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Interaction of Metathioboric Acid with Some Phosphines and Amines

BY S. C. MALHOTRA

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Synthesis of metathioboric acid, $(BHS_2)_x$, was first reported by Stock[1] and later by Wiberg,[2] who obtained both the dimer and the trimer forms by bubbling hydrogen sulfide through a solution of boron tribromide in carbon disulfide. Wiberg also prepared several derivatives by the reaction of the trimer with some appropriate boron compounds, *e.g.*, tris(dimethylamino)borosulfole, $[B(N(CH_3)_2)S]_3$, from trimeric metathioboric acid, $[B(SH)S]_3$, and tris(dimethylamino)borane, $B(N(CH_3)_2)_3$.[3] He has also described an alternate route to obtain tris(dimethylamino)borosulfole from tribromoborosulfole and tris(dimethylamino)borane. With a primary amine, tribromoborosulfole gives tris(alkylamino)borosulfole.

Stock[4] has reported the formation of boron sulfide hexaammoniate by the reaction of the metathioboric acids with ammonia. The product decomposes at 105° to give $B_2(NH)_3$ and at 125° to form BN. There is, however, no report in the literature on the corresponding phosphine adducts.

Boron sulfide and hydrogen sulfide are the products of thermal decomposition of metathioboric acids.[1]

A small amount of diborane is reported to be formed upon bubbling hydrogen through a solution of the trimeric metathioboric acid in the presence of Raney Ni catalyst.[5]

Finally, the structure of trimeric metathioboric acid is discussed by Goubeau.[6]

We have synthesized a new series of complexes of the general formula $R_3P:B_2S_3$ by the interaction of substituted phosphines with metathioboric acid. The synthesis and characterization of these compounds as well as those of the corresponding amine adducts are described below.

Experimental

All materials were handled exclusively in an atmosphere of dry nitrogen. Trimeric metathioboric acid and boron sulfide were prepared as described above.[1] Substituted phosphines were obtained from Metal & Thermit Corporation.

Boron was analyzed by fusion with sodium peroxide, followed by removal of the sodium in the hot water extract by means of a cation-exchange resin and titration with NaOH solution in the presence of mannitol. The two breaks in the titration correspond to boron and phosphorus, respectively. Standard procedures were used for all other elements.

Preparation and Properties of Triphenylphosphine–Boron Sulfide Adduct.—A sample of 2.2 g. (8.4 mmoles) of triphenylphosphine was stirred in benzene (200 ml.) with 1.3 g. (17.1 mmoles) of trimeric metathioboric acid in a 300-ml. round-bottom flask fitted with a reflux condenser. The stirring was continued for 6 hr. at 70°, after which the mass was cooled and filtered and the solid (2.8 g., 7.4 mmoles of adduct) washed twice with benzene and dried under reduced pressure; yield 87%. It is difficultly soluble in tetrahydrofuran and dibromomethane, and decomposes without melting at 180°.

Anal. Calcd. for $(C_6H_5)_3P:B_2S_3$: C, 56.9; H, 4.0; P, 8.1; B, 5.7; S, 25.3; mol. wt., 379.6. Found: C, 54.3; H, 4.0; P, 7.6; B, 5.7; S, 25.8; mol. wt., 355 (in dibromomethane by osmometer method).

Infrared spectrum (KBr, cm.$^{-1}$): 3078 (w), 1960 (w), 1888 (w), 1818 (w), 1588 (w), 1483 (m), 1430 (s), 1300 (sh), 1190 (w), 1163 (w), 1105 (s), 1070 (w), 1025 (m), 1000 (s), 980 (w), 890 (w), 848 (s), 778 (w), 752 (s), 717 (m), and 695 (s).

X-Ray diffraction data for the adduct are given in Table I.

TABLE I

X-RAY DIFFRACTION DATA

$(C_6H_5)_3P:B_2S_3$		$(n\text{-}C_4H_9)_3P:B_2S_3$		$C_5H_5N:B_2S_3$		$((C_6H_5)_2N\text{-}BS)_3$	
d, Å.	*I*/*I*$_0$	*d*, Å.	*I*/*I*$_0$	*d*, Å.	*I*/*I*$_0$	*d*, Å.	*I*/*I*$_0$
9.3	0.10	11.0	0.70	8.8	0.30	11.2	1.00
8.7	0.50	9.0	1.00	7.3	0.70	9.3	0.05
8.6	1.00	7.5	0.30	5.5	0.90	7.6	0.05
8.0	0.20	7.08	0.30	4.75	0.95	6.43	0.10
6.75	0.20	4.97	0.40	4.41	0.10	5.57	0.20
5.57	0.20	4.57	0.40	4.18	0.65	4.82	0.25
4.87	0.10	4.43	0.60	3.88	0.20	4.65	0.20
4.74	0.30	4.27	0.40	3.66	1.00	4.28	0.50
4.66	0.20	4.07	0.20	3.51	0.65	4.13	0.30
4.61	0.90	3.79	0.30	3.20	0.50	3.93	0.05
4.28	0.50			2.97	0.10	3.66	0.05
4.22	0.20			2.89	0.20	3.50	0.05
4.01	0.10			2.72	0.20		
3.89	0.80			2.66	0.25		
3.64	0.10			2.58	0.20		
3.38	0.10						
3.33	0.50						
2.97	0.10						
2.76	0.10						
2.29	0.10						

Proton–N.m.r. Spectra.—$(C_6H_5)_3P:B_2S_3$: One strong peak at 7.15 p.p.m.[7] and several fine structures at between 7.05 and 7.15 p.p.m. $(C_6H_5)_3P$: One strong peak at 7.25 p.p.m. and one medium strong at 7.20 p.p.m. $(C_6H_5)_3PS$: Splitting of the above, resulting in several peaks at between 7.35 and 7.85 p.p.m.

The magnetic susceptibility of $(C_6H_5)_3P:B_2S_3$ is -0.83×10^{-6} c.g.s.

Action of Water.—A sample of 0.70 g. of triphenylphosphine–boron sulfide adduct upon treatment with 150 ml. of water at 25° gave 0.41 g. of triphenylphosphine (infrared), 0.04 g. of boron (as boric acid; calcd., 0.04 g. of boron), and 100.5 cc.[8] of hydrogen sulfide (calcd. 123.8 cc.). No hydrogen was evolved during the reaction.

Action of Pyridine.—The infrared spectrum and X-ray diffraction pattern of the insoluble product obtained from the re-

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[1] A. Stock and O. Poppenberg, *Ber.*, **34**, 399 (1901).

[2] E. Wiberg and W. Sturm, *Z. Naturforsch.*, **8b**, 530 (1953).

[3] E. Wiberg and W. Sturm, *Angew. Chem.*, **67**, 483 (1955).

[4] A. Stock and M. Blix, *Ber.*, **34**, 3042 (1901).

[5] C. J. Barr, *et al.*, U. S. Patent 2,965,450 (to Olin Mathieson Chemical Corporation).

[6] J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **272**, 303 (1953).

[7] With reference to tetramethylsilane.

[8] It does not include the amount dissolved in water under the experimental conditions.

action of the phosphine adduct with pyridine (1:1) were identical with those of the pyridine–boron sulfide adduct. *Anal.* Found: P, 2.1. Insoluble product, 1.31 g.; calculated for combined pyridine and phosphine adducts, based on phosphorus analysis, 1.33 g. The soluble product was triphenylphosphine (infrared), free of boron by flame test.

Preparation and Properties of Tri-*n*-butylphosphine–Boron Sulfide Adduct.—The reaction product of metathioboric acid and excess tri-*n*-butylphosphine in benzene solution at 150° was obtained as needle-like crystals in 80–90% yield and was moderately soluble in benzene and dibromomethane; m.p. 140° dec.

Anal. Calcd. for $(n\text{-}C_4H_9)_3P{:}B_2S_3$: C, 45.0; H, 8.4; B, 6.7; S, 30.0; mol. wt., 319.6. Found: C, 43.2; H, 8.1; B, 6.6; S, 29.1; mol. wt., 286 (in dibromomethane by osmometer method) and 654 (in benzene by boiling point elevation method).

Infrared spectrum (KBr, cm.$^{-1}$): 2985 (s), 2900 (w), 2548 (w), 1465 (s), 1410 (s), 1385 (s), 1290 (s), 1100 (m), 1032 (m), 1010 (m), 970 (sh), 918 (m), 893 (w), 853 (m), 782 (m), and 715 (w).

X-Ray diffraction data for the product are given in Table I.

Preparation of Pyridine–Boron Sulfide Adduct.—Trimeric metathioboric acid and pyridine ($B{:}C_5H_5N = 1{:}0.5$) in carbon disulfide solution gave at 0° a pale yellow precipitate in 80% yield. It is only slightly soluble in tetrahydrofuran and 1,2-dimethoxyethane and decomposes without melting at 69°.

Anal. Calcd. for $C_5H_5N{:}B_2S_3$: C, 30.5; H, 2.5; N, 7.1; B, 11.0; S, 48.8. Found: C, 27.7; H, 2.2; N, 6.4; B, 9.8; S, 43.6. Ratios C:N = 5.0, B:N = 2.0, S:B = 1.5.

Infrared spectrum (KBr, cm.$^{-1}$): 3127 (w), 2988 (w), 1627 (s), 1575 (w), 1490 (w), 1457 (s), 1360 (m), 1283 (m), 1210 (w), 1157 (w), 1088 (s), 1020 (w), 925 (w), 885 (sh), 778 (m), 755 (sh), and 702 (m).

X-Ray diffraction data for the product are given in Table I.

Preparation of Triethylamine–Metathioboric Acid Adduct.—The product of reaction of metathioboric acid with triethylamine (B:amine = 1:0.5) was a light yellow, amorphous solid which decomposed without melting at 60°.

Anal. Calcd. for $(BHS_2)_3{:}1.5(C_2H_5)_3N$: C, 28.5; H, 6.8; N, 5.5; B, 8.5; S, 50.7. Found: C, 28.5; H, 7.0; N, 5.2; B, 8.6; S, 47.7.

Infrared spectrum (KBr, cm.$^{-1}$): 3030 (m), 2740 (m), 2533 (w), 1410 (s), 1300 (m), 1177 (w), 1080 (w), 1042 (m), 925 (w), 840 (w), 782 (w), and 712 (w).

Preparation of Tris(diphenylamino)borosulfole.—The reaction of trimeric metathioboric acid with excess diphenylamine at 45° in carbon disulfide yielded an insoluble product which did not melt below 250°.

Anal. Calcd. for $((C_6H_5)_2N\text{–}BS)_3$: C, 68.3; H, 4.8; N, 6.6; B, 5.1; S, 15.2. Found: C, 68.8; H, 5.0; N, 6.9; B, 5.1; S, 14.8.

Infrared spectrum (KBr, cm.$^{-1}$): 3078 (w), 1592 (s), 1488 (s), 1450 (m), 1335 (s), 1300 (w), 1283 (w), 1250 (s), 1173 (w), 1153 (m), 1075 (m), 1042 (m), 1032 (s), 1015 (s), 1005 (w), 915 (w), 873 (w), 803 (w), 752 (s), 705 (s), and 695 (m).

X-Ray diffraction data for the compound are given in Table I.

Discussion

Triphenyl- and tri-*n*-butylphosphines displace hydrogen sulfide from trimeric metathioboric acid in benzene solution to give rise to a new series of boron sulfide complexes,[9] in accordance with the equation

$$3R_3P + 2(BHS_2)_3 \longrightarrow 3R_3P{:}B_2S_3 + 3H_2S \tag{1}$$

The rate of the reaction is dependent upon the strength of the base. In the case of triphenylphosphine, the reaction proceeds slowly at room temperature but is complete within a few hours at 70°. Although a lower temperature is required for the butyl analog, it is best prepared at 150° and the reaction is complete in less than 4 hr. The same products are formed in either case even when excess phosphines are employed during the reactions.

The phenyl derivative, $(C_6H_5)_3P{:}B_2S_3$ (I), is a difficultly soluble, nonvolatile crystalline solid. Molecular weight data for the compound show it as a simple adduct in which either of the boron atoms may accept a free pair of electrons from the phosphorus atom into its vacant 2p-orbital. The reaction must proceed *via* the breaking of a B–SH bond to enable the free pair of electrons to approach the boron atom with the subsequent formation of hydrogen sulfide. There is no reaction, for example, between boron sulfide, B_2S_3, and triphenylphosphine in benzene even at 200°. Upon treatment with water, the adduct gives free base, boric acid, and hydrogen sulfide according to the equation

$$(C_6H_5)_3P{:}B_2S_3 + 6H_2O \longrightarrow (C_6H_5)_3P + 2H_3BO_3 + 3H_2S \tag{2}$$

That I is a simple addition compound is further evidenced by the fact that pyridine displaces triphenylphosphine from the adduct at 0° as shown below.

$$(C_6H_5)_3P{:}B_2S_3 + C_5H_5N \longrightarrow C_5H_5N{:}B_2S_3 + (C_6H_5)_3P \tag{3}$$

Both the pyridine compound and the free triphenylphosphine are identified by their X-ray diffraction patterns and infrared spectra.

The butyl derivative, $(n\text{-}C_4H_9)_3P{:}B_2S_3$ (II), is moderately soluble in benzene, from which it is crystallized in needle-like form by the addition of a small quantity of *n*-pentane. The molecular weight data for the compound suggest the species $(n\text{-}C_4H_9)_3P{:}B_2S_3$ in dibromomethane and $[(n\text{-}C_4H_9)_3P{:}B_2S_3]_2$ in benzene solutions. II is further characterized by its chemical analysis and infrared spectrum.

Pyridine and triethylamine take different courses upon reaction with metathioboric acid in carbon disulfide solution at 0°. Pyridine behaves in the same fashion as the phosphines, but triethylamine gives an adduct of metathioboric acid without elimination of hydrogen sulfide.

$$3C_5H_5N + 2(BHS_2)_3 \longrightarrow \underset{\text{III}}{3C_5H_5N{:}B_2S_3} + 3H_2S \tag{4}$$

$$3(C_2H_5)_3N + 2(BHS_2)_3 \longrightarrow \underset{\text{IV}}{2[(BHS_2)_3{:}1.5(C_2H_5)_3N]} \tag{5}$$

Molecular weights of the amine products, however, could not be determined because of their insufficient solubility. III is characterized by its independent synthesis from I, as described above, and by its chemical analysis and infrared spectrum. In the latter, the N→B stretching vibration is evident from absorption at 1088 cm.$^{-1}$. IV may be a mixture of salts, the infrared spectrum of which shows absorption at 2740 cm.$^{-1}$ due to NH^+.[10]

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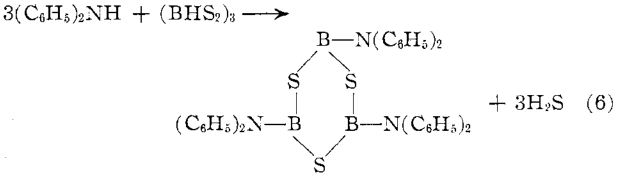
[9] The reaction appears to be general with tertiary phosphines.

[10] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., London, New York, p. 260.

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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CONTRIBUTION NO. 1195 FROM THE
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Studies of Boranes. XII. Nuclear Magnetic Resonance Spectra of Gaseous Diborane at High Temperature and Pressure

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The equilibrium reaction

$$B_2H_6 \rightleftarrows 2BH_3$$

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

(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).