droxide in 150 ml. of water. When one-half of the alkali was added, the solids quickly dissolved. This indicates that the normal sulfate salt is more soluble than the bisulfate. An oil separated after all the alkali was added. The oil smelled like burned fish. It was taken up in ether and dried. The ether was evaporated to leave 60 g. of a mixture of viscous liquid and pasty crystals. *Anal.* Calcd. for $(OSiMe_2CH_2NHCH_2SiMe_2-)_x$: neut. equiv., 175.3. Found: neut. equiv., 175.7.

This product was distilled at 23 mm. and yielded 18 g. of cyclic dimer, b.p. 152° at 23 mm., m.p. 45–49. See Table I, compound 9. The residue was heated to 330° at less than 1 mm. but could not be distilled. The residue was apparently a linear polymer of the same composition. It seems quite remarkable that the cyclic six-membered monomer was not produced in preference to the cyclic twelve-membered dimer.

Reaction of Chloromethyltrimethylsilane and Sodium Amide in Liquid Ammonia.—Chloromethyltrimethylsilane (122.5 g., 1 mole) and sodium amide (39 g., 1 mole) were sealed in an autoclave at 10° and liquid anhydrous ammonia was added. The temperature of the autoclave (80 lb. of iron) rose immediately to about 40° indicating a most vigorous reaction. The autoclave was heated to 120° for about $1^1/_2$ hours and cooled to room temperature. The excess ammonia was released and the non-volatile content of the bomb was washed out with ether. The solids (wt. 54 g., calculated 58.5 g. NaCl) were filtered off and the filtrate distilled in a still of about ten plates. During the distillation a gas was evolved ($MeNH_2$) and the boiling behavior of the material was erratic. The product was redistilled without difficulty and found to be essentially pure N-methylhexamethyldisilazane[7] (68 g., 78%), b.p. 148° at 740 mm., $n^{25}D$ 1.4190, d^{25}_4 0.794; sp. ref. 0.3181, calcd.[6] sp. ref. 0.3168. *Anal.* Calcd. for $C_7H_{21}NSi$: Si, 31.9; neut. equiv., 175.4. Found: Si, 31.2; neut. equiv., 176.6, 177.6.

To more firmly establish the identity of the product, it was shaken with benzoyl chloride in aqueous alkali and yielded N-methylbenzamide, m.p. 77.5–78.5°, which showed no depression of m.p. when mixed with authentic N-methylbenzamide, m.p. 80°.

Another sample was shaken with dilute acid. Hexamethyldisiloxane separated, b.p. 100.4° at 742 mm., $n^{25}D$ 1.3752, d^{25}_4 0.759. Sauer[8] reported for this compound a b.p. of 100.4° at 741 mm., $n^{20}D$ 1.3772, d^{20}_4 0.7638. Methylamine hydrochloride was obtained by evaporating the aqueous acid to dryness. Recrystallized once from acetone the hydrochloride melted at 223.5–224.5° and showed no depression when mixed with authentic hydrochloride, m.p. 225–226°.

The reaction that occurred probably can be represented by the equations

$$Me_3SiCH_2Cl + NaNH_2 \longrightarrow Me_3SiNHCH_3 + NaCl$$
$$2Me_3SiNHCH_3 \longrightarrow (Me_3Si)_2NMe + MeNH_2$$

The mechanism whereby the first reaction occurred in liquid ammonia solution is most obscure.

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[7] R. O. Sauer and R. H. Hasek, *ibid.*, **68**, 241 (1946), report a b.p. of 145°.

[8] R. O. Sauer, *ibid.*, **66**, 1707 (1944).

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[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF TECHNICAL GLASSWARE MAINTAINED AT MELLON INSTITUTE BY THE CORNING GLASS WORKS, IN COÖPERATION WITH THE DOW CORNING CORPORATION, AND FROM THE UNIVERSITY OF PITTSBURGH]

Effect of Organosilicon Substituents on the Basic Strength of Amines

BY JOHN E. NOLL,[1a] B. F. DAUBERT AND JOHN L. SPEIER[1b]

The basic dissociation constants of thirteen (silylmethyl)-amines and one β-aminoethylsilicon compound have been determined. Some effects of structure and of various substituents upon both the silicon and nitrogen atoms are described.

The basic dissociation constants of a series of silicon substituted amines[2] were determined to find the effects of organosilicon substituents on the basic strength of amines.

Two methods were used for determining the basic dissociation constants. One method gave dissociation constants at a relatively high ionic strength. In this method a purified sample of amine hydrochloride, analyzed for chlorine to determine its purity, was dissolved in a volume of water to which a known amount of standard hydrochloric acid had been added. The resulting solution was titrated with standard sodium hydroxide. The progress of the titration was followed by means of a Beckman model H-2 *p*H meter. From the curve of *p*H *versus* ml. of base added and the calculated ratio of amine to amine salt, the dissociation constant, *K*, was calculated using the formula

$$pK = \log \frac{[RNH_2]}{[RNH_3^+]} + pOH$$

As long as the ratio of amine to amine salt was small (less than 1:15) *pK* was constant and the value in this range was used. Another method, we will call the extrapolation method, for determining basic dissociation constants, was used to obtain dissociation constants at infinite dilution. This method was particularly suitable for those amines whose salts could not readily be prepared. The amines used in the determinations were carefully purified by distillation under nitrogen. Small quantities of amine were dissolved in known amounts of water and the *p*H of the resulting solution was determined. Standard hydrochloric acid was added in some cases so that a known ratio of amine to amine salt was present. From the *p*H and concentrations at each point, the *pK* was calculated and plotted against the ionic strength. Extrapolation of the curve to infinite dilution gave pK_B.

The two methods gave only slightly different results for the more water-soluble amines. The less soluble amines gave a much lower result by the second method. The *p*H could be determined to a precision of only about ±0.02 *p*H unit. A variation of this magnitude caused a variability of any single value of *K* of about 10%. Each value listed in Table I is the average of from five to eight separate values of *K* taken from a smooth curve of the plot of *pK versus* ionic strength (extrapolation method). The value of *pK* seldom varied by more than 0.2 of a unit over the concentration range used in the determination. The values obtained by

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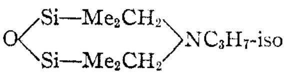
[1] (a) Submitted in partial fulfillment of the requirements for the degree of M.Sc. (b) Please address all communications concerning this work to Dr. John L. Speier, Mellon Institute, Pittsburgh 13, Pa.

[2] J. E. Noll, B. F. Daubert and J. L. Speier, THIS JOURNAL, **73**, 3867 (1951).

these procedures for the dissociation constants are listed in Table I.

TABLE I

BASIC DISSOCIATION CONSTANTS

	Compound	Titration method $K_b \times 10^4$	Extrapolation method $K_b \times 10^4$
1	$MeSiCH_2NH_2$	9.6	8.5
2	$C_6H_5SiMe_2CH_2NH_2$	2.8	2.3
3	$O(SiMe_2CH_2NH_2)_2$	2.0	
4	$EtOSiMe_2CH_2NH_2$[a]		1.5
5	$(EtO)_2SiMeCH_2NH_2$[a]		0.16
6	$(EtO)_3SiCH_2NH_2$[a]		0.027
7	$O(SiMe_2CH_2CH_2NH_2)_2$[b]	5.5	
8	$Me_3SiCH_2NHC_3H_7$-iso	12	6.3
9	$O(SiMe_2CH_2NHC_3H_7\text{-iso})_2$	1.2	2.5
10			1
11	$Me_3SiCH_2NHC_6H_{11}$	17	9.1
12	$O(SiMe_2CH_2NHC_6H_{11})_2$	1.8	1.3
13	$Me_3SiCH_2NHC_6H_5$		0.00002
14	$(Me_3SiCH_2)_2NH$	14	4[c]
15	iso-$C_3H_7NH_2$	4.3[d]	4.0[d]
16	CH_3NH_2	5.1[d]	
17	NH_3		0.2[d]

[a] The ethoxyl groups in these compounds undoubtedly hydrolyzed and the siloxanes formed. For purposes of calculations, however, the compounds were considered monoamines. [b] This compound was made by treatment of 3-trimethylsilylpropionic acid[3] with sulfuric acid and sodium azide at steam-bath temperatures. It was isolated as the hydrochloride, m.p. 261–263°. *Anal.* Calcd. for $C_8H_{26}OCl Si$: Cl, 24.18. Found: Cl, 24.22, 24.25. [c] Extrapolation of the curve from which this value was obtained to the higher ionic strength used for the titration method gave a value of $K = 10 \times 10^{-4}$. [d] N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932), report the values of pK_b as follows: NH_3, 9.27 (K_b, 1.86×10^{-5}); i-$C_3H_7NH_2$, 10.63 (K_b, 4.27×10^{-4}); CH_3NH_2, 10 (K_b, 4.37×10^{-4}).

In Table II some of the silylmethylamines are compared with selected examples of organic amines. From these examples one can readily see that the α-trimethylsilyl group has a strong effect on an amine in increasing its basic dissociation constant, but that the effect of the phenyl or oxygen-substituted silyl groups is in the opposite direction. Electronegative substituents such as phenyl or oxygen, in general, exhibit such effects of weakening amines.

TABLE II

DISSOCIATION CONSTANTS OF PRIMARY AMINES

Amine	$K_B \times 10^4$	$\frac{K_B}{K_B(MeNH_2)^a}$	$\frac{K_B}{K_B(Me_3SiCH_2NH_2)}$	$\frac{K_B}{K_B(n\text{-}C_3H_7NH_2)^a}$
$Me_3SiCH_2NH_2$	8.5	1.94	1.00	
$MeCH_2CH_2NH_2$[b]	3.9	0.89	0.46	1.00
$C_6H_5SiMe_2CH_2NH_2$	2.3	.53	.27	
$C_6H_5CH_2CH_2NH_2$[c]	0.67	.15	.079	0.17
$EtOSiMe_2CH_2NH_2$	1.5	.34	.17	
$HOCH_2CH_2NH_2$[b]	0.28	.064	.033	0.07
$(EtO)_2SiMe_2CH_2NH_2$	.16	.037	.019	
$(EtO)_3SiMe_2CH_2NH_2$	.027	.006	.0032	

[a] These values calculated using the values of Hall and Sprinkle[b]. [b] N. F. Hall and M. R. Sprinkle, Table I, footnote *d*. [c] W. H. Carothers, C. F. Bickford and G. J. Hurwitz, THIS JOURNAL, 49, 2908 (1927).

In general the effects of such substituents rapidly diminish as the number of intervening carbon atom increases between the substituent and the functional group. However, it has been found for two disiloxanes, $O[SiMe_2CH_2NH_2]_2$ and $O[SiMe_2CH_2CH_2NH_2]_2$, that the latter, a β-substituted amine is considerably stronger than the former, an α-substituted amine, quite contrary to all expectations. These compounds were compared as their hydrochlorides by the titration method at equal concentrations under strictly comparable conditions and their apparent K_b values were found to be 2.0×10^{-4} and 5.5×10^{-4}, respectively. No good explanation for this can be offered at this time.

Table II shows that the effect of phenyl or oxygen activity through two carbon atoms is qualitatively the same as when they act through a silicon and a carbon, but that quantitatively the effect is reduced in the latter case. For example, replacement of one methyl group by a phenyl group reduces the value of K_B to 27% of that of trimethylsilylmethylamine, while a similar replacement in n-propylamine causes a reduction in K_B to only 17%. In every case where reasonable comparisons can be made between a silylmethylamine and a similar organic amine, the silylmethylamine appears to be two to five times the stronger base.

The pronounced effect of phenyl or oxygen acting through a silicon atom to reduce the basic strength of amines might be expected to appear as a strengthening effect of equal magnitude in substituted silylacetic acids. The data of Sommer[3] seen in Table III shows, however, that the strengths of the acetic acids are practically unaffected by such structural changes and that a phenyl group weakens the acid slightly instead of strengthening it.

These data in Table III point out the anomaly that the substitution of phenyl or oxygen for a methyl group on the silylacetic acid is practically without effect on the value of K_A for the acids in spite of the pronounced effect such substitution has upon comparable organic acids and also upon the values of K_b for the silylmethylamines.

TABLE III

DISSOCIATION CONSTANTS OF SUBSTITUTED ACETIC ACIDS OF THE FORMULA RCH_2COOH

R	$K_A \times 10^5$	$\frac{K_A}{K_A\mathrm{HOAc}}$
CH_3CH_3	1.51[a]	0.86
$C_6H_5CH_2$	2.19[b]	1.25
$HOCH_2$	2.95[a]	1.70
CH_3Me_2Si	0.60[3]	0.34
$C_6H_5Me_2Si$	.54[3]	.31
$Me_3SiOSiMe_2$	.60[3]	.34

[a] W. Ostwald, *Z. physik. Chem.*, **3**, 369 (1889). [b] J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1008 (1937).

The infrared absorption spectra of these silylmethylamine compounds were obtained. None of these shows any evidence of absorption in the region characteristic of amines with but one exception, N-(trimethylsilylmethyl)-aniline. The complete lack of the absorption characteristic of the NH_2 group, or N–H group, is no doubt related to the other

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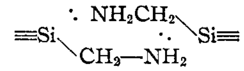
(3) L. H. Sommer, J. R. Gold, G. M. Goldberg and N. S. Marans, *ibid.*, **71**, 1509 (1949).

anomalies found for these compounds. It was thought that perhaps the amines were strongly associated, possibly through coördination somewhat as drawn



If such were true, the amines in non-polar solvents might exhibit abnormally high molecular weights. However, no indication of this was found when the molecular weight of trimethylsilylmethylamine was determined cryoscopically in benzene. The nearly ideal values of 102.5 and 104.3 were found. A value of 103.2 was calculated.

From these data the silylmethylamines all appear to be stronger bases than comparable organic amines. Substituents on the nitrogen show no abnormal effects. Substituents on the silicon atom show effects similar in nature to the same substituents in comparable organic amines.

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[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Nuclear Structure of the Water-soluble Polycarboxylic Acids from Oxidation of Bituminous Coal[1]

BY CLARENCE H. RUOF, T. R. SAVICH[2] AND H. C. HOWARD

The nuclear structures of the polycarboxylic acids prepared by the oxidation of bituminous coal have been studied by fractionation and investigation of the properties of: (1) the free acids, (2) their esters and (3) the methylated nuclei resulting from the hydrogenolysis of the esters. All the physical and chemical properties of these products demonstrate unequivocally the presence of significant amounts of compounds with nuclear structures more complex than the benzene ring. Certain fractions of the hydrogenolysis products contain appreciable amounts of oxygen and have properties corresponding closely to phthalans (isodihydrobenzofurans); the possibility that such ring systems were formed in the hydrogenolysis procedure cannot be excluded. The non-distillable residue of the hydrogenolysis products appears to be a polycyclic structure.

The method of degradation employed—oxidation, followed by esterification, hydrogenolysis and fractionation of the alkylated nuclear structures—is widely applicable to investigations of coal structure. In these reactions the temperature need not exceed 270°, thus minimizing structural changes due to thermal effects.

Controlled oxidation of aqueous alkaline suspensions of bituminous coals results in the conversions of approximately 50% of the carbon to a mixture of water-soluble carboxylic acids, the balance appearing as carbon dioxide.[3] Aliphatic acids—acetic and oxalic acid—have been shown to constitute a minor part of the mixture, usually not more than 10% of the coal carbon, and the balance has been designated as benzenecarboxylic or benzenoid. Individual benzenecarboxylic acids, which are all colorless, stable, crystalline compounds, have been isolated by a number of different workers, using a variety of coals and oxidation procedures. But there are also present yellow, non-crystalline thermally unstable acids which, in aqueous solution, migrate rapidly through parchment; they are not readily volatile but are soluble in low internal pressure solvents such as ethyl ether and the molecular weights of both the free acids and their esters are in the range of the benzenecarboxylic series.

The purpose of the present investigation was to study the nuclear structure of these yellow water-soluble polycarboxylic acids, which appear to be simple enough to offer hope of successful results in structural investigations and yet are sufficiently complex so that information concerning their structure would contribute significantly to our knowledge of coal. The methods used have involved (a) solvent fractionation of the free acids, (b) fractionation of the butyl esters by the action of solvents and by molecular distillation and (c) hydrogenolysis of the butyl esters followed by precision fractionation of the resulting nuclear structures with attached methyl groups. Throughout this series of steps the maximum temperature reached was 270°, thus minimizing thermal alterations of the fragments of the coal polymer.

Determination of molecular and equivalent weights of the acid fractions permits calculation of average functionality and hence average nuclear size. Similar calculations can be made for the ester fractions from values of molecular weights and saponification equivalents and information as to nuclear size follows directly from the molecular weight measurements on the fractions obtained from the hydrogenolysis reaction. In addition, determinations of such properties as density, refractive index, boiling point, viscosity and ultimate composition on the esters and hydrogenolysis fractions has permitted conclusions to be drawn as to chemical structure. The data from all these procedures point to the presence in the mixed acids of nuclear structures of a wide range of sizes—from a single ring to polycyclics of molecular weight of several hundred.

Experimental

Preparation of the Acids.—A suspension of 15 pounds of −100 mesh Pocahontas No. 3 coal in 15 gallons of water and 45 pounds of commercial flake sodium hydroxide was treated with oxygen gas at a total pressure of 900 p.s.i.g. at 270° for 2 to 3 hours in equipment previously described.[4] After cooling to about 90°, the reaction product was pressured out of the autoclave, cooled, filtered, acidified with sulfuric acid and extracted with methyl ethyl ketone in a two-stage countercurrent system. The ketone solution of the acids was concentrated to a sirup in a steam-jacketed

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[1] Presented in part before the Gas and Fuel Division, American Chemical Society, May 9, 1949, Pittsburgh, Penna.

[2] Rensselaer, Indiana.

[3] H. C. Howard, Chap. 9, "Chemistry of Coal Utilization," edited by H. H. Lowry, John Wiley and Sons, Inc., New York, N. Y., 1945.

[4] For a description of the pilot plant for the preparation of these acids see N. W. Franke and M. W. Kiebler, *Chem. Industries*, **58**, 580 (1946). Operating details are given in British Patent 635,088, April 5, 1950.