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Review

Symmetric and asymmetric cleavage of the lighter boron hydrides and of metal salts – the role of the dielectric constant

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This paper is fondly dedicated to Prof. Sheldon G. Shore of Ohio State University on the occasion of his 70th birthday.

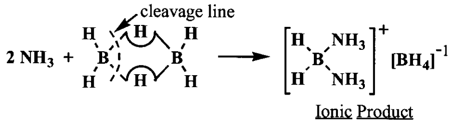
Abstract

Evidence is presented to support the premise that when a base reacts with diborane at low temperatures (− 77 to − 80°C) the variable which determines whether the product will be an ionic substance such as $[H_2B(Base)_2]^+[BH_4^-]$ or a non-ionic substance such as $H_3B(Base)$ is the dielectric constant of the base and the medium. In most cases steric factors do not play a dominant role in the outcome of these direct reactions. © 2000 Elsevier Science B.V. All rights reserved.

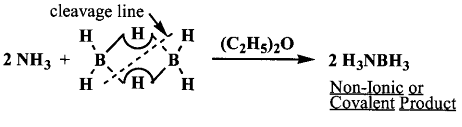
Keywords: Boron hydrides; Symmetrical cleavage; Unsymmetrical cleavage; Bridge bonds; Covalent product; Ionic product; Metal salts; Dielectric constant

1. Introduction

At the conclusion of the work for their PhDs at the University of Michigan in the period 1954–1956 Donald R. Schultz, Sheldon G. Shore, and their coworkers [1,2] had established that the following reactions take place (Eqs. 1 and 2):

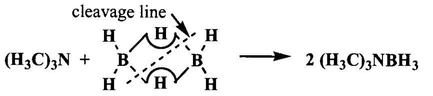


(1)



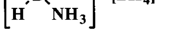
(2)

It was already known from much earlier work by Burg, Brown, et. al. in the laboratory of Prof. H.I. Schlessinger [3] that diborane will react with trimethylamine in accordance with the Eq. (3):



(3)

The ionic compound involving $(CH_3)_3N$, i.e. $H_2B[N(CH_3)_3]_2^+[BH_4]^-$ was unknown at that time. The foregoing observations could be summarized by considering the nature of the reaction which diborane would undergo with different bases. The reaction with trimethylamine was called 'symmetrical cleavage' [2] of the B_2H_6 molecule, Eq. (3), for obvious reasons, while the reaction with ammonia was called 'unsymmetrical cleavage' [2] of B_2H_6, Eq. (1). The reactions can also be identified by the nature of the product. The symmetrical cleavage gives a non-ionic or 'covalent' product, $H_3BN(CH_3)_3$, while reaction with ammonia gives an 'ionic' product:



2. Factors controlling cleavage patterns

Why one Lewis base gives a covalent product and one gives an ionic product has been a source of conjec-

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ture for years. One of the most reasonable differences between the two bases is size. Trimethylamine is significantly larger than ammonia so steric factors could be expected to play a role. In 1975 Shore [4] wrote:

> Of the factors which have been considered to affect the course of bridge cleavage of B_2H_6, two have been experimentally examined and have been discussed in terms of the proposed sequence of steps given above. One factor is steric effect. With increasing bulk of the ligand the tendency for symmetrical cleavage increases. The second factor is a solvent effect (unquote).

A steric effect is so ubiquitous in chemical reactions that there can be no argument over the fact that it is important in some cases; but there can be very real and very valid arguments over whether or not it is the dominating factor in these reactions of B_2H_6. In 1984 Greenwold and Earnshaw [5] wrote the following in their excellent book entitled ‘Chemistry of the Elements’:

> The weak bonds in B_2H_6 are readily cleaved, even by weak ligands to give symmetrical or unsymmetrical cleavage products: (defining equations given) The factors governing the course of these reactions are not fully understood, but steric effects play some role (unquote).

Again steric factors are the variables which can be most easily visualized. In this paper Shore’s second factor [4], the ‘solvent effect’ will be examined carefully. The claim is made here that the solvent effect, as defined by the dielectric constant of the solvent or liquid base, is the differentiating factor in determining whether the ionic or covalent product is obtained. That is, whether one obtains ‘symmetrical’ or ‘asymmetrical’ cleavage of the bridge bonds in diborane, when B_2H_6 reacts with the bases at low temperatures.

3. Reactions of metal salts with bases – role of dielectric constant

Let us go first to the reactions of metal salts for significant background information. When $Co(ClO_4)_2$ is placed in water it dissolves easily to give $Co(H_2O)_6^{2+}$ and $ClO_4^-{}_{(aq.)}$ ions. The explanation usually presented is that the energy of hydration of the Co^{+2} and ClO_4^- ions partially off-sets the lattice energy of the solid and the high dielectric constant of the water (about 80 at 25°C) reduces the forces of attraction between oppositely charged ions to such a degree that the ionic form is stabilized.[1] In contrast, when $CoCl_2$ is placed in triethylamine, one mole of triethylamine is picked up and the covalent $CoCl_2[N(C_2H_5)_3]$ is formed [7]. The base $(C_2H_5)_3N$ has a dielectric constant at 25°C of 2.42 [8]. The product is non-ionic. Water is well known as being one of the very best solvents to stabilize ionic systems (dielectric constant about 80).

Ionic salts frequently dissolve in water, but water isn’t the only solvent to give ionic solutions and ionic products. In 1960 Cotton and Francis [9] reported a preliminary survey of dimethylsulfoxide complexes. The results were somewhat unexpected at the time. Dimethylsulfoxide, $(CH_3)_2SO$, is a tetrahedral molecule with a dielectric constant of 47 at 25°C [10]. (Dimethylsulfoxide in this work is identified as DMSO.[2]) In most cases DMSO coordinates through the oxygen, hence its steric requirements are not trivial. Still ionic compounds of DMSO are formed with many metal salts. In support of this claim, representative data from Cotton and Francis [9] are shown in Table 1. Dimethylsulfoxide (dielectric constant 47) shows a coordination pattern very similar to that of H_2O (dielectric constant 80). As expected for a substance with a high dielectric constant such as DMSO, the ionic product is seen with the metal salts.

4. Ionic and covalent products of boron compounds – low temperature reactions

Diborane and DMSO unexpectedly gave an ionic product [11]. The compound BF_3, perhaps because BF_3 is more sterically hindered than a BH_3 unit, does not show an ionic product with either NH_3 or DMSO [9]. This is true even though the dielectric constants of these bases are high enough to give ionic products with many metal salts [10], and with B_2H_6 [11]. According to this author, the case of BF_3 is one in which steric factors are extremely important. Fluoride atoms or ions are not as compressible or distortable as are hydrogen atoms or ‘ions’ in $[H_2B(NH_3)_2]^+$, hence formation of $[F_2B(NH_3)_2]^+$ or

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[1] In considering solubility the entropy term is large and important, but the reduction of force between ions by a liquid of high dielectric constant is crucial. Note that the force between two electric charges, Q_1 and Q_2, and separated by a distance, r, is given by:

$$\text{Force} = \frac{Q_1 Q_2}{4\pi r^2 \varepsilon}$$

where ε is the permittivity of the homogeneous medium separating the two charges. This permittivity, ε, is $\varepsilon_o \cdot \varepsilon_r$ where ε_o is the vacuum permittivity (a definable constant) and ε_r is the dielectric constant of the medium. Thus, ions in water (dielectric constant at 25°C = 80) have 1/80 of the attractive force acting between them as do the same ions in vacuum with the same separation. See [6].

[2] The dipole moment of DMSO is 3.9 D, hence ionic attraction to a metal cation is high. The dielectric constant (permittivity) is 47 at 25°C.

$[F_2B(DMSO)_2]^+$ can be much more difficult than formation of $[H_2B(NH_3)_2]^+$ [12,13]. $[F_2B(NH_3)_2]^+$ is prepared at high temperature[3] [12].

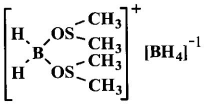
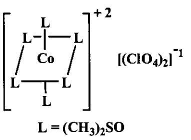
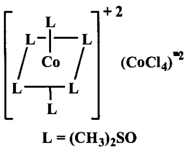
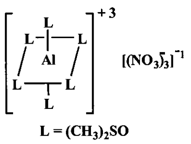
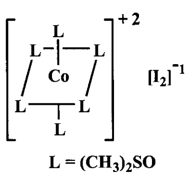
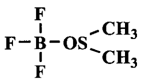
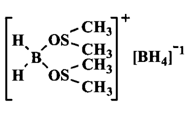
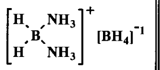


Table 1
Compounds formed by DMSO with various metal salts [9] [a]

Formula	Structural Formula	Color	Comments
$Co(DMSO)_6(ClO_4)_2$		Pink	Data available to support structure shown. Coordination through oxygen [8]. Mag. Moment = 5.01.
$Co(DMSO)_3Cl_2$		Deep Blue	Spectral Data [8] support formula. Mag. Moment = 4.83. Supports formula.
$Al(DMSO)_6(NO_3)_3$		White	Structures not measured but assumed from formula.
CoI_2•6DMSO		Red	Structure assumed from formula.
$Cr(ClO_4)_3$•6DMSO	$[Cr(DMSO)_6]^{+3}$ cation $[ClO_4]_3^-$ anions	Deep Green	Structure assumed from formula.
F_3BDMSO		White	Non ionic structure seen with BF_3. Coordination through oxygen [8].
B_2H_6•2DMSO No covalent structure seen in this study.		White	See G.E. McAchron and S.G. Shore [11]. Explodes above -6°C.

[a] Dielectric constant of DMSO = 47 at 25°C.

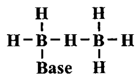
Table 2
Cleavage patterns of B_2H_6 as it undergoes reactions with NH_3 and the methylamines – the role of the dielectric constant

Reagents (Data from Reactions)	Solvent When Used	Temperature of Reaction	Dielectric Constant of Amine or Solvent	Nature of the Product
$B_2H_6 + NH_3$ Reference 2.	None except excess NH_3	-77°C and below m.pt.	25 at -77°C	
B_2H_6 + H_2NCH_3 References 12, 14, & 15	None except excess $(CH_3)NH_2$	-77°C and below m.pt. = -92°C	18 Extrapolated value at -78°C.	Mostly ionic, $\{H_2B[(CH_3)NH_2]_2\}^+$ Very small amount non-ionic.
B_2H_6 + $HN(CH_3)_2$ References 14-16, & 19	None except excess $(CH_3)_2NH$	-77°C and below m.pt. = -96°C	8 Extrapolated value at -78°C.	Mostly non-ionic, $(CH_3)_2NBH_3$. Very little ionic product.
B_2H_6 + $N(CH_3)_3$ Reference 3.	None except $(CH_3)_3N$	25°C	2.55 at 25°C. Estimated at -78°C = 5.	Exclusively non-ionic, $(CH_3)_3NBH_3$.
$LiBH_4$ + $[NH_4]_2SO_4$ or $LiBH_4$ + NH_4Cl References 1b & 2.	Diethylether Slurry	About 25°C	Ether = 4.3 at 25°C. Formed Et_2OBH_3?	H_3NBH_3 No ionic product.

In a series of papers Shore [13] and his students, and in a separate study Kodama and Inoue [14], investigated the reaction patterns of the methylamines with diborane. Beachley [15] also studied the reaction of B_2H_6 with methylamine. Data and dielectric constant values[2] [9,10] are shown in Table 2. In each case dielectric constant values of the amines are extrapolated to the temperature at which that amine was combined with B_2H_6. It is appropriate to note that in preparing the original 'diammoniate of diborane' close control of temperature and other conditions was needed to obtain reproducible results [1b]. The dielectric constants of the amines will rise as the temperature falls. Temperature controls a critical variable in these reactions, i.e., the dielectric constant.

In all of these cases, other than the synthesis of H_3NBH_3, diborane and the reacting base were condensed together at very low temperatures (−196°C) and the system was then allowed to warm up. In general, the reactants were held at −77°C for several hours in the synthesis process. Without this step confusing synthesis results were often seen [1b]. It is reasonable to ask what happens and why is the dielectric constant crucial?

The most widely accepted model, so far, for the reaction of B_2H_6 and bases at low temperatures involves the cleavage of one bridge bond to give as an intermediate [2,11,16]:



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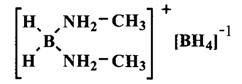
[3] The ions $[ClHB(Base)_2]^+$, $[Cl_2B(Base)_2]^+$, and $[F_2B(Base)_2]^+$ are known but they have been formed under extreme conditions by substitution on existing ionic structures [12]. For example, $[ClHB(NR_3)_2]^+$ and $[BrHB(NR_3)_2]^+$ have been prepared from the $[H_2B(NR_3)_2]^+$ cation by treatment with Cl_2 or Br_2. The ion $[Cl_2B(NR_3)_2]^+$ has been formed by treating the hydrogen containing ion with ICl. Evidence for $[F_2B(NR_3)_2]^+$ was obtained but the pure product was not isolated. The product $\{(FSO_3)_2B[N(CH_3)_3]_2\}^+$ was also reported. Some steric factors can be overcome if severe conditions can be used. See also [20,21].

The next step is the one in which the decision between an ionic or non-ionic product is made. If the liquid in which the intermediate is immersed has a high dielectric constant the ions can be formed, separated, and stabilized. If the dielectric constant in the reaction site is low the non-ionic product should form. Ions are not stabilized in liquids of low dielectric constant.

The data for NH_3 and the alkylamines are interesting. For NH_3 with a dielectric constant of 25 only the ionic product is seen. This does not mean that the ions are widely separated, but only that the ionic form is favored in solution, usually as ion-pairs [2].

For trimethylamine the dielectric constant at 25°C, where this reaction can be carried out, is 2.55. At low temperature (-77°C) the estimated dielectric constant is 5. The sole product in all reactions is the non-ionic or 'covalent' species. No ionic product is formed in the authors experience. For methylamine the dielectric constant is estimated as 18 at -77°C. The product is predominantly the ionic form:



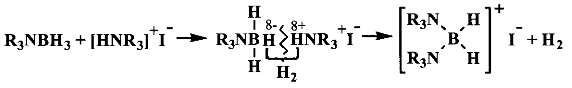
A small amount of the non-ionic form was seen [13a,14,15]. For dimethylamine with a dielectric constant estimated at -77°C of about 8 (extrapolated value) the product formed at -77°C is predominantly the non-ionic (or covalent) form, $(CH_3)_2HNBH_3$. Only a very small amount of the ionic form was seen [13a,14].

Other examples exist. In 1972, Finn and Jolly [17], in a beautiful set of experiments, established that when a measured quantity of water and an excess of diborane were allowed to react at -130°C, where hydrolysis was not destroying the product too rapidly, a dihydrate of diborane, $B_2H_6{\cdot}2H_2O$, was formed. At -112°C about 3% of this dihydrate hydrolyzed in 1 h. Convincing infrared evidence was obtained supporting the structure $[H_2B(OH_2)_2]^+[BH_4^-]$ for the dihydrate. Temperatures were maintained well below -112°C. This structure and the observed reactions are those expected for a weak base with a dielectric constant well above 80 at the low temperatures used. Rapid hydrolysis was expected and observed. Following through with the alkyl derivatives of water, an interesting set of data [17] was obtained. For ethanol a very unstable compound $B_2H_6{\cdot}2EtOH$ was found (this compound decomposed by solvolysis in 1 h at -130°C). At -60°C the dielectric constant for ethanol is 64 [8]. For methanol the data suggested complexes with a formula of $1.7H_3COH{\cdot}B_2H_6$. For methanol at -113°C the dielectric constant given is 64 [8]. Ionic products, though very unstable, would be expected. The bases are weak and each contains an acidic proton. Dimethylether has a dielectric constant of 5.02 [8]. As far as this author can find, dimethylether reacts with diborane at low temperature to give only the NON-ionic product. The same is true for the diethylether.

There is no question that steric factors are important in reactions – not only in the final products but even in the transition state [17]. On the other hand, there is enough room around the H_2B^+ species for two trimethylamine or two triethylamine molecules. The ions $\{H_2B[N(CH_3)]_2\}^+$ and $\{H_2B[N(C_2H_5)_3]_2\}^+$ are known and will be discussed subsequently [12]. All of the observations described above involved the direct reaction of diborane and a particular base at low temperature. The dielectric constant played a key role. On the other hand, it is possible to make boron cations by other means [11,18,19].

5. Reactions at higher temperatures

Miller and Muetterties [12], prepared boron cations of the form $H_2BD_2^+$ where D is a donor molecule of the type NR_3, PR_3, AsR_3, and SbR_3. These were made in one of three ways – not by the direct reaction of the base and B_2H_6 at low temperature. The most versatile process [12] was the reaction of the base borane adduct (i.e. H_3BNR_3) with the 'onium' iodide or PF_6^- salt (i.e. $HNR_3^+I^-$) at high temperatures (100–180°C). The process is illustrated by:



This is a high temperature process which is completely different than the direct reaction of B_2H_6 and a base at very low temperatures. Using this procedure and variations of it they prepared $\{H_2B[N(CH_3)_3]_2\}^+[PF_6]^-$, $H_2B[P(CH_3)_2]_2^+[PF_6]^-$, and other species which also have even more severe steric requirements. Most of these compounds are very stable [12].[4]

Another way to make species such as $[H_2B(NR_3)_2]^+X^-$ is by replacing a base such as the ammonia [15] in $H_2B(NH_3)_2^+$, with HNR_2 or NR_3 to give species $H_2B[NH(CH_3)_2]_2^+$ or $[H_2B(NR_3)_2]^+$. Other examples exist. Miller and Muetterties also reported a third synthesis for $H_2BD_2^+$ cations (D is a donor molecule (Lewis base)) in which a borane compound such as H_3BNR_3 is heated to 100–180°C in the presence of excess B_2H_6. Salts of the form $[H_2B(NR_3)_2^+]_2B_{12}H_{12}^{2-}$ are found in the products [12]. Dielectric constants are not of concern in these very high temperature reactions.

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[4] According to Ref. [13] salts of $[H_2B(NR_3)_2]^+PF_6^-$ ($R = CH_3$, C_2H_5, etc.) have amazing stability. They have been recovered without change from concentrated sulfuric, hydrochloric, and nitric acids after standing near 100°C for long periods of time.

6. Conclusions

In summary, evidence has been presented indicating that when bases react with B_2H_6 at low temperatures, the dielectric constant of the base (or in some cases the solvent or both) plays a defining and not too surprising role in determining whether the product will be ionic (non-symmetrical cleavage) or non-ionic (symmetrical cleavage). The existence of species such as $\{H_2B[OS(CH_3)_2]_2\}^+$, $\{H_2B[P(CH_3)_3]_2\}^+$, and $[F_2B(NR_3)_2]^+$ suggests to this author that steric factors are not the differentiating variable in the cleavage of diborane with NH_3 and $N(CH_3)_3$. Shore's second effect in the form of dielectric constant determines the direction of the process.

Acknowledgements

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