bands[31-33] in the 2400-2200-cm^{-1} region and a single band in the H-B-H deformation region.[30-33] Thus the six bands of diborane dihydrate can be accounted for by assuming the presence of $BH_2(H_2O)_2^+$ and BH_4^-.

The assignment of the high-frequency doublet in the dihydrate spectrum (with peaks at 2750 and 2720 cm^{-1}) to the $BH_2(H_2O)_2^+$ ion deserves some comment. These frequencies are about 150 cm^{-1} higher than those previously found for the B-H stretching in $BH_2X_2^+$ salts.[27-30] However, all the $BH_2X_2^+$ salts which have been previously studied have had X ligands which are relatively strong donors, usually with donor atoms less electronegative than oxygen. In $BH_2(H_2O)_2^+$, the high electronegativity of the oxygen atoms causes the boron orbitals used in the B-O bonds to have a high degree of p character. Consequently the boron orbitals used in the BH bonds have a high degree of s character, and the BH bonds are extraordinarily strong and have a very high stretching frequency.[34] We may similarly argue that the water molecules in $BH_2(H_2O)_2^+$ are relatively poor donor molecules and that consequently the BH bonds are more nearly like those in free BH_2^+. In the latter species the boron orbitals would be sp-hybrid orbitals and the B-H bonds would be stronger than those in which the boron is essentially sp^3 hybridized.

The ν_H/ν_D ratios for the BH_4^- bands have normal values—1.39, 1.36, and 1.39—and, as expected, the B-O stretching frequency was essentially unaffected by deuteration. The ν_H/ν_D ratios for the $BH_2(H_2O)_2^+$ bands are somewhat high (1.48 and 1.55) but not unreasonable.

A similar infrared study of the B_2D_6-H_2O system yielded little information because the broad H_2O deformation band in the 1700-1600 cm^{-1} region obscured the B-D stretching bands of BD_4^-. A band was observed at 1850 cm^{-1}, as well as a weak band near 2700 cm^{-1}, presumably due to $BD_2(H_2O)_2^+$ and $BH_2(H_2O)_2^+$, respectively. Perhaps the latter species can be accounted for by a small amount of hydrogen-deuterium exchange.

Acknowledgments.—We are grateful to Professor Leo Brewer for providing the infrared instrumentation. This work was supported by the U. S. Atomic Energy Commission.

[31] T. C. Waddington, *J. Chem. Soc.*, 4783 (1958).
[32] C. J. H. Schutte, *Spectrochim. Acta*, **16**, 1054 (1960).
[33] E. H. Coker and D. E. Hofer, *J. Chem. Phys.*, **48**, 2713 (1968).
[34] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

Notes

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF CALIFORNIA, AND THE INORGANIC
MATERIALS RESEARCH DIVISION, LAWRENCE BERKELEY
LABORATORY, BERKELEY, CALIFORNIA 94720

The Reaction of Heptasulfur Imide with Diborane

BY MARSHALL H. MENDELSOHN AND WILLIAM L. JOLLY*

Received December 7, 1971

It is known that heptasulfur imide reacts with boron trichloride and boron tribromide to give S_7NBCl_2[1] and S_7NBBr_2,[2] respectively. In this note we report the results of our study of the reaction of heptasulfur imide with diborane. This study was undertaken to determine whether the reaction gives an analogous product (S_7NBH_2), a borane adduct ($S_7NH\cdot BH_3$), or a diborane derivative such as $S_7NB_2H_5$.

Results and Discussion

The reaction of heptasulfur imide with diborane was carried out in various ether solvents, at either room temperature or 0°. The experimental results, summarized in Table I, show that, with diborane in excess, 0.5 mol of diborane reacts per mole of S_7NH and that 1 mol of hydrogen is formed per mole of S_7NH. This stoichiometry corresponds to the reaction $S_7NH + 0.5B_2H_6 \rightarrow S_7NBH_2 + H_2$.

TABLE I

STOICHIOMETRY OF THE REACTION OF S_7NH WITH B_2H_6

Solvent	Temp, °C	Amt, mmol S_7NH	Amt, mmol B_2H_6	Measd H_2/S_7NH	Time of meas, hr	B_2H_6 consumed/ S_7NH
Monoglyme[a]	23	0.288	0.41	1.11[b]	17	0.49
Monoglyme	23	0.992	0.72	1.35[b]	64.5	...
Monoglyme	0	0.574	0.516	1.0[c]	66	0.495
	23			1.15[b]	24	
THF[a]	23	0.386	0.356	0.99	67	0.505
THF	23	0.616	0.50	1.13[b]	65.5	...
THF	23	0.567	0.264	1.09[b,d]	145	...
THF	0	0.611	0.593	1.02	497	0.52
THF	0	0.302	0.0716	1.31[b,d]	978	...
Dioxane	23	0.505	0.633	2.20[b]	319	...
Diethyl ether[a]	0	0.575	0.292	0.98	260	...

[a] Reaction mixture not stirred. [b] Traces of H_2 still being evolved, due to slow decomposition. [c] Stopped purposely to pump out excess B_2H_6. [d] Listed as H_2/B_2H_6.

When the reaction is carried out in diethyl ether at 0°, some of the product precipitates as a white, crystalline ether adduct, $S_7NBH_2\cdot Et_2O$. Similar adducts can be obtained from the other ethers by vacuum evaporation of the solvent and removal of excess diborane. The compounds undergo rapid hydrolysis with excess water at room temperature: $S_7NBH_2\cdot \text{ether} + 3H_2O \rightarrow S_7NH + B(OH)_3 + 2H_2 + \text{ether}$.

The ^{11}B nmr spectrum of S_7NBH_2 in diethyl ether solution consists of a 1:2:1 triplet due to coupling with the two protons of the BH_2 group. The Raman spectrum of the diethyl ether adduct has lines at 2419 and 2409 cm^{-1}, characteristic of terminal BH_2 groups, and lines at 766 and 750 cm^{-1}, typical S-N stretching frequencies.

[1] H. G. Heal, *J. Inorg. Nucl. Chem.*, **20**, 165 (1961).
[2] H. G. Heal, *J. Chem. Soc.*, 4442 (1962).

As can be noted from Table I, the only products that were stable (as determined by hydrogen evolution) were those obtained from diethyl ether and tetrahydrofuran. The diethyl ether adduct is stable at room temperature in the absence of air and moisture, and the product from tetrahydrofuran is stable at 0°. Hydrogen, hydrogen sulfide, and ether were identified as decomposition products of the tetrahydrofuran and monoglyme adducts at room temperature.

A white solid pyridine adduct, $S_7NBH_2 \cdot C_5H_5N$, was isolated from the reaction of $S_7NBH_2 \cdot Et_2O$ with pyridine. Pure samples of this compound were stable indefinitely *in vacuo* at 0° and could be kept in an ordinary closed bottle at room temperature for as long as 5 days without decomposition. However, impure samples decomposed within 1 or 2 days.

When the reaction of heptasulfur imide and diborane is carried out with an excess of S_7NH in tetrahydrofuran at 0°, the reaction does not stop with the formation of S_7NBH_2, as evidenced by the continued slow evolution of hydrogen. Presumably the following subsequent reaction occurs: $S_7NH + S_7NBH_2 \rightarrow (S_7N)_2BH + H_2$. However, the reaction was incomplete after 1 month and was not further studied.

Experimental Section

Reagents and Procedure.—Heptasulfur imide was prepared by the usual method[3] and was purified by one recrystallization from methanol followed by repeated recrystallizations from carbon tetrachloride until the solutions were colorless and the solid melted at 113–114° (lit.[4] mp 113.5°). The infrared spectrum agreed with that reported in the literature.[4] Diborane was made by the reaction of potassium borohydride with phosphoric acid[5] and purified by vacuum distillation through a −112° trap. Tetrahydrofuran, diethyl ether, and dioxane were distilled from lithium aluminum hydride immediately before use. Monoglyme (1,2-dimethoxyethane) was distilled first from calcium hydride and then from lithium aluminum hydride. Pyridine was distilled from potassium hydroxide, and carbon tetrachloride was distilled from phosphorus pentoxide.

Approximately 10 ml of solvent was vacuum distilled into a 50-ml flask containing a known weight of heptasulfur imide. A known amount of diborane was condensed into the reaction vessel, and the vessel was allowed to warm to either room temperature or 0°. At various times the evolved hydrogen was collected using a Toepler pump, measured in a gas buret, and identified by mass spectroscopy. To isolate the crystalline product $S_7NBH_2 \cdot Et_2O$, an all-glass system was employed. The apparatus was sealed off after addition of the reactants and was provided with a break-seal for removal of hydrogen and a side arm for washing the product by decantation. The product was then removed in a drybox. *Anal.* Calcd for $S_7NBH_2 \cdot C_4H_{10}O$: C, 14.76; H, 3.69; N, 4.30; S, 69.01. Found: C, 14.86; H, 3.69; N, 4.45; S, 68.68.

A sample of S_7NBH_2 prepared in tetrahydrofuran was treated with a 500-fold excess of distilled water. The evolved hydrogen was collected and measured as described above. The precipitated S_7NH was collected by filtration, air-dried, and then weighed. It was identified by its infrared spectrum.[4] The boric acid formed was determined by a standard double-titration method.[6] *Anal.* Calcd for S_7NBH_2 prepared from 0.386 mmol of S_7NH: H_2, 0.772 mmol; $B(OH)_3$, 0.386 mmol; S_7NH, 0.386 mmol. Found: H_2, 0.773 mmol; $B(OH)_3$, 0.393 mmol; S_7NH, 0.31 mmol.

Raman Spectrum.—The following lines were observed for the diethyl ether adduct (cm^{-1} ± 3 cm^{-1}): 2969 (w), 2930 (w–m), 2419 (w), 2409 (sh), 1471 (w), 1452 (w–m), 1442 (sh), 1324 (w), 1181 (w–m), 1091 (w–m), 1005 (w), 870 (w–m), 851 (sh), 832 (w), 766 (w–m), 750 (w–m) 602 (m), 476 (vs), 458 (m), 437 (m), 292 (s), 251 (m), 213 (vs), 201 (s), 178 (m), 153 (s). The Raman spectrometer consisted of a Spectra-Physics 125 helium–neon laser with line filter (35 mW) and a Spex 1401 monochromator equipped with an ITT FW-130 photomultiplier tube.

Nmr Spectra.—The samples for the ^{11}B nmr spectra were prepared and recorded in 12-mm o.d. tubes containing diethyl ether, in which the compound is only slightly soluble. For this reason the spectra were computer averaged over 10–150 scans. The spectrum consisted of a 1:2:1 triplet centered 33.5 ppm upfield from an external reference peak of boron trichloride, with $J_{B-H} = 136$ Hz. A Varian Model V4311 high-resolution nmr spectrometer operated at 8.134 MHz was used for the boron spectra. Proton spectra of samples prepared from monoglyme and diethyl ether were recorded in CS_2 using a Varian A-60 spectrometer. Although the samples decomposed in CS_2, the spectra did indicate the presence of the coordinated ether. For the sample from diethyl ether, a triplet at 1.98 ppm and a quartet at 4.75 ppm, relative to TMS, were observed, while from monoglyme two singlets at 4.63 and 4.67 ppm and a complex pattern centered at 4.87 ppm were noted. The complexity of the latter spectrum indicates that only one of the oxygen atoms of monoglyme was coordinated to S_7NBH_2.

X-Ray Diffraction.—Some preliminary X-ray diffraction data on a single crystal of $S_7NBH_2 \cdot C_4H_{10}O$ correspond to the space group *Pnma* and the unit cell dimensions (Å) $a = 15.80$, $b = 13.16$, and $c = 6.75$.

Preparation and Characterization of $S_7NBH_2 \cdot C_5H_5N$.—The pyridine adduct was prepared by addition of excess, dry pyridine to the solid $S_7NBH_2 \cdot Et_2O$. The solution was evaporated to a volume of 0.2–0.3 ml, and dry CCl_4 was then added. A white solid was precipitated and was washed with a small amount of chilled CCl_4. The infrared spectrum of a Nujol mull recorded with a Perkin-Elmer Model 137B Infracord spectrophotometer consisted of the following peaks (cm^{-1} ± 10 cm^{-1}): 2415 (m), 2353 (sh), 1618 (m), 1186 (m), 1157 (w), 1139 (sh), 1131 (s), 1100 (m–s), 1025 (w), 1013 (w), 977 (w), 961 (sh), 953 (m), 943 (s), 929 (w), 917 (m), 775 (m), 768 (m), 751 (s), 687 (s). A sample melting at 87.5–88° was analyzed. *Anal.* Calcd for $S_7NBH_2 \cdot C_5H_5N$: C, 18.17; H, 2.14; N, 8.48; S, 67.92; B, 3.3. Found: C, 18.97, H, 2.08; N, 8.62; S, 67.98; B, 3.2 (as a B_2O_3 residue). A proton nmr spectrum showed the protons on the pyridine ring, but we were unable to see the protons attached to boron.

Acknowledgment.—We wish to thank Dr. James Shear at the U. S. Department of Agriculture Western Regional Research Laboratory for recording the Raman spectrum, Dr. Allan Zalkin of the Lawrence Berkeley Laboratory for the X-ray diffraction data, and Dr. James Neely and John Illige for recording the ^{11}B nmr spectra. This research was supported by the U. S. Atomic Energy Commission.

---

[3] M. Becke-Goehring and E. Fluck, *Inorg. Syn.*, **8**, 103 (1966).

[4] H. G. Heal and J. Kane, *ibid.*, **11**, 193 (1969).

[5] A. D. Norman and W. L. Jolly, *ibid.*, **11**, 15 (1969).

[6] A. I. Vogel, "Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1961, pp 252–254.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY,
EAST LANSING, MICHIGAN 48823

Niobium(IV) Halide Complexes of *N*,*N*-Dimethylformamide. Synthesis and Spectra

BY K. KIRKSEY AND J. B. HAMILTON*

Received August 25, 1971

N,*N*-Dimethylformamide resembles water and methanol in its solvent properties, but unlike these it is a nonhydroxylic solvent. With anhydrous halides such as TiX_4 (X = Cl, Br, I)[1] and $ZrCl_4$[2] it reacts to form

---

[1] J. Archambault and R. Rivest, *Can. J. Chem.*, **38**, 1331 (1960).

[2] A. Clearfield and E. J. Malkiewick, *J. Inorg. Nucl. Chem.*, **25**, 237 (1963).