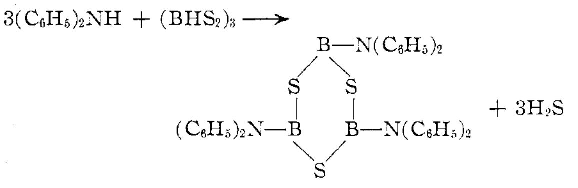
Finally, we have cited a case in which a secondary amine, such as diphenylamine, reacts with trimeric metathioboric acid in carbon disulfide solution to form the corresponding tris(amino)borosulfole. The reaction appears to be analogous to the one reported by Wiberg[3] in which tribromoborosulfole reacts with a primary amine to form tris(alkylamino)borosulfole and hydrogen bromide. The absence of an -NH stretching vibration at about 3300 cm.$^{-1}$ in the infrared absorption spectrum supports its structure.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Studies of Boranes. XII. Nuclear Magnetic Resonance Spectra of Gaseous Diborane at High Temperature and Pressure

BY RILEY SCHAEFFER AND FRED TEBBE

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The equilibrium reaction

$$B_2H_6 \leftrightarrows 2BH_3$$

is one of the commonly postulated reactions in the field of boron hydride chemistry. No direct observations of the BH_3 molecule have been made nor has it proven possible to determine experimentally the values of the equilibrium constants for the reaction. Studies of kinetics of many reactions show that the rate of dissociation of diborane is fairly rapid and is in general not rate limiting. Bauer has considered the problem of describing the thermodynamics and kinetics of the diborane-borane equilibrium and by using a variety of indirect types of information has given some useful estimates.[1] In particular, he notes that the reported nuclear magnetic resonance spectrum of diborane implies a half-time for the dissociation reaction of longer than 0.01 sec. The experimental n.m.r. studies by both Ogg and Shoolery which led to Bauer's estimate were made in the liquid state (presumably below the normal boiling point of $-92.5°$)[2,3] and it appeared worthwhile to extend the temperature range for the measured diborane n.m.r. spectrum as far as possible. This paper reports studies carried out on gaseous diborane at temperatures up to 123°.

Experimental

Nuclear magnetic resonance spectra of diborane were observed at 60 and 19.3 Mc./sec. using a Varian DP-60 spectrometer. Samples of diborane were sealed into cells constructed from thick-walled 6-mm. Pyrex tubing shaped to provide a cavity approximately 2.4 mm. in i.d. and 3 cm. long at the bottom of a longer section of 1-mm. capillary which served as a handle. Spectra were observed over a temperature range in the conventional manner using standard Varian accessories. Coupling constants were measured by a side-band technique, but no effort was made to determine chemical shift values.

Results and Discussion

Both proton and boron spectra were observed but the noise level present in studies of the proton spectra was sufficiently large so that relatively little meaningful data could be obtained. Consequently, most efforts were expended on the determination of the boron spectra. The pressures utilized, the temperature range studied, and the coupling constants observed are recorded in Table I.

TABLE I

^{11}B N.M.R. OF GASEOUS DIBORANE

P, atm.	Temp., °C.	Coupling constants
29.2	96.8	45.3, 134
24.4	30	45.8, 134.8
79.5	100	46.3, 131
84.4	123	44.2, 137
59.5	30	...

The pressures necessary to obtain observable spectra were sufficiently large so that no line broadening interfered with observations. The observed spectra were identical in all cases with the ones reported earlier for diborane below $-90°$.

Clearly the conditions utilized in this study, which probably represent the extreme dictated by safety, did not reach the temperature range in which exchange reactions are of sufficient importance to be observed by the n.m.r. technique. At these temperatures and pressures diborane decomposition was sufficiently rapid so that observations could not be extended beyond a few minutes and severe problems would probably attend efforts to extend the range still further.

It is perhaps particularly worthwhile noting that one would have expected partial collapse of the diborane spectrum if only a single one of the bridge bonds had broken. Thus, the studies of Gaines indicate that for diborane in various ether solutions the breaking of a single bridge bond becomes an important process at temperatures well below 100° with the resultant collapse of the triplets to a seven-line multiplet.[4] Even in those studies no further changes resulting from rupture of the second bridge could be observed. The activation energy necessary for single bond breakage might be expected to be substantially smaller than that required for complete dissociation of diborane into two borane molecules (probably not greatly in excess of half). Clearly even this activation energy is still

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[1] S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 5575 (1956).

[2] R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954).

[3] J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

[4] D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

too large to allow rapid exchange under the conditions of the present study.

Although no new precise numerical figures for either the rate or the equilibrium for the diborane dissociation have been added to the literature by the present study, future calculations of these will be more severely limited by the data reported here for studies over an extended temperature range.

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Some Convenient Methods for Preparing Bis(triphenyltin) Sulfide and Related Compounds

BY EUGENE J. KUPCHIK AND PETER J. CALABRETTA

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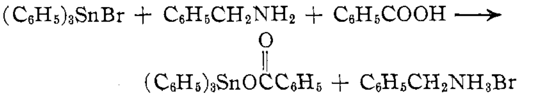
It was reported previously that triphenyltin bromide reacts with ammonia in anhydrous diethyl ether to give bis(triphenyltin) oxide and ammonium bromide.[1]

$$2(C_6H_5)_3SnBr + 2NH_3 + H_2O \longrightarrow (C_6H_5)_3SnOSn(C_6H_5)_3 + 2NH_4Br \qquad (1)$$

The conversion of triphenyltin bromide to bis(triphenyltin) oxide (82% yield) can also be accomplished with benzylamine.

$$2(C_6H_5)_3SnBr + 2C_6H_5CH_2NH_2 + H_2O \longrightarrow (C_6H_5)_3SnOSn(C_6H_5)_3 + 2C_6H_5CH_2NH_3Br \qquad (2)$$

In this reaction triphenyltin bromide and benzylamine probably form a complex which undergoes hydrolysis on exposure to the moisture in the air to give the observed products. The ability of organotin compounds to give complex addition compounds with ammonia or amines is well known.[2–6] The low hydrolytic stability of these complexes has been mentioned.[7] If benzoic acid is added to the reaction mixture before exposing it to the air the products are triphenyltin benzoate (80%) and benzylammonium bromide (87%).



$$(C_6H_5)_3SnBr + C_6H_5CH_2NH_2 + C_6H_5COOH \longrightarrow (C_6H_5)_3SnO\overset{O}{\overset{\|}{C}}C_6H_5 + C_6H_5CH_2NH_3Br \qquad (3)$$

Equation 3 represents a convenient method for preparing triphenyltin esters of carboxylic acids in high yield. High yields have been obtained with bridgehead carboxylic acids.[8]

When carbon disulfide is used as a solvent in reaction 1, bis(triphenyltin) sulfide is formed in high yield. The other products are ammonium bromide and ammonium thiocyanate.

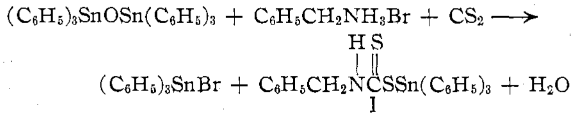
$$2(C_6H_5)_3SnBr + 4NH_3 + CS_2 \longrightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + NH_4SCN + 2NH_4Br \qquad (4)$$

The use of bis(triphenyltin) oxide in place of the triphenyltin bromide also results in a high yield of bis(triphenyltin) sulfide.

$$(C_6H_5)_3SnOSn(C_6H_5)_3 + 2NH_3 + CS_2 \longrightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + NH_4SCN + H_2O \qquad (5)$$

In reactions 4 and 5 hydrogen sulfide probably is formed by reaction between the ammonia and the carbon disulfide. Ammonia is known to react with carbon disulfide to give ammonium dithiocarbamate, which decomposes at room temperature to give hydrogen sulfide and ammonium thiocyanate.[9] In (4) hydrogen sulfide or ammonium sulfide reacts either directly with the triphenyltin bromide or with a possible complex formed between the triphenyltin bromide and ammonia. In (5) the hydrogen sulfide or ammonium sulfide reacts with the bis(triphenyltin) oxide to produce the observed products.

It has been found that bis(triphenyltin) oxide reacts with benzylammonium bromide in carbon disulfide to give triphenyltin bromide (70%) and triphenyltin N-benzyldithiocarbamate (I) (60%).



$$(C_6H_5)_3SnOSn(C_6H_5)_3 + C_6H_5CH_2NH_3Br + CS_2 \longrightarrow (C_6H_5)_3SnBr + \underset{\text{I}}{C_6H_5CH_2\overset{H}{\overset{|}{N}}\overset{S}{\overset{\|}{C}}SSn(C_6H_5)_3} + H_2O \qquad (6)$$

I can also be obtained (94% yield) by allowing sodium N-benzyldithiocarbamate to react with triphenyltin bromide. Perhaps the most convenient method for preparing I (85% yield) involves adding benzylamine to a carbon disulfide solution of bis(triphenyltin) oxide.

$$(C_6H_5)_3SnOSn(C_6H_5)_3 + 2C_6H_5CH_2NH_2 + 2CS_2 \longrightarrow 2\text{I} + H_2O \qquad (7)$$

In (7) N-benzyldithiocarbamic acid probably is formed by reaction between the benzylamine and the carbon disulfide. This compound then immediately reacts with the bis(triphenyltin) oxide to give I and water. In (6) the benzylammonium bromide probably first reacts with the bis(triphenyltin) oxide to give triphenyltin bromide, benzylamine, and either triphenyltin hydroxide or bis(triphenyltin) oxide. The triphenyltin hydroxide or bis(triphenyltin) oxide then reacts as in (7).

Bis(triphenyltin) oxide also reacts with ammonium bromide in carbon disulfide to give triphenyltin bromide (72%) and bis(triphenyltin) sulfide (90%).

I decomposes on heating to give bis(triphenyltin) sulfide in high yield. This decomposition can be conveniently carried out by refluxing an acetonitrile

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