[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF CORNELL UNIVERSITY]

The Reactions of Decaborane with Dimethylamine

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Adducts containing 1, 2, and 3 moles of dimethylamine per mole of decaborane have been prepared and characterized by their X-ray powder diffraction patterns and by their ability to release decaborane upon treatment with acid. Phase studies have provided evidence for the existence of the tetra- and pentaminates. At about 0° or above the aminates undergo an aminolytic reaction, probably involving the loss of BH_3 groups from the B_{10} skeleton of $B_{10}H_{14}$, producing a material which appears to form a B_9 amide upon acid treatment.

Little information is available on the acceptor properties of decaborane, $B_{10}H_{14}$, although ammonia and amine addition compounds of B_5H_9,[2] B_4H_{10}[3] and B_2H_6[4] have been studied. Stock[5] reported that $(NH_3)_6{\cdot}B_{10}H_{14}$ was formed by the evaporation of a liquid ammonia solution of decaborane and that the adduct decomposed reversibly at room temperature leaving "but slightly changed" decaborane. Schaeffer[6] and Toeniskoetter have found hexa-, tetra- and triammoniates, and have some evidence for penta-, di- and monoammoniates. Burg[2] has mentioned that decaborane behaves similarly to B_5H_9 in its reaction with trimethylamine, but he gave no details. B_5H_9 takes up two molecules of trimethylamine and at higher temperatures yields two molecules of $Me_3N:BH_3$ plus a BH polymer. With quinoline,[7] decaborane forms a 1:1 adduct which is used for the colorimetric analysis of decarborane.

In our work the reactions of dimethylamine with decaborane were selected for study because dimethylamine, being a stronger electron pair donor than ammonia, was expected to form more stable addition compounds than ammonia. In this paper the compositions of the adducts will be specified by two numbers separated by a colon, indicating, respectively, the number of moles of dimethylamine per mole of decaborane, *e.g.*, 2:1 stands for $(Me_2HN)_2{\cdot}B_{10}H_{14}$.

Experimental

Purification of Materials.—Crude decaborane of about 95% purity was purified by high vacuum sublimation at room temperature. Dimethylamine, supplied by the Matheson Company, was of 98.2% purity and was dried with barium oxide before use. The experiments were performed in a glass high vacuum system or in an atmosphere of dry nitrogen.

Analysis.—Samples were dissolved in a water–sulfuric acid–methanol mixture, and aliquots were analyzed for dimethylamine by Kjeldahl distillation. Aliquots taken for boron analysis were evaporated nearly to dryness with excess sodium hydroxide, oxidized by adding concentrated nitric acid very cautiously to avoid the loss of boron-containing fumes and titrated in the presence of mannitol.

The General Reaction of Dimethylamine with Decaborane.—When solid $B_{10}H_{14}$ is treated with amine a series of aminates tends to form.

$$B_{10}H_{14} + nMe_2HN = (Me_2HN)_n{\cdot}B_{10}H_{14}$$

A large excess of amine will favor complete reaction of the solid decaborane so that it will not be present in the solid product. However, the presence of excess amine favors aminolysis and the formation of solid aminolytic products which contaminate the aminates. By working at low temperatures where aminolysis does not occur, excess amine can be used to produce the higher aminates. When these higher aminates are warmed, amine and lower aminates are formed. If the temperature and amine concentration are maintained sufficiently low, aminolysis can be avoided; slow aminolysis occurs at 0° (but not at −15°) in excess liquid amine and at room temperature under an amine pressure of a few mm. Hg. The use of a solvent favors the rapid and complete conversion of decaborane to a mixture of the 2:1 and 3:1, but the mixture must be chilled or converted to pure 2:1 to avoid aminolysis at room temperature.

Preparation of Dimethylamine Decaborane, $Me_2HN{\cdot}B_{10}H_{14}$.—Dimethylamine (0.14 mole) was treated with 0.019 mole of decaborane at −78° for 30 hr., forming a voluminous white solid. This product was pumped at −78° and as it warmed slowly to nearly room temperature, thereby converting higher aminates to the 2:1. No sublimate formed on the −78° cold finger of the reactor as the sample was pumped and heated slowly to 58°, thus demonstrating the absence of volatile **1**:1 and decaborane in the product at that temperature. Sublimation with pumping for 12 hr. at 65° produced about 3 g. of white 1:1, leaving a yellow aminolyzed residue.

Analysis of Sublimate.—Calculated for $Me_2HN{\cdot}B_{10}H_{14}$: Me_2HN, 26.9; $B_{10}H_{14}$, 73.1. Found: Me_2HN, 28.5, 28.8 and 28.9; $B_{10}H_{14}$, 70.7, 71.4, 70.9 and 71.0. Empirical composition, $(Me_2HN)_{1.09}{\cdot}B_{10}H_{14}$.

The sublimate gave a distinct X-ray powder pattern which is listed in Table I, and the residue gave a pattern characteristic of aminolytic products of decaborane.

Other and less satisfactory means of preparing the 1:1 are (1) the reaction of gaseous dimethylamine in nitrogen with excess decaborane in very dilute solution in dry heptane, (2) the reaction of gaseous dimethylamine in nitrogen with decaborane vapor in nitrogen, (3) the incomplete reaction for 4 hours at −78° between solid decaborane and excess liquid dimethylamine, and then removal of the amine by pumping as the sample warmed to room temperature and separation of the 1:1 and unreacted decaborane from the 2:1 by room temperature vacuum sublimation. No hydrogen was formed in these reactions, indicating that the 1:1 is an aminate rather than an amide.

At room temperature the 1:1 is insoluble in benzene, cyclohexane, chloroform or ether, and is soluble, apparently with decomposition, in water, aqueous ammonia, methanol, acetone, acetophenone or ethyl acetate. It slowly gains weight and becomes yellow in air, and it reacts explosively with concentrated HNO_3. When heated, the 1:1 decomposes to a gas and a viscous yellow liquid at about 96°.

Preparation of Bis-(dimethylamine)-decaborane, $(Me_2HN)_2{\cdot}B_{10}H_{14}$.—Excess gaseous dimethylamine, diluted with nitrogen, was passed through 0.6 g. of decaborane dissolved in 80 ml. of dry heptane at 0°. The white solid which formed was filtered in the reactor and washed with dry pentane. Dry nitrogen was passed through the reactor for 17 hr. at room temperature to evaporate the adhering solvent and to remove the amine released in the conversion of the 3:1 to the 2:1. The reactor came to a

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[1] Abstracted from Ph.D. thesis submitted by S. J. Fitch, Feb. 1958. Monsanto Chemical Co., St. Louis, Mo.

[2] (a) A. B. Burg, *Rec. Chem. Prog.*, **15**, No. 4, 158 (1954); (b) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 123.

[3] (a) R. W. Parry and G. Kodama, THIS JOURNAL, **79**, 1007 (1957); (b) A. B. Burg and F. G. A. Stone, *ibid.*, **75**, 228 (1953); (c) W. V. Hough, M. D. Ford and L. V. Edwards, "Abstracts of Papers," 132nd Meeting, American Chemical Society, September, 1957.

[4] (a) S. H. Bauer, *Encyclopedia of Chem. Tech.*, First Supplementary Volume, 103 (1957); (b) F. G. A. Stone, *Quart. Rev.*, **9**, 184 (1955).

[5] A. Stock and E. Pohland, *Ber.*, **62B**, 90 (1929).

[6] George W. Schaeffer, private communication.

[7] W. H. Hill and M. S. Johnson, *Anal. Chem.*, **27**, 1300 (1955).

TABLE I

X-RAY POWDER DIFFRACTION DATA

$Me_2HN\cdot B_{10}H_{14}$		$(Me_2HN)_2\cdot B_{10}H_{14}$		$(Me_2HN)_3\cdot B_{10}H_{14}$	
d-Spacing, Å.	Intensity	*d*-Spacing, Å.	Intensity	*d*-Spacing, Å.	Intensity
7.03	S	7.31	s	7.50	vw
6.30	vw	6.34	vs	7.32	vw
5.64	vs	5.82	s	6.89	m
4.59	vs	4.78	vvs	6.30	s
4.40	vs	4.53	vvs	5.87	vw
4.03	w[a]	4.31	w	5.34	vvs
3.66	w	3.92	vvs	4.85	vvw
3.48	w	3.58	m	4.43	vs
3.10	w	3.53	vw	4.22	m
2.91	m[a]	3.21	vw	3.99	vs
2.71	m	2.94	vvw	3.64	vs
2.63	m	2.46	vvw	3.50	vvw
2.40	w			3.34	w
				3.20	w
				2.94	w
				2.86	vvw
				2.44	vvw
				2.19	vvw
				2.09	vw

[a] Broad.

constant weight corresponding to a product composition of $(Me_2HN)_{2.005}.B_{10}H_{14}$.

Anal. Calcd. for $(Me_2HN)_2\cdot B_{10}H_{14}$: Me_2HN, 42.44; $B_{10}H_{14}$, 57.56. Found: Me_2HN, 41.4, 41.5, 42.8; $B_{10}H_{14}$, 57.5.

The X-ray pattern is given in Table I.

The 2:1 also can be prepared in very high purity and quantitative yield by the reaction at −45° between solid decaborane and excess liquid amine, followed by removal of excess amine at −45° and then at room temperature. The evolved amine was found to be free of hydrogen.

The solubilities and thermal decomposition of the 2:1 are very similar to those described for the 1:1.

Preparation of Tris-(dimethylamine)-Decaborane, $(Me_2HN)_3\cdot B_{10}H_{14}$.—Solid products having an X-ray pattern attributed to the 3:1 (Table I) and compositions of 2.91:1 and 2.71:1 were made by the reaction of solid decaborane with liquid dimethylamine and by the reaction of decaborane dissolved in isopentane with gaseous dimethylamine, but phase studies demonstrate the existence of the 3:1 much more clearly. The 3:1 undergoes a slow aminolytic degradation when stored at room temperature.

Phase Studies.—Attempts to determine the pressure-composition phase diagrams at 25 or 0° by adding increments of dimethylamine to solid decaborane or to decaborane dissolved in heptane were unsuccessful because of the slow approach to equilibrium under those conditions. However, when excess dimethylamine was added to decaborane at −15° or below, the products were formed as voluminous solids which exposed the underlying decaborane to further reaction and permitted the reaction to go to completion in a relatively short time. Therefore, phase studies were performed by adding a measured excess of dimethylamine to a known amount of decaborane at constant temperature and withdrawing the excess amine to a trap at a lower temperature until the residual sample reached a constant composition. The aminate which had formed was identified by determining the amount of amine which had been withdrawn, and then the sample temperature was increased or the collection temperature was decreased in order to form the next lower aminate. Success of the method depended on a choice of suitable sample and collection temperatures for forming the various aminates in a reasonable length of time.

The initial excess of amine was measured out at the same values of *P*, *V* and *T* in each run, the amount which would be so obtained being accurately checked beforehand by titration with standard acid.

The amounts of amine withdrawn from the sample in successive withdrawals were estimated by *P*-*V*-*T* readings; when the sample had reached a constant composition the combined withdrawals were identified tensiometrically as being dimethylamine and were titrated to determine accurately the composition of the residual solid. The amine withdrawn from the samples always could be condensed completely at −196°, thereby showing the absence of hydrogen evolution in the aminate formation. The data are given in Table II.

TABLE II

RECORD OF WITHDRAWALS OF AMINE FROM SAMPLE

	Run A	Run B
Mmoles of Me_2HN	9.94_7	9.94_1
Mmoles of $B_{10}H_{14}$	1.340	1.181
Mole ratio Me_2HN to $B_{10}H_{14}$	7.42_3:1	8.41_7:1
Time of initial reaction, hr.	58	59
Temp. of initial reaction, °C.	−15	−63

Run A

	Conditions for successive amine withdrawals				
No.	Sample temp., °C.	Collection temp., °C.	Collection time, hr.	Moles Me_2HN withdrawn per mole $B_{10}H_{14}$ in reactor (by *P*-*V*-*T*)	Composition of residual solid (by titration)
1	−15	−78	8	4.41	
2	−15	−78	48	0.01	
3	−15	−78	40	.0001	3.00_7:1
Held for 16.5 hr. at 0° without collection of amine					
4	0.0	−78	26	0.011	2.99_6:1
5	0.0	−78	18	.0006	
6	0.0	−196	8	.45	
7	23	−78	24	.46	
8	23	−78	21	.05	
9	27.0	−78	24	.01	
10	27.0	−78	22	.0001	2.02_5:1
11	Max. 28	−78	44	.0003	
Run B					
1	−63	−78	48	3.45	
2	−63	−78	11	0.013	
3	−63	−78	42	.003	
4	−63	−78	23	.093	4.92_8:1
5	−63	−78	28	.0001	
6	−63	−78	19	.002	
7	−63	−196	10	.81	
8	−63	−196	24	.19	
9	−63	−196	12	.04	3.87_0:1
10	−63	−196	5	.05	
11	0.0	−78	16	.76	
12	0.0	−78	24	.06	
13	0.0	−78	24	.02	
14	0.0	−78	40	.002	3.03_0:1
15	30.0	−78	32	.95	
16	46	−78	12	5×10^{-7}	2.04_4:1

Run A.—Formation of the 3:1 is clearly shown by the rapid amine loss in withdrawal 1 and subsequent negligible loss in 2 and 3. Increasing the sample temperature to 0° (4 and 5) did not alter the composition appreciably, showing that the decomposition pressure of the 3:1 at 0° is less than about 2.5 mm., the vapor pressure of dimethylamine at the trap temperature of −78°. However, its decomposition pressure is appreciable at 0°, as shown by the rapid amine loss to the −196° trap in 6. Its decomposition pressure is greater than 2.5 mm. at 23°, and conversion of 3:1 to 2:1 is shown in 6 to 11. The sample remaining after 11 gave the 2:1 X-ray pattern and the analysis: Me_2HN, 42.15; $B_{10}H_{14}$, 57.56. Calculated for 2:1: Me_2HN, 42.44; $B_{10}H_{14}$, 57.56.

Run B.—Following a rapid amine loss during withdrawal 1, the formation of a stable phase with a composition close to 5:1 is shown in withdrawals 2 to 6. After the collection temperature was reduced to −196° in 7, the amine loss was rapid during withdrawals which included compositions greater than 4:1 (withdrawals 7 and 8), but slow when the compositions were less than 4:1 (withdrawals 9 and 10).

This suggests that a 4:1 adduct could have been prepared by collection of amine in a trap at, say, −100°. Formation of the 3:1 is shown in 11 to 14, and the 2:1, in 15 and 16. Analysis of the residual solid from 16: Me_2HN, 44.03; $B_{10}H_{14}$, 57.16, 56.57. The slightly high amine content is attributed to an aminolytic reaction such as was observed in the 1:1 formation at 65°. Other evidence indicates that aminolysis of the 2:1 occurs upon the addition of amine above 0°. The X-ray pattern of the sample from 16 showed, in addition to the 2:1 pattern, a weak line which matches a strong line of the aminolytic products.

Recovery of Decaborane from its Aminates.—When a benzene or heptane suspension of the 1:1, 2:1 or 3:1 is treated with aqueous hydrochloric acid, decaborane is regenerated and extracted by the hydrocarbon layer, from which it can be recovered in high yields by evaporation of the solvent. Concurrent decomposition of the decaborane with hydrogen evolution eliminates hope of recovering it quantitatively by this method.

Aminolytic Products.—Repeated experiments have shown that when solid decaborane in excess liquid amine is warmed to 0° or slightly above, the solid aminate which is present under those conditions suffers an aminolytic attack which apparently results in the partial destruction of the B_{10} framework of the molecule. No hydrogen is evolved in the reaction, and the aminolytic products are formed as a dense, immiscible liquid layer which covers the unreacted solid and causes the reaction to become quite slow. The conditions for the reaction are not critical, but the composition of the white solid remaining after the evaporation of excess amine depends on the method of amine removal; values for the atomic ratio of boron:nitrogen ranging from 3.31 to 4.17 have been obtained. The products give a reproducible X-ray pattern, but those formed at higher temperatures show marked differences in the relative intensities of some lines. On pyrolysis under vacuum between about 73 and 109° the aminolytic products lose hydrogen, amine and a small amount of colorless volatile solid. Evolution of hydrogen and amine resumes at about 207°, and there is left a yellow resin of high boron content which continues to lose hydrogen slowly above 500°.

Acid-treated Aminolytic Products.—When the aminolytic products are treated with aqueous acid, decaborane is not regenerated, but hydrogen evolution occurs and a material which may be called an "amide" is formed.

In a typical experiment the aminolytic products were formed by condensing excess dimethylamine on 2.8 g. of $B_{10}H_{14}$ at −78° and agitating the mixture at about the boiling point of the amine, 6.9°, until all solids had reacted. The excess amine was evaporated in a stream of dry nitrogen at room temperature. The solid which remained was cooled slightly by a brief immersion in a Dry Ice bath and 160 ml. of methanol was added, apparently without effect. When 70 ml. of 3 *N* H_2SO_4 was added and the cold mixture was warmed slightly, the solid dissolved with hydrogen evolution, forming a clear solution which was then evaporated without protection from air. As the solution became more concentrated and its boiling point increased, a solid formed, melted and floated to the surface where it solidified upon cooling. This solid product melts at about 97°, is soluble in organic solvents, reacts explosively with concentrated nitric acid, gives a reproducible X-ray pattern and is slightly volatile. Attempts to purify the "amide" by sublimation, recrystallization and chromatography were unsuccessful because of the continuing formation of another solid. Different samples have been obtained with boron:nitrogen atomic ratios of 9.45, 9.12 and 9.07. The substance may be a B_9 amide.

Discussion

The 1:1 adduct appears to be a donor–acceptor molecule since it can be sublimed at room temperature; if it were the dimethylammonium salt, $(Me_2H_2N)^+(B_{10}H_{13})^-$, it would be much less volatile. It apparently sublimes without dissociation, for it can be sublimed with constant pumping from a flask maintained at 33° to the cooler walls of the flask. The reaction of solid decaborane with gaseous dimethylamine is very slow at room temperature, and if the 1:1 adduct dissociated during sublimation with pumping, much of the amine would undoubtedly be lost and the sublimate would contain a larger fraction of decaborane. There is no evidence as to whether the higher aminates are molecular addition compounds or dimethylammonium salts.

The evidence for the existence of the 4:1 and the 5:1 is not completely convincing, but it is supported by the existence[6] of 4:1, 5:1 and 6:1 adducts with ammonia.

In analogy to the aminolysis of the other boranes, one may speculate that the aminolysis of decaborane involves the removal of one or two BH_3 groups by the amine, leaving B_9H_{11} or B_8H_8 residues. These could then be stabilized by coördination to other amine molecules, as is the $Me_3N:B_3H_7$ residue[3c] from the aminolysis of B_4H_{10}. Formation of a B_9 amide by acid treatment of the aminolytic products would be in accordance with their formulation as amine-stabilized B_9H_{11}. The justifications for considering the product from the acid treatment to be a B_9 amide are (1) hydrogen is lost in its formation, and atomic ratio of boron to nitrogen in the material is approximately 9:1, (2) it cannot be an aminate since its nitrogen is not lost to hot aqueous acid, (3) it cannot be a dimethylammonium salt since it is insoluble in the aqueous acid and (4) it cannot be an imide since two of the positions about the nitrogen atom are blocked by methyl groups.

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