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

Effect of Replacement of Carbon by Silicon in Trimethylamine on the Stabilities of the Trimethylboron Addition Compounds. Estimation of the Resonance Energy for Silicon–Nitrogen Partial Double Bond[1]

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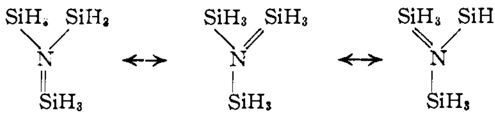
N-Silyldimethylamine, N-methyldisilylamine and trisilylamine have been prepared by the reaction of silyl bromide with dimethylamine, methylamine and ammonia, respectively. The new compound N-silyldimethylamine has unusual properties: strong absorption by dimethylamine hydrobromide, instability toward decomposition, detectable association in the gas phase and high melting point. It is suggested that the latter three of these properties are due to the formation of intermolecular nitrogen–silicon coördinate bonds. The heat of dissociation of this coördinate bond is estimated to be about 5.5 kcal./mole. Only N-silyldimethylamine forms an addition compound with trimethylboron. The addition compound is more highly dissociated in the gas phase than trimethylamine–trimethylboron. The systematic decrease in the stability of the addition compounds with the replacement of the carbon by silicon atoms is attributed largely to partial double-bond resonance stabilization of the free silylamine. The resonance energy in silyldimethylamine is estimated to be about 9 kcal./mole.

The fact that the silicon–halogen bonds are shorter than the sums of normal covalent radii has been interpreted as due to partial double bond character in the bonds.[2] More recently this concept, along with some admittedly arbitrary assumptions, has been extended to estimate the degree of double, single and ionic bond character.[3] As a result of the analysis of bond lengths and quadrupole coupling constants it is found that the double, single and ionic character for C–Cl bond in methyl chloride are 0, 82 and 18%, respectively, while for Si–Cl bond in silyl chloride are 29, 34 and 37%, respectively.

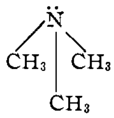
A different explanation has been advanced by Pitzer to explain the shortness of the Si–F bond.[4] According to Pitzer the bond distances of the first row elements are influenced by the valence shell–valence shell electron repulsions while those of the second row elements are influenced by the inner shell–valence shell electron repulsions. In a bond between a first and a second row element these repulsive forces are small and, hence, the bond lengths are shorter than those calculated from the covalent radii. Pitzer concludes that 3d orbitals are not available for additional bonds of significant strength. However, it is difficult to apply a similar interpretation for the shortening (0.11 Å.) of Si–Cl bond in silyl chloride since in this case only inner shell–valence shell interactions should be important.

A clearer appreciation of the importance of partial double bonds may be gained by the examination of the properties of trimethylamine and trisilylamine.[5] Trimethylamine is pyramidal and combines readily with trimethylboron.[6] Trisilylamine, on the other hand, is planar[7] and does not combine with trimethylboron.[8] These observations may be understood if it is assumed that trisilylamine is stabilized by resonance forms involving partial double bonds.[7,8] They are difficult to rationalize on the basis of Pitzer's proposal.



The results of Mays and Dailey indicate that the contribution of the ionic resonance form in silyl chloride ($H_3Si^+Cl^-$) is approximately twice that in methyl chloride ($H_3C^+Cl^-$). This suggests that the silyl group has a greater electron-repelling effect (+I effect) than the methyl group and that, therefore, trisilylamine should be a stronger base than trimethylamine. The fact to the contrary implies that the resonance effect is greater than the inductive (+I) effect.

There appears to be no chemical evidence that the silyl group does have a greater +I effect than the methyl group.[9] It was considered that a study of the relative base strengths of a series of amines in which the carbon atoms in trimethylamine are systematically replaced by silicon atoms (I–IV) might provide such a clue. The smaller resonance



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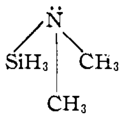

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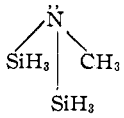

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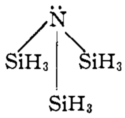

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[1] Abstracted in part from the dissertation presented by Samuel Witz to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Ph.D., February, 1954.

[2] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, Chap. VII. See, however, A. F Wells, *J. Chem. Soc.*, 55 (1949), for a more recent discussion of the applicability of bond lengths for the study of bond types.

[3] J. M. Mays and D. P. Dailey, *J. Chem. Phys.*, **20**, 1695 (1952).

[4] K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

[5] R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953), have studied the behavior of certain aromatic amines containing the trimethylsilyl group as *meta* and *para* substituents. Their results may also be taken as chemical evidence for the participation of silicon in partial double bond formation.

[6] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *ibid.*, **66**, 435 (1944).

[7] K. Hedberg and A. J. Stosick, Abstracts of the XII International Congress of Pure and Applied Chemistry, N. Y., Sept. 10–13, 1951, p. 543.

[8] A. B. Burg and E. S. Kuljian, THIS JOURNAL, **72**, 3103 (1950).

[9] L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951), report that *t*-butylacetic acid is a stronger acid than trimethylsilylacetic acid and that neopentylamine is a weaker base than trimethylsilylmethylamine. They interpret this to mean that the trimethylsilyl group has a greater +I effect than the *t*-butyl group. However, it is our opinion that in these aliphatic compounds, the neopentylamine is an abnormally weak base ($Kb = 1.6 \times 10^{-4}$ compared to $K_b = 4.9 \times 10^{-4}$ for *n*-propylamine) and the *t*-butylacetic acid is an abnormally strong acid. These abnormalities are probably due to steric effects similar to those suggested for straight chain aliphatic amines and acids (H. C. Brown, M. D. Taylor and S. Sujishi, *ibid.*, **73**, 2464 (1951). The conclusions drawn about the inductive effect of the trimethylsilyl group must be viewed with some caution.

TABLE I

SOME PROPERTIES OF SILYLMETHYLAMINES

Properties	$(CH_3)_3N$	$(SiH_3)(CH_3)_2N$	$(CH_3)(SiH_3)_2N$	$(SiH_3)_3N$
Absorption by $(CH_3)_{3-n}H_nNHBr$	......	Strong	None	None
M.p., °C.	-117.1[11]	$+3.3$ to 3.4	-124.1 to -124.6	-105.7[13]
$\Delta H_{vap.}$, kcal./mole	5.5[11]	14.0 (Subl.)	6.8[12]	7.0[13]
Dev. of mol. wt. of gas, %	......	2.1 (p 58 mm.) 3.1 (p 150 mm.)	....	0.9 (p 67 mm.) 1.5 (p 143 mm.)
Thermal decomposition	Stable	Very unstable	Stable	Stable

possibility in silyldimethylamine (II) might lead to the manifestation of the +I effect which is masked in trisilylamine. If this were the case, then silyldimethylamine should be a stronger base than trimethylamine.

Results

The relative base strengths of the amines have been determined by investigation of the reactions of the amines with trimethylboron. Silyldimethylamine-trimethylboron was isolated and characterized, but no evidence for the addition of methyldisilylamine or trisilylamine to trimethylboron was obtained at −112°. Thus, silyldimethylamine is a stronger base toward trimethylboron than the other two silylamines.

Comparison of the gas phase dissociation studies at 24° showed that trimethylamine is a much stronger base than silyldimethylamine. At a total pressure of 62 mm., silyldimethylamine–trimethylboron was almost 100% dissociated while trimethylamine–trimethylboron is only 10% dissociated.[10]

The saturation pressures of solid silyldimethylamine–trimethylboron were measured from −30 to −5°. The results may be expressed by the equation $\log P = -2685/T + 11.968$. The heat of sublimation, assuming complete dissociation in the gas phase, is 24.6 kcal./mole.

The silylamines were prepared by reaction of silyl bromide with the methylamines and ammonia according to the following stoichiometry

$$nSiH_3Br + (n + 1)(CH_3)_{3-n}NH_n = (CH_3)_{3-n}(SiH_3)_nN + n(CH_3)_{3-n}NH_nHBr$$
$$n = 1, 2 \text{ and } 3$$

The silylamines were recovered in 80–85% yields. Since there is a competition for the hydrogen bromide between the silylamines and the methylamine, the fact that methylamine hydrobromides are formed shows that these are more stable than the silylamine hydrobromides. This indicates that the replacement of a hydrogen atom by a silyl group decreases the base strength.

Silyldimethylamine, a compound previously unreported, exhibited a number of peculiar properties when compared with the other amines. It was strongly absorbed by the amine-hydrobromide while methyldisilylamine and trisilylamine were not. The melting point of silyldimethylamine, 3.3–3.4°, was abnormally high; the others melt below −100°. The deviation of silyldimethylamine from perfect gas behavior, although slight, was greater than that of trisilylamine indicating that some association in the gas phase occurred. Finally, silyldimethylamine was much less stable toward decomposition than the others. The products of the decomposition could not be identified. These unusual properties are summarized in Table I.

Discussion

The Resonance Energy in Silylamines.—The relative stabilities of the amine–trimethylboron addition compounds suggest that the basicities are in the order $(CH_3)_3N > (SiH_3)(CH_3)_2N > (CH_3)(SiH_3)_2N \sim (SiH_3)_3N$. Therefore, no evidence that the +I effect of the silyl group is greater than that of the methyl group was obtained. The fact that silyldimethylamine–trimethylboron is completely dissociated in the gas phase did not permit a quantitative study of the dissociation equilibrium by convenient methods.

A rough estimate of the heat of dissociation may be made, however, from the heat of sublimation of silyldimethylamine–trimethylboron. The sublimation of an addition compound may be considered as consisting of two processes, the evaporation to the undissociated molecule and the dissociation of the molecule.

$$AB(s) = AB(g) \qquad \Delta H_1$$
$$AB(g) = A(g) + B(g) \qquad \Delta H_2$$
$$AB(g) = (1 - \alpha)AB(g) + \alpha A(g) + \alpha B(g) \qquad \Delta H_3$$

The three enthalpy terms are related by the expression $\Delta H_3 = \Delta H_1 + \alpha\Delta H_2$, where α is the degree of dissociation of AB(g). For silyldimethylamine–trimethylboron ΔH_3 is known so that it is necessary to estimate ΔH_1 in order to obtain ΔH_2.

The heat of sublimation, ΔH_1 for silyldimethylamine–trimethylboron is estimated by calculating the value corresponding to the same change in state for trimethylamine–trimethylboron and then correcting for the difference due to the differences in the van der Waals effects of a silyl and a methyl group.

The heat of sublimation of trimethylamine–trimethylboron is calculated from data in the literature[6] to be 15.0 kcal. at 0°.[14] A comparison of hydrocarbons, R–CH_3, with structurally similar silylhydrocarbons, R–SiH_3, shows that the replacement of a methyl group by a silyl group increases

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[10] The value for trimethylamine–trimethylboron is based on data given in ref. 6 and is for a metastable state. The saturation pressure of the addition compound at 24° is 2 mm., but even at this pressure the dissociation is about 55%.

[11] J. G. Aston, *et al.*, THIS JOURNAL, **66**, 1171 (1944).

[12] H. J. Emeleus and N. Miller, *J. Chem. Soc.*, 819 (1939).

[13] A. Stock and K. Somieski, *Ber.*, **54**, 740 (1921).

[14] The heat of sublimation of hexamethylethane at 25° is 10.24 kcal. (F. D. Rossini, "Selected Values of Properties of Hydrocarbons," Natl. Bur. Standards Circ. 461, U. S. Government Printing Office, Washington, D. C., 1941). The difference between this and the heat of sublimation of molecular trimethylamine-trimethylboron is 4.7 kcal. This small difference between these relatively unlike molecules lends confidence to our extrapolation from trimethylamine-trimethylboron to silyldimethylamine-trimethylboron.

the heat of vaporization by 0.6–1.0 kcal.[15] The heat of sublimation of silyldimethylamine–tri-trimethylboron is, therefore, about 16 kcal.

Since the observed heat of dissociation of silyldimethylamine–trimethylboron to the components is 24.6 kcal., the gaseous heat of dissociation is approximately 8.5 kcal. Comparing this with the heat of dissociation of trimethylamine–trimethylboron, which is 17.6 kcal.,[6] it is seen that the replacement of the methyl group by a silyl group reduces the heat of dissociation by about 9 kcal.

This decrease may be attributed either to a weakening of the nitrogen–boron bond in the addition compound or to a stabilization of the free silyldimethylamine molecule. It is necessary to consider at least three effects in seeking an explanation: the steric, polar and resonance effects.

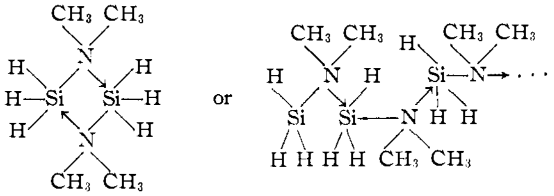
Examination of Fisher–Hirschfelder models shows that the steric requirement of the silyl group is somewhat smaller than that of the methyl group. The longer silicon–nitrogen bond (using normal covalent radii) compensates for the larger bulk of the silyl group. The orbital repulsions should be smaller in the silicon–nitrogen bond than in the carbon–nitrogen bond, so that the nitrogen with the coördination number of four should be more favored with a silicon–nitrogen bond than with the carbon–nitrogen bond. Thus, the consideration of steric effects due to interactions between both bonded and non-bonded atoms would indicate that trisilylamine should be a stronger base than trimethylamine.

Current theories of organic chemistry, the electronegativities and the calculations of Mays and Dailey, all suggest that the second row element, silicon, should have a greater +I effect than the first row element, carbon. These considerations lead to the conclusion that the nitrogen–boron bond in silyldimethylamine–trimethylboron should be stronger than that in trimethylamine–trimethylboron. In the absence of definite chemical evidence to support this conclusion, it must be considered tentative. Regardless of the nature of the polar effect of the silyl group, it appears unlikely that its contribution is as large as 9 kcal.

It appears likely to us that the decrease of 9 kcal. represents predominantly the stabilization of the free silyldimethylamine and that this is approximately the resonance energy of the molecule. The resonance energy in methyldisilylamine and trisilylamine are then greater than 18 and 27 kcal., respectively. This accounts for the low basicity of these compounds.

The Unusual Properties of Silyldimethylamine.—The high melting point of silyldimethylamine may be explained if it is assumed that intermolecular coördination of nitrogen to silicon takes place instead of intramolecular partial-double bond formation in the solid. The solid then consists of bridge dimers or higher polymeric units.

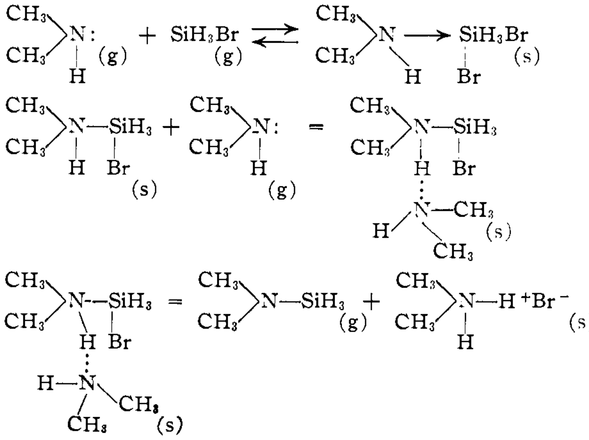
The heat of dissociation of the coördination bond may be estimated to be about 5.5 kcal. The heat of sublimation of unassociated silyldimethylamine is the sum of the heat of fusion and the heat of vaporization of unassociated molecules. Values of 1.5 and 7 kcal. are approximated for these on the basis of the heat of fusion of trimethylamine, 1.5 kcal.,[11] and the heat of vaporization of the other silylamines (see Table I). The observed heat of sublimation of 14.0 kcal. minus 8.5 kcal. yields 5.5 kcal./mole, the heat of dissociation of the coördinate bond.



The absence of association in the other amines is explained as follows. Trimethylamine is unassociated because carbon does not readily accept an electron pair. Methyldisilylamine is unassociated since the second silyl group introduces a resonance energy of more than 9 kcal., a degree of stabilization greater than can be obtained by formation of another silicon–nitrogen bond.

The observation of the slight gas phase association of silyldimethylamine suggests that the associated molecules may consist of cyclic dimers. With an entropy of dissociation of about 40 e.u., a heat of dissociation of 5.5 kcal. makes the free energy of dissociation highly negative at room temperature. However, if two coördinate bonds are formed per cyclic dimer, then the heat of dissociation is 11 kcal. and this would bring the free energy of dissociation to a value where the association would become perceptible.

An explanation for the strong absorption of silyldimethylamine by dimethylamine hydrobromide necessitates an assumption of the mechanism of the reaction of the amines with silyl bromide. Taking the reaction of methylamine with silyl bromide as an example, it is proposed that the first step is the formation of a coördination compound between the two molecules. This is followed by the removal of hydrogen bromide by the excess amine. This scheme of reactions is consistent with the facts that silyl halides form solid compounds with amines and that the first step may be reversed by employing excess hydrogen bromide.



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(15) The data for the hydrocarbons are taken from ref. 14 and those for the silylhydrocarbons from S. Tannenbaum, S. Kaye and G. F. Lewenz, THIS JOURNAL, **75**, 3753 (1953). The heats of vaporization for the silylhydrocarbons were calculated at the same temperature as those for which the heats are given in ref. 14.

The third step in the reaction represents a competition for the proton between the aliphatic amine and the silylamine. Silyldimethylamine is sufficiently basic to keep the equilibrium somewhat toward the left. Thus it is removed from the solid with some difficulty. In the case of methyldisilylamine and trisilylamine the feebly basic nature of these compounds shifts the equilibrium completely to the right.

The last property which requires an explanation is the thermal instability of silyldimethylamine. It seems likely that the products are trimethylamine and the higher silylamines, the decomposition being a disproportionation reaction. Such a disproportionation is thermodynamically favored by the resonance stabilization of the higher silylamines and kinetically by the association of the silyldimethylamine. However, since the products of decomposition could not be actually determined, this explanation must be considered as tentative.

Further work toward the understanding of the chemistry of the silicon hydrides is in progress.

Experimental Part

Apparatus.—A Stock-type high vacuum line was employed and temperatures were measured with appropriate vapor pressure thermometers.[16] Quantities expressed in cc. are for gases at S.T.P.

Ammonia.—Tank ammonia was dried over sodium and fractionally distilled at −112°. The product was tensiometrically homogeneous at −45.2° with a vapor pressure of 405 mm. (lit. 405.2 mm.).[17]

Methylamine.—Methylamine was generated from methylamine hydrochloride solution by treating with potassium hydroxide, distilled through −40°, dried over potassium hydroxide and then over sodium, and finally distilled from −80°. The product was tensiometrically homogeneous at −18.6° with a vapor pressure of 422 mm. (lit. 422 mm.).[6]

Dimethylamine.—Anhydrous dimethylamine (commercial) was dried over sodium hydroxide pellets and fractionally distilled from −80°. The product was tensiometrically homogeneous at 0° with a vapor pressure of 565 mm. (lit. 564.7 mm.).[18]

Trimethylboron.—Trimethylboron was prepared and purified by the method described by Brown.[19] The product was tensiometrically homogeneous with a vapor pressure of 681 mm. at −22.9° (lit. 680 mm.).

Silyl Bromide.—The procedure described by Stock and Somieski for the reaction between bromine and silane was modified for the preparation of silyl bromide.[20] The modification allowed: (1) a larger quantity of silyl bromide to be synthesized with a more compact apparatus, (2) a larger conversion of silyl bromide to be obtained (80–90% compared to 55% by Stock and Somieski) and (3) a shorter period for the reaction (3–5 hr. compared to 7 hr.). These improvements were obtained by maintaining the bromine as a solid at −40 to −50° and allowing silane vapor at its saturation pressure at −120° to react with it. Since the vapor pressure of silyl bromide is negligible at −120° it condensed at this temperature and was prevented from forming polybromosilanes.

The bromination apparatus consisted of two concentric ring-sealed tubes with test-tube bottoms. The inner cold finger tube was 7 × 1.6 cm. and the outer tube 19 × 3.5 cm. This was connected to the high vacuum line by a stopcock (lubricated with fluorocarbon grease). A safety blow-off tube was attached to the reaction system. A weighed quantity of bromine was condensed on the cold finger at −196° (by filling the cold finger with liquid nitrogen) and silane condensed in the outer tube at −196°. The liquid nitrogen bath around the outer tube was then replaced by a −120° bath (ethyl ether slush), the top of the bath being kept 5–8 cm. below the tip of the cold finger. The temperature of the cold finger was next carefully allowed to rise to −45 ± 5° by removing the liquid nitrogen and using ether and Dry Ice as the refrigerant. *The temperature of the cold finger must not be allowed to rise above −30° because above this temperature spontaneous ignition occurs.* The reaction was essentially complete when the bromine had disappeared from the cold finger (3–5 hr.). A small amount of unreacted bromine diffused to the −120° region. This was removed by allowing the reaction mixture to stand over mercury overnight.

The components of the reaction were separated by fractional distillation and condensation in the vacuum line. Silane was recovered by distillation through −150°, hydrogen bromide by distillation from −120°, and polybromosilanes as residue at −95°. The silyl bromide prepared in this manner exerted a vapor pressure of 698–700 mm. at 0° (lit. 710 mm.).[20] Table II summarizes the results of three typical experiments and compares them with those obtained by Stock and Somieski.

TABLE II

QUANTITIES OF REACTANTS AND PRODUCTS INVOLVED IN THE PREPARATION OF SILYL BROMIDE

Run no.	SiH_4 used, cc.	Br_2 used, cc.	SiH_4 recovered, cc.	SiH_3Br recovered, cc.	Conversion of SiH_4 to SiH_3Br, %
Stock and Somieski[20]	498	366	299	110	55
1	493	331	228	213	80
2	1200	1080	146	967	92
3	2138	1400	988	1006	87

Silyldimethylamine. Synthesis.—The preparation of pure silyldimethylamine has not been previously reported in the literature. Emeleus and Miller observed a reaction between silyl chloride and dimethylamine but were not successful in isolating silyldimethylamine from the reaction products.[12]

The same type of apparatus was used for the amination of silyl bromide in this and the following experiments. It consisted of a liter reaction bulb connected through a U-tube and a Stock-valve to the high vacuum line. A blow-off manometer was attached to the reaction bulb. The procedure for carrying out the reaction was the same in all three cases.

Dimethylamine, 139.4 cc., was distilled into the reaction bulb and then 69.8 cc. of silyl bromide distilled into the U-tube. Upon allowing the two to warm to room temperature a copious quantity of white precipitate formed. The pressure in the system became constant after ten minutes and corresponded to 29 cc. of gas. When the U-tube was cooled to −196° a trace of a non-condensable gas was found. This was pumped out and the material volatile at room temperature distilled out of the reaction bulb. The volume of the distillate recovered was 30 cc. By continuing the distillation for 12 hr. longer, a total of 67 cc. of volatile material was obtained.[21]

The mixture was distilled through a series of U-tubes at −63, −100 and −196°. The silyldimethylamine condensed in the −100° U-tube with a trace of more volatile component. By distilling for short intervals at −63°, the impurity was removed. A total of 59 cc. of tensiometrically homogeneous dimethylsilylamine with a vapor pressure of 309 mm. at 0° was obtained. The yield was 84%. The other volatile products were 5.3 cc. of silane and 3.1 cc. of an unidentified product which condensed at −63°.

Silyldimethylamine was stored at either −80° or −196° in order to prevent its decomposition. In the gas phase at room temperature the rate of decomposition was sufficiently slow to permit its manipulation in the vacuum line.

Melting Point.—Silyldimethylamine melted sharply at 3.3–3.4° in a sealed capillary tube under its own vapor pressure. After one-half hour at 4°, the m.p. decreased to 3.0–

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(16) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(17) F. Henning and A. Stock, *Z. Physik.*, **4**, 226 (1921).

(18) A. Simon and J. Hunter, *Z. Elektrochem.*, **41**, 28 (1935).

(19) H. C. Brown, THIS JOURNAL, **67**, 374 (1945).

(20) A. Stock and K. Somieski, *Ber.*, **51**, 989 (1918).

(21) The recovery of the volatile products may be hastened by warming the precipitate to 50° without seriously decreasing the yield of silyldimethylamine.

3.4°. The decomposition in the liquid state was, thus, rather rapid.

Vapor Pressure.—Solid silyldimethylamine was sufficiently stable for vapor pressure measurements. At 0°, the vapor pressure of an initially pure solid sample remained constant at 310 mm. for one-half hour, decreased to 309 mm. in 2 hr., and decreased further to 304 mm. in 5 hr. with an appearance of a liquid phase. Numerous attempts to separate the products of decomposition were unsuccessful. It appears that the products have the same order of volatility which suggests that the decomposition is a disproportion to trimethylamine and methyldisilylamine. At lower temperatures the rate of decomposition was slower.

The results of measurements on two independent samples are shown in Fig. 1 in the form of the usual log P *vs.* $1/T$ plot. In run 1, the vapor pressures were observed as the sample was warmed from −45 to −9° and then as it was cooled down again to −45°. In run 2 the pressures were observed as the temperature was raised. The data are reasonably represented by the same straight line, indicating that little, if any, irreversible decomposition had occurred. Below −40° the pressures show slight positive deviation from the line. The equation of the straight line is $\log P = -3070/T + 13.726$. The pressures calculated from the equation are within ±0.5 mm. of the observed values. The heat of sublimation is calculated as 14.0 kcal./mole, assuming complete dissociation in the vapor state.

Molecular Weight of the Gas.—The apparent molecular weight of the gaseous silyldimethylamine was determined by vapor density measurements. The deviations were somewhat greater than expected so that a number of determinations were made on freshly purified samples. The results are given in Table III.

TABLE III

APPARENT MOLECULAR WEIGHT OF SILYLDIMETHYLAMINE AT 25–30°

Mass, g.	Pressure, mm.	Apparent mol. wt.
Calculated for $SiH_3(CH_3)_2N$		75.2
0.0356	23.0	76.4
.0438	28.0	76.2
.0900	58.0	76.8
.1195	77.0	76.8
.2373	149.5	77.5

Chemical Analysis.—The following series of reactions were utilized to establish the chemical composition

$$SiH_3(CH_3)_2N + 2HBr = SiH_3Br\uparrow + (CH_3)_2HNHBr\downarrow$$

$$(CH_3)_2HNHBr + NaOH(aq) = (CH_3)_2HN\uparrow + H_2O + NaBr(aq)$$

Silyldimethylamine was treated with a measured excess of hydrogen bromide at room temperature. The excess hydrogen bromide and silyl bromide were removed, separated from one another by fractional distillation, and identified by their vapor pressures. The dimethylamine hydrobromide was then dissolved in concentrated sodium hydroxide and the dimethylamine recovered and identified by its vapor pressure. The aqueous solution was neutralized and titrated for bromide with standardized silver nitrate. The results of a typical analysis are given in Table IV.

TABLE IV

RESULTS OF CHEMICAL ANALYSIS OF SILYLDIMETHYLAMINE

Chemicals	Obsd., cc.	Calcd., cc.
$SiH_3(CH_3)_2N$, used	15.6[a]	15.6
HBr, used	31.9	31.2
SiH_3Br, formed	15 0	15.6
$(CH_3)_2HN$, formed	14 6[b]	15.6
Br^-	15.5	15.6

[a] A correction of 1.3% was made for deviation of the gas perfect behavior at the measured pressure of 34.0 mm. and temperature of 25°. [b] Separation from water was difficult, presumably due to hydrate formation (see S. U. Pickering, *J. Chem. Soc.*, 141 (1893), and W. C. Somerville, *J. Phys. Chem.*, **35**, 2412 (1931)).

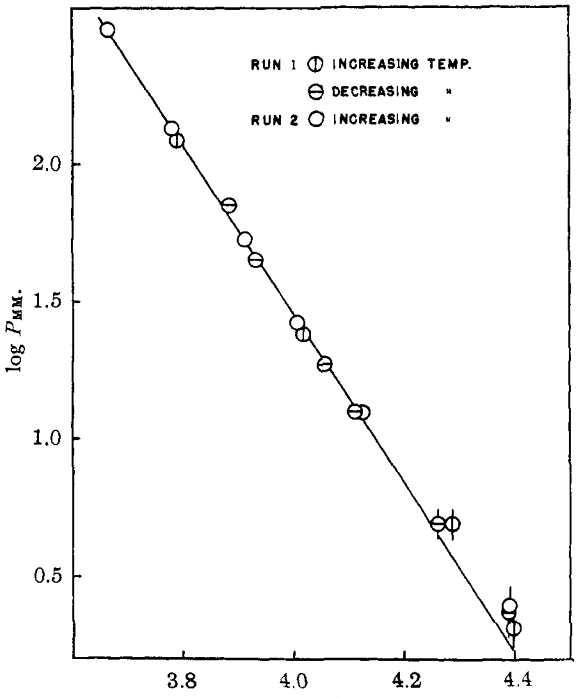

Fig. 1.—Saturation pressure of silyldimethylamine.

Methyldisilylamine.—Methyldisilylamine has been previously prepared from silyl chloride and methylamine.[12]

Stoichiometric quantities of silyl bromide, 102.8 cc., and methylamine, 154.2 cc., were combined at room temperature. White precipitation occurred immediately. After 1 hr. the total pressure of the gas in the reaction vessel corresponded to 49.7 cc. (calcd. 51.4 cc.). A trace of non-condensable gas, 2 cc., was observed and was pumped out. The volatile products were distilled out at room temperature and in 15 min., 52.4 cc. of distillate was collected (vapor pressure 212 mm. at 0°). This was purified by distillation from −78° through a series of U-tubes kept at −95, −112 and −196°. The desired product was obtained in the −95° trap but additional quantities were recovered from the condensate in the −112° trap by repeated redistillation through −95°. The total volume of methyldisilylamine collected was 43.5 cc. The product was tensiometrically homogeneous with a vapor pressure of 193 mm. at 0° (lit., 192 mm.).[12] The m.p. was determined to be −124.1 to −124.6°.

Trisilylamine.—Trisilylamine has been previously prepared from silyl chloride and ammonia.[13]

Stoichiometric quantities of silyl bromide, 244.8 cc., and ammonia, 325.5 cc., were combined at room temperature. Precipitation of a white solid occurred immediately. After 1 hr. the total pressure of the gas corresponded to 90 cc. (calcd. 82 cc.). The mixture was allowed to stand overnight at room temperature, whereupon the volume of the gas decreased to 81 cc. The volatile products were distilled out at room temperature and in 15 min. 80 cc. of distillate collected (vapor pressure 123 mm. at 0°). The mixture was distilled from −45° through U-tubes at −100 and −196°. Most of the trisilylamine was obtained in the −100° trap. A small additional quantity of product was recovered by distilling the −196° fraction from −100° until the correct vapor pressure at 0° was obtained. The product was tensiometrically homogeneous with a vapor pressure of 110 mm. at 0° (lit. 109 mm.[13]).

Although the molecular weight of the compound has been previously determined, we have re-measured it in order to have a standard with which to compare the deviations observed for the molecular weight of silyldimethylamine. The results together with the value determined by Stock and Somieski are 108.9 (142.9 mm.), 108.6 (91.0 mm.)[13] and 108.3 (67.2 mm.). The pressure of the gas is given in the parentheses, calcd. for $(SiH_3)_3N$ 107.3.

Silyldimethylamine-Trimethylboron.—This compound has not been previously reported in the literature.

Composition and Gas Phase Dissociation.—Silyldimethylamine, 17.5 cc., was treated with an excess of trimethylboron, 22.5 cc., at room temperature. The total pressure was 478 mm. and a liquid phase was observed. The system was cooled to −78° and the volatile product distilled out. The distillate, 6.0 cc., was identified as trimethylboron by its vapor pressure of 31 mm. at −78° (lit., 32.5 mm.[22]). Hence, 17.0 cc. of silyldimethylamine had combined with 16.5 cc. of trimethylboron. At 0°, the solid product had a vapor pressure of 146 mm. (138 mm. calcd. for purified sample). When completely vaporized at 24° and 72.5 mm., the volume of the gas was 33.0 cc. (calcd. for complete dissociation 34.0 cc.). It is concluded that the compound is almost completely dissociated under these conditions.

A duplicate experiment in which 15.0 cc. of silyldimethylamine and 40.0 cc. of trimethylboron were employed showed that 14.5 cc. of trimethylboron was consumed. The total volume of the sample at 26° and 62 mm. was 28.0 cc. (calcd. for complete dissociation 29.5 cc.). Minute droplets of colorless liquid were observed which did not evaporate. Since the total volume of the vessel was 378 cc., this indicates that slow decomposition was occurring.

Vapor Pressure and Melting Point.—A tensiometrically homogeneous sample of the addition compound was obtained by distillation from −50° and condensation at −78°. The saturation pressures were measured at various temperatures without observation of any irreversible decomposition. The results may be summarized by the equation $\log P = -2685/T + 11.968$ in the range −30 to −5°. The data are given in Table V with the values calculated from the equation. Assuming complete dissociation of the compound and the Clausius–Clapeyron relations, the heat of sublimation is calculated to be 24.6 kcal./mole.

TABLE V

SATURATION PRESSURES OF SILYLDIMETHYLAMINE-TRIMETHYLBORON

T, °C.	−31.4	−27.3	−18.2	−14.8	−9.1	−4.6	0
P_{mm}, obsd.	7.6	11.2	27.2	37.8	63.7	93.8	...
P_{mm}, calcd.	7.3	11.2	27.5	37.8	63.4	93.7	138

The melting point was 16.3–17.0° in a sealed capillary.

Acknowledgment.—This work was made possible by a Frederick Gardner Cottrell grant from the Research Corporation.

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[22] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, Vol. III, p. 218. Same as ref. 14.

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

An Absorption–Extrapolation Light Scattering Method[1]

BY FRED W. BILLMEYER, JR.

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The particle size of a polystyrene dispersion has been determined by a light scattering method in which transmission measurements are made as a function of wave length. The data are extrapolated to infinite wave length, where the usual small particle light scattering treatment is valid. The results are in satisfactory agreement with the size determined by other light scattering methods.

Introduction

Three different methods of observation have been developed for measuring particle sizes and molecular weights by light scattering. All of these yield essentially equivalent information, but each of them is different from the others in its detailed application and its suitability to certain scattering systems.

The first of these techniques is the dissymmetry method developed by Debye[2] in which scattered light intensity is measured as a function of angle of observation. Scattering functions, dependent upon particle shape, are used to interpret the data in terms of particle size and molecular weight.

A second method is also based on the measurement of scattered light intensity. This is the extrapolation method of Zimm[3] in which data are obtained over as large an angular range as possible and then extrapolated to zero angle. This method is now considered to give the most accurate and precise determinations of molecular weight and size. It is less dependent upon assumptions of particle shape, but requires rather elaborate equipment and considerable skill and care in its application.

The third method, particularly suitable for use with highly scattering systems, is the transmission technique described by Doty.[4] In this method the reduction in light transmission of a colloidal solution due to scattering is measured instead of the scattered light intensity itself. The technique is complementary to the dissymmetry method, measurements being made at a series of wave lengths instead of a series of angles. Again a set of scattering functions based upon specific particle shapes and distributions is used to interpret the results.

The theory of a fourth method, which we have called the absorption-extrapolation technique, has been outlined by Cashin and Debye.[5] Like Doty's transmission method, this procedure uses a standard spectrophotometer to measure total scattering by transmission in a colloidal system. As in Zimm's extrapolation method, scattering functions dependent upon particle shape are not needed for the evaluation of molecular weight.

In the absorption–extrapolation method, the absorption[6] measurements are made at several wave lengths and extrapolated to infinite wave length. Where lack of a suitable range of wave lengths is not a limiting factor,[4] the method combines many of the advantages of other techniques. For example, it has been useful in measuring the particle sizes of dispersions of polymers. This paper describes its application to an aqueous dispersion of polystyrene.

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[1] Presented at the 124th National Meeting of the American Chemical Society, Chicago, Ill., September 9, 1953.

[2] P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).

[3] B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

[4] P. Doty and R. F. Steiner, *ibid.*, **18**, 1211 (1950).

[5] W. M. Cashin and P. Debye, *Phys. Rev.*, **75**, 1307A (1949).

[6] Throughout this paper the term absorption will imply loss in transmission due to scattering only.