

## Proton transfer equilibria between *m*-substituted benzoic acids and the carbinol base of crystal violet in apolar aprotic solvents : A comparison between toluene-phase and aqueous-phase strengths of the acids

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A detailed study on proton transfer equilibria between twelve *m*-substituted benzoic acids and the carbinol base of crystal violet, the reference base, in toluene at 20°C and 28°C shows that toluene-phase strengths of the acids as compared to their aqueous-phase acidities are more than 4.5 times sensitive to the substituent's structure effects.

Proton transfer studies in apolar aprotic solvents ( $\epsilon < 15$ ,  $\mu < 8.3 \times 10^{-30}$  cm,  $E_T^N = 0.0-0.3$ )<sup>1</sup> are of significant interest. In such solvents, complications due to specific solute-solvent interactions encountered in protic and dipolar aprotic solvents are reduced to a minimum, if not eliminated. Despite this only a limited number of systematic studies on acidity measurements in such solvents have been made<sup>2-11</sup>.

Acidity measurements in an apolar aprotic solvent necessitate the use of an appropriate reference base. Davis and her school in their pioneering researches developed an indirect procedure where the 'test' acid and bromophthalein magenta E, the indicator acid, were allowed to compete for diphenylguanidine, the reference base, in benzene. Benzene-phase strengths of forty-eight carboxylic acids were thus determined<sup>2,3</sup>. A direct method for determining benzene-phase acidities was devised by Palit and his co-workers who introduced the colourless carbinol form of crystal violet, 4, 4', 4'' - tris dimethylamino triphenylcarbinol, as the reference base. Acidities of different carboxylic acids, phenols, nitro/fluoro-alcohols in benzene were thus measured<sup>4-7</sup>. Recently, the study on acid-triarylmethane dye carbinol base reactions in apolar aprotic solvents was extended to boron chelating simple acids such as dicarboxy, hydroxy carboxy, dihydroxy acids as well as boron

complexed acids (hydrogen spiroborates) and carbinol bases derived from crystal violet and three other triphenylmethane dyes (malachite green, brilliant green and ethyl violet) using toluene as the solvent of choice. The results were utilised towards predicting the optimum reagent for boron determination by solvent extraction-spectrophotometry<sup>8,9</sup>. In another investigation, toluene-phase basicities of carbinol bases of six triarylmethane dyes (malachite green, brilliant green, methyl violet, crystal violet, ethyl violet and victoria pure blue BO) were measured using *m*-toluic acid and salicylic acid as the reference acids<sup>10</sup>. Subsequently, a study on structural effects of four 'select' substituents having different blends of I and R effects from *meta*- or *ortho*-position on toluene-phase proton transfer from benzoic acid to the carbinol base of crystal violet indicated a significant enhancement in the substituent's electronic effect on the strength of benzoic acids when transferred from water to toluene and a definite predominance of the proximity polar effect over the steric effect in a substituent's '*ortho* effect' on toluene-phase acidities<sup>11</sup>. A systematic investigation on measurements of acidities in apolar aprotic solvents is thus of obvious interest. Herein, are reported the results on proton transfer equilibria between twelve *m*-substituted benzoic acids and the carbinol base of crystal violet in toluene, the apolar aprotic solvent of

Table 1 - Values of association constant ( $\log K$ ) and acid exponent ('n') for reactions of *m*-substituted benzoic acids with crystal violet carbinol in toluene at  $28.0 \pm 0.1^\circ\text{C}$ .

| Acid                                                       | $pK_a^*$<br>(Water) | $\log K$<br>(Toluene) | 'n'  |
|------------------------------------------------------------|---------------------|-----------------------|------|
| Benzoic Acid                                               | 4.20                | 1.65                  | 0.91 |
| <i>m</i> -Fluorobenzoic Acid                               | 3.86                | 3.11                  | 1.09 |
| <i>m</i> -Chlorobenzoic Acid                               | 3.83                | 3.15                  | 1.07 |
| <i>m</i> -Bromobenzoic Acid                                | 3.81                | 4.02                  | 1.29 |
| <i>m</i> -Iodobenzoic Acid                                 | 3.85                | 4.38                  | 1.41 |
| <i>m</i> -Methylbenzoic Acid                               | 4.27                | 1.59                  | 0.90 |
| <i>m</i> -Methoxybenzoic Acid                              | 4.09                | 2.22                  | 1.05 |
| <i>m</i> -Phenoxybenzoic Acid                              | 3.95                | 2.30                  | 0.98 |
| <i>m</i> -Benzoylbenzoic Acid                              | 3.85                | 2.64                  | 0.93 |
| $\alpha, \alpha, \alpha$ -Trifluoro- <i>m</i> -toluic Acid | 3.75                | 3.65                  | 1.12 |
| <i>m</i> -Cyanobenzoic Acid                                | 3.60                | 4.56                  | 1.23 |
| <i>m</i> -Nitrobenzoic Acid                                | 3.49                | 4.92                  | 1.28 |

\* Ref (2)

choice, and a comparative analysis of toluene-phase and aqueous-phase strengths of the acids.

### Materials and Methods

The chemicals used were of either analytical grade or highly purified by standard procedures<sup>12</sup>. Toluene was chosen as the reference apolar aprotic solvent because of its low toxicity (Threshold Limit value, 100 ml/m<sup>3</sup>)<sup>1</sup>. 4, 4', 4'' - tris dimethylaminotriphenyl carbinol (the carbinol form of crystal violet) which is colourless was employed as the reference base. Toluene solution of the carbinol base was prepared by basification of a  $10^{-5}$  M aqueous solution of crystal violet with  $\sim 2$  M NaOH followed by extraction into toluene following a standard procedure<sup>4</sup>.

*Meta*-substituted benzoic acids, in which substituents transmit their field-inductive influences to the -COOH group with little, if any, interference by resonance and various proximity effects, form a convenient set of substrates for quantitative studies on structure-activity relationships. A set of twelve *m*-substituted benzoic acids having substituents with Hammett constants ( $\sigma_m$ )<sup>13,14</sup> ranging from -0.069 to

Table 2 - Values of association constant ( $\log K$ ) and acid exponent (n) for reactions of *meta*-substituted benzoic acids with crystal violet carbinol in toluene at  $20.0 \pm 0.1^\circ\text{C}$  and  $28.0 \pm 0.1^\circ\text{C}$

| Acid                                                       | $\log K$<br>(Toluene) |      | 'n'  |      |
|------------------------------------------------------------|-----------------------|------|------|------|
|                                                            | 20°                   | 28°  | 20°  | 28°  |
| Benzoic Acid                                               | 1.79                  | 1.65 | 0.95 | 0.91 |
| <i>m</i> -Bromobenzoic Acid                                | 4.17                  | 4.02 | 1.31 | 1.29 |
| <i>m</i> -Iodobenzoic Acid                                 | 4.67                  | 4.38 | 1.48 | 1.40 |
| <i>m</i> -Methoxybenzoic Acid                              | 2.39                  | 2.22 | 1.09 | 1.05 |
| <i>m</i> -Phenoxybenzoic Acid                              | 2.68                  | 2.30 | 1.02 | 0.98 |
| <i>m</i> -Benzoylbenzoic Acid                              | 3.26                  | 2.64 | 1.05 | 0.93 |
| $\alpha, \alpha, \alpha$ -Trifluoro- <i>m</i> -toluic Acid | 3.78                  | 3.65 | 1.11 | 1.12 |
| <i>m</i> -Cyanobenzoic Acid                                | 4.89                  | 4.56 | 1.29 | 1.23 |

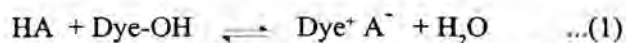
0.71 were employed: Benzoic acid ( $\sigma_m = 0.00$ ), *m*-fluorobenzoic acid ( $\sigma_m = 0.34$ ), *m*-chlorobenzoic acid ( $\sigma_m = 0.37$ ), *m*-bromobenzoic acid ( $\sigma_m = 0.39$ ), *m*-iodobenzoic acid ( $\sigma_m = 0.35$ ), *m*-methylbenzoic acid ( $\sigma_m = 0.069$ ), *m*-methoxybenzoic acid ( $\sigma_m = 0.12$ ), *m*-phenoxybenzoic acid ( $\sigma_m = 0.25$ ), *m*-benzoylbenzoic acid ( $\sigma_m = 0.35$ ), *m*-cyanobenzoic acid ( $\sigma_m = 0.56$ ),  $\alpha, \alpha, \alpha$ -trifluoro-*m*-toluic acid ( $\sigma_m = 0.43$ ) and *m*-nitrobenzoic acid ( $\sigma_m = 0.71$ ).

### Procedure

The equilibrium of the reaction between an acid ( $10^{-4}$  to  $10^{-2}$  M) and the carbinol base of crystal violet ( $10^{-5}$  M) in dry toluene producing a coloured ion-pair was conveniently measured at 610 nm in a 160 A Shimadzu UV-VIS recording spectrophotometer with cuvet thermostating facility at  $20.0 \pm 0.1^\circ\text{C}$  and  $28.0 \pm 0.1^\circ\text{C}$ . The molar absorptivity ( $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) of crystal violet dye cation in toluene was found to be 3.21.

### Results and Discussion

Acid (HA) - dye carbinol base (Dye-OH) equilibria in toluene producing a coloured ion-pair ( $\text{Dye}^+ \text{A}^-$ ) can be represented as



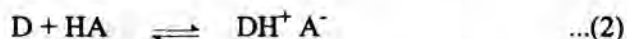
The water molecule formed being hydrogen bonded

Table 3 - Values of  $\log K$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$  (in molar units) in toluene, benzene and water media

| Acid                                                       | $\log K$ | $\Delta H^\circ$<br>(kJ/mol) | $\Delta S^\circ$<br>(kJ/K/mol) | $T\Delta S^\circ$<br>(kJ/mol) | $\Delta G^\circ$<br>(kJ/mol) | $\Delta H$<br>$T\Delta S^\circ$ |
|------------------------------------------------------------|----------|------------------------------|--------------------------------|-------------------------------|------------------------------|---------------------------------|
| Reference Base = Crystal Violet Carbinol in toluene (28°C) |          |                              |                                |                               |                              |                                 |
| Benzoic Acid                                               | 1.65     | -31                          | -0.07                          | -21                           | -9.5                         | 1.5                             |
| <i>m</i> -Bromobenzoic Acid                                | 4.02     | -33                          | -0.03                          | -10                           | -23.1                        | 3.4                             |
| <i>m</i> -Iodobenzoic Acid                                 | 4.38     | -61                          | -0.12                          | -36                           | -25.3                        | 1.7                             |
| <i>m</i> -Methoxybenzoic Acid                              | 2.22     | -35                          | -0.08                          | -22                           | -12.8                        | 1.6                             |
| <i>m</i> -Phenoxybenzoic Acid                              | 2.30     | -80                          | -0.22                          | -67                           | -13.3                        | 1.2                             |
| <i>m</i> -Benzoylbenzoic Acid                              | 2.64     | -132                         | -0.39                          | -117                          | -15.2                        | 1.1                             |
| $\alpha,\alpha,\alpha$ -Trifluoro- <i>m</i> -toluic Acid   | 3.65     | -27                          | -0.02                          | -6                            | -21.1                        | 4.4                             |
| <i>m</i> -Cyanobenzoic Acid                                | 4.56     | -71                          | -0.15                          | -45                           | -26.3                        | 1.6                             |
| * Reference Base = 1,3-Diphenylguanidine in benzene (25°C) |          |                              |                                |                               |                              |                                 |
| Benzoic Acid                                               | 5.30     | -68.04                       | -0.126                         | -37.55                        | -30.37                       | 1.8                             |
| <i>m</i> -Chlorobenzoic Acid                               | 6.08     | -79.80                       | -0.151                         | -45.00                        | -34.74                       | 1.8                             |
| <i>m</i> -Methylbenzoic Acid                               | 5.18     | -69.30                       | -0.132                         | -39.34                        | -29.87                       | 1.8                             |
| <sup>b</sup> In water medium (25°C)                        |          |                              |                                |                               |                              |                                 |
| Benzoic Acid                                               | -4.20    | 0.37                         | -0.080                         | -23.8                         | 24.2                         | -0.020                          |
| <i>m</i> -Chlorobenzoic Acid                               | -3.83    | 0.084                        | -0.073                         | -21.7                         | 21.8                         | -0.004                          |
| <i>m</i> -Bromobenzoic Acid                                | -3.81    | -0.25                        | -0.074                         | -22.1                         | 21.8                         | 0.011                           |
| <i>m</i> -Cyanobenzoic Acid                                | -3.60    | -0.17                        | -0.070                         | -20.8                         | 20.6                         | 0.008                           |
| <i>m</i> -Methoxybenzoic Acid                              | -4.09    | 0.25                         | -0.077                         | -22.9                         | 23.2                         | -0.011                          |
| <i>m</i> -Methylbenzoic Acid                               | -4.27    | 0.29                         | -0.080                         | -23.8                         | 24.1                         | -0.012                          |

\*Ref : 2, <sup>b</sup> Ref : 16

to one of the species present in the system<sup>4,11,15</sup>, Eq. (1) is re-expressed as



where D symbolises the dye carbinol base and  $DH^+ A^-$  the ion-pair. The data for toluene-phase equilibria between each of the acids selected and the carbinol base of crystal violet (D) fitted well with the expression,

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

$K$ , the association constant and 'n' the acid exponent for the acid (at  $28.0 \pm 0.1^\circ\text{C}$ ) evaluated from the

intercept and slope respectively of the linear regression analysis of  $\log([DH^+ A^-]/[D])$  on  $\log [HA]$  data were compiled in Table 1,  $[DH^+ A^-]/[D]$ , the indicator ratio being computed from spectrophotometric data.

'n' the acid exponent

Values of 'n' are non-integral and generally close to unity (Table 1). In an apolar aprotic solvent, a carboxylic acid, HA would undergo intermolecular hydrogen bonding to form acid-acid anion homoconjugate complex acids,  $H(A \cdots (HA)_m)$ ,  $m \geq 1$ . The greater stability of the conjugate  $(A \cdots (HA)_m)^-$  over  $A^-$  renders the homoconjugate complex acid significantly stronger than the simple

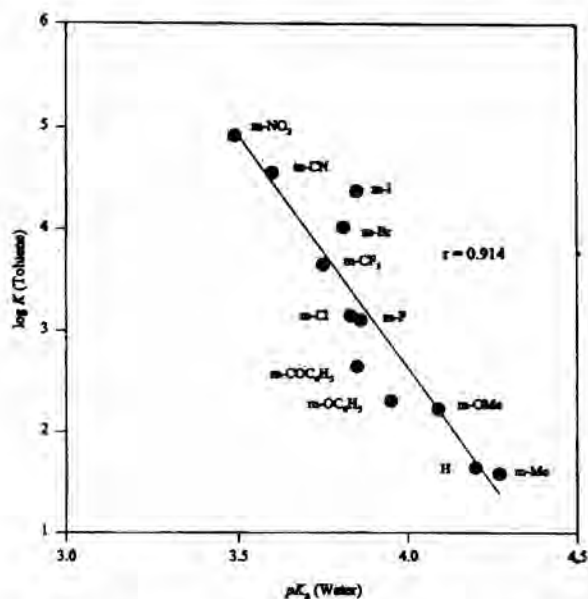


Fig. 1.  $\log K$  (toluene) vs.  $pK_a$  (water) plot for *meta*-substituted benzoic acids.

monomer acid,  $HA^{2-11,16}$ . A fraction of  $HA$  molecules would however remain inactive in the form of simple dimers. The observed values of 'n' are thus ascribed to overlapping reactions of the carbinol base (D) with both the simple  $HA$  and complex homoconjugated  $H[A \cdots (HA)_m]$  acids. 'n' is thus a measure of the degree of homoconjugation of  $HA$  and  $DH^+A^-$  symbolises the ion-pair irrespective of the number of  $HA$  molecules associated to a  $D$  molecule at equilibrium. Obviously, Eq. (2) is a too simplistic description of the  $D$ - $HA$  reaction in toluene and similar solvents.

As seen from Table 1, the values of 'n' for the set of *m*-substituted benzoic acids though generally lie within  $\pm 0.1$  of unity, are significantly greater for four acids: *m*-bromo, *m*-iodo, *m*-cyano and *m*-nitro benzoic acids. This is not surprising as sufficiently polarisable and strong enough acids would undergo more extensive homoconjugation. As expected, the acids with larger 'n' act as 'extra' strong in toluene and have larger  $K$  illustrated vividly by the magnitude of differences in  $\log K$  among four *m*-halobenzoic acids having nearly identical  $pK_a$  (water) values (Table 1). It is worth pointing that 'n' for an acid is not strictly a constant and may depend on acid concentration<sup>10</sup> to a degree determined by its effect on the extent of homoconjugation.

#### Log K scale of toluene-phase acidities

'n' being not strictly a constant, the association constant,  $K$  is simply an equilibrium concentration

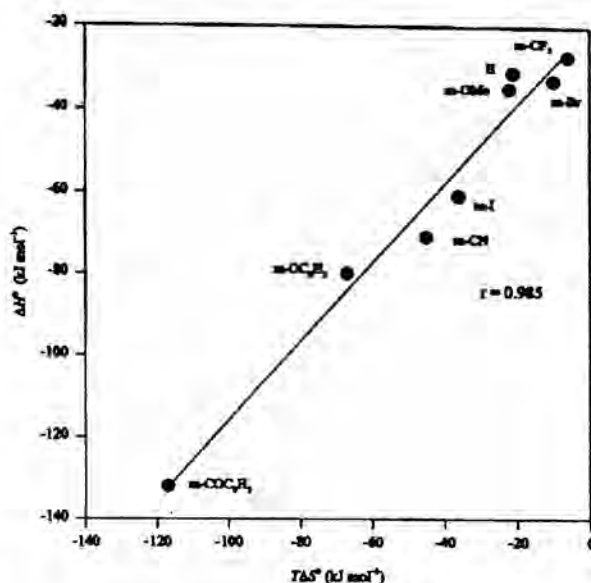


Fig. 2.  $\Delta H^\circ$  vs.  $T\Delta S^\circ$  plot for association of *meta*-substituted benzoic acids with carbinol base of Crystal Violet in toluene.

quotient, and not a true thermodynamic constant. However, the variation of 'n' over the acids of the entire set is small enough ( $\pm 0.25$ ) (Table 1) for attempting  $\log K$ , not unjustifiably, as indices of toluene-phase acidities. The order of toluene-phase strengths according to  $\log K$  (toluene) scale is thus: *m*-nitro- $\rightarrow$  *m*-cyano- $\rightarrow$  *m*-iodo- $\rightarrow$  *m*-bromo- $\rightarrow$  *m*-trifluoromethyl- $\rightarrow$  *m*-chloro- $\rightarrow$  *m*-fluoro- $\rightarrow$  *m*-benzoyl- $\rightarrow$  *m*-phenoxy- $\rightarrow$  *m*-methoxy- $\rightarrow$  hydrogen- $\rightarrow$  *m*-methylbenzoic acid.

The order, however, parallels only roughly to the order based on their ionisation constants,  $pK_a$  (water) or the Hammett constants of the substituents ( $\sigma_m$ ): *m*-nitro- $\rightarrow$  *m*-cyano- $\rightarrow$  *m*-trifluoromethyl- $\rightarrow$  *m*-bromo- $\rightarrow$  *m*-chloro- $\rightarrow$  *m*-benzoyl- $\approx$  *m*-iodo- $\approx$  *m*-fluoro- $\rightarrow$  *m*-phenoxy- $\rightarrow$  *m*-methoxy- $\rightarrow$  hydrogen- $\rightarrow$  *m*-methylbenzoic acid<sup>2,17</sup>.

Deviations from the exact parallelism between the two acidity scales is not surprising. The largest discrepancy is with the polarisable acids, *m*-iodo and *m*-bromo benzoic acids which as noted already, act 'extra' strong in toluene owing to extensive homoconjugation. In fact, the processes dominating the fundamental acid-base reactions are quite different in water and toluene. Whereas these processes are hydration and ionisation in water, various manifestations of hydrogen-bonding, ion-association become predominant in toluene. However, the linear regression analysis of  $\log K$  (toluene) on  $pK_a$  (water) (Fig. 1) leads to the correlation:

$$\log K = -4.59 pK_a + 20.99 \quad (n = 12, r = 0.914) \quad \dots(4)$$

which is statistically significant<sup>18</sup> at a level better than 1% for the correlation coefficient ( $r$ ) as judged by F-test and better than 0.1% for the regression coefficient as judged by Student's  $t$ -test.

Thus, the structural (mainly field-inductive) effects of a *meta*-substituent on proton transfer from -COOH group of benzoic acid molecule gets magnified by as large as more than 4.5 times when transferred from highly polar water to apolar toluene, in general agreement with the prediction of Kirkwood-Westheimer model<sup>19</sup> for the influence of solvent's dielectric constant, on substituent's electronic effects on the dissociation constant of benzoic acid. The large enhancement in the sensitivity to substituent's structure effects makes  $\log K$  significantly closer towards the measure of 'intrinsic' acidities than  $pK_a$ , the 'intrinsic' acidities for the *m*-substituted benzoic acids as measured by their 'gas-phase' acidities<sup>20</sup> being related to  $pK_a$  as

$$\log K \text{ (gas-phase)} = -10.19 pK_a - 198.13 \quad \dots(5)$$

#### Effect of temperature on $\log K$ and ' $n$ '

A comparison of the data on  $\log K$  and ' $n$ ' for toluene phase HA-D equilibria at 20.0°C and 28.0°C

for eight *meta*-substituted benzoic acids (Table 2) shows that although there was not any significant variation in ' $n$ ', the association constant ( $K$ ) decreases considerably with temperature for each of the acids. It is thus reasonable to attempt an estimate of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for toluene-phase HA-D equilibria, assuming the variation of  $\log K$  with  $T^{-1}$  linear over the range : 20° - 28°C. A comparison of  $\Delta H^\circ$  data (Table 3) for toluene-phase proton transfer from *meta*-substituted benzoic acids with those for benzene-phase<sup>2</sup> and aqueous-phase<sup>17</sup> proton transfer shows clearly that whereas the reaction is significantly exothermic in toluene or benzene (-30 to -130 kJ mol<sup>-1</sup>), is generally endothermic in water (0.08 to 0.37 kJ mol<sup>-1</sup>). Further,  $\Delta G^\circ$  is negative in toluene or benzene whereas it is positive in water (Table 3). The value of  $\Delta S^\circ$  though generally remains within -20 to -150 JK<sup>-1</sup> mol<sup>-1</sup> in all the three solvents, rises considerably for *m*-phenoxy and *m*-benzoyl benzoic acids in toluene (Table 3). Interestingly these two acids act too weak in toluene (Fig. 1). Their extra

weakness can thus be ascribed to their large negative entropy ( $T\Delta S^\circ$ ) factor. It is worth noting that although the separate contributions of  $\Delta H^\circ$  and  $T\Delta S^\circ$  to  $\Delta G^\circ$  for the toluene-phase proton transfer vary in an erratic manner from one to another (Table 3) there exists interestingly a linear correlation between  $\Delta H^\circ$  and  $T\Delta S^\circ$  over the set of acids, at a level of significance<sup>18</sup> better than 1% (Fig. 2).

$$\Delta H^\circ = 0.96 T\Delta S^\circ - 20 \quad (n = 8, r = 0.985) \quad \dots(6)$$

Thus, with increasing degree of proton transfer between an acid and the dye carbinol base there is an enhanced restraint on the freedom of motion of the reactant molecules. Contrarily, no such linear correlation between  $\Delta H^\circ$  and  $T\Delta S^\circ$  for ionisation of substituted benzoic acids in water could be observed<sup>2,17</sup>, thus supporting the conclusion reached from the  $\log K$  versus  $pK_a$  correlation that  $\log K$  (toluene) values as compared to  $pK_a$  (water) values are much better measures for structure effect on acidity.

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