

Acid-Base Equilibrium Constant and Dipole Moment of Tribenzylammonium Picrate in Benzene from Measurements of Dielectric Constant

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The equilibrium constant for the dissociation of tribenzylammonium picrate into picric acid and tribenzylamine in benzene at 30° and 40° C has been determined from the variation of dielectric constant with concentration. The heat of reaction is in the neighborhood of 11.4 kilocalories per mole. The dipole moment of tribenzylammonium picrate, 12.0×10^{-18} esu, is substantially the same as found previously for the picrates of the more strongly basic alkylamines. The dipole moment of picric acid, 1.75×10^{-18} esu, was also determined.

I. Introduction

The measurement of dielectric constant has been used rather infrequently as a quantitative method for studying association and other mass law equilibria in dilute solutions. The procedure, however, has been employed successfully to determine the dimerization constants of a number of carboxylic acids in benzene [1].¹ Although the method has more limited application than do methods based on colligative properties, it has certain advantages and, in particular, is free from assumptions regarding the validity of Raoult's law.

In this investigation, the measurement of dielectric constant is used to determine the equilibrium constant for the reaction between picric acid and a relatively weak tertiary amine, tribenzylamine, in benzene. Such acid-base equilibria are well suited for study because of the relatively large dipole moment of the salt compared to that of the component acid and base. In a previous investigation of the picrates of various alkylamines of sufficient basic strength to prevent measurable dissociation into free acid and base [2], it was found that the picrates of tertiary amines, but not those of primary and secondary amines, showed no significant association in benzene. Consequently, association of the salt should not be a complicating factor in the reaction with tribenzylamine.

II. Equipment and Procedure

The equipment and procedure have been described [2]. Tribenzylammonium picrate was prepared in the same manner as the other picrates. The melting point was 190° C. Because of the rather low solubility of the picrate in benzene, only the more dilute solutions were prepared in the usual manner with the addition of stock solution directly to the solvent or solution in the cell. The more concentrated solutions were prepared in flasks and introduced separately into the cell.

III. Experimental Results

The experimental data obtained at 30° and at 40° C are given in the first three columns of table 1. N_2 is the stoichiometric mole fraction of the solute and $\Delta\epsilon$ the difference in dielectric constant between the solution and the solvent.

The gradual decrease in the quantity, $\Delta\epsilon/N_2$, with increasing dilution indicates that the salt is partly dissociated into picric acid and tribenzylamine. The equilibrium constant for this reaction, $Bz_3NH^+ \dots Pi^- = Bz_3N + HPi$, can be determined by a procedure similar to that described previously [2]. Regarding the change in dielectric constant as the sum of three independent contributions that are linear functions of the concentrations of the acid, base, and salt, respectively,

$$\Delta\epsilon = k_A \alpha N_2 + k_B \alpha N_2 + k_S (1 - \alpha) N_2 \quad (1)$$

or

$$\alpha = \frac{k_S - \Delta\epsilon/N_2}{k_S - k_A - k_B}$$

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Experimental data and acid-base equilibrium constant for tribenzylammonium picrate in benzene

$N_2 \times 10^4$	$\Delta\epsilon$	$\Delta\epsilon/N_2$	α	$K_N \times 10^5$
30° C				
0.899	0.0073 ₉	82.2	0.591	7.68
1.081	.0093 ₃	86.8	.566	7.98
1.585	.0159 ₇	100.7	.491	7.51
1.698	.0173 ₇	102.3	.483	7.66
2.327	.0262 ₁	112.6	.427	7.41
3.467	.0420	121.1	.381	8.13
4.127	.0525	127.2	.349	7.72
7.038	.0985	140.0	.280	7.66
$k_A + k_B = 6.2 \quad k_S = 192.0^a \quad K_N = 7.71 \times 10^{-5}^a$				
40° C				
0.907	0.0054 ₆	60.2	0.699	14.7
1.613	.0127 ₇	79.2	.594	14.0
2.186	.0194 ₃	89.1	.539	13.8
4.126	.0441	106.9	.440	14.3
4.986	.0554	111.1	.417	14.9
5.867	.0695	118.5	.376	13.3
7.500	.0914	121.9	.357	14.9
8.198	.1019	124.3	.343	14.7
$k_A + k_B = 6.0 \quad k_S = 186.2^a \quad K_N = 14.3 \times 10^{-5}^a$				

^a Obtained from least squares solution of eq 3, as shown in figure 1.

where α is the fraction of salt dissociated, and k_A , k_B , and k_S are the proportionality constants for the acid, base, and salt, respectively. k_A and k_B were determined experimentally at 30° C from the dielectric constants of dilute solutions of picric acid and of tribenzylamine and then calculated for 40° C on the assumption that the dipole moment remains unchanged. The expression for the equilibrium constant,

$$K_N = \frac{(k_S - \Delta\epsilon/N_2)^2 N_2}{(\Delta\epsilon/N_2 - k_A - k_B)(k_S - k_A - k_B)}, \quad (2)$$

then contains only one unknown quantity in addition to K_N . In order to solve for k_S and K_N , it is convenient to rearrange eq 2 in the following linear form,

$$\Delta\epsilon/N_2 + [K_N(k_S - k_A - k_B)]^{1/2} Z - k_S = 0, \quad (3)$$

where

$$Z = [(\Delta\epsilon/N_2 - k_A - k_B)/N_2]^{1/2}. \quad (4)$$

The solution obtained by the method of least squares is shown graphically in figure 1, where $\Delta\epsilon/N_2$ is plotted as a function of Z . The intercept yields k_S . K_N is then determined from the

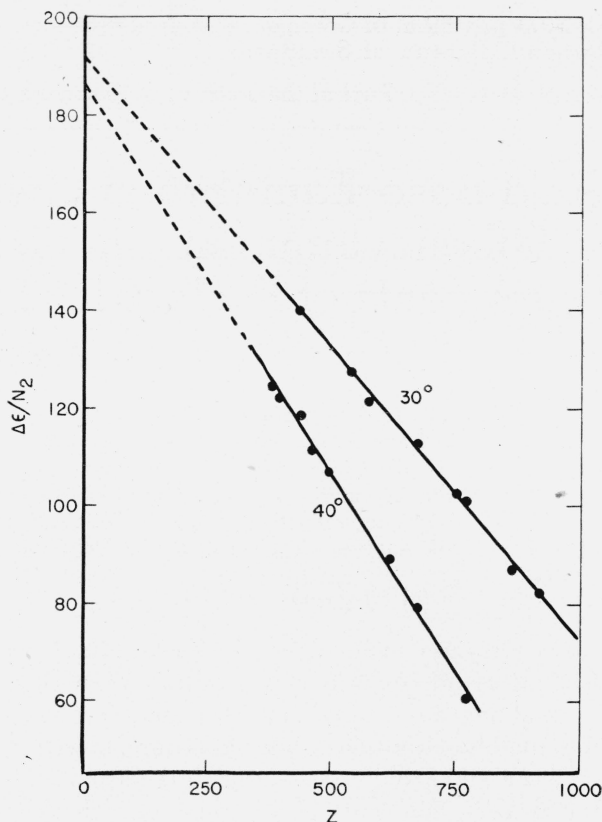


FIGURE 1. Graphical representation of data for tribenzylammonium picrate in benzene in accordance with equations 3 and 4.

slope of the line. These values are included in table 1. For comparison, values of α and of K_N at each concentration² are given, respectively, in the fourth and fifth columns.

There appear to be few or no data in the literature on the heats of reaction, or neutralization, of picric acid with amines in inert media, although such data should prove of interest with regard to relative basic strengths. The heat of reaction for picric acid and tribenzylamine, calculated from the equilibrium constant at the two temperatures, is in the neighborhood of 11.4 kcal/mole.

The dipole moment of tribenzylammonium picrate, calculated from k_S at either 30° or 40° C, is 12.0×10^{-18} esu. As the dipole moment of picric acid apparently has not been reported previously, the experimental data are given in table 2. The various symbols have been defined either in this or the previous paper. The moment of picric acid (1.75)

² The equilibrium constants also may be expressed in moles per liter rather than in mole fraction by multiplying K_N by the factor, $(1,000d)/M$, where, as a sufficient approximation for the dilute solutions involved, d is the density of the solvent and M its molecular weight.

appears to be a little larger than that of phenol (1.5 to 1.6) [3]. The value calculated for picric acid, however, may be subject to greater uncertainty, because of the neglect of atomic polarization, than is usually the case. Nonpolar molecules containing highly polar but symmetrically placed, substituents frequently have a relatively high atomic polarization [4]. If the atomic polarization is assumed to be the same as that of 2,4,6-trinitrobenzene [5], the moment calculated for picric acid is 1.57.

TABLE 2. *Experimental data (30° C) and dipole moment, μ , of picric acid in benzene*

$N_2 \times 10^3$	$\Delta\epsilon$	$\Delta\epsilon/N_2(k_A)$
0.000	-----	4.58
1.769	0.0081	4.58
5.522	.0253	4.58
9.152	.0418	4.57
12.40	.0570	4.60
$\Delta d/N_2 = 1.31$		
$P_2 = 106.0 \quad P_B = 44.6 \quad \mu = 1.75 \times 10^{-18} \text{esu.}$		

IV. Discussion

It has been suggested [6] that tribenzylammonium picrate may exist in tautomeric equilib-

rium between two forms in media of low dielectric constant, one form being a true salt and the other a molecular addition compound. In view of the fact that the moment of tribenzylammonium picrate is practically the same as for the trialkylammonium picrates, this possibility seems unlikely. Acids, however, do form hydrogen bonded complexes rather than salts with certain very weak bases. An interesting question arises as to whether, as the strength of the base is decreased, the transition from salt formation to hydrogen bonding occurs gradually or abruptly. Although tribenzylamine is a substantially weaker base than the trialkylamines, the proton transfer from acid to base appears to be equally complete in the two cases.

V. References

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