197. *A Comparative Study of the Basicity of Some Silylamines.*

By A. W. Jarvie and D. Lewis.

Determination of the heat of mixing with chloroform has been used to measure the electron donor ability of the silylamines. The influence of steric factors has been investigated and it has been found that the electron donor power of the silylamines decreases as the bulk of the groups on either the silicon or the nitrogen atom is increased.

Considerable evidence indicates that the silylamines are less basic than their carbon analogues. Burg and Kuljian [1] observed that trisilylamine was a poorer electron donor than trimethylamine. It does not form complexes with diborane or trimethylboron, and the complexes formed with boron trichloride and boron trifluoride are too unstable to be used for the measurement of base strength.[2] *NN*-Dimethylmethylsilylamine and *NN*-dimethyltrimethylsilylamine form 1 : 1 complexes with methyl iodide but the di- and tri-silylamines, *N*-methyldi(methylsilyl)amine, and tri(methylsilyl)amine do not react with methyl iodide.[3] Silazane polymers co-ordinate with copper ions but lose the copper to ethylenediamine which is a stronger donor, and polymers with Si–N–C bonds are more powerful donors than those with Si–N–Si bonds.[4] The results of a dipole-moment study on a series of *N*-alkyltrimethylsilylamines indicate that the electronegativity of the nitrogen atom in the silylamines is much reduced relative to dimethylamine.[5] A similar effect is observed with silicon–oxygen compounds. West [6] has shown that the ethers are stronger bases than the alkoxysilanes and that both these classes of compound are much stronger bases than the siloxanes.

It is now generally accepted that decrease in the electron donor power of electronegative atoms attached to silicon is due to d_π–p_π bonding between the lone pairs on the electronegative atom and the vacant 3*d*-orbitals of the silicon. Evidence for this type of bonding has been reviewed by several workers.[7] Although d_π–p_π bonding may be the main

---

[1] Burg and Kuljian, *J. Amer. Chem. Soc.*, 1950, **72**, 3103.
[2] Sujishi and Witz, *J. Amer. Chem. Soc.*, 1957, **79**, 2447.
[3] Ebsworth and Emeléus, *J.*, 1958, 2150.
[4] Minné and Rochow, *J. Amer. Chem. Soc.*, 1960, **82**, 5625.
[5] Cook and Mills, *J. Phys. Chem.*, 1961, **65**, 252.
[6] West, Whatley, and Lake, *J. Amer. Chem. Soc.*, 1961, **83**, 761.
[7] (*a*) Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332; (*b*) Craig, *ibid.*, 1959, 997; (*c*) Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 112; (*d*) Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp. 94—103.

factor responsible for the decrease in basicity of silicon-nitrogen and silicon-oxygen compounds, it seems likely that steric hindrance may be an important contributing cause. Emeléus and Ebsworth[3] have observed that the stability of the addition complexes of *NN*-dimethylsilylamines with trimethylboron decreases as the number of methyl groups attached to the silicon atom increases. This is likely to be a steric rather than an electronic factor.

The quantitative determination of the basicity of the silylamines is complicated by the instability of the silicon–nitrogen bond, which is cleaved rapidly by mineral acids, organic acids, Lewis acids, phenols, and alcohols. Therefore the more normal methods for determining pK_a values cannot be used.

The purpose of the present work has been to correlate the basicities of the alkylsilylamines with those of the aliphatic amines, and an attempt has been made to assess the relative importance of steric factors. The method used was to determine the heat of mixing of the silylamines with chloroform. As Gordy[8] has observed, heat-of-mixing data must be interpreted with caution: the amount of heat evolved will be dependent on several factors and may not be an exact measure of the hydrogen-bonding power of the donor. However, it has been shown by previous workers that this is a reasonable method of determining the relative electron donor ability of amines, ethers,[9] etc., and it seems likely that it will be a useful tool for estimating the influence of steric factors on the basicity of the silylamines.

EXPERIMENTAL

Calorimetry.—The apparatus and method used were identical with those employed by Tamres and his co-workers.[9b] The results are probably accurate to within 5% although in those cases where the heat of mixing is low (*e.g.*, hexamethyldisilazane) the error may be as high as 10%. Several determinations were made on each compound. The results were reproducible within the error of the experiment.

Materials.—Hexamethyldisilazane was prepared as described by Sauer and Hasek.[10] The purified material had b. p. 126°, n_D^{20} 1·4070 (Found: Neut. equiv., 164. Calc. for $C_6H_{19}NSi_2$: Neut. equiv., 161). *N*-Methyl-, *N*-ethyl-, *N*-isopropyl-, *N*-t-butyl-, *NN*-dimethyl- and *NN*-diethyl-trimethylsilylamine were prepared from trimethylchlorosilane and the corresponding aliphatic amine. The b. p.s. for refractive indices, and neutralisation equivalents of the purified materials are as follows: *N*-methyltrimethylsilylamine,[10] b. p. 71°, n_D^{20} 1·3899 (Found: Neut. equiv., 103. Calc. for $C_4H_{13}NSi$: Neut. equiv., 103); *N*-ethyltrimethylsilylamine,[10] b. p. 90—91°, n_D^{20} 1·3930 (Found: Neut. equiv., 117. Calc. for $C_5H_{15}NSi$: Neut. equiv., 117); N-*isopropyltrimethylsilylamine*, b. p. 102—103°, n_D^{20} 1·3944 (Found: Neut. equiv., 134. $C_6H_{17}NSi$ requires Neut. equiv., 131); *N*-t-butyltrimethylsilylamine,[11] b. p. 121—123°, n_D^{20} 1·4055 (Found: Neut. equiv., 148. Calc. for $C_7H_{19}NSi$: Neut. equiv., 145); *NN*-dimethyltrimethylsilylamine, b. p. 85°, n_D^{20} 1·3958 (Found: Neut. equiv., 114. Calc. for $C_5H_{15}NSi$: Neut. equiv., 117); *NN*-diethyltrimethylsilylamine,[10] b. p. 126°, n_D^{20} 1·4101 (Found: Neut. equiv., 145. Calc. for $C_7H_{19}NSi$: Neut. equiv., 145). *N*-Ethyltriethylsilylamine[11] was prepared from triethylchlorosilane and ethylamine and had b. p. 166—167°, n_D^{20} 1·4290 (Found: Neut. equiv., 161. Calc. for $C_8H_{21}NSi$: Neut. equiv., 159). Triethylsilylamine[10] was obtained by treatment of triethylchlorosilane with liquid ammonia and had b. p. 137° (Found: Neut. equiv., 134. Calc. for $C_6H_{17}NSi$: Neut. equiv., 131). Hexamethylcyclotrisilazane,[12] prepared from dimethyldichlorosilane and liquid ammonia, had b. p. 188°, n_D^{20} 1·4439 (Found: Neut. equiv., 71. Calc. for $C_6H_{21}N_3Si_3$: Neut. equiv., 73). *NN*-Diethyldimethylsilanediamine[12] was obtained from dimethyldichlorosilane and ethylamine; it had b. p. 138—139°, n_D^{20} 1·4134 (Found: Neut. equiv., 70. Calc. for $C_6H_{18}N_2Si$: Neut. equiv., 73). Hexamethyldisiloxane,[13]

---

[8] Gordy and Stanford, *J. Chem. Phys.*, 1941, **9**, 204.

[9] (*a*) Searles and Tamres, *J. Amer. Chem. Soc.*, 1951, **73**, 3704; (*b*) Tamres, Searles, Leighly, and Mohrman, *ibid.*, 1954, **76**, 3983; (*c*) Marvel, Copley, and Ginsberg, *ibid.*, 1940, **62**, 3109.

[10] Sauer and Hasek, *J. Amer. Chem. Soc.*, 1946, **68**, 241.

[11] Pike, *J. Org. Chem.*, 1961, **26**, 232.

[12] Larsson and Smith, *Acta Chem. Scand.*, 1949, **3**, 48.

[13] Sauer, *J. Amer. Chem. Soc.*, 1944, **66**, 1707.

prepared by hydrolysis of trimethylchlorosilane, had b. p. 100°, n_D^{20} 1·3764. Ethoxytrimethylsilane was a Hopkin and Williams " Purified " product which was dried ($CaSO_4$) and fractionally distilled. The middle fraction used for the determinations had b. p. 75°, n_D^{20} 1·3738. Chloroform was washed five times with water, dried ($CaCl_2$), and fractionally distilled.

The Reaction of Methyl Iodide with NN-*Diethyltrimethylsilylamine.*—The silylamine (8 g.) was dissolved in methyl iodide (8 g.); and a brown oily material was slowly deposited. After about 12 hr. a white solid began to separate. This was allowed to accumulate for 3 days, then filtered off (yield, 2 g.). The substance did not contain silicon; it is possible that the material is diethyldimethylammonium iodide (Found: I, 56·4; N, 6·1. Calc. for $C_6H_{16}IN$: I, 55·4; N, 6·1%).

TABLE 1.

Heats of mixing (*M*) with chloroform (in cal./mole of solution)

	Compound	Heat of mixing at 17° (*M*)
(I)	n-Butylamine	714 *
(II)	Di-n-butylamine	810 *
(III)	Diethylamine	866 *
(IV)	Di-isopropylamine	935 *
(V)	Tri-n-butylamine	438 *
(VI)	Triethylamine	870 *
(VII)	*N*-Methyltrimethylsilylamine	355
(VIII)	*N*-Ethyltrimethylsilylamine	315
(IX)	*N*-Isopropyltrimethylsilylamine	174
(X)	*N*-t-Butyltrimethylsilylamine	98
(XI)	*NN*-Dimethyltrimethylsilylamine	359
(XII)	*NN*-Diethyltrimethylsilylamine	102
(XIII)	Hexamethyldisilazane	28
(XIV)	Hexamethylcyclotrisilazane	196
(XV)	*NN*-Diethyldimethylsilanediamine	364
(XVI)	Triethylsilylamine	272
(XVII)	*N*-Ethyltriethylsilylamine	102

* Temperature of measurement not recorded (ref. 9*b*).

TABLE 2.

	Compound	*M*	$\Delta\nu_{OH}$ Phenol *	$\Delta\nu_{NH}$ Pyrrole *
(XVIII)	Hexamethyldisiloxane	−80	169	75
(XIX)	Ethoxysilanetrimethyl	499	271	138
(XX)	Diethyl ether	597 †	282	149

* Ref. 6. † Measured at 25° (ref. 9*a*).

DISCUSSION

Examination of the calorimetric data in Table 1 shows that when chloroform is used as reference acid the alkylsilylamines are in general weaker bases than the aliphatic amines. Tamres[9b] has suggested that chloroform should not be a very bulky electron acceptor molecule. The large chlorine atoms are bound to the second atom from the nitrogen and the first atom, the hydrogen, is not closely or rigidly bound to the nitrogen. However, comparison of the calorimetric data for ethoxytrimethylsilane and hexamethyldisiloxane with the spectroscopic data obtained by West[6] indicates that chloroform as a reference acid is considerably bulkier than either phenol or pyrrole. West measured the relative basicity of a variety of siloxanes, alkoxysilanes, and ethers by determining the frequency shift of OH and NH bands on hydrogen-bond formation. By using phenol and pyrrole as reference acids it was found that the electron donor power of hexamethyldisiloxane was about two thirds of that of ethoxytrimethylsilane. When the heat of mixing with chloroform is used as a measure of basicity ethoxytrimethylsilane is found to be a relatively good electron donor whereas the donor power of hexamethyldisiloxane is too weak to be measured. These changes in relative basicity, shown in Table 2, are probably due to steric interaction between the bulky trimethylsilyl group and the chloroform molecule.

It has been demonstrated that carbon and silicon compounds of analogous structure do not have the same molecular shapes. Trimethylamine is a tetrahedral molecule whereas trisilylamine[14] is planar; hexamethyldisilazane is easily prepared in good yield whereas

---

[14] Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.

di-t-butylamine has been obtained in only poor yield,[15] the difficulty in formation has been attributed to steric strain.[16] Therefore, the observed differences in the hydrogen bonding ability of hexamethyldisilazane and *N*-t-butyltrimethylsilylamine will not be due entirely to electronic effects but will also involve a steric factor.

The effect of increasing the size of the alkyl substituent on the nitrogen is demonstrated in the series of compounds (VII)—(X), Table 1. It is interesting to note that the dipole moment [5] is almost constant throughout this series, which shows that, in this case as in most others, extension of the alkyl chain causes little change in polar effects within the molecule. The observed decrease in hydrogen bonding ability as the bulk of the groups on the nitrogen is increased would seem, therefore, to be due to steric factors. Similarly, increasing the size of the substituents on the silicon atom causes a decrease in the basicity of the silylamines [compare compounds (VIII) and (XVII)].

Pike [11] reports that *N*-alkylsilylamines react more slowly than *NN*-dialkylsilylamines with silanols. Since *NN*-dimethylsilylamines form addition compounds with methyl iodide and trimethylboron [3] it may be assumed that these compounds are relatively strongly basic. The authors suggest, therefore, that the reaction rate may be dependent on the basicity and that the *N*-alkylsilylamines are weaker bases than the *NN*-dialkylsilylamines. Although this may be true in some cases, since the relative basicity of a compound will be dependent on the reference acid, it cannot be accepted as a generalisation. With chloroform as a reference acid *NN*-diethyltrimethylsilylamine is a weaker base than several of the *N*-alkylsilylamines. Furthermore, *NN*-diethyltrimethylsilylamine fails to give an addition complex with methyl iodide. The white solid isolated from the reaction of methyl iodide with *NN*-diethyltrimethylsilylamine did not contain silicon, showing that methyl iodide cleaves the silicon–nitrogen bond.

It has been pointed out by West [6] that deformation of the normal Si–O–Si bond angle might reduce the d_π–p_π overlap and that this might account for the fact that hexamethylcyclotrisiloxane is rather more basic than linear methylpolysiloxanes. However, Craig [7a] has drawn attention to the greater flexibility in steric requirements for d_π–p_π bond formation because the five orthogonal 3*d*-orbitals of the silicon allow of overlap over a wide range of bond angles. Preliminary work on some five-membered cyclosilazanes and the calorimetric result obtained for hexamethylcyclotrisilazane indicate that in five- and six-membered rings the effect of bond-angle deformation on d_π–p_π overlap is not very important.

Owing to the lack of comparative evidence it is impossible to determine whether the observed steric hindrance is, in the terminology of Brown, *B* or *F* in origin.[17] Comparison of our results with those obtained by West for disiloxanes and alkoxysiloxanes would suggest that *F* strain was more important in these cases. Many of the methods which have been used to study the influence of steric factors on basicity in the aliphatic and aromatic amines cannot be adapted to the silylamines because the silicon–nitrogen bond is readily cleaved by the reagents which are used as reference acids. It may be possible to elucidate further the effect of steric factors on the basicity of the silylamines by comparison of heats of mixing with chloroform and bromoform, or by an infrared study of hydrogen bonding with ethers of various sizes and shapes.[18]

We thank Imperial Chemical Industries Limited, Nobel Division, for the gift of chemicals and Dr. M. Williams and Mrs. B. Taylor for microanalyses.

CHEMISTRY DEPARTMENT,
COLLEGE OF ADVANCED TECHNOLOGY, BIRMINGHAM, 4.
[*Received, July 19th,* 1962.]

---

[15] Klages and Sitz, *Chem. Ber.*, 1959, **92**, 2606.

[16] Brown, Barbaras, Berneis, Bonner, Johannesen, Grayson, and Le Roi Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 1.

[17] Brown, Bartholomay, and Taylor, *J. Amer. Chem. Soc.*, 1944, **66**, 435.

[18] Gordy and Stanford, *J. Amer. Chem. Soc.*, 1940, **62**, 497.