The preparation of the phosphonic and phosphinic acids has been reported recently.[2]

(2) G. O. Doak and L. D. Freedman, THIS JOURNAL, **74**, 753 (1952); L. D. Freedman and G. O. Doak, *ibid.*, **74**, 2884 (1952).

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Effect of N-Monosubstitution on the Basic Properties of Ethylenediamine[1]

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Introduction

In connection with the determination of formation constants of complex ions containing various diamine ligands, it became necessary to know the consecutive dissociation constants for the two acid ions of the diamines. The results are reported here since the majority of these constants have not previously been determined. Furthermore, in view of the fact that most of the diamines are derivatives of ethylenediamine by N-monosubstitution, these dissociation constants reflect qualitatively the effect of substitution on the basic character of the nitrogen atoms.

Experimental

Aqueous solutions of the purified diamines[3] were standardized against hydrochloric acid. Precautions were taken to eliminate absorption of carbon dioxide during the titrations.

The consecutive dissociation constants of the acid ions of the diamines were determined by the method suggested by Bjerrum.[4] The titrations of standard solutions (*ca.* 0.15 *M*) of hydrochloric acid 1.0 molar in potassium chloride and 0.1 molar in barium chloride[5] by known quantities of the diamines were followed by means of *p*H measurements at 25° with a hydrogen electrode. Two platinized platinum electrodes were employed as a means of checking the potential. In general these electrodes were in good agreement; when the readings began to diverge, new electrodes were substituted. The calomel electrode was connected to the titration flask through a saturated potassium chloride–agar salt bridge. Immediately before and after each titration, the potential attributed to the calomel electrode was determined by measuring a standard acid solution of defined hydrogen ion concentration (0.005 *N*) and the same chloride concentration as the metal salt solutions titrated. The *p*H values from the above measurements were then used in computing the *pK* values for the dissociation constants of the acid ions of the diamines.

Results

Table I contains a summary of the values for the *pK*'s and the corresponding equilibrium constants for the two acid ions of the eight diamines investigated. From the data of this table it appears that N-monoalkyl substitution in the ethylenediamine molecule has only a slight influence on the values of the dissociation constants of the acid ions. N-Monoalkylol substitution, on the other hand, increases the acid strengths of both these ions. It is well established that monoalkyl substitution in the ammonia molecule results in an increase in basicity of the nitrogen. Reasoning by analogy, then, the constant K_{AH_2} presumably refers to the ionization of the proton which is on the primary amino group in an N-monoalkyl substituted ethylenediamine. On the contrary, replacing one hydrogen in ammonia with an OH group (*i.e.*, hydroxylamine) brings about a marked lowering of the basicity of the nitrogen.[6] Therefore, in the case of the hydroxyethylenediamines the dissociation constants can be identified with a particular amino group with much less certainty. In fact, the nitrogen on which substitution has taken place may now be the one of lesser basicity. However, an unqualified conclusion seems unwarranted from these data alone.

TABLE I

pK AND K VALUES FOR THE DISSOCIATION OF THE ACID IONS OF DIAMINES IN SOLUTIONS 1 MOLAR IN KCl AND 0.1 MOLAR IN $BaCl_2$

Diamine	pK_{AH_2}	pK_{AH}	$K_{AH_2} \times 10^8$	$K_{AH} \times 10^{10}$
$NH_2CH_2CH_2NH_2$[a]	7.44	10.17	3.63	0.676
$NH_2CH_2CH_2NHCH_3$	7.42	10.32	3.80	0.48
$NH_2CH_2CH_2NHCH_2CH_3$	7.42	10.36	3.80	0.437
$NH_2CH_2CH_2NHCH_2CH_2OH$	6.83	9.82	14.8	1.52
$NH_2CH_2CH_2NHCH_2CH(OH)CH_3$	6.94	9.86	11.5	1.38
$NH_2CH_2CH_2NHCH_2CH_2CH_2OH$	6.78	9.67	16.6	2.14
$NH_2CH_2CH(NH_2)CH_3$[b]	7.10	9.97	7.95	1.07
$NH_2CH_2CH(OH)CH_2NH_2$	7.94	9.57	1.15	2.70

[a] The following values were obtained for ethylenediamine by Bjerrum (ref. 4, p. 207) in 1 *M* KCl and 0.1 *M* $BaCl_2$ at 30° by means of the hydrogen electrode: $pK_{AH_2} = 7.34$ and $pK_{AH} = 10.08$. G. A. Carlson, J. P. McReynolds and F. H. Verhoek (THIS JOURNAL, **67**, 1334 (1945)) using the glass electrode and in the presence of 1 *M* KCl and 0.05 *M* $BaCl_2$ at 30° obtained the values 7.19 and 9.92. [b] Carlson, *et al.* (footnote *a*), in the presence of 0.5 *M* KCl and 0.05 *M* $BaCl_2$ at 30° and using the glass electrode obtained values for propylenediamine of 7.07 and 9.83 for pK_{AH_2} and pK_{AH}, respectively.

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(1) From the Ph.D. Thesis of L. J. Edwards, University of Michigan, June, 1950.

(2) Department of Chemistry, University of Colorado, Boulder, Colorado.

(3) R. N. Keller and L. J. Edwards, THIS JOURNAL, **74**, 215 (1952).

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

(5) For subsequent titrations in which the values for the constants determined here were made use of, complex-forming metal ions replaced the barium ions.

(6) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 98.

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The Oxidation of Tetramethyl-1,3-bis-(*p*-tolyl)-disiloxane to 1,3-Bis-(*p*-carboxyphenyl)-tetramethyldisiloxane

BY DANIEL W. LEWIS AND GORDON C. GAINER

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In connection with certain studies on substituted arylsilicon compounds, it seemed of interest to prepare some carboxyphenyl-substituted siloxanes. Several orienting experiments involving application of the usual oxidizing procedures to *p*-tolyl-containing organosilicon compounds indicated that a mild oxidation was required, lest the carbon–silicon bond be also attacked. During the course of these investigations, there was reported the oxidation of 2-acetyl-5-trimethylsilylthiophene to (5-trimethyl-