

suggests that the partial excess entropies for PbO(l) in this system have quite large negative values. Presumably these negative entropies must be related to the increased order created in these mixtures through the formation of the complex borate anions. It would be of considerable interest to pursue this problem further by the study of other highly complex-forming mixtures such as, *e.g.*, PbO-SiO₂. For this system free energy data have been reported by Richardson and

Webb.¹³ A calorimetric investigation has been initiated.

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The Photochemistry of Borazine. Preparation of B-Monohydroxyborazine, Diborazinyl Ether, and B-Monoaminoborazine¹

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Products of the photochemical reactions of low-pressure mixtures of borazine and oxygen and borazine and water vapor have been identified by mass and infrared spectra as B₃N₃H₅OH (B-monohydroxyborazine) and (B₃N₃H₅)₂O (diborazinyl ether). The ether derivative is the more stable compound and can be isolated in small quantities. The product of the photochemical reaction of borazine with ammonia is identified as B₃N₃H₅NH₂ (B-monoaminoborazine).

Introduction

Borazine chemistry has developed greatly in the past few years. One area of borazine chemistry that has not been explored extensively is photochemistry. Little work has been reported on the reactions of borazine that are photosensitized by a second reagent or which require absorption of light by the borazine molecule. It has been shown that borazine does absorb ultraviolet light in four diffuse bands starting at about 1995 Å and extending into the vacuum region.² In this paper we describe results that illustrate the potential advantages of photochemical pathways for the synthesis of borazine derivatives. The systems selected for study are borazine-oxygen, borazine-water vapor, and borazine-ammonia.

Experimental Section

The reaction vessel was constructed from a round-bottom 2-l. Pyrex flask fitted with two side arms as shown in Figure 1. A double-wall quartz immersion well capable of transmitting light down to 1800 Å was set into a standard taper joint at the neck of the flask. The volume between the outer walls of the immersion well was evacuated prior to the start of the experiment. The light source was a Hanovia medium-pressure Hg lamp, which provides an intense region of radiation around 1850 Å. To maintain the vessel at room temperature, the lamp was cooled by circulating precooled nitrogen through the immersion well. The reaction vessel was joined on one side to a series of four cold traps and on the other side directly to the vacuum pumps. The reaction products were pumped through the cold traps starting at -35° and continuing to -45, -80, and -196°. These traps were cooled in slush baths of 1,2-dichloroethane-Dry Ice, chloro-

benzene-Dry Ice, acetone-Dry Ice, and liquid nitrogen, respectively. The products in each trap were analyzed mass spectrometrically. Infrared spectra of products with low volatility were obtained by means of solid films in a low-temperature infrared cell. This cell was assembled from a 9-cm Pyrex infrared cell fitted with a standard taper joint for insertion of a copper jacket to accommodate a 0.5-in. KBr window. The jacket and window were cooled by thermal conduction from an internal cold reservoir containing liquid nitrogen. The window assembly could be rotated from the position used for deposition of a sample from one of the traps to a position of alignment with the optical path. Spectra were obtained with Perkin-Elmer Model 337 grating spectrophotometer.

In the borazine-oxygen system the reagents were mixed in the reaction vessel by first adding borazine at the desired pressure and then adding O₂ from an auxiliary reservoir at an excess backing pressure. The quantity of O₂ added was determined from the ratio of the volumes of the reaction vessel and reservoir and the change of O₂ pressure in the reservoir. In separate experiments the total pressures of the reactants were varied between 10 and 40 mm, while the pressure ratio of borazine to oxygen was varied between 2:1 and 1:3. The exposure times ranged from 10 min to 1 hr.

In the borazine-water system H₂O was added to the reaction vessel first. Borazine was then added from a reservoir at an excess backing pressure. Since it is known that water and borazine react thermally under certain conditions,³ the pressure of H₂O was always maintained below its vapor saturation point. Experiments were conducted with reactants at a total pressure of about 13 mm and pressure ratios of borazine to water varying between 2:1 and 1:2. Borazine-ammonia mixtures initially were in a molar ratio of 7:1 at a total pressure of 16 mm. The irradiation time in all cases was 20 min.

Borazine was prepared from LiBH₄ and NH₄Cl.⁴ An impurity, B₂H₅NH₂, noted from its infrared spectrum, was removed as a

(1) Work supported by the Army Research Office (Durham) and the Advanced Research Projects Agency.

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

(3) E. Wiberg, K. Hertwig, and A. Bolz, *Z. Anorg. Chem.*, **256**, 177 (1948); see also W. E. Weibrecht, Ph.D. Thesis, Cornell University, 1964.

(4) G. W. Schaeffer, R. Schaeffer, and R. I. Schlesinger, *J. Am. Chem. Soc.*, **73**, 1612 (1951).

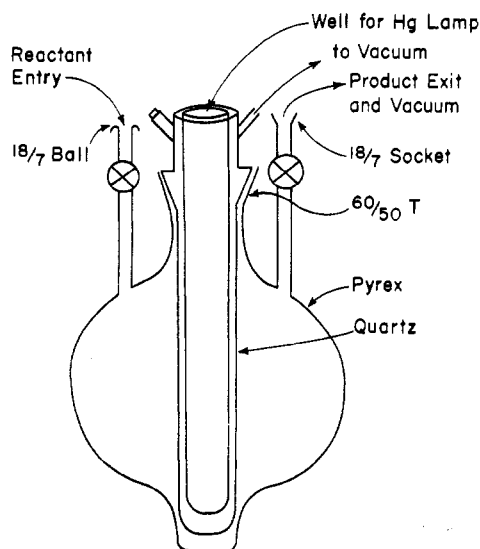
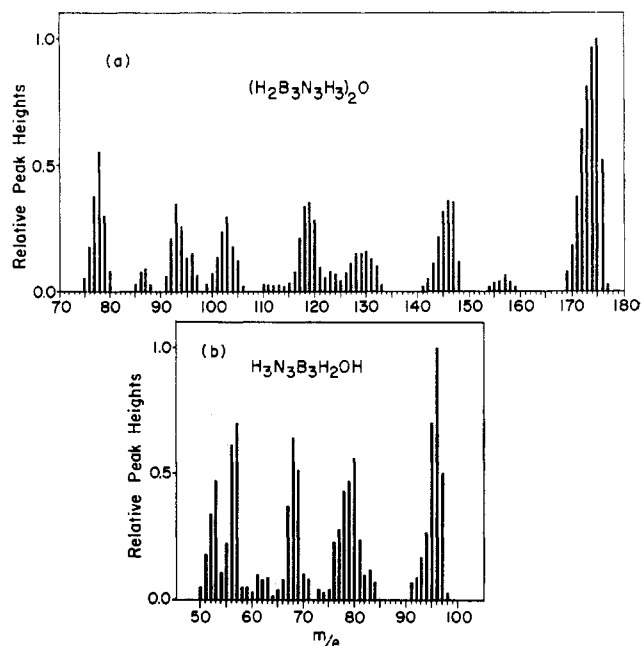


Figure 1.—Reaction vessel.

nonvolatile ammonia adduct but could not be separated by distillation. Removal of this impurity was essential since it inhibited formation of photochemical products. The oxygen and water were purified by repeated distillation. In some experiments oxygen and water highly enriched in ^{18}O were used.

Results

Borazine–Oxygen System.—The volatile compounds obtained from the borazine–oxygen reaction and deposited in each of the four cold traps were analyzed in a 12-in. 60° mass spectrometer.⁵ Most of the products were retained in the -35° trap with little or no product in the -45° trap. The -80 and -196° traps contained unreacted borazine and nonvolatile white solids. The -196° trap also contained a small quantity of ammonia. The composition of material in the -35° trap was dependent upon the initial pressure ratio of the reactants. With oxygen in excess of borazine the material condensed in the -35° trap showed a mass spectrum with the major ion grouping between m/e 169 and 176. An extended mass spectrum of this component is shown in Figure 2a. Under conditions with excess borazine in the reactant mixture the mass spectra of the material condensed at -35° showed major ion groupings in the ranges of m/e 91–97, 127–133, and 169–176. Mass spectral traces for the products obtained when $^{18}\text{O}_2$ was used in place of $^{16}\text{O}_2$ indicated that the ion groups at m/e 169–176 and 91–97 were displaced 2 mass units to higher mass. This showed that the molecular precursors associated with these spectra contain only one atom of oxygen. From the ^{10}B – ^{11}B isotope structure, the mass spectral pattern in the m/e range 91–97 was interpreted as a three boron atom structure with superposition of the parent ion and the parent ion minus H atoms. The high-mass grouping between m/e 169 and 176 was interpreted as a six boron atom structure with superposition of the parent ion and the parent minus H atoms. The components containing an oxygen atom were thus identified with the molecular formulas $\text{B}_3\text{N}_3\text{H}_6\text{O}$ and

Figure 2.—(a) Partial mass spectrum of $(\text{B}_3\text{N}_3\text{H}_6)_2\text{O}$. (b) Partial mass spectrum of $\text{B}_3\text{N}_3\text{H}_5\text{OH}$.

$\text{B}_6\text{N}_6\text{H}_{10}\text{O}$. The component with m/e grouping between 127 and 133 did not contain an oxygen atom and was identified from previously published data as borazanaphthalene.⁶ By noting the changes in ion intensity ratios as the sample was depleted of the more volatile components, it was possible to establish the relative order of volatility as $\text{B}_3\text{N}_3\text{H}_6\text{O} > \text{B}_6\text{H}_6\text{N}_{10}\text{O} \sim \text{B}_5\text{N}_5\text{H}_8$. By applying background corrections for ions arising from $\text{B}_5\text{N}_5\text{H}_8$ and $\text{B}_6\text{N}_6\text{H}_{10}\text{O}$ a partial mass spectrum for $\text{B}_3\text{N}_3\text{H}_6\text{O}$ was derived. This spectrum is shown in Figure 2b. It should be noted that the ion fragmentation patterns of $\text{B}_3\text{N}_3\text{H}_6\text{O}$ and $\text{B}_6\text{N}_6\text{H}_{10}\text{O}$ are complicated since different ions of the same mass containing the same number of B atoms may be formed by splitting off neutral fragments containing N and H atoms and O and H atoms in certain combinations.

Infrared spectra of the products associated with m/e groupings between 91 and 97 and 169 and 176 were obtained from samples prepared as solid films. Products from the reaction of oxygen with excess borazine were condensed in a -35° trap. The trap was then warmed gradually and the volatile component $\text{B}_3\text{N}_3\text{H}_6\text{O}$ was deposited on a cold KBr window. The spectrum of this material is shown in Figure 3b. A spectrum of the higher molecular weight product $\text{B}_6\text{N}_6\text{H}_{10}\text{O}$ was obtained in a similar manner but using excess oxygen in the reactant mixture. In this case the sample collected in the -35° trap was pumped for about 1 hr before the trap was warmed. The spectrum of this material is shown in Figure 3a.

Borazine–Water Reactions.—Mass spectrometric analysis of the products of the borazine–water reaction indicated that the main product condensed in the -35° trap had mass groupings between m/e 169 and 176.

(5) R. F. Porter and R. C. Schoonmaker, *J. Phys. Chem.*, **62**, 234 (1958).(6) A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, *J. Am. Chem. Soc.*, **83**, 1337 (1961).

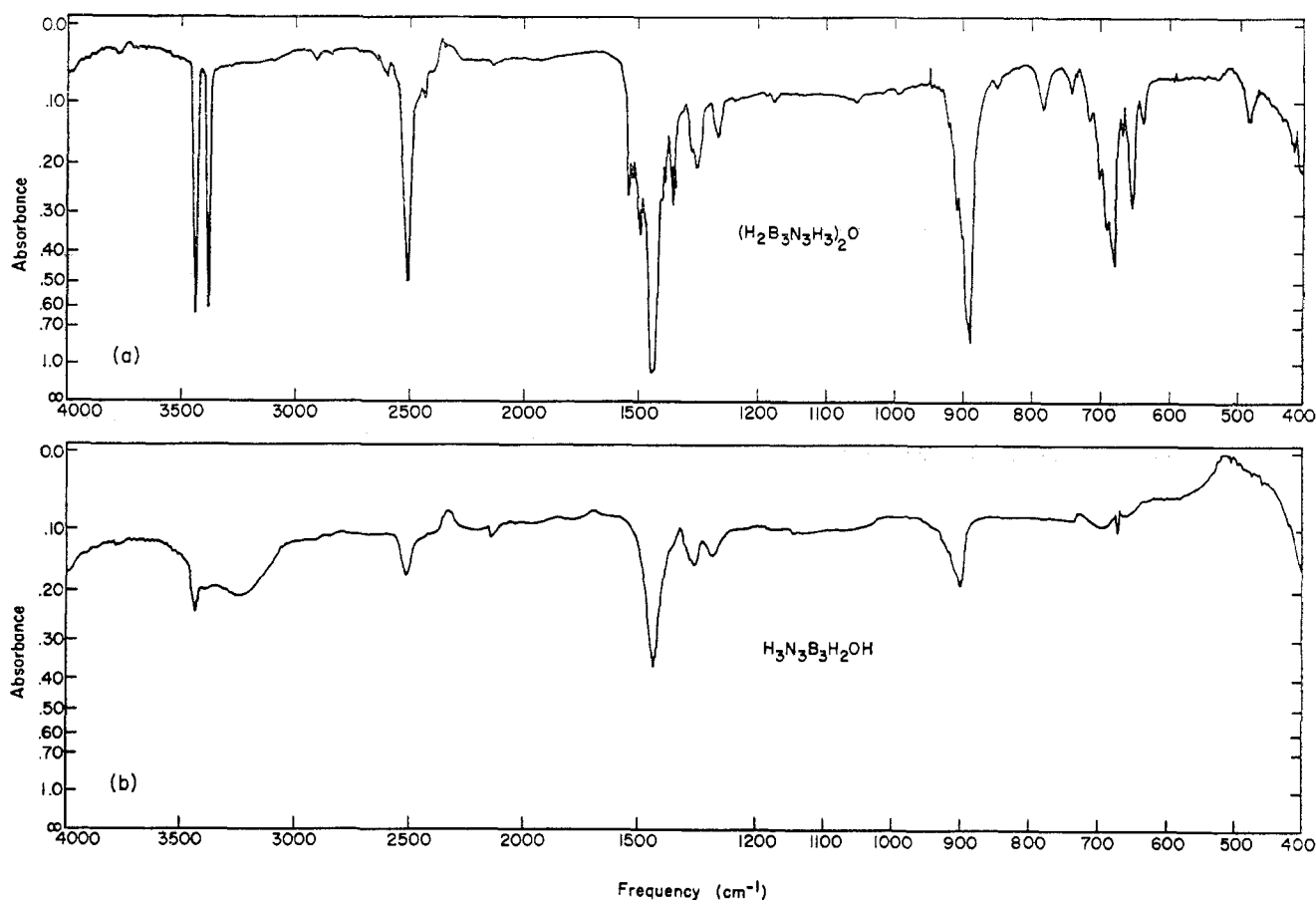


Figure 3.—(a) Infrared spectrum of $(B_3N_3H_5)_2O$ (solid film). (b) Infrared spectrum of $B_3N_3H_5OH$ (solid film).

Since this compound reacts with water, it was necessary to pump on the condensed sample for 1–2 hr after preparation to ensure that unreacted water vapor was removed from the system. Infrared spectra of solid films of the product were identical with that in Figure 2a. Spectra obtained with a sample prepared from borazine and $H_2^{18}O$ indicated shifts in weak bands at 1289 and 1260 cm^{-1} to 1278 and 1242 cm^{-1} while a band shoulder at 690 cm^{-1} disappeared.

Borazine-Ammonia Reaction.—Analyses of the borazine-ammonia reaction products condensed in the cold traps indicated that only the -35° trap contained a new compound. The -45° trap contained little or no product while the -80 and -196° traps contained mostly unreacted starting material. The -35° trap contained a product which is liquid at room temperature and has a vapor pressure of about 2.8 mm at 25° . A portion of the mass spectrum of the compound is shown in Figure 4. The main ion grouping between m/e 90 and 96 is interpreted as a three boron atom structure with a parent mass corresponding to $B_3N_4H_7$ and fragmentation with loss of H atoms. The vapor-phase infrared spectrum of the compound is shown in Figure 5.

Discussion

$B_3N_3H_6O$ and $B_6N_6H_{10}O$.—From the mass spectral and infrared data it is proposed that the main products of the photochemical oxidation of borazine are B-mono-

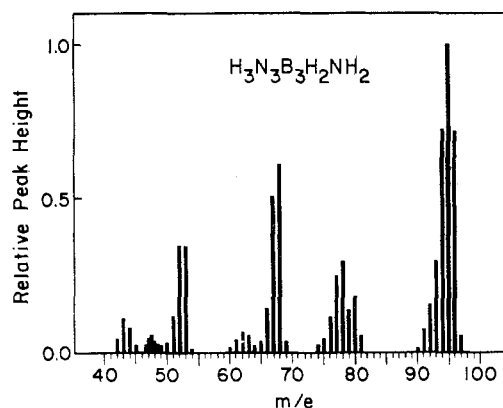
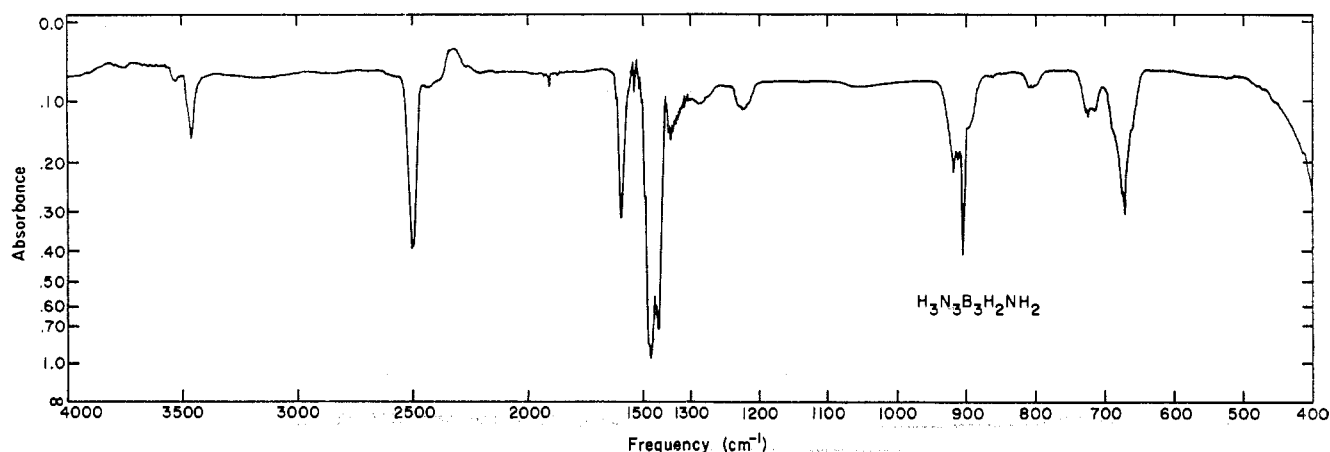


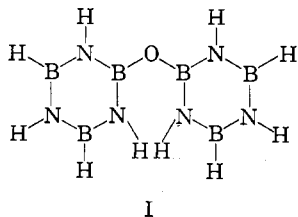
Figure 4.—Partial mass spectrum of $B_3N_3H_5NH_2$.

hydroxyborazine ($B_3N_3H_6O$) and diborazinyl ether ($B_6N_6H_{10}O$). The low-temperature infrared spectrum of $B_3N_3H_6O$ shows N–H, O–H, and B–H stretching frequencies at 3440, 3250, and 2510 cm^{-1} , respectively. A B–N ring stretching frequency at 1435 cm^{-1} and lower frequency ring deformation vibrations were also observed. The low-temperature infrared spectrum of $B_6N_6H_{10}O$ shows two N–H stretching frequencies at 3440 and 3380 cm^{-1} , a B–H stretching frequency at 2505 cm^{-1} , B–N ring vibrations around 1425 cm^{-1} , and lower frequency deformation vibrations.

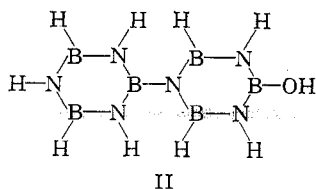
The shift in the band at 1260 to 1242 cm^{-1} upon substitution of ^{18}O for ^{16}O is interpreted as evidence for a

Figure 5.—Infrared spectrum of gaseous $B_3N_3H_5NH_2$.

B-O asymmetric stretching frequency. Several of the frequencies agree with the values attributed to the fundamental vibrations for borazine⁷ in the gas phase. For the latter compound it was necessary to consider not only the ether configuration



but also the isomers of the hypothetical hydroxy derivative of diborazinyl:



Present evidence does not tend to support the existence of II. The presence of an O-H group is supported by neither the infrared spectrum nor the mass spectrum which would be expected to show major fragmentation resulting from loss of an O-H group to give a prominent ion grouping beginning at m/e 159 and extending to lower masses. This would be the same as the major ion fragment from diborazinyl.⁸

An interesting feature of the infrared spectrum of the ether is the appearance of two N-H stretching frequencies of about equal intensity. This may be a splitting due to intermolecular interactions in the solid or to intramolecular interactions in the molecule. It is interesting to note that for a molecule with coplanar borazine rings, a B-O-B bond angle of only about 120° is required to bring two H atoms from adjacent rings into close proximity (I). This type of splitting apparently is not observed in the solid films of the hydroxy derivative or in KBr pellets of diborazinyl.⁶

Difficulties were encountered in isolating the B-mono-hydroxyborazine due not only to the fact that other compounds of low volatility were also produced but repeated evaporation-condensation procedures could not be used because of the instability of the compound. The best procedure for the preparation of the ether derivative is to use a reactant mixture of water with an excess of borazine.

$B_3N_4H_7$.—Mass and infrared spectra for $B_3N_4H_7$ indicate this compound to be B-monoaminoborazine. The mode of ion fragmentation for this compound is similar to that for borazine.⁸ In both compounds ion fragments arise by loss of a mass unit (or units) corresponding to NH_4 , BNH_3 , BNH_4 , BN_2H_4 , and BN_2H_5 . The infrared spectrum of $B_3N_4H_7$ (Figure 5) is also similar to that for gaseous borazine.⁷ The band at 3460 cm^{-1} and the weaker band at 3540 cm^{-1} may be attributed to N-H stretching vibrations from the ring and the NH_2 group. The band at 2505 cm^{-1} is attributed to the B-H asymmetric stretch. A key feature is the band at 1590 cm^{-1} which is interpreted as an NH_2 "scissor" vibration.⁹ The B-N ring stretching vibration in $B_3N_4H_7$, which is of the type E' in borazine, apparently is split into two components at 1460 and 1440 cm^{-1} .

Samples of B-monoaminoborazine could be maintained in the condensed phase at -35° for several hours without extensive decomposition. However, the compound in the vapor phase partially decomposed after a few hours at room temperature to borazine and ammonia. The compound can be condensed and evaporated without serious loss by decomposition. In this sense the monoamino derivative appears to be more stable than B-triaminoborazine.¹⁰

Mechanisms.—In the borazine-water reaction it is presumed that the initial photochemical act involves light absorption by the borazine molecule since H_2O does not absorb strongly between 1800 and 2000 Å.

(8) A.P.I. Mass Spectral Data, Serial No. 1346, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa., 1956.

(9) See for example group frequency analysis by N. B. Colthup, L. H. Daly, and S. E. Wiberly in the Introduction to "Infrared and Raman Spectroscopy," Academic Press, Inc., New York, N. Y., 1964.

(10) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 3561 (1959).

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