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EQUILIBRIA AND KINETICS OF REACTIONS BETWEEN CARBOXYLIC ACIDS AND THE CARBINOL BASE OF CRYSTAL VIOLET IN APOLAR APROTIC SOLVENTS: RELATIVE STRENGTHS OF *m*- AND *o*-SUBSTITUTED BENZOIC ACIDS IN TOLUENE

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Equilibria and kinetics of proton-transfer reactions in toluene between a set of *m*- and *o*-substituted (methyl, methoxy, chloro, nitro and hydroxy) benzoic acids and the carbinol base (colourless) of Crystal Violet were studied spectrophotometrically. The data on equilibrium and kinetic parameters were critically analysed. The rate constant for the forward step of the acid–carbinol equilibrium was found to be an appropriate criterion for determining acidities in toluene. Toluene-phase acidities were found to be significantly more susceptible than aqueous-phase acidities to the structure of the substituents, particularly for the *m*-substituted acids. Quantitative analysis of the substituent effect on toluene-phase acidities using the Fujita–Nishioka model for the extended Hammett equation showed that the predominant factor contributing to the '*ortho* effect' for benzoic acid–dye carbinol reactions in toluene is the proximity polar effect rather than the steric effect for most of the *o*-substituents © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

The solution phase acidity/basicity of a solute reflects its intrinsic proton-donating/accepting power and the effect of the solvent, which is often clouded by its own acidity/basicity, dielectric constant, polarizability and various solute–solvent interactions. An apolar aprotic solvent ($E_T^N = 0{\cdot}0–0{\cdot}3$) of low dielectric constant ($\varepsilon < 6$) offers significant advantages for investigating proton-transfer processes as specific solute–solvent interactions would be greatly minimized and the proton transfer is expected to be direct. Despite these advantages, there have been far fewer investigations on rate equilibria of proton-transfer reactions in apolar aprotic solvents than in protic and dipolar aprotic solvents. Moreover, since many organic reactions are carried out in hydrocarbons and halocarbons, the measurement of acid/base properties in such solvents is of significant interest. However, the determination of the strength of an acid/base in such a solvent which cannot by itself act as a base/acid requires the use of an appropriate reference base/acid. Indicator acids such as 2,4-dinitrophenol, picric acid, 2,4,6-trinitro-*m*-cresol, Bromophenol Blue and Bromophthalein Magenta E have been found useful as reference acids for determining the basicities of various aliphatic and aromatic amines, *N*-heterocyclics and diaryl- and triarylguanidines in several apolar aprotic solvents. Results of equilibria[1] and kinetics[2] of organic base–indicator acid associations have been reviewed.

Davis and co-workers, the pioneers in the area, developed an indirect method for determining the relative strengths of 19 aliphatic and 47 aromatic carboxylic acids in benzene by studying the equilibrium of association for the carboxylic acids with 1,3-diphenylguanidine, the reference base, in the presence of Bromophthalein Magenta E which competes for the base.[1, 3, 4] A direct method for determining relative acidities in benzene was devised by Palit and co-workers, who introduced the carbinol base of Crystal Violet as a reference base. Acid–dye carbinol base reactions in an apolar aprotic medium are interestingly slow enough for their kinetics to be monitored by ordinary spectrophotometry. They studied both the equilibria and kinetics of benzene-phase reactions of various carboxylic acids, phenols, fluoro and nitro alcohols and mercury(II) chloride (Lewis acid) with the carbinol base of Crystal Violet[5–7] or Ethyl Violet.[8]

Sen Gupta and co-workers applied the procedure for evaluating equilibrium and kinetic parameters for toluene-phase reactions of chelating acids for boron and the

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boron-complexed acids (hydrogen spiroborates) with different triphenylmethane dye carbinols and utilized the data for the selection of optimum solvent extraction–spectrophotometric reagent systems for boron determination.[9, 10] Further, they determined the relative toluene-phase basicities of six triarylmethane dye carbinols and correlated the basicities with σ_R^+ parameters of their *p*-alkylamino substituents.[11] However, there has not been reported any systematic study on the effect of substituent structures on the strengths of acids in such apolar aprotic solvents, particularly by any direct method. Since organic acids in apolar solvents undergo aggregation and homoconjugation to varying extents, it is judicious to consider a set of acids of very similar chemical type to minimize complications while interpreting the results. A spectrophotometric investigation on the equilibria and kinetics of the toluene-phase proton transfer between a set of selected *o*- and *m*-substituted [$CH_3(+R, +I)$, OCH_3 $(-I<+R)$, Cl $(-I>+R)$ and NO_2 $(-I, -R)$ benzoic acids and the carbinol of Crystal Violet was undertaken with the objectives of determining a scale of toluene-phase acidities and shedding some light on the intrinsic-only factors for the '*ortho* effect.' The results obtained are critically discussed here.

EXPERIMENTAL

The chemicals used were either of analytical-reagent grade or highly purified by standard procedures. Toluene was chosen as the reference apolar aprotic solvent because of its relatively low toxicity. 4,4′,4″-Tris(dimethylamino)triphenyl carbinol, which is colourless, was employed as the reference base. The toluene solution of the carbinol base was prepared by basification of a 10^{-5} M aqueous solution of Crystal Violet [4,4′,4″-tris(dimethylamino)triphenyl chloride] with 2 M NaOH and subsequent extraction into toluene in accordance with a standard procedure.[5]

Choice of acids. A set of benzoic acids substituted at the *m*- and *o*-positions with groups of varying *R* (resonance) and *I* (inductive) effects, CH_3 $(+I, +R)$, OCH_3 $(+R>-I)$, Cl $(-I>+R)$ and NO_2 $(-I, -R)$, were selected to study their structural influences (polar-ordinary and proximity and steric) on the proton transfer from the —COOH group. Salicylic acid was also included in the set to study the enhancement of acidity due to chelation in toluene as compared with water.

Procedure. The equilibrium and kinetics of the reaction between the carbinol base of Crystal Violet, Dye-OH (10^{-6}–10^{-5} M), and an acid (HA) (10^{-4}–10^{-2} M) in dry toluene, producing a coloured ion associate, Dye^+A^-, were measured with a Shimadzu 160 A UV–VIS recording spectrophotometer at 610 nm at 28 ± 0·1 °C. The molar absorptivity of Crystal Violet cation (Dye^+) in toluene at 28 °C was found to be $5{\cdot}9\times10^4$ l mol^{-1} cm^{-1}.

RESULTS AND DISCUSSION

Carbinol bases (colourless) of triarylmethane dyes [Malachite Green, Brilliant Green, Methyl Violet, Crystal Violet, Ethyl Violet and Victoria Pure Blue BO (Dye-OH)] react with acidic substrates [(HA): aliphatic and aromatic carboxylic acids, phenols, fluoro and nitro alcohols, hydrogen spiroborates] in benzene, toluene and other apolar aprotic media to form coloured ion associates (Dye^+ A^-):[5–11]

$$\text{Dye-OH} + \text{HA} \rightleftharpoons \text{Dye}^+\ \text{A}^- + \text{H}_2\text{O} \qquad (1)$$

It has been argued that the water molecule formed is hydrogen bonded to one of the species present in the system.[5–11] Thus, equation (1) can be rewritten as

$$\text{D} + \text{HA} \rightleftharpoons \text{DH}^+\text{A}^- \qquad (2)$$

where D represents a dye carbinol and DH^+A^- the ion associate.

Equilibrium results

The equilibrium data for the toluene-phase reaction of the set of *m*-and *o*-substituted benzoic acids (HA) with the carbinol base of Crystal Violet (D) were found to fit well the equation

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

The values of *n*, the overall acid exponent, and log*K*, the association constant {obtained from the linear log ($[DH^+A^-]/[D]$) vs log [HA] plot} are given in Table 1.

The overall acid exponent (n)

As can be seen from Table 1, *n* is non-integral and usually greater than unity. This is explained as being due to overlapping reactions of the simple monomer acid (HA) and acid–acid anion homoconjugate complex acids, $H[A\cdots(HA)_m]$ $m\geqslant1$ (such complex acids, which are stronger than the simple HA, are known to form in toluene-like media[1]) with the carbinol base of Crystal Violet in toluene. Hence *n* is a measure of the number of HA molecules associated with a D molecule at equilibrium. As one would expect, the value of *n* has been found to be larger for stronger acids which allow a greater degree of homoconjugation (see Table 1). The comparatively small value of *n* for salicylic acid reflects strong intramolecular hydrogen bonding in the salicylate anion which would inhibit seriously its homoconjugation. It is worth pointing out that the value of *n* for an acid is not strictly a constant and may depend on acid concentration,[11] specific solvent[7] and temperature.[7] In fact, *n* is a composite parameter and equals of $f-r$, where *f* and *r* are the individual acid exponents for the forward and reverse steps of the equilibrium [equation (2)], respectively [see equation (10)].

Association constant (*K*). As *n* is not a true constant, the

Table 1. Values of association constant (log$K$), overall acid exponent (n), individual rate constants (logk_1, logk_{-1}) and individual acid exponents (f, r) for substituted benzoic acids–Crystal Violet carbinol base reactions in toluene at 28·5±0·1 °C

Acid	pK_a (water)	Log$K$ (±2%)	n (±3%)	Logk_1 (±2%)	Logk_{-1} (±2%)	f (±3%)	r (±3%)
Benzoic acid	4·20	1·85	0·98	1·75	−0·10	1·39	0·41
o-Methylbenzoic acid	3·91	1·96	1·19	1·99	0·03	1·67	0·48
m-Methylbenzoic acid	4·27	1·74	0·93	1·46	−0·28	1·37	0·44
o-Methoxybenzoic acid	4·09	2·73	1·13	2·70	−0·03	1·58	0·45
m-Methoxybenzoic acid	4·09	2·29	1·11	2·09	−0·20	1·48	0·37
o-Chlorobenzoic acid	2·94	4·11	1·23	4·72	0·62	1·70	0·48
m-Chlorobenzoic acid	3·83	3·96	1·29	3·99	0·03	1·57	0·28
o-Nitrobenzoic acid	2·17	5·38	1·33	7·25	1·87	2·05	0·72
m-Nitrobenzoic acid	3·49	5·24	1·30	7·91	2·67	2·21	0·91
o-Hydroxybenzoic acid	3·00	4·80	1·12	5·55	0·75	1·57	0·45

association constant (K) is simply an equilibrium concentration ratio and not a true thermodynamic constant. However, the variation in n among the acids selected is small enough (see Table 1) to employ log$K$ values not unjustifiably as indices of toluene-phase acidities. A plot of log$K$ (toluene) vs pK_a (water) (Figure 1) yields two distinct straight lines, one for the *m*-substituted benzoic acids only and the other for the *o*-substituted acids.

***m*-Substituted benzoic acids.** The orders of the strengths of these acids in solvents as diverse as water and toluene are exactly parallel (see Table 1), indicating the predominance of the substituent's field-inductive effect on proton transfer from the —COOH group. Log$K$ is related to the pK_a for the acids by

$$\log K = -4{\cdot}76\ \mathrm{p}K_a + 21{\cdot}96 \qquad (4)$$

The large enhancement (4·76-fold) of the susceptibility of proton transfer to the nature of the substituent on changing the medium from water ($\varepsilon = 78$) to toluene ($\varepsilon = 2{\cdot}38$) substantiates further that the influence of a *m*-substituent is predominantly an electrostatic field effect exerted through both the molecule and the surrounding solvent sheath.

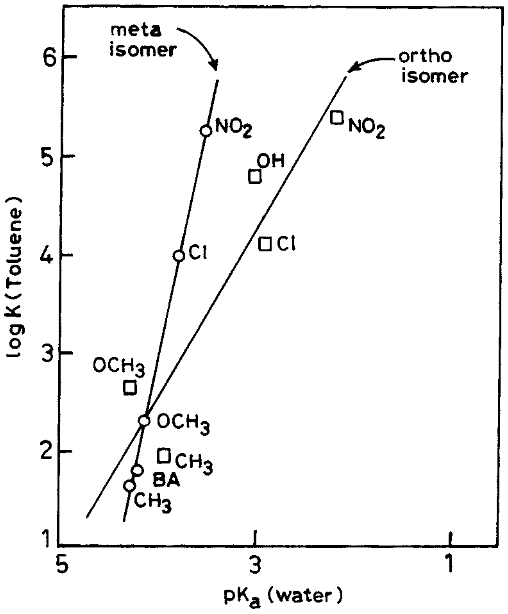

Figure 1. Comparison of the strengths of (○) *m*- and (□) *o*-substituted benzoic acids in toluene and water as measured by log$K$ (toluene) and pK_a (water)

***o*-Substituted benzoic acids.** The log$K$ vs pK_a plot for the *o*-isomers (Figure 1) can be represented by

$$\log K = -1{\cdot}77\ \mathrm{p}K_a + 9{\cdot}49 \qquad (5)$$

Comparison with that for the *m*-isomers [Figure 1; equation (4)], taken as the 'normal' behaviour, indicates clearly that *o*-isomers are either too weak in toluene or too strong in water. Further, the order of their log$K$ values is not the same as that of their pK_a values (see Table 1). An *o*-substituent would influence the reaction centre of a substrate through a number of intrinsic 'effects' such as resonance, steric and intramolecular hydrogen bonding, besides the field-inductive effect. However, in a solvating medium some of these effects may be significantly affected. In water, steric interference of an *o*-substituent (with a $+R$ effect) bare or hydrated with the hydrated —COOH group would inhibit its resonance (acid-weakening) with the aromatic ring. Hydration would contribute to further enhancement of the acidity by disrupting the chelated structure, if any, of the non-dissociated acid, whereas in non-solvating toluene acidities would be influenced primarily by the substituent's intrinsic-only factors. Thus, on changing the solvent from water to toluene the, acidity of an *o*-isomer undergoes a considerable reduction compared with that for the *m*-isomer. Obviously, the log$K$ values rank significantly better as indices for the intrinsic strengths of *o*-substituted benzoic acids than their pK_a values. The case of salicylic acid is an exception. Its anomalously high acidity in water is preserved in toluene (see Table 1) and even in the gas phase.[12] This must be due to the stabilization of the conjugate base, the salicylate anion by the same strong intramolecular hydrogen bonding involving the phenolic hydrogen and the carboxylate anion in all the three media. Thus, the overall effect of an *o*-substituent on proton transfer from the —COOH group in a benzoic acid molecule is contributed to by field-inductive, resonance, steric, cheltion (in both the undissociated acid and its conjugate base), solvation and possibly other less significant factors.

Kinetic results

The toluene-phase reaction between a substituted benzoic acid (HA) and the carbinol base (D) of Crystal Violet [equation (2)] under the conditions employed, $C_{HA} \gg C_D$ (see Experimental), follows first-order kinetics:

$$k = \frac{2 \cdot 303}{t} \log\left(\frac{X_e}{X_e - X_t}\right) \qquad (6)$$

where k is the rate constant and X_e and X_t are the absorbances of the ion associate (DH^+A^-) at equilibrium and at time t. The rate constant (k), however, depends upon C_{HA}, the total acid concentration. In an apolar aprotic solvent, a carboxylic acid (HA) exists as an equilibrium mixture of the monomer acid, HA, and the stronger homoconjugate acid–acid anion complex acids, $H(A \cdots HA)$, $H[A \cdots (HA)_2]$, etc.,[1] the proportion of the latter increasing with increase in C_{HA}. Thus, the overall proton-donating power of a carboxylic acid solution in such solvents increases with increase in C_{HA}. On the assumption that both the forward and reverse steps of the equilibrium [equation (2)] are influenced by the acid, equation (2) can be expressed as

$$D + f\mathrm{HA} \rightleftharpoons DH^+A^- + r\mathrm{HA} \qquad (7)$$

where DH^+A^- symbolizes the coloured ion associate irrespective of the number of HA molecules associated with a D molecule and f and r are the individual acid exponents for the forward and reverse steps of the equilibrium, respectively. If k_1 and k_{-1} represent the rate constants for the forward and reverse steps, respectively, it follows that

$$k = k_1[\mathrm{HA}]^f + k_{-1}[\mathrm{HA}]^r \qquad (8)$$

$$K = \frac{k_1}{k_{-1}} \qquad (9)$$

$$n = f - r \qquad (10)$$

Algebraic manipulations of equations (8), (9) and (10) lead to the relationship

$$\log\left(\frac{k}{K + [\mathrm{HA}]^{-n}}\right) = f \log[\mathrm{HA}] + \log k_{-1} \qquad (11)$$

Plots of the left-hand side of equation (11) vs log [HA] were found to be linear for all the acids selected. Logk_{-1} (intercept) and f (slope) obtained by the least-squares method and logk_1 and r calculated using equations (9) and (10), respectively, are given in Table 1.

The strength of an acid in an apolar aprotic solvent as determined in terms of its association constant (K) with a dye carbinol (when the n values do not differ widely) is thus due to the interplay of at least four parameters, k_1, k_{-1}, f and r.

Individual acid exponents (f, r)

The acid exponent f for the forward step can be interpreted as the mean aggregation number of HA species, HA, $H(A \cdots HA)$, $H[A \cdots (HA)_2]$, etc., reacting with the dye carbinol in the forward step, the acid reacting effectively as an f-mer, $(HA)_f$. The f values, as expected, are generally greater than unity and non-integral (see Table 1). Further, the magnitude of f (1·4–2·2) shows an upward trend with increase in the strength of HA.

The acid exponent r for the reverse step is much smaller (0·3–0·9) (see Table 1) and can be interpreted as the number of HA molecules released from the f-mer, $(HA)_f$, after the equilibrium of its reaction with the dye carbinol has been attained. The degree of homoconjugation in the ion associate $DH^+ [A^- \cdots (HA)_{n-1}]$ (where n is the overall acid exponent) symbolized as DH^+A^- would depend on the relative affinity of the base A^- between the acids DH^+ and HA and differ from f. In fact, when HA is considerably stronger than DH^+ (the conjugate acid of the dye carbinol), n could exceed f and r and may even become negative.[5–7, 11]

Individual rate constants (k_1, k_{-1})

As can be seen from Table 1, the magnitude for the rate constant of the forward step, k_1, is much greater than the rate constant for the reverse step, k_{-1}, and both the parameters vary considerably over the set of acids. However, compared with k_{-1}, k_1 for an acid is significantly more sensitive to the strength of the acid. Further, the magnitudes of k_1 and f and also those of k_{-1} and r follow a similar trend (see Table 1), pointing to the catalytic role of the acid in both the forward and reverse steps of the equilibrium [equation (2)].

Log k_1 scale of toluene-phase acidities

An acidity scale in terms of logk_1 would be meaningful only if the acids do not have significantly different f values. This scale would be of greater intrinsic value than that in terms of log$K$ as the latter depends on the interplay of at least four parameters (k_1, k_{-1}, f and r) as against two (k_1 and f) for the former. The variation observed in f over the different acids is ±0·42. However, it seems justifiable to infer that neglecting the variation would not invalidate the general conclusions reached on the basis of the logk_1 scale of acidities. As can be seen from Table 1, the logk_1 acidity

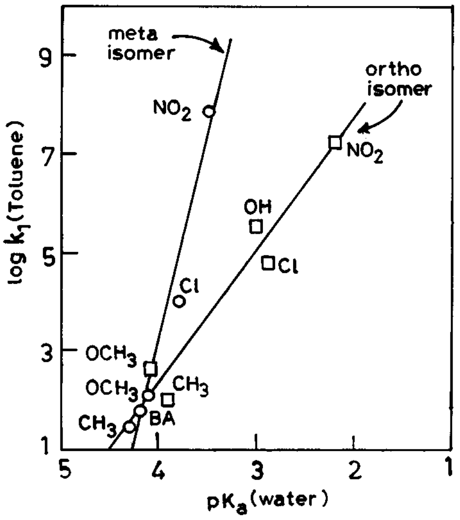

Figure 2. Comparison of the strengths of (○) *m*- and (□) *o*-substituted benzoic acids in toluene and water as measured by $\log k_1$ (toluene) and pK_a (water)

scale runs parallel to the $\log K$ scale for either isomer (*o*- or *m*-). Further, the $\log k_1$ vs pK_a plot (Figure 2), like the $\log K$ vs pK_a plot, yields two separate straight lines, one for the *m*-substituted acids:

$$\log k_1 = -8{\cdot}27\, pK_a + 36{\cdot}33 \tag{12}$$

and the other for the *o*-substituted acids:

$$\log k_1 = -2{\cdot}66\, pK_a + 12{\cdot}99 \tag{13}$$

However, the slope of the $\log k_1$ vs pK_a plot is considerably greater than that of the corresponding $\log K$ vs pK_a plot [equations (4) and (5)]. Obviously, $\log k_1$ values are significantly more sensitive than $\log K$ values to the structure of the substituent and thus better indices of intrinsic acidities.

Quantitative treatment of substituent effect on toluene-phase strengths of benzoic acids by Hammett methodology

The simple Hammett equation:

$$\log K_x = \rho\sigma_x + C \tag{14}$$

where K_x is the equilibrium (or rate) constant of a reaction for the substituted substrate, σ_x is the substituent (x) constant pertaining to its electronic effects only, ρ, the reaction constant, is a measure of the sensitivity of the reaction to the electronic perturbation and C corresponds to the equilibrium or rate constant for the unsubstituted substrate, applies to *m*- and *p*-substituents only. However, for *o*-substituents which exert, in addition to the ordinary electronic effect (common to *m*- and *p*-substituents), various proximity effects such as direct field effect, steric effect and chelation effect to various extents in different physical-organic systems, the simple Hammett equation (14) no longer applies and an extended form must be used. An equation proposed by Fujita and Nishioka[13] has been found to be obeyed for reactions of *o*-substituted benzoic acids except those whose conjugate bases undergo significant chelation (e.g. salicylic acid) and was used in this study to estimate the relative contribution of various components of the total effects of *o*-substituents on the toluene-phase acidity of benzoic acids. The equation is

$$\log K_{ortho} = \rho\sigma_o + \delta E_s + fF + C \tag{15}$$

where K_{ortho} is the equilibrium or rate constant of a reaction for the *o*-substituted substrate, σ_o, E_s and F are the substituent parameters for the ordinary polar effect ($\sigma_o \equiv \sigma_p$),[13] the primary steric effect and the proximity polar effect respectively, ρ, δ and f are the susceptibility constants corresponding to σ_o, E_s and F, respectively, and C is the intercept. It may be noted that the Fujita–Nishioka model [equation (15)], although obeyed by the substituents OCH_3, OC_2H_5 and OC_6H_5 capable of forming intramolecular H-bonds with the undissociated carboxylic group, does not contain any term representing this factor. This is corroborated by a chemometric analysis of *o*-substituent effects which indicated that the chelation effect in the undissociated acid is not as significant as to be necessary to express it explicitly.[14]

The $\log k_1$ data for the toluene-phase reactions of substituted benzoic acids with the carbinol base of Crystal Violet were correlated with equation (14) for the *m*-isomers and with the equation (15) for the *o*-isomers by the method of multiple linear regression analysis, and the levels of significance of the correlation coefficient (R) and the regression coefficients (ρ, δ, f) were examined statistically. The calculations were carried out on a UPTRON DS-86 PCS computer and the results are discussed below.

Substituent parameters employed

Except for the *o*-OH group, which undergoes significant chelation with carboxylate anion, all the other substituents considered (*m*- and *o*-methyl, -methoxy, -chloro and -nitro) were included in the regression analysis. The ‘ordinary polar effect’ parameters σ_m [equation (14)] and σ_o ($\equiv\sigma_p$)

Table 2. Substituent parameters (σ_m, $\sigma_p \equiv \sigma_o$, E_s and F) used for correlation

Substituent	σ_m[a]	σ_o[a] ($\equiv\sigma_p$)	E_s[b]	F[c]
Methyl	−0·07	−0·17	−1·24	−0·04
Methoxy	0·12	−0·27	−0·55	0·26
Chloro	0·37	0·23	−0·97	0·41
Nitro	0·71	0·73	−1·01(⊥)[d]	0·67

[a] From Ref. 15.
[b] From Ref. 13.
[c] From Ref. 16.
[d] For minimum dimension—perpendicular orientation. E_s for the maximum dimension—coplanar orientation is −2·52 (‖).

Table 3. Correlation results of reactivity data with equations (14) and (15)

Benzoic acid	Solvent	Log K	ρ^{a}	δ^{a}	f^{a}	C^{b}	n^{c}	R^{d}	Result of F-test on R (level of significance)	Result of t-test on ρ, δ and f (level of significance)
m-Substituted	Toluene	Logk_1	8·28	—	—	1·57	5	0·981	Better than 1%	Better than 0·5%
o-Substituted	Toluene	Logk_1	2·27	− 0·64	4·57	1·75	5	0·999	Better than 5%	Better than 5%
m-Substituted	Water	pK_a	0·99	—	—	− 4·21	11	0·969	Better than 1%	Better than 0·5%
o-Substituted	Water	pK_a	1·00	− 0·33	1·28	− 4·05	13	0·979	Better than 1%	Better than 0·05%

[a] Regression coefficient.
[b] Intercept.
[c] Number of points involved in the correlation.
[d] Multiple correlation coefficient.

[equation (15)] are from the compilations of McDaniel and Brown[15] and the proximity polar effect parameters, F [equation (15)], are the Swain Lupton constants as improved and extended by Hansch *et al.*[16] The primary steric effect parameters, E_s [equation (15)] are the Taft constants[17] as modified by Kutter and Hansch[18] with H as the reference substituent $[E_s(\mathrm{H})=0]$[13] instead of CH_3 (in original E_s values). For the non-symmetrical NO_2 group, the E_s value for the minimum dimension, i.e. perpendicular orientation to the aromatic ring, was adopted since the *o*-NO_2 substituent was found to correlate best with this E_s value rather than that for the maximum dimension corresponding to its coplanar orientation with the ring, for proton-transfer reactions of benzoic acids in water and benzene.[13] The values of the parameters σ_m, σ_o ($\equiv\sigma_p$), E_s and F for methyl, methoxy, chloro and nitro substituents are given in Table 2.

Results of correlation

The results of the correlation of logk_1 (toluene) data with equations (14) and (15) for the substituted benzoic acids and the level of significance for the correlation coefficient (R) and the regression coefficients (ρ, δ and f) are given in Table 3. Table 3 also includes correlation results of pK_a (water) of the acids. The correlation results reveal that the strength of an *o*-substituted benzoic acid is sensitive more to the proximity effects than to the ordinary polar effects of the substituent ($\delta+f>\rho$). The present analysis demonstrates further that the major factor contributing to the proximity effect, usually referred as '*ortho* effect', is the proximity polar effect and not the steric effect ($fF>\delta E_s$) for methoxy, chloro and nitro substituents (see Tables 2 and 3) on benzoic acid–dye carbinol reactions in toluene. However, the opposite holds true for the methyl substituent ($\delta E_s>fF$). A similar conclusion is obtained from the correlation analysis of pK_a data for 13 *o*-substituted benzoic acids where also the steric effect is the dominant factor for the alkyl substituents only.

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