

Contribution from the Department of Chemistry,  
Cornell University, Ithaca, New York 14853**A Kinetic Study of Ion-Molecule Reactions in Borazine. Some Chemical Properties of the Borazine Cation and the Borazinium Ion**

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Ion-molecule reactions of *N*-trimethylborazine, borazine, and borazine in H<sub>2</sub>, He, Ne, CH<sub>4</sub>, and Kr have been studied under photon impact with 10.2 eV radiation. Protonation of borazine to yield H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup> (the borazinium ion) and subsequent reaction of this species to yield H<sub>5</sub>B<sub>6</sub>N<sub>6</sub>H<sub>6</sub><sup>+</sup> are the major processes occurring in the borazine systems. Protonation from H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> to form H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> is the only process observed in the *N*-trimethylborazine system. In the H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub><sup>+</sup>-H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> reaction the proton transferred is initially bound to boron. In the H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>-H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub> reaction the proton transferred originates from an exocyclic methyl group. CNDO calculations on H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup> support mass spectral evidence that protonation of borazine occurs at a nitrogen site and dissociative proton transfer at a boron site. The second-order rate constant for the disappearance of H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub><sup>+</sup> is 1.3 × 10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> and that for H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> is about 9.5 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>.

**Introduction**

Chemical ionization studies of borazine-alkane mixtures have shown that the borazinium ion, H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup>, is quite stable thermodynamically. This suggests the possible importance of this ionic species as an intermediate in strong acid media or in radiolysis experiments. In this paper we report an investigation of the chemical behavior of the borazine cation and the borazinium ion with respect to their precursor, the borazine molecule. The experiments described were performed with a low-pressure ion-molecule reactor utilizing the hydrogen α resonance line as the source of ionizing radiation. Under the experimental conditions employed the borazine cation is the only species generated initially, facilitating interpretation of ion-molecule reactions in this system.

**Experimental Section**

For these studies a mass spectrometer used previously for chemical ionization measurements was modified to accommodate a photoionization source.<sup>1</sup> Different types of ion sources were used for qualitative and quantitative measurements. Source A, used primarily to obtain high ion intensity levels for mechanistic studies, is shown in Figure 1. The repeller consisted of four stainless steel rings spaced to provide a voltage gradient of 1.2 V/cm down the reaction chamber. Light entered the source through a 1-mm thick, 1-in. o.d. LiF window. Source B, used for quantitative rate measurements, is also shown in Figure 1. For this source the reaction chamber consisted of a 0.375-in. cubical cavity in a 0.75 × 0.50 × 0.40-in. block of type 304 stainless steel. Since the measurement of source pressure was an important quantity in these experiments, the inlet system was designed to minimize pressure gradients through the inlet lines. An independent pressure calibration was subsequently obtained by study of the NH<sub>3</sub><sup>+</sup>-NH<sub>3</sub> proton transfer reaction. Light entered the source through a 0.030 × 0.250-in. slit centered 0.477 cm from the base of the cavity. This slit was covered by a 1-mm thick LiF window held in place with Dow Corning 732 RTV adhesive. The repeller was a 0.250 × 0.250 × 0.001-in. piece of stainless steel foil located 0.673 cm from the base of the cavity. The repeller was insulated from the reaction chamber by a ceramic feed-thru, and the applied voltage could be varied from 0 to about 20 V positive with respect to the reaction chamber. Unless otherwise noted the electric field used with source B was 14.8 V/cm. The ion exit slit was 0.003 by 0.250-in. The ion drawout potential was 300 V negative with respect to the reaction chamber, and the ion acceleration potential was held at +2000 V.

The light source was a hydrogen resonance lamp similar to that described by Ausloos.<sup>2</sup> The lamp window was attached to the body of the lamp by a 0.5-in. Cajon Ultratorr fitting. Under normal operating conditions the principal source of radiation was the 10.2 eV Lyman α line of hydrogen. Lithium fluoride is an effective filter for radiation above 11.9 eV,<sup>2</sup> and in test experiments with methane (ionization potential = 12.7 eV),<sup>3</sup> CH<sub>4</sub><sup>+</sup> was not detectable.

**Material Preparation**

Borazine was prepared by the reduction of *B*-trichloroborazine (Alfa Inorganics) with NaBH<sub>4</sub> using triethylene glycol-dimethyl ether as solvent, according to the method of

Hohnstedt and Haworth.<sup>4</sup> The borazine was purified by trap-to-trap distillation and the purity checked by ir and mass spectra.

The *N*-trimethylborazine was prepared from CH<sub>3</sub>NH<sub>3</sub>Cl and NaBH<sub>4</sub> under a helium atmosphere using NaBH<sub>4</sub>-dried 1,2-dimethoxyethane as solvent by a method similar to that of Beachley.<sup>5</sup> This compound was purified by trap-to-trap distillation followed by reaction with excess BCl<sub>3</sub> to remove the remaining ether impurity. Sample purity was checked by ir and mass spectra.

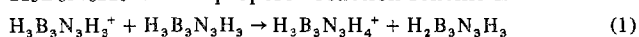
A mixture of all the possible B-deuterated *N*-trimethylborazines was prepared from CH<sub>3</sub>NH<sub>3</sub>Cl and NaBD<sub>4</sub> under conditions similar to those used in the *N*-trimethylborazine preparation. Mass spectra of the product showed that the D/H ratio at the boron sites was about 2/1.

The *B*-trideuterioborazine was prepared by the photolysis of 3 mm of borazine in 75 mm of D<sub>2</sub>, using an Hanovia medium-pressure mercury lamp purged with dry nitrogen.<sup>6</sup> The photolysis vessel was equipped with a quartz immersion well which transmitted light down to 180 nm. The product was analyzed by ir and mass spectra and found to be better than 99% deuterated, measured as atomic deuterium.

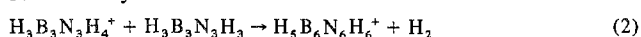
The CH<sub>4</sub> used was Matheson Research grade and the CD<sub>4</sub> was obtained from Merck Sharpe and Dohme.

**Chemistry of the Borazine Cation and Borazinium Ion**

Radiation from the H<sub>2</sub> lamp at 10.2 eV is sufficient to ionize borazine (ionization potential = 10.09 eV)<sup>7</sup> without fragmentation. At low source pressures only the parent ion of borazine was observed but as the pressure was increased the borazinium ion (H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup>) and an ion species with composition H<sub>5</sub>B<sub>6</sub>N<sub>6</sub>H<sub>6</sub><sup>+</sup> appeared. The effect of source pressure on the relative intensities of these ions for the pure borazine system is illustrated in Figure 2. At the highest source pressure the intensity of the H<sub>5</sub>B<sub>6</sub>N<sub>6</sub>H<sub>6</sub><sup>+</sup> ion was about 80% of the total ionization, while the relative intensity of the H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup> ion reached a nearly stationary value of about 0.20. Figure 3 illustrates the effect of repeller voltage on the relative ion intensities in the borazine system. The ratio I<sub>H<sub>5</sub>B<sub>6</sub>N<sub>6</sub>H<sub>6</sub><sup>+</sup></sub>/I<sub>H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup></sub> decreased markedly as the repeller voltage was increased, inferring a slower reaction with decreasing residence time of the precursor ions. This observation and kinetic considerations based on the data in Figure 2 support a consecutive reaction mechanism with H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup> as the precursor to H<sub>5</sub>B<sub>6</sub>N<sub>6</sub>H<sub>6</sub><sup>+</sup>. The data do not support parallel reaction mechanisms leading to H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup> and H<sub>5</sub>B<sub>6</sub>N<sub>6</sub>H<sub>6</sub><sup>+</sup>. The proposed reaction scheme is



followed by:



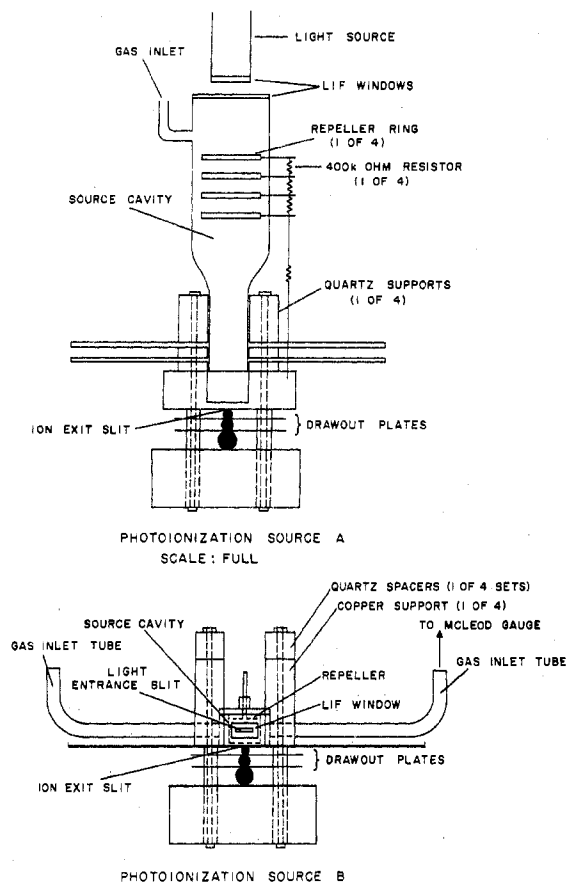


Figure 1. Photoionization sources: source A used for qualitative studies, source B for quantitative measurements.

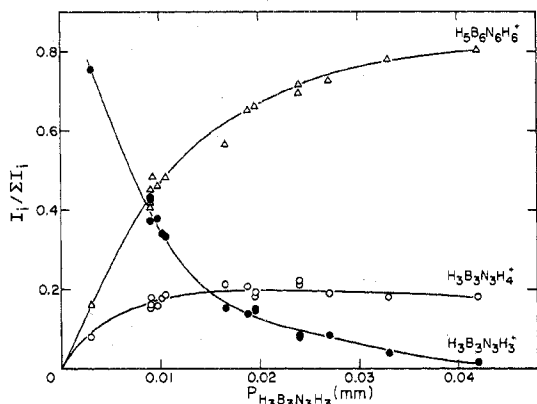


Figure 2. Effect of source pressure on the relative intensities of ions in the mass spectra of borazine (ionizing radiation = 10.2 eV).

There was no observation of the singly charged dimer ion of borazine,  $H_6B_6N_6H_6^+$ , analogous to the  $C_{12}H_{12}^+$  ion formed by a three-body process in benzene.<sup>8</sup>

Further information regarding the reaction mechanism was obtained by studies with *B*-trideuterioborazine (source B). The effect of source pressure on the relative intensities of the ions in this system is shown in Figure 4. The relative intensities of  $D_3B_3N_3H_4^+$  (highest mass number = 85) and  $D_5B_6N_6H_5D^+$  (highest mass number = 167) remained small throughout the pressure range investigated, while the  $D_3B_3N_3H_3D^+$  ion intensity rapidly leveled off to about 15% of the total ionization.

Shown in Figure 5 is a plot of the ratio  $I_{D_3B_3N_3H_4^+}/I_{D_3B_3N_3H_3D^+}$  vs. pressure. These data were obtained using source A in which the McLeod gauge pressure is proportional to, but somewhat higher than, the actual source pressure. The observed ratio

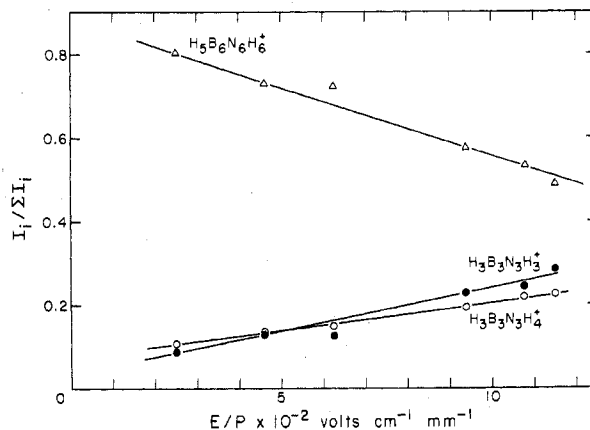


Figure 3. Effect of repeller voltage changes on the relative intensities of the ions in the mass spectra of borazine.

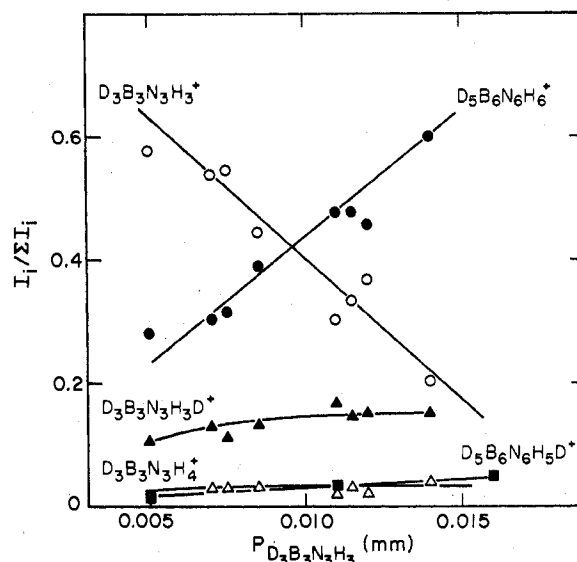


Figure 4. Effect of source pressure on the relative intensities of the ions in the mass spectra of *B*-trideuterioborazine.

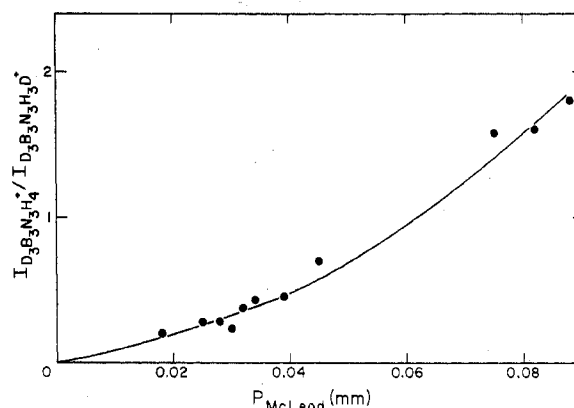
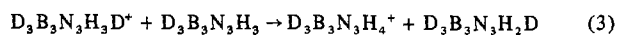


Figure 5. Effect of source pressure on the  $I_{D_3B_3N_3H_4^+}/I_{D_3B_3N_3H_3D^+}$  ratio in the mass spectra of *B*-trideuterioborazine.

$I_{D_3B_3N_3H_4^+}/I_{D_3B_3N_3H_3D^+}$  decreased with decreasing source pressure, indicating the proton (or deuteron) transfer occurs from a boron site. The ratio  $I_{D_3B_3N_3H_4^+}/I_{D_3B_3N_3H_3D^+}$  vs. pressure shows linear behavior in the low-pressure region, indicating a pseudo-first-order proton transfer reaction



as the source of  $D_3B_3N_3H_4^+$ . This behavior would not be



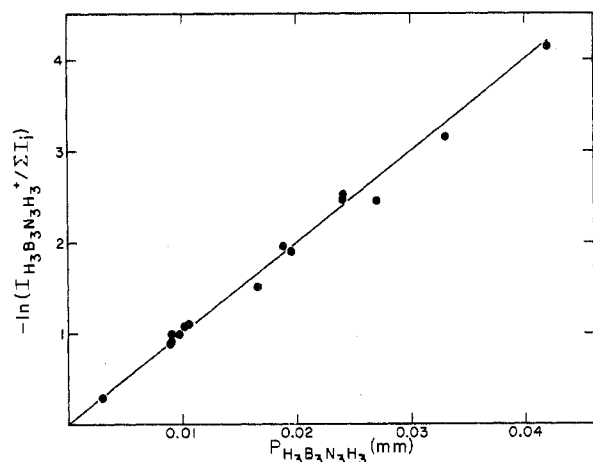


Figure 6. Plot of  $-\ln(I_{H_3B_3N_3H_3^+}/\Sigma I_i)$  vs.  $P_{H_3B_3N_3H_3}$  for the pure  $H_3B_3N_3H_3$  system.

Table III. Bimolecular Rate Constants for the Reaction  $H_3B_3N_3H_3^+ + H_3B_3N_3H_3 \rightarrow$  Products at Various  $E/P$  Ratios

$I_{H_3B_3N_3H_3^+}/\Sigma I_i$	$E/P, V \text{ cm}^{-1} \text{ mm}^{-1}$	$k, \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
0.088	250	$1.2 \times 10^{-9}$
0.132	460	$1.3 \times 10^{-9}$
0.125	625	$1.6 \times 10^{-9}$
0.230	938	$1.4 \times 10^{-9}$
0.245	1080	$1.4 \times 10^{-9}$
0.283	1150	$1.3 \times 10^{-9}$

where  $\tau$  is the residence time of the ions in the source,  $P_{H_3B_3N_3H_3}$  is the pressure of borazine in the source,  $R$  is the gas constant, and  $T$  is taken as  $300^\circ \text{ K}$ . A plot of  $-\ln(I_{H_3B_3N_3H_3^+}/\Sigma I_i)$  vs.  $P_{H_3B_3N_3H_3}$  is shown in Figure 6. The plot exhibits the expected linear behavior, and the slope of the line yields  $k\tau/RT$ . As will be noted subsequently, use of the free-flight residence time,  $\tau_{ff}$ , calculated from electrostatic considerations, gives concordant rate constants in the pressure range covered in this study. The free-flight residence time is given by

$$\tau_{ff} = (2dm/eE)^{1/2} \quad (12)$$

where  $d$  is the distance from the center of the light entrance slit to the ion exit slit measured in centimeters,  $m$  is the mass of the  $H_3B_3N_3H_3^+$  ion,  $e$  is the electrostatic charge, and  $E$  is the electric field in statvolts. From the data in Figure 6 we obtain  $k = 1.3 \pm 0.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  with  $\tau_{ff} = 2.3 \times 10^{-6} \text{ sec}$ . Table III lists rate constants calculated from measurements at different  $E/P$  values. It is noted that  $k$  is essentially invariant over the  $E/P$  range investigated, indicating that in the pressure range of these experiments the collisional effects on ion mobility are not a major factor in defining  $\tau$ . Calculations from the observed rate constant and  $\tau_{ff}$  indicate that an  $H_3B_3N_3H_3^+$  ion encounters about five collisions at a source pressure of 0.045 mm and about one collision at a pressure of 0.010 mm.

In an effort to extend the range of the investigation to lower borazine source pressures a number of experiments were conducted with mixtures of borazine and various diluents ( $H_2$ , He,  $CH_4$ , Ne, Kr). Apparent rate constants for the disappearance of  $H_3B_3N_3H_3^+$ , calculated in the same manner as above, are summarized in Table IV. Results obtained with  $CH_4$ , Ne, and Kr are consistent with those obtained for pure borazine at higher pressures. A marked increase in the apparent rate constant was noted when  $H_2$  or He was used as the diluent. We believe this effect is primarily an artifact due to the experimental conditions. At the low source pressures used in this study (0.010–0.080 mm) gas flow from the ion

Table IV. Apparent Bimolecular Rate Constants for the Reaction  $H_3B_3N_3H_3^+ + H_3B_3N_3H_3 \rightarrow$  Products in Various Diluents

System	Compo- sition	No. data points	$k, \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}{}^a$
$H_2$ - $H_3B_3N_3H_3$	30:1	39	$3.3 \pm 0.5 \times 10^{-9}$
He- $H_3B_3N_3H_3$	30:1	17	$2.3 \pm 0.2 \times 10^{-9}$
$CH_4$ - $H_3B_3N_3H_3$	30:1	3	$1.9 \pm 0.2 \times 10^{-9}$
Ne- $H_3B_3N_3H_3$	50:1	5	$1.7 \pm 0.2 \times 10^{-9}$
Kr- $H_3B_3N_3H_3$	30:1	7	$1.1 \pm 0.2 \times 10^{-9}$

<sup>a</sup> Error limits represent one standard deviation.

Table V. Apparent Bimolecular Rate Constants for the Reaction  $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$

System	Compo- sition	No. data points	$k, \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}{}^a$
$NH_3$	Pure	21	$2.0 \pm 0.4 \times 10^{-9}$
$H_2$ : $NH_3$	40:1	8	$3.8 \pm 0.5 \times 10^{-9}$
Ar: $NH_3$	50:1	9	$2.3 \pm 0.4 \times 10^{-9}$

<sup>a</sup> Error limits represent one standard deviation.

Table VI. Rate Constants at Various Pressures for the Reaction  $D_3B_3N_3H_3^+ + D_3B_3N_3H_3 \rightarrow$  Products

$P_{D_3B_3N_3H_3}, \text{ mm}$	$I_{D_3B_3N_3H_3^+}/\Sigma I_i$	$k, \text{ cm}^3 \text{ mole-cule}^{-1} \text{ sec}^{-1}$
0.007	0.540	$1.2 \times 10^{-9}$
0.0075	0.544	$1.1 \times 10^{-9}$
0.0085	0.445	$1.3 \times 10^{-9}$
0.0115	0.336	$1.3 \times 10^{-9}$
0.012	0.370	$1.1 \times 10^{-9}$
0.014	0.204	$1.5 \times 10^{-9}$

exit slit is primarily effusive, leading to density adjustment of the two gases. Thus the partial pressure of borazine in the source is actually higher than that assumed from the sample composition and the measured pressure. To check this effect with a known ion-molecule reaction, studies were conducted with pure  $NH_3$  and mixtures of  $NH_3$  in  $H_2$  and Ar. Rate constants were obtained for the reaction



The results are summarized in Table V. The value of  $k_2 = 2.0 \pm 0.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  is in reasonable agreement with the results of electron impact<sup>14,15</sup> and charge exchange<sup>16</sup> studies  $0.8$ – $1.8 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  and the value of  $2.3 \pm 0.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  obtained in the photoionization work of Sieck.<sup>17</sup> Substantially higher values of  $k_2$  were obtained from measurements with  $NH_3$ - $H_2$  mixtures following the trend observed in the borazine systems.<sup>18</sup> Rate constant data for the  $D_3B_3N_3H_3^+$ - $D_3B_3N_3H_3$  reaction are given in Table VI. The averaged value of  $k_2$  ( $1.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ) is essentially that for the reaction of the hydrogenated species indicating little or no kinetic isotope effect.

Using the free-flight residence time approximation the rate constant for reaction 10 was obtained from a pseudo-first-order rate expression. Measurements with source pressures of  $H_3B_3N_3(CH_3)_3$  between 0.001 and 0.005 mm give an averaged value for  $k_2$  of  $9.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  with an estimated uncertainty of about  $\pm 25\%$ .

## Discussion

The photoelectron spectrum of borazine<sup>7,12,19</sup> indicates that for ionization energy of 10.2 eV the borazine cation formed will be in its ground electronic state with some vibrational excitation. Electronic excitation to the first electronic state of the cation requires a photon energy of 11.4 eV, which is essentially excluded by the LiF filter.

A number of theoretical calculations for the borazine

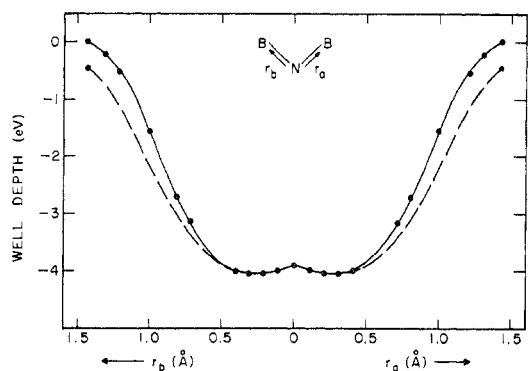
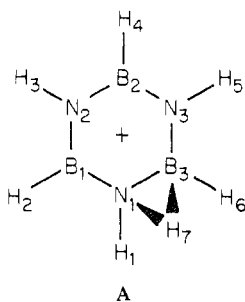
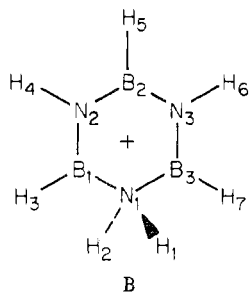


Figure 7. Energy calculations for borazine protonation. (—) Height of proton above the ring = 1.1 Å. (---) Estimated minimum energy contour.

molecule have been reported.<sup>20</sup> In view of the successful application of CNDO calculations for predicting structures of hydrocarbon ions,<sup>21</sup> we have used this procedure to estimate the relative stabilities of the borazinium ion for a series of structures in which the coordinates for the added proton are varied.



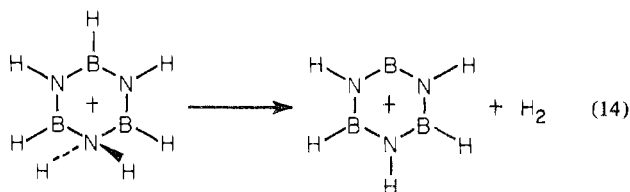
Structure A is a dynamic model which allows for internal rearrangement of the proton. The internal coordinates for the borazine ring were taken from electron diffraction data.<sup>22</sup> The added proton was allowed to move along a B-N bond at a fixed distance above the plane of the molecule. A minimum in the energy was found for a proton distance 1.10 Å above a nitrogen atom and about 0.3 Å from a nitrogen between a B-N pair. The calculations were quite insensitive to the coordinates of the proton in the region near a nitrogen atom, indicating a considerable uncertainty in the proton's location. The energy of the system rises rapidly as the proton approaches a boron atom. The minimum energy for the structure with the proton located directly above a boron atom occurs at a B(3)H(7) distance of 1.23 Å. Results of these calculations are shown in Figure 7. The small barrier at the bottom of the potential well may result by restricting the H(7)N(1)H(1) bond angle at 90°. An increase in this angle from 90° reduces the minimum energy slightly and flattens the curve.



Structure B has two equivalent hydrogens bound to a nitrogen atom in a pseudo-tetrahedral configuration. Without reparameterization of the B-N distances the minimum energy for this structure occurs at an NH<sup>+</sup> distance of 1.09 Å and

an H(1)N(1)H(2) angle of about 108°. This structure is analogous to the thermodynamic (most stable) structure calculated for protonated benzene.<sup>21</sup> The minimum energy calculated for structure B is about 0.2 eV higher than that for A. Structures A and B were refined by allowing  $r(\text{N}(1)\text{B}(1))$  and  $r(\text{N}(1)\text{B}(3))$  to vary together until new energy minima were reached at about  $r(\text{N}(1)\text{B}(1)) = r(\text{N}(1)\text{B}(3)) = 1.52$  Å. Structure B remained about 0.2 eV higher in energy than A. It should be noted, however, that CNDO procedures tend to favor bridged structures<sup>23</sup> and our calculations may overestimate the stability of A relative to B. However, the calculations indicate that protonation of borazine should occur at a site near the nitrogen unless there is an excess internal energy for activation of the proton. Proton transfer from CH<sub>5</sub><sup>+</sup> to borazine is a highly exothermic process releasing about 3.7 eV (the difference between the proton affinities of borazine<sup>24</sup> and CH<sub>4</sub><sup>25</sup>). In chemical ionization studies of borazine-CH<sub>4</sub> mixtures it was observed that a reaction between CH<sub>5</sub><sup>+</sup> and borazine leads to H<sub>2</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub><sup>+</sup> with loss of an H atom bound initially to a boron.<sup>1</sup> In this case the proton transferred is apparently activated sufficiently to surmount the top of the potential barrier and dissociative proton transfer occurs unless there are stabilizing collisions. It is difficult to explain the observation that the deuteron transferred from CD<sub>5</sub><sup>+</sup> (reaction 8) or the proton from H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub><sup>+</sup> (reaction 1) is also removed in the subsequent reaction to form H<sub>3</sub>B<sub>6</sub>N<sub>6</sub>H<sub>6</sub><sup>+</sup> (reactions 9 and 2) unless the proton is in a unique chemical environment or is activated in the H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup> intermediate.

Using 8.8 eV for the proton affinity of borazine,<sup>24</sup> 11.5 eV for the appearance potential of H<sub>2</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub><sup>+</sup> from borazine,<sup>26</sup> and well established values<sup>27</sup> for the ionization potential of H and dissociation energy of H<sub>2</sub>, we obtain for the process



$\Delta H$  (eq 14) = 2.2 eV, indicating the minimum energy required for the process. The process involving loss of H<sub>2</sub> from H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup> leading to the H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>2</sub> radical is not observed, as indicated by the CI mass spectral data for the CH<sub>4</sub>-D<sub>3</sub>-B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> mixture shown in Table I. This is probably due to the greater thermodynamic stability of ·H<sub>2</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> relative to H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>2</sub>, and is consistent with photochemical observations on the two radicals.<sup>28</sup>

A phenomenological collision cross-section,  $\sigma$ , for the collision of borazine with H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub><sup>+</sup> may be obtained by writing the rate constant for H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub><sup>+</sup> disappearance as  $k = \sigma d / \tau_{ff}$ , where  $d$  and  $\tau_{ff}$  have been previously defined. This formulation yields  $\sigma_B \approx 63$  Å<sup>2</sup>. A similar calculation for *N*-trimethylborazine yields  $\sigma_{TMB} \approx 57$  Å<sup>2</sup>. These compare with  $\sigma_{NH_3} \approx 44$  Å<sup>2</sup> calculated from the rate constant for reaction 11.

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**Registry No.** *N*-Trimethylborazine, 1004-35-9; borazine, 6569-51-3; H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>4</sub><sup>+</sup>, 56629-81-3; H<sub>3</sub>B<sub>6</sub>N<sub>6</sub>H<sub>6</sub><sup>+</sup>, 56629-82-4; H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, 56687-66-2; H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, 56629-83-5; H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub><sup>+</sup>, 56629-84-6.

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## Basicity and Ion-Molecule Reactions of Trimethylarsine in the Gas Phase Determined by Ion Cyclotron Resonance Spectroscopy

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The gas-phase ion-molecule reactions of trimethylarsine have been investigated by ion cyclotron resonance spectroscopy. Reaction pathways, rate constants, and product distributions were determined by the variation of electron energy and by trapped-ion and double-resonance techniques. The parent ion reacts with  $(\text{CH}_3)_3\text{As}$  to give  $(\text{CH}_3)_5\text{As}_2^+$  and a methyl radical. The two principal fragment ions,  $(\text{CH}_3)_2\text{As}^+$  and  $\text{C}_2\text{H}_4\text{As}^+$ , react to give the protonated parent ion and also undergo condensation reactions. The gas-phase basicity (proton affinity) of trimethylarsine is determined to be 209.3 kcal/mol [relative to  $\text{PA}(\text{NH}_3) = 201 \text{ kcal/mol}$ ] from investigations of proton-transfer equilibria. This result is consistent with previously established trends in the basicities of group 5 hydrides and their methyl derivatives.

### Introduction

The gas-phase ion chemistry of the series  $(\text{CH}_3)_n\text{EH}_{3-n}$ , where E is a group 5 element, has been the subject of several studies. Molecules which have been examined include  $\text{NH}_3$ ,<sup>3-9</sup>  $\text{CH}_3\text{NH}_2$ ,<sup>5,10-12</sup>  $(\text{CH}_3)_2\text{NH}$ ,<sup>5,10-12</sup>  $(\text{CH}_3)_3\text{N}$ ,<sup>5,10-12</sup>  $\text{PH}_3$ ,<sup>8,13-18</sup>  $\text{CH}_3\text{PH}_2$ ,<sup>19</sup>  $(\text{CH}_3)_2\text{PH}$ ,<sup>19</sup>  $(\text{CH}_3)_3\text{P}$ ,<sup>19</sup> and  $\text{AsH}_3$ .<sup>18,20</sup> Of particular interest are the trends in gas-phase basicity of these compounds. Comparison of gas-phase basicities with condensed phase values, when the latter data are available, yields quantitative information on the effect of solvation on basicity.<sup>11,19,21-23</sup>

This paper reports the investigation by ion cyclotron resonance (ICR) spectroscopy of the gas-phase ion chemistry and basicity of  $(\text{CH}_3)_3\text{As}$  for the purpose of comparison with previously studied congeneric compounds.

### Experimental Section

The general features of ICR instrumentation and its operation in trapped-ion experiments have been previously described.<sup>24-26</sup> All experiments were performed at room temperature.

Reaction paths were identified by observing reactant and product ion intensities as a function of electron energy<sup>16,27</sup> and by double-resonance experiments.<sup>24</sup> Spectral intensities in the figures have been corrected to ion abundance by dividing the measured intensity by ion mass.<sup>24,25</sup>

Pressure measurements were made using a Schulz-Phelps gauge located adjacent to the ICR cell. This gauge is calibrated for each gas for a given emission current (5  $\mu\text{A}$ ) and magnetic field (6 kG) against an MKS Instruments Baratron Model 90H1-E capacitance manometer in the region  $10^{-5}$ – $10^{-3}$  Torr, where linear variation of gauge current with pressure is observed. Pressures in the trapped ion experiments were in the range  $10^{-7}$ – $10^{-5}$  Torr. The principal error in the rate constants (estimated to be  $\pm 20\%$ ) arises from uncertainties in pressure measurements. Mass spectra of  $(\text{CH}_3)_3\text{As}$  recorded with

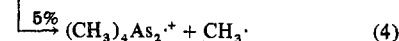
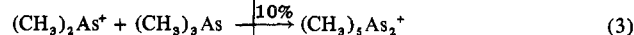
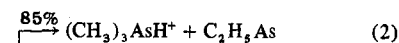
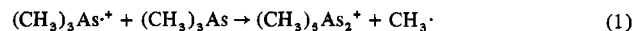
the Schulz-Phelps gauge on and off demonstrated that no significant pyrolysis was occurring on the filament.

$(\text{CH}_3)_3\text{As}$  was obtained from Alfa Products. Mass spectral analysis revealed no detectable impurities.  $\text{CF}_3(\text{CH}_2)_3\text{NH}_2$  was provided by Professor R. W. Taft (University of California, Irvine, Calif.). Other chemicals were readily available reagent grade materials and were used as supplied except for treatment using freeze-pump-thaw cycles to remove noncondensable impurities.

### Results

**Mass Spectrum.** The mass spectrum of  $(\text{CH}_3)_3\text{As}$  at low pressure ( $10^{-6}$  Torr) at 70 eV agreed with the reported spectrum.<sup>28</sup> The fragments present at 18 eV, the electron energy at which the trapped ion experiments were performed, include  $(\text{CH}_3)_3\text{As}^+$  ( $m/e$  120, 38%),  $(\text{CH}_3)_2\text{As}^+$  ( $m/e$  105, 35%),  $\text{C}_2\text{H}_4\text{As}^+$  ( $m/e$  103, 25%), and  $\text{C}_2\text{H}_2\text{As}^+$  ( $m/e$  101, 2%).

**Ion-Molecule Reactions.** Figures 1 and 2 illustrate the variation of ion abundance with time.<sup>29</sup> The principal reactions in  $(\text{CH}_3)_3\text{As}$  parallel those of  $(\text{CH}_3)_3\text{P}$ .<sup>19</sup> Like  $(\text{CH}_3)_3\text{P}^+$ , the parent ion  $(\text{CH}_3)_3\text{As}^+$  ( $m/e$  120) does not react to give the protonated parent ion. Instead it undergoes exclusively the condensation reaction 1 to form  $(\text{CH}_3)_5\text{As}_2^+$  ( $m/e$  225), which is also formed in the clustering reaction 3 of  $(\text{CH}_3)_2\text{As}^+$  ( $m/e$  105) with the parent neutral.



Other reactions of  $(\text{CH}_3)_2\text{As}^+$  include proton transfer to