A STUDY ON ION-PAIR FORMATION IN PETROLEUM SOLVENT

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Spectrophotometric measurements of the basic indicator *p*-naphtholbenzein (PNB) in benzene in the presence of trichloroacetic acid were made. Tri-n-butylammonium trichloroacetate salt was added to a mixture of the indicator and trichloroacetic acid and the extent of the reaction was measured.

It is assumed that ion-pair is formed in absence of salts. This indicator showed no reaction with added salts in the presence of acid, at least up to an indicator concentration of $5 \times 10^{-4} M$. When the PNB concentration was increased to $5 \times 10^{-3} M$, and the concentration of CCl_3COOH was the same, the addition of tri-n-butyl ammonium trichloroacetate produced small increases in the concentration of the free base. The changes in absorbance due to added salt were too small to justify calculations of the values for any homoconjugate ion-pair stability constants.

INTRODUCTION

In our earlier investigations [1,2] we studied two indicator bases, namely 4-dimethylamino-4-nitro stilbene and dimethyl yellow. It was quite evident that both of them undergo complicated reactions in the presence of added acids, e.g. trichloroacetic acid, HCl, and diphenyl phosphate. It was not possible to decide whether there was ion-pair formation alone, quadrupole formation or homoconjugate ion-pair formation. The addition of the appropriate salts of di-n-butylamine and tri-n-butylamine to equimolar solutions of any of the two indicators and an acid prodiced no change in the absorption spectra of the indicators up to $5 \times 10^{-4} M$ in the latter's stoichiometric concentration. When the indicator and an 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 formation of homoconjugate ion-pair of the acid salt with a molecule of acid according to

$$HA + B A^+ + A^- \longrightarrow HAB H^+ + A^-,$$

$$K_H = \frac{(HAB \ H+A^-)}{(B H^+ + A^-)(HA)}$$

In this reaction $B H^+ A^-$ represents the added amine salt, and $HAB H^+ A^-$ represents the acid solvates of amine salts. Free acid is removed by such reaction and the acid which is available for reaction with the indicator is decreased

this more free indicator will appear.

Beacause of the lack of satisfactory information regarding the indicator—acid equilibria, it was not possible to calculate the equilibrium constants of the above change.

In this communication we report spectrophotometric measurements of the basic indicator *p*-naptholbenzein (PNB) in benzene in the presence of trichloroacetic acid. Tri-n-butylammonium trichloroacetate salt was added to a mixture of the indicator and trichloroacetic acid, and the extent of the reaction was measured.

EXPERIMENTAL

Material

Indicator. *p*-Naphthol benzeine (PNB) was (Eastman White Label Product) recystallized twice from ethanal [3].

Acids. Trichloroacetic acid (CCl_3COOH) was (Merck, A.R. product) dried by dissolving in a 25% excess of benzene (by volume) 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 [4].

Amines. Tri-n-butylamine (Matheson, Coleman and Bell) was stored over KOH pellets, refluxed over fresh KOH and distilled through a Vigreaux column. B.p.214°.

Amine Salts. Tri-n-butylammonium trichloroacetate was prepared from equivalent quantities of the amine and the acid dissolved in benzene.

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

(Found: C 48.17, Cl 30.77, H 8.13, N 4.2. Calcd for $C_{14}Cl_3H_{28}NO_2$; C 48.16, Cl 30.53, H 8.03, N 4.01%).

The analysis was performed by the Alfred Bernhardt Micro Analytical Laboratory.

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

Procedure

Preparation of Solutions. Solutes 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 $25^O \pm 0.10^O$. More dilute solutions were prepared by taking appropriate volumes of the concentrated solutions, using burette.

Spectrophotometry. The spectra were obtained on a Cary model 14 double-beam spectrophotometer equipped with a thermostat cell compartment which was maintained at 25° by a water-bath with a circulating pump. Quartz cells (Pyrocell) were used, and were calibrated before use by the method of Haupt [5]. The four cells used had the following path lengths: 0.0100, 0.1070, 0.9408 and 4.7912 cm.

RESULTS AND DISCUSSION

The purpose of this work is to examine the reaction between the basic indicator *p*-naphthol—benzein with trichlorocacetic acid in the absence and presence of tri-n-butylammonium trichloroacetate using a spectrophotometric method at 25°. The data is presented in the following sections.

This indicator was studied in acetic acid solution by Kolthoff and Bruckenstein [6], in addition to other investigators [7]. Hume and Hummelstedt reported that it was too weak a basic to react with diphenyl phosphate in glacial acetic acid [8]. It was found in the present work that it reacted with diphenyl phosphate in benzene. The absorption curves which were obtained were quite different in character from those reported by Higuchi *et al.* [3], who made their measurements in acetic acid solutions.

Figure 1 shows the family of curves obtained when $1.57 \times 10^{-5}M$ *p*-naphtholbenzein was mixed with different concentrations of trichloroacetic acid in benzene. The results are also shown in Table 1, together with calculated values of the K_p, the ion-pair formation constant
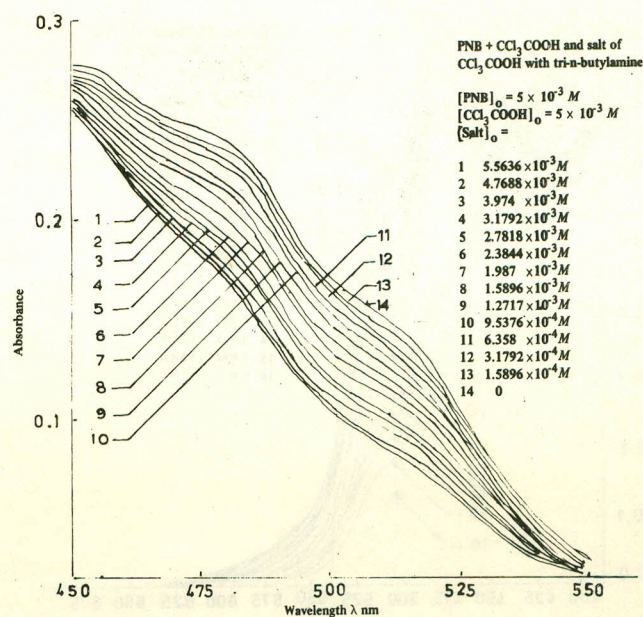

Fig. 1. Visible absorption spectra of *p*-naphtholbenzein and CCl_3-COOH in benzene at 25.0 ± 0.1^O.

Table 1. Reaction of PNB with CCl_3COOH in benzene at 25° $(B)_0 = 1.57 \times 10^{-5}M; b = 4.791/cm, a_M$ (for B) = 1.60×10^3 cm$^2/M$

Conc. of CCl_3COOH $(M \cdot 10^4)$	Absorbance Å at 512.5 nm	K_p $M^{-1} \cdot 10^{-2}$
5.95	0.230	4.49
7.94	0.240	4.47
9.92	0.260	4.16
19.8	0.325	4.06
29.8	0.375	4.17
39.7	0.395	3.73
49.6	0.425	4.00
59.5	0.442	3.90
69.4	0.460	4.04
79.4	0.472	4.66
99.2	0.505	5.00

$K_p = (4.23 \pm 0.47)10^2/M$

according the following equilibrium

$$B + HA \rightleftharpoons BHA$$
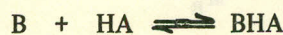
Where B, the basic indicator, HA, acid, and BHA the ion-pair.

It can be seen from the Fig. 1 that the basic form absorbs strongly at 512.5 nm with an estimated molar absorptivity coefficient of 1.60×10^3 cm$^2/M$. The ion-pair absorbs more strongly at the same wavelength, with an absorptivity of 7.75×10^3. The equations which were
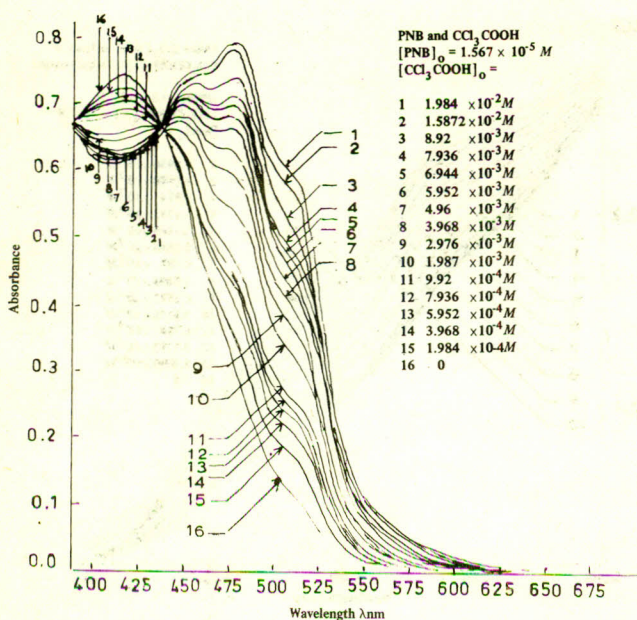
Fig. 2. Visible absorption spectra of p-naphtholbenzein, CCl_3COOH and tri-n-butyl-ammonium trichloroacetate in benzene at 25.0± 0.1°.

used for the calculation of K_p are given below:

$$A = A_B + A_{BHA}$$

$$= a_{M_B} \, b \, (B) + a_{M_{BHA}} \, b \, (BHA)$$

where total A is the absorbence, A_B absorbance due to the basic indicator, A_{BHA} is the absorbance due to the ion-pair, a_M is the absorptivity of the indicater, (B) is the concentration of the indicator, a_{MBHA} the absorptivity of ion-pair, (BHA) concentration of ion-pair and b is the cell length.

If the stoichiometric equation is represented as $(B)_0 = (B) + (BHA)$ and $(HA)_0 = (HA) + (BHA)$ then $(HA) = (HA)_0 - (BHA)$ and $(B) = (B)_0 - (BHA)$.

substituting for (B) in the above equation we have

$$A = a_{MB} \, b \, [\, (B)_0 - (BHA) \,] + a_{M_{BHA}} \, b \, (BHA)$$

$$(BHA) = \frac{A - a_{M_B} \, b \, (B)_0}{b \, (a_{M_{BHA}} - a_{M_B})}$$

but

$$K_p = \frac{(BHA)}{(B)(HA)} = \frac{A - a_{MB} \cdot b \, (B)_0}{b \, (a_{M_{BHA}} - a_{M_B})} \times$$

$$\frac{1}{(B)_0 - \frac{A - a_{MB} \, b \, (B)_0}{b \, (a_{M_{BHA}} - a_{M_B})} \times}$$

$$\frac{1}{(HA)_0 - \frac{A - a_{M_B} \, b \, (B)_0}{b \, (a_{M_{BHA}} - a_{M_B})}}$$

The fact that K_p values in the concentration range $(5.95 \times 10^{-4}/9.92 \times 10^{-3})M$ is almost constant $(4.23 \pm 0.47) \, 10^2/M$ indicates that the above assumption, namely the ion-pair formation, is a reasonable and acceptable one. This was not abserved in the previous basic indicators studied by us where a mixture of aggregates was suggested.

This is evidently a simple reaction under the conditions of this study. While the precision is not very good (12%), there are no trends in the calculated values.

This indicator like the others investigated earlier, showed no reaction with added salts in the presence of acid, at least up to an indicator concentration of $5 \times 10^{-4}M$. When the PNB concentration was raised to $5 \times 10^{-3}M$, and the concentration of CCl_3COOH was the same, the addition of tri-n-bulylammonium trichloroacetate produced small increases in the concentration of the free base. The changes in absorbance due to added salt were too samll to justify calculations of the values for any homoconjugate ion-pair stability constants, K_H. Fig. 2 shows the spectra obtained with the added salt. The ordinate is greatly expanded to show the differences in absorbance caused by the added salt. This latter conclusion is significant because it shows that there must be specific structural effects which may be more important than electrostatic effects in determining whether unsymmetrical triple ions form. Bruckenstein and Saito have reported that in $0.01M$ solution (in benzene) a stronger base (like dodecylamine) enhanced the basicity of a weaker base (like N,N-dimethyl benzylamine) when both were titrated with an acid like benzoic acid. This effect is seen after the end-point of the stronger base, and in the presence of an excess of acid.

Their conclusion is that strong interaction can occur between the ion-pair BH^+X^- and $B'H^+X'^-$, suggesting that ionic aggregates containing different cations are more stable than aggregates containing several identical cations. It is quite possible that this occurs at higher concentrations and with the particular bases which they studied. In the present work no such interaction was observed.

This points to a specificity of structure.

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