

showed no depression of melting point when mixed with an authentic sample of the derivative of formaldehyde, m. p. 165°. The derivative contained only a trace of silicon. At 150° a similar mixture after nineteen hours showed no signs of having reacted in any way.

**Preparation of bis-(Acetoxymethyl)-dimethylsilane (Dimethylsilylenedimethanol Diacetate).**—bis - (Chloromethyl)-dimethylsilane (292 g., 1.85 moles), potassium acetate (412 g., 4.2 moles) and glacial acetic acid (300 ml.) were heated together and shaken in a stainless steel autoclave at 118–130° for four hours and at 148–160° for sixteen hours. The contents of the autoclave were then washed once with water to remove the salts and most of the acid present. The water insoluble liquid was distilled. The only compound found, other than acetic acid, was bis-(acetoxymethyl)-dimethylsilane (339 g., 90%), b. p. 124° at 27 mm., 223° at 739 mm.,  $n_D^{25}$  1.4309–1.4310,  $d_4^{25}$  1.0135. Molar refraction: Calcd.<sup>8</sup> for (AcOCH<sub>2</sub>)<sub>2</sub>-SiMe<sub>2</sub>: 52.34. Found: 52.17. Anal. Sap. equiv. Calcd. for (AcOCH<sub>2</sub>)<sub>2</sub>SiMe<sub>2</sub>: 102.2. Found: 102.6, 102.1.

bis-(Acetoxymethyl)-dimethylsilane (110 g.) was dissolved in a ten-fold excess of dry methanol and acidified with three drops of concentrated hydrochloric acid. Periodically during three weeks methyl acetate was removed by distillation. Each time methanol was added to restore the solution to its original volume and the solution was permitted to stand at room temperature for several days before more methyl acetate was removed. The solution was distilled, after no further amount of methyl acetate appeared to form. bis-(Hydroxymethyl)-dimeth-

ylsilane (dimethylsilylenedimethanol) was obtained as a colorless, odorless, viscous liquid, completely soluble in water; b. p. 130° at 27 mm.,  $n_D^{25}$  1.4611,  $d_4^{25}$  0.993. Molar refraction: Calcd.<sup>8</sup> for (HOCH<sub>2</sub>)<sub>2</sub>SiMe<sub>2</sub>: 33.38. Found: 33.20. Saponification number, 12.7. Anal. Calcd. for C<sub>4</sub>H<sub>12</sub>O<sub>2</sub>Si: Si, 23.3. Found: Si, 23.2, 23.3.

### Summary

Some of the reactions of the chlorides of tetramethylsilane have been studied. These compounds showed a tendency, under certain conditions, toward cleavage of the substituted methyl group from the silicon atom. The dichloromethyl group was found to be more easily cleaved than the chloromethyl group. Hydrolysis of the addition product of trimethylsilylmethylmagnesium chloride and phenyl isocyanate was shown to result in the formation of acetanilide, thus revealing the ease of cleavage of *beta* carbonyl silicon compounds.

The new compounds, bis-(chloromethyl)-dimethylsilane, dimethylsilylenedimethanol diacetate, dimethylsilylenedimethanol, and dichloromethyltrimethylsilane were prepared and characterized during the investigation.

PITTSBURGH, PA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

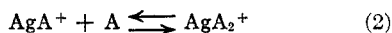
## The Basic Strengths of Amines as Measured by the Stabilities of Their Complexes with Silver Ions

BY RICHARD J. BRUEHLMAN<sup>1</sup> AND FRANK H. VERHOEK

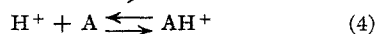
The relationship of the basic strengths of amines as determined by the stability of their ammonium ions to their strengths as measured by the stability of their complexes with silver ion has been discussed repeatedly. It has been stated that a parallelism between the two measures exists<sup>2</sup> and that a parallelism does not exist.<sup>3,4</sup> Except for the last paper cited,<sup>4</sup> the conclusions have commonly been based on a consideration of the instability or association constants for the over-all reaction



where A represents the amine. It was pointed out,<sup>5</sup> however, that each such constant contains an equilibrium constant for the reaction



in which the ion reacting with the amine is different for each amine considered, and that a more just comparison is that between the two reactions



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(2) Larsson, *Z. physik. Chem.*, **A169**, 215 (1934).

(3) Britton and Williams, *J. Chem. Soc.*, 796 (1935).

(4) Vosburgh and Cogswell, *THIS JOURNAL*, **65**, 2412 (1943).

(5) Carlson, McReynolds and Verhoeck, *ibid.*, **67**, 1334 (1945).

Accordingly the equilibrium constants of reactions (3) have been measured for several amines and compared with those for reactions (4) measured in similar systems. The equilibrium constants of reactions (2) were also measured.

The equilibrium constants were determined by means of pH measurements on solutions of amine, silver ion, acid and neutral salt according to the method of Bjerrum,<sup>6</sup> on selected groups of primary, secondary, and tertiary amines of varied basic strength. The selection was severely limited by the requirements that the amine be reasonably soluble in water, that it form complexes in such a pH range that silver oxide would not precipitate out, that it have a basic strength different from other members of the group, and that the complex formed be sufficiently soluble that a solid phase did not form. This paper reports equilibrium constants for the formation of amines of silver ion with five primary amines, three secondary amines, and four pyridines. In order to estimate the validity of the comparison of equilibrium constants for equations (3) and (4) at a single temperature, temperature coefficients over a ten-degree temperature interval were determined in most cases.

In addition, equilibrium constants were deter-

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

mined for the formation of copper amines with two of the pyridines.

### Experimental

The  $pH$  measurements were made with a glass electrode and a Coleman Style 200  $pH$  Electrometer. The glass and calomel electrodes were mounted in a specially designed glass apparatus that was thermostated at 25 or 35°; the two compartments were connected through ungreaed stop-cocks by a saturated potassium nitrate bridge. The electrometer was adjusted for asymmetry and temperature by using buffer solutions prepared from samples of potassium acid phthalate, potassium dihydrogen phosphate and disodium hydrogen phosphate and sodium tetraborate decahydrate furnished by the National Bureau of Standards.

Each  $pH$  measurement was made on a separate sample prepared by adding a known amount of amine from a weight buret to a 100-ml. sample of a standard solution of metal ion, acid, and neutral salt, precautions being taken to prevent absorption of carbon dioxide. Fifty milliliters of the solution thus prepared was used to rinse the glass electrode chamber and the remaining 50 ml. was used for the measurement.

All of the amines were research grade materials obtained from Eastman Kodak Co. General treatment involved refluxing for eight to twelve hours over barium oxide or potassium hydroxide, followed by distillation through a packed column, taking the middle fraction boiling within 0.2–0.3°. Boiling points in all cases agreed well with those in the literature. As a further precaution, the amines of high basic strength were titrated with standard acid to determine the neutral equivalents; these agreed with the theoretical values. All amines except ethylamine and  $\beta$ -methoxyethylamine, which were used as standardized solutions, were used as the pure amine.

### Results

**Dissociation Constants of the Amines.**—Since it is necessary to know the acid dissociation constants of the amines for the calculation of the formation curves, these were determined in solutions of the same ionic strength as the solutions containing the complex-forming metal ion. Varying amounts of amines were added to standard solutions 0.525  $M$  in potassium nitrate and 0.100  $M$  in nitric acid. The results are given in Table I. Each value reported here represents an average of 10–12 determinations at different ratios of amine concentration to amine salt concentration.

**Metal Ammine Formation.**—The over-all and successive association constants for the systems studied were calculated from accurately-drawn large-scale plots of the formation curves ( $\bar{n}$ , the average number of moles of amine combined with one mole of silver ion, *vs.*  $p[A]$ , the negative

TABLE I  
THE ACID DISSOCIATION CONSTANTS OF AMINES IN 0.5  $M$   
POTASSIUM NITRATE SOLUTIONS

Amine	$pK_{AH}$ at 25°	$pK_{AH}$ at 35°	$\Delta pK_{AH}/\Delta t$
Pyridine	5.45	5.35	0.010
$\alpha$ -Picoline	6.20	6.08	.012
$\gamma$ -Picoline	6.26	6.14	.012
2,4-Lutidine	6.99	6.86	.013
Ethylamine	10.81	10.48	.033
Isobutylamine	10.72	10.40	.032
Ethanolamine	9.74	9.51	.023
$\beta$ -Methoxyethylamine	9.45		
Benzylamine	9.62	9.32	.030
Morpholine	8.70		
Piperidine	11.28		

logarithm of the concentration of free amine) by the method of Bjerrum.<sup>5,6</sup> Each formation curve was plotted from 15–25 separate points, each point representing a  $pH$  measurement on an individually prepared sample of known concentrations of amine, acid, metal ion and neutral salt. The standard solutions to which known amounts of the amines were added were 0.500  $M$  in potassium nitrate, 0.1000  $M$  in nitric acid and 0.0250  $M$  in silver nitrate. Table II gives a summary of the values obtained for the silver amines at 25° and 35°;  $k_1$  is the equilibrium constant for equation

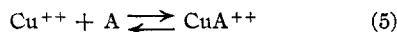
TABLE II  
ASSOCIATION CONSTANTS OF SILVER AMMINES IN 0.5  $M$   
POTASSIUM NITRATE

Amine	Temp., °C.	$\log k_1$	$\Delta \log k_1/\Delta t$	$\log k_2$	$k_1/k_2$	$\log K_2$
Pyridine	25	2.04	0.011	2.18	0.72 <sup>a</sup>	4.22
	35	1.93		2.07	.72	4.00
$\alpha$ -Picoline	25	2.27	.011	2.41	.72	4.68
	35	2.16		2.30	.72	4.46
$\gamma$ -Picoline	25	2.24	.010	2.46	.60	4.70
	35	2.14		2.36	.60	4.50
2,4-Lutidine	25	2.47	.011	2.61	.58	5.18
	35	2.36		2.60	.58	4.96
$\beta$ -Methoxyethylamine	25	2.95		3.39	.36	6.34
Ethanolamine	25	3.13	.012	3.55	.37	6.68
	35	3.01		3.43	.37	6.47
Isobutylamine	25	3.38	.016	3.86	.33	7.24
	35	3.22		3.70	.33	6.92
Ethylamine	25	3.37		3.93	.28	7.30
	30°	3.30	.016	3.84	.29	7.14
	35	3.21		3.77	.28	6.98
Ammonia <sup>b</sup>	25	3.29		3.83	.29	7.12
Benzylamine	25	3.29	.016	3.85	.28	7.14
	35	3.13		3.69	.28	6.82
Morpholine	25	2.25		2.67	.38	4.98
Diethylamine <sup>c</sup>	30	2.98		3.22	.58	6.20
Piperidine	25	3.03		3.45	.38	6.48

<sup>a</sup> Vosburgh and Cogswell (ref. 4) obtained a ratio of 0.78 from solubility measurements. <sup>b</sup> Obtained by Bjerrum (ref. 6) in 0.5  $M$  ammonium nitrate solution;  $pK_{AH} = 9.26$ . <sup>c</sup> Obtained by Carlson, McReynolds and Verhoeck (ref. 5) in solutions of the same concentration as above;  $pK_{AH} = 10.96$ .

(3),  $k_2$  that for equation (2) and  $k_2$  that for equation (1). It is estimated that the former values are precise to 0.05 logarithmic unit.

For comparison with the values for the silver amines, measurements of the equilibrium constants for the reaction



and those for the addition of further amine molecules to cupric ion were made with pyridine and  $\gamma$ -picoline at 25°. The solutions used were 0.500  $M$  in potassium nitrate, 0.1000  $M$  in nitric acid and 0.0300  $M$  in cupric nitrate. Table III gives the results.

TABLE III

ASSOCIATION CONSTANTS OF CUPRIC AMINES IN 0.5  $M$  POTASSIUM NITRATE AT 25°

Amine	$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	$\log K_4$
Pyridine	2.52	1.86	1.31	0.85	6.54
$\gamma$ -Picoline	2.82	2.15	1.61	1.16	7.74
Ammonia <sup>a</sup>	3.99	3.34	2.73	1.97	12.03

<sup>a</sup> Measured by Bjerrum in 0.5  $M$  ammonium nitrate solutions.

### Discussion

Since silver ion is a Lewis acid, the equilibrium constants for equations (3) and (4) for a series of amines measure the strengths of the amines relative to two different reference acids. If the relative strengths of the amines are independent of the reference acid, a plot of the logarithm of  $k_1$  against the negative logarithm of the dissociation constant of the substituted ammonium ion would be expected to give a straight line of unit slope. Such a plot for the data at 25° from Tables I and II is given in Fig. 1.

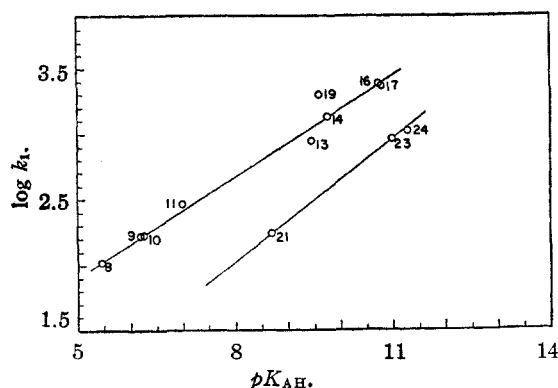


Fig. 1.—Variation of the first association constant of silver amines with the strength of the amine relative to hydrogen ion at 25°. Amines are numbered as in Fig. 2.

It is evident that a straight line relationship is obtained, but that the data fall into two groups. The pyridines and primary amines lie on one curve, and the secondary amines on another. Thus a secondary amine and a primary amine which have the same strength relative to hydrogen ion will differ in strength by a factor of about 3.5 when measured relative to silver ion.

It is also evident that the lines obtained are not of unit slope; the slopes are about one-fourth. Although the curves are drawn with different slopes for the two groups, it cannot be definitely stated that the slopes should be different, since the number of points is small. The slopes will be changed somewhat by a change in temperature, but the data in the tables show that the temperature coefficients are sufficiently alike that this change will not be great. The slope of approximately one-fourth may then be taken as real, and indicates a very great compression of the range of basicities when silver ion is used as a standard acid to measure the basic strength. Thus two amines which differ in strength by a factor of ten thousand when measured relative to hydrogen ion will differ only by a factor of ten when measured relative to silver ion.

It is seen from Table II that the ratio of  $k_1/k_2$ , although larger for the pyridines than for the other amines, is in all cases of the order of unity, and that  $\log K_2$  is about twice  $\log k_1$ . This modifies the statements made in the introduction because it means that  $\log K_2$  will vary in a similar fashion to  $\log k_1$ , so that except for a factor of two, comparisons of  $\log K_2$  with  $pK_{AH}$  will be valid. This is convenient, because it permits the use of the large number of values of  $K_2$  available in the literature, obtained on systems to which the present technique is not applicable, for comparison. Figure 2 shows a plot of these data as  $\log K_2$  vs.  $pK_{AH}$ ; in drawing conclusions from the figure one must remember that the ordinate of each point, and consequently the slopes of the curves

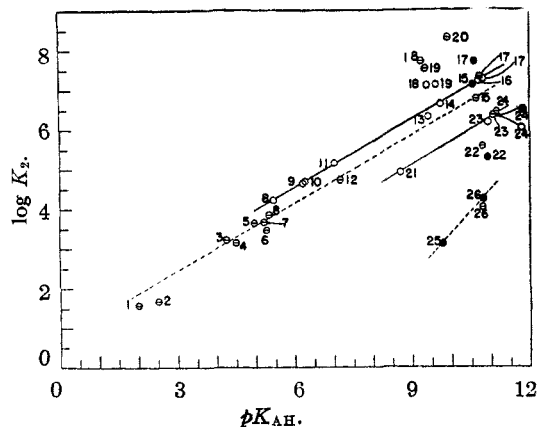


Fig. 2.—Variation of the over-all association constant of silver amines with the strength of the amine relative to hydrogen ion:  $\ominus$ , Larsson;  $\bullet$ , Britton and Williams;  $\circ$ , this paper; 1,  $p$ -nitroaniline; 2,  $m$ -nitroaniline; 3,  $\alpha$ -naphthylamine and  $\beta$ -naphthylamine; 4, aniline; 5, quinoline; 6,  $p$ -toluidine; 7, pseudo-cumidine; 8, pyridine; 9,  $\alpha$ -picoline; 10,  $\gamma$ -picoline; 11, 2,4-lutidine; 12,  $s$ -collidine; 13,  $\beta$ -methoxyethylamine; 14, ethanolamine; 15, methylamine; 16, isobutylamine; 17, ethylamine; 18, ammonia; 19, benzylamine; 20, ethylenediamine; 21, morpholine; 22, dimethylamine; 23, diethylamine; 24, piperidine; 25, trimethylamine; 26, triethylamine.

would be decreased by one-half if  $\log k_1$  was plotted. The full lines are drawn through the values obtained in this investigation; they are represented by the equations

$$\log K_2 = 0.577 pK_{AH} + 1.08$$

$$\log K_2 = 0.577 pK_{AH} - 0.02$$

for the upper and lower curves, respectively. The dotted lines are drawn through the points of Larsson<sup>2</sup> for the primary amines and through the tertiary amine points of Britton and Williams.<sup>3</sup> The curve for Larsson's data lies below that for this investigation because his values are for a 50-50 alcohol water mixture; if, as he reports, the values in water are 0.3 to 0.6 logarithmic units higher than in the alcohol solution, the dotted line will coincide with the full line for the primary amines.

The figure confirms the smaller range of basic strengths relative to silver ion and shows that the aliphatic tertiary amines comprise a third group, although the slope of the curve for the latter is uncertain since only two points are available. It is this difference between primary, secondary, and tertiary amines which has led to the belief that there is no relationship between the basic strengths of the amines measured relative to the two standard acids; actually within the three groups there is a parallelism between the two measures, although the ratios of strengths of two bases is not the same in the two systems.

The explanation for the smaller range of base strengths referred to silver ion as compared to hydrogen ion is not immediately obvious. Evidently a change in the groups attached to the nitrogen atom which makes a great change in its tendency to coordinate with a proton makes little change in its tendency to coordinate with a silver ion. This is probably connected with the larger size of the silver ion as compared to the hydrogen ion, but the exact mechanism is obscure. That the effect is not peculiar to the silver ion is shown by the correspondence of the data on the copper complexes to those for the silver complexes.

Nor is it clear why the silver ion separates the aliphatic amines into three groups. It is tempting to attribute this to the increasing importance of steric effects with increasing substitution on the nitrogen, yet this can hardly be the explanation. The silver ion is not large enough to interfere with any of the groups on the amines investigated.

A further problem appears in the position of the pyridines, which do not lie with the tertiary aliphatic amines. It may be noted, however, that resonance structures are possible in a compound of silver ion with pyridine which are not possible with tertiary aliphatic amines, nor for compounds of hydrogen ion with pyridine. These would tend to cause the pyridine complexes to be more stable as compared to those of the aliphatic amines, raising them above the position of tertiary aliphatic amines of the same strengths relative to hydrogen ion. From this point of view, the fact that the points for the pyridine complexes lie on the same curve as those for the primary aliphatic amines is fortuitous.

### Summary

1. The association constants for the reactions of silver ion with groups of primary aliphatic amines, secondary amines and pyridines have been measured, together with similar constants for cupric ion and two pyridines, and temperature coefficients.
2. When the logarithm of the first association constant is plotted against the  $pK$  value for the corresponding substituted ammonium ion, two straight lines are obtained: one for the pyridines and primary aliphatic amines, and one for the secondary amines. Data from the literature indicate that tertiary aliphatic amines lie on a third curve.
3. The slope of the curve obtained is approximately one-fourth, indicating a much smaller range of basic strengths when measured against silver ion as a reference acid than when measured against hydrogen ion.

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