[Contribution from the John Harrison Laboratory of Chemistry, University of Pennsylvania]

The Interaction of Disiloxane with Aluminum Halides[1]

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$(SiH_3)_2O$ has been shown to react rapidly with $(CH_3)_4Al_2Br_2$ to give the new volatile "electron-deficient" compound $(CH_3)_4Al_2(OSiH_3)_2$. Disiloxane reacts at low temperatures with aluminum halides to give the corresponding silyl and silylene halides and monosilane.

During recent years, much interest has been shown in simple compounds containing the SiH_3 or "silyl" group,[2-7] which may be regarded as the inorganic analogs of methyl compounds. Recent work by Emeléus and Onyszchuk[5] has shown that disiloxane or "disilyl ether," $(SiH_3)_2O$, reacts rapidly at low temperatures with BF_3 and BCl_3 to give SiH_3OBF_2 and SiH_3OBCl_2, respectively. Voronkov, Dolgov and Dmitrieva[8] have demonstrated that $[(CH_3)_3Si]_2O$ and aluminum halides react on heating at approximately 100° to give $(CH_3)_3SiX$ (X = Cl, Br or I).

The present communication describes the reaction of disiloxane with $(CH_3)_4Al_2Br_2$, Al_2Cl_6, Al_2Br_6 and Al_2I_6.

Experimental

Apparatus.—All work was carried out in a Pyrex glass vacuum system. Stopcocks were lubricated with Apiezon N grease in preference to Silicone grease in order to eliminate the possibility of foreign silicon compounds appearing through attack on the grease by the substances handled.

All pressure readings (as in molecular weight or vapor pressure determinations) were made with a glass bourdon gauge in order to eliminate contamination and possible reaction of compounds with mercury. An all-glass apparatus involving no ground glass joints or stopcocks was employed when determining the vapor pressure of $(CH_3)_4Al_2(OSiH_3)_2$.

Capillary melting point tubes were filled by condensing compounds in the tubes while attached to the vacuum system and then sealing them off.

All temperatures below 0° were measured by an iron-constantan thermocouple, which was calibrated by comparison with an iron–constantan thermocouple standardized by the National Bureau of Standards.

Disiloxane.—This was prepared by the hydrolysis of SiH_3I,[9] which was itself prepared from SiH_4 and HI.[9] The purity of the disiloxane used was checked by determining its molecular weight (found, 78.0; calcd., 78.2) and its vapor pressure at −63.5° (found, 63.4 mm.; literature value, 63.5 mm.[10]). Its infrared spectrum was identical with that given previously.[11]

Aluminum Halides.—Commercial reagent grade Al_2Cl_6 and Al_2Br_6 were used without further purification. Al_2I_6 was prepared from aluminum and iodine,[12] and $(CH_3)_4Al_2Br_2$, from aluminum and methyl bromide.[13]

Experimental Procedure.—All handling of the Al_2X_6 compounds was carried out in a nitrogen-filled dry box. The $(CH_3)_4Al_2Br_2$ was handled exclusively in the vacuum system. Weighed amounts of aluminum halide were transferred to approximately 30-cc. glass tubes (Apparatus A) which were then attached to the vacuum system. Weighed amounts of disiloxane were distilled in at −196°; the tubes were then sealed off and brought to the desired temperature conditions during the course of the reactions. All the volatile contents of the reaction tubes were then transferred to the vacuum system, separated by conventional methods of fractional condensation in, or distillation from, cold baths, and identified and weighed. Glass reaction tubes containing a ground glass joint and a stopcock (Apparatus B) were used in place of Apparatus A in some experiments.

The experimental results are given in detail below and are summarized in Table I.

Table I

Reaction of Disiloxane with Aluminum Halides[a]

Note: Values enclosed in parentheses are for yields obtained on reaching room temperature. Values not enclosed are final yields.

Reaction no.	Compd.	Al_2X_6[b] present	SiH_3X	SiH_2X_2	SiH_4	Recovery of Si,[c] %
1	$(CH_3)_1Al_2Br_2$	0.606	(0.967)	.....	.....	(95.0)
2	Al_2I_6	1.241	(.718)	(0.00)	(0.218)	(46.8)
			.913	.258	.426	79.9
3	Al_2I_6	0.253	(.646)	(.00)	(.324)	(48.5)
4	Al_2Br_6	.954	(.297)	(.453)	(.836)	(79.3)
			.297	.639	.836	88.6
5	Al_2Br_6	.358	(.907)	(.00)	(.101)	(50.4)
			1.112	.00	.309	71.0
6	Al_2Br_6	1.020	(0.333)[d]	(.00)[d]	(.167)[d]	(25.0)[d]
			(.184)	(.231)	(.512)	(46.5)
			.515	.534	.679	86.4
7	Al_2Cl_6	0.899	(.222)	(.447)	(.743)	(70.6)
			.328	.514	1.048	94.5
8	Al_2Cl_6	0.214	(.809)	(.00)	(0.196)	(50.2)

[a] The data reported in columns 4–7 are the quantities of products recovered based on one mole of $(SiH_3)_2O$ consumed. [b] Quantity of aluminum halide initially present in each reaction per mole of $(SiH_3)_2O$ consumed. [c] Percentage of silicon in the $(SiH_3)_2O$ consumed which was recovered in volatile compounds. [d] Quantities recovered at −65°.

Reaction 1. $(CH_3)_4Al_2Br_2$ **and** $(SiH_3)_2O$.—$(CH_3)_4Al_2Br_2$ (0.720 mmole) and $(SiH_3)_2O$ (3.151 mmoles) were combined in an apparatus of type "B" at −50°. It was observed that a solid adduct was produced at this temperature since the liquid $(SiH_3)_2O$ and $(CH_3)_4Al_2Br_2$ formed a solid on contact. At −20° this changed to a liquid which could not be resolidified by cooling to −30°. It appeared therefore that some decomposition of the initial product had occurred on warming.

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All volatiles were removed from the reaction vessel at −40°. These could not be separated quantitatively, but a small amount of pure SiH_3Br was obtained by repeated distillation (mol. wt. found, 108, calcd., 111). A comparison of the infrared spectrum of the volatiles with published spectra of SiH_3Br[14] and $(SiH_3)_2O$[11] indicated that these were the only compounds present. A molecular weight of the mixture showed the presence of 1.149 mmoles of SiH_3Br and 1.963 mmoles of $(SiH_3)_2O$.

A white, slightly volatile solid which remained in the reaction vessel was removed slowly from a bath at −23° by continuous pumping. Yield of $(CH_3)_4Al_2(OSiH_3)_2$ was 0.565 mmoles; mol. wt. found, 204, calcd., 208. Vapor pressure was 3 mm. at 0°.

Analysis of $(CH_3)_4Al_2(OSiH_3)_2$.—0.531 mmole of product was hydrolyzed in 30% KOH and the gaseous products were measured; 5.107 mmoles of gas was produced (calcd., 5.31 mmoles of H_2 and CH_4). An aliquot of the gas was cycled through a palladium sponge to remove hydrogen. The gas contained 59.6% CH_4, calcd. 60.0%; mol. wt. found, 15, calcd., 16.0.

Silicon was determined as SiO_2[15] and aluminum as the 8-hydroxyquinolate[16]; Si found, 26.45%, calcd., 26.97%; Al found, 24.9%, 25.6%, calcd., 25.9%.

Reaction 2. Al_2I_6 and $(SiH_3)_2O$.—Al_2I_6 (0.335 mmole) and $(SiH_3)_2O$ (1.075 mmoles) were combined in an apparatus of type "B" and allowed to react at −65°. The Al_2I_6 turned yellow immediately. No liquid phase was obtained. After one hour the volatiles were removed at −65°. The volatile fraction (0.216 mmole) had a mol. wt. of 42, indicating that it consisted mainly of SiH_4 together with very little $(SiH_3)_2O$. (Consequently the $(SiH_3)_2O$ already had reacted, presumably to form an adduct.) The volatiles were returned and the temperature of the vessel was raised to −50° and kept between −40 and −50° for one hour, after which the volatiles were again removed. The temperature of the vessel was raised to that of the room for a half hour during which time more volatiles were produced. These were removed and combined with the other volatile products. A white solid remained. Fractionation of the volatiles yielded: SiH_3I (0.772 mmole; mol. wt. found, 158, calcd., 158; vapor pressure at 0°, found, 122.9 mm., literature value,[9] 123.9 mm.); SiH_4 (0.234 mmole; mol. wt. found, 33.0, calcd., 32.1); and HI (0.239 mmole; mol. wt. found, 124 calcd., 128).

The SiH_3I was returned to the reaction tube and was then allowed to remain in contact with the solid residue for one hour at 0°. Fractionation of the volatiles yielded: SiH_3I (0.282 mmole; mol. wt. found, 157, calcd. 158; vapor pressure at 0°, found, 123.3 mm., literature value,[9] 123.9 mm.); SiH_2I_2 (0.242 mmole; mol. wt. found, 278, calcd. 284; vapor pressure at 29°, found, 17.7 mm., literature value,[17] 17.9 mm.); and SiH_4 (0.248 mmole; mol. wt. found, 33.1, calcd., 32.1).

The residue was heated for 2.5 hours at 80–100° and then warmed with a smoky gas flame for 15 minutes. Volatiles were produced and on fractionation yielded: SiH_3I (0.210 mmole; mol. wt. found, 157, calcd. 158); SiH_2I_2 (0.277 mmole; mol. wt. found, 283, calcd., 284); and SiH_4 (0.224 mmole; mol. wt. found, 32.0, calcd., 32.1).

Reaction 3. Al_2I_6 and $(SiH_3)_2O$.—Al_2I_6 (0.25 mmole) and $(SiH_3)_2O$ (1.975 mmole) were combined in an apparatus of type "A" at −76°, held at this temperature for 15 minutes and raised to room temperature over a period of one hour, during which time bubbling occurred. When all volatiles were removed, a white solid remained. Fractionation of the volatiles yielded: SiH_3I (0.639 mmole; mol. wt. found, 158, calcd., 158; vapor pressure at 0°, found, 124.3 mm., literature value,[9] 123.9 mm.); $(SiH_3)_2O$ (0.986 mmole; mol. wt. found, 78.3, calcd., 78.2; vapor pressure at −64°, found, 61.4 mm., literature value,[10] 62.0 mm.); and SiH_4 (0.320 mmole, identified by comparison with published infrared spectrum[18]).

Reaction 4. Al_2Br_6 and $(SiH_3)_2O$.—Al_2Br_6 (1.01 mmoles) and $(SiH_3)_2O$ (1.059 mmoles) were combined in an apparatus of type "A" at −63°, held at this temperature for 25 minutes and raised to room temperature over a period of 35 minutes during which time bubbling occurred. On removal of all volatiles a viscous yellow liquid remained. Fractionation of the volatiles yielded: SiH_3Br (0.315 mmole; mol. wt. found, 108, calcd., 111; vapor pressure at −63.5°, found, 27.8 mm., literature value,[10] 27.3 mm.); SiH_2Br_2 (0.480 mmole; mol. wt. found, 186, calcd., 190; vapor pressure at 0°, found, 52.6 mm., literature value,[10] 52.8 mm.); and SiH_4 (0.885 mmole; mol. wt. found, 34.0, calcd., 32.1).

The yellow residue slowly decomposed on standing at room temperature. Heating first at 80° for 3 hours and then with a smoky flame for a few minutes yielded volatiles and a white solid. Fractionation of the volatiles yielded: SiH_2Br_2 (0.197 mmole; mol. wt. found, 186, calcd., 190; vapor pressure at 0°, found, 52.7 mm., literature value,[10] 52.8 mm.), and HBr (0.882 mmole; mol. wt. found, 78.0, calcd., 81.0).

Reaction 5. Al_2Br_6 and $(SiH_3)_2O$.—Al_2Br_6 (0.462 mmole) and $(SiH_3)_2O$ (1.740 mmole) were combined in an apparatus of type "A" at −65°, held at this temperature for 25 minutes and raised to room temperature over a period of 45 minutes during which time bubbling occurred. A white solid remained on removing the volatiles. Fractionation of the volatiles yielded: SiH_3Br (1.170 mmoles) and $(SiH_3)_2O$ (0.450 mmole), identified as described in reaction 1, and SiH_4 (0.131 mmole; mol. wt. found, 33.0, calcd., 32.1).

The residue was heated first at 100° for one hour and then with a smoky gas flame for a few minutes, producing more volatiles. Fractionation yielded: SiH_3Br (0.265 mmole; mol. wt. found, 108, calcd. 111) and SiH_4 (0.268 mmole; mol. wt. found, 32.6, calcd., 32.1).

Reaction 6. Al_2Br_6 and $(SiH_3)_2O$.—Al_2Br_6 (2.05 mmoles) and $(SiH_3)_2O$ (2.01 mmoles) were combined in an apparatus of type "B" at −65° and held at this temperature for one hour. A yellow slush formed. Volatiles were distilled off at −65° and on fractionation yielded: SiH_3Br (0.667 mmole; mol. wt. found, 110, calcd., 111), SiH_4 (0.334 mmole; mol. wt. found, 32.6, calcd., 32.1), and HBr (0.174 mmole; mol. wt. found, 82.0, calcd., 80.9).

On raising the temperature of the residue to −50° a yellow viscous liquid was produced. Very slight decomposition occurred between −50 and −40° during one hour. When the reaction vessel was raised to room temperature vigorous bubbling occurred, and after one hour a viscous yellow material remained. Fractionation of the volatiles yielded: SiH_3Br (0.369 mmole; mol. wt. found, 110, calcd., 111; vapor pressure at −63.5°, found, 28.0 mm., literature value,[10] 27.3 mm.), SiH_2Br_2 (0.464 mmole; mol. wt. found, 188, calcd., 190; vapor pressure at 0°, found, 52.0 mm., literature value,[10] 52.8 mm.), and SiH_4 (1.030 mmoles; mol. wt. found, 32.3, calcd., 32.1).

The residue was heated as in reaction 5. A brown solid was produced, together with volatiles which on fractionation yielded: SiH_2Br_2 (0.610 mmole; mol. wt. found, 187, calcd., 190; vapor pressure at 0°, found, 52.0 mm., literature value,[10] 52.8 mm.).

Reaction 7. Al_2Cl_6 and $(SiH_3)_2O$.—Al_2Cl_6 (2.305 mmoles) and $(SiH_3)_2O$ (2.565 mmoles) were combined in an apparatus of type "A" at −75°, held at this temperature for 10 minutes, and raised to room temperature over a period of 40 minutes during which time bubbling occurred. After a half hour at room temperature the volatiles were separated from the white solid. Fractionation yielded: SiH_3Cl (0.571 mmole; mol. wt. found, 65.6, calcd., 66.5; vapor pressure at −64.5°, found, 131 mm., literature value,[10] 132 mm., confirmed by comparison with published infrared spectrum[19]); SiH_2Cl_2 (1.148 mmoles; mol. wt. found, 101, calcd., 101; vapor pressure at −46°, found, 58.0 mm., literature value,[10] 60.3 mm., confirmed by comparison with published infrared spectrum[20]); and SiH_4 (1.905 mmoles; mol. wt. found, 33.0, calcd., 32.1, confirmed by comparison with published infrared spectrum[18]).

Heating the residue first at 80–85° for one hour, and then with a smoky gas flame for a few minutes, liberated more volatiles which on fractionation yielded: SiH_3Cl (0.272

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mmole; mol. wt. found, 65.6, calcd., 66.5, confirmed by comparison with published infrared spectrum[19]); SiH_2Cl_2 (0.170 mmole; mol. wt. found, 99.1, calcd., 101, confirmed by comparison with published infrared spectrum[20]); and SiH_4 (0.782 mmole; mol. wt. found, 33.1, calcd., 32.1, confirmed by comparison with published infrared spectrum[18]).

Reaction 8. Al_2Cl_6 and $(SiH_3)_2O$.—Al_2Cl_6 (0.580 mmole) and $(SiH_3)_2O$ (3.430 mmoles) were combined in an apparatus of type "A" at −78°, held at this temperature for 10 minutes, and raised to room temperature over a period of 40 minutes during which time bubbling occurred. The volatiles were removed from the white and gray solids and on fractionation yielded: SiH_3Cl (2.185 mmoles; mol. wt. found, 66.3, calcd., 66.5, confirmed by comparison with published infrared spectrum[19]); $(SiH_3)_2O$ (0.728 mmole; mol. wt. found, 78.1, calcd. 78.2; vapor pressure at −63.5°, found, 62.0 mm., literature value,[10] 63.5 mm.); and SiH_4 (0.530 mmole; mol. wt. found, 33.0, calcd., 32.1, confirmed by comparison with published infrared spectrum[18]).

Reaction 9. SiH_3Cl and Al_2Cl_6.—Tensimetrically pure SiH_3Cl (0.579 mmole) and Al_2Cl_6 (0.281 mmole) were combined in an apparatus of type "A," held at −70° for a few minutes and warmed slowly over a period of one hour to room temperature during which time no apparent reaction occurred. Fractionation of the volatiles produced only SiH_3Cl; 99.5% of the starting SiH_3Cl was recovered. An infrared spectrum indicated that no other materials were present.

Results and Discussion

Tetramethyldisiloxydialuminum.—$(CH_3)_4Al_2Br_2$ and $(SiH_3)_2O$ react at −50° to give a solid adduct which decomposes at low temperatures. The overall reaction may be represented by the equation

$$(CH_3)_4Al_2Br_2 + 2(SiH_3)_2O \longrightarrow (CH_3)_4Al_2(OSiH_3)_2 + 2SiH_3Br$$

Vapor density measurements on the new compound show it to be the dimer $[(CH_3)_2Al(OSiH_3)]_2$. This is of considerable theoretical interest since it is therefore an "electron deficient" molecule, and it is also the first known volatile compound containing an Si–O–Al linkage.

The compound is a white solid, melting at 41–42° and may be sublimed in the vacuum system. Vapor pressures in the range 45 to 105° are represented by the equation $\log p = -2252/T + 7.761$, giving an extrapolated boiling point of 109–112°. Its molar heat of vaporization in this range is 10,300 cal./mole and the Trouton constant is 26.9. The compound is completely stable at −78°, but decomposes at a slow but measurable rate at room temperature to give SiH_4 and an unidentified, non-volatile viscous liquid. The vapor pressure plot begins to deviate from linearity at 105° and decomposition is therefore rapid at this temperature.

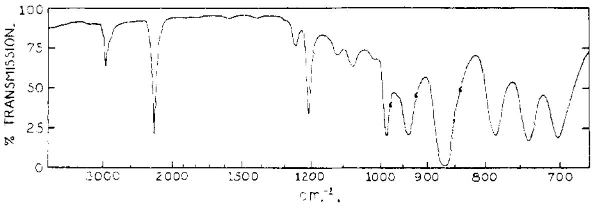

Fig. 1.—Infrared absorption spectrum of $(CH_3)_4Al_2(OSiH_3)_2$. A Perkin-Elmer model 21 double beam recording spectrophotometer with a sodium chloride prism was used. The spectrum was made at 20° on a pure gaseous sample at 3.5 mm. pressure, in a 10 cm. cell having potassium bromide windows.

The frequencies observed were 2940 cm.⁻¹, medium, C–H stretch; 2194 cm.⁻¹, strong, Si–H stretch; 1255 cm.⁻¹, weak; 1207 cm.⁻¹, strong, CH_3 deformation; 1115 cm.⁻¹, weak; 1072 cm.⁻¹, weak; 985 cm.⁻¹, strong; 937 cm.⁻¹, strong; 866 cm.⁻¹, very strong; 774 cm.⁻¹, strong; 738 cm.⁻¹, strong; 702 cm.⁻¹, strong.

Disiloxane and Aluminum Trihalides.—All the aluminum trihalides investigated were found to cleave the Si–O linkage in $(SiH_3)_2O$ at low temperatures (see Table I). Reaction commenced at approximately −78°. Some evidence for initial adduct formation was noted, *e.g.*, reaction 2. On raising the temperature by increments to room temperature over periods of one to two hours, it was observed that the rate of reaction increased after each rise in temperature and then slowly decreased. SiH_3X and small amounts of SiH_4 were liberated in all cases. Experiments in which the ratios of disiloxane to halide were varied significantly were conducted with each aluminum halide.

The chief reaction occurring between −78° and room temperatures appeared to be analogous to that between $(SiH_3)_2O$ and boron halides,[5,21] *viz.*

$$2(SiH_3)_2O + Al_2X_6 \longrightarrow 2SiH_3OAlX_2 + 2SiH_3X$$

The yields of SiH_3X based on the amounts of disiloxane consumed in this type of reaction were 71.8, 64.6, 90.7 and 80.9% for reactions 2, 3, 5 and 8, respectively. The siloxyaluminum halide formed was a non-volatile, presumably polymeric solid.

In those experiments where greater proportions of aluminum halide were used, it was observed that SiH_2X_2 was formed in addition to the SiH_3X, and that larger amounts of silane were produced (reactions 4 and 7). However, if in other experiments where similar proportions were used, the SiH_3X was recovered from the reaction vessel at low temperatures as soon as it was formed (reactions 2 and 6), less SiH_2X_2 and SiH_4 were produced. Small amounts of hydrogen halide were evolved in some instances.

In several experiments all the volatiles were removed from the reaction tubes, which were then warmed gently. In these cases, further quantities of SiH_3X, SiH_2X_2 and SiH_4 were formed (reactions 2, 4, 5, 6 and 7).

From reaction 9 it is clear that the formation of SiH_4 and SiH_2X_2 is not due to a simple catalytic disproportionation of the SiH_3X by unreacted Al_2X_6. Reaction 2 indicates that the siloxyaluminum halide may react further with the SiH_3X formed to produce SiH_2X_2 and SiH_4. This type of reaction is favored in those experiments where larger proportions of aluminum halides are used.

The cleavage of such a strong linkage as Si–O at low temperatures, as demonstrated in the above experiments, is completely consistent with other reported reactions of SiH_3 compounds: *e.g.*, the low-temperature interaction of $(SiH_3)_2O$ with boron halides.[5] Analogous reactions employing alkyl ethers proceed less readily: $(CH_3)_2O$ and aluminum chloride yield the methyl halide at 190°,[22] while

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[21] Very recently an analogous reaction between $[(CH_3)_3Si]_2O$ and aluminum halides has been reported by N. F. Orlov, *Doklady Akad. Nauk. S.S.S.R.*, **114**, 1033 (1957).

[22] W. Menzel and M. Froehlich, *Ber.*, **75B**, 1055 (1942).

$(CH_3)_2O$ and boron halides yield the methyl halide at 76°.[23] The greater rate of reaction of the silicon ether may be explained by the formation of a halogen–silicon coördinate bond involving vacant silicon 3d orbitals[2] in the rate-controlling step.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Reaction of Hydroxylamine and its N-Methyl Derivatives with Diborane

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Hydroxylamine–borane and N-methylhydroxylamine–borane have been prepared in impure form as solids at −112°. These lose H_2 on warming to room temperature. Pure N,N-dimethylhydroxylamine–borane has been prepared as a volatile liquid, which is relatively stable at room temperature. The decomposition of the borane complex is catalyzed by B_2H_6 and by the decomposition residues. The role of B_2H_6 in the decomposition is interpreted in terms of a proposed reaction scheme.

The reactions of the N-methylhydroxylamines and diborane differ in several important ways from the previously discussed[1] reactions of diborane with the O- and O,N-methylhydroxylamines. In the case of the O-methyl derivatives the stoichiometry of the reaction with B_2H_6 was very good to excellent; experimental ratios of CH_3ONR_2/B_2H_6 were always very close to 2.00. In the case of the N-methylhydroxylamines these ratios were in the range 1.8 to 1.92 (values which deviate from 2.00 by an amount significantly greater than the errors in experimental measurements). Reasons for these observations have been found in the properties of the hydroxylamine–borane complexes. The pure compound $HON(CH_3)_2BH_3$ was unusually stable for a compound containing hydridic and protonic hydrogens in the same molecule, but it displayed extreme sensitivity toward various catalysts which promote its decomposition. The possible role of such catalysts is considered herein.

The Reaction of Diborane and Hydroxylamine.—Diborane and solid anhydrous hydroxylamine either gave no reaction over the temperature range −186 to −96° or gave unpredictable explosive interaction. In the presence of diethyl ether as a reaction medium diborane and an ether suspension of anhydrous hydroxylamine reacted in approximate agreement with the equation

$$nB_2H_6 + 2nNH_2OH \xrightarrow[Et_2O]{-112°} 2(H_3BNH_2OH)_n$$

Hydrogen evolution was trivial under these conditions but stoichiometric reaction ratios, $HONH_2/B_2H_6$, invariably were relatively poor even in ether[2] as can be seen in Table I.

If the temperature of the ether-insoluble hydroxylamine adduct of diborane was allowed to rise slowly above −112°, hydrogen was liberated. The total number of moles of H_2 per mole of hydroxylamine used approached 1 at 25°. The product remaining after loss of one mole of hydrogen was a white solid which dissolved in water, methanol and ethanol with the evolution of small amounts of hydrogen. The material was insoluble in liquid ammonia, ether, benzene, toluene and 1,4-dioxane. The product remaining after the loss of two moles of hydrogen dissolved only with difficulty in water but readily in dilute acid or base. A polymer of the type $[-H_2BNH_2O-]_n$ would be reasonable for the 25° decomposition product. Additional B–N cross-linking would be expected for the 125° material. Above 70° the borane group itself begins to undergo direct pyrolysis.[3] A very marked decrease in the rate of hydrogen evolution was observed after two-thirds of a mole of H_2 per mole of hydroxylamine had been evolved.[4] As in the previously discussed case of methoxyamine–borane,[1] the observation correlated with an increase in the viscosity of the reacting mass. It is assumed that increasing rigidity of the polymer prevented free interaction of the acidic and hydridic hydrogen in the addition complex. A more detailed correlation with compound structure or reaction mechanism is not now available.

TABLE I

SUMMARY OF THE PROPERTIES OF THE BORANE ADDITION COMPOUNDS OF HYDROXYLAMINE AND ITS N-METHYL DERIVATIVES

Compound	M.p., °C.	Volatility	Ratio amine/ B_2H_6 in prep.[b]	Approx. temp. at which 50% dec. in 24 hr., °C.
$HONH_2BH_3$	Solid at −78°	None (dec.)	1.8–2.1	−75 (impure)
$HONHCH_3BH_3$	Liquid[a] at −78°	None	1.92	15 (impure)
$HON(CH_3)_2BH_3$	2–4°	6 mm. at 25°	1.92	25 (impure) 55 (pure)

[a] Sample impure; low melting point may be due to impurities. [b] Each value is a result of several runs. The theoretical value is 2.

The Reaction of Diborane and N-Methylhydroxylamine.—This reaction, conducted only in

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(1) T. C. Bissot, D. H. Campbell, R. W. Parry, THIS JOURNAL, **80**, April (1958).

(2) The advantages of diethyl ether as a solvent in some boron hydride reactions have been demonstrated previously. Emeleus and Stone (*J. Chem. Soc.*, 840 (1951)) observed poor stoichiometry for the reaction between diborane and non-solvated hydrazine, but Steindler and Schlesinger (THIS JOURNAL, **75**, 756 (1953)) obtained the compound $H_3BNH_2NH_2BH_3$ with excellent stoichiometry in the presence of diethyl ether.

(3) This statement is based on fact that H_2 loss from the analogous compound $CH_3ON(CH_3)_2BH_3$, which contains no protonic hydrogens, begins near 70°.

(4) More detailed information on this phenomenon is available in "The Chemistry of Boron Hydrides and Related Hydrides," W.A.D.C. Technical Report 56-318, 1956.