

Steric Effects. II. Base-Catalyzed Ester Hydrolysis

Marvin Charton

Contribution from the Department of Chemistry, School of Science,
Pratt Institute, Brooklyn, New York 11205.

Received November 13, 1974

Abstract: Correlation of eight sets of rate constants for base-catalyzed hydrolysis of XCO_2R , where X is alkyl with the equation, $\log k_X = \alpha\sigma_{1X} + \beta\sigma_{RX} + \psi_{vX} + h$, shows that electrical effects of alkyl groups are unimportant in this reaction. Correlation of 13 sets of rate constants for XCO_2R , where R is alkyl with the equation, $\log k_X = \psi_{BvX} + h$, gave excellent results. Comparison of the ψ_B values with the ψ_A values previously obtained shows that the basic assumption of Taft in his separation of polar and steric effects is unwarranted; it is at best an approximation. It has also been shown that the σ^* values for alkyl groups are actually related to the v steric parameters by the equation, $\sigma^*_X = mv_X + c$, and that the electrical effects of alkyl groups certainly with respect to base-catalyzed ester hydrolysis are essentially constant.

In his separation of polar and steric effects, Taft¹ makes the assumption that the steric effect upon the esterification of carboxylic acids or the acid-catalyzed hydrolysis of their esters is of the same magnitude as the steric effect upon the base-catalyzed hydrolysis of the esters. This assumption is basic to the Taft separation of electrical and steric effects. Its verification is of the greatest significance. Previous efforts at solving this problem have been reviewed in detail by Shorter.² We may represent the acid-catalyzed hydrolysis or esterification of carboxylic acids which has been shown to depend only upon the steric effect of substituents³ as

$$\log k_X = \psi_{AvX} + h_A \quad (1)$$

The effect of substituents on the base-catalyzed hydrolysis of esters can be represented by eq 2. In these equations, v is a steric parameter related to the Van der Waals radius of X, while σ_1 and σ_R are measures of the localized and delocalized electrical effects of the group X. What we wish to determine then, is whether ψ_A is equal to ψ_B . If they are not significantly different, the Taft assumption is justified

whereas, if they are significantly different, the Taft assumption must be in error. To test the assumption, it is necessary to determine values of ψ_A and ψ_B . Values of ψ_A are available from our previous work;³ values of ψ_B are determined here. We first examine the application of eq 2 to various sets of base-catalyzed hydrolysis of esters. In the sets studied, which are reported in Table I, only alkyl substituents are present. Results of the correlations with eq 2 are set forth in Table II. Values of σ_1 are taken from our collection.⁴ Values of σ_R were obtained from eq 3. The necessary σ_p values are from McDaniel and Brown.⁵ Values of v are from our previous work. The Et_2CH substituents in sets 1-3 and 6-8 were excluded from the correlations with eq 2 as σ_1 and σ_R constants were not available for this substituent. Lack of availability of substituent constants also prevented the correlation of sets 9-13 with eq 2.

$$\log k_X = \alpha\sigma_{1X} + \beta\sigma_{RX} + \psi_{BvX} + h_B \quad (2)$$

$$\sigma_R = \sigma_p - \sigma_1 \quad (3)$$

Inspection of the results in Table II reveals that α and β

Table I. Data used in Correlations

1	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 70% v/v MeAc-H ₂ O at 24.8 ^a Me, 4.65; Et, 2.20; Pr, 0.881; Bu, 0.659; BuCH ₂ CH ₂ , 0.608; <i>i</i> -Pr, 0.550; <i>i</i> -PrCH ₂ , 0.218; <i>t</i> -Bu, 0.0223; Et ₂ CH, 0.0083	8	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 85% w/w EtOH-H ₂ O at 50 ^d Me, 38.7; Et, 24.7; Pr, 12.2; <i>i</i> -Pr, 5.72; Bu, 13.3; <i>i</i> -PrCH ₂ , 3.34; <i>s</i> -Bu, 2.36; <i>t</i> -Bu, 0.241; BuCH ₂ , 14.5; Et ₂ CH, 0.154; BuCH ₂ CH ₂ , 12.7; BuCH ₂ CH ₂ CH ₂ , 13.3
2	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 70% v/v MeAc-H ₂ O at 35 ^a Me, 8.22; Et, 4.06; Pr, 1.68; Bu, 1.33; BuCH ₂ CH ₂ , 1.19; <i>i</i> -Pr, 1.03; <i>i</i> -PrCH ₂ , 0.450; <i>t</i> -Bu, 0.0456; Et ₂ CH, 0.0184	9	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 85% w/w EtOH-H ₂ O at 25 ^e Ph(CH ₂) ₃ , 2.69; Ph(CH ₂) ₄ , 2.28; <i>c</i> -C ₆ H ₁₁ CH ₂ , 0.509; <i>i</i> -PrCH ₂ - CH ₂ , 1.86; <i>s</i> -BuCH ₂ , 0.411; Et ₂ CH, 0.0154; Pr ₂ CH, 0.0106; Bu ₂ CH, 0.0100; Me, 6.92; Et, 3.55; Pr, 1.83; <i>c</i> -C ₆ H ₁₁ , 0.360
3	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 70% v/v MeAc-H ₂ O at 44.7 ^a Me, 13.5; Et, 6.83; Pr, 2.99; Bu, 2.45; BuCH ₂ CH ₂ , 2.21; <i>i</i> -Pr, 1.80; <i>i</i> -PrCH ₂ , 0.863; <i>t</i> -Bu, 0.0874; Et ₂ CH, 0.0371	10	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 85% w/w EtOH-H ₂ O at 35 ^e Ph(CH ₂) ₃ , 6.19; Ph(CH ₂) ₄ , 5.21; <i>c</i> -C ₆ H ₁₁ CH ₂ , 1.20; <i>i</i> -PrCH ₂ CH ₂ , 4.31; <i>s</i> -BuCH ₂ , 0.963; Et ₂ CH, 0.0384; Pr ₂ CH, 0.0282; Bu ₂ CH, 0.0255; Pr, 4.25; <i>c</i> -C ₆ H ₁₁ , 0.848
4	k , $\text{XCO}_2\text{CH}_2\text{Ph} + \text{OH}^-$ in 56% w/w MeAc-H ₂ O at 25 ^b H, 25.83; Me, 0.06960; Et, 0.03428; Pr, 0.01774; Bu, 0.01370; <i>i</i> -PrCH ₂ , 0.004457; BuCH ₂ , 0.01143; BuCH ₂ CH ₂ CH ₂ , 0.01125	11	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 85% w/w EtOH-H ₂ O at 45 ^e Ph(CH ₂) ₃ , 13.2; Ph(CH ₂) ₄ , 11.3; <i>c</i> -C ₆ H ₁₁ CH ₂ , 2.66; <i>i</i> -PrCH ₂ CH ₂ , 9.04; <i>s</i> -BuCH ₂ , 2.20; Et ₂ CH, 0.0968; Pr ₂ CH, 0.0656; Bu ₂ CH, 0.0635; Pr, 9.18; <i>c</i> -C ₆ H ₁₁ , 1.92
5	k , $\text{XCO}_2\text{Me} + \text{OH}^-$ in 40% dioxane-water at 35 ^c Me, 19.3; Et, 14.7; Pr, 7.44; <i>i</i> -Pr, 5.23; Bu, 5.96; <i>i</i> -PrCH ₂ , 2.12; <i>s</i> -Bu, 1.49; <i>t</i> -Bu, 0.676	12	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 85% w/w EtOH-H ₂ O at 55 ^e Ph(CH ₂) ₃ , 26.8; Ph(CH ₂) ₄ , 21.9; <i>c</i> -C ₆ H ₁₁ CH ₂ , 5.65; <i>i</i> -PrCH ₂ CH ₂ , 18.9; <i>s</i> -BuCH ₂ , 4.65; Et ₂ CH, 0.215; Pr ₂ CH, 0.154; Bu ₂ CH, 0.153; Pr, 19.0; <i>c</i> -C ₆ H ₁₁ , 4.03
6	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 85% w/w EtOH-H ₂ O at 25 ^d Me, 6.21; Et, 3.63; Pr, 1.72; <i>i</i> -Pr, 0.801; Bu, 1.92; <i>i</i> -PrCH ₂ , 0.427; <i>s</i> -Bu, 0.308; <i>t</i> -Bu, 0.0254; BuCH ₂ , 2.07; Et ₂ CH, 0.0157; BuCH ₂ CH ₂ , 1.79; BuCH ₂ CH ₂ CH ₂ , 1.84	13	k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 87.8% w/w EtOH-H ₂ O at 30 ^f Bu(CH ₂) ₄ , 0.134; <i>i</i> -Pr, 0.0483; <i>t</i> -Bu, 0.00505; Me, 0.481; Et, 0.226; Pr, 0.132; Bu, 0.126; BuCH ₂ , 0.131
7	10^3k , $\text{XCO}_2\text{Et} + \text{OH}^-$ in 85% w/w EtOH-H ₂ O at 35 ^d Me, 13.6; Et, 8.31; Pr, 3.94; <i>i</i> -Pr, 1.84; Bu, 4.42; <i>i</i> -PrCH ₂ , 1.02; <i>s</i> -Bu, 0.735; <i>t</i> -Bu, 0.0635; BuCH ₂ , 4.81; Et ₂ CH, 0.0409; BuCH ₂ CH ₂ , 4.06; BuCH ₂ CH ₂ CH ₂ , 4.30		

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Table II. Results of Correlations with Equation 2

Set	α	β	ψ	h	r^a	F^b	r_{12}^c	r_{13}^c	r_{23}^c
1	-2.29	4.70	-2.89	2.41	0.985	43.41 ^g	0.495	0.367	0.158
2	-1.79	4.72	-2.80	2.65	0.986	46.37 ^g	0.495	0.367	0.158
3	-1.09	4.52	-2.70	2.83	0.986	46.67 ^g	0.495	0.367	0.158
4	-1.34	10.7	-2.98	1.38	0.993	96.20 ^f	0.897 ⁱ	0.581	0.762 ^l
5	4.50	-4.22	-1.93	1.94	0.983	49.15 ^f	0.287	0.228	0.0845
6	2.03	3.55	-2.96	2.80	0.982	62.82 ^f	0.578	0.166	0.054
7	1.75	3.76	-2.90	3.14	0.982	61.53 ^f	0.578	0.166	0.054
8	1.43	3.53	-2.76	3.48	0.981	60.52 ^f	0.578	0.166	0.054

Set	s_{est}^d	s_{α}^d	s_{β}^d	s_{ψ}^d	s_h^d	n^e
1	0.158	5.27 ^p	4.58 ^o	0.273 ^f	0.482 ^h	8
2	0.149	4.97 ^p	4.31 ^o	0.257 ^f	0.454 ^h	8
3	0.144	4.80 ^q	4.17 ^o	0.249 ^f	0.439 ^h	8
4	0.183	9.13 ^q	5.26 ⁿ	0.409 ^h	0.180 ^h	8
5	0.122	1.52 ^k	2.52 ⁿ	0.187 ^f	0.336 ^h	9
6	0.148	4.37 ^p	3.96 ^o	0.225 ^f	0.422 ^f	11
7	0.146	4.32 ^p	3.91 ^o	0.222 ^f	0.417 ^f	11
8	0.140	4.15 ^p	3.75 ^o	0.213 ^f	0.400 ^f	11

^a Multiple correlation coefficient. ^b F test for significance of regression. Superscripts indicate confidence levels. ^c Partial correlation coefficient of σ_I on σ_R , σ_I on ν , σ_R on ν . ^d Standard errors of the estimate, α , β , ψ , and h . Superscripts indicate confidence level of "Student t " test. ^e Number of points in the set. ^f 99.9% confidence level (CL). ^g 99.5% CL. ^h 99.0% CL. ⁱ 98.0% CL. ^j 97.5% CL. ^k 95.0% CL. ^l 90.0% CL. ^m <90% CL. ⁿ 80.0% CL. ^o 50% CL. ^p 20% CL. ^q <20.0% CL. The confidence level of the partial correlation coefficients is less than 90% unless otherwise indicated.

Table III. Results of Correlation with Equation 4

Set	ψ	h	r^a	F^b	s_{est}^c	s_{ψ}^c	s_h^c	n^d
1	-2.65	1.80	0.987	262.3 ^e	0.153	0.164 ^e	0.149 ^e	9
2	-2.57	2.03	0.987	262.6 ^e	0.149	0.159 ^e	0.144 ^e	9
3	-2.50	2.22	0.987	264.5 ^e	0.144	0.154 ^e	0.139 ^e	9
4	-4.10	1.09	0.968	90.64 ^e	0.319	0.430 ^e	0.283 ^f	8
5	-1.98	2.23	0.992	387.9 ^e	0.0666	0.100 ^e	0.0842 ^e	8
6	-2.72	2.15	0.982	271.7 ^e	0.161	0.165 ^e	0.146 ^e	12
7	-2.66	2.46	0.981	261.1 ^e	0.160	0.164 ^e	0.145 ^e	12
8	-2.53	2.86	0.982	266.5 ^e	0.151	0.155 ^e	0.137 ^e	12
9	-2.63	2.13	0.993	692.6 ^e	0.129	0.0999 ^e	0.101 ^e	12
10	-2.58	2.45	0.992	477.7 ^e	0.133	0.118 ^e	0.127 ^e	10
11	-2.51	2.74	0.991	463.4 ^e	0.131	0.117 ^e	0.126 ^e	10
12	-2.44	2.99	0.992	466.6 ^e	0.127	0.113 ^e	0.122 ^e	10
13	-2.61	0.880	0.984	178.0 ^e	0.115	0.196 ^e	0.148 ^e	8

^a Correlation coefficient. ^b F test for significance of the correlation. ^c Standard errors of the estimate, ψ , and h . ^d Number of points in the set. ^e 99.9% CL (confidence level). ^f 99.0% CL.

Table IV. Solvents and Temperatures for the Comparison of ψ_A and ψ_B^a

System	Acidic Hydrolysis		Basic Hydrolysis		Set
	Solvent	T	Solvent	T	
A	70% v/v MeAc-H ₂ O	24.8	70% v/v MeAc-H ₂ O	24.8	1
B	70% v/v MeAc-H ₂ O	35	70% v/v MeAc-H ₂ O	35	2
C	70% v/v MeAc-H ₂ O	44.7	70% v/v MeAc-H ₂ O	44.7	3
D	70% v/v MeAc-H ₂ O	25	70% v/v MeAc-H ₂ O	24.8	1
E	60% MeAc-H ₂ O	25	56% w/w MeAc-H ₂ O	25	4
F ₁	EtOH	25	85% w/w EtOH-H ₂ O	25	6
F ₂	EtOH	25	85% w/w EtOH-H ₂ O	25	9
G ₁	60% v/v EtOH-H ₂ O	24.86	85% w/w EtOH-H ₂ O	25	6
G ₂	60% v/v EtOH-H ₂ O	24.86	85% w/w EtOH-H ₂ O	25	9

^a The substrate is XCO₂Et unless otherwise noted. In system E, in basic hydrolysis, the substrate is XCO₂CH₂Ph and, in systems F₁, F₂, in acidic hydrolysis, the substrate is XCO₂H.

Table V. Comparison of ψ_A and ψ_B

System	ψ_A	s_{ψ_A}	ψ_B	s_{ψ_B}	$\Delta\psi$	t_A	t_B	n_A	n_B
A	-2.06	0.0784	-2.65	0.164	-0.59	7.526 ^a	3.598 ^b	9	9
B	-1.98	0.0770	-2.57	0.159	-0.59	7.662 ^a	3.711 ^b	9	9
C	-1.82	0.0743	-2.50	0.154	-0.68	9.152 ^a	4.416 ^b	9	9
D	-2.49	0.112	-2.65	0.164	-0.16	1.429 ^c	0.976 ^d	11	9
E	-2.36	0.0522	-4.10	0.430	-1.74	33.33 ^a	4.047 ^b	4	8
F ₁	-2.48	0.0705	-2.72	0.165	-0.24	3.404 ^c	1.455 ^c	3	12
F ₂	-2.48	0.0705	-2.63	0.0999	-0.15	2.128 ^d	1.502 ^c	3	12
G ₁	-1.12	0.155	-2.72	0.165	-1.60	10.32 ^e	9.697 ^a	3	12
G ₂	-1.12	0.155	-2.63	0.0999	-1.51	9.742 ^e	15.11 ^a	3	12

^a Superscripts indicate confidence levels of "Student t " tests for the significance of the difference between ψ_A and ψ_B . ^a 99.9% CL. ^b 99.0% CL. ^c 80% CL. ^d 50% CL. ^e 90.0% CL.

are generally not significant for these sets. We have therefore correlated the data with the modified Taft equation (eq 4). Results for these correlations are given in Table III. All of the sets studied gave excellent results; correlations were significant at the 99.9% confidence level. Best results were obtained for sets 1-3 and 6-12 when the value³ 1.51 was used for ν for Et₂CH.

$$\log k_X = \psi_{B\nu X} + h_B \quad (4)$$

The Taft assumption may now be tested. Table IV contains the substrates, solvents, and temperatures for acidic and basic hydrolysis of esters under comparable conditions. In Table V are values of $\Delta\psi$ and t_A and t_B , the latter of which are "Student *t*" tests for the significance of the difference between ψ_A and ψ_B . Inspection of the results in Table V shows that, in most of the systems studied, ψ_A and ψ_B are significantly different from each other. We are forced to the conclusion that the Taft assumption is incorrect. Supporting this conclusion is the fact that all of the $\Delta\psi$ values have the same sign. Had the differences in $\Delta\psi$ been due to experimental error, we would have expected that there would be as many positive $\Delta\psi$ values as there were negative $\Delta\psi$ values. There are two possible explanations for the difference between ψ_A and ψ_B . In the first of these, we note that all of the $\Delta\psi$ values are negative which suggests that the steric effect is greater in the case of the base-catalyzed hydrolyses than it is in the case of the acid-catalyzed hydrolyses. This is particularly interesting in view of the point made by Taft that the intermediate in acid-catalyzed hydrolysis differed from that in base-catalyzed hydrolysis by the presence of two additional protons. If both transition states were equally close to the intermediate (which is more hindered than the reactant), then the acid-catalyzed reaction should be somewhat more sterically hindered than the base-catalyzed reaction. Since this is not the case, it may be that the transition state in the base-catalyzed reaction is closer to the intermediate than is the transition state in the acid-catalyzed reaction.

The alternative explanation is that the difference between ψ_A and ψ_B is caused by a difference in the extent to which the two transition states are solvated. As the acid-catalyzed hydrolysis transition state bears a positive charge, and the base-catalyzed transition state bears a negative charge, and the reactions have been studied in polar solvents, this would not be at all surprising.⁶

We believe we have also shown in this work that the electrical effects of alkyl groups are essentially constant. This is in agreement with the observed σ_I and σ_R values of simple alkyl groups which are constant within experimental error. It seems to us that the existence of different values of σ^* for alkyl groups is probably an artifact.⁷ We believe that the existence of different σ^* values for alkyl groups can be explained, at least in part, as follows. From eq 4 we may write for alkyl substituents the following relationships for basic hydrolysis of esters

$$\log k_{XB} = \psi_{B\nu X} + h_B \quad (5)$$

$$\log k_{MeB} = \psi_{B\nu Me} + h_B \quad (6)$$

while for acidic hydrolysis, we may write the equations

$$\log k_{XA} = \psi_{A\nu X} + h_A \quad (1)$$

$$\log k_{MeA} = \psi_{A\nu Me} + h_A \quad (7)$$

According to Taft¹

$$\sigma^*_X = (1/2.48)[\log(k_X/k_{Me})_B - \log(k_X/k_{Me})_A] \quad (8)$$

From equations 1, 3, 4, and 5, we obtain

$$\sigma^*_X = (1/2.48)(\psi_{B\nu X} + h_B - \psi_{B\nu Me} - h_B - \psi_{A\nu X} - h_A + \psi_{A\nu Me} + h_A) \quad (9)$$

$$= (1/2.48)[\psi_{B\nu X} - \psi_{A\nu X} - (\psi_{B\nu Me} - \psi_{A\nu Me})] \quad (10)$$

$$= (1/2.48)(\Delta\psi_{\nu X} - \Delta\psi_{\nu Me}) \quad (11)$$

$$= (1/2.48)\Delta\psi(\nu_X - \nu_{Me}) \quad (12)$$

Then

$$\sigma^*_X = m\nu_X + c \quad (13)$$

We have taken σ^* constants from the compilation of Taft¹ and correlated them with eq 13. The ν constants are from our collection.³ The σ^* constants used were Me, 0; Et, -0.10; Pr, -0.115; *i*-Bu, -0.125; Bu, -0.13; *t*-BuCH₂, -0.165; *i*-Pr, -0.19; Et₂CH, -0.225; *t*-Bu, -0.30; *s*-Bu, -0.21; *c*-C₆H₁₁CH₂, -0.06; *c*-C₆H₁₁, -0.15; *t*-BuMeCH, -0.28. The results of the correlation with eq 13 are m , -0.139; c , -0.164; correlation coefficient, 0.732; F test for significance of regression, 12.68 (confidence level 99.5%); standard errors of the estimate, m , and c (CL in parentheses) 0.0599; 0.0390 (99.0%), and 0.0430 (20.0%); number of points in data set, 13. The results are obviously significant, and eq 13 is validated. It must be noted, however, that the correlation coefficient squared, which measures that fraction of the data accounted for by the correlation equation is 0.5358. Thus, about 46% of the data is unaccounted for. A possible explanation of this is as follows. In the calculation of σ^* constants from eq 8, Taft made use of average values of $\log(k_X/k_{Me})_B$ and $\log(k_X/k_{Me})_A$. As not all the substituents studied were present in all the data sets used as sources of k values, the composition of the average values of $\log(k_X/k_{Me})$ used varies with substituents. Since $\Delta\psi$ depends on the particular system chosen, the σ^* values reported by Taft will include varying values of $\Delta\psi$.

In conclusion, we feel that we have established two vital points regarding the Taft separation of electrical and steric effects. (1) The Taft assumption that steric effects are identical in esterification and acid catalyzed ester hydrolysis and in base-catalyzed ester hydrolysis is at best an approximation and is frequently false. (2) Alkyl groups do not differ significantly in their electrical effects, certainly in base catalyzed ester hydrolysis and probably in general. The σ^* values of alkyl groups do not reflect differences in electrical effects but rather involve steric factors.

References and Notes

- (1) R. W. Taft in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 556.
- (2) J. Shorter in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Ed., Plenum Press, New York, N.Y., 1973, p 71.
- (3) M. Charton, *J. Am. Chem. Soc.*, **97**, 1552 (1975).
- (4) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).
- (5) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
- (6) This explanation was called to our attention by Professor Robert W. Taft.
- (7) The constancy of σ_I values and the variance of σ^* values for alkyl groups must be reconciled

$$\sigma^*_X = 5.92 \sigma_X + 0.096$$

(M. Charton, unpublished results). Thus, the σ^* scale may be considered to be an expanded σ_I scale. Substituents which have essentially the same σ_I constants appear to have different σ^* constants. To the extent that the differences in σ^* are real, we attempt here to account for them.