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Preparation and Properties of Diborane Diphosphine

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Of the compounds formed by the hydrides of boron, diborane diammine $B_2H_6{\cdot}2NH_3$, has been investigated most extensively. This compound was first prepared by Stock,[1] and from its properties he concluded that it was a salt, $(NH_4)_2(B_2H_4)$, derived from the dibasic acid, $H_2(B_2H_4)$. Schlesinger and Burg[2] have reported that the low temperature reaction of metallic sodium on a solution of diborane diammine in liquid ammonia, gave results that could be explained only on the basis of a monobasic salt being formed. Therefore, they believed that the structure of diborane diammine is best represented by the formula, $NH_4(BH_3NH_2BH_3)$. When $B_2H_6{\cdot}2NH_3$ is heated rapidly to 200°, a volatile cyclic compound, $B_3N_3H_6$, is formed,[3] the six-membered ring having alternate boron and nitrogen atoms.

The similarities and differences between phosphine and ammonia led us to investigate the action of phosphine on diborane and the nature of the product so obtained.

Two volumes of phosphine react with one volume of diborane to form a white unstable compound of empirical composition $B_2H_6{\cdot}2PH_3$ or $BH_3{\cdot}PH_3$.[4] The reaction takes place slowly in the gas phase at temperatures above $-30°$, and fairly rapidly in the liquid phase above $-110°$. The product, diborane diphosphine, dissociates above $-30°$ into diborane and phosphine, the dissociation pressure at 0° being about 200 mm. No evidence for the corresponding dissociation of diborane diammine has ever been reported.

Diborane diphosphine is formed from the gas phase as long, white, crystalline needles, and from the liquid phase as a microcrystalline mass. It is spontaneously inflammable in air, and rapidly decomposed by water with the formation of hydrogen, phosphine and boric acid. On heating rapidly to 200°, large quantities of hydrogen and a non-volatile, unidentified residue are formed, but no volatile product corresponding to $B_3N_3H_6$, which is formed under comparable conditions, has been isolated.

The compound dissolves with difficulty in liquid ammonia at its melting point without apparent reaction. A true phosphonium salt, PH_4Br, slowly dissolves under the same conditions with complete evolution of the phosphine in the compound, and the formation of ammonium bromide. If the solution of diborane diphosphine in liquid ammonia or the solid compound in liquid ammonia is warmed to approximately $-60°$, phosphine is slowly evolved. The rate of evolution increases with increasing temperature, the maximum evolution at 0° taking place within twenty minutes. The maximum evolution of phosphine corresponds to between 52 and 58% of the total, an average of seven determinations being 55.5%. The resulting solution evolves no more phosphine even on standing for months dissolved in liquid ammonia at room temperature. When the solvent ammonia is pumped off, a white solid remains, whose composition is approximated by the formula $B_2H_6{\cdot}PH_3{\cdot}NH_3$.

Gaseous ammonia has been found to react slowly with diborane diphosphine with the displacement of 21 to 75% of the phosphine in the compound, depending chiefly on the temperature and the time of reaction. An interpretation of the above reaction may involve the fact that at temperatures much above $-30°$, the quantity of diborane formed by the dissociation of diborane diphosphine, $B_2H_6{\cdot}2PH_3 \rightleftarrows B_2H_6 + 2PH_3$, is sufficient to cause one to expect direct action between diborane and ammonia.[5]

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(1) A. Stock and E. Kusz, *Ber.*, **56B**, 807 (1923); A. Stock and E. Pohland, *ibid.*, **59B**, 2213 (1926); A. Stock, E. Wiberg, H. Martini and A. Nicklas, *ibid.*, **65B**, 1711 (1932).

(2) H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

(3) A. Stock and E. Pohland, *Ber.*; **59B**, 2216 (1926); S. H. Bauer, THIS JOURNAL, **60**, 524 (1938); H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.*, **60**, 1296 (1938).

(4) While this work was in progress, Schlesinger and Burg[2] reported in a footnote the formation of this compound, but no details have been published. However, Professor Schlesinger has been kind enough to inform us of the results of his work with Dr. Burg. These results are given in the following footnote of this paper.

(5) Professor Schlesinger's private communication states that he and Dr. Burg have found that at $-40°$, gaseous ammonia reacts with diborane diphosphine with the displacement of 50% of the phosphine. They believe that two compounds containing diborane, phosphine and ammonia exist, namely, $B_2H_6{\cdot}PH_3{\cdot}NH_3$ and $B_2H_6{\cdot}PH_3{\cdot}2NH_3$. The latter compound is quite unstable, losing one mole of ammonia at $-30°$. Trimethylamine displaces 100% of the phosphine from diborane diphosphine, with the formation of borine trimethylamine and phosphine. They have also noted that phosphine reacts with borine carbonyl with the formation of carbon monoxide and diborane diphosphine.

The product formed by the reaction of liquid ammonia on diborane diphosphine is a white pasty solid the stability of which is much greater than that of diborane diphosphine itself. It evolves hydrogen slowly over a period of time, either in the solid state or in solution in liquid ammonia, in which it is readily soluble. It burns with difficulty in air, and dissolves readily in water to form a clear solution. This solution evolves hydrogen, 10% of the hydrogen attached to boron being liberated in six hours, but no phosphine is liberated during this time. If the formula of diborane phosphine ammine is expressed as a phosphonium salt, $PH_4(BH_3NH_2BH_3)$, it would be expected that both liquid ammonia and water would liberate phosphine from the compound. Therefore, the ammonium salt, $NH_4(BH_3PH_2BH_3)$, seems more probable.

When diborane phosphine ammine was heated rapidly to 200°, $B_3N_3H_6$ was formed in yields of 30%, calculated on the nitrogen content. No volatile compounds containing phosphorus were detected.

Hydrogen chloride reacts with diborane diphosphine to form chlorinated derivatives, displacing hydrogen in volume equivalent to the hydrogen chloride introduced. Under controlled conditions, the following reaction takes place

$$B_2H_6\cdot 2PH_3 + 2HCl = B_2H_4Cl_2\cdot 2PH_3 + 2H_2$$

The product so formed is a clear, water-white, viscous, non-volatile liquid, which may further react with hydrogen chloride. The product with an empirical composition $B_2H_2Cl_4\cdot 2PH_3$ is usually formed as a white, crystalline solid, melting with decomposition near 68°. By the use of high pressures of hydrogen chloride above 0°, it can be converted to $BCl_3\cdot PH_3$.[6]

Four possible formulas have been considered for the compound formed by diborane and phosphine: [I], $(PH_4)_2B_2H_4$, corresponding to the formula $(NH_4)_2B_2H_4$ for the diammine suggested by Stock and Wiberg,[7] appears to be inadequate to account for the properties of the compound. [II], $BH_3\cdot PH_3$. If the simple monomer, borine phosphine, were capable of existence in the gas phase for a few minutes at room temperature, it could be detected easily by gas analysis. The results of numerous analyses have given no indication that borine phosphine exists as a stable gas; however, this does not preclude the possibility of its existence in the solid state. The monomeric form for the solid gives the simplest explanation for the reaction with hydrogen chloride, inasmuch as only when two, four and six moles of hydrogen chloride are introduced (for each mole of diborane in the compound) do the products appear to be homogeneous. The reactions with ammonia cannot be accounted for on the basis of the monomeric form, unless it is converted to the dimeric form by the ammonia, which is entirely possible. [III], $PH_4(BH_3PH_2BH_3)$, corresponding to $NH_4(BH_3NH_2BH_3)$ for the diammine, can be used to account for the reactions of the compound formed by diborane and phosphine. The salt-like nature of this compound is, however, not well defined, inasmuch as it will dissolve in liquid ammonia at −75° without the liberation of phosphine. [IV], $B_2H_6\cdot 2PH_3$ is unsatisfactory from many points of view, but it implies the mode of formation and decomposition of the compound and does not emphasize any salt-like character of the compound. It seems probable that without a more extended study of the other hydrides of boron, especially B_4H_{10} and B_5H_9, more definite conclusions may not be drawn concerning the salts or addition compounds formed from diborane.

Experimental

Description of Apparatus.—The apparatus was adapted from the type used by Stock and his co-workers[7] and Schlesinger and his co-workers.[8] The use of stopcocks instead of mercury valves was found to be permissible in situations where the grease was exposed to diborane at low pressures for short periods of time.

Analytical Methods.—The reactants were measured in a calibrated globe and distilled into the reaction tubes with liquid nitrogen. After the reaction had taken place the excess gases were pumped off from the reaction tube into a gas buret by means of a Toepler pump. Wherever possible, these gases were separated by fractional condensation before entering the buret. Diborane was determined by the increase in volume on hydrolysis or the volume of residual hydrogen. Phosphine was determined by the decrease in volume on treatment with 0.1 *N* silver nitrate solution.

Preparation of Diborane.—Diborane was prepared by the method of Schlesinger and Burg[9] as modified by Stock and Sütterlin.[10] Hydrogen saturated with boron tri-

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[6] A. Besson, *Compt. rend.*, **110**, 516 (1890), originally prepared this compound by the reaction of equal volumes of gaseous boron trichloride and phosphine below 20°.

[7] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, 1933, p. 125; E. Wiberg, *Ber.*, **69**, 2816 (1936).

[8] H. I. Schlesinger and his co-workers, particularly A. B. Burg, have published twelve papers on the Hydrides of Boron in THIS JOURNAL, the last of which is **61**, 1078 (1939).

[9] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **53**, 4321 (1931).

[10] A. Stock and W. Sütterlin, *Ber.*, **67B**, 407 (1934).

bromide at 25° was passed through an electric arc 7 cm. in length at a pressure of 10 mm., and a rate of 500 cc. per minute.[11] The arc produced by a 10,000 volt, 500 volt-ampere transformer proved to be 50% more efficient for the ultimate yield of diborane than the arc produced by a 25,000 volt, 1000 volt-ampere transformer. Yields of 16 cc. of gaseous diborane per cc. of liquid boron bromide (measured at 0°) were obtained. About 85% of the BBr_3 used passed through the arc unchanged.

Preparation of Diborane Diphosphine.—When a mixture of diborane and phosphine was kept at a temperature of −20 to 0°, the pressure slowly decreased over a period of eight to fourteen hours, and long, white, crystalline needles were formed filling the void of the reaction tube. With the reaction tube cooled to −78°, the gases which did not take part in the reaction were pumped out and analyzed. The composition of the residue in the reaction tube, determined by fourteen experiments, is described by the formula $B_2H_6{\cdot}(2.00 \pm 0.04)PH_3$. In a typical preparation, 15.0 cc. of diborane and 39.2 cc. of phosphine with an initial pressure of 1.8 atmospheres at 0° produced in six hours a yield of 92% of diborane diphosphine. Neglecting 1.3 cc. of hydrogen formed during this time, the composition of the product was $B_2H_6{\cdot}2.02PH_3$.

The degree to which the reaction takes place is influenced mostly by pressure, an increase from 0.6 to 6.0 atmospheres increasing the yield of product from 72 to 98%. The rate of reaction is also markedly influenced by pressure; at 0° after two to three hours the pressure in the reaction tube is quite independent of the original pressure of the reactants. High concentrations of phosphine and long time of reaction are favorable factors for high yields. The extent of secondary decomposition is increased by high temperatures and long periods of reaction.

Liquid diborane does not react with liquid phosphine at an appreciable rate much below −110°, but above that temperature liquid phosphine reacts within two or three hours with either gaseous or liquid diborane. When insufficient pressure of phosphine is left to maintain the liquid phase, the reaction apparently ceases. For this reason, the temperature should be kept as low as possible to reduce the vapor pressure of the phosphine, and the quantity of unreactive material in the gas phase without reducing the rate of reaction to too great a degree. Using a tube of 6 cc. volume, containing 25.9 cc. of diborane and 60.8 cc. of phosphine at −100°, a yield of 98% in three hours reaction time was obtained. The composition of the product is described by the formula $B_2H_6{\cdot}2.01PH_3$.

Of the two sets of conditions which have been used to prepare diborane diphosphine, the low temperature reaction is the more desirable, because of the increased rate and the elimination of any side reactions in which hydrogen is formed.

Diborane diphosphine dissociates to form one volume of diborane and two volumes of phosphine. An equilibrium exists which can be approached from either side.

$$B_2H_6{\cdot}2PH_3 \rightleftharpoons B_2H_6 + 2PH_3$$

At 0°, this pressure is about 200 mm. Other pressure measurements include: at +25°, 1400 mm.; at −11°, 71 mm.; and at −21°, 11 mm. Since the time required for equilibrium to be established is unusually long, and considerable quantities of hydrogen are formed by secondary decomposition during this time, the precision of the measurements of pressure is quite low.[12]

Pyrolysis of Diborane Diphosphine.—A mixture of 63.6 cc. of PH_3 and 33.9 cc. of B_2H_6 was stored overnight at 0° to form diborane diphosphine in equilibrium with its gaseous constituents. An electric sleeve furnace preheated to 200° and calibrated to maintain that temperature was placed around the reaction tube for fifteen minutes. The tube was cooled to −195°, and 76.7 cc. of hydrogen pumped out. Warming to −77°, 10.5 cc. of a mixture of diborane and phosphine was pumped off. On warming to room temperature, no more gas was evolved. The residue in the tube was a yellowish-white, greasy-looking solid covering the walls of the tube. Under comparable conditions, the pyrolysis of diborane diammine produces up to 40% of $B_3N_3H_6$.

Diborane Diphosphine and Ammonia.—While the solid diborane diphosphine dissolves with difficulty[13] in liquid ammonia at −75° with no apparent reaction, at higher temperatures the rate of solution is quite rapid, and phosphine is evolved. The evolution of phosphine was followed by cooling the tube to −78° and pumping off the phosphine together with some ammonia. At the end of the experiment, the solvent ammonia was pumped off completely. The results of the reaction are shown in Table I. The quantities of diborane diphosphine and ammonia used are expressed as cc. of gas. The fraction of the total phosphine given off in the reaction is expressed as per cent. evolved. The ratio of the sum of the ammonia introduced plus the phosphine calculated to be left in the compound, to the diborane in the compound, is shown in the eighth column. The last column shows the volume of hydrogen evolved; this is a measure of the secondary decomposition during the reaction.

The reaction of gaseous ammonia and diborane diphosphine is in all probability complicated by the decomposition of diborane diphosphine into diborane and phosphine, and thus by the possibility of direct reaction taking place between diborane and ammonia in the gas phase. It is also possible that the formation of phosphine in excess of 50% in the reaction with liquid ammonia is due to this reaction. Part B of Table I shows the results of the gas phase reaction.

Diborane Phosphine Ammine.—The product of the reaction of liquid ammonia on diborane diphosphine is best expressed as $B_2H_6{\cdot}PH_3{\cdot}NH_3$ although the analysis is not exact. The sum of the phosphine plus the ammonia bears the correct relation to the formula.

Pyrolysis of Diborane Phosphine Ammine.—A sample containing 24.1 cc. of diborane, 22.0 cc. of phosphine and

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(11) All volumes referred to in this paper are at standard conditions of temperature and pressure.

(12) The slowness with which this equilibrium is established may very well be due to the reaction involving the borine molecule ($B_2H_6 \rightleftharpoons 2BH_3$) as has been suggested by Schlesinger and Burg[2] for the formation of diborane diammine.

(13) At a temperature just above the melting point of ammonia, 0.079 g. of diborane diphosphine (18.4 cc. B_2H_6 and 37.1 cc. PH_3 as gases) dissolve appreciably in 0.285 g. of liquid ammonia (375.8 cc. of gas) in twenty-nine hours. Solution is complete in forty-eight hours.

TABLE I

REACTION OF AMMONIA AND DIBORANE DIPHOSPHINE

Expt.	B_2H_6, cc.	PH_3, cc.	NH_3, cc.	Temp., °C.	Time	% PH_3 evolved	$\frac{NH_3 + PH_3}{B_2H_6}$	H_2 evolved, cc.
A. Liquid Phase Reaction								
1	19.9	39.7	155.0	0	20 min.	56		0.1
				20	5 days	56	2.00	1.0
2	21.0	42.8	162.4	0	20 min.	52		0.2
				20	5 days	52	2.01	1.0
3	22.2	43.5	154.6	−25	40 min.	50		
				+25	1 hr.	54	2.07	0.6
4	23.3	43.8	162.2	−33	1 day	38		
					2 days	51		
					3 days	53		
				+25	3 days	58	2.12	2.0
B. Gas Phase Reaction								
1	46.5	92.1	85.8	−33	3 days	21		
			27.6	+20	24 hrs.	73	2.04	41.3
2	45.4	87.9	163.4	0	40 hrs.	63	2.04	28.5
3	41.5	81.9	103.5	0	3 min.	31		
					24 hrs.	75	2.04	27.7
4	13.6	27.6	51.8	0	5 min.	60		0.1
				20	3 mo.	63	2.01	7.6

21.3 cc. of ammonia was heated in a sealed tube to 200° for fifteen minutes; 90.4 cc. of hydrogen and 2.1 cc. of $B_3N_3H_6$ were formed, while 1.5 cc. of phosphine, 0.2 cc. of B_2H_6 and 0.5 cc. of NH_3 were left unreacted. The vapor pressure of the $B_3N_3H_6$ was 79 mm. at 0° as compared with the reported value of 85 mm. at 0°. Thus, about 30% of the nitrogen in the diborane phosphine ammine was converted to the cyclic compound.

Reaction of Hydrogen Chloride on Diborane Diphosphine.—The results of the reaction of hydrogen chloride on solid diborane diphosphine are shown in Table II. The volume of the reactants is shown in the second, third and fourth columns, while the hydrogen produced and the hydrogen chloride introduced are shown in the last two columns.

Soon after one mole of hydrogen chloride is introduced into diborane diphosphine, the product begins to liquefy. When liquefaction is complete the product has the empirical composition $B_2H_4Cl_2 \cdot 2PH_3$. On addition of more hydrogen chloride, a mixture of solid and liquid is obtained, and when the composition is $B_2H_2Cl_4 \cdot 2PH_3$, it is completely solid. On further reaction with hydrogen chloride, the product can be converted completely into $BCl_3 \cdot PH_3$. When $BCl_3 \cdot PH_3$ is treated with diborane, a liquid containing boron, hydrogen, chlorine and phosphorus is obtained, but its composition could not be established definitely. When a tube containing $B_2H_2Cl_4 \cdot 2PH_3$ is heated rapidly the solid melts about 68° with decomposition. On warming the tube to 100° for an hour, a liquid is formed, and crystals of $BCl_3 \cdot PH_3$ sublime

TABLE II

REACTION OF HYDROGEN CHLORIDE ON DIBORANE DIPHOSPHINE

Expt.	B_2H_6, cc.	PH_3, cc.	HCl, cc.	Temp., °C.	Time, hr.	Press., atm.	$\frac{HCl}{B_2H_6}$	$\frac{H_2 \text{ evolved}}{B_2H_6}$
1	17.7	34.3	38.2	− 26	12	0.2	2.02	1.95
			89.7	− 20	6	0.3		2.92
				+ 25	1		4.00	3.68
2	22.2	44.4	50.8	− 77	24	4.5		1.07
				− 20	0.7	4.0	2.01	1.89
				0	12	0	2.01	2.33
3	10.2	20.2	73.0	− 20	10	3.0		2.93
				+ 25	1		4.05	3.96
4	18.8	37.6	74.9	− 77	2	4.0		0.85
				− 33	0.3	4.5		2.54
					17	1.7		3.30
				0	1	1.2		3.85
				100	1	0	4.00	4.59
5	19.5	39.5	78.1	− 33	2	4.0		1.78
					15	3.5		2.50
				0	72	0	4.00	4.00

to the top of the tube. Small amounts of hydrogen are formed at the same time.

Density of $BCl_3 \cdot PH_3$ in the Gas Phase.—40.3 cc. of $BCl_3 \cdot PH_3$ weighs 0.1230 g. The calculated weight of this volume of gas, if complete dissociation is assumed, and the product acted as a perfect gas, would be 0.1340 g.

Decomposition Pressure of $BCl_3 \cdot PH_3$.—The pressure of $BCl_3 \cdot PH_3$ was determined between −11 and +25°, the results being expressed by the equation $\log p = 11.137 - 2810/T$. The maximum deviation of the observed from the calculated pressures does not exceed 0.5 mm.

Reaction of Hydrogen Bromide on Diborane Diphosphine.—Hydrogen bromide reacts in much the same way as hydrogen chloride, the reaction of liquid hydrogen bromide at −78° taking place very rapidly.

Summary

1. Diborane and phosphine react to form a white unstable solid. The reaction takes place in the gas phase above −30° and in the liquid phase above −110°. The properties of the substance were studied and its probable structure discussed.

2. The action of ammonia on diborane diphosphine has been investigated over a temperature range of −75 to +25°. Liquid ammonia has been found to displace from 52 to 58% and gaseous ammonia up to 75% of the phosphine in diborane diphosphine.

3. The action of hydrogen chloride and hydrogen bromide on diborane diphosphine was found to result in the splitting out of hydrogen attached to boron. The compounds $B_2H_4Cl_2 \cdot 2PH_3$, $B_2H_2Cl_4 \cdot 2PH_3$ and $BCl_3 \cdot PH_3$ have been obtained by this reaction.

4. Attempts to prepare a volatile compound $B_3P_3H_6$, the analog of the cyclic compound $B_3N_3H_6$, were unsuccessful.

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Dipole Moment, Induction and Resonance in Tetra-, Penta- and Hexa-substituted Benzenes

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The dipole moments of a great many poly-substituted benzenes have been measured by numerous investigators, but the loan by Dr. S. O. Morgan of the Bell Telephone Laboratories of fourteen such compounds, only one of which had been previously measured, has given us an unusual opportunity for the study of a large number of closely related compounds obtained from a single source. In the cases of most of the poly-substituted benzenes, departures of the moments from the values calculated as the resultants of the moments produced by the individual substituents have been attributed to mutual repulsion between adjacent atoms, which has since been shown by X-ray and electron diffraction to produce little distortion in most cases, and to mutual induction between adjacent groups, which calculation has shown to be sufficient to account for the observed discrepancies. More recently, the development of our ideas of resonance has brought the explanation not only of differences in moment between mono-substituted aromatic and aliphatic hydrocarbons, but also of a few seeming discrepancies in the moments of poly-substituted benzenes not previously accounted for. Although Groves and Sugden[1] have refined the method of calculating the inductive effect of a dipole upon the various atoms of the molecule containing it, the calculation retains the fundamental uncertainty inherent in the treatment of a distribution of charges as a single dipole located at a point and in the decision as to the proper location of this point. This uncertainty is serious only in calculating the inductive effects of the dipole upon the immediately adjacent atoms, but it is just these effects which make up the major part of the inductive shifts produced by the dipole. Although reasonable and, at times, very satisfactory results have been obtained on the basis of plausible assumptions in both the more and the less refined calculations, the inductive effect will be treated here in an empirical manner, rendered convenient by the number of but slightly differing compounds under examination.

Consideration of the moments obtained in the present work, like that of nearly all poly-substituted benzenes previously treated, loses a certain amount of precision because of the solvent effect, as the low volatility of the substances has

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[1] Groves and Sugden, *J. Chem. Soc.*, 1992 (1937).