by diluting commercial sodium silicate (Grasselli 20WW Grade, containing 28.4% $SiO_2$ and 8.72% $Na_2O$).

Five hundred and eighty-five milliliters of this solution was then run into 415 ml. of 1.52 normal hydrochloric acid at 20° with violent agitation. The solution of sodium silicate was added in a stream about 0.1 inch in diameter directed into the vortex of the stirred acid, addition being complete in about 5 minutes. The resulting solution of polysilicic acid had a *p*H of 1.65, and was 1 molar with respect to $SiO_2$. Sol A: Half of the above solution of polysilicic acid was aged for 1 hour at 25°. Sol B: The other half of the above solution was aged for 2 hours at *p*H 1.65, 25°; then the *p*H was raised to 2.25 by the addition of 2 *N* NaOH and the sol aged further for 4.5 hours at 25°.

Sols A and B were mixed with a 2.0 molar solution of aniline hydrochloride in the proportions shown in Table I, stirred for 5 minutes, saturated with sodium chloride by adding solid salt and stirring for five minutes, and then centrifuged in order to isolate the complex.

TABLE I

| Expt. | Volume of sol, ml. | Volume of 2 molar DEAH,[a] ml. | Solid NaCl added | Separated complex |
|---|---|---|---|---|
| 1 | 500 A | 250 | 200 | 80 ml. heavy viscous fluid |
| 2 | 500 A | 125 | 166 | 50 ml. heavy fluid, more viscous than 1 |
| 3 | 500 B | 250 | 200 | 198 ml. white soft paste containing emulsified brine |
| 4 | 500 B | 125 | 166 | 156 ml. white soft paste containing emulsified brine |
| 5 | None | 250 plus 250 $H_2O$ | 133 | Clear solution—no phase separation |

[a] DEAH, diethylaniline hydrochloride.

The compositions of the recovered complexes, based on analyses for silica, nitrogen, chlorine and sodium are shown in Table II. It is evident that as the age of the sol increases, the ratio of silica to diethylaniline hydrochloride in the complex also seems to increase; this is probably due to the diminishing combining power of the silicic acid as it polymerizes. In experiment 2 there was not enough excess amine hydrochloride to combine with all the silica, but after the sol had been aged, as in 4, this quantity of the amine salt was more nearly adequate. The ratio of hydrogen chloride to diethylaniline in the complex approximates unity.

TABLE II

| Experiment | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Recovered complex, ml. | 80 | 50 | 198 | 156 |
| grams (approx.) | 100 | 62 | 250 | 195 |
| $SiO_2$, % | 24.99 | 33.90 | 11.48 | 12.67 |
| Diethylaniline (nitrogen analysis), % | 35.2 | 31.4 | 13.7 | 10.0 |
| NaCl (sodium analysis), % | 1.91 | 1.63 | 15.95 | 27.4 |
| HCl (Total chloride minus chloride equivalent to sodium), % | 9.77 | 8.47 | 4.10 | 2.19 |
| Mol ratio in complex: $\left(\frac{HCl}{\text{diethylaniline}}\right)$ | 1.14 | 1.10 | 1.2 | 0.9 |
| Mol ratio in complex: $\left(\frac{SiO_2}{\text{diethylaniline}}\right)$ | 1.77 | 2.69 | 2.09 | 3.15 |
| Mol ratio in original solution: $\left(\frac{SiO_2}{\text{diethylaniline}}\right)$ | 1.0 | 2.0 | 1.0 | 2.0 |
| $SiO_2$ recovered in complex, % | 83 | 56 | 96 | 82 |
| Diethylaniline recovered, % | 48 | 52 | 46 | 52 |

In the cases of the liquid complexes obtained in experiments 1 and 2, the total water in the complex can be estimated by difference, assuming that the sodium chloride is present as emulsified, saturated brine and subtracting this water from the total. This calculation gives 14.3% water in complex 1, and 21.5% in complex 2. However, no attempt was made to dehydrate the complex, and probably only a portion of this water was in chemical combination with the silica.

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## The Ultraviolet Absorption Spectra of Two Arylalkylphosphinic Acids and Related Compounds

BY H. H. JAFFÉ AND LEON D. FREEDMAN

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The ultraviolet absorption spectra of a number of arylphosphonic and diarylphosphinic acids were reported in a recent paper from this Laboratory.[1] We have now determined the absorption spectra of (*o*-bromophenyl)-ethylphosphinic and (*p*-nitrophenyl)-ethylphosphinic acids. Table I lists the wave lengths of the absorption maxima and the corresponding molar extinction coefficients for these compounds and several related arylphosphonic and diarylphosphinic acids.

TABLE I

| Compound | $\lambda_{max}$ | $\epsilon_{max}$ |
|---|---|---|
| $BrC_6H_5$ | 264.5[a] | 163 |
| $o\text{-}BrC_6H_4PO_3H_2$ | 270.5[a] | 847 |
| $(o\text{-}BrC_6H_4)_2PO_2H$ | 275[a] | 1780 |
| $(o\text{-}BrC_6H_4)C_6H_5PO_2H$ | 273.5[a] | 1430 |
| $(o\text{-}BrC_6H_4)C_2H_5PO_2H$ | 271[a] | 1010 |
| $(p\text{-}O_2NC_6H_4)C_2H_5PO_2H$ | 266[b] | 8100 |

[a] Secondary band. [b] Primary band.

Our previous data showed that the absorption spectra of unsymmetrical diarylphosphinic acids ($ArAr'PO_2H$) may be calculated by averaging the extinction coefficients of the corresponding symmetrical diarylphosphinic acids ($Ar_2PO_2H$ and $Ar'_2PO_2H$).[1] A similar relationship holds approximately for the arylalkylphosphinic acids, if it is assumed that the absorption of diethylphosphinic acid is negligible compared to the absorption of diarylphosphinic acids in the region 240 to 300 mμ. This assumption is reasonable in view of the facts that phosphoric acid does not absorb appreciably in this region, and that the ethyl radical is not a chromophore. The primary band [observed in (*p*-nitrophenyl)-ethylphosphinic acid] and the secondary band [observed in (*o*-bromophenyl)-ethylphosphinic acid] occur at shorter wave lengths than would have been predicted; the molar extinction coefficients, however, can be calculated with an error of less than 20% by means of the above relationship.

*o*-Bromobenzenephosphonic acid has an ultraviolet absorption approximately 5 times as intense as that of bromobenzene. This intensification is outside the limits 1.5 to 4 reported previously.[1] Otherwise, the data reported in the present paper on the absorption spectra of *o*-bromobenzenephosphonic, bis-(*o*-bromophenyl)-phosphinic and (*o*-bromophenyl)-phenylphosphinic acids are in agreement with the generalizations made in the previous paper.

The ultraviolet absorption spectra were determined by the procedure previously used.[1] All measurements were made with 1.0-cm. silica cells in a temperature controlled room (21 ± 2°). The molar extinction coefficient, $\epsilon$, was calculated from the equation: $\epsilon = D/lc$, where $D$ = optical density, $l$ = absorption cell thickness in cm., and $c$ = the concentration of the sample in moles per liter.

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(1) H. H. Jaffé and L. D. Freedman, THIS JOURNAL, **74**, 1069 (1952).

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]

BY R. N. KELLER[2] AND L. J. EDWARDS

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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 |
| $NH_2CH_2CH(OH)CH_2NH_3$ | 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-