General Acid Catalysis in Benzoic Acid–Crystal Violet Carbinol Base Reactions in Toluene

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ABSTRACT: Kinetics of benzoic acid–dye carbinol base reactions in an apolar aprotic solvent exhibit a complex dependence on the concentration of the acid, indicating the occurrence of general acid catalysis, the acid playing the dual role of the substrate and the catalyst. The complex kinetic behavior observed for 23 ortho- and meta-substituted benzoic acids has been traced to overlapping participations of the monomer acid, hyperacidic open chain homoconjugated complex (dimeric and trimeric) acids, and nonreactive cyclic dimer and trimer acids. It has been found that although the degree of proton transfer in the transition state is 50–60% when the acid acts exclusively in the monomeric form, it gets enhanced to as high as more than 90% when the role of homoconjugated complex acids is taken into consideration. © 2012 Wiley Periodicals, Inc. Int J Chem Kinet 44: 570–576, 2012

INTRODUCTION

Apolar aprotic solvents ($E_T^N = 0.0 - 0.3$) [1] offer particular advantages for studying proton transfer reactions. In these solvents, specific solute–solvent interactions are greatly minimized, if not eliminated and proton transfer is expected to occur directly. Physicochemical studies of acid–base reactions in an apolar aprotic solvent between a series of acids and a reference base are of significant aid in setting up an acidity scale considerably more intrinsic than the common pK_a (H₂O or DMSO) scale, which is subjected to strong specific solvation effects. Among the different bases tried, a triarylmethane dye carbinol base, particularly Crystal Violet carbinol base, 4,4',4"-*tris*(dimethylamino) triphenyl carbinol, has been found to be an appropriate choice for the reference base. This colorless carbinol base reacts with a variety of acids (HA) ranging from simple carboxylic acids, phenols, nitro-/fluoroalcohols to complex hydrogen spiroborates in toluene and other apolar aprotic media, producing a colored ion associate [2–19].

Timescales for these proton transfer reactions are interestingly as long as several minutes, and the progress of the reactions is conveniently monitored by ordinary spectrophotometry. The reactions, in general, follow pseudo–first-order kinetics with respect to the dye carbinol base concentration. Their rate constants (k), on the other hand, vary with acid concentrations (C_{HA}).

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The variation, however, did not follow any simple pattern, indicating the occurrence of general acid catalysis, an acid playing the dual role of the substrate and the catalyst [2–4,7–14]. The complex *k* versus C_{HA} variation is not unexpected in view of the possibility of HA existing as a hyperacidic homoconjugated complex acid, H(A···(HA)_m ($m \ge 1$), a nonreactive cyclic dimer (HA)₂, etc., besides the monomeric HA in an apolar aprotic medium [2–24]. The *k* versus C_{HA} variation has been probed in detail to determine the constants of catalysis by such different acidic species for a series of 23 meta- and ortho-substituted benzoic acids in their toluene-phase reactions with Crystal Violet carbinol base, the reference base.

Correlations of both simple and composite catalytic constants of the substituted benzoic acids with their toluene-phase equilibrium reactivity parameters and also with substituent parameters have been analyzed with the focus on evaluating the contribution of homoconjugated complex acids in catalyzing acid–base reactions in apolar aprotic media. The results are 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. Crystal Violet carbinol base, 4',4'',4'''-tris(dimethylamino) triphenyl carbinol (Fig. 1), which is colorless, was employed as the reference base.

Crystal Violet carbinol base was prepared by precipitating a 100-mL aqueous solution containing \sim 100 mg of Crystal Violet dye [4,4',4"-tris (dimethylamino) triphenyl chloride] with ~2 M NaOH followed by extraction of the carbinol base precipitated into \sim 200-mL of toluene. The toluene extract was separated and subjected to freeze-drying to obtain Crystal Violet carbinol base as a powder (mp 180°C). Elemental analysis results (C, 76.85%; H, 7.88%; N, 10.94%) as against C, 77.08%, H, 8.02%; N, 10.79% required for $C_{25}H_{31}N_3O$; IR peak data in Nujol (3350 cm⁻¹, bonded OH); ¹H NMR signals in carbon tetrachloride $(2.90 \text{ ppm, s}, 18\text{H}, 3\text{N} (\text{CH}_3)_2; 6.55 \text{ ppm, d}, 6\text{H}, J =$ 10 Hz, aromatic H; 7.00 ppm, d, 6H, J = 10 Hz, aromatic H; 7.28 ppm, s, ¹H, C-OH) and freezing point depression in benzene confirmed the structure of the carbinol base (Fig. 1). Twenty-three substituted benzoic acids, H; meta-Me, OMe, OPh, F, Cl, Br, I, COPh, CF₃, CN, NO₂, ortho-Me, OMe, OEt, OPh, OAc, F, Cl, Br, I, COPh, and NO₂ benzoic acids, were employed for the study.



Figure 1 Structure of Crystal Violet carbinol base.

All stock solutions of Crystal Violet carbinol base and meta- or ortho-substituted benzoic acids were prepared by dissolving their weighed amounts in dry toluene.

Kinetics of the reaction between an acid, HA $(C_{HA} \sim 10^{-4} - 10^{-2} \text{ M}, \text{ higher molarity order being})$ employed for relatively weaker acids and lower order for stronger acids) and the colorless carbinol base of Crystal Violet, Dye-OH ($C_D = 2.5 \times 10^{-5}$ M), in dry toluene, producing a colored ion associate, Dye⁺A⁻, were monitored by absorbance measurements of the ion associate at 610 nm in a Teflon-stoppered quartz cuvette using a 160A Shimadzu UV-vis spectrophotometer at 28.0 \pm 0.1°C. The sampling time for absorbance recordings during the reaction was every 5 to 10 s. Forty to sixty minutes was required to attain the reaction equilibrium. The molar absorptivity (\in) of Crystal Violet cation (Dye⁺) in toluene was found 3.3×10^4 dm³ mol⁻¹ cm⁻¹ at 28.0°C and wavelength 610 nm.

RESULTS AND DISCUSSION

Acid–Dye Carbinol Base Reaction Kinetics in Toluene

Substituted benzoic acids (HA) react with Crystal Violet carbinol base (Dye-OH) in toluene to form colored ion associates (Dye $^+A^-$):

$$A + Dye-OH \rightleftharpoons Dye^+A^- + H_2O$$
 (1)

It has been argued that the water molecule formed (Eq. (1)) is hydrogen bonded to one of the species of system and that they exist as one entity [25]. Taking into consideration the possibility of HA existing not simply as a monomer but effectively as a *n*-mer due to formation of reactive open chain (homoconjugated acid–acid anion complex acids) and nonreactive cyclic acid multimers in toluene, the apolar aprotic solvent [20–24], Eq. (1), can be reexpressed as

$$n\mathrm{HA} + \mathrm{D} \rightleftharpoons \mathrm{DH}_n^+ \mathrm{A}_n^- \tag{2}$$

where D and $DH_n^+A_n^-$ represent the colorless carbinol base of Crystal Violet and the colored ion associate, respectively. The absorbance data for the reaction equilibrium (Eq. (2)) for members of the present set of meta- and ortho-substituted benzoic acids in toluene fitted the expression

$$K = \frac{\left[\mathrm{DH}_n^+ \mathrm{A}_n^-\right]}{\left[\mathrm{D}\right]\left[\mathrm{HA}\right]^n} \tag{3}$$

where *K* is the association constant and *n* is an acid exponent. Values of log *K* and *n* for the 23 acids chosen here were determined as the intercept and regression coefficient, respectively, of the linear regression of log $((A_{eq})/(b - A_{eq}))$ on log [HA] $(n = 7-8, R^2 = 0.994-0.996, F$ (481.41–969.36)-level significance on *R* better than 0.1%), where A_{eq} and *b* are the absorbances of DH_n⁺A_n⁻ at 610 nm at equilibrium and when converted totally from D (by the use of excess HA), respectively, and [HA] $\simeq C_{HA}$, are given in Tables I and II.

As seen, values of n are close to or greater than unity. A similar behavior was observed for many

Table I Equilibrium Parameters (log K, *n*) for Toluene-Phase Reactions of *Meta* Substituted Benzoic Acids with Crystal Violet Carbinol Base at $28.0 \pm 0.1^{\circ}$ C

Substituent	$\log K^a$	n^a
Н	1.78	0.98
Me	1.74	0.93
OMe	2.29	1.11
OPh	2.30	0.98
F	3.12	1.09
Cl	3.96	1.29
Br	4.02	1.29
Ι	4.38	1.41
COPh	2.63	0.93
CF ₃	3.65	1.12
CN	4.55	1.23
NO ₂	4.92	1.28

^aRefs. [11,17]

Table II Equilibrium Parameters (log K, n) for Toluene-Phase Reactions of Ortho-Substituted Benzoic Acids with Crystal Violet Carbinol Base at $28.0 \pm 0.1^{\circ}$ C

Substituent	$\log K^a$	n ^a
H	1.78	0.98
Me	1.96	1.19
NO ₂	5.38	1.33
F	2.36	0.94
Cl	2.85	0.98
Br	3.04	0.98
Ι	3.53	1.10
OMe	2.87	1.18
OEt	2.55	1.12
OPh	1.94	1.04
OAc	3.43	1.08
COPh	2.83	0.92

^aRefs. [11,16]

other acids in apolar aprotic solvents [2–24]. This has been ascribed to overlapping participations of open chain dimeric and multimeric homoconjugated complex acids $H(A \cdots (HA)_m \ (m \ge 1)$ in the reaction with the carbinol base (D) in apolar aprotic media [2–24]. The value of the acid exponent (*n*) for an acid depends upon its concentration, temperature, and solvent [10,17–24].

The time course of the absorbance data (A_t) for the reaction, Eq. (2), under the condition, $C_{HA} \gg C_D$ (vide the Experimental section) conforms excellently to pseudo–first-order reversible kinetics for the acids of the following set:

$$A_{t} = A_{\rm eq} - (A_{\rm eq} - A_{0})e^{-kt}$$
(4)

where A_0 is the absorbance at t = 0. The overall rate constant, k, was determined from the exponential regression of A_t on $t(n = 15-20; R^2 = 0.996-0.999,$ F (1241.23–8246.17)-level of significance on R better than 0.1% and t-level of significance on the regression coefficient (k) better than 0.1%). The rate constant of the relatively more reactive acids, *meta-* and *ortho*nitro benzoic acids for which the lower limit of C_{HA} was extended close to C_D, however, was obtained by an appropriate second-order procedure.

The rate constant (k) data, however, exhibit a complex dependence on C_{HA} (vide the Supporting Information), indicating the occurrence of general acid catalysis in the reaction (Eq. (3)), an acid playing the dual role of the acid and the catalyst. The rate constant (k) data obtained at varying acid concentrations, C_{HA} ($\sim 10^{-4}-10^{-2}$ M) and a fixed C_D (2.5 × 10⁻⁵ M) when examined for the pattern of k versus C_{HA} variation, in fact, fits excellently an expression describing general acid catalysis:

$$k = k_{\alpha}C_{\mathrm{HA}} + k_{\beta}C_{\mathrm{HA}}^2 + k_{\gamma}C_{\mathrm{HA}}^3 \tag{5}$$

for all the acids. k_{α} , k_{β} , and k_{γ} were obtained as regression coefficients from cubic regression of k on C_{HA} $(n = 7-9; R^2 = 0.957-.999, F (133.66-17369.14)$ -level of significance on R better than 0.1%, and t-levels of significance on k_{α} , k_{β} , and k_{γ} better than 0.1%, 0.1%, and 0.5%, respectively). k_{α} , k_{β} , and k_{γ} (Tables III and IV) represent constants for catalysis of toluene-phase HA-D reactions (Eq. (2)) by monomeric, dimeric, and trimeric HA species, respectively.

Dimeric HA species in an apolar aprotic medium may exist as a nonreactive cyclic dimer, (HA)₂, as well as a hyperacidic open chain homoconjugated acid-acid anion complex acid, H(A···HA), depending on the acid concentration used. k_{β} , thus, refers to the net catalytic constant for the homoconjugated dimer acid over the cyclic acid dimer. k_{β} can, in fact, be positive or negative. k_{γ} , similarly, refers to the net catalytic constant for the reactive homoconjugated complex acid, $H(A \cdots (HA)_2)$ over the cyclic trimer. Thus, the complex pattern of k versus C_{HA} variation originates from overlapping participations of HA, $(HA)_2$, $H(A \cdots HA)$, $(HA)_3$, and $H(A \cdots (HA)_2)$ species in toluene-phase HA-D reactions (Eq. (2)). A similar behavior has been observed for many other acids in apolar (also dipolar) aprotic media while studying not only reactions with dye carbinol bases [2-4,7-14] but also ethyl diazoacetate-carboxylic acid interactions, [26,27] the inversion of *l*-menthone [28] and diazodiphenylmethane-carboxylic acid reactions [29,30]. It is further seen unless C_{HA} is high enough, k_{α} term is the dominant contributor to k (Eq. (5)) (Tables III and IV); C_{HA} generally ranges within $10^{-4}-10^{-2}$ M.

It is of interest to see how sensitive is $\log k_{\alpha}$ as a toluene-phase reactivity parameter to substituent parameters. Results of correlation analysis of $\log k_{\alpha}$ on substituent parameters $\sigma_{\rm I}$, $\sigma_{\rm R}$ (Table V) for meta-substituted acids according to Taft's model [31]:

$$\log k_{\alpha} = \alpha \sigma_{\rm I} + \beta \sigma_{\rm R} + h \tag{6}$$

and on σ_{I} , σ_{R} , and v (Table V) for ortho-substituted acids according to Charton's model [32] is

$$\log k_{\alpha} = \alpha \sigma_{\rm I} + \beta \sigma_{\rm R} + \psi v + h \tag{7}$$

along with the best regression equations obtained are given for both meta- (Eq. (8)) and ortho- (Eq. (9)) substituted benzoic acids in Table VI.

The field and resonance effects of the substituents on the basis of their partial regression (β) coefficients contribute to log k_{α} in the ratio 66:34 ($\alpha' = 0.88$, $\beta' =$ 0.46) for meta- and 61:39 ($\alpha' = 0.80$, $\beta' = 0.52$) for ortho-substituted benzoic acids. It may be noted that the addition of the steric effect parameter (v) to Eq. (9) for log k_{α} makes the correlation nonsignificant, The *t*-level of significance on ψ (Eq. (7)) becomes as worse as >80%.

Composite Catalytic Constant

As an alternative to Eq. (5), the following expression in terms of a composite catalytic constant (k_{cat}) and an

Meta	k_{lpha}	k_{eta}	k_{γ}	$k_{\rm cat}$	
Substituent	$(10^2 \text{ L mol}^{-1} \text{ min}^{-1})$	$(10^3 L^2 mol^{-2} min^{-1})$	$(10^5 \text{ L}^3 \text{ mol}^{-3} \text{ min}^{-1})$	$(10^2 L^p mol^{-p} min^{-1})$	р
Н	0.195			0.220	1.03
Me	0.117	-	-	0.105	0.97
OMe	0.261	_	_	0.231	0.97
OPh	0.676	-	-	0.561	0.96
F	2.47	30.1	-	9.08	1.17
Cl	3.62	-	-	3.29	0.99
Br	3.93	-	-	4.93	1.03
Ι	3.71	-	-	2.37	0.93
COPh	3.16	-	-	3.72	1.03
CF ₃	5.30	171	-	39.4	1.25
CN	10.4	2250	-	458	1.40
NO ₂	23.7	-	-	331	1.28

Table III Catalytic Constants (k_{α} , k_{β} , k_{γ} , according to Eq. (5) and k_{cat} with Exponent *p* According to Eq. (10)) Evaluated from $k(min^{-1})$ versus C_{HA} (M) for Meta-Substituted Benzoic Acids–Crystal Violet Carbinol Base Reactions in Toluene at 28.0 + 0.1°C

in Toluene a	n Toluene at 28.0 + 0.1°C							
Ortho Substituent	$\frac{k_{\alpha}}{(10^2 \mathrm{L} \mathrm{mol}^{-1} \mathrm{min}^{-1})}$	k_{β} (10 ³ L ² mol ⁻² min ⁻¹)	k_{γ} (10 ⁵ L ³ mol ⁻³ min ⁻¹)	$\frac{k_{\text{cat}}}{(10^2 \text{ L}^p \text{ mol}^{-p} \text{ min}^{-1})}$	р			
Н	0.195	_	-	0.220	1.03			
Me	0.143	0.0554	_	0.222	1.09			
NO ₂	11.3	9030		2280	1.51			
F	0.784	_	_	1.51	1.12			
Cl	1.43	54.1	_	19.5	1.18			
Br	1.18	234	-306	99.83	1.15			
Ι	1.24	251	-625	36.2	1.36			
OMe	0.371	1.00	-	0.798	1.11			
OEt	0.290	_	_	0.390	1.06			
OPh	0.141	-0.599	0.209	0.728	1.47			
OAc	2.04	200	-432	17.2	1.23			
COPh	1.07	78.5	-	84.9	1.56			

Table IV Catalytic Constants (k_{α} , k_{β} , k_{γ} according to Eq. (5) and k_{cat} with Exponent *p* According to Eq. (10)) Evaluated from $k(\min^{-1})$ versus C_{HA} (M) for Ortho-Substituted Benzoic Acids–Crystal Violet Carbinol Base Reactions in Toluene at 28.0 + 0.1°C

Table V	Substituent Parameters Employed for
Correlatio	ns of log k_{α} and log k_{cat} According to Models,
Eqs. (6) at	nd (7)

Substituent	$\sigma^a_{ m I}$	$\sigma^a_{ m R}$	v^b	
Н	0	0	0	
Me	-0.01	-0.16	0.52	
OMe	0.30	-0.58	0.32	
OEt	0.28	-0.57	0.32	
OPh	0.40	-0.48	0.32	
OAc	0.38	-0.23	0.32	
F	0.54	-0.48	0.27	
Cl	0.47	-0.25	0.55	
Br	0.47	-0.25	0.65	
Ι	0.40	-0.16	0.78	
COPh	0.28^{c}	0.15^{d}	$0.50(\perp)^e$	
CF ₃	0.40	0.11	0.91	
CN	0.57	0.08	0.40	
NO ₂	0.67	0.10	$0.57(\perp)^f$	

^aRef. [33].

^bRef. [34].

^cTaft's σ_F [35].

^{*d*}Calculated as $\sigma_p - \sigma_F$ [35].

^eRefs. [34, 36]. ^fCalculated according to [37].

overall kinetic acid exponent (*p*):

$$k = k_{\rm cat} C_{\rm HA}^{\rm p} \tag{10}$$

fitted excellently k versus C_{HA} data for the acids. Values of k_{cat} and p determined from nonlinear regression analysis of k on C_{HA} (n = 7-9, $R^2 = 0.987-0.999$, F (311.90–622.91)-level of significance on R better 0.1% and *t*-levels of significance on k_{cat} and *p* better than 1% and 0.5%, respectively) are presented in Tables III and IV. Meta- and ortho-substituent effects on log k_{cat} are found expressible according to Eqs. (6) and (7), respectively, and the best regression results (Eqs. (11) and (12)) are presented in Table VI. The steric factor contribution to log k_{cat} for ortho-substituted acids was found not enough statistically significant. As estimated from partial regression (β) coefficients, the relative contribution of field and resonance effects on log k_{cat} is 61:39 ($\alpha' = 0.82$, $\beta' = 0.53$) for meta- and 53:47 ($\alpha' = 0.75$, $\beta' = 0.66$) for ortho-substituted acids.

Catalytic Constants (log k_{α} or log k_{cat}) versus the Equilibrium Association Constant (log K) Correlation

To see how far applicable is the Marcus theory [38,39] for toluene-phase proton transfer reactions between benzoic acids and Crystal Violet carbinol base, quadratic regression analysis of log k_{α} and log k_{cat} on log K was carried for both meta- and ortho-substituted benzoic acids. However, the results were statistically nonsignificant in each case. On the other hand, linear regression of log k_{α} and log k_{cat} on log K yielded statistically significant results (Table VII).

Furthermore, the values of the regression coefficient, the Brønsted exponent (*b*) [40,41] in log k_{α} versus log *K* relations for both meta- and ortho-substituted benzoic acids, 0.59 and 0.53, respectively, satisfy the condition: 0 < b < 1 (Eqs. (13) and (14) in Table VII) and demonstrate the applicability of the Brønsted relationship [40,41] to acid–dye carbinol base reactions

	Model	Best Regression Equations	n	R^2	F and F Level on	-Significance R Better Than	<i>t</i> -Level Significance on the Regression Coefficients Better Than
Meta-substituted benzoic acids	(6)	$\log k_{\alpha} = 3.02 \sigma_{\rm I} + 1.29 \sigma_{\rm R} + 1.36 (8)$	12	0.971	153.24	(0.1%)	α : 0.1%; β : 0.1%
	(6)	$\log k_{\rm cat} = 4.66 \sigma_{\rm I} + 2.45 \sigma_{\rm R} + 1.26 (11)$	12	0.937	67.36	0.1%	α : 0.1%; β : 0.1%
Ortho-substituted benzoic acids	(7)	$\log k_{\alpha} = 2.24 \sigma_{\rm I} + 1.17 \sigma_{\rm R} + 1.36 (9)$	12	0.840	23.71	0.1%	α : 0.1%; β : 0.5%
	(7)	$\log k_{\rm cat} = 4.62 \sigma_{\rm I} + 3.24 \sigma_{\rm R} + 1.89 (12)$	12	0.909	44.81	0.1%	α : 0.1%; β : 0.1%

Table VI Results of Regression Analysis of Catalytic Constants ($\log k_{\alpha}$ and $\log k_{cat}$) on Substituent Parameters According to the Models Equations (6) and (7)

Table VII Results of Linear Regression Analysis of $\log k_{\alpha}$ and $\log k_{cat}$ on $\log K$ for Meta- and Ortho-Substituted Benzoic Acids in Toluene

	Best Regression Equations	n	R^2	F and F on F Bett	-Significance R Level er Than	<i>t</i> -Level Significance on the Regression Coefficient Better Than
Meta-substituted benzoic acids	$\log k_{\alpha} = 0.33 + 0.59 \log K \ (13)$	12	0.854	58.37	0.1%	0.1%
	$\log k_{\rm cat} = 0.81 \log K \ (15)$	12	0.701	25.76	0.1%	0.1%
Ortho-substituted benzoic acids	$\log k_{\alpha} = 0.33 + 0.53 \log K \ (14)$	12	0.849	56.08	0.1%	0.1%
	$\log k_{\rm cat} = 0.96 \log K \ (16)$	12	0.774	37.59	0.1%	0.1%

in toluene. The transition state of the reaction is thus sufficiently dipolar where 50–60% proton transfer has occurred. Furthermore, evidence to the dipolar nature for the transition state is afforded by the observation of increasing log k_{α} with increasing dielectric constant (ε_r) of apolar aprotic solvents. On going from toluene ($\varepsilon_r = 2.38$) [1] to chlorobenzene ($\varepsilon_r = 5.62$) [1], log k_{α} (at 28.0 ± 0.1°C) increases from 2.39 to 2.70 for *meta*- fluorobenzoic acid and from 1.89 to 2.24 for *ortho*-fluorobenzoic acid.

On the other hand, the regression coefficient (*b*), the Brønsted exponent in log k_{cat} versus log *K* relation, is much larger for both meta- and ortho-substituted acids, 0.81 and 0.96, respectively, (Eqs. (15) and (16), Table VII). The large increase in the Brønsted exponent (*b*) while changing the acid catalytic constant from the monomer acid constant k_{α} to the composite constant, k_{cat} (Table VII), is obviously a reflection of the role of hyperacidic homoconjugated acid complexes in enhancing the extent of proton transfer in the transition state of acid–base reactions in an apolar aprotic solvent.

CONCLUSIONS

The complex kinetic behavior of benzoic acid-dye carbinol base reactions in an apolar aprotic solvent with respect to C_{HA} variations has been traced to overlapping catalysis by the monomer acid, HA and hyperacidic homoconjugated complexes, $H(A \cdots (HA)_m)$ with $m \ge 1$. The dominant catalytic role is, however, due to the monomer HA. Both the monomer acid catalytic constant, k_{α} , and the composite constant k_{cat} conform significantly to the Brønsted relation for proton transfer. The Brønsted exponent (b) for log k_{cat} versus $\log K$ correlation indicates to a degree of proton transfer as high as more than 90% in the transition state of the reactions, highlighting the role of homoconjugated acid complexes in catalyzing the reactions. Substituent effect analysis shows no significant contribution of steric factors to the catalytic constants of ortho-substituted benzoic acids. The field and resonance components contribute as 66:34 and 61:39 patterns to log k_{α} and as 61:39 and 53:47 to log k_{cat} , respectively, for meta- and ortho-substituted acids.

SUPPORTING INFORMATION

Tables S1–S23 of the Supporting Information containing the experimental overall rate constant, $k \, (\text{min}^{-1})$ versus acid concentration, C_{HA} (M) data at 28.0 \pm 0.1°C for reactions of 23 ortho- and meta-substituted benzoic acids with Crystal Violet carbinol base (the reference base) in toluene are available in the online issue at www.wileyonlinelibrary.com.

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