THE STUDY OF PROTON TRANSFER REACTION IN APOLAR – APROTIC SOLVENTS

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Abstract

The study of proton transfer reactions plays an important role in structural theories in chemistry. Solution phase acidities or basicities observed reflect intrinsic proton donating or accepting power of the solute as well as the solvent effect.

Apolar – aprotic solvents of low dielectric constant ($\epsilon < 6$) are of significantly less complications as specific solute – solvent interactions are greatly minimized and proton transfer is expected to be direct.

Introduction

Basic triphenylmethane dyes such as crystal violet on nucleophilic attack hydroxide ion and get colourless covalent carbinols. However, these colourless carbinol base react with an acid to form coloured dye carbenium ions and water, and not simply added a proton.

$$(4 - NR_2Ar)_3\,C - OH + HA \rightleftharpoons (4 - NR_2\,Ar)_3\,C^+ + A^- + H_2O$$
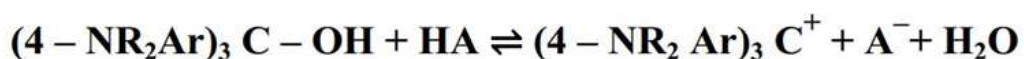
Colourless dye – carbinol	Acid	Coloured dye Carbenium ion

The carbinol bases of triarylmethane dyes are thus classified as pseudo – bases or more appropriately aquo – base.

A number of triphenyl methane dye cations are well known as solvent extraction – spectrophotometric reagents in trace determination of elements such as boron, antimony, cadmium, gallium, indium, cobalt, silver, tantalum, uranium, phosphorus, zinc, chlorine, germanium, gold, thallium, tungsten, molybdenum, bromine, silicon, vanadium, chromium, tellurium, bismuth, etc.

Association constant K for the reactions of triphenylmethane dye carbinols (D) with a reference acid HA in toluene:

$$D + HA \rightleftharpoons DH^+ A^-$$

The association constant for the equation is thus,

$$K = \frac{[DH^+A^-]}{[D][HA]}$$

In the present study HA stands for unsubstituted and a selected set of ortho and meta – substituted benzoic acids and D for the carbinol base of crystal violet (the reference base chosen for the study).

It is worth nothing that K, as defined, is an equilibrium concentration quotient rather than equilibrium constant. The solutions employed in such studies are usually sufficiently dilute.

Experimental

The reaction of a benzoic acid (HA) with the carbinol base of crystal violet (dye – OH) in toluene gives coloured ion – pair (**dye⁺A⁻**). In the reaction between a dye carbinol (dye – OH) and an acid (HA) is an apolar aprotic solvent,

$$HA + dye - OH \rightleftharpoons dye^+ A^- + H_2O \text{ --------------(1)}$$
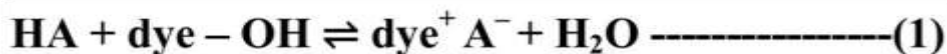
The water molecule formed has been arranged to be associated with any of the species present in the system and they exist as one entity. The reaction is more conveniently represented as

$$\underset{\substack{(dye - carbinol) \\ colourless}}{D} + \underset{\substack{Acid \\ colourless}}{HA} \rightleftharpoons \underset{\substack{(Ion - pair) \\ coloured}}{DH^+A^-} \text{ ---------------(2)}$$

Where D and DH^+A^- respectively stand for colourless ion – pair

$$K = \frac{[DH^+A^-]}{[D][HA]^n} \quad\text{-----------------(3)}$$

respectively was found to be described by

Where K, association constant; n acid exponent, usually > 1 and non – integral interpreted as due to overlapping associations of complex homoconjugate anion **(A^- ...... HA)** along with simple anion A^- with the dye cation.

The reaction kinetics was found to follow,

$$k = \frac{2.303}{t} \log \frac{X_e}{Xe-x} \quad\text{-----------------(4)}$$

Where X and Xe are the absorbance of the DH+A – at time *t* and at equilibrium; k is the rate constant. This is the standard rate equation for a pseudounimolecular reversible reaction.

k, however, was found to depend on CHA as

$$k = k_\alpha\, C_{HA} \pm k_\beta\, C^2_{HA} \quad\text{-----------------(5)}$$

The acid thus seems to play the dual role of acid and catalyst. kα the catalytic constant was determined from the intercept of $\frac{k}{C_{HA}}$ Vs $C_{HA.}$ the extrapolated plot of

Assuming that both the forward and the backward steps of the reaction (Eq^n – 2) be influenced by the acid as

$$D + f\,HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} DH^+A^- + rHA \quad\text{-----------------(6)}$$

and using the obvious relations,

$$n = f - r \quad\text{-----------------(7)}$$

$$K = \frac{k_1}{k_{-1}} \quad\text{-----------------(8)}$$

$$k = k_1\,[HA]^f + K_{-1}\,[HA]^r \quad\text{-----------------(9)}$$

the following equation was obtained

$$\log\left\{\frac{k}{K+[HA]^{-n}}\right\} \log k_{-1} + f \log [HA] \quad \text{----------------(10)}$$

Plots of L.H.S. Vs log [HA] of Eqn. – 10 were found linear for all the acid carbinol solvent combinations tried in this study. Log k_{-1} (intercept) and f (slope) were obtained by the method of least squares. Log k_1 from Eq. (8) and r from Eq^n (7) were then calculated.

Discussion

Log K acidity scale

Log K can be used to measure relative strengths of acids in tolune strictly when the n values are same. Since n values for the acids in the set do not differ sufficiently ($0.93 < n \leq 1.35$), the log K scale for tolune phase acidity seems justifiable. The toluence phase acidity order in log K.

o – Bromo - > o – Fluoro - > o – Hydroxy - > o – Chloro> m – Bromo - > m – Chloro - > m – Fluro - > o - methyl - > Hydrogen - > Methyl Benzoic Acid does not run exactly parallel to the order of aquous – phase acidity in pKa.

o – Bromo - > o – Chloro - > o – Hydroxy - > o – Fluoro - > m – Bromo - > m – Chloro - > m – Fluro - > o – Methyl - > Hydrogen - > m – Methyl Benzoic Acid. Further, the log K (toluene Vs pKa (water) plot leads to two distinct separate lines.

(A)   Log K = - 5.05 pKa + 22.5 for m – isomer.

(B)   Log K = - 2.75 pka + 9.58 for o – isomer.

(A)   meta – isomer line

The high value of the slope (5.05) can be ascribed to greater fieldeffect of the substituent (x) in the solvent of low effective dielectric constant (D_E) in accordance with krickwood – westheimer equation.

$$\log \frac{K_X}{K_H} = \frac{e\mu_X \cos\theta}{2.303 \, RTD_E Y^2}$$

Since a meta substituents influence is predominantly field – inductive least complicated from other effects such as resonance, steric, chelation etc. in fact, the acidity order for meta – substituted acids was found very exactly the same in toluene and water m – Br - > m – cl - > m – F - > H - > m – CH$_3$ – benzoic acid.

(B)   Ortho – isomer line

Considerably lower value of the slope (2.75) of log K Vs pKa line for ortho – isomers indicates that the effect of an ortho – substituent is not predominantly electrostatic and that possible proximity effects due to steric hinderance. Ortho – substituted acids are very weak in toluene or too strong in water indicating the role of salvation in ortho effect. Infact the acidity order for ortho – acids in toluene.

o – Br - > o – F - > o – OH - > o – Cl - > o – CH$_3$ - > - hydrogen – benzoic acid differs from that in water

o – Br - > o – Cl - > o- OH - > o – F - > o – CH$_3$ -> hydrogen – benzoic acid.

DFT Calculations

DFT calculations were doing using B3LYP/6 – 31G (D) basis set Gaussion – 03 programme along with the graphical interface Gauss view – 03. The calculations were performed independently for the colourless carbinol form and the product formed during the reaction of Carbinol base of Crystal violet and benzoic acid.

The results obtained for different parameters such as Bond Length, Bond Angle and Dipole moment were analysed critically. Thus it is in accordance with the experimental fact that the complex formed during the reaction between carbinol base of CV and benzoic acid in an apolar aprotic medium, toluene, is polar in nature and is an ion – associate.

Conclusions

1) Dye carbinol – equilibria and kinetics provide a direct method for the determination of acidities and basicities in apolar aprotic solvents.

2) Toluene – phase log K or Log k$_1$ appears to be better measures of intrinsic acidities / basicities than the equous phase pK$_a$/pK$_R$.

3) DFT calculations also confirms the formation of an ion – associate during the reaction in toluene.

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