] B. Z. Egan and S. G. Shore, *J. Amer. Chem. Soc.*, **83**, 4717 (1961).

[12] R. W. Parry and S. G. Shore, *ibid.*, **80**, 15 (1958).

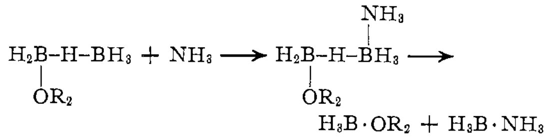
[13] S. G. Shore and C. L. Hall, *ibid.*, **88**, 5346 (1966); **89**, 3947 (1967).

probable. This would agree with the above reactions being the rate-determining steps.

The role of fairly basic ethers such as dimethyl ether and tetrahydrofuran in promoting symmetrical cleavage of diborane is well established.[3,4] These ethers form a $H_3B\cdot$ether adduct which is a likely intermediate for the reaction of diborane with ammonia in these solvents. The less basic ethers investigated here behave differently: no indication for $H_3B\cdot$ether adduct formation of diethyl ether, diisopropyl ether, and monoglyme was found.[6,14] However, experiments by Gaines and Schaeffer demonstrate that some interaction between these ether solvents and boron hydrides occurs although the specific type of interaction is not known yet.[15] A $B_2H_6\cdot$ether adduct was suggested as the reactive intermediate analogous to the $B_2H_6\cdot NH_3$ adduct postulated for the diborane–ammonia reaction.

The following two mechanisms give a plausible explanation for the increase of symmetrical cleavage product yields in the investigated ether solvents, assuming in each case the formation of the above-mentioned $B_2H_6\cdot$ether adduct upon dissolution of diborane in the ethers

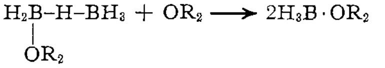
(a)



$$\underset{\underset{\displaystyle \mathrm{OR_2}}{|}}{\mathrm{H_2B}}\mathrm{\text{-}H\text{-}BH_3} + \mathrm{NH_3} \longrightarrow \underset{\underset{\displaystyle \mathrm{OR_2}}{|}}{\mathrm{H_2B}}\mathrm{\text{-}H\text{-}}\overset{\overset{\displaystyle \mathrm{NH_3}}{|}}{\mathrm{B}}\mathrm{H_3} \longrightarrow \mathrm{H_3B\cdot OR_2} + \mathrm{H_3B\cdot NH_3} \qquad (6)$$

$$\mathrm{H_3B\cdot OR_2} + \mathrm{NH_3} \longrightarrow \mathrm{H_3B\cdot NH_3} + \mathrm{OR_2} \qquad (7)$$

(b)

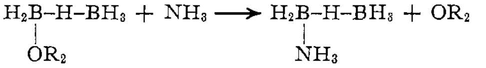


$$\underset{\underset{\displaystyle \mathrm{OR_2}}{|}}{\mathrm{H_2B}}\mathrm{\text{-}H\text{-}BH_3} + \mathrm{OR_2} \longrightarrow \mathrm{2H_3B\cdot OR_2} \qquad (8)$$

$$\mathrm{H_3B\cdot OR_2} + \mathrm{NH_3} \longrightarrow \mathrm{H_3B\cdot NH_3} + \mathrm{OR_2} \qquad (9)$$

Mechanism a implies that $B_2H_6\cdot OR_2$ complex formation favors the attack of an ammonia base on the boron atom *not* linked with the ether base. Mechanism b implies an equilibrium between the $B_2H_6\cdot OR_2$ adduct and an $H_3B\cdot OR_2$ adduct. Although there is no experimental evidence for the formation of the latter product, it still could be formed in concentrations below the limit of detection. Since for both mechanisms the yield of the symmetrical cleavage product is expected to increase with the base strength of the ethers it is not possible to differentiate.

The yield of H_3BNH_3 in diethyl ether drops to the value obtained in *n*-hexane if the order of addition is reversed and gaseous diborane is added to an ammonia–diethyl ether solution. Apparently some other faster reaction outweighs the influence of the ether solvent. The following two reactions have to be taken into consideration: either the rate for the $B_2H_6\cdot NH_3$ complex formation is much higher than for the $B_2H_6\cdot$ether complex reaction, or base exchange according to eq 10 occurs. Both reactions would have the effect of reducing the yield of symmetrical cleavage product.



$$\underset{\underset{\displaystyle \mathrm{OR_2}}{|}}{\mathrm{H_2B}}\mathrm{\text{-}H\text{-}BH_3} + \mathrm{NH_3} \longrightarrow \underset{\underset{\displaystyle \mathrm{NH_3}}{|}}{\mathrm{H_2B}}\mathrm{\text{-}H\text{-}BH_3} + \mathrm{OR_2} \qquad (10)$$

The first explanation seems to be more likely because base exchange would be operative also in all other reactions reducing the H_3BNH_3 yield.

Experimental Section

General Data.—Standard vacuum-line techniques were used throughout. Nonvolatile compounds were handled under a cover of dry nitrogen. The solvents were stored over $LiAlH_4$ and vacuum distilled into the reaction vessel. Ammonia was dried over sodium. Ir spectra were recorded for Nujol mulls on a Perkin-Elmer 337 instrument from 4000 to 400 cm^{-1}. X-Ray powder patterns were taken with a Siemens Kristalloflex IV instrument using nickel-filtered copper Kα radiation. The patterns of milligram samples were recorded in sealed capillaries using a camera; larger samples were investigated with a goniometer in the air.

Reaction of Diborane with Ammonia in Organic Solvents.—All reactions except as specifically noted were carried out using the following conditions. As the reaction vessel a tube with a 35-mm diameter and a length of 150 mm was used which was attached to an inlet of the vacuum line with a 14/35 joint. The total volume of this system was 110 ml, with about 100 ml being immersed in a cooling bath. A 20-ml sample of solvent was condensed into the tube from a $LiAlH_4$–solvent suspension and 1.00 mmol of diborane was dissolved in the solvent. The solution was thermostated for 0.5 hr at the temperatures listed in Tables I and II and stirred vigorously with a magnetic bar. Gaseous ammonia (2.00 mmol) was added by quickly turning a stopcock which connected the dissolved diborane with the ammonia reservoir (volume of reservoir 190 ml). The vapor pressure decrease was followed on a manometer connected to the reservoir. The gas-phase reaction of diborane with ammonia took place only to a small extent as could be seen from the traces of ether-insoluble material covering the walls of the reaction vessel. The volatile material was fractionated after 1 hr, if the reaction temperature was -44 or $-63°$, and after 5 hr, if it was $-83°$. Only a trace of ammonia (between 0.3 and 0.7 ml) but no diborane or hydrogen was collected. For the reactions in *n*-hexane special care was taken to prevent any contamination with traces of ether. The vacuum system was pumped out for 2 days and *n*-hexane was taken from different bottles. If monoglyme is used as solvent, it is essential to keep the solution below $-20°$ during fractionation in order to prevent further reaction of $H_2B(NH_3)_2BH_4$.[16]

The reactions with *n*-hexane as solvent were repeated with a different reaction vessel which had only a total volume of 25 ml, thereby reducing reaction in the gas phase. No difference in yields of reaction products was found.

(a) **Ether-Soluble Fraction.**—The white residue nonvolatile at room temperature was first washed out with *n*-hexane and then extracted with diethyl ether. The ether was pumped off *in vacuo*. All ether-soluble fractions consisted of pure H_3BNH_3 which were weighed and characterized by their X-ray powder patterns and ir spectra. H_3BNH_3 prepared in this way melted sharply in a sealed capillary under nitrogen between 112 and 114° while gassing strongly. Characterization of H_3BNH_3 by its ir spectrum and X-ray powder pattern does not exclude the possibility of contamination by amorphous decomposition products such as $(H_2BNH_2)_n$. However, the sharp melting point and the thermal stability mentioned below make probable that a very pure substance was obtained.

Samples of H_3BNH_3 prepared in this way sublimed nearly quantitatively without decomposition if heated in a dynamic vacuum of 10^{-2} Torr at 60°. The melting point of the resublimed product was unchanged, if sublimation was carried out at 60° and was slightly lowered, if temperatures close to 100° were used. A 0.94-mmol sample in an evacuated glass ampoule did not evolve any H_2 within 2 months at room temperature and was after this period completely soluble in diethyl ether. A 1.30-mmol sample evolved at 60° within 24 hr only 0.6 cm^3 of H_2. At 72° H_2 evolution became considerable (from 1.49 mmol of H_3BNH_3 in 24 hr, 25 cm^3 of H_2).

(b) **Ether-Insoluble Fraction.**—An ether-insoluble fraction $H_2B(NH_3)_2BH_4$ was formed which precipitated from the organic solvents in the form either of a novel crystalline modification or of a mixture with the modification reported in the literature.[4] Although the conditions favoring either modification are not really understood, it seems that lower temperatures favor the formation of the literature modification. In mixtures the new modification transformed at room temperature within a couple of days into the literature modification.

The identity of the material with the new modification was proved by the following facts.

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(14) G. E. McWood and L. J. Paridon, *J. Phys. Chem.*, **63**, 1302 (1959).

(15) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963); D. F. Gaines and R. Schaeffer, *J. Amer. Chem. Soc.*, **86**, 1505 (1964).

(16) $H_2B(NH_3)_2BH_4$ decomposes in monoglyme above $-20°$ into H_2, H_3BNH_3, and other products which will be reported shortly.

(1) The ir spectra of samples with the new modification were identical with the spectrum of $H_2B(NH_3)_2BH_4$ prepared according to the literature.[17] It is not surprising that differences in crystal structure do not show up in the spectra because the ir absorptions are fairly broad whereas these differences should amount to less than 10 cm^{-1}.

(2) The compound could be dissolved in liquid ammonia and recovered without any apparent sign of decomposition, such as hydrogen evolution. If the solvent was pumped off at −83°, the literature modification was formed. Ir spectra of the substance before dissolution and after removal of ammonia were identical.

(3) An ether-insoluble sample of 0.316 g gave 3.91 units of $H_2/H_2B(NH_3)_2BH_4$ upon hydrolysis with glacial acetic acid and dilute HCl. After pumping off all volatile material, the residue showed the X-ray patterns of boric acid and of $H_2B(NH_3)_2Cl$ reported by Schultz and Parry.[18]

The unstable modification of $H_2B(NH_3)_2BH_4$ is shown by the following *d* values (in Å): 5.03 (w), 4.74 (m), 4.62 (m), 4.37 (vs), 4.19 (w), 4.00 (m), 3.75 (w), 3.63 (m), 3.52 (w), 3.44 (m), 3.41 (s), 3.13 (m), 3.04 (w), 2.99 (w), 2.92 (m), 2.83 (m), 2.71 (w), 2.66 (w), 2.37 (w).

Reaction of Diborane with Ammonia in Liquid Ammonia.—The procedure described in ref 17 was used except that a −96° trap was taken to freeze out impurities from the diborane–nitrogen gas stream and no fritted cylinder was used. This tended to plug. After removal of ammonia the solid residue was extracted with diethyl ether stirring the suspension for 1 hr at room temperature. In two experiments 0.009 g of H_3BNH_3 was isolated from 0.246 g of crude product and 0.045 g of H_3BNH_3 from 0.779 g, corresponding to 4 and 5.8% yields of H_3BNH_3. The samples were again characterized by ir spectra and X-ray powder patterns. Further extraction with diethyl ether produced no more H_3BNH_3 which proves that H_3BNH_3 was not formed by decomposition of $H_2B(NH_3)_2BH_4$ in the ether slurry.

$H_2B(NH_3)_2BH_4$ precipitated even from liquid ammonia in the form of either the literature modification or the new modification, or a mixture of both. Rapid removal of solvent at temperatures above −78° gave the new modification; slow removal from a cooling bath at −83° produced the one already reported.

Attempted Reaction of Ammonia–Borane with Sodium Borohydride.—A 1.15-mmol sample of H_3BNH_3 was dissolved in 20 ml of monoglyme and 3.34 mmol of $NaBH_4$ was added. At room temperature no trace of hydrogen was formed within 8 hr. After heating the solution at 60° for 12 hr, monoglyme was pumped off. A 1.04-mmol amount of H_3BNH_3 (=91%) was recovered by extraction with diethyl ether.

Attempted Reaction of Ammonia–Borane with Ammonium Chloride.—The reaction of 0.88 mmol of H_3BNH_3 with an equimolar amount of dry NH_4Cl was investigated with monoglyme and liquid ammonia as solvents. No hydrogen was produced within 10 days at room temperature in either solvent. The X-ray powder patterns of the nonvolatile residues contained only the reflections of the starting materials.

Acknowledgment.—I am very grateful to Doz. Dr. E. Schnell and Mr. W. Strele, both of this institute, for patiently recording and discussing numerous X-ray powder patterns.

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[17] S. G. Shore, K. W. Boedekker, and J. A. Patton, *Inorg. Syn.*, **9**, 4 (1967).

[18] D. R. Schultz and R. W. Parry, *J. Amer. Chem. Soc.*, **80**, 4 (1958).

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The Prediction of Gas-Phase Lewis Acid–Base Dissociation Heats with an Empirical Four-Parameter Equation

BY WILLIAM L. JOLLY,* JOHN D. ILLIGE, AND MARSHALL H. MENDELSOHN

Received July 15, 1971

The Drago–Wayland four-parameter equation for predicting Lewis acid–base dissociation heats has been extended to gaseous compounds, most of which are considered as adducts of cationic acids and anionic bases. By use of the empirically evaluated parameters for 14 acids and 12 bases, the heats of 105 different dissociations are reproduced with an average error of ±3.9 kcal/mol. The method gives poor results for adducts in which the dissociated bonds are either weakened by lone-pair repulsions or affected by unusual π-bonding effects.

In 1952, Mulliken[1] showed theoretically that the dissociation energy of a Lewis acid–base adduct can be partitioned into a "no-bond" part and a "dative" or covalent part. In 1954, Edwards[2] showed that the free energies (or logarithms of equilibrium constants) of Lewis acid–base reactions can be reproduced by the two-term four-parameter equation

$$\log \frac{K}{K_0} = \alpha E_n + \beta H$$

where K is the equilibrium constant for the reaction of a base with a particular acid and K_0 is the constant for the corresponding reaction of a reference base. The parameters α and β are empirical constants characteristic of the acid, and E_n and H are independent parameters for the base. More recently, Drago and Wayland[3] used a similar equation to reproduce the *heats* of dissociation of Lewis acid–base adducts

$$\Delta H = E_A E_B + C_A C_B \tag{1}$$

Two empirical parameters, E_A and C_A, were assigned to each acid, and two empirical parameters, E_B and C_B, were assigned to each base. The E_AE_B term was interpreted as a measure of electrostatic interaction energy, and the C_AC_B term was interpreted as a measure of covalent bond energy. By application of eq 1 to reactions of neutral acids and bases in the gas state or in poorly solvating solvents (for which the dissociation heats ranged from 0.5 to 18.0 kcal/mol), it was possible to correlate the dissociation heats with an average error of approximately ±0.1 kcal/mol.

Dissociation heats are available for an extensive set of gaseous compounds, not considered by Drago and

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[1] R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

[2] J. O. Edwards, *ibid.*, **76**, 1540 (1954); **78**, 1819 (1956).

[3] R. S. Drago and B. B. Wayland, *ibid.*, **87**, 3571 (1965).