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The Photochemical Exchange of Borazine with Deuterium[1]

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The photochemical exchange of borazine with deuterium was studied with 1849-Å radiation. Quantum yields for the initial stages of the reaction were determined. The quantum yield for the production of B-monodeuterated borazine was not affected by the initial pressure of borazine but increased with increase in D_2 pressure, reaching a limiting value of 0.93 ± 0.14. The quantum yield was not affected by the intensity of absorbed radiation but was greatly affected by the addition of He, N_2, or H_2. For a fixed D_2 pressure the quantum yield for the production of $B_3N_3H_5D$ increased with addition of He or N_2 and reached a limiting value of unity but decreased for addition of H_2. A radical and an excited-state mechanism are discussed and the excited-state mechanism is shown to be consistent with the experimental observations.

Introduction

Borazine reacts photochemically in the gas phase with NH_3, O_2, H_2O,[2a] CH_3OH, and C_2H_5OH[2b] to give B-monosubstituted derivatives. Thermal reactions of borazine with H_2O[3] and CH_3OH[4] usually lead to B-trisubstituted addition compounds. The thermal reaction with D_2 yields B-mono-, di-, and trisubstituted deuterioborazines.[5] Borazine and deuterium also exchange photochemically. At present only qualitative information on the photochemical reaction has been obtained. To extend our understanding of the photochemical mechanisms, experiments were undertaken to obtain quantum yields. The borazine and D_2 reaction was chosen for study since it appeared to be the simplest for analysis.

Experimental Section

In preliminary experiments the products of the borazine–deuterium photolysis were analyzed using two types of reaction vessels each equipped with an immersion well to house the Hg lamp. One was joined to a mass spectrometer through a small pinhole[6] and the other was joined to a 10-cm infrared cell.

For the quantum yield determinations the apparatus used is shown in Figure 1. The source is a Hanovia medium-pressure Hg lamp which yields about 15% of its total energy in the far-uv mainly at 2537 and 1849 Å. The lamp temperature was controlled by passing precooled dry N_2 through the lamp housing. The lens holder assembly and monochromator was also purged with dry N_2. Parallel light entered the reaction cell through a fused-quartz lens[7] capable of transmitting 1849-Å radiation. The reaction cell was equipped with fused-quartz windows[7] and was joined by a stopcock to a vacuum line for transfer of gases. The monochromator was a 0.25-m Jarrel Ash model equipped with a grating blazed for 1900 Å. It wss used to monitor the 1849-Å radiation passing through the cell. It should be noted that borazine absorbs only below 2000 Å[8] and therefore the Hg lamp is essentially a monochromatic source of the 1849-Å line. The photomultiplier was an EMI 9558 (Q) model with an S-20 spectral response. The output from the photomultiplier was amplified with a Cary Model 31 vibrating-reed electrometer from the Applied Physics Corp. before being displayed on a Varian G-2000 strip chart recorder.

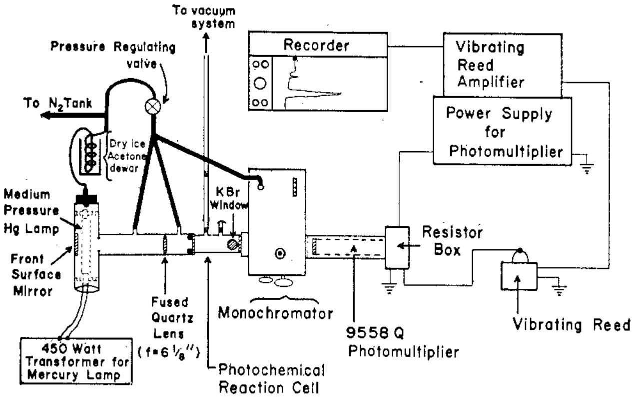

Figure 1.—Quantum yield apparatus.

The general procedure was to measure the initial rate of the photochemical reaction of $B_3N_3H_6$ and D_2 at a constant intensity by determining the amount of product produced in a known time. The relative intesnity of the 1849-Å radiation absorbed by $B_3N_3H_6$ (I_A) was calibrated to absolute intensity with an N_2O actinometer. The Hg lamp and N_2 flow were turned on and the 1849-Å line was monitored with time until a constant intensity was reached. Then the region from 1800 to 1900 Å was scanned several times so that the initial intensity (I_0) could be determined. Purified[2a] borazine was expanded into the reaction cell and the intensity (I) of the 1849-Å line passing through the cell was measured. Finally D_2 was added to the reaction cell initiating the reaction. During the course of the reaction the 1849-Å line was monitored to check for any variation in intensity. When the photolysis was completed, the products were condensed into a U tube, which was joined to the reaction cell through a ball joint and stopcock. The stopcock to the U tube was then closed and the HD and D_2 were pumped away from the condensed borazines so that the sample could be analyzed without interference from any thermal reaction.

The amounts of HD and $B_3N_3H_5D$ produced in the reaction were determined by mass spectral analysis. The analysis of

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[1] (a) Work supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency. (b) Taken in part from a thesis submitted by M. P. Nadler in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School of Cornell University.

[2] (a) G. Lee and R. F. Porter, *Inorg. Chem.*, **6**, 648 (1967); (b) M. Nadler and R. F. Porter, *ibid.*, **6**, 1739 (1967).

[3] E. Wiberk and A. Boltz, *Ber.*, **73**, 209 (1940).

[4] D. T. Haworth and L. F. Hohnstedt, *J. Am. Chem. Soc.*, **81**, 842 (1959).

[5] G. H. Dahl and R. Schaeffer, *ibid.*, **83**, 3034 (1961).

[6] R. F. Porter and F. A. Grimm, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968, pp 94–100.

[7] General Electric Type 151 fused quartz.

[8] J. R. Platt, H. B. Klevens, and G. W. Schaeffer, *J. Chem. Phys.*, **15**, 598 (1947).

$B_3N_3H_5D$ was found to be the more reliable, since an appreciable correction had to be made for an HD impurity in the D_2. Equation 1 was used to determine the pressure of $B_3N_3H_5D$ in the

$$P_{B_3N_3H_5D} = \left[\frac{I'_{82}}{I'_{81} + I'_{82}}\right] P^0_{B_3N_3H_6} \qquad (1)$$

presence of an excess of $B_3N_3H_6$, where $P^0_{B_3N_3H_6}$ is the initial pressure of borazine. In this equation I'_{82} is the ion intensity for *m/e* 82, corrected for the ^{15}N contribution from $^{11}B_3N_3H_6{}^+$. The I'_{81} is the ion intensity of *m/e* 81, corrected for fragmentation and ^{10}B isotopic contributions from $B_3N_3H_5D$. The pertinent relationships are $I'_{82} = I_{82} - 0.0114I_{81}$ and $I'_{81} = I_{81} - 2.03I'_{82}$, where I_{81} and I_{82} are the observed ion intensities at *m/e* 81 and 82, respectively.

The relative intensity $[I_A = I_0(1 - (I/I_0)]$ of the 1849-Å line absorbed by the borazine sample was calibrated to absolute intensity in einsteins per second by using an N_2O actinometer. The quantum yield for the production of N_2 in the N_2O photolysis at 1849 Å is 1.44,[9] so the absolute intensity I_a can be calculated using

$$I_a = \frac{\Delta(N_2)/\Delta t}{1.44} \qquad (2)$$

The amount of N_2 produced in the photolysis of N_2O was determined mass spectrometrically by isotope dilution of N_2O with a small quantity of $^{15}N_2$.[10] The initial compositions were $(^{15}N_2)/(N_2O) = 0.00980 \pm 0.00029$ and $(^{15}N_2)/(N_2O) = 0.00834 \pm 0.00025$. These mixtures were photolyzed under identical conditions as used in the photochemical reaction of $B_3N_3H_6$ and D_2. The N_2O mixture was then frozen at liquid N_2 temperature and the intensities of *m/e* 28 from $^{14}N_2$ and *m/e* 30 from $^{15}N_2$ were measured with care to correct for the background intensity at *m/e* 28. The final pressure of $^{14}N_2$ produced in the photolysis was calculated from the expression

$$P_{^{14}N_2} = \frac{I_{28}}{I_{30}} \frac{(^{15}N_2)}{(N_2O)} P^0_{N_2O} \qquad (3)$$

Then $P_{^{14}N_2}$ was converted to moles and the absolute intensity I_a in einsteins per second was calculated from eq 2. A calibration curve of relative intensity (I_A) *vs.* absolute intensity (I_a) was plotted with the actinometer results so that I_a could be determined from the relative intensity (I_A). Finally

$$\Phi_{\beta D} = \frac{\Delta(\beta D)/\Delta t}{I_a} \qquad (4)$$

where β is used as a symbol for $B_3N_3H_5$ and $\Delta(\beta D)$ is in moles.

Results

Stoichiometry.—The preliminary mass spectral information indicated that mono-, di-, and trideuterated borazines were produced along with HD and H_2. Infrared spectra of the reaction products indicated that exchange occurred only at the B atoms. Figure 2 shows the results obtained by following the ion intensities of $D_2{}^+$ and HD^+ while the reaction proceeded and the intensity of $H_2{}^+$ at the termination of photolysis. These data indicate that over a prolonged period of irradiation an equilibrium among the partially deuterated species in the reaction is approached. It should be noted (Figure 2) that in the first few minutes of irradiation the drop in $D_2{}^+$ intensity corresponds to the increase in HD^+ intensity. Mass spectral analysis of the products obtained for less than 2% exchange per boron atom (or about 6% in $B_3N_3H_5D$) showed that $B_3N_3H_5D$ and HD were produced in equimolar quantities to within 5–15% experimental error. (See Table I.) Under these conditions the reaction stoichiometry can be written

$$B_3N_3H_6 + D_2 \xrightarrow{h\nu} B_3N_3H_5D + HD \qquad (5)$$

and quantum yields could be obtained without appreciable error due to the presence of dideuterated borazines.

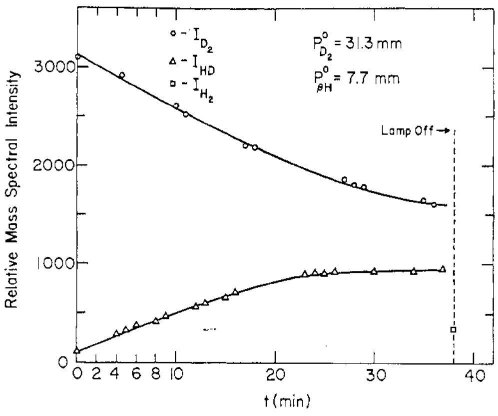

Figure 2.—Plot of mass spectral intensities *vs.* time for I_{D_2}, I_{HD}, and I_{H_2} during the photolysis of $B_3N_3H_6$ and D_2. $P^0_{B_3N_3H_6} = 7.7$ mm; $P^0_{D_2} = 31.3$ mm.

Table I

Stoichiometric Measurements of $P_{B_3N_3H_5D}$ and P_{HD} in the Photochemical Reaction of $B_3N_3H_6$ and D_2

P_{HD}, mm	$P_{B_3N_3H_5D}$, mm	$P_{B_3N_3H_4D_2}$, mm	$P^0_{B_3N_3H_6}$, mm	$P^0_{D_2}$, mm	$\frac{P_{B_3N_3H_5D}}{P^0_{B_3N_3H_6}} \times 100$
0.035	0.032	0.000	0.93	6.6	3.4
0.022	0.025	0.000	0.86	4.6	2.9
0.057	0.053	0.000	1.0	75	5.3
0.049	0.041	0.000	0.80	5.2	5.1
0.020	0.033	0.000	0.40	7.8	8.3
0.25	0.42	0.05	1.0	28.2	42

In the initial stages of this study erratic behavior in the determination of quantum yields was observed. It was found that after a series of irradiation experiments, the rate of deuterium exchange increased notably. However, it was also observed that the reaction cell became conditioned in a way to accelerate thermal exchange greatly. Mass spectral analysis of products for the photolysis of pure borazine in a "fresh" cell indicated the formation of diborazinyl ether.[2a] After several irradiations of pure borazine in the same cell the ether was no longer observed, nor could any other product be detected. Since borazine and H_2O react photochemically to yield diborazinyl ether,[2a] it appears that during the initial series of irradiations surface H_2O is removed by reaction. The cell then becomes "activated" in some manner so as greatly to increase the rate of the thermal exchange. Dahl and Schaeffer[5] noted a thermal reaction at about 100° and reported the products to be mono-, di-, and trideuterated borazines, but they were not able to make any quantitative measurements of the rate except to note that it was

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(9) N. R. Greiner, *J. Chem. Phys.*, **47**, 4373 (1967).

(10) Purity: 97% $^{15}N_2$, obtained from Bio-Rad Laboratories.

TABLE II

QUANTUM YIELD DATA FOR THE PHOTOCHEMICAL REACTION OF $B_3N_3H_6$ AND D_2

Run no.	$P^0{}_{\beta H}$, mm	$P^0{}_{D_2}$, mm	t, sec	$10^{-3}I_A$	$10^{10}I_a$, einsteins/sec	$P_{\beta D}$, mm	$[\Delta(\beta D)/\Delta t]_{photo}$, mol/sec	$[\Delta(\beta D)]/\Delta t_{thermal}$, mol/sec	$\Phi_{\beta D}$
1	0.99	21.1	1000	1.95	5.20	0.032	3.5×10^{-10}	0	0.67
2	0.99	105	1000	2.14	5.72	0.051	5.0×10^{-10}	0	0.87
3	0.99	39.1	1005	2.24	6.00	0.038	3.75×10^{-10}	0	0.62
4	0.99	4.0	2060	1.90	5.10	0.024	1.1×10^{-10}	0	0.22
5	0.70	10.2	1100	1.71	4.55	0.019	1.7×10^{-10}	0	0.37
6	2.0	37.1	830	2.7	7.25	0.038	4.5×10^{-10}	0	0.62
7	10.8	11.3	1050	3.5	9.4	0.030	2.8×10^{-10}	0	0.30
8	3.9	84.0	800	2.5	6.7	0.047	5.8×10^{-10}	0	0.87
9	2.1	68.0	1000	1.5	4.0	0.040	3.9×10^{-10}	0	0.97
10	0.99	27.4	1242	2.3	6.1	0.11	4.9×10^{-10}	4.0×10^{-10}	0.80
11	0.99	53.6	900	1.7	4.55	0.11	4.3×10^{-10}	8.0×10^{-10}	0.94
12	1.0	56.6	785	2.1	5.6	0.11	4.9×10^{-10}	8.4×10^{-10}	0.88
13	1.0	19.2	1120	2.7	7.15	0.070	3.3×10^{-10}	2.8×10^{-10}	0.46
14	0.99	12.0	1300	1.9	5.1	0.059	2.7×10^{-10}	1.8×10^{-10}	0.53
15	0.99	32.1	1015	2.0	5.4	0.080	3.0×10^{-10}	4.7×10^{-10}	0.56
16	1.0	5.4	1850	1.9	4.8	0.033	0.97×10^{-10}	0.80×10^{-10}	0.20

affected by surface conditions. In the experiments with an "activated" cell it was necessary to obtain the thermal contribution to the reaction rate. The thermal reaction was found to be first order in D_2 pressure,[11] and for $P^0{}_{\beta H} = 1.0$ mm and a temperature of 25°

$$\left[\frac{\Delta(\beta D)}{\Delta t}\right]_{thermal} = (1.5 \pm 0.2) \times 10^{-6} P^0{}_{D_2}\ (\text{mm/sec}) \quad (6)$$

Results of experiments in the "activated" cell were then corrected by the relationship

$$\left[\frac{\Delta(\beta D)}{\Delta t}\right]_{photo} = \left[\frac{\Delta(\beta D)}{\Delta t}\right]_{total} - P^0{}_{D_2}(1.5 \pm 0.2) \times 10^{-6} \quad (7)$$

Results of such calculations are shown in Figure 3 and Table II. It was found that more accurate quantum yields could be obtained by exposing the cell to the atmosphere before each experiment, thereby inhibiting the thermal reaction (see Figure 3 and Table II). It should be noted that the photochemical rate was not notably affected by surface conditions.

When a Vycor plate was placed in front of the reaction cell to filter radiation below 2000 Å, the exchange reaction was not observed, confirming that the excitation was associated with the 1849-Å line. In other experiments the borazine used was distilled at −80° to reduce the residual Hg concentration by a factor in excess of 10^3. Reaction rates were unaffected by the reduction in Hg concentration showing that photosensitization by excited Hg atoms was not a major effect.

Quantum Yields.—Table II summarizes the results of 16 quantum yield determinations. Figure 3 is a plot of $\Phi_{\beta H}$ *vs.* $P^0{}_{D_2}$; the data (points indicated by ○ and ●) for $P^0{}_{\beta H} = 1.0$ mm show a pressure dependence on D_2. The curve rises sharply at lower D_2 pressures and then levels off with increased D_2 pressure, resulting in a limiting quantum yield of 0.93 ± 0.14.

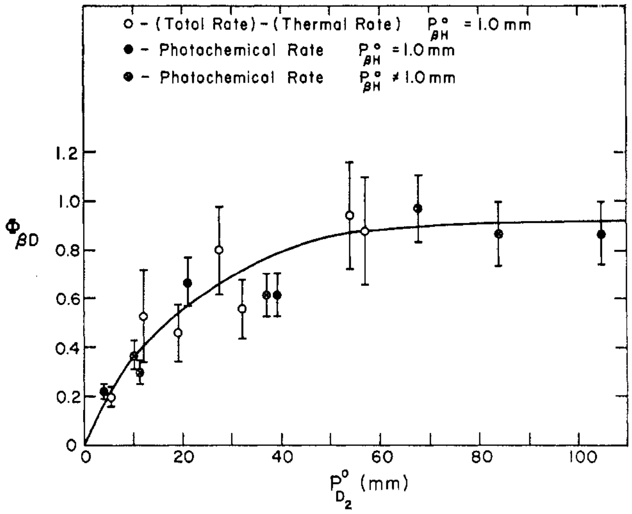

Figure 3.—Plot of quantum yield of βD *vs.* $P^0{}_{D_2}$.

The initial borazine pressure varied from 0.70 to 10.8 mm (Table II and Figure 3) and for the experiments with equal $P^0{}_{D_2}$, $\Phi_{\beta D}$ was the same within 15% experimental error, even though $P^0{}_{\beta H}$ varied by a factor of 15.

Figure 4 shows a plot of log I_A *vs.* log $[\Delta(HD)/\Delta t]$ for $P^0{}_{D_2} = 5$ mm and $P^0{}_{\beta H} = 1.0$ mm. The slope of the straight line is 1.0 ± 0.3, which indicates that $\Phi_{\beta D}$ should not vary with I_a from the definition of $\Phi_{\beta D}$ (eq 4). We note from the data in Figure 3 and Table II that $\Phi_{\beta D}$ does not vary significantly with I_a. We can now write a rate equation of the form

$$\frac{\Delta(HD)}{\Delta t} = \frac{\Delta(\beta D)}{\Delta t} = K I_a{}^{1.0 \pm 0.3} (P^0{}_{D_2})^n \quad (8)$$

The results of quantum yield experiments in which He, N_2, or H_2 was added are shown in Figure 5 and Table III. For conditions of constant D_2 pressure, $\Phi_{\beta D}$ increases with increase in P_{He} or P_{N_2} and ap-

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[11] Unpublished work by E. Yeung and R. F. Porter at Cornell University agrees with this result.

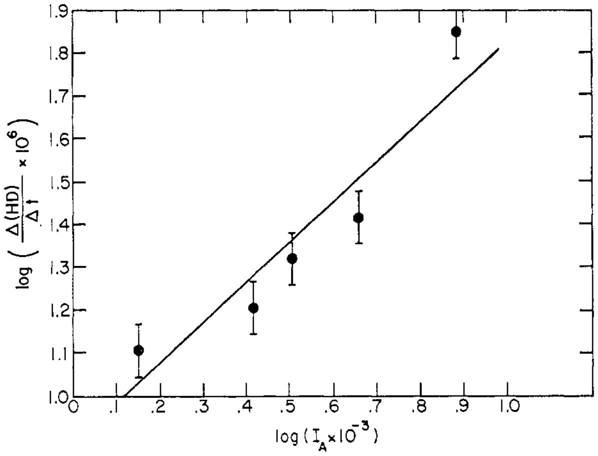

Figure 4.—Plot of log [$\Delta(HD)/\Delta t$] *vs.* log I_A. $P^0_{D_2}$ = 5 mm; $P^0_{\beta H}$ = 1.0 mm. Upper limit of slope 1.30; lower limit of slope 0.65.

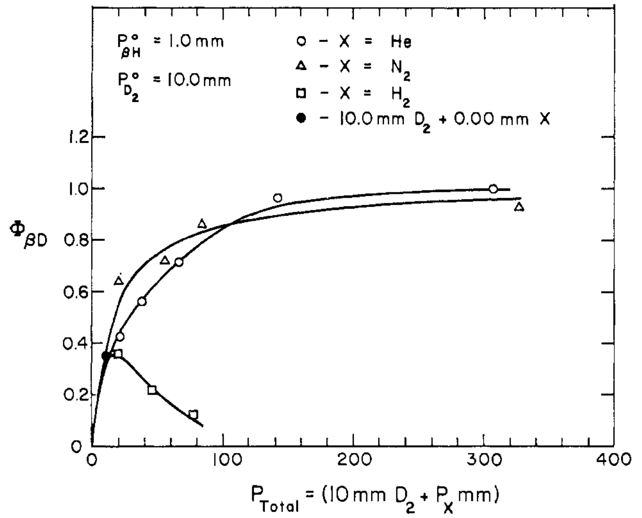

Figure 5.—Plot of quantum yield of βD *vs.* P_{total}, where P_{total} = 10 mm of $D_2 + P_X$ and X = He, N_2, or H_2. $P^0_{\beta H}$ = 1.0 mm; $P^0_{D_2}$ = 10.0 mm.

proaches unity. We note by comparing Figures 3 and 5 that $\Phi_{\beta D}$ is approximately the same when $P^0_{D_2} = P_X + 10$ mm of D_2. It should also be noted (Table III) for $P_{He}/P_{D_2} \approx 700$ that $\Phi_{\beta D} \approx 1$. The experiments conducted with H_2 added show that $\Phi_{\beta D}$ decreased as P_{H_2}/P_{D_2} increased (Figure 5 and Table III). For a 50:50 mixture of H_2 and D_2 we note that $\Phi_{\beta D}$ is smaller than for the same total pressure of D_2 (Tables II and III). In the region of constant quantum yield we note $\Phi_{\beta D} = 0.54 \pm 0.05$ in 50:50 mixtures of $H_2 + D_2$, while for pure D_2, $\Phi_{\beta D} = 0.93 \pm 0.14$. Stoichiometric measurements on the amounts of βD and HD produced with a 50:50 mixture of $H_2 + D_2$ show that [HD] = [βD] for ≤5% reaction.

Table III

Effect of He, N_2, and H_2 Gases on the Quantum Yield for the Photochemical Reaction of $B_3N_3H_6$ with D_2

Added gas (X)	P_X, mm	P_{D_2}, mm	$\Phi_{\beta D}$
Helium	11.3	10.4	0.45
	28.0	9.9	0.56
	57.2	9.9	0.73
	130	10.0	0.98
	297	10.4	1.0
	~700	~1	~1
Nitrogen	10.2	10.0	0.64
	46	10.0	0.72
	75	10.0	0.86
	316	10.4	0.93
Hydrogen	9.5	10.4	0.36
	35.3	10.4	0.22
	68.2	10.1	0.12
	30.0	32.2	0.56
	44.2	44.2	0.49
	133	131	0.57

Discussion

The primary purpose of this discussion will be to propose a reasonable mechanism for the photochemical reaction between borazine and deuterium. A radical and an excited-state mechanism will be discussed, and then, based on the experimental evidence, the latter will be shown to be more plausible.

A. Radical Mechanism.—The primary step could be of the form

$$\beta H \xrightarrow{h\nu} \beta + H \qquad (9)$$

where the H atoms come from a boron in borazine. The direct reaction between β and D_2 can be eliminated first of all because it is thermodynamically unfavorable,[12,13] and secondly because such a simple mechanism does not give the kinetic dependences found experimentally. The most likely source of D atoms is

$$H + D_2 \rightleftarrows HD + D \qquad (10)$$

with an activation energy $E_a = 7.3 \pm 1.0$ kcal/mol.[14,15] Dissociation of D_2 by a third body or at the walls would not produce a steady-state concentration of D atoms in the time of the photochemical reaction.[13] Deuterated borazine must be produced by steps such as

$$\beta + D \longrightarrow \beta D \qquad (11)$$

or

$$\beta H + D \longrightarrow \beta D + H \qquad (12)$$

It is difficult to write a mechanism including eq 9, 10, 11, and/or 12 that agrees with the experimental results. With a mixture of $H_2 + D_2$ another reaction is possible

$$D + H_2 \rightleftarrows HD + H \qquad (13)$$

This reaction has about the same rate as reaction 10.[13] Thus, in a 50:50 mixture of $H_2 + D_2$, β and/or βH would have to compete with H_2 for D atoms resulting in a decrease in the amount of βD produced and an

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(12) V. I. Vedeneyev, L. V. Gurnich, V. M. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," Edward Arnold Ltd., London, 1966 [bond strength of β-H taken from data on BH, B_2H_6, B_5H_9, and HBO].

(13) G. Boato, G. Careri, A. Cimino, Z. Molivari, and G. G. Volpi, *J. Chem. Phys.*, **24**, 783 (1956).

(14) A. Farkas and L. Farkas, *Proc. Roy. Soc.* (London), **A152**, 124 (1935).

(15) W. R. Schultz and D. J. LeRoy, *Can. J. Chem.*, **42**, 2480 (1964).

increase in the amount of HD. However, the experimental results show that [βD] = [HD] under these conditions for short periods of irradiation. The high-pressure He experiments also indicate that reaction 10 is not probable. The exciting wavelength of 1849 Å is equivalent to 170 kcal/mol and the β–H bond strength is about 85 kcal/mol[12] leaving 85 kcal/mol excess. Assuming most of the excess energy is taken up by H atoms in the form of kinetic energy, it can be calculated how many He collisions would bring the "hot" H atom below the activation energy of reaction 10. It is found that less than 20 collisions between "hot" H atoms and He should be sufficient. This would indicate that the quantum yield should start decreasing after $P_{He}/P_{D_2} > 20$, but Figure 5 shows that the quantum yield levels off at unity even when $P_{He}/P_{D_2} \approx 30$ and is still unity for $P_{He}/P_{D_2} = 700$ (Table III).

The above information and the observation that upon radiation of pure borazine no β_2 or H_2 was formed in notable quantities seem to be inconsistent with a radical mechanism. It is quite possible that, even though 1849 Å is more energy than necessary to break a β–H bond in borazine, the molecule could remain stable in an excited state for a sufficient time to react with D_2. In the photolysis of benzene at 1849 Å an excited-state mechanism is proposed even though 1849 Å is sufficient to break a C–H bond in benzene.[16]

B. Excited-State Mechanism.—We can write a primary step as

$$\beta H \xrightarrow{h\nu} \beta H^* \qquad (14)$$

A knowledge of the electronic states and uv spectrum of borazine is now necessary. Figure 6B shows an absorption spectrum of gaseous borazine from 1800 to 2100 Å[17] and Figure 6A shows an emission spectrum of the source in the same region. Rector, *et al.*,[18] found that the structureless band peaked at 1710 Å. This band is assigned to a $^1A_1' \rightarrow {}^1E'$ transition which is strongly allowed.[8,19] The band having vibrational structure from 1840 to 2000 Å is assigned to a $^1A_1' \rightarrow {}^1A_2'$ transition which is electronically forbidden but weakly allowed through coupling with an E′ vibration.[8,19] The $^1A_1' \rightarrow {}^1A_1'$ transition is said to be hidden near 1850 Å.[18] Molecular orbital theory predicts that borazine has only three low-lying singlets.[19] Note that the 1849-Å line lies at the edge of the vibrational structure superimposed on the strongly allowed band (see Figure 6).

A radiative lifetime can be calculated for the $^1E'$ state using

$$\tau^0 = \frac{3.5 \times 10^8}{\bar{\nu}_m{}^2 \epsilon_m \Delta\nu_{1/2}}$$

where $\bar{\nu}_m$ is the mean frequency for the absorption band (cm^{-1}), ϵ_m is the maximum molar extinction coefficient (M^{-1} cm^{-1}), and $\Delta\bar{\nu}_{1/2}$ is the half-width (cm^{-1}).

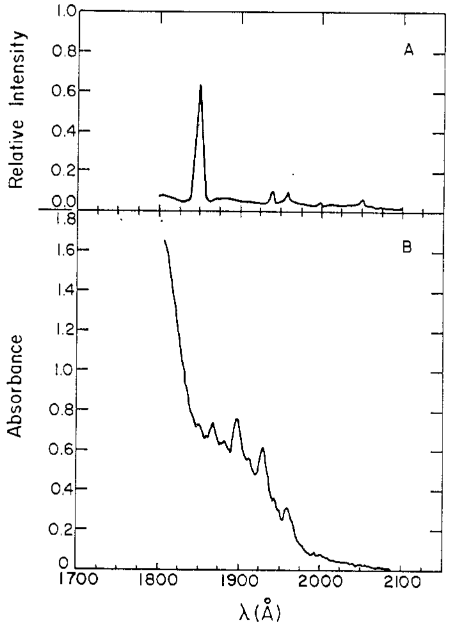

Figure 6.—A. Ultraviolet emission spectrum of the medium-pressure Hg lamp used for photolysis. B. Ultraviolet absorption spectrum of gaseous borazine. $P_{B_3N_3H_6} \approx 1$ mm; λ 1800–2100 Å.

Using the data from the paper by Rector, *et al.*,[18] $\bar{\nu}_m = 58{,}400$ cm^{-1}, $\epsilon_m = 1.3 \times 10^4\ M^{-1}$ cm^{-1}, and, assuming that the band is symmetric with $\Delta\bar{\nu}_{1/2} = 7400$ cm^{-1}, $\tau^0{}_{^1E} \approx 1.1 \times 10^{-9}$ sec. The lifetimes of the $^1A_2'$ and $^1A_1'$ states are much longer since transitions to these states are electronically forbidden. A lower limit on the lifetime of the reacting state can be set by calculating the collision frequency at the lowest pressure required for maximum quantum yield. Using $Z_{1,2} = N_2\pi\sigma^2{}_{1,2}(8RT/\pi M_r)^{1/2}$ [where subscripts 1 and 2 refer to βH* and D_2, respectively], $\sigma_1 = 5.2 \times 10^{-8}$ cm[20] and $\sigma_2 = 1.5 \times 10^{-8}$ cm,[21] and using 76 mm for the lowest pressure required to reach maximum quantum yield, we find $Z_{1,2} = 1.2 \times 10^9$ collisions/sec. This means that, to a rough order of magnitude, the reacting species must live for 10^{-9} sec to have 1 collision with a D_2 molecule. The $^1E'$ state cannot have many collisions with D_2 molecules at $P_{D_2} = 76$ mm and is most likely not the reacting state. Figure 3 shows that at low pressures some deactivation is taking place or not enough reacting states are formed. Figure 5 shows that it is the total pressure of gases other than borazine which affects $\Phi_{\beta D}$.

Using the above information, it is possible to write a mechanism which satisfies the experimental data [(v) indicates vibrational excitation]

$$\beta H \xrightarrow{h\nu} \beta H^{*(v)} \xrightarrow{\text{fast}} \beta H^* \qquad (I)$$

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[16] K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

[17] Thanks are due to Andrew Kaldor for running the spectrum of borazine.

[18] C. W. Rector, G. W. Schaeffer, and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949).

[19] C. C. J. Roothaan and R. S. Milliken, *ibid.*, **16**, 118 (1948).

[20] W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, submitted for publication.

[21] "Handbook of Chemistry and Physics," 48th ed, The Chemical Rubber Co., Cleveland, Ohio, 1967–1968, p F-16.

$$\beta\mathrm{H} \xrightarrow{h\nu} \beta\mathrm{H}'^{(\mathrm{v})} \xrightarrow{\text{fast}} \beta\mathrm{H}' \qquad \text{(II)}$$

$$\beta\mathrm{H}^* \xrightarrow{\text{slow}} \beta\mathrm{H}'^{(\mathrm{v})} \xrightarrow{\text{fast}} \beta\mathrm{H}' \qquad \text{(III)}$$

$$\beta\mathrm{H}^* + \mathrm{M} \longrightarrow \beta\mathrm{H}' + \mathrm{M} \qquad \text{(IV)}$$

$$\beta\mathrm{H}^* \longrightarrow \beta\mathrm{H} + h\nu \qquad \text{(V)}$$

$$\beta\mathrm{H}' + \mathrm{D_2} \longrightarrow \beta\mathrm{D}^{(\mathrm{v})} + \mathrm{HD}^{(\mathrm{v})} \xrightarrow{\text{fast}} \beta\mathrm{D} + \mathrm{HD} \qquad \text{(VI)}$$

$$\beta\mathrm{H}' \longrightarrow \beta\mathrm{H} + h\nu \qquad \text{(VII)}$$

where M = He, N_2, H_2, D_2, etc.

The reacting states can be assumed to be $^1A_2'$ and/or $^1A_1'$ since these states live long enough to have many collisions with D_2 molecules. The βH* state could be the $^1E'$ state since the $^1A_1'(\mathrm{gr}) \rightarrow {}^1E'$ transition is strongly allowed and 1849 Å falls within the transition. Step II is neglected since the transition involved is only weakly allowed. Step VII can also be neglected since the transition involved is electronically forbidden. If we assume that step III is much slower than IV and can be neglected as a source of βH′, then $\mathrm{d}[\beta\mathrm{D}]/\mathrm{d}t$ can be calculated as

$$\frac{\mathrm{d}[\beta\mathrm{D}]}{\mathrm{d}t} = k_{\mathrm{VI}}[\beta\mathrm{H}'][\mathrm{D_2}]$$

$$\frac{\mathrm{d}[\beta\mathrm{H}']}{\mathrm{d}t} = k_{\mathrm{IV}}[\beta\mathrm{H}^*][\mathrm{M}] - k_{\mathrm{VI}}[\beta\mathrm{H}'][\mathrm{D_2}] = 0$$

$$[\beta\mathrm{H}'] = \frac{k_{\mathrm{IV}}[\beta\mathrm{H}^*][\mathrm{M}]}{k_{\mathrm{VI}}[\mathrm{D_2}]}$$

$$\frac{\mathrm{d}[\beta\mathrm{H}^*]}{\mathrm{d}t} = 0 = I_{\mathrm{a}} - k_{\mathrm{IV}}[\beta\mathrm{H}^*][\mathrm{M}] - k_{\mathrm{V}}[\beta\mathrm{H}^*]$$

$$[\beta\mathrm{H}^*] = \frac{I_{\mathrm{a}}}{k_{\mathrm{IV}}[\mathrm{M}] + k_{\mathrm{V}}}$$

Finally

$$\frac{\mathrm{d}[\beta\mathrm{D}]}{\mathrm{d}t} = \frac{k_{\mathrm{IV}}[\mathrm{M}]I_{\mathrm{a}}}{k_{\mathrm{IV}}[\mathrm{M}] + k_{\mathrm{V}}} \qquad (15)$$

and

$$\Phi_{\beta\mathrm{D}} = \frac{k_{\mathrm{IV}}[\mathrm{M}]}{k_{\mathrm{IV}}[\mathrm{M}] + k_{\mathrm{V}}} \qquad (16)$$

If $[\mathrm{M}] \rightarrow 0$, then $\Phi_{\beta\mathrm{D}} \rightarrow k_{\mathrm{IV}}[\mathrm{M}]/k_{\mathrm{V}}$ and if $[\mathrm{M}] \rightarrow \infty$, then $\Phi_{\beta\mathrm{D}} \rightarrow 1$. These results are consistent with data in Figure 3 where $[\mathrm{M}] = [\mathrm{D_2}]$ and Figure 5 where $[\mathrm{M}] = [\mathrm{D_2} + \mathrm{He}]$ or $[\mathrm{D_2} + \mathrm{N_2}]$. Note that in step VI the βD formed is in the ground electronic state. If this were not the case, the mechanism would not agree with the $H_2 + D_2$ experiments. It was observed that in a 50:50 mixture of $H_2 + D_2$, $\Phi_{\beta\mathrm{D}}$ was decreased by almost a factor of 2. If the following step is added to the mechanism

$$\beta\mathrm{H}' + \mathrm{H_2} \xrightarrow{k_{\mathrm{VIII}}} \beta\mathrm{H} + \mathrm{H_2} \qquad \text{(VIII)}$$

then

$$\frac{\mathrm{d}[\beta\mathrm{D}]}{\mathrm{d}t} = \frac{k_{\mathrm{IV}}k_{\mathrm{VI}}[\mathrm{M}][\mathrm{D_2}]I_{\mathrm{a}}}{\{k_{\mathrm{VI}}[\mathrm{D_2}] + k_{\mathrm{VIII}}[\mathrm{H_2}]\}\{k_{\mathrm{IV}}[\mathrm{M}] + k_{\mathrm{V}}\}} \qquad (17)$$

Note: $[\mathrm{M}] = [\mathrm{H_2} + \mathrm{D_2}] = 2[\mathrm{H_2}] = 2[\mathrm{D_2}]$ for a 50:50 mixture of $H_2 + D_2$. If k_{IV} is the same for H_2 and D_2 and we also assume that $k_{\mathrm{VI}} \approx k_{\mathrm{VIII}}$, then

$$\frac{\mathrm{d}[\beta\mathrm{D}]}{\mathrm{d}t} = \frac{2k_{\mathrm{IV}}k_{\mathrm{VI}}[\mathrm{D_2}]^2I_{\mathrm{a}}}{\{2k_{\mathrm{IV}}[\mathrm{D_2}] + k_{\mathrm{V}}\}2k_{\mathrm{VI}}[\mathrm{D_2}]} = \frac{k_{\mathrm{IV}}[\mathrm{D_2}]I_{\mathrm{a}}}{2k_{\mathrm{IV}}[\mathrm{D_2}] + k_{\mathrm{V}}} \qquad (18)$$

and

$$\Phi_{\beta\mathrm{D}} = \frac{k_{\mathrm{IV}}[\mathrm{D_2}]}{2k_{\mathrm{IV}}[\mathrm{D_2}] + k_{\mathrm{V}}} \qquad (19)$$

If $[\mathrm{D_2}] \rightarrow 0$, then $\Phi_{\beta\mathrm{D}} \rightarrow k_{\mathrm{IV}}[\mathrm{D_2}]/k_{\mathrm{V}}$ and if $[\mathrm{D_2}] \rightarrow \infty$, then $\Phi_{\beta\mathrm{D}} \rightarrow {}^1/_2$.

These results agree with the experimental observations, and it can be concluded from the $H_2 + D_2$ experiments that the reaction of βH′ with either D_2 or H_2 deactivates the excited borazine. At present it is uncertain how the electronic energy is dissipated in these reactions. Molecular orbital calculations[22–24] agree that the $^1A_2'$ state is about 6.5 eV above the ground state which is equivalent to 150 kcal/mol. Borazine is a large molecule so part of the energy could be redistributed into vibrational and rotational degrees of freedom. Some of the energy is undoubtedly lost as kinetic energy in βH and kinetic and/or vibrational energy in HD.

From the foregoing analysis it is not possible to rule out a mechanism involving a triplet intermediate for βH′. The energy of the lowest triplet state of borazine has been established by analogy with benzene,[19] but as yet there are no experimental data locating the position of this state.

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