

Effect of Molecular Acid–Base Dissociation of Salts on Conductometric Titration Curves in Acetonitrile¹

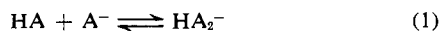
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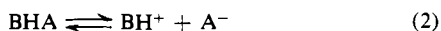
Salts of weak acids and primary, secondary, and tertiary amines are subject to molecular acid–base dissociation in acetonitrile: $BHA \rightleftharpoons B + HA$. When the acid HA has a large homoconjugation constant $K_2 = [HA_2^-]/[A^-][HA]$ and the molecular formation constant K_f of the salt $K_f = [BHA]/[B][HA]$ is less than infinity, the conductance of the salt may be much greater than that which corresponds to the calculated value from the ionic dissociation constant of the salt: $K_{BHA}^d = [BH^+][A^-]/[BHA]$, K_{BHA}^d (denoted as K_d in this paper) being $\ll K_2$ because of homoconjugation. With known values of K_f , K_d , and K_2 , equations have been derived which allow the calculation of conductometric titration curves of an acid with an amine B under the above conditions. Such curves exhibit a maximum in conductance. A relation has been derived which allows the calculation of K_f from the location of the maximum and of K_d from the conductance at the maximum. Also, a relation has been derived which allows the calculation of $K_d K_f$ from the early portion of the titration curves. Conductometric titration curves at 25° of 3,5-dinitrobenzoic acid with 2,4,6-trimethylpyridine, 2,4-dimethylpyridine, 4-methylpyridine, pyridine, *N,N*-dimethylbenzylamine, *N,N*-diethylaniline, and aniline, respectively, in acetonitrile are presented and the values of K_f and K_d of the various dinitrobenzoates are reported. Provided there are no specific solvation effects it is shown that $p(K_d K_f)_{AN} - (pK_{BH^+}^f)_{H_2O}$ should be a constant: $(K_{BH^+}^f)_{H_2O} = [BH^+]/[B][H_3O^+]$. Actually, this difference was found to be equal to 10.1 for the pyridines and *N,N*-dimethylbenzylamine. For the anilines the difference was 11.3. From the experimental results the dissociation constant of 3,5-dinitrobenzoic acid in AN has been calculated to be $10^{-16.1}$ as compared to $10^{-2.82}$ in water.

Introduction

Conductometric titration curves of a weak acid, HA , with a weak base, B , in acetonitrile as solvent generally exhibit a maximum² between 50% neutralization and the equivalence point if the homoconjugation constant, K_2 , which denotes the formation constant of HA_2^- for the reaction



is much larger than the ionic dissociation constant, K_d , for the salt



and if the formation constant, K_f , for the salt



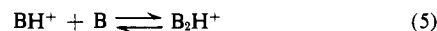
is also large and the concentration of acid being titrated is not too small. Such maxima have also been observed in acetone³ and in methyl isobutyl ketone.⁴

When, however, reaction 3 is incomplete, the conductance at the equivalence point becomes greater than that computed on the basis of (2) owing to (1) and the much greater ionic dissociation of $B(HA)_2$ than BHA . Thus the interpretation of the present results differs from that of the earlier work² in that the reaction



is assumed complete and K_f is assigned finite values. In the work reported here a single acid, 3,5-dinitrobenzoic, HDNB, has been titrated with a series of bases of decreasing strength, and only in the case of collidine was it necessary to take into account the incomplete ionic dissociation of $B(HA)_2$.

The increase in conductance at, and beyond, the equivalence point is also enhanced if, in addition to reaction 1, homoconjugation of the base occurs



and the salt B_2HA has an appreciably larger ionic dissociation constant than BHA . This effect has been observed by Coetzee, *et al.*,⁵ and we have noted it in the titration of 0.02 *M* HDNB with diphenylguanidine, but not with the bases used in the present work.

Titration of a given acid with a series of bases of decreasing strength, assuming K_d to be independent of B , results in a progressive shift of the equilibrium 3 to the left and increasing conductance at the equivalence point with reference to a salt that is not subject to such acid–base dissociation. With increasing conductance $[A^-]$ becomes continuously smaller than $[HA_2^-]$, and $[HA_2^-]$ approaches $[BH^+]$. The increase in conductance continues until a maximum value is attained. With further decrease in K_f the conductance at the equivalence point starts to decrease. It is shown in this paper that the molecular acid–base dissociation constants of the salts, $1/K_f$, affect the entire conductometric titration curves.

The main objectives of this paper are to calculate K_f and K_d from the characteristics of conductometric titration curves at different initial concentrations of

(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-63.

(2) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **85**, 426 (1963).

(3) P. J. R. Bryant and A. W. H. Wardrup, *J. Chem. Soc.*, 895 (1957).

(4) C. E. Gracias, Ph.D. Thesis, University of Minnesota, 1961.

(5) J. F. Coetzee, G. Padmanabhan, and G. Cummingham, *Talanta*, **11**, 93 (1964).

acid. Equations have been derived to find, under specified conditions, K_f from the location of and K_d from the value of the conductance at the maximum. Also, under specified conditions the product $K_f K_d$ can be evaluated from the initial slope of the titration curve. K_f can then be calculated using a value of K_d obtained from the conductance at the maximum. A simple relation between $K_d K_f$ in acetonitrile and the acid strength of BH^+ in water is derived and confirmed experimentally. Furthermore, with experimentally determined values of K_2 , K_d , and K_f and the independently measured ionic mobilities of A^- , HA_2^- , and BH^+ , titration curves have been computed for comparison with those observed. In these computations the independently measured² value of $K_2 = 1.7 \times 10^4$ has been used and activity coefficients of unity have been assumed, except where ion concentrations have been large enough to require the use of the Debye-Hückel theory. Although not indicated by the notation, the salts are considered to be ion pairs, e.g., BH^+A^- .

In addition to the expressions for K_f , K_d , and K_2 , there is conservation of acid

$$C_a = [HA] + 2[HA_2^-] + [A^-] + [BHA] \quad (6)$$

and of base

$$C_b = [B] + [BHA] + [BH^+] \quad (7)$$

and electrical neutrality

$$[BH^+] = [HA_2^-] + [A^-] \quad (8)$$

Elimination of $[A^-]$ and $[HA_2^-]$ from K_2 , K_d , and (8) gives

$$[BHA] = [BH^+]^2 / K_d \{1 + K_2[HA]\} \quad (9)$$

whereas K_f and (7) combine to give

$$[BHA] = K_f [HA] \{C_b - [BH^+]\} / \{1 + K_f [HA]\} \quad (10)$$

from which

$$[BH^+]^2 \{1 + K_f [HA]\} + K_d K_f [HA] \{1 + K_2 [HA]\} \{[BH^+] - C_b\} = 0 \quad (11)$$

To obtain the titration curve a reasonable estimate of $[HA]$ is used in (11) to compute $[BH^+]$ and these values then used in (9) to give $[BHA]$ and in the expressions for K_f , K_d , and K_2 to give $[B]$, $[A^-]$, and $[HA_2^-]$, respectively. If the correct value of $[HA]$ has been used, the conservation eq. 6 and 7 are satisfied. The curves of Figure 1 were computed for $C_a = 0.0015 M$ HDNB and representative values of K_f and K_d , where it will be noted that the conductance at the maximum increases with K_d although the shape of the curves is similar for both values of this constant. On the other hand, for given values of K_f , K_d , and K_2 , the shape varies greatly with C_a (cf. Figures 2 and 3).

Evaluation of $K_d K_f$ from the Initial Portion of an Experimental Titration Curve of Very Dilute Solutions of HDNB. In solutions more dilute than about $5 \times$

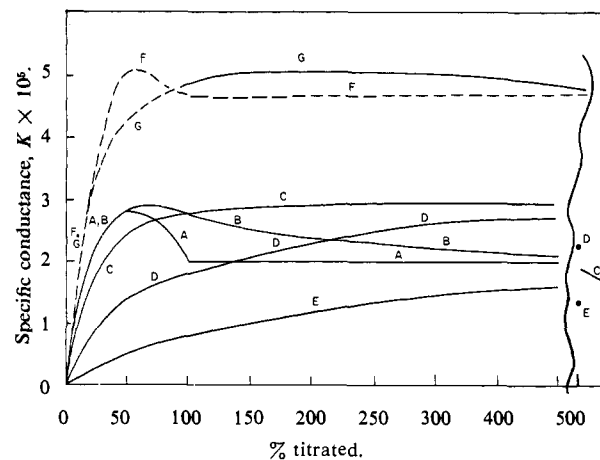


Figure 1. Calculated conductometric titration curves of 0.0015 M HA with B at various values of K_f : A, $K_f = \infty$; B, $K_f = 10^4$; C, $K_f = 10^3$; D, $K_f = 10^2$; E, $K_f = 10^1$. $K_d = 0.80 \times 10^{-5}$; dotted curves for $K_d = 5 \times 10^{-5}$. F, $K_f = \infty$; G, $K_f = 10^3$. $K_2 = 1.7 \times 10^4$; $\Lambda_0 BH^+A^- = 190$ and $\Lambda_0 BH^+AHA^- = 130$ in all cases.

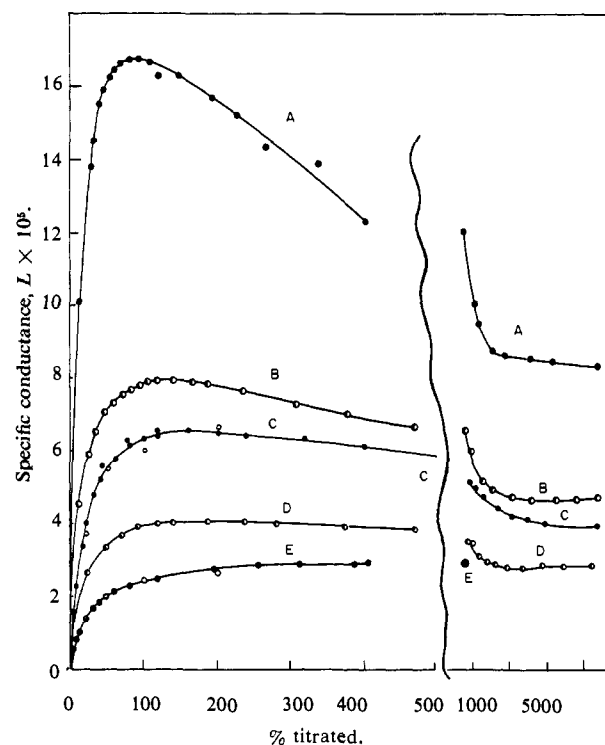
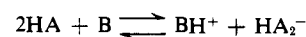


Figure 2. Conductometric titration curves of 3,5-dinitrobenzoic acid (HDNB) with collidine and lutidine: A, 0.0114 M ; C, 0.00382 M ; E, 0.00153 M HDNB with collidine; \bullet — \bullet experimental, \circ — \circ calculated points; B, 0.00748 M ; D, 0.00374 M HDNB with lutidine, experimental points.

$10^{-3} M$, the principal acid-base reaction up to 40% titrated is



with an equilibrium constant

$$K = \frac{[BH^+][HA_2^-]}{[HA]^2[B]} = K_d K_f K_2 \quad (12)$$

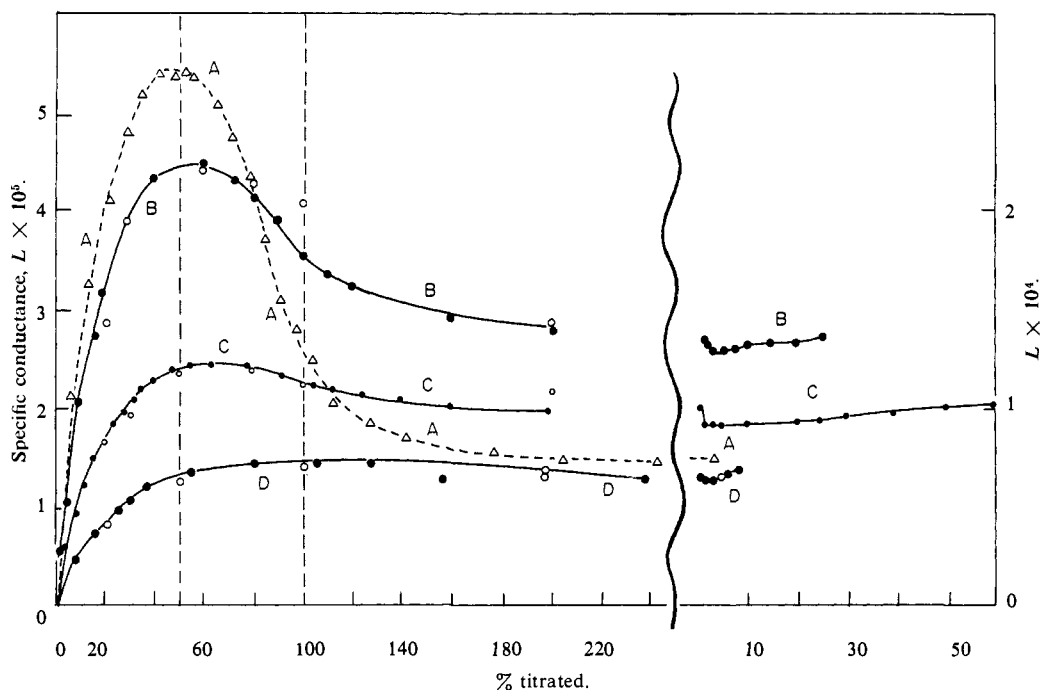


Figure 3. Conductometric titration curves of 3,5-dinitrobenzoic acid with *N,N*-dimethylbenzylamine: A, $1.87 \times 10^{-2} M$; B, $2.68 \times 10^{-3} M$; C, $1.34 \times 10^{-3} M$; and D, $6.70 \times 10^{-4} M$ HDNB. Curve A, right-hand ordinate; curves B, C, and D, left-hand ordinate; —●— experimental, —○— calculated points.

Since $[A^-] \ll [HA_2^-]$ and $[B(HA)_2]$ is negligible in these solutions, it follows from eq. 8 that $[BH^+] = [HA_2^-]$. $[BH^+]$ is in turn related to the observed specific conductance of the solution, L

$$L = [BH^+] \Lambda_{0B(HA)_2} 10^{-3} \quad (13)$$

and

$$\frac{10^3 L}{[HA]} = \Lambda_{0B(HA)_2} \sqrt{K_d K_f K_2 [B]} \quad (13a)$$

From the slope of the plot of $L/[HA]$ vs. $\sqrt{[B]}$, which is $\Lambda_{0B(HA)_2} 10^{-3} \sqrt{K_d K_f K_2}$, the product $K_d K_f$ is calculated knowing K_2 and $\Lambda_{0B(HA)_2}$. Values of $[HA]$ and $[B]$ are calculated in the following way.

At a given point on the initial portion of the titration curve, a value of $[BH^+]$, assumed equal to $[HA_2^-]$, is obtained from the conductance using ionic conductances at infinite dilution. An approximate value of $[HA]$ is calculated from $[HA_2^-]$ using eq. 6, neglecting $[A^-]$ and $[BHA]$. The above values of $[HA]$ and $[BH^+]$ when introduced in eq. 9 yield an approximate value of $[BHA]$, the value of K_d being obtained from the maximum of the titration curve. A better value of $[HA]$ is then evaluated from eq. 6 by introducing the approximate values of $[BHA]$ and $[HA_2^-]$, again neglecting $[A^-]$. If necessary, the above operations can be repeated. The equilibrium concentration of the free base $[B]$ is calculated from eq. 7 using the above values of $[BHA]$ and $[BH^+]$.

Calculation of K_f and K_d from the Location and Height of the Maximum on the Titration Curve, Respectively. Differentiating eq. 11 implicitly once with respect to C_b , the analytical concentration of base added, eq. 14

results. Since the contribution of A^- to the conductance

$$\frac{d[HA]}{dC_b} K_f \{ K_d [BH^+] + 2[HA] K_d K_2 \{ [BH^+] - C_b \} - K_d C_b + [BH^+]^2 \} + \frac{d[BH^+]}{dC_b} \{ 2[BH^+] + K_f [HA] \{ 2[BH^+] + K_d \{ 1 + K_2 [HA] \} \} - K_d K_f [HA] \{ 1 + K_2 [HA] \} \} = 0 \quad (14)$$

in the region of the maximum is small compared to that of HA_2^- , the location of the maximum in $[BH^+]$ may be regarded as identical with the maximum in conductance. To express $d[HA]/dC_b$ in terms of $d[BH^+]/dC_b$, eq. 15, which is derived from eq. 2, 9,

$$[BH^+]^2 + K_d \{ 1 + 2K_2 [HA] \} [BH^+] + K_d \{ 1 + K_2 [HA] \} \{ [HA] - C_a \} = 0 \quad (15)$$

10, and 14, is differentiated implicitly once with respect to C_b . Equation 16 results

$$\frac{d[HA]}{dC_b} = \left[\frac{[K_d + 2K_d K_2 [HA] + 2[BH^+]]}{C_a K_2 - 1 - 2K_2 \{ [HA] + [BH^+] \}} \right] \frac{1}{K_d} \frac{d[BH^+]}{dC_b} \quad (16)$$

Substituting eq. 16 into eq. 14 and setting $d[BH^+]/dC_b = 0$ as a condition at the maximum, eq. 17 is obtained.

$$[HA]_m = \frac{1}{2} [C_a - 1/K_2] - [BH^+]_m \quad (17)$$

With 3,5-dinitrobenzoic acid $1/K_2 \ll C_a$ (Figures 2-4); hence eq. 17 can be written

$$[\text{HA}]_m = C_a/2 - [\text{BH}^+]_m \quad (17a)$$

where the subscript m denotes the maximum. Under conditions that $[\text{HA}_2^-]_m \gg [\text{A}^-]_m$, it can be shown from eq. 17a, 6, and 7 that

$$K_f = 1/C_a \{ C_{b,m}/C_a - 1/2 \} \quad (18)$$

and that

$$[\text{BH}^+]_m = \frac{C_a \sqrt{K_d K_2}}{2\{1 + \sqrt{K_d K_2}\}} \quad (18a)$$

Also

$$[\text{BHA}]_m = [\text{HA}]_m = \frac{C_a}{2\{1 + \sqrt{K_d K_2}\}} \quad (18b)$$

$$[\text{B}]_m = 1/K_f \quad (18c)$$

and

$$[\text{A}^-]_m = \sqrt{\frac{K_d}{K_2}} \quad (18d)$$

It is interesting to note that under the specified conditions K_f is calculated from the location of the maximum (eq. 18) and has no relation to the conductance at the maximum. On the other hand, K_d is found from the conductance at the maximum (eq. 18a) which, at a given value of C_a , should be independent of K_f . This is seen to be the case in curves A, B, and C in Figure 1. For curve D in Figure 1 the value of K_f is only 10^2 and the constant conductance at the maximum is not approached until about 2000% excess of base is added. When K_f is only 10 (curve E), salt formation is so incomplete that the maximum is not attained even with a 50-fold excess of base.

Experimental

Chemicals. Acetonitrile was purified and dispensed as previously described.² The conductivity of the pure solvent was $1-2 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^{-1}$, while the water and ammonia content were $2 \times 10^{-3} M$ and $2 \times 10^{-6} M$,² respectively.

3,5-Dinitrobenzoic acid was purified, and perchloric acid in anhydrous acetic acid was prepared as described elsewhere.²

N,N-Dimethylbenzylamine, an Eastman Kodak White Label product, was used without further purification. The water content was 0.01% as determined by Karl Fischer titration. The purity as determined from titration with perchloric acid in glacial acetic acid was 99.7%. Crystal violet served as indicator.

Pyridines. The following pyridines were used: 2,4,6-trimethylpyridine (denoted as collidine), a Matheson technical grade product; 2,4-dimethylpyridine (denoted as lutidine), a Barnett technical grade product; 4-methylpyridine (picoline), an Eastman Kodak

White Label product; pyridine, a Merck reagent grade product.

The pyridines were purified by shaking 100-150 ml. for 6 hr. over 5 g. of Merck reagent grade potassium hydroxide. The shaking was repeated twice with fresh potassium hydroxide. The pyridines were then shaken for 6 hr. over 5 g. of freshly activated Linde Type 4A Molecular Sieve, and the shaking was repeated using a fresh molecular sieve. The samples were finally distilled at atmospheric pressure under nitrogen and were stored under nitrogen. Observed and literature⁶ boiling points were, respectively: collidine 168, 169°; lutidine 158, 158°; picoline 142, 144°; and pyridine 112, 114°.

N,N-Diethylaniline and Aniline. These were Eastman Kodak White Label products. *N,N*-Diethylaniline was distilled at 10 mm. pressure. Aniline was distilled over zinc dust at atmospheric pressure, b.p. 183°, lit.⁶ b.p. 184°.

Diethylanilinium perchlorate was obtained from Dr. S. Bruckenstein.⁷

Conductance Measurements. The conductance cell with a cell constant of 0.224 and thermostat has been described previously.² An Industrial Instruments, Inc., Model RCM 15 conductivity bridge in conjunction with a Heathkit 0.1 $\mu\text{f.}$ decade condenser was used for conductivity measurements. All measurements were made at $25 \pm 0.05^\circ$. Pure base or a concentrated solution in acetonitrile was added from an ultramicroburet and volume changes were negligible. The procedure for the conductometric titrations was described previously.²

Experimental Results

Mobility of BH^+ . The mobility at infinite dilution of the 3,5-dinitrobenzoate ion and its homoconjugate ion, HDNB-DNB⁻, previously has been found to be 100 and 46, respectively.² In Table I are presented conductance data in acetonitrile of diethylanilinium

Table I. Conductance of Perchlorates in Acetonitrile at 25°

—Lutidinium—		N,N-Dimethylbenzylammonium		—Diethylanilinium—	
$M \times 10^3$	Λ	$M \times 10^3$	Λ	$M \times 10^3$	Λ
0.500	174.4	1.09	156	0.211	169
1.00	169.6	2.03	148	0.408	165.5
2.00	159.4	4.04	137	0.818	156
5.00	143.5			1.21	150.5
				1.94	144
				2.61	141
				3.47	138.5
	$\Lambda_0 = 191$		$\Lambda_0 = 174$		$\Lambda_0 = 184$

perchlorate solutions and of equimolar mixtures of the following bases with perchloric acid in acetonitrile: *N,N*-dimethylbenzylamine and lutidine. The perchloric acid solution was prepared by diluting a 0.495 *M* stock solution of perchloric acid in anhydrous acetic

(6) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960.

(7) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, 78, 2974 (1956).

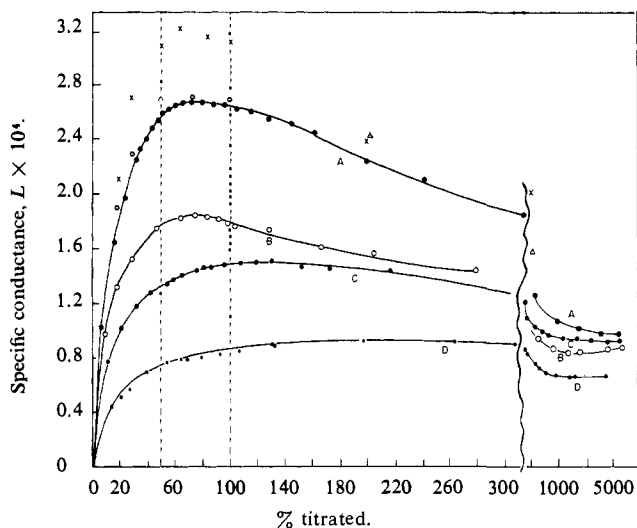


Figure 4. Conductometric titration curves of $1.87 \times 10^{-2} M$ 3,5-dinitrobenzoic acid with methylpyridines: A, collidine; B, lutidine; C, picoline; D, pyridine; $-\times-$ calculated points for collidine, using approximate eq. 13; $-\triangle-$ considering BH^+AHA^- formation (see text).

tively, with the calculated values of 344, 371, and 358, indicates all the perchlorates are extensively dissociated in acetonitrile. As the solutions in Table I were dilute, no viscosity corrections were necessary. The mobilities of the pyridinium, picolinium, and collidinium ions have been assumed equal to that of the lutidinium ion, while that of the anilinium ion is assumed equal to that of the diethylanilinium ion.

Viscosity Corrections. Several conductance measurements have been made in solutions containing relatively large concentrations of free base. In such instances a viscosity correction of the conductance values is necessary. The viscosity of the following solutions of some bases was determined: 0.55 and 1.01 *M* lutidine, 0.364 and 0.378 cp.; 0.53 and 1.05 *M* diethylaniline, 0.370 and 0.402 cp. The values for lutidine were employed for all the pyridine bases, while those for aniline were assumed to be the same as for *N,N*-diethylaniline. At high base concentrations in Figures 2 to 5, where the solution viscosity differs significantly from that of the solvent, correction has been made by interpolation of the above data. The pure solvent has a viscosity of 0.345 cp.

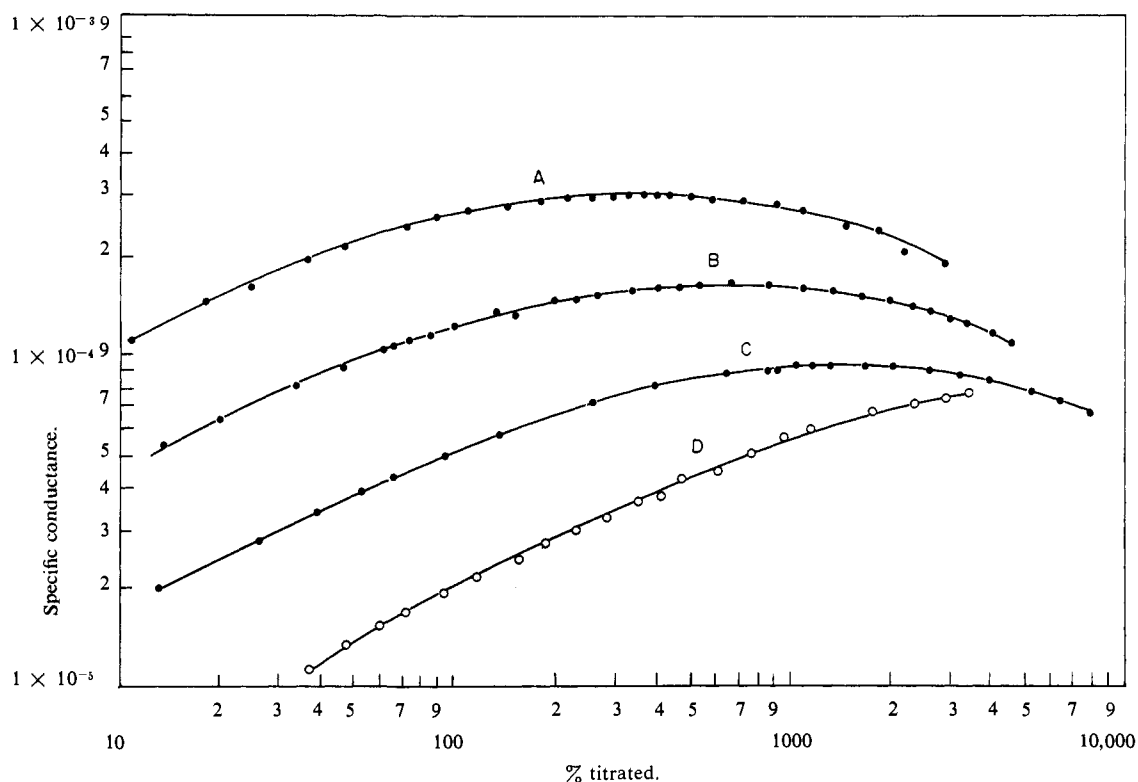


Figure 5. Conductometric titration curves of 3,5-dinitrobenzoic acid with *N,N*-diethylaniline and aniline: A, 0.036 *M*; B, 0.0187 *M*; C, 0.010 *M* HDNB with *N,N*-diethylaniline; D, 0.0187 *M* HDNB with aniline (abscissa and ordinate on logarithmic scales).

acid with acetonitrile and used immediately after dilution.

From a Λ vs. \sqrt{C} plot and Coetzee's values of $\lambda_{ClO_4^-} = 104$,⁸ values of λ_{BH^+} were found equal to 80 for diethylanilinium, 87 for lutidinium, and 70 for *N,N*-dimethylbenzylammonium. Comparison of experimental Onsager slopes of 880, 720, and 580, respec-

(8) J. F. Coetzee and I. M. Kolthoff, *J. Am. Chem. Soc.*, **79**, 6110 (1957).

Experimental Titration Curves of 3,5-Dinitrobenzoic Acid (HDNB) with Various Weak Bases. Experimental titration curves of approximately 1×10^{-3} to $1.8 \times 10^{-2} M$ HDNB with collidine, lutidine, picoline, pyridine, and *N,N*-dimethylbenzylamine are presented in Figures 2, 3, and 4. Figure 5 presents titration curves of HDNB with *N,N*-diethylaniline and aniline. In this figure both ordinate and abscissa are on logarithmic scales. The maxima are extremely flat, but their

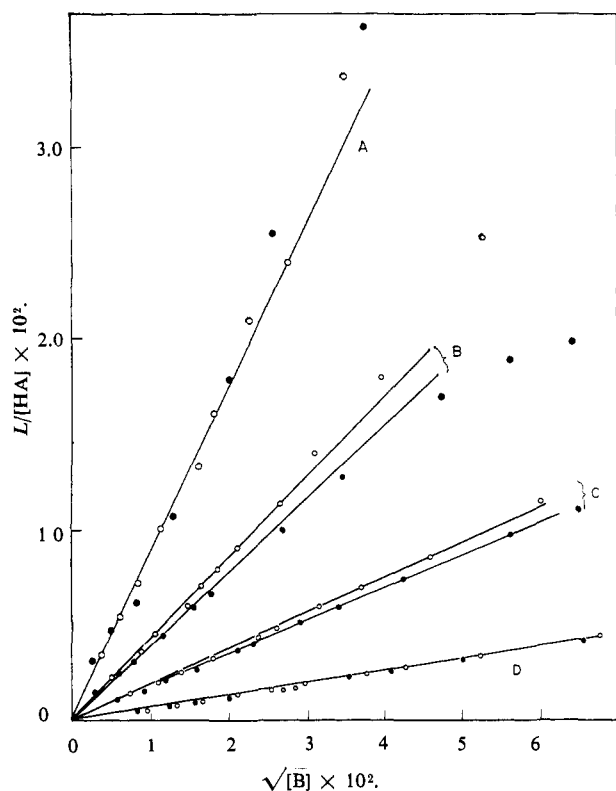


Figure 6. Plot of $L/[HA]$ vs. $\sqrt{[B]}$ from initial portion of the conductometric titration curve of HDNB with methylpyridines in dilute solution: A, collidine; B, lutidine; C, picoline; D, pyridine; \bullet —, 3.82×10^{-3} , \circ —, 1.53×10^{-3} M HDNB. Slopes: A, 0.86, 0.86; B, 0.38, 0.42; C, 0.17, 0.18; D, 0.062, 0.062.

exact location is difficult to estimate when the ordinary numerical scale is used for the abscissa. A logarithmic ordinate scale permits the presentation of titration curves at widely differing concentrations of HDNB and permits a better estimate of the location of the maximum.

Calculation of $K_d K_f$ from Initial Part of Titration Curves. Plots of $L/[HA]$ vs. $\sqrt{[B]}$ from the initial portion of the titration of HDNB with the various pyridines and those of N,N-diethylaniline are shown in Figures 6 and 7, respectively. Using eq. 13a, calculated values of $K_d K_f$ are presented in the last column of Table II. Below an example is given of the calculation of $[HA]$ and of $[B]$ in the titration of $C_a = 0.00153$ M HDNB with collidine: concentration of base added, $C_b = 1.20 \times 10^{-3}$ M; observed conductance 2.28×10^{-5} ; $\Delta_{B(HA)_2} = 130$; $[BH^+] = [HA_2^-] = 1.76 \times 10^{-4}$ M. As a first approximation $[HA] \cong C_a - 2[BH^+] = 1.18 \times 10^{-3}$. From eq. 9, $[BHA]_{app} = 2.1 \times 10^{-4}$, using $K_d = 7.0 \times 10^{-6}$ which is obtained from the maximum conductance in the titration curve.

As a second approximation

$$[HA] = C_a - 2[BH^+] - [BHA] = 9.7 \times 10^{-4} \quad (6)$$

$$[B] = C_b - [BH^+] - [BHA] = 8.2 \times 10^{-4} \quad (7)$$

From eq. 13a, $K_d K_f = 2.3 \times 10^{-3}$.

When K_f is of the order of 10^3 or greater, salt formation in the early portion of the titration curve is almost

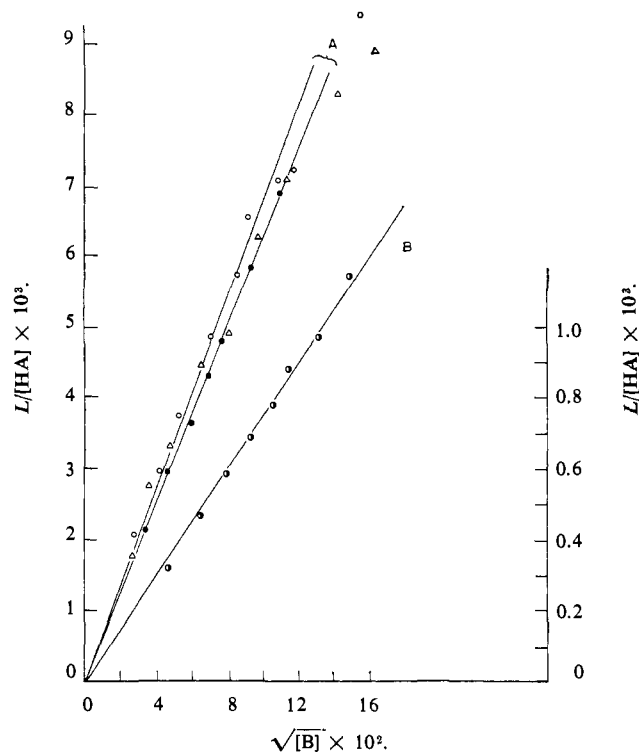


Figure 7. Plot of $L/[HA]$ vs. $\sqrt{[B]}$ from initial portion of titration curve of HDNB with N,N-diethylaniline and aniline: A, \triangle —, 0.0360, \circ —, 0.0187, \bullet —, 0.010 M HDNB with N,N-diethylaniline; B, 0.0187 M HDNB with aniline. Left-hand ordinate to curve A, right-hand ordinate to curve B. Slopes: A, 0.068, 0.068; B, 0.0075.

quantitative. Under these conditions $[B]$ is extremely small and the calculated values of $[B]$ vary greatly with very small errors in the determined conductance. This situation prevails in the titration of HDNB with N,N-dimethylbenzylamine, and no reliable value of $K_d K_f$ can be found from the early portion of the titration curve.

K_f and K_d from Location and Height of Maximum of Titration Curve. The location of the maximum in the conductometric titration of 3,5-dinitrobenzoic acid with the various bases and the corresponding values of K_f calculated according to eq. 18 and the values of K_d calculated from the conductance at the maximum according to eq. 18a are entered in Table II. In all instances $[A^-]_m$ is less than 20% of $[HA_2^-]_m$, and eq. 18 and 18a are applicable.

When the maximum is very flat, the exact location of the maximum is difficult to establish. Under such circumstances three values of its location have been taken, one before, one estimated as much beyond, and one midway between the two. The following average values of K_d and K_f were found in the titration of HDNB with various bases: collidine 0.7×10^{-5} and 2.3×10^2 ; lutidine 2×10^{-6} and 1.6×10^2 ; picoline 1.2×10^{-6} and 6×10^1 ; pyridine 4×10^{-7} and 3×10^1 ; N,N-dimethylbenzylamine 1.0×10^{-5} and 5×10^3 ; N,N-diethylaniline 2×10^{-6} and 7. The product $K_f K_d$ obtained from the above data is also entered in Table II and compared with that obtained from the initial portion of the titration curve. No maximum was found in the titration curve of 0.0187 M HDNB with aniline.

Table II. K_f and K_d Calculated from Maximum in Conductometric Titration Curves of HONB with Bases

Base	[HDNB], $M \times 10^3$	C_{bm} , $M \times 10^3$	Sp. conduct. at max.	[BH ⁺] _{1m} , $M \times 10^3$ (eq. 18 ^a)	[HA] _{1m} , $M \times 10^3$ (eq. 18 ^a)	[BHA] _{1m} , $M \times 10^3$ (eq. 6)	[B] _{1m} , $M \times 10^3$ (eq. 7)	[A ⁻] _{1m} , $M \times 10^6$ (eq. 18d)	$K_d \times 10^6$ (eq. 18a)	K_f (eq. 18)	$K_d K_f$ (av.) from	
											max.	initial part of curve
N,N-Dimethyl- benzylamine	18.7	...	2.65×10^{-4}	2.27
	2.68	1.55	4.50×10^{-5}	0.388	0.92	0.98	10	4.7×10^3
	1.34	0.87	2.48×10^{-5}	0.214	0.43	0.48	13	4.9×10^3
Collidine	0.67	0.60 ± 0.1^b	1.45×10^{-5}	0.125	0.18	0.27	Av. 10	3.7 ± 0.15 $\times 10^{2b}$
	18.7	15	2.7×10^{-4}	2.1	7.3	7.4	5.0	1.9	7.4	1.9×10^2
	3.82	6.1	7.0×10^{-5}	0.49	1.4	1.4	4.2	1.9	6.7	2.4×10^2	...	2.5×10^{-3}
Lutidine	1.53	5.4	2.8×10^{-5}	0.195	0.54	0.61	4.5	1.9	8.5	2.2×10^2
	18.7	15	1.83×10^{-4}	1.4	9.2	6.7	7.2	1.1	1.8	1.6×10^2
	7.43	9.7	7.9×10^{-5}	0.61	3.1	3.2	5.9	1.1	2.3	1.7×10^2	...	5.3×10^{-4}
Picoline	3.74	11 ± 4^b	4.0×10^{-5}	0.31	1.5	1.6	9.1	1.1	2.3	1.6 ± 0.4 $\times 10^{2b}$
	18.7	26 ^b	1.49×10^{-4}	1.15	8.3	8.4	16.5	0.82	2.1	$6 \pm 1.5 \times 10^6$...	1×10^{-4}
	18.7	37 ^b	0.93×10^{-4}	0.715	8.6	8.7	28.0	0.50	1.2	$3 \pm 0.8 \times 10^6$...	1.3×10^{-6}
N,N-Diethyl- aniline	36.0	1.4×10^{2b}	3.0×10^{-4}	2.38	15.6	15.6	126	1.0	2.2	7 ± 4^b	...	1.7×10^{-5}
	18.7	1.1×10^{2b}	1.6×10^{-4}	1.29	8.1	8.1	100	1.0	1.5	10 ± 5^b	...	1.5×10^{-5}
	10.0	1.5×10^{2b}	0.92×10^{-4}	0.73	4.2	4.3	145	1.0	1.6	7 ± 3^b	...	1.5×10^{-5}

^a From conductance of salt, K_d was calculated to be 0.9×10^{-5} . ^b Extremely flat maximum; exact location uncertain.

$K^d_{B(HA)_2}$ (B is Collidine; HA is HDNB). This is calculated from the titration curve of HDNB solutions more concentrated than $1 \times 10^{-2} M$ with collidine from 10–40% titrated. In these solutions extensive $B(HA)_2$ formation occurs. The following procedure is used in the calculation of $K^d_{B(HA)_2}$. (a) From the conductance an approximate value of $[BH^+]$ is calculated using eq. 13, neglecting $[A^-]$ and $[HB_2^+]$. (b) As a first approximation $[HA]$ is calculated from eq. 6, neglecting $[A^-]$, $[BHA]$, and $[B(HA)_2]$, i.e., $[HA] = C_a - 2[BH^+]$. (c) Knowing $[HA]$ and $[BH^+]$ approximately, an approximate value of $[BHA]$ is calculated from eq. 10. (d) From the above value of $[BHA]$, $[B]$ is calculated from the known value of K_f . (e) Next eq. 19 (cf. eq. 11) is used to calculate $[B(HA)_2]$

$$C_b = [B] + [BH^+] + [BHA] +$$

$$[B(HA)_2] + 2[HB_2^+] \quad (19)$$

neglecting $[HB_2^+]$, as the analytical concentration of base, C_b , never exceeds $6 \times 10^{-3} M$ in the mixture used for the present study. (f) A better approximation of $[HA]$ is obtained in step b by including the $[BHA]$ and $[B(HA)_2]$ terms in eq. 6, and the entire cycle is repeated until constant values of $[HA]$ and $[B(HA)_2]$ are obtained. Finally, $K^d_{B(HA)_2}$ is calculated, taking $[BH^+] = [HA_2^-]$. In a sample calculation, collidine in a concentration of $3.00 \times 10^{-3} M$ was added to $1.87 \times 10^{-2} M$ HDNB. The observed conductance was $1.64 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. Since $\Lambda_{B(HA)_2} = 119$, $[BH^+]_1$ equals 1.4×10^{-3} (subscript 1 denotes first cycle). $[HA]_1$ is found from step b to be 1.6×10^{-2} . Next, $[BHA]_1 = 3.8 \times 10^{-3}$ from step c taking $K_d = 0.70 \times 10^{-5}$, $K_2 = 1.7 \times 10^4$, and $f^2 = 0.78$ (calculated from the limiting Debye-Hückel expression). Taking $K_f = 3.3 \times 10^2$, the following values of $[B]_1$ and $[B(HA)_2]_1$ are obtained from steps d and e: 1.60×10^{-4} and $1.08 \times 10^{-3} M$, respectively. After five cycles, the final values of $[BH^+]$ and $[B(HA)_2]$ are 1.4×10^{-3} and $5.6 \times 10^{-4} M$, respectively, yielding a value of $K^d_{B(HA)_2}$ equal to 3×10^{-3} . Use of this value has been made in the calculation of the titration curve of 0.0187 M HDNB with collidine in Figure 4.

Discussion

The equations derived in this paper are valid only when K^d_{BHA} (denoted by K_d in this paper) is very small as compared to $K^d_{B(HA)_2}$. When these two dissociation constants are large, as in titrations with tetraalkylammonium hydroxides, the titration curve is monotonous and does not exhibit a maximum.

Comparison of curves C and D in Figure 2 illustrates the fact that the conductance at the maximum increases with increasing K_d . Curve C refers to collidine with K_d of 7×10^{-6} and curve D to lutidine with $K_d = 2 \times 10^{-6}$.

Under the conditions specified, the conductance at the maximum in the titration of HDNB with a given base, according to eq. 18a, should be proportional to the initial concentration, C_a , of the acid. From Table II it appears that this relation holds in the titration of HDNB with N,N-dimethylbenzylamine, collidine, and lutidine. For example, in the titration of 3.82×10^{-3} and $1.53 \times 10^{-3} M$ HDNB with collidine, the ratio of

the C_a values is 2.5 while the ratio of the conductance at the maximum is 2.5.

According to eq. 18 the location of the maximum approaches 50% titrated with increasing values of K_f and of C_a , the initial concentration of the acid. Figures 2 and 3 clearly illustrate this effect of C_a . When K_f is equal to infinity, the maximum in the titration curve is found at 50% titrated ($C_{b,m} = C_a/2$). With values of K_f of 10^4 and C_a of $10^{-3} M$ the maximum occurs at 60% titrated ($C_{b,m} = 0.6C_a$); with $C_a = 10^{-2}$, $C_{b,m} = 0.51C_a$. Quite generally K_f must be smaller than about 10^4 in order to derive its value from the location of the maximum in the conductometric titration curve. The other extreme is that $K_f C_a$ is very small. When $1/K_f C_a$ is of the order of 10 or greater, the term $1/2$ in eq. 18 can be neglected and eq. 18 reduces to (cf. eq. 18c)

$$C_{b,m} = 1/K_f = [B]_m$$

This means that $C_{b,m}$, the analytical concentration of base at the maximum, becomes independent of C_a . This is the situation in the titration of 3,5-dinitrobenzoic acid with N,N-diethylaniline (see Table II), where $C_{b,m} = 1.3 \pm 0.2 \times 10^{-1} M$. Under these conditions the maximum is very flat and its location cannot be found with an accuracy greater than about 10 to 20%.

When the square root of the product $K_d K_2$ is considerably smaller than 1, eq. 18a becomes

$$2[BH^+]_m = C_a \sqrt{K_d K_2} \quad (18a')$$

and K_d is calculated very simply. Also, under these conditions eq. 18b approaches

$$[BHA]_m = [HA]_m = C_a/2 \quad (18b')$$

i.e., at the maximum 50% of the acid is present in the undissociated form and 50% as salt. This situation is approached in the titration of HDNB with several weak bases. For example, from the data in Table II it is seen that in the titration with pyridine $[HA]_m = [BHA]_m$ and K_d (from eq. 18a) = 4×10^{-7} .

The conductometric titration curves of a weak acid with a base in which the maximum value of $[BH^+]$ is about 2.5×10^{-3} or less can be calculated using eq. 6, 7, 9, and 11 and applying a series of successive approximations described in the Introduction, knowing K_f , K_d , K_2 , and ion mobilities. The agreement between experimental and calculated curves is highly satisfactory, as can be seen from Figures 2, 3, and 4. Significant differences between the two curves are found when $[BH^+]$ becomes greater than about $2.5 \times 10^{-3} M$, when formation of undissociated $B(HA)_2$ can no longer be neglected.

When $B(HA)_2$ formation must be considered, the factor $1 + K_f[HA]$ in eq. 10 and 11 is replaced by the factor $1 + K_f[HA] + K_f K_d K_2 [HA]^2 / K_{B(HA)_2}^d$, while eq. 9 remains unchanged. The procedure of calculation of the titration curve then becomes identical with that neglecting $B(HA)_2$, except that $[B(HA)_2]$ is introduced into eq. 6. The calculated (using the limiting Debye-Hückel expression) and experimental curves in the titration of 0.0187 M HDNB solutions with collidine are presented in Figure 4 and are in satisfactory agreement. When the excess of base is

greater than 200%, the calculated conductance becomes smaller than the experimental value because of HB_2^+ formation.

From the data presented in Table II, it appears that K_d increases considerably with increasing number of methyl groups in the substituted pyridine, probably as a result of decreasing hydrogen bonding in the salt.

There is no simple relation between K_f of the various substituted pyridinium 3,5-dinitrobenzoates and the strength of the bases in water. Such a relation also involves K_d of the salts in acetonitrile. Qualitatively it is easily shown that, other things being equal, the salt formation becomes more complete with decreasing dissociation of the salt. Considering the dissociation constant K_{HA}^d of an acid and the formation constant of the base cation $K_{BH^+}^f$ in acetonitrile we obtain

$$(K_{HA}^d K_{BH^+}^f)_{AN} = \frac{[BH^+][A^-]}{[HA][B]} = (K_d K_f)_{AN} \quad (20)$$

in which K_d and K_f refer to BHA.

In aqueous medium BHA is highly dissociated and the neutralization of the acid HA by B is represented by the over-all reaction $B + HA \rightleftharpoons BH^+ + A^-$.

In our experiments in acetonitrile the same acid has always been used. Therefore the difference between K_{HA}^d in water and in acetonitrile is in all instances the same. Provided there are no specific solvation effects, it is to be expected that $p(K_d K_f)_{AN} - (pK_{BH^+}^f)_W$ should be a constant. From the data in the last column in Table III it appears that this is true for pyridine and its methyl derivatives, the above difference being equal to 10.1. In a previous paper⁹ we have found that for

Table III. Relation between $(K_d K_f)_{AN}$ and $(K_{BH^+}^f)_W$ ($HA = 3,5$ -Dinitrobenzoic Acid)

Base	$p(K_d K_f)_{AN}$ from initial part of titra- tion curve	$-(pK_{BH^+}^f)_W$	$(p(K_d K_f)_{AN} - (pK_{BH^+}^f)_W)$
2,4,6-Collidine	2.6	7.45 ^a	10.25
2,4-Lutidine	3.3	6.79 ^a	10.1
4-Picoline	4.0	6.02 ^b	10.0
Pyridine	4.9	5.17 ^b	10.1
N,N-Dimethyl- benzylamine	1.2 ^c	8.93 ^d	10.1
N,N-Diethylaniline	4.7	6.56 ^d	11.35
Aniline	6.7	4.62 ^d	11.3

^a A. Gero and J. Markham, *J. Org. Chem.*, **16**, 1835 (1951).

^b H. Brown and X. Mihm, *J. Am. Chem. Soc.*, **77**, 1723 (1955).

^c $K_d K_f$, average value from maximum in titration curve (Table II) since this product cannot be evaluated from the initial part of the titration curve.

^d N. Hall and M. Spinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

the Hammett nitroaniline indicators, $K_{BH^+}^f$ in acetonitrile is 10^5 times greater than that in water. Coetzee and Padmanabhan¹⁰ found the same ratio for aliphatic secondary and tertiary amines. If this relation also holds for the pyridines, we find that (cf. eq. 20) $(p(K_d K_f)_{AN} = p(K_d K_f)_{AN} - (pK_{BH^+}^f)_{AN} = p(K_d K_f)_{AN} - (pK_{BH^+}^f)_W + 5.0 = 10.1 + 5.0 = 15.1$.

(9) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).

(10) G. Padmanabhan, Ph.D. Thesis, University of Pittsburgh, 1963.

Thus, the dissociation constant of 3,5-dinitrobenzoic acid in acetonitrile is found to be $10^{-15.1}$ as compared to $10^{-2.82}$ in water,¹¹ a difference of 12.3 pK units. The value of $p(K_d K_f)_{AN} - (pK_{BH^+})_W$ is 1.2 units greater for aniline and diethylaniline than for the substituted

(11) J. Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

pyridines, indicating that $K_{BH^+}^f$ for the former two bases in only $10^{3.8}$ instead of 10^5 times greater in AN than in water. This result is in excellent agreement with that of Coetzee and Padmanabhan,¹⁰ obtained by potentiometric measurements with the glass electrode, who found $K_{BH^+}^f$ for aniline $10^{3.8}$ times greater in AN than in water.

d-Orbital Participation in Silane Conjugation

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A substituent interference experiment on the intensity of the 1L_b bands in phenylsilanes demonstrates that the SiH_3 group actually does withdraw electrons from the benzene ring into Si 3d-orbitals. Such an experiment has general applicability for ascertaining participation of d-orbitals in a conjugation scheme.

Introduction

Although 3d-orbital participation is frequently advanced as the explanation for some of the differences in the properties of organosilicon as compared to organic compounds, definitive evidence for such participation has been lacking. Reviews of the possible effects of postulated availability of the 3d-orbitals of silicon are available.^{1,2}

In this paper a spectroscopic experiment is reported which should show quite definitely whether or not a group utilizes d π -orbitals in interacting with a benzene ring. The experiment is applied to phenylsilanes; the results clearly require the silicon 3d-orbitals to strongly interact with the π -orbitals of the phenyl ring.

When a silicon atom is attached to a phenyl ring, two effects become apparent. The silicon, being more electropositive than carbon, has an inductive effect of releasing electrons into the ring (+ I effect).³ Resonance interaction between the silicon and the ring, however, either releases or withdraws π -electrons. Some of the principal resonance structures expected for phenyltrimethylsilane based on the postulated availability of the 3d-orbitals are shown below.

Contributions from structure III, which represents a type of hyperconjugation previously postulated for alkylbenzenes,⁵ tend to reinforce the inductive effect of

the silicon represented by structure II. Contributions from structures IV and V oppose the inductive and hyperconjugative effects by withdrawing electrons from the ring into the d-orbitals of the silicon ($-T$ effect). Much of the work of previous investigators in this field has been devoted to determining the relative magnitudes of these opposing effects. In this paper some attention is also given to this problem.

Previous investigations have used dipole moment measurements,^{6,7a} reaction kinetics,⁷ and nuclear magnetic resonance spectroscopy⁸ to determine these magnitudes. Taken individually, these results are inconclusive and, in some cases, contradict the results of other investigations. However, when all the results are examined as a whole, a definite trend emerges. The greater portion of the evidence points to the silicon having a small + I effect and a slightly larger $-T$ effect.

d-Orbital Perturbation of the Benzene Analog $^1A \rightarrow ^1L_b$ Transition

For substituted benzenes of C_{2v} or higher symmetry, the probability of the 2600-Å. benzene analog transition ($^1A \rightarrow ^1L_b$) is related to the electronic distributions (in both ground and excited states) of the ring alone.^{9,10} The unique feature of this transition is that it is forbidden in benzene itself, but, upon either C_{2v} mono-substitution or *para* disubstitution, the transition becomes allowed with the transition moment perpen-

(1) C. Eaborn, "Organosilicon Compounds," Academic Press, Inc., New York, N. Y., 1960, pp. 94-113.

(2) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

(3) Clark, Murrell, and Tedder⁴ in distinguishing between inductive effects on π - and σ -electrons in halobenzenes have pointed out that if there is sufficient repulsion between a lone pair on the substituent group and the π -distribution, then it is possible to have $-I_\Sigma$ and $+I_\pi$. In $-SiH_3$, however, the absence of a lone pair makes it highly likely that I_π is quite small and parallel to I_Σ .

(4) D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1250 (1963).

(5) (a) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941); (b) E. B. Berliner and F. J. Bonhus, *ibid.*, **68**, 2355 (1946); **70**, 854 (1948).

(6) (a) C. Curran, R. Witucki, and P. McCusker, *ibid.*, **72**, 4471 (1950); (b) H. Soffer and T. DeVries, *ibid.*, **73**, 5817 (1951); (c) A. Freiser, M. V. Eagle, and J. Speier, *ibid.*, **75**, 2821 (1953).

(7) (a) J. D. Roberts, E. A. McElhill, and R. Armstrong, *ibid.*, **71**, 2923 (1949); (b) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 4101 (1953); (c) J. Speier, *ibid.*, **75**, 2930 (1953); (d) R. A. Benkeser and P. E. Brumfield, *ibid.*, **73**, 4770 (1951); (e) C. Eaborn, *J. Chem. Soc.*, 4858 (1956); C. Eaborn and D. E. Webster, *ibid.*, 4449 (1957).

(8) R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **81**, 5352 (1959); R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

(9) A. L. Sklar, *J. Chem. Phys.*, **10**, 135 (1942); *Rev. Mod. Phys.*, **14**, 232 (1942).

(10) L. Goodman, I. G. Ross, and H. Shull, *J. Chem. Phys.*, **26**, 474 (1957).