

SPECTROPHOTOMETRIC STUDY OF ASSOCIATION IN PETROLEUM SOLVENT

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This is a spectrophotometric study of the effect of added amine salts on the reactions of some basic indicator with the diphenyl phosphate and trichloroacetic acid in benzene at 25°. The indicator used was *p,p'*-dimethylamino azobenzene (dimethyl yellow). The added amine salts were the di-*n*-butyl ammonium and tri-*n*-butyl ammonium salts of the acid under study.

Equilibrium constants for the indicator reactions with various acids at stoichiometric indicator concentrations from 10^{-5} to $5 \times 10^{-5} M$ were obtained.

However, the uncertainty in their values are large which made it difficult to decide the exact type of aggregate. Namely ion-pair, quadrupole or homoconjugate ion-pair. It is likely that all the three species coexist in the solutions which were studied.

The addition of the appropriate salts of di-*n*-butylamine and tri-*n*-butylamine to equimolar solutions of indicator and acid produced no change in the absorption spectra of the indicator up to $5 \times 10^{-4} M$ in the latter's stoichiometric concentration. When the indicator and acid were both approximately $2.5 - 5 \times 10^{-3} M$ the addition of the corresponding amine salt caused an increase in the concentration of the free indicator. This was attributed to the reaction:



or to higher aggregates of the same sort. It is concluded that no unsymmetrical cationic triple ions were formed. It would appear that structural effect rather than electrical effects are decisive in determining the formation of such particles.

INTRODUCTION

Bronsted recognized that acid-base reaction did not yield free protons but rather consisted of proton transfer from an acid of one system to the base of a second system. The extent of such reaction is determined by the strength of acid, the basicity of the base and the dielectric constant of the solvent. In general three types of solvents are recognized. First type of solvents like water are capable of reacting as bases and acids (self-ionization). A second type consists of solvents which can react as bases, e.g. dimethyl ether. The third type consists of so-called inert solvents which do not take part directly in proton transfer like benzene or CCl_4 . This paper is concerned with the third type of acid-base reactions in the benzene. Benzene has low dielectric constant (about 2.28 at 25°) [1], therefore, the concentration of ionic species will be very small and charged particles will tend to form ion-pairs and higher aggregates.

Bjerrum [2] was the first to treat the formation of such species depending on electrostatic considerations. The association of ion-pair could be calculated from the equation:

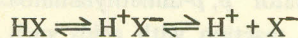
$$K = \frac{4 \pi N}{1000} \frac{e^2}{DKT} Q(b)$$

where K is the association constant, $b = e^2/aDKT$, a is an empirical distance parameter, N is Avogadro's number, D the dielectric constant of solvent, K is Boltzmann constant, e is the electronic charge, T is absolute temperature and the term $Q(b)$ is a complex function of b which Bjerrum computed for values of b from 1 to 15.

Later Fuoss and Kraus [3-8] tested the theory of Bjerrum by measuring the electrical conductivity of various quaternary ammonium salts in dioxane-water mixture and dielectric constant from 2.2 (pure dioxane) to 84 (water). Most of the work which was reported by these investigators was concerned with quaternary ammonium salts.

Kraus found that amine salt (tri-isoamyl ammonium picrate) forms a hydrogen-bonded ion-pair which had a much smaller dissociation constant in benzene than the corresponding quaternary ammonium compound. This indicates that in acid-base reactions the ion-pair formed in solvents with low dielectric constants could not be examined on the basis of simple electrostatic theory. Kolthoff and Bruckenstein [9, 10] succeeded in extending the theory of Bronsted to acid-base reaction in glacial acetic acid by taking account of ion-pair formation and the formation of higher aggregates. The dielectric constant of acetic acid at 25° is 6.13. Kolthoff and Bruckenstein used an indirect method to calculate the acidity constants of acids in this medium.

An acid HX is assumed to react in acetic acid in the following way:



The first step is called ionization. This is true acid-base reaction, forming ion-pair. The second step is dissociation.

Kolthoff and Bruckenstein found that higher aggregates, triple ions or quadrupoles were also formed in solutions of acids and bases in acetic acid.

The autoprotolysis constant of acetic acid and the overall dissociation constants of a number of acids, bases and salts were determined potentiometrically by using a saturated chloranil electrode and a silver-silver chloride electrode [11, 12].

Acetic acid as solvent has a low dielectric constant, but is quite polar and strongly solvate solutes very strongly. Number of acid-base reactions were studied by different workers in solvents with low dielectric constant solvents like carbon tetrachloride, chloroform, chlorobenzene and *o*-dichlorodbenzene [13, 14].

In this work benzene was used as solvent. It is a good solvent for many organic molecules but is poor solvent for electrolytes in general.

Acid-base reaction of phenolic indicators like bromophthalein Magenta E and 2,4-dinitrophenol were studied in benzene by Davis and his coworkers [15, 16]. They found that in dilute solution ($10^{-5}M$ indicator) diphenyl guanidine react simply to form ion-pairs. According to Davis, alkylamines also reacted with this indicator to form ion-pairs.

Bruckenstein and Saito studied the reactions of large number of amines with a number of relatively strong acids in benzene [17].

The authors found that 1:1, 2:1 (acid-base) and 3:1 complexes in some cases. The 1:1 salts were more strongly aggregated at higher concentration than the other varieties,

the salts of the primary amines aggregated more strongly than the secondary amine and the latter aggregated more strongly than the tertiary amines.

Steigman and Lorenz [18] investigated the reactions of several indicator phenols in benzene with several bases, in the absence and presence of added amine salts. The indicators included 2,4-dinitrophenol and bromophthalein Magenta E. The bases included di-*n*-butylamine and diphenyl guanidine.

Earlier workers had reported that the addition of di-*n*-butyl ammonium *p*-toluene sulfonate to a mixture of di-*n*-butylamine and 2,4-dinitrophenol in benzene produced a marked increase in the yield of dinitrophenolate. Steigman and Lorenz found that the enhancement of the reaction was due to the formation of unsymmetrical triple ions and that the triple ions were anionic in nature, they also found that quaternary ammonium salts like bromides added to benzene solutions of the quaternary ammonium salt of either 2,4-dinitrophenol or bromophthalein Magenta E produced a marked shift in the spectra of the phenolate compounds and showed in other ways that some stable mixed unsymmetrical aggregate was formed.

The present work was initiated in order to examine the reactions of basic indicator in benzene with various acids and in particular to see whether added salts would enhance the reactions of the indicator and to see if there is any stabilization of unsymmetrical cationic triple ions.

The basic indicator dimethyl yellow (*p,p'*-dimethyl aminoazo benzene) was studied in benzene in the presence of acids such as trichloroacetic acid and diphenyl phosphate.

Salts like tri-*n*-butyl ammonium trichloroacetate was added to mixtures of basic indicator and trichloroacetic acid and the extent of reaction was measured in each case. Similar experiments were performed with di-*n*-butyl ammonium diphenyl phosphate as additives.

EXPERIMENTAL

Materials

Indicator. *p, p'*-Dimethylamino, azo benzene (dimethyl yellow, DMY) was a reagent grade material of Matheson, Coleman and Bell. It was recrystallized according to the method of Kolthoff and Bruckenstein [9], and was dried under reduced pressure (KOH) at 50°.

Acids. Diphenyl phosphate (DPP) was an industrial sample supplied by the Stauffer Chemical Co. contaminated to the extent of 50% with the monophenyl compound.

It was extracted in a Soxhlet apparatus with cyclohexane and the extract was recrystallized three times from the same solvent. It appeared in the form of white needles.

These were dried in a vacuum oven at 35°.

The assay determined by titration with NaOH according to the method of Davis [19] showed 100% purity.

Trichloro acetic acid (CCl_3COOH) was a Merck A.R. product. It was dried by dissolving in a 25% excess of benzene (by vol) and distilling off 25% of the solvent.

The actual concentration in benzene was established by titrating with NaOH according to the method of Bruckenstein and Saito [17].

Amines. Tertiary butylamine (Matheson, Coleman and Bell) was stored over KOH pellets, refluxed over fresh KOH and distilled through a Vigreux column (b.p. 76–77°).

Di-n-butylamine was (Matheson, Coleman and Bell) was purified in the same manner (b.p. 157°).

Tri-n-butylamine (Matheson, Coleman and Bell), was purified in the same way (b.p. 214°).

Diphenyl guanidine was (American Cyanamid Corp.) recrystallized according to the method of Lorenz [20]. The final product was dried in vacuum oven at 85°.

Amine Salts. n-Butylammonium trichloroacetate was prepared from equivalent quantities of the amine and the acid dissolved in methanol.

The solvent was removed in a rotary evaporator and the solid was recrystallized twice from methanol.

n-Butylammonium diphenyl phosphate was prepared in a similar fashion in benzene as solvent. It was then recrystallized twice from benzene. (Calcd for: $\text{C}_{20}\text{H}_{30}\text{NPO}_4$: 63.2, H 7.9, N 3.7, P 8.2% Found: C 62.97, H 8.07, N 3.78, P. 35%).

The analysis was performed by the Alfred Bernhardt Microanalytical Laboratory. Tri-n-butyl ammonium trichloroacetate was prepared from the amine and the acid in benzene. The solvent was removed by rotary evaporation. The solid was recrystallized from benzene. Calcd for $\text{C}_{14}\text{Cl}_3\text{H}_{28}\text{NO}_2$: C 48.16, Cl 30.53, H 8.03, N 4.01%. Found: C 48.17, Cl 30.77, 8.13 N 4.2%.

The analysis was performed by the Alfred Bernhardt Microanalytical Laboratory.

Solvent. Benzene was a spectroquality reagent grade product of Matheson, Coleman and Bell. It was refluxed with calcium hydride for several hours and then distilled. The distillate was stored in all-glass bottles in a dessicator over Drierite.

Procedures

Preparation of Solutions. Solutes (mostly solids) were weighed directly into 100, 50 or 25 ml volumetric flasks. These were then filled to the mark while immersed in a constant-temperature-bath maintained at $25 \pm 0.1^\circ$.

More dilute solutions were prepared by taking appropriate volumes of the concentrated solutions, using a burette

and made up to the required volume.

Spectrophotometry. The spectra were obtained on a Cary model 14 double-beam spectrophotometer equipped with a thermostat cell compartment which was maintained at 25°, a water-bath with a circulating pump. Quartz cells (Pyrocill Co.) were used, and were calibrated before use by the method of Haupt [21]. The four cells which were used had the following path lengths: 0.0100, 0.1070, 0.9468 and 4.7912 cm.

RESULTS AND DISCUSSION

The purpose of this work was to study the acid–base reaction in benzene as nonaqueous solvents and to see the effect of added salts to this reaction.

Basic indicator *p, p*-dimethylaminoazo benzene was chosen to such reaction with acids such as CCl_3COOH and diphenyl phosphate. In order to calculate such effect it was necessary to measure the equilibrium constants of the reactions of this indicator with the same acids in the absence of added salts.

The basic indicator *p, p*-dimethylaminoazo benzene (DMY), is a well-known and widely used azo compound. It is known that in benzene it dimerizes to an unknown extent at higher concentrations. In the present work it was found that at $10^{-5}M$ the coefficient was $2.89 \times 10^4 \text{ cm}^2/M$ and that at $5 \times 10^{-3}M$ the coefficient was 3.55×10^4 .

In addition it is known that the base undergoes a *cis*–*trans*-isomerization when light is absorbed and the two isomeric forms have different spectra [22].

Because of the complications associated with this indicator, a limited number of studies were carried out of its reaction with an acid. The acid chosen was diphenyl phosphate. Figure 1 shows the spectrum of this indicator in benzene in the presence of varying concentrations of diphenyl phosphate.

Since the basic form absorb at 407.1 nm and the ion-pair of the indicator salt absorb at 522.5, either concentration of the free base or that of the ion-pair of the indicator salt could be estimated spectrophotometrically.

For the acid which was studied ion-pair formation constant (K_p) homoconjugate formation constants (K_s) and quadrupole formation constants (K_Q) were calculated. The following equations were used in the calculations. The symbols A, B, HA, BH^+A^- , B (HA)₂, (BHA)₂ represent the absorbance, base, the acid, the ion-pair, the homoconjugate ion-pair and the quadrupole. The symbols *b* and a_M represent the cell-bath length in centimeters and the molar absorptivity in cm^2/M . Brackets around these symbols stand for molar concentrations, the subscript zero

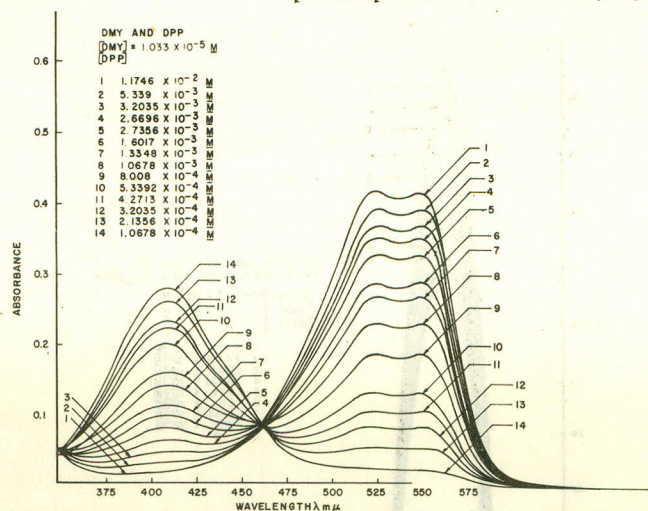
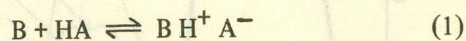


Fig 1 Absorbance vs wavelength for DMY and DPP in benzene at 25°C

outside a bracket represents the stoichiometric concentration of the particular species



$$K_p = \frac{[BH^+ A^-]}{[B][HA]} \quad (2)$$

$$[B]_0 = [BH^+ A^-] + [B] \quad (3)$$

$$[HA]_0 = [BH^+ A^-] + [HA] \quad (4)$$

$$[B] = \frac{A}{a_M \times b} \quad (5)$$

$$[BH^+ A^-] = \frac{A'}{a_M \times b} \quad (6)$$

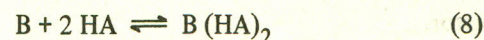
A, A' are the absorbance of free base and ion-pair since either concentration can be determined spectrophotometrically either

$$K_p = \frac{[B]_0 - [B]}{[B][HA]} = \frac{[B]_0 - \frac{A}{a_M \times b}}{\frac{A}{a_M \times b} \left[[HA]_0 - \left([B]_0 - \frac{A}{a_M \times b} \right) \right]} \quad (7)$$

or

$$K_p = \frac{\frac{A'}{a_M \times b}}{\left([B]_0 - \frac{A}{a_M \times b} \right) \left([HA]_0 - \frac{A'}{a_M \times b} \right)} \quad (7')$$

The equations for calculating homoconjugate ion-pair formation constant follow:



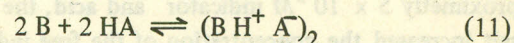
$$K_s = \frac{[B(HA)_2]}{[B][HA]^2} = \frac{[B]_0 - [B]}{[B] \left[[HA]_0 - 2([B]_0 - [B]) \right]^2} \quad (9)$$

$$K_s = \frac{[B]_0 - \frac{A}{a_M \times b}}{\frac{A}{a_M \times b} \left[[HA]_0 - 2 \left([B]_0 - \frac{A}{a_M \times b} \right) \right]^2} \quad (10)$$

or

$$K_s = \frac{\frac{A}{a_M \times b}}{\left([B]_0 - \frac{A'}{a_M \times b} \right) \left([HA]_0 - 2 \left(\frac{A'}{a_M \times b} \right) \right)^2} \quad (10')$$

The equations used for calculating the quadrupole formation constants are given below:



$$K_Q = \frac{[(BH^+ A^-)_2]}{[B]^2 [HA]^2} = \frac{\frac{1}{2} ([HA]_0 - [HA])}{[B]^2 [HA]^2} \quad (12)$$

$$= \frac{\frac{1}{2} \left([B]_0 - \frac{A}{a_M \times b} \right)}{\left(\frac{A}{a_M \times b} \right)^2 \left[[HA]_0 - \left([B]_0 - \frac{A}{a_M \times b} \right) \right]^2} \quad (13)$$

or

$$K_Q = \frac{\frac{A}{a_M \times b}}{\left([B]_0 - \frac{2A}{a_M \times b} \right)^2 \left([HA]_0 - 2 \frac{A}{a_M \times b} \right)^2} \quad (13')$$

Table 1 shows the concentrations of diphenyl phosphate end of the indicator, together with the measured absorbances of the solutions and the calculated values of the three constants.

It was decided to base these calculations on the ion-pair, its absorptivity coefficient obtained from limiting spectra in high acid concentration, was 4.46×10^4 at 522.5 nm for $10^{-5} M$ indicator, and 4.32×10^4 at the same wavelength for $5 \times 10^{-5} M$ base.

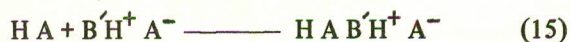
From this table it is possible to conclude that the reaction is quite complex, and that none of the three assumed equilibria adequately describes the behaviour of the indicator.

The ion-pair formation constant increases steadily with increasing acid concentration, the behaviour of the ion-pair constant would suggest that some higher aggregates also being formed.

However, the homoconjugate constant (K_s) decreases steadily with increasing acid, and this suggests that it is not the main product. The quadrupole formation (K_Q) at first decreases with increasing acid, and then increases. However, there is a marked effect of indicator concentration. The average constant at $10^{-5}M$ is about ten times greater than that calculated for the $5 \times 10^{-5}M$ solution. It is possible that all the three equilibria and others (like hexapole formation) are simultaneously occurring.

The difference in K_Q at the two indicator concentration levels is not due to indicator dimer formation. Since the other constants are not affected in the same way. It is possible that an additional equilibrium (not specified) is involved at the higher concentrations of di-n-butyl ammonium diphenyl phosphate.

In solutions containing $10^{-5}M$ indicator and acid, the addition of the salt (up to $4.6 \times 10^{-3}M$). However, in approximately $5 \times 10^{-3}M$ indicator and acid, the addition of salt increased the concentration of the free indicator. The effect was attributed to the formation of the homoconjugate ion-pair of the acid salt with a molecule of the acid and an attempt was made to calculate an equilibrium constant for the reaction of HA with B^+HA^- .



$$B = \frac{A}{a_M b}, BH^+A^- = (B)_0 - (B) \quad (16)$$

$$[HA] = \frac{[BH^+A^-]}{K_p [B]} \quad (17)$$

$$[H A B^+H^+A^-] = [HA]_0 - [HA] - [BH^+A^-] \quad (18)$$

$$[B^+H^+A^-] = [B^+H^+A^-]_0 - [H A B^+H^+A^-] \quad (19)$$

$$K_H = \frac{[H A B^+H^+A^-]}{[B^+H^+A^-][HA]} \quad (20)$$

In this reaction $B^+H^+A^-$ represents the added amine salt. $H A B^+H^+A^-$ represents the acid solvates of amine salts.

If free acid is removed by such a reaction, the acid

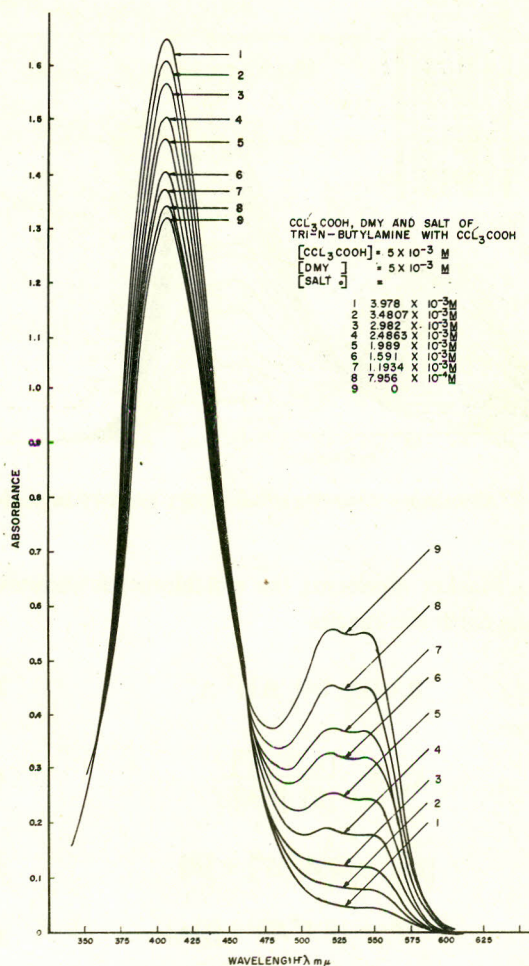


Fig. 2. Absorbances vs wavelength CCl₃COOH, DMY and salt of tri-n-butylamine with CCl₃COOH in benzene at 25°C.

which is available for reaction with the indicator is decreased, and more free indicator will appear. For calculation of the molar absorptivity the index of the base was determined at 407 nm and at the concentration of interest ($5 \times 10^{-3}M$) and was found to be $3.55 \times 10^4 \text{ cm}^2/M$.

In solution of $4.76 \times 10^{-3}M$ indicator and $4.76 \times 10^{-3}M$ DDP a value was calculated for the ion-pair formation constant (K_p) from the absorbance at 407 nm. It was 66.3. The corresponding value for the molar absorptivity of the ion-pair was calculated from the concentration and the absorbance of the solution at 522.5 nm. When the ion-pair formation constant was calculated from the ion-pair absorption at 522.5 nm the value of K_p was 5.4×10^1 , assuming that the absorptivity of the salt is 4.32×10^4 at this wavelength. Both sets of constants were used for the calculation of the homoconjugate ion-pair formation constant (K_H).

The results are given in Table 2, the subscripts 1 and 2 refer to the two different calculations and the different parameters used in each calculation. Neither set of calcu-

Table 1. Reaction of DMY with DPP in benzene at 25°

(DPP) <i>M</i>	Absorbance at 522.5 nm	$K_p M^{-1}$	$K_s M^{-2}$	$K_Q M^{-3}$
[(A). [B] ₀ = 1.003 × 10 ⁻⁵ M b = 0.941 cm, $a_M = 4.46 \times 10^4$ cm ² /M]				
1.07 × 10 ⁻⁴	0.025	5.98 × 10 ²	3.91 × 10 ⁶	2.80 × 10 ¹¹
2.14 × 10 ⁻⁴	0.055	7.11 × 10 ²	3.42 × 10 ⁶	1.87 × 10 ¹¹
3.20 × 10 ⁻⁴	0.085	7.97 × 10 ²	2.54 × 10 ⁶	1.52 × 10 ¹¹
4.27 × 10 ⁻⁴	0.107	8.07 × 10 ²	1.97 × 10 ⁶	1.20 × 10 ¹¹
5.34 × 10 ⁻⁴	0.135	8.93 × 10 ²	1.69 × 10 ⁶	1.20 × 10 ¹¹
8.01 × 10 ⁻⁴	0.190	1.08 × 10 ³	1.33 × 10 ⁶	1.21 × 10 ¹¹
1.07 × 10 ⁻³	0.230	1.14 × 10 ³	1.09 × 10 ⁶	1.15 × 10 ¹¹
1.33 × 10 ⁻³	0.270	1.36 × 10 ³	1.04 × 10 ⁶	1.39 × 10 ¹¹
1.60 × 10 ⁻³	0.290	1.40 × 10 ³	9.0 × 10 ⁵	1.36 × 10 ¹¹
2.14 × 10 ⁻³	0.325	1.61 × 10 ³	7.70 × 10 ⁵	1.63 × 10 ¹¹
2.67 × 10 ⁻³	0.350	1.89 × 10 ³	7.20 × 10 ⁵	2.08 × 10 ¹¹
3.20 × 10 ⁻³	0.365	2.09 × 10 ³	6.7 × 10 ⁵	2.93 × 10 ¹¹
3.74 × 10 ⁻³	0.377	2.36 × 10 ³	6.65 × 10 ⁵	3.01 × 10 ¹¹
4.27 × 10 ⁻³	0.390	3.08 × 10 ³	7.20 × 10 ⁵	4.95 × 10 ¹¹
5.34 × 10 ⁻³	0.420			
9.61 × 10 ⁻³	0.420			
$K_p = (1.42 \pm 0.72) \times 10^3$ $K_s = (1.53 \pm 1.07) \times 10^6$ $K_Q = (1.99 \pm 1.05) \times 10^{11}$				
[(B). [B] ₀ = 5.63 × 10 ⁻⁵ , b = 0.941 and 0.107 cm $a_M = 4.32 \times 10$ cm ² /M]				
1.75 × 10 ⁻⁴	0.120	3.22 × 10 ²	1.94 × 10 ⁶	1.76 × 10 ¹⁰
2.63 × 10 ⁻⁴	0.207	3.86 × 10 ²	1.76 × 10 ⁶	1.46 × 10 ¹⁰
3.51 × 10 ⁻⁴	0.275	3.97 × 10 ²	1.20 × 10 ⁶	1.20 × 10 ¹⁰
4.38 × 10 ⁻⁴	0.370	4.51 × 10 ²	1.10 × 10 ⁶	1.19 × 10 ¹⁰
6.14 × 10 ⁻⁴	0.505	4.73 × 10 ²	8.18 × 10 ⁵	8.92 × 10 ⁹
7.61 × 10 ⁻³	0.590	5.07 × 10 ²	7.71 × 10 ⁵	8.87 × 10 ⁹
8.77 × 10 ⁻³	0.720	5.37 × 10 ²	6.53 × 10 ⁵	7.85 × 10 ⁹
1.32 × 10 ⁻³	1.06	6.47 × 10 ²	5.28 × 10 ⁵	8.15 × 10 ⁹
1.75 × 10 ⁻³	0.147	7.59 × 10 ²	4.26 × 10 ⁵	9.02 × 10 ⁹
2.63 × 10 ⁻³	0.187	1.0 × 10 ³	4.20 × 10 ⁵	1.24 × 10 ¹⁰
3.51 × 10 ⁻³	0.212	1.28 × 10 ³	3.80 × 10 ⁵	1.78 × 10 ¹⁰
4.38 × 10 ⁻³	0.220	1.27 × 10 ³	3.00 × 10 ⁵	1.70 × 10 ¹⁰
5.27 × 10 ⁻³	0.227	1.33 × 10 ³	2.60 × 10 ⁵	1.78 × 10 ¹⁰
6.14 × 10 ⁻³	0.240	1.98 × 10 ³	3.22 × 10 ⁵	3.78 × 10 ¹⁰
7.01 × 10 ⁻³	0.247	2.75 × 10 ³	3.81 × 10 ⁵	7.09 × 10 ¹⁰
1.23 × 10 ⁻³	0.260	—	—	—
1.40 × 10 ⁻³	0.260	—	—	—
$K_p = (9.39 \pm 6.8) \times 10^2$ $K_s = (7.51 \pm 5.3) \times 10^5$ $K_Q = (1.81 \pm 1.62) \times 10^{10}$				

Table 2. Reaction of DMY and DPP in the presence of di-n-butylammonium diphenylphosphate in benzene at 25° $[B]_0 = 4.76 \times 10^{-3} M$, $[HA]_0 = 4.76 \times 10^{-3} M$, $a_{M_1} = 4.32 \times 10^4 \text{ cm}^2 M^{-1}$, $K_{P_1} = 54 M^{-1}$, $b = 0.0100 \text{ cm}$, $a_{M_2} = 3.83 \times 10^4 \text{ cm}^2 M^{-1}$, $K_{P_2} = 66.3$

Concn of salt (M)	Absorbance at 522.5 nm	K_{H_1}, M^{-1}	K_{H_2}, M^{-1}
	0.355	—	—
8.65×10^{-3}	0.315	1.07×10^3	2.56×10^3
1.30×10^{-3}	0.290	1.29×10^3	9.19×10^3
1.51×10^{-3}	0.265	3.04×10^3	2.28×10^3
1.78×10^{-3}	0.245	6.00×10^3	4.40×10^3
2.30×10^{-3}	0.210	6.14×10^3	2.48×10^3
3.33×10^{-3}	0.125	4.33×10^3	2.76×10^3
4.33×10^{-3}	0.055	3.84×10^4	2.73×10^4
5.41×10^{-3}	0.035	1.29×10^4	1.77×10^4
7.57×10^{-3}	0.00	—	—

$K_{H_1} = (1.43 \pm 1.74) \times 10^4$
 $K_{H_2} = (2.20 \pm 1.23) \times 10^4$

Table 3. Reaction of DMY with CCl_3COOH in the presence of added tri-n-butylammonium trichloroacetate in benzene at 25°

$$[B] = 5.00 \times 10^{-3}, [HA]_0 = 5.00 \times 10^{-3}, \\ b = 0.010 \text{ cm}, K_p = 87 M^{-1}$$

Concn of salt (M)	Absorbance at 407 nm	K_H, M^{-1}
0	1.322	—
1.19×10^{-3}	1.370	3.30×10^2
1.59×10^{-3}	1.40	5.89×10^2
1.99×10^{-3}	1.460	3.89×10^3
2.49×10^{-3}	1.500	5.11×10^3
2.98×10^{-3}	1.560	6.66×10^3
3.48×10^{-3}	1.600	1.03×10^4
3.98×10^{-3}	1.640	2.83×10^4
3.97×10^{-3}	1.690	5.56×10^3
6.46×10^{-3}	1.696	4.74×10^3

$K_H = (7.23 \pm 7.78) \times 10^3$

lations yields a satisfactory constant for the homoconjugate ion-pair of the dibutylamine salt.

It can be concluded that if one considers the great uncertainty in the ion-pair formation constant and the almost certain presence of other indicator salt species which were

ignored in the calculation and therefore, the absence of more exact information about the reaction between the indicator and the acid leads to such uncertainty (K_H). Because of the complexities associated with the reaction of DMY with acids, no attempt was made to calculate ion-pair or any other constant for the system DMY-trichloroacetic acid in benzene. The effect of added salt was investigated.

When both the indicator and acid were $5 \times 10^{-5} M$ the addition of tri-n-butylammonium trichloroacetate up to $3.96 \times 10^{-4} M$ produced no change in the absorption spectrum. Higher concentration of the salt produced an increase in the concentration of the free base. Fig. 2 shows this effect.

Table 3 shows the results with the calculated values of the homoconjugate ion-pair formation constant (K_H).

It was assumed that the molar absorptivity of the free base was $3.55 \times 10^4 \text{ cm}^2/M$, ion-pair formation constant (K_p) for single solution in which both the acid and indicator had the same initial concentration $5.0 \times 10^{-3} M$ was calculated and found to be $87/M$.

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