concentrations is attributed to one or both of two factors, the co-extraction of $TlCl_3$ or the ionization of $HTlCl_4$ in highly dilute ether solutions.

The directly measured extraction coefficient, K_T, showed a first-order dependence on the concentration of hydrogen ion. The quantity K', involving formation constants and activity coefficients, also showed such a relationship when plotted against the $HClO_4$ concentration as in Fig. 4. The linear acid dependence agrees with the idea that $HTlCl_4$ is the extracted species and in addition indicates that the activity coefficient of the hydrogen ion is constant at a given ionic strength.

The acid dependence is expressed in equations 1 and 4 and if these truly represent the data one would expect the curves of Fig. 4 to pass through the origin. The fact that they do not, indicates that at lower acid concentrations some other process is taking place which could be either the ionization of $HTlCl_4$ in ether or the co-extraction of $TlCl_3$.

Conclusions

The following results and conclusions can be drawn from this study.

The extraction was found to have a negative temperature coefficient in the range of 20 to 30°. An average value of ΔH of 9.7 ± 0.5 kcal. per mole was found under the conditions of the experiments.

In order to explain the reduced extraction at high acidities a non-extractable species with formula H_2TlCl_5 was postulated. The data were used to calculate its formation constant as 3.0×10^{17}.

The empirical formula of the extracted species was found to be close to $HTlCl_4$.

At a given ionic strength and acid concentration the extraction equilibrium constant was found to be essentially constant, independent of the chloride concentration except when this was quite low. The lack of constancy was possibly due to ionization of $HTlCl_4$ in the ether phase or to coextraction of the $TlCl_3$ species.

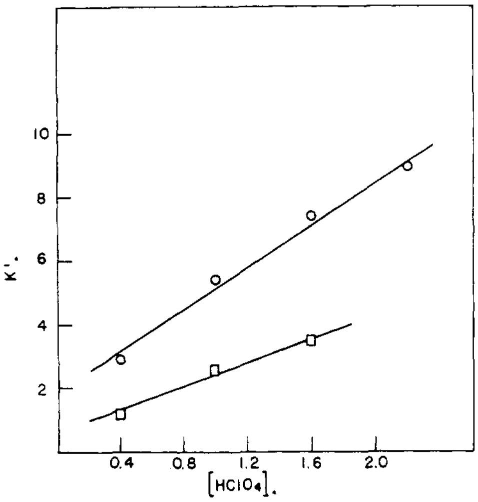

Fig. 4.—Dependence of K' upon $HClO_4$ concentration: ○, 3.0 M total salt and acid concentration; □ 2.0 M total salt and acid concentration.

The extraction was found to have a linear dependence on the hydrogen ion concentration in agreement with the supposition that $HTlCl_4$ was the species extracted. The fact that the extraction did not extrapolate to zero at low acidity agrees with the idea that $TlCl_3$ is extracting or that $HTlCl_4$ is ionizing in the ether phase. Values of the extraction coefficient at 30° are about 2.3 at an ionic strength of 2 and 4.3 at an ionic strength of 3 and relatively high acidities.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Solid Arsenic Hydrides

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RECEIVED OCTOBER 3, 1956

Various methods for preparing solid arsenic hydrides have been evaluated as to yield and product composition. Atom ratios of hydrogen/arsenic as high as 0.52 have been observed for solid hydrides. A method has been developed for preparing an unstable, volatile arsenic hydride (probably biarsine, As_2H_4) from arsine by use of a silent electrical discharge.

I. Introduction

The literature contains many conflicting statements regarding the solid arsenic hydrides. Not only the compositions of these hydrides, but also their methods of preparation, have been the subject of dispute.[1] We have evaluated various preparative methods in terms of both yield and hydrogen content of the product. Several new preparative methods have been developed, including a method for the preparation of an unstable, volatile hydride (probably biarsine). Some studies of the adsorption of arsine on arsenic have been made, in an attempt to elucidate the nature of the solid arsenic hydrides.

II. Results and Discussion

A. Reduction of Arsenic Solutions. 1. Reduction by $SnCl_2$.—Weeks and Druce[2] reported that a brown, amorphous arsenic hydride may be prepared by the action of an ether solution of stannous chloride on a solution of arsenic trichloride in aqueous hydrochloric acid

$$2AsCl_3 + 4SnCl_2 + 2H^+ + 2Cl^- = As_2H_2 + 4SnCl_4$$

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[1] See, for example, "Gmelins Handbuch der Anorganischen Chemie," System-Nummer 17, Verlag Chemie, G. m. b. H., Weinheim/Bergstrasse, 1952, pp. 195–200.

[2] E. J. Weeks and J. G. F. Druce, *Chem. News*, **129**, 31 (1924).

By using standardized solutions of $SnCl_2$ and $AsCl_3$ we have found that the stoichiometry of the *aqueous* reaction corresponds to the formation of elementary arsenic rather than an arsenic hydride. It is difficult to understand why the synthetic method of Weeks and Druce (differing only by the use of an *ether* solution of $SnCl_2$) should produce a solid hydride rather than elementary arsenic. Therefore we repeated the procedure of Weeks and Druce several times. In no case was the dark brown product found to contain any hydrogen other than that in the strongly adsorbed impurities (*e.g.*, H_2O, alcohol, HCl). The marked reducing properties of the material are, in general, identical with those of finely divided arsenic.

2. Reduction by Metals.—When certain metals (as granules or small chunks) are added in excess, to solutions of $AsCl_3$ or As_2O_3 in 6 *M* HCl (or, in the case of aluminum, 3 *M* NaOH), brown-black precipitates form, along with large amounts of hydrogen (and some arsine). The results of such experiments are summarized in Table I. The empirical formulas are the average values from several experiments. The best products were consistently obtained by the use of powdered magnesium, although the yields were never as great as those obtained by the use of granulated zinc. It is interesting that practically no solid product was obtained when calcium was the reducing agent. This may be caused by the extremely rapid reaction of calcium with water and by the fact that the calcium chunks floated on the surface of the solution.

TABLE I

REDUCTION OF 0.24 *M* As(III) SOLUTIONS BY METALS

Metal	Soln.	Yield, %	Empirical formula of solid product
Mg	HCl	~25	$AsH_{0.19}$
Zn	HCl	~85	$AsH_{0.04}$
Al	HCl	~18	$AsH_{0.025}$
Al	NaOH	~85	$AsH_{0.035}$
Ca	HCl	0	.....

An important method of isolating trace amounts of arsenic for subsequent analysis involves the quantitative reduction to arsine by zinc in hydrochloric or sulfuric acid solution.[3] Apparently little or no solid product is obtained when the arsenic concentration is very low.

3. Reduction by Miscellaneous Reducing Agents.—The reduction of $AsCl_3$ in 6 *M* HCl by chromous chloride gave a product of composition $AsH_{0.02}$ when the chromous chloride was in excess, and a product of composition $AsH_{0.002}$ when the $AsCl_3$ was in excess.

The addition of lithium hydride chunks to a solution of sodium arsenite gave no solid product. In this respect lithium hydride resembles calcium. Perhaps some reduction to arsine took place in the case of these powerful reducing agents.

B. Electrolytic Reduction of Arsenic Solutions.—Davy[4] was the first to report the formation of a brown precipitate when a solution of potassium hydroxide was electrolyzed using an arsenic cathode. Weeks[5] stated that the brown material obtained from a similar experiment was a solid arsenic hydride, but he gave no analytical data. Olszewsky[6] obtained a similar product by electrolyzing a solution of arsenious acid, using platinum electrodes.

We chose mercury as a cathode principally because of its high overvoltage for hydrogen evolution. Since hydrogen overvoltage increases with both increasing current density and decreasing temperature, we usually cooled the electrolytic cell as much as possible without unduly increasing the resistance. It is well known that arsine is liberated when an arsenic solution is reduced at a mercury cathode,[7,8] and we suspected that the presence of arsine was necessary for the formation of "solid arsenic hydrides."

The results are summarized in Table II. It will be noted that the ratio of hydrogen to arsenic in the product was high for those runs in which the electrolyte was acidic and cold. On the other hand, yields (based on electrical efficiency) were low under these conditions. It was observed that when the electrolytic experiments were started, the brown precipitate did not form at the surface of the mercury cathode, rather it formed homogeneously throughout the catholyte. We suspected that this phenomenon was caused by the reaction of dissolved arsine with the As(III) in the solution. It has been reported that arsine and arsenious acid react to give arsenic.[9]

We did not vary the concentration of As(III) in the electrolyte. It is known, however, that, as the concentration of As(III) decreases, the ratio of solid product to liberated arsine also decreases. In fact, when the concentration of As(III) is sufficiently small, quantitative yields of arsine gas are obtained.[3,8] It is probably significant that, in the reduction of As(III) solutions by sodium amalgam, the proportion of arsenic appearing as the metal (or solid hydride?) decreases with decreasing As(III) concentration.[10]

C. Oxidation of Arsine. 1. Oxidation by As(III).—Since our observations of the electrolysis of As(III) solutions led us to suspect that at least part of the solid product was formed by the reaction between arsine and As(III), we performed some experiments in which arsine was passed through As(III) solutions. The reaction of arsine with arsenious acid in sulfuric acid solution at room temperature was found to be so slow as to be an impractical synthetic method. We were unable to collect enough product to analyze. However, arsine reacts more rapidly with $AsCl_3$ in 6 *M* HCl. The product from such an experiment was found to have the empirical formula $AsH_{0.021}$. It thus seems likely that only a minor fraction of the product from the electrolytic preparations was formed by the reaction of arsine with arsenious acid.

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(3) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1950.

(4) H. Davy, *Phil. Trans. Royal Soc.* (*London*), **100**, 31 (1810).

(5) E. J. Weeks, *Chem. News*, **128**, 54 (1924).

(6) K. Olszewsky, *Arch. Pharm.*, [3] **13**, 563 (1878).

(7) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York, N. Y., 1941, p. 261.

(8) F. S. Aumonier, *J. Soc. Chem. Ind.*, **46**, 341 (1927).

(9) J. N. Friend, "A Textbook of Inorganic Chemistry," Vol. VI, Part IV, Chas. Griffin and Co., Ltd., London, 1938, p. 91.

(10) N. Konopik and K. Szlaczka, *Monatsh.*, **83**, 290 (1925); *C. A.*, **46**, 7413b (1952).

TABLE II

ELECTROLYTIC REDUCTION OF ARSENIC(III) SOLUTIONS

(15 g. As_2O_3 per l. of catholyte)

Run	Av. temp., °C.	Supporting electrolyte	Anode type	Current density, amp./cm.²		Voltage		Hours, run	Yield, g.	Atom ratio H/As	Mole ratio AsH_3/H_2[a]
				Initial	Final	Initial	Final				
1	46	0.18 M H_2SO_4 .063 M Na_2SO_4	C	0.052	0.052	25	17	3	4.51	0.056	0.0181
2	12	.18 M H_2SO_4 .063 M Na_2SO_4	C	.052	.052	22	22	3	0.35	.193	.0845
3	56	1.8 M H_2SO_4 0.063 M Na_2SO_4	C	.052	.052	6.2	6	4	4.23	.048	.0258
4	28	.18 M H_2SO_4 .063 M Na_2SO_4	C	.052	.052	21	18	3	3.10	.0034	.448
5	5	.18 M H_2SO_4 .063 M Na_2SO_4	C	.052	.052	25	23	8	0.81	.227	.0822
6	16	.5 M NaOH	C	.052	.0173	35	60	11	9	.029	.0435
7	7	1.8 M H_2SO_4 0.063 M Na_2SO_4	Pt	.052	..	8	..	9	2	.156	.091
8	10	.18 M H_2SO_4 .063 M Na_2SO_4	Pt	.052	.043	22	40	11.5	2.07	.072	.0793
9	7	None	Pt	8.6×10^{-4}	8.6×10^{-3}	120	120	2	1.27	.001	.367
10	10	.063 M Na_2SO_4 H_2 bubbled through soln.	Pt	0.016	0.028	62	20	6	0.5	.025	.0161
11	5	0.18 M H_2SO_4 .063 M Na_2SO_4	Pt	.052	.035	26	22	6	0.33	.258	.0771
12	8	.88 M H_3PO_4 .12 M NaH_2PO_4	Pt	.035	.035	30	30	9	0.74	.168	.0478

[a] Mole ratio AsH_3/H_2 in gas from vacuum thermal decomposition of vacuum heated product.

2. Oxidation by $SnCl_4$.—Moser and Brukl[11] reported the preparation of a hydride of the composition As_4H_2 by the oxidation of arsine by stannic chloride in aqueous hydrochloric acid. We repeated their experiments, but under conditions such that the $SnCl_4$ was always in excess. (Moser and Brukl kept the arsine in excess.) Our products had the average empirical formula $AsH_{0.18}$.

D. Decomposition of Arsine by a Silent Electrical Discharge.—Ogier[12] decomposed arsine in a discharge tube and obtained only 85.6% of the theoretical amount of hydrogen gas. This datum corresponds to a solid residue of the composition $AsH_{0.43}$. We repeated this experiment twice, using a closed discharge tube, and obtained solids with calculated compositions $AsH_{0.20}$ and $AsH_{0.23}$.

E. Disproportionation of Biarsine (?).—In preliminary experiments it was found that, when arsine was passed through a silent electrical discharge tube followed by a trap cooled to −196°, a yellow-brown solid formed in the trap.

Nast[13] has isolated small amounts of biarsine, As_2H_4, from the volatile products in the hydrolysis of magnesium aluminum arsenide. Pure biarsine was reported to be extremely unstable, decomposing to arsine and a solid red hydride of the approximate composition $AsH_{0.62}$. We suspected that, in our preliminary experiments with the discharge tube, the arsine had been decomposed to, among other things, hydrogen and biarsine. Presumably the biarsine, in turn, decomposed at the cold trap into arsine and the yellow-brown solid which we observed.

Further experiments indicated that we could, indeed, isolate a volatile material (not arsine) from the discharge tube products. This material (which may have been a mixture of biarsine and higher polymers such as As_3H_5 and As_3H_3) could be partially condensed in traps cooled to −80° and almost completely condensed in traps cooled to −120°. It partially decomposed to a bright yellow non-volatile hydride (and probably arsine and/or hydrogen) during the processes of condensation and vaporization. The yellow hydride, on warming to room temperature, turned red and finally brown. The volatile material was too unstable to analyze directly, but several samples of the solid hydride were analyzed. The average of several analyses corresponded to the empirical formula $AsH_{0.52 \pm 0.07}$.

F. Ammonolysis of Sodium Arsenide.—When ammonium chloride is added to a liquid ammonia solution of $NaAsH_2$, arsine is liberated and a finely divided brown precipitate of arsenic forms. This precipitated arsenic was found to contain only negligible amounts of hydrogen, in agreement with the findings of Johnson and Pechukas.[14]

G. Adsorption of Arsine on Arsenic.—The arsenic prepared by the method of Weeks and Druce ("As_2H_2") was found to be extremely finely divided. One sample had a surface area of 120 m.²/gram.

The adsorption of arsine on a similar sample of arsenic at −78.5° was found to show some hystere-

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[11] L. Moser and A. Brukl, *Monatsh.*, **45**, 25 (1924).

[12] J. Ogier, *Ann. chim. phys.*, [5] **20**, 17 (1880).

[13] R. Nast, *Chem. Ber.*, **81**, 271 (1948).

[14] W. C. Johnson and A. Pechukas, THIS JOURNAL, **59**, 2065 (1937).

sis in an adsorption–desorption cycle, but there was no strong bonding between the arsine molecules and the arsenic.

III. Experimental[15]

A. Analysis.—The solid arsenic hydrides were analyzed by thermal decomposition in a vacuum manifold. Weighed samples were heated *in vacuo* until the arsenic sublimed vigorously. The evolved gases were Toepler-pumped through, successively, a tube of Ascarite (to absorb CO_2, HCl and H_2O), a trap cooled to −78° (to trap H_2O, alcohol, etc.), and a trap cooled to −196° (to trap AsH_3). The non-condensable gas was usually assumed to be hydrogen; occasionally this was checked by a molecular weight determination or by mass-spectrometric analysis. Arsine was identified by its vapor pressure at the melting point of CS_2: lit.[14] 35 mm., found 34–36 mm. Usually the molar ratio AsH_3/H_2 in the gaseous decomposition products was approximately 0.05. The hydrogen contents of the solid hydrides were calculated from the molecular hydrogen and arsine evolved in the thermal decompositions.

B. Electrolytic Reduction of Arsenic Solutions. 1. Apparatus.—The anode compartment was a cylindrical tube 100 mm. long with a 40-mm. fritted disc at the lower end. Two types of anodes were used. One was a graphite rod 12 mm. in diameter. The other was a 1 × 10 cm. strip of platinum sheet. The cathode compartment was a one-liter "tall form" beaker, equipped with a stirrer. A pool of mercury (1/2 inch deep) in the bottom of the cathode compartment served as the cathode. Electrical contact was made to the mercury by a platinum-tipped wire passing through a tube. In some experiments, the cell was cooled externally with ice-water.

2. General Procedure.—Fifteen grams of arsenious oxide was dissolved in 25 ml. of 5 *M* sodium hydroxide. The solution was diluted with water and the appropriate amount of sulfuric acid to a volume of one liter.

In run no. 12, phosphoric acid was used instead of sulfuric acid. The catholyte for run no. 9 was prepared by dissolving arsenious oxide in hot water. The catholyte of run no. 6 was half-molar sodium hydroxide. The anolytes were the same as the catholytes in acid or base composition, but lacking in arsenious oxide. In run no. 6 the platinum anode was immersed directly in the catholyte.

At the end of each run, the mercury was removed with a separatory funnel, and the product was collected in a fritted funnel by vacuum filtration. The product was washed with water and dried for at least eight hours *in vacuo* over magnesium perchlorate.

Table II summarizes the data for each experiment.

C. Decomposition of Arsine by a Silent Electrical Discharge.—The discharge tube was similar to the usual ozone generator. It consisted of a glass cylindrical "finger" within and concentric with another glass cylinder. The discharge tube could be closed by means of stopcocks located at either end. The capacity of the tube was 63 cc.; the inner and outer cylinders were separated by about 0.5 cm. When in operation, 20,000 volts (60 cycles) were applied across the gap (one electrical contact was made to a salt solution in the inner "finger"; the other contact was made to aluminum foil wrapped around the outer cylinder). The results of two static experiments with AsH_3 are given in Table III.

TABLE III

S.E.D. DECOMPOSITION OF AsH_3 TO $AsH_x + (3/2 - x/2)H_2$

Voltage	Time (min.)	Initial mmoles AsH_3	Mmoles AsH_3 dec.	Moles H_2 formed per mole AsH_3 dec.	x (calcd.)
20,000	11	0.254	0.253	1.400	0.20
20,000	10	.696	.279	1.385	.23

In the first experiment, the discharge tube was flamed after pumping out the hydrogen and unreacted arsine in an attempt to decompose the residual brown solid hydride. Only 0.0050 mmole of H_2 and 0.0035 mmole of AsH_3 were obtained (corresponding to 0.010 mmole of H_2 total). One calculates that 0.016 mmole of H_2 were combined in the solid hydride; the deficiency was probably caused by incomplete thermal decomposition. (The peculiar shape of the discharge tube prevented efficient flaming.)

D. Disproportionation of "Biarsine."—The experiments may be divided in two classes: (1) those in which arsine was pumped through the discharge tube at low pressure (<1 mm.), and (2) those in which the arsine was carried through the discharge tube by a large excess of hydrogen gas (*ca.* 1 atm.). The former experiments were characterized by the formation of brown solid deposits in the tubing leading from the discharge tube. This phenomenon was probably caused by the glow discharge, which extended beyond the discharge tube itself. In the latter experiments, the brown deposit was limited to the interior of the discharge tube. In general, both methods involved the decomposition of about 5% of the arsine.

The gases leaving the discharge tube were usually first passed through a −120° trap and then through a −196° trap. After complete passage of the arsine through the discharge, the system was pumped down to about 10 μ pressure. The −120° trap was then closed off and *slowly* warmed to room temperature, thereby decomposing the "biarsine."

The trap was then evacuated. The red-brown solid residue was gently heated with a flame until it was black and the evolved arsine and hydrogen were measured. The remaining arsenic metal was dissolved in warm nitric acid and the solution was analyzed for arsenic by the molybdenum-blue colorimetric method.[3] For every 100 cc. of arsine passed through the discharge with one atmosphere of hydrogen, about 0.01 mmole of arsenic was obtained in the form of the solid hydride in the first trap (0.014 mmole in the low pressure experiments).

In Table IV, the results of five experiments are summarized.

TABLE IV

ANALYSIS OF SOLID DECOMPOSITION PRODUCT OF "BIARSINE"

Mmoles H_2 evolved during thermal decn.	Mmoles AsH_3 evolved during thermal decn.	Mmoles As remaining after thermal decn.	Calcd. empirical formula
0.0024	0.00261	0.0270	$AsH_{0.43}$
.00294	.00357	.0244	$AsH_{0.59}$
.0140	.0162	.119	$AsH_{0.57}$
.00157	.00367	.0210	$AsH_{0.57}$
.00354	.00327	.0356	$AsH_{0.43}$

In several qualitative experiments, the material in the −120° trap was not allowed to decompose completely, but was distilled to various places in the vacuum line. It was noted that, after distilling the material from a glass receptacle, a film of yellow solid remained which, when warmed to room temperature, turned red-brown. The material seemed to be relatively stable in the gaseous state, even at room temperature.

IV. Conclusions

The experimental data indicate that whenever one attempts to form elementary arsenic in the presence of arsine, the solid product contains not only arsenic, but also varying amounts of firmly held hydrogen. If we conclude that the presence of arsine is essential to the formation of these solid arsenic hydrides, then it is explained why a weak reducing agent like stannous chloride will only reduce As(III) to elementary arsenic. (Stannous chloride is thermodynamically incapable of reducing As(III) to arsine.)

It is very unlikely that the hydrogen of these solid hydrides exists as molecular hydrogen or arsine adsorbed on arsenic. Perhaps the solid hy-

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(15) For detailed experimental data, the reader is referred to University of California Radiation Laboratory Report UCRL-4707, "Solid Arsenic Hydrides," June 7, 1956. The data on the preparation of arsine, the chemical reduction of As(III) solutions, the oxidation of arsine, the ammonolysis of sodium arsenide and the adsorption studies are presented in that report.

drides prepared by certain methods consist of hydrogen and arsine occluded in cracks and holes in arsenic particles, but it is difficult to explain the very hydrogen-rich solids of composition $AsH_{0.5}$ in this manner. When macro amounts of these latter hydrides are available, various physical-chemical studies may elucidate their structure.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Reaction of Silylamines with Boron Trifluoride. Methyl- and Silylaminoboron Difluorides

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RECEIVED DECEMBER 17, 1956

N-Silyldimethylamine, N-methyldisilylamine and trisilylamine react with boron trifluoride to yield dimethylaminoboron difluoride, N-methylsilylaminoboron difluoride and disilylaminoboron difluoride, respectively, and silyl fluoride. The variation in the physical properties of the aminoboron difluorides is discussed. Silylaminoboron difluorides decompose to form borazole derivatives and silyl fluoride. New vapor pressure data for silyl fluoride and N,N',N''-trimethyl-B,B',B''-trifluoroborazole were obtained.

With trimethylboron as the reference acid, the base strengths of silylamines show the following order: $(CH_3)_3N > (SiH_3)(CH_3)_2N > (CH_3)(SiH_3)_2N \sim (SiH_3)_3N$.[1] Neither methyldisilylamine nor trisilylamine forms an addition compound with trimethylboron and, therefore, their relative base strengths are not known.

With the object of completing this order, the reactions of the silylamines with boron trifluoride were investigated. Boron trifluoride appeared to be a suitable reference acid since Burg and Kuljian had reported that trisilylamine–boron trifluoride forms reversibly in the range −78 to −40° with a solid–gas equilibrium pressure of 3.7 mm. at −55°.[2] Although we found evidence for the formation of amine–boron trifluoride addition compounds, we could not measure the equilibrium pressures. This difficulty arose because secondary reactions, which yield aminoboron difluorides and silyl fluoride, occurred too rapidly. The nature of this secondary reaction is similar to that reported for the silylamine–boron trichloride system[2] and is the subject of the present paper.

Results and Discussion

Reaction of Silylamines with Boron Trifluoride.—Silyldimethylamine, methyldisilylamine and trisilylamine all absorbed an equimolar quantity of boron trifluoride at −80° to form white solids. Silyl fluoride was liberated slowly and at −80° less than an equivalent of it was formed in 16 hours.

When the amine–boron trifluoride mixtures were warmed to 25° about an equivalent of silyl fluoride was obtained. The formation of silyl fluoride was rapid in the methyldisilylamine and silyldimethylamine systems but was slow in the trisilylamine system. In the trisilylamine–boron trifluoride system, the total pressure indicated that trisilylamine–boron trifluoride was completely dissociated at partial pressures of 27 mm. of the components. After several days, however, almost an equivalent of silyl fluoride was obtained.

Along with silyl fluoride, substituted aminoboron difluorides were obtained. Dimethylaminoboron difluoride,[3] N-methylsilylaminoboron difluoride and disilylaminoboron difluoride were isolated from the silyldimethylamine, methyldisilylamine and trisilylamine systems, respectively. The silylaminoboron difluorides have not previously been reported in the literature.

The results suggest that the reactions of the silylamines with boron trifluoride proceed in two steps: (1) absorption of boron trifluoride to form an addition compound and (2) the elimination of silyl fluoride from the addition compound to form aminoboron difluoride.

$$(SiH_3)_2N{:} + BF_3 = (SiH_3)_3N{:}BF_3 \qquad (1)$$

$$(SiH_3)_3N{:}BF_3 = SiH_3F + (SiH_3)_2N{=}BF_2 \qquad (2)$$

The heats of formation of the addition compounds in the gas phase, from the amine and boron trifluoride, can be estimated and correlated with the results. According to Brown and Johannesen, the heat of formation of trimethylamine-boron trifluoride is −28 kcal./mole.[4] We have suggested that the substitution of a silyl group for a methyl group increases the heat of formation by about 9 kcal. for each successive substitution.[1] Hence, the approximate heat of formation of silyldimethylamine–boron trifluoride is −19 kcal., for methyldisilylamine–boron trifluoride −10 kcal., and for trisilylamine–boron trifluoride −1 kcal.

The last value is compatible with the observed gas phase non-association in the trisilylamine–boron trifluoride system.[5] The rapid formation of silyl fluoride in the methyldisilylamine–boron trifluoride and silyldimethylamine–boron trifluoride systems at 25° is compatible with heats of for-

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[1] S. Sujishi and W. Witz, THIS JOURNAL, **76**, 4631 (1954).

[2] A. B. Burg and E. S. Kuljian, *ibid.*, **72**, 3103 (1950).

[3] (a) J. F. Brown, Jr., *ibid.*, **74**, 1219 (1952); (b) A. B. Burg and J. Banus, *ibid.*, **76**, 3903 (1954).

[4] H. C. Brown and R. B. Johannesen, *ibid.*, **75**, 16 (1953).

[5] The value of −1 kcal. for the heat of formation of trisilylamine–boron trifluoride appears on first consideration to be too small to account for the formation of the solid adduct at −80°. However, A. B. Burg and Sr. A. A. Green (*ibid.*, **65**, 1838 (1943)) report that trimethylamine–boron trifluoride molecules form associated aggregates even in the gas phase. In the solid state, therefore, strong dipole forces between the addition compound molecules could stabilize the adduct.