[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Pyrolysis of the Borazine–Methanol Adduct

BY DANIEL T. HAWORTH AND L. F. HOHNSTEDT[1]

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As reported in the literature, borazine reacts with excess methanol at room temperature to form a 1:3 adduct, $B_3N_3H_6 \cdot 3CH_3OH$. Pyrolysis of this adduct at 100° has been reported to give 3 moles of H_2 per mole of adduct and a volatile monomer CH_3OBNH, which would represent the only case of a monomeric species of empirical formula corresponding to a borazine derivative. Our repeated pyrolyses of $B_3N_3H_6 \cdot 3CH_3OH$ gave the predicted amount of H_2. The other products observed are ammonia–trimethoxyborane, $H_3NB(OCH_3)_3$ (which has a gas phase molecular weight close to that calculated for CH_3OBNH), B-trimethoxyborazine $[B_3(OCH_3)_3N_3H_3]$, a little methanol and a non-volatile white solid of composition intermediate between BN and $[B(OCH_3)NH]_x$. $B_3(OCH_3)_3N_3H_3$ sublimes *in vacuo* at 60°, reacts quantitatively with methanol at 100° to produce $H_3NB(OCH_3)_3$, and changes to a non-volatile solid when heated alone at 100°. It appears highly improbable that a stable CH_3OBNH monomer can be prepared by reaction of borazine and methanol. The reaction of borazine on mixing with ethanol is similar to that with methanol except that partial ethanolysis to break the borazine ring occurs at room temperature and even lower. B-Triethoxyborazine may be obtained from borazine–ethanol mixtures by heating at 100°. The same compound melting at 53–54° was prepared for comparison by the interaction of $B_3Cl_3N_3H_3$ with $NaOC_2H_5$.

Introduction

A volatile monomeric compound CH_3OBNH has been suggested as one of the products of the pyrolysis of the 1:3 borazine–methanol adduct.[2-4] This is of interest because it corresponds to a depolymerized borazine $B_3(OCH_3)_3N_3H_3$ and would represent the only example of such a monomeric B–N analog of acetylene.[5]

We find in agreement with references 3 and 4 that borazine reacts with excess methanol at room temperature to form a 1:3 borazine–methanol adduct. As reported, pyrolysis at 100° and slightly higher yields three moles of hydrogen per mole of adduct. However, the other readily volatile products were identified by us as the addition compound ammonia–trimethoxyborane and a small amount of methanol. No volatile monomeric CH_3OBNH was produced in any of our pyrolysis runs. The methanol previously[3] ascribed to the decomposition of CH_3OBNH into BN and CH_3OH may be explained by the fact that the pyrolysis products include a non-volatile polymer of composition intermediate between that of $(CH_3OBNH)_x$ and $(BN)_x$, so that the elements of methanol must have been released from some of the $B_3N_3H_6 \cdot 3CH_3OH$ on pyrolysis. This polymeric product was converted into a substance approximating BN in formula only after prolonged heating at 400°.

Furthermore the pyrolysis products included the borazine $B_3(OCH_3)_3N_3H_3$. This suggested the possibility that the first step in the pyrolysis was the formation of B-trimethoxyborazine (eq. 1)

$$B_3N_3H_6 \cdot 3CH_3OH \longrightarrow 3H_2 + B_3(OCH_3)_3N_3H_3 \quad (1)$$

If part of the $B_3(OCH_3)_3N_3H_3$ polymerized with liberation of CH_3OH, the CH_3OH could then attack the remaining $B_3(OCH_3)_3N_3H_3$ to produce the observed $H_3NB(OCH_3)_3$ (eq. 2)

$$B_3(OCH_3)_3N_3H_3 + 6CH_3OH \longrightarrow 3H_3NB(OCH_3)_3 \quad (2)$$

To test this hypothesis B-trimethoxyborazine was prepared by the reaction of sodium methoxide and B-trichloroborazine[6] (eq. 3) and then treated with

$$B_3Cl_3N_3H_3 + 3NaOCH_3 \longrightarrow 3NaCl + B_3(OCH_3)_3N_3H_3 \quad (3)$$

methanol at 100–120°. As described in the Experimental part, the reaction was in quantitative agreement with eq. 2. However, when samples of B-trimethoxyborazine were subjected to the same heating in the absence of added methanol, only a trace of ammonia-trimethoxyborane was formed even though considerable quantities of methanol were produced and all the methoxyborazine was converted to non-volatile material. Therefore the decomposition of $B_3N_3H_6 \cdot 3CH_3OH$ to liberate hydrogen must be more complex than the single reaction indicated by equation 1.

The reaction of ethanol with borazine was investigated with efforts to produce $B_3N_3H_6 \cdot 3C_2H_5OH$ by direct combination. Mixing borazine and ethanol at temperatures as low as −30° resulted in partial ethanolysis to give $B(OC_2H_5)_3$ and NH_3. If the 1:3 borazine–ethanol adduct is the first product of the interaction of its constituents, it undergoes further reaction with ethanol under the experimental conditions used.

Experimental

Materials.—Borazine was prepared by the reduction of $B_3Cl_3N_3H_3$ with $NaBH_4$ in triethylene glycol–dimethyl ether solvent.[7]

$B_3Cl_3N_3H_3$ was prepared by the reaction of BCl_3 and NH_4Cl.[8] The methanol after fractionation in a high vacuum system exhibited a vapor tension of 30 mm. at 0.0° (lit. 30.4 mm.).

Apparatus.—In general standard vacuum line equipment was used which is described elsewhere.[9]

Formation and Pyrolysis of $B_3N_3H_6 \cdot 3CH_3OH$.—Samples of borazine and methanol, with methanol in excess of the stoichiometric amount required to form $B_3N_3H_6 \cdot 3CH_3OH$, were condensed together in a bomb tube attached to the vacuum line. The tube and its contents were allowed to warm from −196° to room temperature and kept at the latter temperature for 6 hr. During this time a glassy transparent solid was formed. The tube was then opened to the vacuum line and the unconsumed methanol was distilled

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(1) Communications regarding this article should be directed to L. F. Hohnstedt, Department of Chemistry, St. Louis University.

(2) The name borazine has been recommended to replace borazole for $B_3N_3H_6$.

(3) E. Wiberg and A. Bolz, *Ber.*, **73B**, 209 (1940).

(4) E. Wiberg, *Naturwissenschaften*, **35**, 212 (1948).

(5) Wiberg has also reported the existence of monomeric $CH_3BNC_6H_5$, but Becher reports that repetition of the Wiberg procedure gives a trimer and that no monomer can be isolated. E. Wiberg and K. Hertwig, *Z. anorg. allgem. Chem.*, **257**, 138 (1948). H. J. Becher, *ibid.*, **289**, 262 (1956).

(6) J. R. Gould and C. Pearl, RMI-440-Q1 (Oct. 9, 1952).

(7) L. F. Hohnstedt and D. T. Haworth, to be published.

(8) C. A. Brown and A. W. Laubengayer, THIS JOURNAL, **77**, 3699 (1955).

(9) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, **Inc.**, New York, N. Y., 1948.

out and measured. The bomb tube was sealed off and heated at 100–120° for 4–5 hr. after which it was opened and H_2 was measured volumetrically. The data are listed in Table I.

TABLE I[a]

Exp.	$B_3N_3H_6$	CH_3OH added	CH_3OH re-covered	CH_3OH re-tained	$B_3N_3H_6$/CH_3OH (retained)	H_2	$B_3N_3H_6$/H_2
1	12.2	40.6	4.1	36.5	1/2.99	26.5	1/2.17[c]
2	21.7	79.5	14.4	65.1	1/3.00	*b*	
3	64.3	200.3	7.5	192.8	1/2.99	194.2	1/3.02
4	73.7	231.8	10.8	221.0	1/2.99	219.2	1/2.97
5	12.8	44.7	5.9	38.8	1/3.03	38.1	1/2.97
6	27.4	92.4	10.3	82.1	1/2.99	81.1	1/2.96

[a] All volumes are reported as cc. at S.T.P. [b] Not measured. [c] Heating time was less than 1 hour.

Volatile Products of Pyrolysis of $B_3N_3H_6 \cdot 3CH_3OH$.—After removal of hydrogen, the products volatile at room temperature were fractionated using a train of U-tubes cooled to −45, −78 and −196°. Most of the ammonia–trimethoxyborane was stopped by −45° and any methanol was retained by −78°. Since ammonia–trimethoxyborane is largely dissociated at room temperature the methanol was separated by condensing all these volatile products in a U-tube at −196° and then replacing the −196° bath with a −45° bath and allowing the methanol to move out of the U-tube. The methanol was identified by its vapor pressure of 31 mm. at 0°. A white solid with an appreciable vapor pressure was retained at −45°.

The gas phase molecular weight of the material retained by the −45° bath was in the range of 59–61. This would appear to be consistent with CH_3OBNH (mol. wt. = 56.87); however, an infrared spectrum indicated the presence of ammonia and methyl borate which suggested that the volatile solid was 1:1 ammonia–trimethoxyborane adduct.[10] The spectrum of a sample of ammonia–trimethoxyborane prepared by mixing methyl borate and ammonia in a 1:1 ratio proved to be identical with that of the −45° fraction. Furthermore the equilibrium pressure over the solid agrees with that reported for the ammonia–trimethoxyborane,[11] as shown in Table II.

TABLE II

PRESSURE OVER THE −45° FRACTION

$$\log p(\text{mm.}) = 12.365 - \frac{3010.0}{T} \text{ (for } H_3NB(OCH_3)_3)^{11}$$

T(°C.)	Obsd. (mm.)	Calcd. (mm.)
0.0	21	20.7
1.3	24	23.2
9.7	49	47.3
16.2	85	86.1
17.9	97	98.8
19.8	110	109
22.6	133	139
23.5	155	154
26.0	188	186

Identification of the volatile solid was confirmed by analysis. Calcd. for $H_3NB(OCH_3)_3$: B, 8.95; N, 11.58. Found: B, 8.94, 8.93; N, 11.64, 11.62.

Identification of B-Trimethoxyborazine.—Sublimation at 55° of the residual solids in the bomb tube yielded $B_3(OCH_3)_3N_3H_3$ which was identified by its m.p. of 110–111° (lit.[6] 112–112.5°) and analysis. Calcd. for $B_3(OCH_3)_3N_3H_3$: B, 19.03; N, 24.63. Found: B, 19.0, 19.0; N, 24.20, 24.51.

A sample of the non-volatile solids remaining after sublimation contained B and N in a 1:1 ratio, but the B and N content accounted for only 73.5% by weight of the sample which presumably also contained the elements of CH_3OH.

Preparation of $B_3(OCH_3)_3N_3H_3$.—4.4 g. of B-trichloroborazine and 5.0 g. of sodium methoxide were reacted for 5 hr. in refluxing chlorobenzene. The solvent was distilled off under vacuum and 2.2 g. of the borazine (53.9% yield) was obtained by vacuum sublimation at 60°.

Methanolysis of $B_3(OCH_3)_3N_3H_3$.—Measured samples of $B_3(OCH_3)_3N_3H_3$ and CH_3OH were mixed and heated at 100° for 4 hr. in sealed Pyrex tubes. Methanolysis occurred according to eq. 2 to consume completely the methanol and give stoichiometric amounts of ammonia–trimethoxyborane. Typical results are listed in Table III. For comparison this table includes the data for the pyrolysis of the B-trimethoxyborazine itself at the same conditions. It is of interest to observe that the borazine evolves methanol on pyrolysis but only relatively small amounts of ammonia–trimethoxyborane. Thus the data of run no. 6 are consistent with reaction of the added methanol according to eq. 2 accompanied by decomposition of some of the excess borazine to produce methanol and a little ammonia–trimethoxyborane.

TABLE III[a]

	$B_3(OCH_3)_3$-N_3H_3 used	CH_3OH added	Ratio $\frac{B_3(OCH_3)_3N_3H_3}{CH_3OH}$	$H_3NB(OCH_3)_3$ Theor.	$H_3NB(OCH_3)_3$ Obsd.	CH_3OH Re-covered
(1)	8.6	0.0	1/0.0	...	0.0	8.17
(2)	11.0	0.0	1/0.0	...	0.2	5.00
(3)	10.2	0.0	1/0.0	...	1.1	6.5
(4)	5.8	13.5	1/2.33	6.75	6.7	0.0
(5)	10.0	25.0	1/2.50	12.5	9.2	0.0
(6)	8.3	21.8	1/2.63	10.9	11.2	4.9
(7)	11.3	68.0	1/6.01	34.0	35.7	0.0
(8)	6.95	41.7	1/6.00	20.8	20.5	0.0

[a] All volumes are reported in cc. at S.T.P.

Blank.—32.4 cc. of CH_3OH and 32.3 cc. of NH_3 were heated to 120° for 4 hr. in a Pyrex bomb tube. 31.5 cc. of CH_3OH and 32.0 cc. of NH_3 were recovered from the tube; only a trace of material which might have been $H_3NB(OCH_3)_3$ was formed.

Ethanol-Borazine Reaction.—Measured samples of borazine and ethanol were condensed together at −196° and allowed to warm to reaction temperature, at which they were maintained for 4 to 7 hr. The mixtures were then cooled to −196° and any H_2 formed at the reaction temperature was measured. Then the mixture was rewarmed to reaction temperature and volatile materials were distilled into the vacuum line and fractionated. The reaction temperatures studied were −45, −30, −23, 0° and room temperature. In all cases ethanol was present in greater than 3:1 mole ratio with respect to borazine. There was no evidence of reaction at −45°, but at other reaction temperatures H_2 was evolved and NH_3 could be isolated from the volatile product mixture. In some runs $B(OC_2H_5)_3$ could be isolated but in others it appeared that in addition to NH_3 the volatile material contained a mixture of C_2H_5OH and $B(OC_2H_5)_3$ which could not be separated by the technique used. In no case was there any apparent stoichiometric relationship between the amounts of H_2, NH_3 and $B(OC_2H_5)_3$ produced. The borazine–ethanol reaction may be complex as is that of borazine–methanol (see below).

B-Triethyoxyborazine.—In the above reactions the solids remaining in the reaction tubes after pumping off all volatile materials at room temperature were heated to 100° for several hours. Further H_2, NH_3 and $B(OC_2H_5)_3$ or $B(OC_2H_5)_3$–C_2H_5OH mixture were produced. The remaining solids were heated to 40° in a high vacuum and $B_3(OC_2H_5)_3N_3H_3$ sublimed away from a non-volatile white residue. The $B_3(OC_2H_5)_3N_3H_3$, m.p. 53–54°, was identified by comparison with a sample of this substance prepared by the reaction of $B_3Cl_3N_3H_3$ with $NaOC_2H_5$. Four g. of $B_3Cl_3N_3H_3$ and 4.4 g. of $NaOC_2H_5$ reacted in refluxing chlorobenzene for 4 hr. The solvent was distilled away under vacuum and the resulting solids were warmed to 40° in a high vacuum. A white crystalline material melting at 53–54° sublimed out of the heated zone and was collected in a −80° trap. It was identified as $B_3(OC_2H_5)_3N_3H_3$ by molecular weight and analytical data. Calcd. for $B_3(OC_2H_5)_3N_3H_3$: B, 15.26; N, 19.76; mol. wt. 212.7. Found: B, 15.3, 15.4; N, 19.73, 19.83; mol. wt. (by benzene m.p. depression), 193–205.

Analyses.—Samples of alkoxyborazines were digested at 100° in a small amount of concd. H_2SO_4. Non-volatile solids were treated similarly, except that a few drops of 30% H_2O_2 was added to the H_2SO_4. Boron was determined by titration of the mannitol complex, nitrogen by the Kjeldahl analysis.

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(10) J. Goubeau and U. Böhm, *Z. anorg. allgem. Chem.*, **266**, 161 (1951).

(11) W. H. Schechter, U. S. Patent 2,629,732.

Discussion

The data given in the experimental part show that the pyrolysis of 1 : 3 borazine–methanol adduct at 100-120° gives the volatile ammonia–trimethoxyborane and not the suggested CH_3OBNH. Assuming complete dissociation in the gas phase the observed molecular weight of the complex would be 60.46, one-half that for $H_3NB(OCH_3)_3$. The observed value of 59–61 supports this assumption. The isolation of the trimer $B_3(OCH_3)_3N_3H_3$ by vacuum sublimation at 55° makes it appear improbable that there was present any stable monomer CH_3OBNH which was not detected by reason of its being retained by the solids in the bomb tube. The existence of any such monomer stable with regard to polymerization at room temperature appears to be highly doubtful.

Pyrolysis of the borazine–methanol adduct evidently proceeds by at least two paths, one of which probably is represented by eq. 1 and another of which may well be an intermolecular polymerization of the borazine–methanol adduct to liberate H_2 and some methanol and to form a polymer $B_xN_xH_y(OCH_3)_y$. Of course, intramolecular reaction to give CH_3OH is not precluded and the data are obscured by the fact that the trimethoxyborazine produced during the pyrolysis is itself changed into a non-volatile residue, methanol and a little ammonia–trimethoxyborane when subjected alone to similar pyrolysis.

Methanol and Pyrex react to give methyl borate.[12] However, a blank, as described in the Experimental part, indicated that no significant amount of methyl borate was produced in this fashion under the pyrolysis conditions.

The borazine–methanol adduct was practically unattacked by excess liquid methanol, whereas borazine underwent partial ethanolysis to $B(OC_2H_5)_3$ and NH_3 at temperatures as low as −30°. An attempt to displace the methanol from the borazine–methanol adduct by ethanol at 25° resulted in partial ethanolysis of the adduct. At 0° ethanol was observed to have no effect on the borazine–methanol adduct.

These observations might tempt one to speculate as to the relative reactivity of methanol and ethanol toward borazine–alcohol adducts. However, the adducts, especially $B_3N_3H_6{\cdot}3CH_3OH$, appear to be only slightly soluble in their corresponding alcohols. Therefore the observed differences in behavior may well be due to differences in solubility, and the apparent stability of $B_3N_3H_6{\cdot}3CH_3OH$ may arise from the slowness of a heterogeneous phase reaction occurring at the surface of the adduct.

Some preliminary experiments support this suggestion. A sample of $B_3N_3H_6{\cdot}3CH_3OH$ was partially dissolved in benzene. When methanol was added to the resulting solid–solution mixture, the remaining solid rapidly dissolved with evolution of a gas from the solid surface, although such evolution did not occur when the adduct initially dissolved in the benzene. This suggests that further studies of the reaction of borazines with alcohols should be carried out in neutral solvent. Also, to prepare $B_3N_3H_6{\cdot}3C_2H_5OH$ and other kinds of related adducts one should consider the reaction of the desired borazine and alcohol in solvents in which the adduct formed will be relatively insoluble. If no such solvent can be found, then the addition of dilute solutions of the alcohol to solutions of the borazine may be considered.

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ST. LOUIS, MISSOURI

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[12] R. F. Porter, *J. Phys. Chem.*, **61**, 1260 (1957).

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DIVISION, NATIONAL CHEMICAL LABORATORY]

Hydrogen Ion Equilibria and the Interaction of Cu^{II} and Co^{II} with Bovine Serum Albumin

BY HIRA LAL*

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The interaction of Cu^{II} and Co^{II} with bovine serum albumin has been followed by titration and distribution dialysis studies. It has been shown that Co^{II} is bound to bovine albumin through its imidazole sites. The existence of compound sites through which the first two cupric ions are bound to bovine albumin has been confirmed; a log k^0 value of 6.8 ± 0.3 for the intrinsic affinity of these sites for Cu^{II} has been obtained. It has been shown that the subsequent binding of cupric copper with bovine albumin occurs 1:1 with the imidazole sites. Evidence has been presented that cupric copper is partially hydrolyzed and bound as such to the protein in the neutral *p*H region.

Previous studies in acetate buffer medium of *p*H 6.5 have indicated that bovine albumin contains a class of two "compound" sites through which the first two cupric ions are bound to the protein molecule.[1] The nature of these sites, adduced essentially from electrophoretic studies, is such as to cause a release of two protons per metal ion bound.[1,2] If these sites do exist, a direct evidence for their presence should be obtainable from titration studies. Studies in buffer solutions have also revealed that Co^{II} is bound to the carboxyl

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* Indian Institute of Technology, Worli, Bombay 18.

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[2] H. Lal and M. S. N. Rao, *ibid.*, **79**, 3050 (1957).