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# Kinetics and Mechanism of Proton Transfer between Disubstituted Benzoic Acids and Carbinol Base of Crystal Violet in Chlorobenzene

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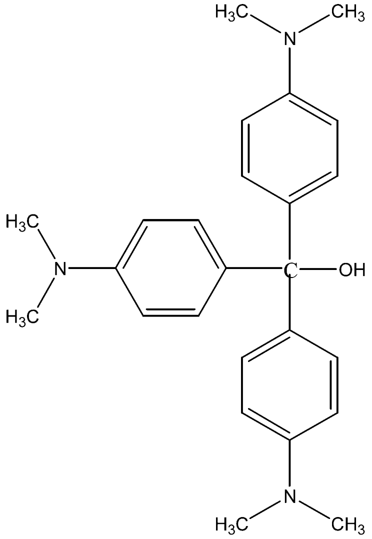
An investigation on the detailed kinetics of proton transfer between a set of di- and monofluoro- and chloro- (2,3-, 2,5-, 2,6-, 3,5-, 2-, and 3-) benzoic acids (HA) and Crystal Violet carbinol base in chlorobenzene favors a mechanism in terms of fast equilibrium between HA and D to form a H-bonded complex, D···HA, followed by rate-limiting proton transfer along the H-bond to form the colored ion pair $DH^+A^-$ under the combined influence of monomer HA catalyst, nonreactive cyclic dimer $(HA)_2$ inhibitor, and hyperacidic homoconjugated complex $H(HA_2)$ catalyst through a transition state with nearly 60% charge separation.

Proton-transfer studies in apolar aprotic solvents (dielectric constant, $D < 15$; dipole moment, $\mu < 8.3 \times 10^{-30}$ Cm; and Dimroth−Reichardt's normalized solvent polarity parameter, $E_T^N$ ca. 0.0−0.3)[1] are of significant interest. Complications from specific solute−solvent interactions due to the solvent's own acidity and/or basicity are minimized in these solvents, and proton transfer is expected to be direct. Further, time scales for proton-transfer processes in such solvents may be considerably rather abnormally long and vary from several milliseconds to as long as a few hundred seconds depending on the acid and/or the base used.[2−14] In fact, reactions of a variety of oxygen acids, e.g., aliphatic and aromatic carboxylic acids, phenols, hydrogen spiroborates corresponding to dihydroxy, hydroxyl carboxy, and dicarboxy acids, nitro- and fluoro-alcohols with carbinol bases of several triarylmethane dyes, e.g., Malachite Green, Brilliant Green, Methyl Violet, Crystal Violet, Ethyl Violet, and Victoria Pure Blue BO in benzene, toluene, and other apolar aprotic solvents, exhibit slow enough kinetics that can be conveniently monitored by ordinary spectrophotometry of the colored ion pair product.[2−4,7,9−14] An investigation on the reactions of a set of disubstituted (2,3-, 2,5-, 2,6-, 3,5-difluoro- and dichloro-) benzoic acids with the carbinol base of Crystal Violet in chlorobenzene that too display similar "slow" kinetics has shown that the reactions follow second-order reversible kinetics and interestingly exhibit characteristics of general acid catalysis. Here, we present a critical discussion of the results on detailed kinetics of the reactions along with chemometric analysis of disubstituent effects on kinetic reactivity of benzoic acid as the model substrate with the goal of shedding light on the mechanism of such slow proton-transfer processes.

## Experimental Section

The chemicals used were either analytical reagent grade or highly purified by standard procedures. Chlorobenzene ($E_T^N$ = 0.188),[1] among aromatic $\pi$-electron donor solvents, being very inert as compared to benzene or toluene was chosen as the reference apolar aprotic solvent. Crystal Violet carbinol base, 4,4′,4″-tris(dimethylamino) triphenylcarbinol (Chart 1), which is colorless, was employed as the reference base. Chlorobenzene solution of the carbinol base was prepared by basification of a $10^{-5}$ M aqueous solution of Crystal Violet [4,4′,4″-tris-(dimethylamino) triphenylchloride] with ~2 M NaOH and subsequent extraction into chlorobenzene in accordance with a standard procedure.[6]

**CHART 1: Structure of Crystal Violet Carbinol Base**



**Choice of Acids.** A set of disubstituted chloro- and fluorobenzoic acids (2,3-, 2,5-, 2,6-, 3,5-) including the corresponding monosubstituted benzoic acids were selected to study kinetics of proton transfer from the −COOH group. Halogen (Cl-, F-) substituents were chosen to avoid H-bonding interactions between the ortho substituents and the −COOH group.[14]

Kinetics of the reaction of an acid, HA ($10^{-5}$−$10^{-4}$ M), with the colorless carbinol base of Crystal Violet, Dye-OH ($10^{-5}$ M), in dry chlorobenzene producing a colored ion pair, $Dye^+A^-$, were monitored by absorbance measurements of the ion pair at 610 nm in a Teflon stoppered quartz cuvette using a 160A Shimadzu UV−vis spectrophotometer at temperatures of 28.0 and 20.0 ± 0.1 °C. The molar absorptivity ($\epsilon$) of Crystal Violet cation ($Dye^+$) in chlorobenzene was found to be $1.65 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ at 28 °C.

## Results and Discussion

**Acid−Carbinol Base Reaction Kinetics in Chlorobenzene.** The equilibrium constant ($K$) values of the acid (HA)−Crystal

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**TABLE 1: Values of Equilibrium Constant (log *K*) for Reactions of Mono- and Disubstituted Chloro- and Fluorobenzoic Acids with Crystal Violet Carbinol Base in Chlorobenzene at 28.0 ± 0.1 °C**

| acids | log $K$ ($M^{-1}$) |
|---|---|
| benzoic acid | 3.04 |
| *o*-chlorobenzoic acid | 3.99 |
| *m*-chlorobenzoic acid | 3.92 |
| 2,3-dichlorobenzoic acid | 4.83 |
| 2,5-dichlorobenzoic acid | 4.91 |
| 2,6-dichlorobenzoic acid | 5.39 |
| 3,5-dichlorobenzoic acid | 4.91 |
| *o*-fluorobenzoic acid | 3.70 |
| *m*-fluorobenzoic acid | 3.92 |
| 2,3-difluorobenzoic acid | 4.24 |
| 2,5-difluorobenzoic acid | 4.24 |
| 2,6-difluorobenzoic acid | 4.48 |
| 3,5-difluorobenzoic acid | 4.45 |

Violet carbinol base (Dye-OH) reaction in chlorobenzene,

$$\mathrm{HA} + \text{Dye-OH} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{Dye^+A^-} + \mathrm{H_2O} \qquad (1)$$

for the acids of the set are very high[15] (vide log $K$ values in Table 1), and the reverse rate constants ($k_r$) of the reactions as compared to their forward rate constants ($k_f$) are too small to consider. Because water formed in the reaction has been argued to be associated with one of the species and they exist as one entity,[16] the acid−carbinol base reaction can be re-expressed as

$$\mathrm{HA} + \mathrm{D} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{DH^+A^-} \qquad (2)$$

where D is Crystal Violet carbinol base (colorless) and $\mathrm{DH^+A^-}$ is the colored ion pair product. It may be pointed out that maximum correction in log $K$ (+0.03) due to possibility of acid dimerization in chlorobenzene based on the upper limit of dimerization constant of $10^3\ \mathrm{M^{-1}}$ [17,18] remains well within ±0.04 unit, the limits of deviation of log $K$ (Table 1).

Absorbance data during the course of reaction for a fixed concentration of $D$ and varying concentrations of HA conform to satisfactory second-order reversible kinetics:

$$\ln\left\{\frac{[\mathrm{D}]_t - [\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{D}]_t - [\mathrm{D}]_{\mathrm{eq}} + \sqrt{Q}}\right\} - \ln\left\{\frac{[\mathrm{D}]_0 - [\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{D}]_0 - [\mathrm{D}]_{\mathrm{eq}} + \sqrt{Q}}\right\} = -k_f\sqrt{Q}t \qquad (k_f \gg k_r) \quad (3)$$

where

$$Q = \left([\mathrm{HA}]_0 - [\mathrm{D}]_0 + \frac{1}{K}\right)^2 + 4\frac{[\mathrm{D}]_0}{K}$$

$[\mathrm{D}]_0$, $[\mathrm{D}]_{\mathrm{eq}}$, and $[\mathrm{D}]_t$ were computed as $b/\epsilon$, $(b - X_e)/\epsilon$, and $(b - X_t)/\epsilon$, respectively, where $b$, $X_e$, and $X_t$ are absorbances at 610 nm for completely converted D to $\mathrm{DH^+A^-}$ by use of excess HA, at equilibrium, and at time "*t*", respectively. $\epsilon$ is the molar absorptivity of $\mathrm{DH^+A^-}$ at 610 nm, and $[\mathrm{HA}]_0$ is the initial [HA].

The plots $\log\{[\mathrm{D}]_t - [D]_{\mathrm{eq}}/[D]_t - [D]_{\mathrm{eq}} + \sqrt{Q}\}$ versus $t$ are found to be all linear.

It may be noted that acid−carbinol base reactions in apolar aprotic media reported earlier,[2−4,7,9−14] which did not include disubstituted benzoic acids that were too slow, were studied at $10^2$−$10^3$-fold excess acid concentrations when pseudo first-order conditions prevailed. The magnitude of second-order forward rate constant ($k_f$) for acid−carbinol base reactions is however found to vary with initial acid concentration $[\mathrm{HA}]_0$ but not with $[\mathrm{D}]_0$, indicating the reactions are general acid catalyzed, the acid playing the dual role of the substrate and the catalyst. More interestingly, $k_f$ generally rises with $[\mathrm{HA}]_0$ to a maximum at $\sim 6 \times 10^{-5}$ M $[\mathrm{HA}]_0$ and thereafter keeps falling up to $\sim 1 \times 10^{-4}$ M $[\mathrm{HA}]_0$. Interestingly at $\sim 1 \times 10^{-4}$ M, there is a sharp decrease in the rate of fall of $k_f$ and subsequently there is very slow fall in $k_f$ up to $10^{-3}$ M. Not unexpectedly, the rising segment on $k_f$ versus $[\mathrm{HA}]_0$ profile could not be observed for 2-F, 3-F, and H-benzoic acids, their lowest concentration in the study being well above $6 \times 10^{-5}$ M. In fact, $k_f$ shows a parabolic dependence on $[\mathrm{HA}]_0$ over the range $10^{-5}$−$10^{-4}$ M (Figure 1), and the behavior over this range conforms to the equation:

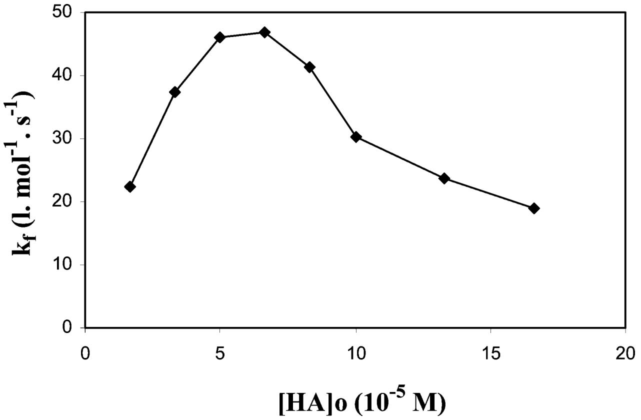


**Figure 1.** $k_f$ versus $[\mathrm{HA}]_0$ plot for 2,5-dichlorobenzoic acid (concentration range $1.66 \times 10^{-5}$ to $1.66 \times 10^{-4}$ M) as the sample acid.

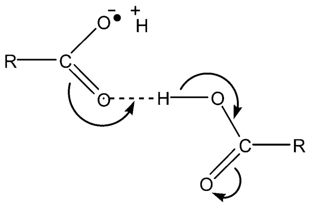
**TABLE 2: Values of Catalytic Constants ($k_\alpha$ and $k_\beta$) for Reactions of Mono- and Disubstituted Chloro- and Fluorobenzoic Acids with Crystal Violet Carbinol Base in Chlorobenzene at 28.0 ± 0.1 °C**

| acids | $k_\alpha$ (28 °C) ($10^5$ L$^2$ mol$^{-2}$ s$^{-1}$) | $k_\beta$ (28 °C) ($10^9$ L$^3$ mol$^{-3}$ s$^{-1}$) |
|---|---|---|
| *o*-chlorobenzoic acid | 4.90 | 2.90 |
| *m*-chlorobenzoic acid | 4.68 | 2.60 |
| 2,3-dichlorobenzoic acid | 14.7 | 12.6 |
| 2,5-dichlorobenzoic acid | 15.4 | 12.5 |
| 2,6-dichlorobenzoic acid | 32.0 | 28.8 |
| 3,5-dichlorobenzoic acid | 19.1 | 15.2 |
| *o*-fluorobenzoic acid | 0.536 | 0.143 |
| *m*-fluorobenzoic acid | 0.637 | 0.156 |
| 2,3-difluorobenzoic acid | 5.02 | 2.60 |
| 2,5-difluorobenzoic acid | 5.73 | 4.20 |
| 2,6-difluorobenzoic acid | 7.32 | 5.00 |
| 3,5-difluorobenzoic acid | 6.09 | 4.00 |

$$k_f = k_\alpha[\mathrm{HA}]_0 - k_\beta[\mathrm{HA}]_0^2 \qquad (4)$$

The $k_f/[\mathrm{HA}]_0$ versus $[\mathrm{HA}]_0$ plots for the acids are found linear with $r^2 = 0.83$−$0.99$. The catalytic constants $k_\alpha$ (a third-order rate constant) and $k_\beta$ (a fourth-order rate constant) determined respectively from intercept and slope of $k_f/[\mathrm{HA}]_0$, versus $[\mathrm{HA}]_0$, plots are characteristics of the acid substrate for a given solvent and temperature (Table 2). Obviously, the kinetic situation for the reactions under study is far from simple. The term quadratic in $[\mathrm{HA}]_0$ in eq 4 indicates the possibility of acid dimers to participate in the overall reaction. In apolar aprotic solvents, carboxylic acid monomer−dimer equilibrium may exist with a dimerization constant ($K_{12}$) of $1 \times 10^3\ \mathrm{M^{-1}}$ at 25 °C for benzoic acids as the upper limit.[17,18] The dimer acid $[\mathrm{HA}]_2$ in such inert media is believed to be a cyclic dimer known to be present in the gas phase.[19,20] With the acid dimer content at acid

**CHART 2**



concentrations $10^{-5}$−$10^{-4}$ M being from 0 to 15% only, the error in approximating monomeric acid concentration [HA] by the initial total concentration of the acid in terms of monomer only, $[HA]_0$ is insignificant. The acid in cyclic dimer $(HA)_2$ form, it may be noted, is not a reactive species.[19,20] We now propose the following mechanism for acid (HA)−carbinol base (D) reaction incorporating the catalytic role of HA and the acid dimerizing effect of apolar aprotic solvents, and attempt to interpret the $k_f$ versus $[HA]_0$ relation (eq 4):

$$\mathrm{D} + \mathrm{HA} \overset{K_H}{\rightleftharpoons} \mathrm{D\cdots HA} \tag{5}$$

$$\mathrm{D\cdots HA} + \mathrm{HA} \xrightarrow{k_1} \mathrm{DH^+A^-} + \mathrm{HA} \tag{6}$$

$$\mathrm{D\cdots HA} + (\mathrm{HA})_2 \xrightarrow{k_2} \mathrm{DH^+A^-} + 2\mathrm{HA} \tag{7}$$

where D···HA is a 1:1 H-bonded intermediate complex plausibly formed by fast diffusional approach of D, and HA is in fast equilibrium with D and HA and undergoes conversion to the product $DH^+A^-$ under the catalytic influence of monomer HA and dimer $(HA)_2$ as the rate-limiting step.

The expression for $k_f$ according to this scheme

$$k_f = k_1K_H[\mathrm{HA}] + k_2K_HK_{12}[\mathrm{HA}]^2 \tag{8}$$

is equivalent to eq 4 for $k_f$ with $k_\alpha = k_1K_H$ and $k_\beta = -k_2K_HK_{12}$, and as shown $[HA] \approx [HA]_0$, for $[HA]_0$ up to $1 \times 10^{-4}$ M.

The first term in eq 4, $k_\alpha[HA]_0$, may thus be interpreted as due to catalysis of proton transfer from HA to D along the H-bond in D···HA complex to form $DH^+A^-$ by monomeric HA possibly by H-bonding interaction, whereas the second term $-k_\beta[HA]^2$ may be interpreted as due to inhibition of conversion of D···HA to $DH^+A^-$ by cyclic dimer $(HA)_2$, which has no free −COOH group for H-bonding interaction and stabilizes D···HA complex. The complex kinetic behavior observed may now be explained. On increasing $[HA]_0$ from $1 \times 10^{-5}$ to $6 \times 10^{-5}$ M when the monomer content decreases from 100% to 90% and the cyclic dimer content increases from 0% to 10%, $k_f$ keeps rising but with a gradually decreasing slope. On further increase in $[HA]_0$ up to $1 \times 10^{-4}$M when the monomer content decreases to 85% and the cyclic dimer content increases to 15%, $k_f$ keeps decreasing. The subsequent observation as described earlier on very slow fall in $k_f$ over $1 \times 10^{-4}$ to $1 \times 10^{-3}$ M $[HA]_0$ can be accounted for as due to formation of hyperacidic open chain dimer known as homoconjugate acid−acid anion complex acid $H(HA_2)$ (Chart 2)[17,20,21] and/or open chain trimer acid[17,18] although in small proportions. The catalytic action of open chain dimer or trimer superimposed on catalytic action of monomer and inhibitory action of cyclic dimer could be a reason for this kinetic behavior. A line of reasoning similar in several ways was put forward for reactions such as ethyl diazoacetate−carboxylic acids in benzene,[22] ethyl diazoacetate−halogenoacetic acids in apolar aprotic solvents,[23] and diazodiphenylmethane−carboxylic acids in apolar solvents[18,20] to explain their complicated kinetics.

The foregoing analysis thus lends support to the mechanism for acid [HA]−carbinol base (D) reaction in an apolar aprotic solvent as consisting of a fast equilibrium between the reactants (D and HA) and a H-bonded intermediate D···HA followed by proton transfer along the H-bond in D···HA to form the ion pair $DH^+A^-$ as the rate-limiting step under combined influence of monomer HA catalyst, nonreactive cyclic dimer $(HA)_2$ inhibitor, and hyperacidic open chain dimer $H(HA_2)$ catalyst, the contribution of each species depending on the magnitude of $[HA]_0$.

**Chemometric Analysis of Disubstituent Effects on Catalytic Constant for Benzoic Acid−Crystal Violet Carbinol Base Reaction in Chlorobenzene.** The catalytic constant $k_\alpha$, the liming value of $k_f/[HA]_0$ as $[HA]_0 \rightarrow 0$ (eq 4), is a direct measure of protonation power of HA in the given solvent. A chemometric analysis of the effects of relevant substituent parameters on log $k_\alpha$ with benzoic acid as the model substrate is of natural interest. The approach found most suitable for the set of benzoic acids used in the study, that is, with substituents at both *ortho*- and *meta*-positions, is that of Fujita and Nishioka.[24]

$$\log k = \rho\sigma_{m,p\ o\equiv p} + fF_o + \delta E_o^S + h \tag{9}$$

which treats *o*-, *m*-, and *p*-substituents on the same standard. In this model, $\sigma$ represents ordinary electronic effect and $\sigma_o \equiv \sigma_p$ is assumed. *F* represents the proximity electronic effect, and $E^S$ is the primary steric effect for *ortho*-substituents. $\rho$, $f$, and $\delta$ are susceptibility constants for $\sigma$, $F$, and $E^S$, respectively. Values of relevant $\sigma$, $F$, and $E^S$ are given in Table 3. Based on the Fujita−Nishioka model (eq 9) and the assumption of additivity for substituent effects, multiple linear regression of log $k_\alpha$ for difluoro- and dichloro- (2,3-, 2,5-, 2,6-, 3,5-) and monochloro- (2-, 3-) benzoic acids in chlorobenzene leads to the following correlation as statistically the most significant:

$$\log k_\alpha = 1.503 \sum_{m,o} \sigma_{m,o\equiv p} + 0.826 \sum_{o} F_o + 4.955 \qquad (n = 10, R = 0.855) \tag{10}$$

which has a correlation coefficient (*R*) significant at better than 5% *F*-level and both the partial regression coefficients ($\rho$ and $f$) significant at better than 0.5% *t*-level. Inclusion of $E_o^S$ parameter makes log $k_\alpha$ correlation non-significant. A comparison of eq 10 to the regression result on log *K*,[15] the other measure for protonation power:

$$\log K = 2.545 \sum_{m,o} \sigma_{m,o\equiv p} + 1.470 \sum_{o} F_o + 2.811 \qquad (n = 10, R = 0.935) \tag{11}$$

having *F*-level of significance for *R* at better than 1% and *t*-level of significance for $\rho$ and $f$ at better than 0.5%, shows that log $k_\alpha$ is only about 0.6 times as sensitive as log *K* to variations in both of the substituent parameters. This is, as expected, reflected in the Bronsted slope of log $k_\alpha$ versus log *K* correlation:

$$\log k_\alpha = 0.615 \log K + 3.167 \qquad (n = 10, R = 0.969) \tag{12}$$

having *R* significant at better than 1% *F*-level and the regression coefficient significant at better than 0.5% *t*-level. The result may be interpreted to indicate that around 60% of the proton transfer occurs at the transition state of acid−carbinol base reactions. Considerably dipolar nature of the transition state is also supported by the lower value of $k_\alpha$ observed for *o*-chlorobenzoic acid in phenetole having a lower dielectric constant as compared

**TABLE 3: Substituent Parameters Used for Correlation in the Fujita−Nishioka Model**

| sl. no. | substituents | $(\sum_m \sigma_m)$[a] | $(\sum_o \sigma_{o\equiv p})$[b] | $(\sum_{m,o} \sigma_{m,o\equiv p})$[c] | $(\sum_o F_o)$[d] | $(\sum_o E_o^S)$[e] | log $K$ ($M^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | H | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.04 |
| 2 | 2-F | | 0.06 | 0.06 | 0.43 | −0.46 | 3.70 |
| 3 | 3-F | 0.34 | | 0.34 | | | 3.92 |
| 4 | 2,3-$F_2$ | 0.34 | 0.06 | 0.40 | 0.43 | −0.46 | 4.24 |
| 5 | 2,5-$F_2$ | 0.34 | 0.06 | 0.40 | 0.43 | −0.46 | 4.24 |
| 6 | 2,6-$F_2$ | | 0.12 | 0.12 | 0.86 | −0.92 | 4.48 |
| 7 | 3,5-$F_2$ | 0.68 | | 0.68 | | | 4.45 |
| 8 | 2-Cl | | 0.23 | 0.23 | 0.41 | −0.97 | 3.99 |
| 9 | 3-Cl | 0.37 | | 0.37 | | | 3.92 |
| 10 | 2,3-$Cl_2$ | 0.37 | 0.23 | 0.60 | 0.41 | −0.97 | 4.83 |
| 11 | 2,5-$Cl_2$ | 0.37 | 0.23 | 0.60 | 0.41 | −0.97 | 4.91 |
| 12 | 2,6-$Cl_2$ | | 0.46 | 0.46 | 0.82 | −1.94 | 5.39 |
| 13 | 3,5-$Cl_2$ | 0.74 | | 0.74 | | | 4.91 |

[a] Reference 24. [b] Reference 24. [c] Reference 24. [d] Reference 25. [e] Reference 26.

**TABLE 4: Values of Catalytic Constants ($k_\alpha$ and $k_\beta$) for Reactions of 2,3- and 2,5-Difluorobenzoic Acids with Crystal Violet Carbinol Base in Chlorobenzene at 20.0 ± 0.1 °C**

| acids | $k_\alpha$ (20 °C) ($10^5$ $L^2$ $mol^{-2}$ $s^{-1}$) | $k_\beta$ (20 °C) ($10^9$ $L^3$ $mol^{-3}$ $s^{-1}$) |
|---|---|---|
| 2,3-difluorobenzoic acid | 4.75 | 3.10 |
| 2,5-difluorobenzoic acid | 4.75 | 4.00 |

**TABLE 5: Values of Energy of Activation ($E_a$) and Activation Parameters: Enthalpy of Activation ($\Delta H^{\#}$) and Entropy of Activation for the Reaction of 2,3- and 2,5-Difluorobenzoic Acids with Crystal Violet Carbinol Base in Chlorobenzene**

| acid | $E_a$ (kJ/mol) | $\Delta H^{\#}$ (kJ/mol) | $T$[a]$\Delta S^{\#}$ (kJ/mol) |
|---|---|---|---|
| 2,3-difluorobenzoic acid | 8.25 | 5.75 | −35.16 |
| 2,5-difluorobenzoic acid | 12.8 | 10.3 | −30.10 |

[a] 301 K.

to chlorobenzene [$1.03 \times 10^4$ $L^2$ $mol^{-2}$ $s^{-1}$ in phenetole ($D = 4.22$)[1]; cf., $4.90 \times 10^5$ $L^2$ $mol^{-2}$ $s^{-1}$ in chlorobenzene ($D = 5.62$)[1] at 28 °C].

**Effect of Temperature on $k_\alpha$.** To have an estimate of activation parameters ($E_a$, $\Delta H^{\#}$, $T\Delta S^{\#}$) of HA−D reactions, log $k_\alpha$ was determined also at 20° ± 0.1 °C for 2,3- and 2,5-difluorobenzoic acids as the sample acids (Table 4). The activation parameters were evaluated using the following relations based on Arrhenius and Eyring equations:

$$E_a = \left(\frac{2.303RT_1T_2}{T_2 - T_1}\right)\log\left(\frac{k_{\alpha 2}}{k_{\alpha 1}}\right) \tag{13}$$

$$\Delta H^{\#} = E_a - RT \tag{14}$$

$$\Delta S^{\#} = 2.303R \log k_\alpha - 2.303R \log\left(\frac{kT}{h}\right) - R + \frac{E_a}{T} \tag{15}$$

and are given in Table 5, where $T_1$ and $T_2$ are 293 and 301 K, respectively. A comparison of observed $\Delta H^{\#}$ (5−10 kJ $mol^{-1}$) with the energies of O−H bond in acids (464.4 kJ $mol^{-1}$), C−O bond in carbinols (359.5 kJ $mol^{-1}$), and hydrogen bond (10−40 kJ $mol^{-1}$)[27] indicates the release of a substantial amount of energy from delocalization of positive charge in the incipient Crystal Violet carbocation in the transition state. The latter as already seen is sufficiently dipolar with about 60% proton transfer for the D···HA complex. Further, large negative values of $T\Delta S^{\#}$ (−30 to −35 kJ $mol^{-1}$ at 28 °C) point to considerable loss in the freedom of translational and rotational motion of reactants while forming the transition state. Interestingly, the magnitude of $T\Delta S^{\#}$ is substantially higher than that of $\Delta H^{\#}$, showing that acid−carbinol base reactions in apolar aprotic solvents are clearly entropy driven. The finding is particularly significant. The abnormally "slow" proton-transfer kinetics observed in acid−triarylmethane dye carbinol base reactions in apolar aprotic solvents can now be attributed to their large negative entropy of activation. The transition state being sufficiently polar with nearly 60% charge separation, the large negative $\Delta S^{\#}$ appears contributed not only by restrictions on freedom of motions of the reactant molecules in the transition state but also by an increase in the orientation of apolar solvent molecules around the dipolar transition state.

## Conclusion

The present study provides an explanation for abnormally "slow" proton transfer from acids, HA, to dye carbinol bases, D, in apolar aprotic solvents in terms of a mechanism consisting of a fast equilibrium between the reactant components and an intermediate complex D···HA followed by rate-limiting proton transfer along the H-bond to form the product, $DH^+A^-$, under the combined influence of monomer HA catalyst, nonreactive cyclic dimer $(HA)_2$ inhibitor, and hyperacidic open chain dimer $H(HA_2)$ catalyst through a dipolar transition state with ~60% charge separation accompanied by release of enough energy due to delocalization of charge in the incipient dye carbocation and sufficiently large negative entropy of activation.

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