The spectra of BCl_3 chemisorbed on iron and nickel show two B–Cl stretching bands in the 810–840-cm^{-1} region, the weaker band due to the ^{10}B isotope, the stronger to the ^{11}B isotope (Figure 5 and Table III). The frequencies are in accord with those reported by Katritzky[7] for a number of substituted pyridine–BCl_3 complexes. In the seven complexes he studied, the B–Cl stretching frequencies appeared between 818 and 843 cm^{-1}.

Johnson and Shriver[19] have reported infrared data for one of the few metal–BCl_3 adducts yet prepared, $(C_5H_5)_2WH_2 \cdot BCl_3$. They assigned the B–Cl asymmetric stretch to a band at 755 cm^{-1}, although several bands were found in the 800–850-cm^{-1} region.

Unlike BF_3 chemisorbed on nickel, BCl_3 chemisorbed on nickel was not replaced by carbon monoxide. In fact, exposure of a nickel film containing preadsorbed BCl_3 to CO resulted in an increase in the intensity of the B–Cl stretching bands. This change in intensity is probably related to a change in the dipole moment of adsorbed BCl_3 molecules caused by the chemisorption of CO. The CO bands were very weak, indicating that not much CO was adsorbed.

These results with BF_3 and BCl_3 indicate that transition metal surfaces do indeed exhibit basic properties in appropriate circumstances. The molecules BF_3 and BCl_3 have been shown to adsorb without dissociation on V, Fe, Ni, Pd, and Cu. However, these results do not require that all adsorbed BF_3 and BCl_3 be undissociated but do indicate that those species whose infrared spectra are sufficiently intense to be observed in the spectral region covered are undissociated.

The variation in displacement of BF_3 by CO on the metal surfaces may be correlated with the expected basicities of the different metals. Basic character is expected to increase with an increase in the ease of donating electrons, which will increase as valence-state ionization potentials decrease. From the data in Table V it is seen that the valence-state ionization potentials decrease as one goes from Cu to V across the first-row transition metals. Since BF_3 adsorbs with the metal acting purely as a base, the strength of BF_3 adsorption is expected to directly vary with metal base strength. Thus on V, the strongest base, BF_3 is not displaced by CO, while on Ni, a weaker base, BF_3 is replaced by CO and Fe occupies an intermediate position both with respect to basicity and BF_3 replacement by CO. Not only then has the basicity of transition metal surfaces been shown, but also it is demonstrated that basicity is a useful concept in understanding the properties of adsorbed species.

Table V. Valence-State Ionization Potentials (cm^{-1}) for Removing a d Electron from a $3d^n4s^1$ State

V	51,400	Co	75,000
Cr	57,900	Ni	80,900
Mn	64,100	Cu	86,000
Fe	70,000		

Acknowledgment. This investigation was supported in part by Research Grant No. 00818 from the Air Pollution Control Office, Environmental Protection Agency.

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Photochemistry of Borazine. Evidence for a Borazyne Intermediate[1]

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Abstract: Photolysis of borazine with 1849-Å radiation produces H_2, borazanaphthalene, diborazinyl, and a nonvolatile polymer. The quantum yield for hydrogen formation and the rate of polymer deposition in the presence and absence of inert gases have been studied as functions of pressure. A mechanism is proposed involving internal conversion from an excited singlet state of borazine to a vibrationally excited ground state. Experimental observations indicate that a molecule $B_3N_3H_4$ (a borazyne) is a probable photochemical intermediate. The quantum yield for H_2 production at 1 mm is 0.21 ± 0.02. This value decreases with increasing borazine pressure and with the addition of inert gas (Ar, H_2, and cyclohexane). In equimolar mixtures of borazine and borazine-d_6 rapid photochemical hydrogen–deuterium exchange is observed, and at low pressure the exchange quantum yield varies linearly with pressure.

Qualitative photochemical studies of borazine have shown that borazine reacts in the gas phase with H_2O,[2] NH_3,[2] alcohols,[3,4] and methyl halides[5] to yield B-monosubstituted derivatives. The mechanism of the borazine–D_2 reaction[6] was the first quantitative

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[1] Work supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency through the Materials Science Center, Cornell University.

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[3] M. Nadler and R. F. Porter, *ibid.*, **6**, 1739 (1967).

[4] M. B. Oertel, Ph.D. Thesis, Cornell University, 1971.

[5] M. Oertel and R. F. Porter, *Inorg. Chem.*, **9**, 904 (1970).

[6] M. P. Nadler and R. F. Porter, *ibid.*, **8**, 599 (1969).

study of borazine's photochemistry. We have noted in recent experiments that when pure borazine is photolyzed at 1849 Å a nonvolatile material forms on the window(s) and acts to reduce the apparent incident intensity. At the same time volatile reaction products are observed. In earlier experiments,[6] no measurable amount of borazine photodecomposition was observed. However, the experimental apparatus has since been improved and a greater sensitivity attained. Since further basic information is desired to extend our understanding of the photochemistry of borazine, we have undertaken a quantitative study of the borazine photolysis in the absence of a reacting gas.

Experimental Section

The experimental apparatus for quantitative photochemical determinations is shown in Figure 1. All sections of the optical train were mounted on an optical bench. The light source was a Hanovia medium-pressure Hg arc (No. 679 A, 450 W) with a suitable power supply. Since a unidirectional, parallel beam was desired, the full capacity of the lamp could not be utilized. However, sufficient intensities were achieved to permit photolysis times generally of 1 hr or less. The lamp was mounted in a protective housing consisting of a 3-in. copper cylinder surrounded by 0.25-in. copper cooling coils. Additional cooling of the lamp was accomplished by heat conduction from two copper strips in contact with the ends of the lamp and soldered to the cooling jacket. The first 6 in. of the optical path was also water-cooled to ensure that the cell remained close to room temperature. Light from the source was collimated by a fused quartz lens (General Electric Type 151) that transmitted 1849-Å radiation. The cell consisted of a 40-mm i.d. quartz cylinder 10 cm in length with fused quartz windows (General Electric Type 151) glassblown in place. The volume was 129 cm^3 with about 2% dead space. The cell was connected with a Teflon stopcock to a conventional Hg-free high-vacuum system for the transfer of gases. It was enclosed in a cylindrical sheath to reduce stray light and could be reproducibly mounted in the optical path following cleaning or analysis of its contents. With the exception of optical elements, internal surfaces were covered with ultraflat black paint. The apparatus was purged along the entire length of the optical path with dry N_2.

Since borazine does not absorb uv radiation above 2000 Å,[7] the Hg lamp is essentially a monochromatic source of the 1849-Å resonance line. Thus a 0.25-m Jarrel-Ash monochrometer with a grating blazed for 1900 Å and 500-μ slits was mounted behind the cell and was used as a monitor of the 1849-Å radiation passing through the cell. The output from an EMI 9558(Q) photomultiplier with an S-20 spectral response was amplified with a Cary Model 31 vibrating-reed electrometer (Applied Physics Corp.) and then displayed on a Varian G-2000 strip-chart recorder. The extent of photolysis was most conveniently measured by the determination of the amount of noncondensable gas (*e.g.*, H_2) produced in a known time at a constant lamp intensity. The decomposition of N_2O[8] served as an actinometer to calibrate the relative 1849-Å recorder intensity to an absolute intensity. The method of analysis has been previously described.[6]

Borazine was prepared by the method of Hohnstedt and Haworth[9] by the reduction of *B*-trichloroborazine with $NaBH_4$. To remove possible Hg contamination, the gas was pumped through a −80° trap and the borazine collected at −196°. A high purity was ascertained by examination of infrared spectra taken using a Perkin-Elmer 521 grating spectrophotometer and mass spectra from a Consolidated Engineering Corp. 21-103A mass spectrometer. These instruments were also used for product analyses. Borazine-d_6 was prepared by the reaction of B_2D_6 and ND_3.[10] $D_3B_3N_3H_3$ was prepared by a series of large-scale photolyses of borazine with excess D_2.[11] Airco prepurified argon and Matheson research grade hydrogen and C.P. deuterium (99.5 atom %) were used. Spectranalyzed cyclohexane from Fisher Scientific Co. was dried by refluxing over sodium and by fractional distillation. It was stored under vacuum. All condensable reagents were degassed at −196° just prior to each use.

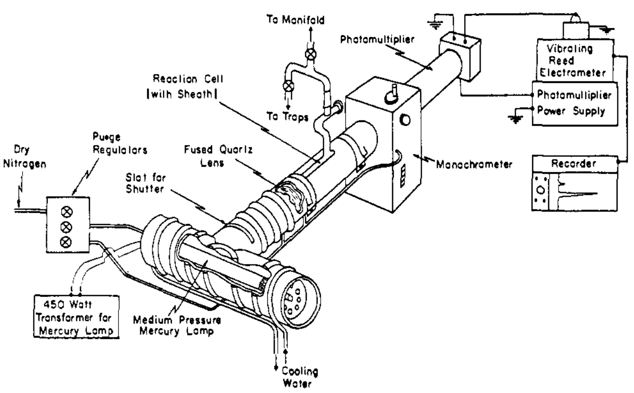

Figure 1. Experimental apparatus.

In all photolyses addition of gas(es) to the cell was made once the source had reached a constant intensity (I_0). The transmitted light was then monitored for the duration of the run. In experiments with pure borazine, photolysis commenced when a known amount of the gas sample was added. A light shutter was introduced when gases were mixed in the cell. These experiments included borazine–inert gas mixtures (Ar, H_2, and cyclohexane) and equimolar mixtures of borazine and borazine-d_6 with added cyclohexane. At the termination of a photolysis, the volatile contents of the cell were passed through two successive traps at −196° to remove all condensables for analysis. Noncondensable gases were transferred through a Toepler pump into a calibrated volume where pressures were measured on a McLeod gauge. For H_2 quantum yield determinations, this volume contained a known pressure of D_2. The amount of H_2 produced was determined by monitoring the relative mass spectral peak heights of H_2^+ and D_2^+.

A decrease in the apparent I_0 was noted following photolysis of borazine. This was attributed to absorption of light by a nonvolatile coating deposited on the window(s) during the irradiation. Therefore, the intensities used in calculations were time averaged. It was essential to clean the cell thoroughly after each experiment. Although the material was hydrolyzed by water vapor in the air, it was necessary to ensure the removal of any boron-containing hydrolysis products such as $B(OH)_3$ by rinsing the cell several times with anhydrous methanol. The cell was then heated in an oven to 300–350° for 6–12 hr under vacuum. It was important to avoid even trace amounts of moisture in the cell since borazine–water mixtures photolyze readily to produce H_2 and solid products.

Results

Photolysis of gaseous borazine at 1849 Å in the absence of another reactant produced H_2, borazanaphthalene ($B_5N_5H_8$), a much smaller amount of diborazinyl ($B_6N_6H_{10}$), and a nonvolatile material which retained some hydrogen atoms. The mass spectra of the $B_5N_5H_8$ and $B_6N_6H_{10}$ agreed well with those in the literature.[12,13] Analysis of the noncondensable gas produced during the photolysis of *B*-trideuterioborazine indicated a composition as follows: H_2, 4.6 ± 1.6%; HD, 90 ± 2%; D_2, 5.4 ± 0.6%. In the photolyses of equimolar mixtures of borazine and borazine-d_6, the same species were obtained in the noncondensable gas, but the relative proportions changed with the total amount of light absorbed. For short irradiation periods the products were mostly H_2 and D_2, but after longer periods appreciable amounts of HD were formed. This is shown in the first section of Table I. Photolyses of these mixtures in the presence of excess

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(8) N. R. Greiner, *ibid.*, **47**, 4373 (1967).

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(10) A. Stock and E. Pohland, *Ber. Deut. Chem. Ges.*, **59**, 2215 (1926).

(11) M. P. Nadler, Ph.D. Thesis, Cornell University, 1969.

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(13) G. Mamantov and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **20**, 348 (1961).

Table I. Isotope Studies Using 50:50 Mixtures of $B_3N_3H_6$ and $B_3N_3D_6$

P^0_T, mm	$P^0_{B_3N_3D_6}/P^0_{B_3N_3H_6}$	$10^6 I_a t$, einsteins	$P_{B_3N_3D_5H}/P_{B_3N_3D_6}$	Φ_{exch}	$P_{H_2}:P_{HD}:P_{D_2}$
1.59	1.01	0	0		
1.55	1.00	0.59	0.27	3.8	100:18:45
1.58	0.99	1.11	1.0	5.0	100:27:45
1.57	0.97	2.21	2.6		100:64:50
1.55	1.00	6.26	2.8		100:100:55
1.09[a]	1.02	1.86			100:26:9
1.04[b]	1.00	3.80			100:36:10

[a] Photolysis in the presence of 12.4 mm of cyclohexane. [b] Photolysis in the presence of 55 mm of cyclohexane.

cyclohexane produced the noncondensable gas composition given in the second section of Table I. Cyclohexane was used because it is transparent to the 1849-Å radiation and can provide many vibrational degrees of freedom for borazine deactivation. Mass spectral analysis of the borazine mixture after photolysis showed appreciable exchange, as indicated by the presence of partially deuterated borazines. A blank run indicated no thermal reaction. In Table I we have given results of quantum yield calculations for the exchange (Φ_{exch}) based on the increase in $B_3N_3D_5H$ or $B_3N_3H_5D$ for short periods of irradiation. These numbers include the unobservable exchanges between like molecules. For longer periods the ratio $B_3N_3D_5H/B_3N_3D_6$ approaches a limiting value of about 3. Data plotted in Figure 2 indicate that this exchange at low pressures varies linearly with the total pressure of the equimolar mixture. These runs were all made at the same integrated intensity ($I_a t$).

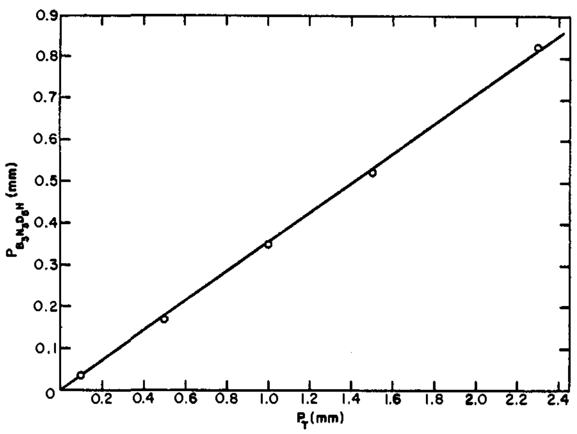

Figure 2. Plot showing the dependence of the photochemical yield of $B_3N_3D_5H$ on the total pressure of borazine in an equimolar mixture of $B_3N_3H_6$ and $B_3N_3D_6$. $I_a t$ was the same for each measurement.

In one series of experiments borazine was photolyzed at a pressure of 5 mm and the polymer coating was allowed to accumulate over several runs. It was found that in each case the H_2 pressure obtained was proportional to an average intensity absorbed by the borazine. This effect was observed even after the apparent incident intensity had been reduced by a factor of 6. However, when the pressure of borazine was increased from 5 to 10 mm the quantity of H_2 produced was reduced for the same amount of light absorbed. A subsequent series of experiments confirmed that the rate of production of H_2 varied inversely as the total pressure of borazine, suggesting a Stern–Volmer-type mechanism involving collisional deactivation. From Figure 3a it can be seen that the quantum yield for H_2 production extrapolated to zero pressure approaches 0.21 and at a borazine pressure of 13.5 mm $\Phi_{H_2} = 0.11$. The quantum yield for the production of polymer cannot be obtained because it is possible to measure only the absorbance (A) and not the concentration. However, a plot of $I_a t/A$ vs. borazine pressure gives a simple linear curve as indicated in Figure 3b. The effects of the addition of inert gas to the borazine are given in Table II. When the data for polymer absorbance are graphed the best straight line through all the points representing H_2 or Ar addition falls just below the polymer plot vs. borazine pressure in Figure 3b. Strictly speaking, the H_2 gas is not inert because it does undergo exchange with the borazine. This process may be another means of quenching.

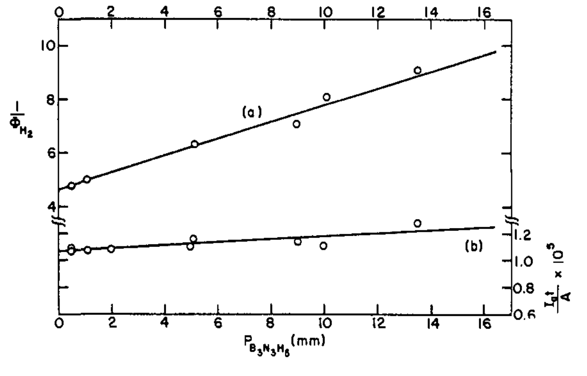

Figure 3. (a) Stern–Volmer-type plot showing the yield of H_2 in the photolysis of borazine as a function of total pressure. (b) Plot indicating the dependence of polymer formation on the total pressure. A = absorbance.

Table II. Effects of Inert Gases on Hydrogen and Polymer Production

Added gas	$P_{B_3N_3H_6}$, mm	P_{gas}, mm	$10^6 I_a t$, einsteins	Polymer absorbance (1849 Å)	Φ_{H_2}
None	0.92	0	1.53	0.194	0.21
Argon	1.0	100	1.82	0.152	
	1.0	260	2.16	0.052	
Hydrogen	1.0	101	1.82	0.101	
	0.97	163	1.87	0.065	
	1.0	311	1.98	0.050	
None	1.0	0	3.04	0.254	0.20
Cyclohexane	1.0	49	3.00	0.064	0.07
None	5.1	0	2.56	0.233	0.16
Cyclohexane	5.0	25	2.58	0.104	0.12

Ultraviolet spectra of the nonvolatile polymeric material on the window(s) (Figure 4) were taken on a Cary 14 uv spectrometer. Spectrum a is of the polymer as deposited. It appears similar to the spectrum of a polymer reported by Shindo and Lipsky[14] in their study of the photolysis of benzene at 1849 Å. Unlike the benzene polymer, which is yellowish brown, the borazine polymer is transparent. When borazine was photolyzed in the presence of excess inert gas, the intensity of the polymer absorption spectrum diminished. When the cell containing the borazine polymer was mounted on the mass spectrometer and heated to 200°, borazine and H_2 were produced and the uv spectrum changed as the film evidently became more condensed. The effect can be seen in spectrum b of Figure 4. The borazine polymer was removed completely over a period of several days in the presence of air and in minutes when the cell was washed using anhydrous methanol. Oxygen introduced into the cell following a photolysis produced no effect on the polymer absorbance. When water vapor was added to the cell, NH_3 was evolved. Apparently the film can be completely hydrolyzed according to the general equation

$$(BNH_n)_x + 3xH_2O \longrightarrow xB(OH)_3 + xNH_3 + (nx/2)H_2 \qquad (1)$$
$$0 < n < 2$$

Determination of the NH_3 pressure produced in the complete hydrolysis of polymer allowed an indirect calculation of the amount of borazine lost to the polymer. The amount of borazine converted to borazanaphthalene and diborazinyl was small and could not be determined, nor could the total borazine loss be conveniently measured. From complete polymer hydrolysis, a lower limit on the borazine disappearance quantum yield at 1.54 mm was calculated to be 0.30. The ratio of the amount of borazine lost in polymer production to the amount of H_2 produced was approximately 1.2. In a hypothetical "polymer" consisting only of borazanaphthalene, the ratio would be the maximum of 2. In the other limit, that of infinitely long chains of fused polyborazines (analogous to graphite or diamond), a minimum value of about 1 would be observed. Although the actual polymer is most likely a mixture of various chain lengths, the average component is formed by the fusion of at least four borazine rings.

An investigation was made to determine if the long-lived triplet state of borazine recently reported by Young, *et al.*,[15] is involved in the formation of $B_5N_5H_8$. In their experiments at 2580 Å, borazine was found to quench the benzene-sensitized phosphorescence of biacetyl. This was interpreted as an indication that borazine was excited to a triplet state which was reported to lie at an energy not higher than 112 kcal/mol (4.86 eV).[15] We have photolyzed 30 mm of a 2:1 mixture of benzene and borazine at 2537 Å using a Vycor filter to eliminate 1849-Å radiation. Under these conditions, $B_5N_5H_8$ could not be detected. Therefore, since the photosensitization of borazine does not lead to the formation of our product, we conclude that the triplet state would be unimportant in a mechanism for borazine photodecomposition.

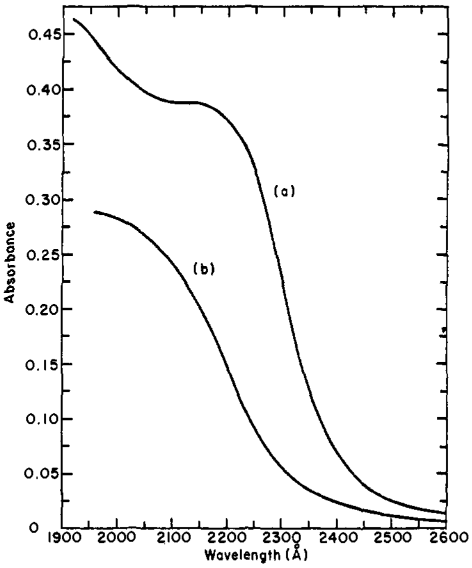

Figure 4. Ultraviolet spectra of (a) polymer produced in the photolysis of borazine and (b) polymer after heating to 200°.

Discussion

The volatile products of the photolysis of borazine at 1849 Å have been previously observed in the decomposition of liquid borazine at room temperature[13] and of gaseous borazine in a discharge[16] and at elevated temperatures.[17] Under all these conditions high molecular weight residues have been reported.

Experiments with $D_3B_3N_3H_3$ and mixtures of $B_3N_3H_6$ and $B_3N_3D_6$ indicate that the H_2 molecules produced photochemically result from elimination of adjacent hydrogen atoms by an intramolecular process. This is most likely a concerted reaction, since there has been no evidence for radical formation in the photolysis of borazine at this wavelength.[6] If hydrogen atoms were produced in the primary step of the photolysis, one would expect to observe a statistical distribution of H_2, HD, and D_2 when equimolar mixtures of $B_3N_3H_6$ and $B_3N_3D_6$ are irradiated, regardless of the length of the photolysis period. It is also significant that the limiting ratio of $B_3N_3D_5H/B_3N_3D_6$ at equilibrium is 3. This indicates that exchange is occurring at three sites rather than at all six. It is known that photochemical exchange between borazine and D_2 occurs only at the boron sites.[6] It should be noted that in the photolysis of *B*-trideuterioborazine, intermolecular exchange between the boron and nitrogen sites is not significant, as indicated by the predominance of HD in the noncondensable gas produced.

The observation that the rate of H_2 production decreases with increasing initial borazine pressure in the system is consistent with the following type of mechanism.

$$B_3N_3H_6 + h\nu \xrightarrow{I_a} B_3N_3H_6^* \qquad \text{excitation} \qquad (2)$$

$$B_3N_3H_6^* \xrightarrow{k_i} B_3N_3H_6' \qquad \text{internal conversion} \qquad (3)$$

$$B_3N_3H_6' \xrightarrow{k_d} B_3N_3H_4 + H_2 \qquad \text{decomposition} \qquad (4)$$

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(14) K. Shindo and S. Lipsky, *J. Chem. Phys.*, 45, 2292 (1966).
(15) W. F. Young, F. Grein, J. Passmore, and I. Unger, *Can. J. Chem.*, 49, 233 (1971).
(16) O. T. Beachley, Jr., Ph.D. Thesis, Cornell University, 1963.
(17) P. C. Moews, Jr., Ph.D. Thesis, Cornell University, 1960.

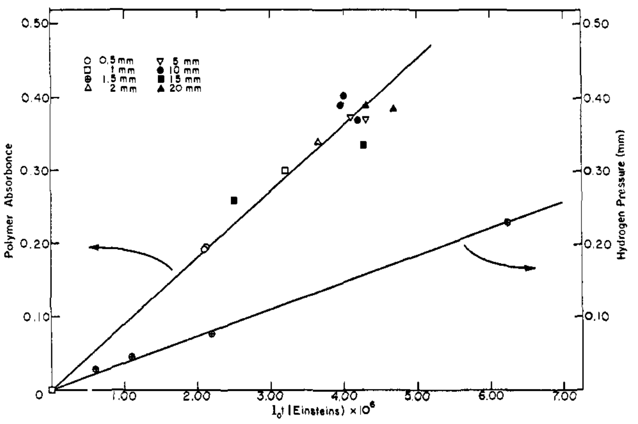


Figure 5. Plot indicating the dependence of polymer and H_2 formation on absorbed light intensity in the photolysis of borazine. Borazine pressures are indicated by a key in the upper left corner.

$$B_3N_3H_6' + M \xrightarrow{k_q} B_3N_3H_6 + M \qquad \text{quenching} \qquad (5)$$

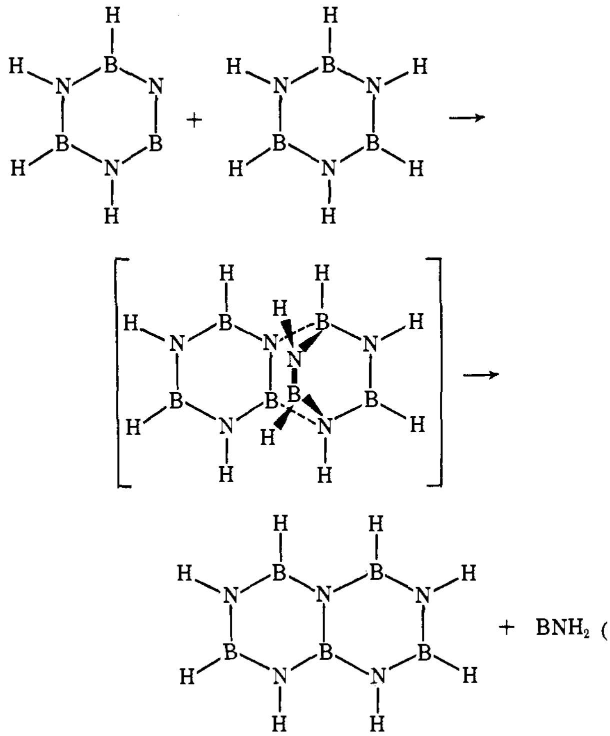
$$B_3N_3H_4 + B_3N_3H_6 \longrightarrow$$
$$B_5N_5H_8 + (BNH_2) \longrightarrow \text{polymer} \qquad \text{multiple ring formation} \qquad (6)$$

Using a steady-state approximation in $B_3N_3H_6^*$ and $B_3N_3H_6'$, we find

$$\frac{d(H_2)}{dt} = k_d(B_3N_3H_6') = \frac{k_dI_a}{k_d + k_q(M)} \qquad (7)$$

It can be seen in Figure 5 that the H_2 production is indeed linear in intensity for constant (M). An approximately linear dependence is also observed for the polymer production even when (M) is varied. Noting that $(d(H_2)/dt)/I_a$ is the quantum yield for hydrogen production, a plot of $1/\Phi_{H_2}$ *vs.* (M) should yield a linear curve. This dependence has been experimentally observed (Figure 3). There is also seen a slow rise in the ratio I_at/A with borazine pressure for the polymer. This quantity is the closest one can come to an expression of $1/\Phi_{\text{polymer}}$. In these reactions, M may be a borazine molecule, another molecular species, or the wall. In the case where M is a borazine molecule, quenching may also result from intermolecular hydrogen exchange. The decrease in polymer deposition noted when an inert gas or additional borazine is present parallels the effect on H_2 production. It can be seen from the data in Table II and Figure 3 that cyclohexane appears to be most effective in quenching the formation of H_2 and polymer.

The above data indicate a definite relationship between hydrogen and polymer production. Reaction 6 is a possible path leading to the formation of borazanaphthalene and polymer following H_2 elimination. One can visualize the attack of $B_3N_3H_4$ on borazine as analogous to a Diels–Alder reaction with borazine as the "diene." There is some precedent for suggesting that $B_3N_3H_4$ is a borazyne intermediate. The organic analog benzyne has been considered as an intermediate in certain types of reactions,[18,19] although not in the



(6′)

benzene photolysis. The vibrational excitation and forced strain present in the above transition species as well as a desirable degree of π delocalization that could be attained in a planar structure might cause the elimination of the H–B–N–H unit and thereby the formation of borazanaphthalene. Further reactions of borazine, borazanaphthalene, and the BNH_2 monomers could lead to polymeric materials and/or high molecular weight borazine derivatives. Diborazinyl, which appears to be a minor product, could result from a direct insertion of borazyne into a B–H or N–H bond on a borazine molecule.

It is thought on the basis of the ultraviolet spectrum of borazine that upon absorption at 1849 Å the primary act is the formation of the first excited $^1E'$ state,[6] although there may be some competitive transitions to one of the "forbidden," but vibronically allowed, $^1A_1'$ and $^1A_2'$ states. The reacting species must undergo a number of collisions in order for the observed deactivation to occur in the pressure range studied. At 15 mm of borazine, the time between collisions is $\sim 10^{-8}$ sec. Since the lifetime of the $^1E'$ state[6] is only 1.1×10^{-9} sec, it is probably not directly responsible for the observed products. Shindo and Lipsky[14] have proposed that in the photolysis of gaseous benzene at 1849 Å the photochemical destruction proceeds *via* a vibrationally excited ground electronic state of the molecule. The state formed by initial excitation ($^1E_{1u}$) is too short lived to be affected by collisions.[14] However, a benzene disappearance quantum yield inversely dependent on the pressure of added N_2 was observed. Therefore, they suggested internal conversion to a lower, longer-lived electronic state in which the molecule undergoes reaction or deactivation. The lack of increased fluorescence from the lower lying excited singlet states with increased benzene pressure suggested identification of this state with the ground state. Thus a crossover from the $^1E_{1u}$ (S_3) state into an upper vibrational level in the ground-state (S_0) manifold is likely. A similar situation may exist in the case of borazine. The excited

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(18) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967. This book presents an extensive survey of benzyne chemistry.

(19) R. C. F. Brown and R. K. Solly, *Chem. Ind.* (*London*), 181 (1965). In this paper is presented the benzyne–benzene analogy of reaction 6′. The benzyne was generated by the pyrolysis of indantrione and reaction with benzene produced naphthalene, acetylene, and biphenyl.

states and their relative positions are analogous in the two molecules,[20] but emission from borazine excited at 1849 Å has not been detected,[11] indicating little if any radiative decay. Other examples in the literature for which vibrational mechanisms have been proposed are the photodecompositions of 1,3-cyclohexadiene and 1,3,5-hexatriene.[21] In each case H_2 and benzene were produced. Moreover, the H_2 production was quenched by increased pressures in the system. Evidence here too indicated an internal conversion from the initially produced short-lived singlet state to a vibrationally excited ground state that eliminates the H_2. As we reported earlier, based on our evidence one can eliminate the borazine triplet from major participation in the mechanism. We therefore suggest that the species $B_3N_3H_6'$ is a vibrationally "hot" ground electronic state and that H_2 elimination occurs by a process involving the distribution of internal energy. Vibrational relaxation through collisions lowers the energy below a threshold and thereby quenches the elimination reaction. The fact that Ar is an efficient quencher indicates that the elimination reaction has a relatively high energy threshold. The relative amounts of H_2 and D_2 produced in the photolysis of an equimolar mixture of $B_3N_3H_6$ and $B_3N_3D_6$ suggest a frequency factor in the rate which is isotope dependent.[22]

We have noted that the photochemical exchange reaction between $B_3N_3H_6$ and $B_3N_3D_6$ (equimolar mixture) that produces the species $B_3N_3D_5H$ and $B_3N_3H_5D$ has a quantum yield of the order of 4–5 for an initial total pressure of 1.5 mm. These quantum yields (Table I) may be slightly low because we have not considered the more highly mixed species such as $B_3N_3D_4H_2$ and $B_3N_3H_4D_2$ which are formed by subsequent reactions of $B_3N_3D_5H$ and $B_3N_3H_5D$. Figure 2 indicates that at a constant integrated intensity (I_at) the pressure of $B_3N_3D_5H$, and hence its quantum yield, increases linearly with the total pressure of the equimolar mixture. In addition, the approximately constant value of the exchange quantum yield (Table I) over a factor of 2 in I_at indicates that the product yield may be first order in intensity. It would follow that

$$d(B_3N_3D_5H)/dt \propto I_aP_T \tag{8}$$

However, it is clear that as the total pressure of the mixture is increased, the pressure of the product $B_3N_3D_5H$ cannot continue to rise indefinitely for the same I_at. The curve must eventually level off since the quantum yield should reach a limiting value.

On the basis of the evidence presented, we conclude that following initial excitation of the borazine to the $^1E'$ state by the 1849-Å radiation internal conversion occurs to a vibrationally excited ground-state molecule that can subsequently undergo two modes of reaction: (1) decomposition by elimination of H_2 with a relatively high energy threshold and (2) exchange reaction(s) with a relatively low threshold. Hydrogen elimination is reduced with increased pressures in the system, while the exchange reaction rate in the pressure range studied increases with borazine pressure. This increase and the high quantum yield observed suggest an exchange process of low activation energy. The results of these experiments may also be significant in the interpretation of the photochemical reactions of borazine with a second reagent.

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(20) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, 19, 1 (1970).

(21) R. Srinivasan, *J. Chem. Phys.*, 38, 1039 (1963).

(22) It has been determined that the extinction coefficients of borazine and perdeuterioborazine at 1849 Å are 980 and 658 l. mol^{-1} cm^{-1}, respectively. Therefore, in the equimolar mixture the $B_3N_3D_6$ absorbs only about 40% of the light. However, it is noted that the low D_2:H_2 ratio observed following photolysis cannot be completely explained by a consideration of relative light absorption. The experiments with cyclohexane provide a more striking illustration of this fact.

Chemical Ionization Mass Spectrometry of Selected Boron Hydrides

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Abstract: Chemical ionization mass spectra for diborane, tetraborane, pentaborane(9), pentaborane(11), and hexaborane(10) in methane have been obtained. The boron hydrides B_2H_6, B_4H_{10}, and B_5H_{11} are ionized by dissociative proton transfer and hydride abstraction to form $(M - 1)^+$ ions, while B_5H_9 and B_6H_{10} react with a number of hydrocarbon ions to form $(M + 1)^+$ species, and high molecular weight complexes. A new technique for determining the relative ordering of the proton affinities of gaseous molecules is described. The proton affinity of B_5H_9 is found to be intermediate between that for H_2O and H_2S or PA(B_5H_9) = 167 ± 6 kcal/mol. Hexaborane(10) with a proton affinity in excess of 186 kcal/mol is a stronger base than B_5H_9. Proton-transfer reactions of $B_4H_9^+$ indicate that the proton affinity of B_4H_8 is 184 ± 6 kcal/mol. The proton affinity of B_2H_6 is estimated to be 145 kcal/mol. The second-order rate constant for the protonation of B_5H_9 by CH_5^+ is 1.93×10^{-9} cm^3/(molecule sec).

Chemical ionization mass spectrometry is now established as a useful technique capable of providing information on proton affinities of gaseous molecules. Although the technique has been employed extensively for study of organic compounds, its potential for investigation of inorganic systems has not yet been fully developed. For several reasons it appeared to us that the boron hydrides constitute an interesting class of