

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS AND FROM THE TEXAS ENGINEERING EXPERIMENT STATION, COLLEGE STATION, TEXAS]

A Hammett-Taft Polar-Steric Equation for the Saponification Rates of *m*- and *p*-Substituted Alkyl Benzoates¹

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Saponification rate constants at $35.00 \pm 0.01^\circ$ in 60 volume % aqueous dioxane have been determined for 35 *m*- and *p*-substituted alkyl benzoates. For 11 *m*- or *p*-substituted methyl benzoates, $\log k = 0.204 + 2.19\sigma$ with $r = 0.996$ and $s = 0.094$. For 11 alkyl benzoates, $\log k = 0.113 + 1.52\sigma^* + 0.620E_s^c$ with $R = 0.981$ and $s = 0.128$, where E_s^c is the steric substituent constant corrected for hyperconjugation effects. For all 35 esters (including 14 esters which are substituted simultaneously in both the alkyl position and the *m*- or *p*-position), $\log k = 0.174 + 2.22\sigma + 1.53\sigma^* + 0.668E_s^c$ with $R = 0.996$ and $s = 0.108$. It is shown conclusively that the effect of *m*- or *p*-substitution in methyl benzoate is completely independent of the effect of simultaneous substitution in the alkyl position.

For the rate constants for the reactions of diphenyldiazomethanes with benzoic acids in toluene at 25° , it has been shown² that the effect of *m*- or *p*-substitution in diphenyldiazomethane is completely independent of the effect of simultaneous *m*- or *p*-substitution in benzoic acid. For the basic wave number shifts of the 2,4-dinitrophenylhydrazones of substituted acetophenones, it is somewhat less evident³ that the effect of *m*- or *p*-substitution in acetophenone is independent of the effect of simultaneous α -substitution in the same molecule. Consequently, it was desired to investigate this matter further and the saponification rate constants of *m*- and *p*-substituted alkyl benzoates appeared promising as a related study.

In the saponification of *m*- and *p*-substituted alkyl benzoates, the rate constant is a function of Hammett's constant^{4a} σ for the *m*- or *p*-substituent and of Taft's polar constant^{5a} σ^* and steric constant^{5b} E_s for the alkyl substituent. In this reaction series, there are no hydrogens in either position α to the carbonyl group and, consequently, the rate constant is not affected by hyperconjugation⁶ (as used in the present article, "hyperconjugation" has the meaning of " α -hydrogen bonding" as proposed by Kreevoy and Eyring⁷). It was shown in the preceding article⁸ that hyperconjugation effects can be separated quantitatively from steric substituent constants by use of the equation

$$E_s^c = E_s + 0.306(n - 3) \quad (1)$$

where E_s^c is the steric substituent constant corrected for hyperconjugation effects, E_s is Taft's steric substituent constant^{5b} and n is the number of α -hydrogens. E_s^c -Values, calculated by eq. 1, should be more applicable to the reaction series of this article than are E_s -values.

(1) Abstracted from the M.S. thesis of C. P. F., The A. and M. College of Texas, August, 1960.

(2) C. K. Hancock and J. S. Westmoreland, *J. Am. Chem. Soc.*, **80**, 545 (1958); C. K. Hancock, R. F. Gilby, Jr., and J. S. Westmoreland, *ibid.*, **79**, 1917 (1957).

(3) L. E. Scoggins and C. K. Hancock, *J. Org. Chem.*, **26**, 3490 (1961).

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940: (a) p. 188, (b) p. 189.

(5) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956: (a) p. 619, (b) p. 598.

(6) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(7) M. M. Kreevoy and H. Eyring, *ibid.*, **79**, 5121 (1957).

(8) C. K. Hancock, E. A. Meyers and B. J. Yager, *ibid.*, **83**, 4211 (1961).

Saponification rate constants at 35° in 60 volume % aqueous dioxane (60 volumes of dioxane diluted with deionized water to 100 volumes) have been determined by a conductivity method for methyl benzoate, ten *m*- or *p*-substituted methyl benzoates, ten alkyl benzoates and fourteen *m*- or *p*-substituted alkyl benzoates. The resulting rate constants and corresponding substituent constants are given in Tables I, II and III.

TABLE I
SAPONIFICATION RATE CONSTANTS AT 35° IN 60 VOLUME % AQUEOUS DIOXANE AND SUBSTITUENT CONSTANTS FOR *m*- AND *p*-SUBSTITUTED METHYL BENZOATES

R ₁	$M^{-1} \text{ min.}^{-1}$	σ^a	R ₁	$M^{-1} \text{ min.}^{-1}$	σ^a
<i>p</i> -NH ₂	0.0612	-0.660	<i>m</i> -I	6.73	0.352
<i>p</i> -CH ₃ O	.420	-.268	<i>m</i> -Cl	9.13	.373
<i>p</i> -CH ₃	.754	-.170	<i>m</i> -Br	8.63	.391
<i>m</i> -CH ₃	.982	-.069	<i>m</i> -NO ₂	62.6	.710
H	1.74	.000	<i>p</i> -NO ₂	102	.778
<i>p</i> -Br	6.64	.232			

^a Ref. 4a.

TABLE II
SAPONIFICATION RATE CONSTANTS AT 35° IN 60 VOLUME % AQUEOUS DIOXANE AND SUBSTITUENT CONSTANTS FOR ALKYL BENZOATES

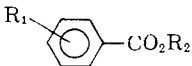
R ₂	$k, M^{-1} \text{ min.}^{-1}$	σ^{*a}	E_s^c ^b	E_s ^c
CH ₃	1.74	0.000	0.00	0.00
C ₂ H ₅	0.553	-.100	-.38	-.07
<i>n</i> -C ₃ H ₇	.379	-.115	-.67	-.36
<i>i</i> -C ₃ H ₇	.0919	-.190	-1.08	-.47
<i>n</i> -C ₄ H ₉	.289	-.130	-0.70	-.39
<i>i</i> -C ₄ H ₉	.240	-.125	-1.24	-.93
<i>s</i> -C ₄ H ₉	.0468	-.210	-1.74	-1.13
<i>i</i> -C ₅ H ₁₁	.234	-.162 ^d	-0.66	-0.35
C ₆ H ₅ CH ₂	.960	.215	-.69	-.38
C ₆ H ₅ (CH ₂) ₂	.504	.080	-.69	-.38
(C ₂ H ₅) ₂ CH	.0162	-.225	-2.59	-1.98

^a Ref. 5a. ^b Ref. 8. ^c Ref. 5b. ^d Ref. 9.

In order to determine the effect of varying *m*- or *p*-substituents, the data of Table I were sub-

(9) A. B. Hoefelmeyer and C. K. Hancock, *ibid.*, **77**, 4746 (1955).

TABLE III
 SAPONIFICATION RATE CONSTANTS AT 35° IN 60 VOLUME % AQUEOUS DIOXANE AND SUBSTITUENT CONSTANTS FOR *m*- AND *p*-SUBSTITUTED ALKYL BENZOATES



R ₁	R ₂	<i>k</i> , M ⁻¹ min. ⁻¹	σ ^a	σ ^{*b}	E _s ^c	E _s ^d
<i>p</i> -CH ₃ O	<i>i</i> -C ₃ H ₇	0.0235	-0.268	-0.190	-1.08	-0.47
<i>p</i> -CH ₃ O	C ₂ H ₅	.134	-.268	-.100	-0.38	-.07
<i>p</i> -F	C ₂ H ₅	.996	.062	-.100	-.38	-.07
<i>m</i> -NO ₂	C ₂ H ₅	19.3	.710	-.100	-.38	-.07
<i>p</i> -NO ₂	C ₂ H ₅	33.0	.778	-.100	-.38	-.07
3,5-(NO ₂) ₂	C ₂ H ₅	998	1.420	-.100	-.38	-.07
<i>p</i> -CH ₃	C ₆ H ₅ CH ₂	0.397	-0.170	.210	-.69	-.38
<i>p</i> -NO ₂	<i>i</i> -C ₃ H ₇	7.56	.778	-.190	-1.08	-.47
<i>p</i> -NH ₂	C ₂ H ₅	0.0194	-.660	-.100	-0.38	-.07
<i>p</i> -NH ₂	<i>i</i> -C ₄ H ₉	.00934	-.660	-.125	-1.24	-.93
<i>p</i> -NH ₂	<i>n</i> -C ₄ H ₉	.0104	-.660	-.130	-0.70	-.39
<i>p</i> -Cl	<i>n</i> -C ₃ H ₇	1.38	.227	-.115	-.67	-.36
<i>p</i> -Cl	<i>i</i> -C ₃ H ₇	0.883	.227	-.162 ^e	-.66	-.35
<i>m</i> -CH ₃	<i>s</i> -C ₄ H ₉	0.0288	-.069	-.210	-1.74	-1.13

^a Ref. 4a. ^b Ref. 5a. ^c Ref. 8. ^d Ref. 5b. ^e Ref. 9.

mitted to linear^{10a} regression analysis to obtain

$$\log k = 0.204 + 2.19\sigma \quad (2)$$

with a linear correlation coefficient *r* of 0.996 and a standard deviation from regression *s* of 0.094. In eq. 2, the parameter 0.204 is the regression value for log *k*^o for unsubstituted methyl benzoate and 2.19 is Hammett's reaction constant^{4b} ρ for this reaction series. It is apparent that the effect of *m*- or *p*-substitution is expressed quite closely by eq. 2.

The effect of varying alkyl substituents was determined by multiple^{10b} regression analysis of the data of Table II. Using hybrid E_s^{5b}-values, the analysis gives the fair relation

$$\log k = -0.042 + 1.84\sigma^* + 0.695E_s \quad (3)$$

(0.010) (0.001)

with a multiple correlation coefficient, *R*, of 0.951 and *s* = 0.202. In eq. 3, the parameter 1.84 is the polar reaction constant ρ* and 0.695 is the steric reaction constant δ. The numbers in parentheses below the last two parameters of eq. 3 are the significance levels as determined by "Student's" *t*-tests.^{10c}

Replacing E_s-values with corrected steric substituent constants⁸ E_s^c there results the much-improved relation

$$\log k = 0.113 + 152\sigma^* + 0.620E_s^c \quad (4)$$

(0.003) (0.001)

with *R* = 0.981 and *s* = 0.128. Equations 3 and 4 are directly comparable since they involve the same number of variables and degrees of freedom. Consequently, comparing *R*- and *s*-values and significance levels of the parameters, it is apparent that eq. 4 provides a better fit for the data. This is as it should be since there can be no hyperconjugation, and E_s^c-values result from the quantitative separation of hyperconjugation effects from steric substituent constants. The hybrid E_s-values include a contribution from hyperconjugation and, there-

fore, should be less applicable to reaction series in which there is no hyperconjugation effect.

For the combined data of Tables I and II, analysis of the multiple regression^{10b} of log *k* on σ, σ* and E_s^c gives

$$\log k = 0.174 + 2.22\sigma + 1.51\sigma^* + 0.664E_s^c \quad (5)$$

with *R* = 0.994 and *s* = 0.116. This equation is almost identical to, and certainly is not significantly different from, the following equation obtained from multiple regression analysis of the data of Table III.

$$\log k = 0.190 + 2.23\sigma + 1.54\sigma^* + 0.692E_s^c \quad (6)$$

with *R* = 0.998 and *s* = 0.114. The close agreement between eq. 5 and 6 strongly indicates that the effect of *m*- or *p*-substitution in methyl benzoate is completely independent of the effect of simultaneous substitution in the alkyl portion. This indication is further substantiated by the following. Using eq. 5, log *k*-values were calculated for the 14 disubstituted esters listed in Table III. For these 14 esters, the average deviation of the calculated log *k*-values from experimental log *k*-values is only 0.077 log unit for a range in experimental log *k*-values of 5.082 log units.

This independence of effects of dual substitution was tested further by inclusion of possibly pertinent interaction factors.¹¹ For the combined data of Tables I, II and III (total of 35 esters), the analysis of the multiple regression of log *k* on σ, σ*, E_s^c, σ·σ* and σ·E_s^c gives

$$\log k = 0.169 + 2.22\sigma + 1.44\sigma^* + 0.684E_s^c - 1.45\sigma\cdot\sigma^* + 0.287\sigma\cdot E_s^c \quad (7)$$

(0.001) (0.001) (0.001) (0.400) (0.200)

with *R* = 0.997 and *s* = 0.108. Significance levels of the parameters, in parentheses, as given by "Student's" *t*-tests,^{10c} show that the interaction factor, σ·σ*, makes no contribution. The multiple regression analysis involving the remaining four

(10) G. W. Snedecor, "Statistical Methods," 5th ed., The Iowa State College Press, Ames, Iowa, 1956: (a) Chap. 6, (b) Chap. 14, (c) pp. 46, 418 and 441.

(11) S. I. Miller, *J. Am. Chem. Soc.*, **81**, 101 (1959).

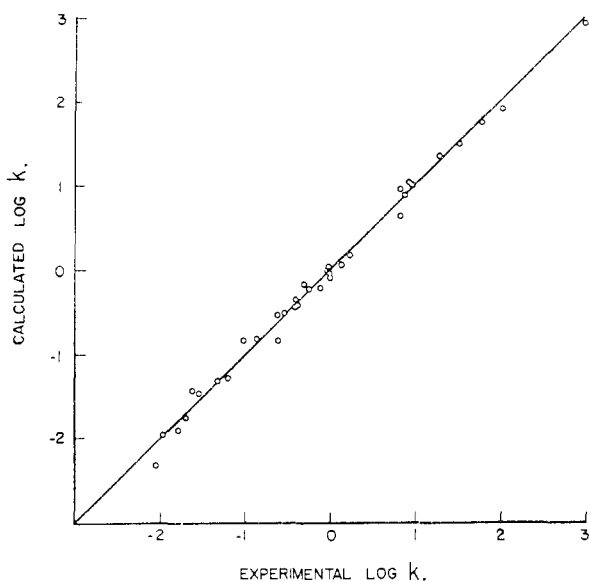


Fig. 1.—Quantitative relationship between experimental log k -values and log k -values calculated from eq. 9 for the saponification of 35 m - and p -substituted alkyl benzoates.

independent variables gives

$$\log k = 0.171 + 2.26\sigma + 1.51\sigma^* + 0.669E_s^c + 0.008\sigma \cdot E_s^c \quad (8)$$

(0.001) (0.001) (0.001) (0.500)

with $R = 0.996$ and $s = 0.108$. From eq. 8, it is evident that the other interaction factor, $\sigma \cdot E_s^c$, makes no contribution either.

Finally, for the combined data of Tables I, II and III, multiple regression analysis gives

$$\log k = 0.174 + 2.22\sigma + 1.53\sigma^* + 0.668E_s^c \quad (9)$$

(0.001) (0.001) (0.001)

with $R = 0.996$ and $s = 0.108$. Equation 9 is almost identical to equations 5 and 6 but is slightly more reliable since it is based on more data. The excellent quantitative relationship given by eq. 9 is shown in Fig. 1.

Experimental

Materials.—The esters were purchased from commercial sources or were prepared by well-known methods. Liquid esters were purified as described previously⁸ while solid esters were purified by recrystallization and dried *in vacuo*. The following three prepared esters were not found in the literature.

3-Pentyl benzoate was prepared by adding benzoyl chloride to a mixture of anhydrous 3-pentanol and pyridine,¹² b.p. 196° at 2.5–3 mm., n_D^{25} 1.4909. *Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; sapon. equiv., 192.26. Found: C, 74.68¹³; H, 8.42¹³; sapon. equiv., 192.33.

sec-Butyl *m*-toluate was prepared as above, b.p. 99–102° at 2.5–3 mm., n_D^{20} 1.4965. *Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; sapon. equiv., 192.26. Found: C, 74.46¹³; H, 8.44¹³; sapon. equiv., 191.19.

Isoamyl *p*-chlorobenzoate was prepared by H_2SO_4 -catalyzed direct esterification; b.p. 122–124° at 3 mm., n_D^{25} 1.5056. *Anal.* Calcd. for $C_{12}H_{15}ClO_2$: C, 63.58; H, 6.67; Cl, 15.64; sapon. equiv., 226.70. Found: C, 63.61¹⁴; H, 6.74¹⁴; Cl, 15.68¹⁴; sapon. equiv., 227.04.

Dioxane was purified as described previously.⁸ Due to limited solubility of some of the esters in lower concentrations of dioxane, it was necessary to use 60 volume % aqueous dioxane (60 volumes of dioxane diluted with deionized water to 100 volumes) in determination of the saponification rate constants.

Determination of Saponification Rate Constants at 35.00 ± 0.01°.—The method used was described previously.⁸ However, for the three fastest reactions, it was necessary to pour the ester and sodium hydroxide solutions quickly into a large test-tube and then immediately immerse a dipping conductivity cell into the reaction mixture in order to follow the reaction.

Duplicate rate constant determinations were made on 27 of the esters and three to five determinations on the other eight esters. The precision of the determinations was comparable to that reported previously.⁸

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(12) J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.*, **54**, 2088 (1932).

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Carbonium Ion Stabilization by Metallocene Nuclei. III. Evidence for Metal Participation¹

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The solvolytic behavior of diastereomeric ferrocenylcarbonyl acetates has been examined and is interpreted as indicating a direct bonding of the metal atom to the cationic carbon of the α -metallocenylcarbonium ions.

Introduction

In the first paper of this series² the unusual reactivity of carbonyl acetates with adjacent metallocenyl substituents was discussed. It had been proposed earlier³ that direct interaction be-

tween electrons of the metal component of the metallocene group and the carbonium ion center was an important factor in stabilizing certain α -metallocenyl carbonium ions. The purpose of this paper is to present additional stereochemical and solvolytic data to support this proposal.

When substituents are located in *ortho* positions of a benzene derivative, steric effects between the

(1) Supported in part by a grant from the National Science Foundation and the Paint Research Institute.

(2) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961).

(3) J. H. Richards and E. A. Hill, *ibid.*, **81**, 3484 (1959).