JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 145–152 (1993)

ACID–BASE EQUILIBRIA AND KINETICS BETWEEN TRIARYLMETHANE DYE CARBINOLS AND ORGANIC ACIDS IN APOLAR APROTIC SOLVENTS: RELATIVE BASICITIES OF DYE CARBINOLS IN TOLUENE

SUSANTA K. SEN GUPTA AND UDAI ARVIND
Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, India

Equilibria and kinetics of acid–base reactions in toluene between a carboxylic acid (*m*-toluic, salicylic acid) and a set of carbinol bases (derived from basic triarylmethane dyes) were studied spectrophotometrically. The results for the equilibrium and kinetic parameters were critically analysed. The rate constant of the forward step of the acid–carbinol base equilbrium was found to provide a suitable scale of basicities in toluene. The basicities of the dye carbinols chosen decrease in the order Ethyl Violet– > Crystal Violet– > Methyl Violet– ≈ Victoria Pure Blue BO– ≫ Brilliant Green– > Malachite Green–carbinol. This is fairly consistent with the order observed in water. A fairly good correlation between base strengths of the carbinols and σ_R^+ parameters of their *para*-alkylamino substituents was obtained.

INTRODUCTION

The carbinol–carbenium ion equilibrium for basic triarylmethane dyes is of major significance in studies on acid–base reactions in both polar and apolar solvents. Crystal Violet in its carbinol form (**1d**) has been used extensively as a reference base for determining the relative acid strengths of a series of carboxylic acids both aliphatic and aromatic and a series of phenols in benzene and similar apolar solvents.[1–5] In another study the carbinol form of Ethyl Violet (**1e**) was used for determining the acidities of fluoroalcohols in benzene.[6] On the other hand, the carbinol forms of Malachite Green (**1a**) and Crystal Violet (**1d**) have been utilised to measure the difference in carbon and proton basicities of a number of nucleophiles in aqueous media.[7,8] Further, a number of triarylmethane dye cations are well known as solvent extraction–spectrophotometric reagents in the trace determination of many elements.[9,10] In a recent physico-chemical study on the selection of reagents for the determination of boron, it has been shown that the base strengths of the carbinol forms of the dyes in toluene, a typical extraction solvent, and in water have key roles in designing extraction–spectrophotometric reagents for the element.[11]

A number of quantitative studies on the carbenium ion–carbinol equilibrium and measurements of the base strengths of the carbinols in the aqueous phase for several basic triarylmethane dyes have been reported.[7,8,12] Recently, for triarylcarbenium ions having no 4-alkylamino substituent, which are much less stable than the dye cations, laser flash photolysis has been employed for studying the kinetics of the carbenium ion–carbinol equilibrium in water and water–acetonitrile media.[13] However, no systematic effort to determine the basicities of dye carbinols or other triarylcarbinols in any apolar aprotic solvent has been reported. To bridge this gap, a systematic investigation of the equilibria and kinetics of the reactions between a set of selected triarylmethane dye carbinols and suitable reference organic acids in toluene was undertaken.

EXPERIMENTAL

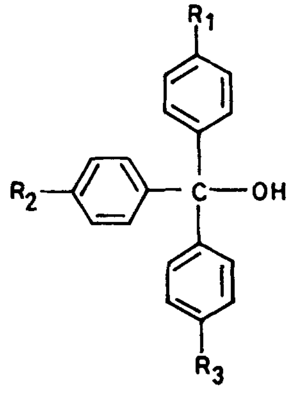
All chemicals were either of analytical-reagent grade or highly purified by standard procedures. Toluene was chosen as the reference apolar aprotic solvent because of its relatively low toxicity. A toluene solution of the carbinol form of a basic triarylmethane dye, which is colourless, was prepared by the basification of an aqueous 10^{-5} M dye solution with 2 M NaOH and subsequent extraction into toluene, followed by drying over sodium wire in accordance with a standard

0894–3230/93/030145–08$09.00

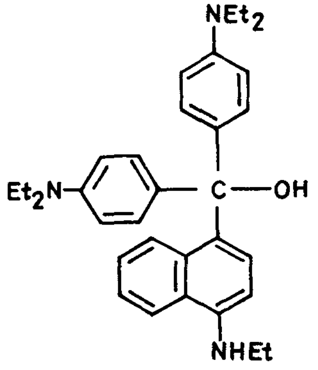
Received 25 February 1992
Revised 24 September 1992

procedure.[1] However, a toluene solution of Malachite Green carbinol (**1a**) was prepared by the direct dissolution of the carbinol (Sigma).

Choice of dyes. 4,4′,4″-Tris- and 4,4′-bis-mono- and -dialkylaminotriarylcarbinols are generally basic enough to undergo toluene-phase proton transfers with many organic acids to a significant extent. Accordingly, the triarylmethane dye cations Malachite Green (MG; 4,4′-bis-$NMe_2Ph_3C^+$), Brilliant Green (BG; 4,4′-bis-$NEt_2Ph_3C^+$), Methyl Violet (MV; 4,4′-bis-NMe_2-4″-$NHMePh_3C^+$), Crystal Violet (CV; 4,4′,4″-tris-$NMe_2Ph_3C^+$), Ethyl Violet (EV; 4,4′,4″-tris-$NEt_2Ph_3C^+$) and Victoria Pure Blue BO (VB; 4,4′-bis-NEt_2Ph_2-4-NHEt-1-$NaphC^+$), which on nucleophilic attack by OH^- are converted into the corresponding colourless carbinols **1a**, **1b**, **1c**, **1d**, **1e** and **2**, respectively, were chosen.



1a : $R_1 = R_2 = NMe_2$, $R_3 = H$
1b : $R_1 = R_2 = NEt_2$, $R_3 = H$
1c : $R_1 = R_2 = NMe_2$, $R_3 = NHMe$
1d : $R_1 = R_2 = R_3 = NMe_2$
1e : $R_1 = R_2 = R_3 = NEt_2$



2

Choice of reference acids. In principle, any acid which has sufficient reactivity for the carbinol forms of the chosen dyes (**1a**–**e**, **2**) in toluene can be employed as a reference acid in determining their relative base strengths. However, preliminary results on equilibria and kinetics of the toluene-phase acid–dye carbinol reactions suggest strongly that salicyclic acid and *m*-toluic acid in combination are the reference acids of convenience.

Procedure. The equilibrium and the kinetics of the reaction between the carbinol form of a basic triarylmethane dye, dye-OH (10^{-6}–10^{-5} M), and a reference acid, HA (10^{-4}–10^{-2} M), in dry toluene which gives rise to the coloured ion pair (dye^+A^-) product, were measured with a Shimadzu 160A UV–visible recording spectrophotometer at 600 nm for **1c**, 610 nm for **1d**, 615 nm for **1e**, 630 nm for **1a** and 640 nm for **1b** and **2** at 28 ± 0·1 °C. The molar absorptivities of the dye cations (dye^+) (10^4 l mol^{-1} cm^{-1}) in toluene at 28 °C were found to be 5·6 for MV, 5·9 for CV, 10·2 for EV, 8·7 for MG, 13·8 for BG and 4·2 for VB.

Base strengths of dye carbinols in water. To see how the toluene-phase relative base strengths of the dye carbinols compare with their aqueous-phase relative base strengths, the equilibrium constant (K_{R^+}) of the reaction

$$dye^+ + H_2O \rightleftharpoons dye\text{-}OH + H^+ \qquad (1)$$

was determined using the equation

$$pK_{R^+} = pH + \log\left(\frac{A_e}{A_0 - A_e}\right) \qquad (2)$$

where A_0 and A_e are the initial and equilibrium absorbances, respectively, of the dye^+ in a buffer solution of suitable pH. The carbenium ion–carbinol equilibrium for the dyes chosen here was monitored for the initial concentration of a dye, $1{\cdot}0 \times 10^{-5}$ M, and at pH 6·88 (for MG and BG) and 9·26 (for MV, CV, EV and VB). pH was measured with a Beckman ϕ71 pH meter. It should be noted that for the dyes considered here, except MG and CV,[7,8] no precise value of pK_{R^+} have been reported previously.

RESULTS AND DISCUSSION

The colourless carbinol form (dye-OH) of a triarylmethane dye cation, an aquo-base,[14] reacts with an acid (HA) in an apolar aprotic solvent producing the coloured ion pair (dye$^+$A$^-$) and H_2O:

$$\text{dye-OH} + \text{HA} \rightleftharpoons \text{dye}^+\text{A}^- + \text{H}_2\text{O} \qquad (3)$$

It is generally argued that the water molecule produced in the reaction is hydrogen bonded to one of the species present in the equilibrium and that they exist as one entity.[1-6,11] Equation (3) can be rewritten as

$$\text{D} + \text{HA} \rightleftharpoons \text{DH}^+\text{A}^- \qquad (4)$$

where D represents the colourless dye carbinol and DH$^+$A$^-$ the coloured ion pair. The magnitude and the kinetics of the equilibrium [equation (4)] would depend on both the base strength of D and the acid strength of HA. Further, it has been found that the kinetics of a number of dye carbinol–organic acid reactions in several apolar aprotic solvents are slow enough to be monitored easily by conventional spectrophotometry.[1,2,5,11] In this respect, salicylic acid for the carbinol of MG (**1a**), BG (**1b**) or CV (**1d**) and *m*-toluic acid for the carbinol of MV (**1c**), CV (**1d**), EV (**1e**) or VB (**2**) were found to be the appropriate reference acids in toluene.

The triarylmethane dye carbinol–acid equilibrium was found to be described by the equation

$$K = \frac{[\text{DH}^+\text{A}^-]}{[\text{D}]\,[\text{HA}]^n} \qquad (5)$$

where n, the acid exponent, was found to be greater than unity and non-integral (see Tables 3–5), as previously reported for many acid–base reactions in apolar aprotic solvents.[1,3,4,6,11,15] This is commonly attributed to the participation of the homoconjugate acid–acid anion complex acid, H(A$\cdots$HA) along with the free monomeric acid, HA; n is generally sensitive to the specific HA, temperature and solvent. K, the concentration ratio, is an association constant and obviously not a true thermodynamic constant. The values of K and n obtained are given in Tables 3–5. Equation (5) is consistent with the equilibrium

$$\text{D} + f\text{HA} \rightleftharpoons \text{DH}^+\text{A}^- + r\text{HA} \qquad (6)$$

where both the forward step and the reverse step are influenced by the acid, HA, and f and r, related by

$$f - r = n \qquad (7)$$

are the individual acid exponents for the forward and the reverse steps, respectively. If k_1 and k_{-1} denote the rate constants for the forward and the reverse steps, respectively,

$$K = k_1/k_{-1} \qquad (8)$$

The reversible reaction [equation (4)] under the conditions employed, $C_{\text{HA}}/C_{\text{dye-OH}} = 10\text{–}10^3$ (see Experimental), was found to follow first-order kinetics:

$$k = \frac{2{\cdot}303}{t}\log\left(\frac{X_e}{X_e - X_t}\right) \qquad (9)$$

where k is the overall rate constant and X_e and X_t are the concentrations of DH$^+$A$^-$ at equilibrium and at time t, respectively, in terms of its absorbance. It follows that

$$k = k_1[\text{HA}]^f + k_{-1}[\text{HA}]^r \qquad (10)$$

A combination of equations (7), (8) and (10) leads to a useful relationship:

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

The plot of the left hand side of equation (11) against log[HA] was found to be linear for each of the dye carbinol–acid systems studied. Similar linear plots have been reported for the reactions of the carbinol of Crystal Violet (**1d**) with many phenols, carboxylic acids and hydrogen spiroborates in benzene and toluene.[1,2,5,11] The values of log k_{-1} and f obtained by least-squares analysis of the above log–log linear plots [see equation (11)] are compiled in Tables 4 and 5, which include also the values of log k_1 and r as calculated using equations (8) and (7), respectively. The results obtained (Tables 1–6) are analysed below.

Log *K* scale of basicities

The values of the association constant (K) for the reactions of a set of triarylmethane dye carbinols (D) with a given reference acid (HA) can be employed to determine the relative base strengths of the carbinols in toluene strictly when the differences in the n values are not sufficiently large [see equation (5)]. The number of HA molecules associated with a D molecule at equilibrium, n, as already indicated, may be non-integral and exceed unity (see Tables 3–5) (it may be noted that DH$^+$A$^-$ symbolically represents the ion pair irrespective of the magnitude of n, the absorbance of the ion pair being insignificantly dependent on n). This can be interpreted as being due to the overlapping associations of the simple anion A$^-$ and the homoconjugate complex anions A$^-\cdots$HA, A$^-\cdots$(HA)$_2$, etc., with a DH$^+$ in an apolar aprotic solvent.[4,15] The magnitude of n has been found to depend on the acid strength of HA,[15] temperature and the nature of the solvent.[4] The results obtained for the reaction of BG–carbinol (**1b**) with salicylic acid further show that n for an acid is not a fixed quantity and increases with increasing concentration of the acid used in its determination (see data for **1b** in Tables 3 and 5). Hence any factor which can influence anion homoconjugation due to hydrogen bonding, $A^- \cdots HA \cdots HA \cdots$, affects the magnitude of n. Keeping these factors in mind, the toluene-phase base strengths of the dye carbinols on the basis of log K values were found to follow the order VB-carbinol (**2**) > CV-carbinol (**1d**) > MV-carbinol (**1c**) against *m*-toluic acid [see Table 4; owing to the much larger magnitude of n, EV-carbinol (**1e**) was not considered in the comparison], BG-carbinol (**1b**) > MG-carbinol (**1a**) against salicylic acid (see Table 5) and CV-carbinol (**1d**) > BG-carbinol (**1b**) against salicylic acid (see Table 3). The combined order of basicities in toluene so

Table 1. Equilibrium and kinetic results of the reactions of various dye carbinols (dye-OH) with *m*-toluic acid (HA) in toluene at 28 ± 0·1 °C

Dye-OH	[HA] × 10^3 (M)	X_e	$\text{Log}\ \frac{[DH^+A^-]}{[D]}$ [b]	k (min^{-1}) (±0·2%)	$\text{Log}\ \frac{k}{K + [HA]^{-n}}$
CV-carbinol (**1d**)	33·3	0·534	0·39	0·389	−2·31
($1{\cdot}25 \times 10^{-5}$ M)	21·7	0·449	0·17	0·242	−2·57
($B^a = 0{\cdot}750$)	16·7	0·405	0·07	0·207	−2·68
	11·7	0·355	−0·05	0·124	−2·98
	6·7	0·261	−0·27	0·086	−3·27
	5·0	0·215	−0·40	0·069	−3·45
MV-carbinol (**1c**)	41·7	0·478	0·32	0·495	−2·06
($1{\cdot}25 \times 10^{-5}$ M)	33·3	0·425	0·18	0·425	−2·15
($B^a = 0{\cdot}705$)	21·7	0·352	0·00	0·284	−2·41
	16·7	0·317	−0·09	0·227	−2·56
	11·7	0·260	−0·23	0·177	−2·75
	6·7	0·190	−0·43	0·132	−3·03
EV-carbinol (**1e**)	21·7	0·310	0·50	1·086	−3·59
($4{\cdot}0 \times 10^{-6}$ M)	16·7	0·254	0·22	1·075	−3·66
($B^a = 0{\cdot}407$)	11·7	0·186	−0·07	0·995	−3·82
	8·3	0·135	−0·30	0·949	−4·00
	6·7	0·108	−0·44	0·898	−4·15
VB-carbinol (**2**)	21·7	0·452	0·42	0·195	−2·93
($1{\cdot}5 \times 10^{-5}$ M)	16·7	0·430	0·34	0·151	−3·07
($B^a = 0{\cdot}625$)	11·7	0·381	0·19	0·108	−3·27
	6·7	0·298	−0·04	0·069	−3·58
	3·3	0·185	−0·38	0·046	−3·93

[a] B = total concentration of the dye carbinol in terms of the absorbance of the completely converted dye cation.

[b] $\frac{[DH^+A^-]}{[D]} = \frac{X_e}{B - X_e}$.

Table 2. Equilibrium and kinetic results of the reactions of various dye carbinols (dye-OH) with salicylic acid (HA) in toluene at 28 ± 0·1 °C

Dye-OH	[HA] × 10^4 (M)	X_e	$\text{Log}\ \frac{[DH^+A^-]}{[D]}$ [b]	k (min^{-1}) (±0·2%)	$\text{Log}\ \frac{k}{K + [HA]^{-n}}$
MG-carbinol (**1a**)	33·3	0·702	0·63	2·077	−6·47
($1{\cdot}0 \times 10^{-5}$ M)	25·0	0·611	0·38	1·510	−6·69
($B^a = 0{\cdot}865$)	20·0	0·485	0·11	1·361	−6·82
	13·3	0·282	−0·31	1·158	−7·13
	10·0	0·165	−0·63	1·146	−7·36
BG-carbinol (**1b**)	16·7	0·554	0·49	2·142	−6·98
($5{\cdot}33 \times 10^{-6}$ M)	13·3	0·455	0·21	1·690	−7·16
($B^a = 0{\cdot}735$)	10·0	0·345	−0·05	1·390	−7·38
	6·7	0·179	−0·49	1·279	−7·70

[a,b] See Table 1.

Table 3. Equilibrium results of the reactions of various dye carbinols (dye-OH) with salicylic acid (HA) in toluene at 28 ± 0·1 °C

Dye-OH	$[HA] \times 10^4$ (M)	X_e	$\text{Log}\,\frac{[DH^+A^-]}{[D]}$ [b]	Log K (±2%)	n (±2%)
CV-carbinol (**1d**)	3·3	0·672	1·38	7·87	1·88
($1{\cdot}15 \times 10^{-5}$ M)	3·0	0·660	1·22		
(B[a] = 0·700)	2·7	0·652	1·13		
	2·3	0·646	1·08		
BG-carbinol (**1b**)	8·3	0·240	−0·31	5·37	1·85
($5{\cdot}33 \times 10^{-6}$ M)	6·7	0·179	−0·49		
(B[a] = 0·735)	5·0	0·118	−0·72		
	3·3	0·060	−1·05		

[a,b] See Table 1.

Table 4[a]. Association constants (K), individual rate constants (k_1, k_{-1}) and acid exponents (n, f, r) for the dye carbinol–*m*-toluic acid reaction in toluene at 28 ± 0·1 °C

Dye-OH	Log K (±2%)	Log k_1 (±2%)	Log k_{-1} (±2%)	n (±2%)	f (±2%)	r (±2%)
CV-carbinol (**1d**)	1·74	1·46	−0·28	0·93	1·37	0·44
MV-carbinol (**1c**)	1·57	1·24	−0·33	0·93	1·25	0·32
EV-carbinol (**1e**)	3·50	1·75	−1·75	1·83	1·09	−0·74
VB-carbinol (**2**)	2·08	1·22	−0·86	0·98	1·24	0·26

[a] Corresponding to the data in Table 1.

Table 5[a]. Association constants (K), individual rate constants (k_1, k_{-1}) and acid exponents (n, f, r) for the dye carbinol–salicylic acid reaction in toluene at 28 ± 0·1 °C

Dye-OH	Log K (±2%)	Log k_1 (±2%)	Log k_{-1} (±2%)	n (±2%)	f (±2%)	r (±2%)
MG-carbinol (**1a**)	6·71	4·41	−2·30	2·44	1·68	−0·76
BG-carbinol (**1b**)	7·18	5·20	−1·98	2·42	1·80	−0·62

[a] Corresponding to the data in Table 2.

obtained, VB-carbinol (**2**) > CV-carbinol (**1d**) > MV-carbinol (**1c**) ≫ BG-carbinol (**1b**) > MG-carbinol (**1a**) [since Δlog K(**1d** − **1b**) ≫ Δlog K(**1d** − **1c**), Tables 3 and 4], is interestingly similar to that in water (on the basis of pK_{R^+} values), viz. CV-carbinol (**1d**) ≈ MV-carbinol (**1c**) > VB-carbinol (**2**) ≫ BG-carbinol (**1b**) > MG-carbinol (**1a**) (see Table 6), except for inversion of the order between **2** and **1d** (or **1c**).

However, it is worth noting that on reducing the concentrations of HA, not only n but also K is significantly lowered [see data for BG-carbinol (**1b**) in Tables 2, 3 and 5]. This can be explained as being due to the considerably greater stability of the homoconjugate

Table 6. Values of pK_{R^+} for various dyes at 28 ± 0·1 °C

Dye	pK_{R^+} (±0·3%)
CV	9·35
MV	9·35
EV	9·49
VB	9·08
MG	6·97
BG	7·43

complex anion $A^- \cdots HA$ over the simple anion A^- [5]. Similar reasonings have been put forward to explain the S-shaped spectrophotometric titration curves of *p*-tolyl-di-*n*-propyl Nile Blue base with moderately strong acids such as salicylic acid in benzene.[15,16] Evidently, the more extensive the anion homoconjugation, the larger is the deviation of the magnitude of n from unity. Hence, for given concentrations of an acid (HA), there should apparently be no significant variation in the magnitude of n with changes in dye carbinol. The prediction is in good agreement with the results (see Tables 1 and 4 and Tables 2 and 5). However, an obvious discrepancy is observed for EV-carbinol (**1e**). When EV-carbinol (**1e**) is substituted for CV-carbinol (**1d**), MV-carbinol (**1c**) or VB-carbinol (**2**) in the reaction with *m*-toluic acid, the magnitude of n undergoes a significant rise from *ca* 1 to *ca* 2. It is worth pointing out also that EV-carbinol (**1e**) in comparison with the other carbinols (**1c**, **1d** and **2**) has a much larger K with *m*-toluic acid (see Table 4). Obviously, in the toluene phase EV-carbinol (**1e**) behaves as a much stronger base than the other carbinols (both K and n are larger). Thus, in an ion associate (DH^+A^-) of EV-carbinol (**1e**) the anion A^- would not have sufficient affinity for the EV-carbenium ion and would prefer homoconjugation to HA, leading to a substantial increment in the magnitude of n. Because of the considerable differences in the magnitudes of n, the relative base strength between EV-carbinol (**1e**) and another dye carbinol (**1c**, **1d** or **2**) on the basis of log K values could not be correctly assessed. This is also in line with the finding that the difference between $\Delta \log K$ and ΔpK_{R^+} is much larger for EV-carbinol (**1e**) and another dye carbinol (1·0–1·8) than for the other pairs of the carbinols (0·0–0·3) (see Tables 4–6). In fact, the base strength of a dye carbinol in a toluene-like solvent as measured by the extent of its conversion to the dye cation at equilibrium in terms of log K is due to a complex interplay of at least four parameters, k_1, k_{-1}, f and r [see equations (7) and (8)].

Log k_1 scale of basicities

Evidently K is not a convenient basis for determining toluene-phase basicities of all the dye carbinols. An alternative which is found to be of more general applicability is k_1, the rate constant for the forward step of the acid–carbinol equilibrium in which the acid, HA, reacts as an f-mer with the dye carbinol, D [see equation (6)]. Log k_1 can reliably be used to determine the relative base strengths of the carbinols in toluene when the f (the acid exponent for the forward reaction step) values do not differ substantially [see equations (6) and (10)]. In contrast to the log K scale of basicities, which depends on four parameters (k_1, k_{-1}, f and r), the log k_1 scale would depend only on k_1 and f. Further, f, which can be interpreted as the mean aggregation number of HA species [HA, $H(A \cdots HA)$, etc.] reacting with D in the forward step should be exclusively a characteristic of the given concentrations of HA in toluene. In fact, with reference to given concentrations of an acid, no significant variation in the values of f could be found among the dye carbinols (see Tables 4 and 5). The f value for EV-carbinol (**1e**), unlike its n value, does not differ substantially from that for another dye carbinol (**1c**, **1d** or **2**). Certainly, k_1 referred to an f value would be a judicious criterion for measuring the relative basicities of the dye carbinols in toluene.

On comparing log k_1 values, the following order of basicities in toluene is observed: EV-carbinol (**1e**) > CV-carbinol (**1d**) > MV-carbinol (**1c**) ≈ VB-carbinol (**2**) (against *m*-toluic acid, see Table 4) and BG-carbinol (**1b**) > MG-carbinol (**1a**) (against salicylic acid, see Table 5). Keeping in view the magnitude of the difference in basicities between CV-carbinol (**1d**) and BG-carbinol (**1b**) as measured by their log K values with reference to salicylic acid (see Table 3), the order of toluene-phase basicities among all the dye carbinols examined can be written as EV-carbinol (**1e**) > CV-carbinol (**1d**) > MV-carbinol (**1c**) ≈ VB-carbinol (**2**) ≫ BG-carbinol (**1b**) > MG-carbinol (**1a**). Interestingly, this order is fairly consistent with that in water (on the basis of pK_{R^+}): EV-carbinol (**1e**) > CV-carbinol (**1d**) ≈ MV-carbinol (**1c**) > VB-carbinol (**2**) ≫ BG-carbinol (**1b**) > MG-carbinol (**1a**) (see Table 6). Thus, the approach based on the rate constants of the forward step (k_1) appears adequate for determining the carbinol basicities in toluene.

It is seen that $\Delta \log k_1 / \Delta pK_{R^+}$ values are 2·0 and 1·7 for the pairs **1d**, **1e** and **1a**, **1b**, respectively (see Tables 4–6). The attenuation in the relative basicities of the dye carbinols due to the aqueous phase can be attributed to the hydration of the dye carbinols and the carbenium ions by hydrogen bonding.

Negative values of r

The acid exponent of the reverse step, r, which equals $f - n$ [see equation (7)] is found to be either positive or negative, depending on the substrates reacting (see Tables 4 and 5). A positive value of r stands for the number of HA molecules released from an f-mer $(HA)_f$ molecule after attaining the equilibrium of its interaction with a D molecule and is, as expected, very small (see Table 4). Negative values of r can be interpreted as being due to further homoconjugation of the anion fragments of the ion associates (DH^+A^-, $DH^+A^- \cdots HA$, etc.) by HA, which is present in large excess (see Experimental). This would obviously be favoured by the higher acidity of HA and the lower acidity of DH^+. This agrees well with the finding that negative values of r are obtained only when the carbinol base or the acid is sufficiently strong as with EV-carbinol (**1e**) or salicylic acid (see Tables 4 and 5).

Base strengths of dye carbinols and through-resonance (σ_{R}^{+}) parameters of their *para* π-electron donor (R) substituents

A triarylcarbinol to triarylcarbenium ion conversion can be considered to pass through a transition state in which a vacant p-orbital is developing at the central carbon atom contiguous to the aryl rings. For the dye carbinols 4,4′-bis- or 4,4′,4″-tris-alkylaminotriarylcarbinols, π-electron donor (R) alkylamino substituents in the 4-position of the aromatic rings thus enter into an extra strong direct resonance interaction with the developing positive charge at the central carbon atom and a decrease in the free energy of the transition state (and of the carbenium ion) due to the more effective spreading of the positive charge is the result.[17] This means that greater the π-electron donor strength of the 4-alkylamino substituents as measured by their through-resonance parameters σ_{R}^{+} (NHMe, −0·58; NMe_2, −0·64; NEt_2, −0·68) [18], the higher is the basicity of the dye carbinol. This agrees well with the order of the base strengths of the triphenylmethane dye carbinols (4-X, 4′-X′, 4″-X″ triphenylcarbinols; X,X′,X″=alkylamino substituents or hydrogen): EV-(X=X′=X″=NEt_2)carbinol (**1e**) > CV-(X=X′=X″=NMe_2)carbinol (**1d**); BG − (X=X′=NEt_2, X″=H)carbinol (**1b**) > MG-(X=X′=NMe_2, X″=H) carbinol (**1a**); CV-(X=X′=X″=NMe_2)carbinol (**1d**) > MV-(X=X′=NMe_2, X″=NHMe)carbinol (**1c**) (see Tables 4 and 5). In fact, both $\log k_1$ and $\mathrm{p}K_{\mathrm{R}^+}$ show a regularly decreasing trend with increase in $\Sigma\sigma_{\mathrm{R}}^{+}$ (i.e. less and less negative) over all the 4-substituents for both the sets of triphenylcarbinols: 4,4′-bis-alkylamino (**1a, 1b**) and 4,4′,4″-tris-alkylamino (**1c, 1d, 1e**) (see Tables 4–6). Further, the values of $\Delta\log k_1/\Delta\Sigma\sigma_{\mathrm{R}}^{+}$ are found to be −2·4 and −9·9 for the sets **1d, 1e** and **1a, 1b**, respectively, whereas the corresponding values for $\Delta\mathrm{p}K_{\mathrm{R}^+}/\Delta\Sigma\sigma_{\mathrm{R}}^{+}$ are −1·2 and −5·8, respectively. The attenuation in the sensitivity of the carbinol basicity to substituent effects by the aqueous phase (2·0 for **1d, 1e** and 1·7 for **1a, 1b**), i.e. $\Delta\log k_1/\Delta\mathrm{p}K_{\mathrm{R}^+}$, can thus be attributed to the reduction of through-resonance in the carbenium ions by hydrogen bonding between water and the nitrogen lone pair of the 4-substituents. Since the σ_{I} values of ethyl- and methylamino substituents differ little (NEt_2, 0·10; NMe_2 0·10; NHMe, 0·12),[18] the reduced relative basicities of the carbinols in the aqueous phase are chiefly due to the inhibition of resonance in the carbenium ions through hydration of its π-electron donating (R) substituents.

It may be noted that although CV-carbinol (**1d**) acts as a stronger base than MV-carbinol (**1c**) in toluene medium, their basicity difference is virtually eliminated on transfer to an aqueous medium (see Tables 4 and 6). In aqueous medium, specific hydration via hydrogen bonding between water and the hydrogen atom of the 4-(=$\overset{+}{\mathrm{N}}$HMe) centre of the MV carbenium ion through its transquinoidal resonance affords extra stability to the carbenium ion and enhanced basicity to the carbinol (**1c**). Clearly, the other dye carbenium ions (EV, CV, BG or MG), which have only dialkylamino (NMe_2 or NEt_2) substituents, would lack such extra stabilization due to specific hydration of a hydrogen-bond donor substituent through transquinoidal resonance.

Further, the higher basicities of 4,4′,4″-tris-dialkylaminotriphenylcarbinols (**1d, 1e**) as compared with the 4,4′-bis-dialkylamino analogues (**1a, 1b**) can be explained on the basis that owing to the additional 4-dialkylamino substituent, delocalization of the positive charge in the CV- or EV-carbenium ion (and in the transition state leading to it) would be more extensive and symmetric than in the MG- or BG-carbenium ion. In fact, extended HMO and CNDO calculations have shown that the positive charge density of the central carbon atom is greater in MG than in CV.[19,20] This also explains the greater sensitivity of the carbinol basicity to substituent effects for 4,4′-bis-dialkylaminotriphenylcarbinols (**1a, 1b**): $\Delta\log k_1/\Delta\Sigma\sigma_{\mathrm{R}}^{+} = -9{\cdot}9$ and $\Delta\mathrm{p}K_{\mathrm{R}^+}/\Delta\Sigma\sigma_{\mathrm{R}}^{+} = -5{\cdot}8$ as compared with the 4,4′,4″-tris-dialkylamino analogues (**1d, 1e**) with values of −2·4 and −1·2, respectively.

However, the parallelism observed between the order of the base strengths of the triphenylmethane dye carbinols (**1a–1e**) and that of the $\Sigma\sigma_{\mathrm{R}}^{+}$ values of their 4-alkylamino substituents does not hold when a 4-alkylaminophenyl group is substituted by a 4-alkylamino-1-naphthyl group. VB-carbinol (**2**), on the basis of the $\Sigma\sigma_{\mathrm{R}}^{+}$ values of its alkylamino substituents [assuming near equality of the σ_{R}^{+} values of NHEt and NHMe on the basis of nearly equal dipole moments (1·64 D) of *N*-methyl- and *N*-ethylanilines[21]] and the higher resonance effect in a 1-naphthyl ring than in a phenyl ring, the conjugating power of a 1-naphthyl group being 1·6 times that of a phenyl group,[22] would rank as a base higher than CV-carbinol (**1d**). The observed basicity ranks are, however, just the reverse (see Tables 4 and 6). The reason may be the steric strain beween the coplaner —NHEt substituent at the 4-position and the *peri*-hydrogen in the 1-naphthyl ring, which would cause the —NHEt group to twist out of the plane of the naphthyl ring and decrease the through-resonance between the positive charge on the central carbon atom and the lone pair of electrons on the 4-NHEt group in the 1-naphthyl ring of VB-carbenium ion (and of the transition state leading to it), and thus render the carbinol less basic. A similar reasoning based on resonance inhibition by the steric effect of a *peri*-proton has been offered to explain why *N,N*-dimethyl-1-naphthylamine is a stronger base than *N,N*-dimethyl-2-naphthylamine.[23]

Acid–base reactions in apolar aprotic solvents of low dielectric constant ($\varepsilon < 6$) as compared with those in water, although largely free from specific solute–solvent interactions, are complicated owing to the possibilities of self-association of acids, homoconjugation of acid anions, formation of hydrogen-bonded acid–base complexes without proton transfer, formation of proton-transfer complexes leading to ion pairing of cations with both simple and homoconjugate anions, hydrogen bonding of acid and other suitable molecules to ion pairs, self-aggregation of ion-pairs, etc., depending on the structure and the concentration of the acids and bases.[14,15,24] However, for acid–dye carbinol base reactions in toluene, the observed regularity between log k_1 and $\Sigma\sigma_R^+$ (or $\Sigma\sigma_R^+ + \Sigma\sigma_I$) rather than $\Sigma\sigma_R$ (or $\Sigma\sigma_R + \Sigma\sigma_I$) of the *para* substituents of the dye carbinols with negative values of $\Delta\log k_1/\Delta\Sigma\sigma_R^+$ ($-2{\cdot}4$ for **1d**, **1e** and $-9{\cdot}9$ for **1a**, **1b**) favours strongly an electron-deficient transition state of the rate-determining step in which the developing positive charge centre is in direct conjugation with the substituents at the 4-position of the aryl rings of a dye carbinol, leading to the formation of the corresponding carbenium ion.

REFERENCES

1. S. R. Bhowmik and S. R. Palit, *J. Indian Chem. Soc.* **44**, 1049–1059 (1967).
2. G. K. Saxena and S. R. Palit, *J. Indian Chem. Soc.* **49**, 351–358 (1972).
3. G. K. Saxena and S. R. Palit, *J. Indian Chem. Soc.* **49**, 971–979 (1972).
4. A. Ghosh and S. R. Palit, *Indian J. Chem.* **12**, 382–386 (1974).
5. A. Ghosh and S. R. Palit, *Indian J. Chem.* **14A**, 19–23 (1976).
6. S. K. De and S. R. Palit *J. Indian Chem. Soc.*, **45** 395–403 (1968).
7. C. D. Ritchie, *Can. J. Chem.* **64**, 2239–2250 (1986).
8. C. D. Ritchie, D. J. Wright, D.-S. Huang and A. A. Kamego, *J. Am. Chem. Soc.* **97**, 1163–1170 (1975).
9. Z. Marczenko, *Microchim. Acta*, **II**, 651–684 (1977).
10. S. Sato, *Anal. Chim. Acta* **151**, 465–472 (1983).
11. S. K. Sen Gupta and O. Balasubramanian, *Bull. Chem. Soc. Jpn.* **64**, 1437–1439 (1991).
12. R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.* 1724–1732 (1949).
13. N. Mathivanan, R. A. McClelland and S. Steenken, *J. Am. Chem. Soc.* **112**, 8454–8457 (1990).
14. R. P. Bell, *The Proton in Chemistry*, 2nd ed., pp. 31–67. Chapman and Hall, London (1973).
15. M. M. Davis, *Acid–Base Behaviour in Aprotic Organic Solvents*, pp. 19–101. NBS Monograph, No. 105, National Bureau of Standards, Washington, DC (1968).
16. M. M. Davis and H. B. Hetzer, *Anal. Chem.* **38**, 451–461 (1966).
17. N. S. Isaacs, *Physical Organic Chemistry*, Longman, Harlow (1987).
18. C. Hansch, A. Leo and W. Taft, *Chem. Rev.* **91**, 165–195 (1991).
19. G. J. Ray, R. J. Kurland and A. K. Colter, *Tetrahedron* **27**, 735–752 (1971).
20. M. K. Kalinowski, J. Stachurski and K. R. Janowski, *Anal. Chim. Acta* **117**, 353–357 (1980).
21. G. Chuchani, in *The Chemistry of the Amino Group*, edited by S. Patai, p. 213. Wiley, Chichester (1968).
22. M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*. McGraw-Hill, New York (1969).
23. J. W. Smith, in *The Chemistry of the Amino Group*, edited by S. Patai, pp. 193–195. Wiley, Chichester (1968).
24. B. H. Robinson, in *Proton Transfer Reactions*, edited by E. Caldin and V. Gold, pp. 121–152. Chapman and Hall, London (1975).