Autorenkollektiv

Inorganic Chemistry

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Richard F. Porter and Laura J. Turbini

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The Chemistry of Technetium

Klaus Schwochau

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Photochemistry of Boron Compounds

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I. Introduction

Scientific interest in the chemistry of boron has expanded noteably in the past 20 years. There has, however, been relatively little emphasis on the photochemistry of boron compounds. Since the volume of published work on boron photochemistry is not excessive, it is possible in this review to include the major fraction of the photochemical literature dating back to the initial work of Stock[99]. This article deals primarily with the inorganic photochemistry of boron compounds. Many simple boron compounds with B-H, B-O, B-N or B-halogen bonds do not absorb radiation in the visible or near UV regions of the optical spectrum. For this reason photochemical experiments with these compounds frequently require the use of sources of short wavelength radiation below 200 nm, a spectral region requiring vacuum optical techniques. This limitation and the need for special handling of boron compounds that may be thermally unstable or highly reactive have probably contributed to the lack of systematic efforts to investigate the photochemistry of these systems. Nevertheless, it is anticipated that the interest in structures of polyhedral boron compounds[68] will be an impetus to further exploration of their photochemical behavior.

With the development of CO_2 lasers, work on the infrared photochemistry of boron compounds is now appearing in the literature. Future work on these compounds with UV laser sources is also expected. In this review the effect of radiation on boron compounds in the photon energy range 0.1 eV (CO_2 laser) to 10.2 eV (H-α line) is examined. The range of tropics extends from the use of photochemical techniques for synthesis of new compounds to the production and isolation of reactive photochemical intermediates. The photochemistry of borazine is most extensively discussed.

Some speculation is inevitable in proposing any photochemical mechanism and some liberty has been taken in this regard in the present discussion. Areas of boron photochemistry are indicated where proposed mechanisms are controversial and where further experimental work is necessary. For example, very little is known about triplet states of boron molecules. Some of these questions may be answered in the future by non-photochemical techniques[30].

II. Boron Hydrides

Interest in the photochemistry of boron compounds dates back as far as 1913 when Alfred Stock[99] investigated the effects of light from a mercury vapor lamp on diborane(6) and on tetraborane(10). In the case of diborane(6) he commented: "UV light will also decompose B_2H_6. The volume of a sample in a quartz tube increased by 1/6 after 24 hours exposure to a mercury-arc lamp, and a pale yellow crystalline substance appeared." Stock also observed that B_4H_{10} decomposition to B_2H_6 is not noticeably influenced by sunlight.

Further observations on the effect of light on diborane(6) did not appear until the 1950's. At that time, Hirata and Gunning[52] studied the mercury-sensitized decomposition, leading to H_2 and B_4H_{10} as the main products. The proposed mechanism involves the mercury-sensitized cleavage of a boron-hydrogen bond followed by recombination of the radicals as follows:

$$B_2H_6 + Hg\,6\,(^3P_1) \longrightarrow B_2H_5 + H + Hg\,6\,(^1S_0) \qquad (1)$$

$$2\,B_2H_5 \longrightarrow B_4H_{10} \qquad (2)$$

It should be noted that as of now there is no direct physical evidence (e. g., ESR spectrum) for the existence of the B_2H_5 radical and *much* of the mechanistic discussion of the photochemistry of diborane(6) is speculative. If Eqs. (1) and (2) represent the correct mechanisms the rate of the quantum yields for H_2 to B_4H_{10} production would be unity. Although this ratio tends towards unity at lower pressures, this simple mechanism did not explain the ratio of two approached at higher pressures. In order to explain this, an additional primary process was proposed, i. e., a disproportionation of two B_2H_5 radicals:

$$2B_2H_5 \longrightarrow B_2H_4 + B_2H_6 \qquad (3)$$

The reactive B_2H_4 is presumed to decay rapidly to pentaboranes and solid product.

Direct photolysis of B_2H_6 using 184.9 nm radiation was reported by Kreye and Marcus[62)] in 1962. A UV absorption spectrum of B_2H_6 is shown in Fig. 1. The spectrum has been interpreted as a σ to π^* transition which is weakly allowed. Thus, the 184.9 nm mercury line is a useful radiation to study the photochemical reactions of this compound. The study of Kreye and Marcus limited itself to low percent conversions, but included variations in light intensity, and diborane(6) pressures. The major products in the photolysis were identified as B_4H_{10}, B_5H_{11}, a polymeric solid, and H_2. The formation of B_4H_{10} and polymer were linked to the proposed primary radical, B_2H_5, in the mechanism:

$$B_2H_6 \xrightarrow{h\nu} B_2H_5 + H \qquad (4)$$

$$B_2H_5 + H \longrightarrow (-B_2H_2-) + 2H_2 \qquad (5)$$

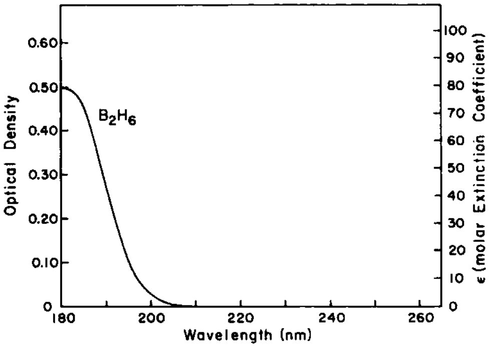

Fig. 1. Ultraviolet absorption spectrum of diborane (6)

$$2B_2H_5 \longrightarrow B_4H_{10} \tag{6}$$

$$2H + M \longrightarrow H_2 \tag{7}$$

The formation of B_5H_{11} is linked to a second intermediate BH_3:

$$B_2H_6 \xrightarrow{h\nu} 2BH_3 \tag{8}$$

$$BH_3 + B_2H_6 \longrightarrow B_3H_7 + H_2 \tag{9}$$

$$B_3H_7 + B_2H_6 \longrightarrow B_5H_{11} + H_2 \tag{10}$$

The overall mechanism for the reaction is consistent with the quantum yields observed for photolysis at various pressures of B_2H_6. Attempts to produce BH_3 by photolysis of diborane(6) in matrix studies have consistently failed. At the present time there is no physical evidence to support this step in the mechanism.

Grimm and Porter$^{41)}$ investigated the photochemical reaction of diborane(6) with oxygen by direct coupling of their photochemical vessel with a mass spectrometer (Fig. 2). Using 184.9 nm radiation, they varied the oxygen/diborane(6) mixtures in molar proportions from 1:1 to 2:1 at total pressures ranging from 12 to 40 torr. The course of the reaction is illustrated in Fig. 3 which shows an initial rise in the formation of $H_2B_2O_3$ (I) and a time-delayed rise in the formation of $H_3B_3O_3$ (II). When the reaction was run with unscrambled mixtures of $^{16}O_2 - {}^{18}O_2$, it was found that the $H_2B_2O_3$ consisted of a non-statistical distribution of isotopic species. This suggested that an O_2 molecule participated directly in the formation of $H_2B_2O_3$. The overall stoichiometry was observed as follows:

$$B_2H_6 + 2O_2 \xrightarrow{h\nu} H_2B_2O_3 + H_2O + H_2 \tag{11}$$

The results suggest the possible addition reaction of O_2 to a diborane-type intermediate in the primary step. Despite the fact that B_2H_6 is the simplest boronhydride, there are a number of unanswered questions regarding the photochemical behavior of this molecule.

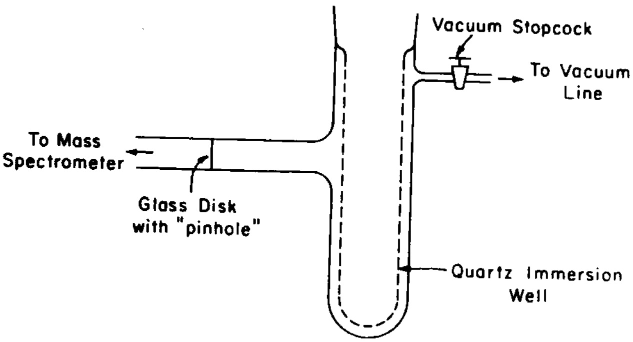

Fig. 2. System for sampling photolysis products in a mass spectrometer

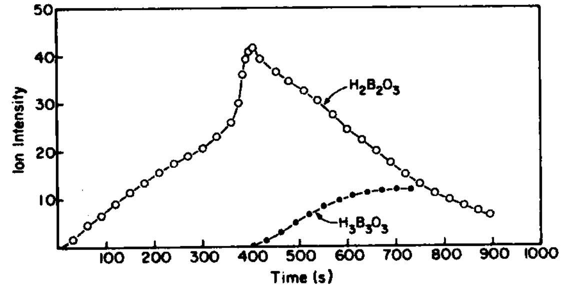

Fig. 3. Data points indicate the course of the photolysis reaction of B_2H_6/O_2 mixture monitored by mass spectral sampling of the reaction products (apparatus of Fig. 2).
Initial conditions: $B_2H_6:O_2 = 1:1$ Total press ≈ 20 torr

In 1956, Burwasser and Pease[18a)] presented preliminary work on pentaborane(9) photolysis, in which they suggested that the major radical formed is B_5H_8. The products identified in their photolysis are H_2, B_2H_6, and a colorless crystalline material, postulated to be $B_{10}H_{14}$. Photolysis of B_5H_9 in the presence of deuterium, produced H_2, HD, and D_2 in the product. This led to the following proposed primary mechanism:

$$B_5H_9 + h\nu \longrightarrow H + B_5H_8 \tag{12}$$

$$H + D_2 \longrightarrow HD + D \tag{13}$$

$$H \text{ or } D + B_5H_9 \longrightarrow B_5H_8 + H_2 \text{ (or HD).} \tag{14}$$

No explanation is presented for the B_2H_6 or $B_{10}H_{14}$ products. More recently, Plotkin and Sneddon[81)] showed the results of Hg-sensitized photolysis of pentaborane(9) leading to a $(B_5H_8)_2$ dimer, H_2, $B_{10}H_{14}$, and a viscous oil. They suggested that the $(B_5H_8)_2$ is formed to the recombination of B_5H_8 radicals. They identify the compound as $2,2'$-$(B_5H_8)_2$ (Fig. 4). This system was studied in detail by Kline and Porter[61)] in an attempt to obtain evidence for the B_5H_8 radical. These investigators were unable to obtain the $(B_5H_8)_2$ dimer in the photolysis of B_5H_9 with di-*t*-butylperoxide which is known to act as a H-abstraction reagent. When mixtures of nonscrambled B_5H_9 and B_5D_9 were investigated, the hydrogen produced for short photolysis periods consisted of H_2 and D_2 with very small quantities of HD, much below an equilibrium proportion. These results are inconsistent with the mechanism described in Eqs. (12), (13), and (14) which is expected to lead to a statistical distribution of hydrogen isotopes. Kline and Porter[61)] also investigated the photolysis of 1-DB_5H_8 and μ-$D_4B_5H_5$. They concluded from the isotopic hydrogen analysis, that the elimination of a hydrogen molecule from any pair of H sites in pentaborane is a random but not strictly statistical process. From these results, a

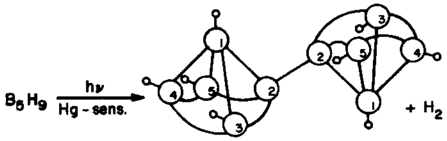

Fig. 4. Pyrolysis product of B_5H_9

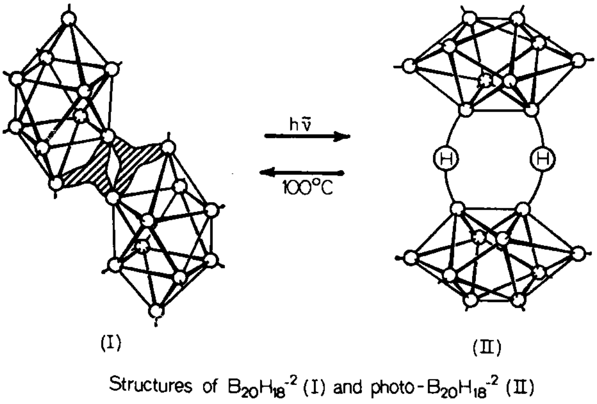
hν̄
100°C
H
H
(I)
(II)
Structures of $B_{20}H_{18}^{-2}$ (I) and photo-$B_{20}H_{18}^{-2}$ (II)

Fig. 5. Photoisomers of $B_{20}H_{18}^{2-}$

mechanism is postulated which involves the formation of B_5H_7 as a primary intermediate leading to the formation of $B_{10}H_{14}$ and $B_{10}H_{16}$. Similar studies with 1-methyl- and 2-methylpentaborane(9) gave methylated derivatives of $B_{10}H_{14}$ and $B_{10}H_{16}$. Photochemical isomerization of these methylboranes was not observed. An interesting photo-isomerization was reported by Hawthorne and Pilling[50)] in 1966. They irradiated $B_{20}H_{18}^{2-}$ (I) in acetonitrile solution to obtain the photoisomer $B_{20}H_{18}^{2-}$ (II), which can be converted back to (I) by heating at 100 °C for 36 hours (Fig. 5).

Trofimenko and Cripps[98)] report that $B_{10}X_{10}^{2-}$ and $B_{12}X_{12}^{2-}$ (X = halogen) undergo photoinduced nucleophilic substitution reactions which are useful in preparing some previously inaccessible polyhedral boranes.

III. Boron-Carbon Compounds

A. Trialkylboranes

The literature contains several articles on the photochemical reactions of trialkylboranes with organic moieties. In some cases it appears that the organic reagent is absorbing the light rather than the borane. Examples of this are the reaction of trialkylboranes with (a) β-substituted α,β-unsaturated carbonyl compounds[15)], (b) with cyclohexene[75)], (c) with cycloocta-27,7-dienone[75)], (d) with acridine[75)], (e) with ethyl acetoacetate[109)], (f) with acetylacetone[109)], and (g) with ethyl 2,2-dimethylacetoacetate[109)]. Iodine has been photolyzed in the presence of triethylborane[1)]. Finally, thioborinates have been produced in the photolysis of 4,4′-bisdimethylaminobenzothiophenone with trialkylboranes[55)], and of phenyl disulfide or methyl disulfide with tri-*n*-butylborane[16)]. In all of these examples, the borane is not the primary photochemical reagent.

There are examples where the trialkylborane is the photochemical excited species. Lissi and Larrondo[69)] studied the Hg-photosensitized decomposition of

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triethylborane. Although they did not analyze the boron-containing products, they proposed two main processes, and possibly a third, which involved the triethylborane in the primary step:

$$Hg^* + (C_2H_5)_3B \longrightarrow Hg + H_2 + \text{products} \qquad (15)$$

$$Hg^* + (C_2H_5)_3B \longrightarrow Hg + C_2H_5 + (C_2H_5)_2B \qquad (16)$$

and probably

$$Hg^* + (C_2H_5)_3B \longrightarrow Hg + C_2H_4 + (C_2H_5)_2BH \qquad (17)$$

The quantum yields determined are 0.3, $\geqslant 0.3$, and $\leqslant 0.07$, respectively.

B. Carboranes

Only a few photochemical reactions of carboranes have been reported in the literature. Plotkin and Sneddon[87)] synthesized a carborane dimer by the Hg-sensitized photolysis of $C_2B_5H_7$ (Fig. 6).

$$C_2B_5H_7 \xrightarrow[Hg]{h\nu} 3,3'\text{-}(2,4\text{-}C_2B_5H_6)_2 + H_2 \qquad (18)$$

Spielman and Scott[98)] obtained improved yields in the synthesis of $C_2B_3H_5$, 1,6-$C_2B_4H_6$ and 1,2-$C_2B_4H_6$ from the photolysis of 2,3-$C_2B_4H_8$. Finally, photochemical chlorination of carboranes has been reported[101)].

C. Organoboron Compunds

There is pertinent literature on the photochemistry of complex organic molecules containing a structurally significant boron atom. The Eastman Kodak group[31, 42,

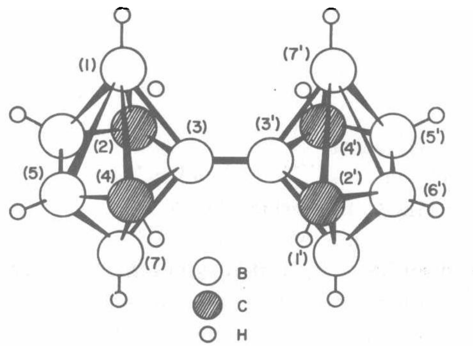

Fig. 6. Photolysis product of $C_2B_5H_7$

PROPOSED STRUCTURE FOR 3,3'-(2,4-$C_2B_5H_6$)$_2$

[43, 44, 113, 114, 115, 116, 117] has been especially active in this area. In general these molecular systems with organic chromophores are photochemically active in the near ultraviolet. Doty and coworkers[31a] report absorption maxima and fluorescence quantum yields for a series of p-substituted phenyldimesitylboranes. Quantum yields and Stoke's shifts are strongly dependent on the dipolar character of the solvent used. From the solvent effect it is inferred that the excited state of the borane is highly polar relative to the ground state.

Photolysis of sodium tetraphenylborate in aqueous solution with 253.7 nm radiation yields products of biphenyl and 1-phenylcyclohexa-1,4-diene as well as other dienes[113]. The yield of biphenyl was decreased when the reaction was run under nitrogen to exclude atmospheric oxygen. These hydrocarbon products were not observed when triphenylborane was irradiated at 253.7 nm under nitrogen in cyclohexane solution[114]. However, when this reaction was run under the same conditions in alcohol solutions, products similar to those observed in borate salt photolyses were obtained[116]. The solvent effect is probably a consequence of the varying capacity of basic solvents to transfer electron pairs to the borane resulting in complexes which exhibit photochemical behavior of tetra coordinate (ate-type) systems. The mechanism of the photochemical reaction of tetraphenylborate anion with singlet oxygen is believed to involve an electron transfer process from the anion to form O_2^-, not direct attack of $^1O_2$ on the borate[31]. Grisdale and coworkers have observed some interesting photochemical rearrangements of hindered tetraarylborates[44]. In the presence of oxygen photolysis of dimesityldiphenylborate anion yields products of 2,4,6-trimethylbiphenyl and (2,4,6-trimethyl-3-biphenylyl)-mestiylphenylborane. Eisch and coworkers[32] have also contributed to our understanding of the photochemical mechanisms in borate systems. Irradiation of sodium tetraphenylborate at 254 nm in anhydrous THF or 1,2-dimethoxyethane leads to products of diphenyl and toluene. Two pathways were proposed to account for these products. From the chemical behavior of this system with organic reagents in aprotic solvents a photochemical mechanism was proposed that involves the formation of an intermediate diphenylborate anion (a carbene analogue).

Irradiation of tribenzylborane in alcoholic solvents gives good yields of toluene. The mechanism of the reaction involves heterolytic cleavage of the benzylcarbon-boron bond[24].

IV. Boron-Nitrogen Compounds

A. Borazine

1. Spectroscopic Studies

Borazine, $(\text{-BH-NH-})_3$, an inorganic isoelectronic analog of benzene, is the single boron compound that has been most completely investigated by photochemical techniques. An early theoretical study of the structure of borazine was made by Hoffmann[53]. A UV absorption spectrum of borazine is shown in Fig. 7. Unlike the

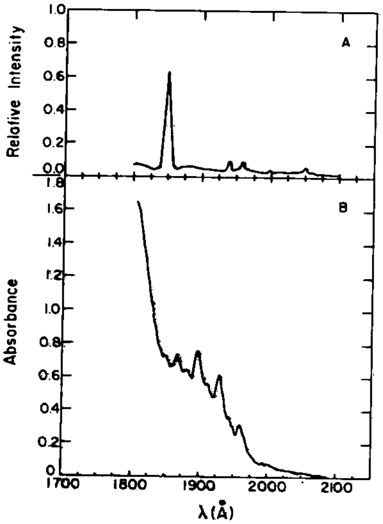

Fig. 7. Ultraviolet absorption spectrum of borazine (B). Curve A is a line spectrum from a medium pressure Hg lamp showing the location of the strong 184.9 nm line in relation to the borazine absorption spectrum

spectrum of diborane(6), the spectrum of borazine exhibits structural features. Before proceeding to the specifics of the photochemical reactions, spectral considerations based on current available physical evidence will be discussed.

The photoelectron spectrum of a molecule gives vertical ionization potentials for photoionization from molecular orbitals of various energies (Table 1). In this manner, it has been used as a convenient method for determining the position and ordering of the orbitals of a given molecule. A majority of the theoretical calculations reported on borazine – which include all valence electrons in the calculations – have suggested that the HOMO is the e′(σ). Those which consider only π electrons and some which consider both σ and π electrons have suggested that the HOMO is

Table 1. Experimental and theoretical vertical ionization potentials for borazine (eV)

	1e″(π)	4e′(σ)	a_2″(π)	3e′(σ)	$1a_2$′(σ)	$3a_1$′(σ)
Experimental						
Boch[13)]	10.09	11.42	12.83	14.75	14.75	13.72
Brundle[17)]	10.14	11.42				
Frost[36)]	11.42	10.09	17.10	13.98	14.70	12.82
Lloyd[70)]	10.14	11.42	12.06	14.76	12.83	13.84
	10.50 sh	11.73				
Theoretical						
Armstrong[4)]	12.70	13.59				
Chalvet[19)]	12.3					
Davies[26)]	11.0	10.2	18.3	14.9	16.7	14.6
Frost[36)]	10.4	9.8	17.7	14.8	16.6	14.0
Kuznesof[64)]		13.72				
Peyerimhoff[85)]	11.69	13.10	14.64	19.14	16.78	15.77

e″(π). In 1970, two research groups independently reported the experimental photoelectron spectrum of borazine. Although both published spectra were superimposable through 16 eV, the interpretations of the data were decidedly different. Frost and co-workers[36)], who based their analysis on theoretical calculations, reported that the e′(σ) level is the HOMO. Lloyd and co-workers[70)], on the other hand, used arguments based on peak contours and vibrational fine structure to interpret the spectrum in terms of an e″(π) HOMO. In 1971, Bock and Fuss[13)] published convincing arguments that the e″(π) orbital is the HOMO. They began with the assigned orbital levels of benzene from its photoelectron spectrum. Introducing a perturbation of D_{3h} symmetry into these levels causes a mixing of molecular orbitals of like symmetry. The smaller the initial energy difference is between the two symmetry-matched orbitals, the larger the interaction. By examining benzene and borazine spectra together, Bock and Fuss were able to correlate all the borazine and benzene bands on the basis of this mixing, assigning the first borazine band at 10.09 eV to the e″(π) orbital. Further proof of the π-assignment comes from examining halogen derivatives of borazine where lowering of the highest occupied σ level and raising of the π level is predicted theoretically. In line with this prediction, they report a 10.66 eV ionization potential for B-trifluoroborazine, $(\text{-BF-NH-})_3$, and 10.55 eV ionization potential for B-trichloroborazine, $(\text{-BCl-NH-})_3$.

On the basis of the ordering of the molecular orbitals, one can determine the symmetry of the low lying electronically-excited states to be $^1A_1$, $^3A_1$, $^1A_2$, $^3A_2$, $^1E'$ and $^3E'$. Transitions from the ground $^1A_1{}'$ state to the $^1E'$state is dipole allowed, but transitions to all the triplet states are spin-forbidden. The $^1A_1{}' \leftarrow {}^1A_1$, and the $^1A_1 \leftarrow {}^1A_2{}'$ transitions are electric dipole-forbidden but become allowed by vibronic coupling to the $^1E'$ level. A vibration of e′ or a_2'' symmetry makes the former absorption allowed, while the latter is allowed only by a vibration of e′ symmetry.

Platt and coworkers[86)] first recorded the UV spectrum of borazine from 225.0 to 170.0 nm in 1947. Later, an attempt was made to locate bands above 200 nm, but none were observed. Improved instrumentation led to a series of papers on the absorption spectrum of borazine in the vacuum ultraviolet. Kaldor[59)] assigns the most intense absorption whose maximum occurs at 165.0 nm to the allowed $^1E' \leftarrow {}^1A_1{}'$ transition. He analyzes the vibrational structure of the remaining absorptions and divides them into 4 progressions: (1) 199.5, 196.1, 192.9, 187.9 and 186.7 nm; (2) 194.4, 191.3, 183.1, and 185.0 nm; (3) 186.0, 182.9 and 179.9 nm; and (4) 187.7, 184.5, and 181.4 nm. Interpreting the 199.5 nm band of the first progression as a hot band, he assigns the spacing e′ symmetry. For progressions (3) and (4) the exciting vibration is not observed but the 0-0 transition for this state is estimated to be at 188.9 nm. Since Kaldor can find no active vibration of a_2'' symmetry, he cannot distinguish the $^1A_1{}'$ and $^1A_2{}'$ states on the basis of the experimental data. However, he has assigned these states according to the sequence observed for the analogous benzene states, which is also the ordering predicted by theoretical calculations.

Yanase and coworkers[118)] examined the UV spectrum of borazine from 210.0 to 185.0 nm, reporting the same vibrational progressions as Kaldor. Yanase interprets the data in terms of a 0-0 transition at 198.4 nm allowed by vibrations of e′ symmetry ($\nu_{17} = 525\ \text{cm}^{-1}$ and $\nu_{13} = 1649\ \text{cm}^{-1}$). Although the latter exciting vibration is not observed experimentally, he suggests that this is due to the weakness of the singal. Despite the fact that Yanase assigns the 1984nm transition to the $^1A_2'$ state without consideration of whether it could also be the $^1A_1'$ state, his calculations of the predicted intensity of the band as a $^1A_2' \leftarrow {}^1A_1'$ transition give good agreement with the observed intensity. This location of the $^1A_2'$ state is in general agreement with that assigned by Kaldor.

A third analysis of the UV absorption spectrum of borazine reported by Bernstein and Reilly$^{12)}$ is not in agreement with Kaldor's assignments. Bernstein interprets the first vibrational progression in the same manner as Kaldor. However, for the second progression he reports a band at 2011 nm (not observed by Kaldor) which he interprets as a ν_1 hot band of a_2'' symmetry. He identifies the 197.5 nm origin of this band as the location of the $^1A_1'$ state.

Table 2 summarizes the theoretical predictions and experimental data on the excited states of borazine. It can be noted that the three excited singlet states of borazine are closely spaced and overlap. Consider, for example, the absorption of 184.9 nm radiation by borazine. It is not clear whether the $^1A_1'$, $^1A_2'$ or $^1E'$ state is reached preferentially. There is a vibrational band at 185.0 nm assigned to the $^1A_2'$ state, and another one nearby at 184.5 nm assigned to the $^1A_1'$ state. The $^1E'$ absorption whose maximum is at 165.5 nm can be thought to begin somewhere in this region as well. Thus, one expects that the potential surface describing this region will allow for facile interconversion. This may be one of the reasons for the repeated failures to observe fluoroescence from borazine. The location of the triplet states of borazine has been studied theoretically. However, the only piece of experimental evidence for the location of a triplet state of this molecule comes from the work of

Table 2. Experimental and theoretical transition energies to the low lying excited state of borazine (eV)

	$^1A_2'$	$^1A_1'$	$^1E'$	$^3A_1'$	$^3A_2'$	$^3E'$
Experimental						
Platt$^{86, 58)}$	6.2	6.7	7.2			
Kaldor$^{59)}$	6.28	6.56	7.55			
Yanase$^{118)}$	6.25					
Kroner$^{63)}$	6.41–6.52	7.13	7.65			
Bernstein$^{12)}$	(7.0)	6.5	7.5			
Theoretical						
Chalvet$^{19)}$ I	6.51	5.74	7.14	5.74	5.82	5.78
Davies$^{25)}$	5.7	6.1	8.8			
Kuznesof$^{64)}$	8.48	9.65	9.86	8.48	7.96	8.27
Perkins$^{84)}$	6.58	7.26	7.51	6.58	6.88	6.58
Peyerimhoff$^{85)}$ I	6.97	8.75	9.57	6.46	8.52	7.30
II	7.88	9.01	9.59	7.93	8.05	8.33
Roothaan$^{93)}$	6.5	7.2	7.7	5.9	6.9	6.4
Young$^{119)}$ I	6.51	7.80	7.30	6.03	6.51	6.05
II	6.52	7.84	7.18	5.57	6.53	5.92
Kroner$^{63)}$	6.45	7.22	7.61			

Young and coworkers[19] who showed a direct relationship between borazine pressure and the quenching of the triplet state of benzene excited at 258.0 nm. These investigators concluded that the triplet state of borazine lies at an energy not higher than 4.9 eV., which is at least 1 eV lower than the calculated values. It was further concluded that the lifetime of the borazine triplet is much shorter than the benzene triplet because of the failure of borazine to transfer its triplet energy to biacetyl. Experiments involving borazine with photoexcited biacetyl show borazine to have the effect of a vibrational quencher. Neither the singlet nor triplet emissions of biacetyl have been quenched by this molecule.

In contrast to borazine, the three corresponding excited singlet states of benzene have a much wider spread of absorbing wavelengths and exhibit easily distinguished vibrational fine structure. Many photolysis experiments have been performed using laser lines tuned to selective excite a particular vibrational level of a particular excited state of benzene. Such experiments are more difficult with borazine. The triplet states of benzene have been located experimentally and quantum yields for fluorescence and phosphorescence at various wavelengths and pressure conditions have been determined.

2. Photochemical Studies

A detailed study of the photochemistry of borazine with 184.9 nm radiation was reported by Neiss and Porter[80] in 1972. Products formed at low pressures (0.1 to 15 Torr) include H_2, borazanaphthalene, diborazinyl, and a polymer. When B-trideuterioborazine was used in the photolysis, HD was produced as the major noncondensible gas. Equimolar mixtures of borazine and borazine-d_6, irradiated for short periods produced predominantly H_2 and D_2, while those samples photolyzed for longer periods produced appreciable amounts of HD. An H-D exchange reaction at boron sites was noted. The ratio $B_3N_3D_5H/B_3N_3D_6$ was determined and used as a measure of this exchange. At low pressures, this ratio varied linearly with the total pressure, reaching a limiting value of 3 at long photolysis times. Quantum yield data from the photolysis of borazine indicates that the production of H_2 depends directly upon the amount of light absorbed by borazine and inversely upon the total pressure of the system. The limiting value of Φ_{H_2}, obtained by extrapolation to zero pressure, is 0.21. This value drops to $\Phi_{H_2} = 0.11$ at 13.5 torr (Fig. 8). The formation of a polymer was noted and found to depend linearly upon $I_a t/A$ (where $I_a t$ is the integrated intensity of light absorbed and A is the absorbance of the polymer). The addition of a low molecular weight inert gas such as H_2 or Ar decreased the production of polymer. No data were reported relative to the quantum yield for the production of H_2 when these inert gases were used. Cyclohexane vapor which is transparent to 184.9 nm light was also added in some experiments since it can provide many vibrational degrees of freedom for collisional deactivation without reacting chemically. The effect of cyclohexane addition was to decrease Φ_{H_2} and the amount of polymer produced.

Borazine + D_2. Nadler and Porter[79] reported on the photochemical exchange reaction of borazine with D_2 at 184.9 nm. Products observed include B-mono-, B-di,

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