Taft σ* Constants, particularly for Halogen-substituted Alkyl Groups, and their Utility in Mechanistic Studies

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To verify the Taft σ* values, data from several reaction series were fitted to the equation log $k = \rho^*\sigma^* + \log k_0$. The calculated σ* values were in good agreement with each other, but certain substituents, especially hydrogen, behave differently in some reaction series. On the basis of the $\sigma^*(CCl_3)$ values obtained from the different reaction series, it is concluded that the acid-catalysed esterification of trichloroacetic acid in an alcohol solution takes place by the normal $A_{AC}2$ mechanism, although the acid-catalysed hydrolysis of ethyl trichloroacetate in aqueous solutions mainly proceeds by the exceptional A–$B_{AC}3$ mechanism. In the case of simultaneous reactions, the Ingold–Taft equation can be employed to estimate the contribution of the normal $A_{AC}2$ mechanism.

Taft σ* constants (originally marked[1] E_σ) were defined[1] by the Ingold–Taft equation (1), where ρ* is a reaction constant

$$\rho^*\sigma^* = [\log(k/k_0)]_B - [\log(k/k_0)]_A \qquad (1)$$

measuring the susceptibility of the reaction series to polar substituents; k/k_0 is the relative rate of hydrolysis or esterification for a substituent of an *o*-substituted benzoate or aliphatic ester reaction series; and the subscripts refer to identical acid- and base-catalysed reaction series, respectively. Later the value 2.48 was given for ρ* to put the polar effects obtained in this manner on about the same scale as for the Hammett σ values.[2,3] The σ* constants are subsequently generally employed as a measure for polar effects in aliphatic compounds, although their significance is often questioned[4,5] but also defended.[6,7]

A necessary criterion for equation (1) to be valid is that the reaction mechanisms of both the acid- and base-catalysed reactions, respectively, are the same for every member of the reaction series and that the transition states differ only by the number of protons, *i.e.* that the reactions take place by the common $A_{AC}2$ and $B_{AC}2$ mechanisms, respectively, as they do in the case of normal esters. However, the hydrolysis of esters with electronegative substituents, which have a measurable neutral hydrolysis by the $B_{AC}3$ mechanism, is now known to proceed by the exceptional acid-catalysed ester hydrolysis mechanism (A–$B_{AC}3$), often accompanied by the normal $A_{AC}2$ mechanism.[8–11] This may limit the applicability of equation (1) or lead to erroneous results. Therefore we considered a critical examination of the σ* values for halogen-substituted alkyl groups to be of importance. Some new σ* values are presented.

ρ*σ* *Correlations.*—Equation (2) was employed for several

$$\log k = \rho^*\sigma^* + \log k_0 \qquad (2)$$

reaction series generally known or assumed to depend on polar factors only, using the best available experimental data. As shown in Table 1 (series 1 and 2), equation (1) can also be employed in the acid- and base-catalysed hydrolyses of esters in water, a case which was not included in the original reaction series by Taft.[1,3,12] The ρ* values, 2.42 ± 0.13 and 2.48 ± 0.12, were found to be, within the limits of the accuracy of the fits, identical with the original value 2.48. Thus the data for ester hydrolyses in water can be used to obtain σ* values. Owing to the possible change in mechanism the procedure may, however, fail if halogen-substituted esters (*e.g.*, methyl dichloroacetate and ethyl trichloroacetate, Table 2) are included.

The protonation equilibria of carboxylic acids, alcohols, and primary alkyl amines and the esterification of carboxylic acids with diazodiphenylmethane were also studied as appropriate reaction series for which new data were available. The results are given in Table 1 (series 3—6). The correlation was found to

Table 1. The values of the reaction constants ρ* and of log k_0 with their standard deviations, calculated by the method of least squares from equations (1) and (2), and the probable errors r of the fit of a single observation[a]

Reaction	k	ρ*	log k_0	r	Substituents R[b]
1. Acid- and base-catalysed hydrolyses of RCO_2Me in water at 298 K	k_B/k_A	2.42 ± 0.13	3.38 ± 0.07	0.120	4, 5, 7—9, 13, 14, 21, 22
2. Acid- and base-catalysed hydrolyses of RCO_2Et in water at 298 K	k_B/k_A	2.48 ± 0.12	3.05 ± 0.07	0.110	4, 6—9, 13, 14, 21, 22
3. Dissociation constants of RCO_2H in water at 298 K	K_a	−1.56 ± 0.04	−4.59 ± 0.03	0.080	1—15, 17, 18, 22, 25
4. Dissociation constants of RCH_2OH in water at 298 K	K_a	−1.43 ± 0.08	−15.91 ± 0.08	0.146	4, 7—9, 13—16, 18, 22, 24, 25
5. Dissociation constants of $RCH_2NH_3^+$ in water at 298 K	K_a	−1.51 ± 0.25	−10.38 ± 0.12	0.251	1, 4—11, 13, 15, 16, 19, 21
6. Esterification of RCO_2H with diazodiphenylmethane in ethanol at 303 K	k	0.99 ± 0.03	−0.178 ± 0.03	0.062	1, 4, 7, 8—12, 14, 15, 18, 20—25

[a] The data used for the reaction series 1—6 are available as a Supplementary Publication, SUP No. 56666 (8 pp.), see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1987, Issue 1. [b] 1 = Bu^t, 2 = Et_2CH, 3 = Bu^s, 4 = Pr^i, 5 = Bu^n, 6 = Bu^i, 7 = Pr^n, 8 = Et, 9 = Me, 10 = $Ph(CH_2)_2$, 11 = $PhCH_2$, 12 = $Cl(CH_2)_2$, 13 = H, 14 = $MeOCH_2$, 15 = $HOCH_2$, 16 = Ph, 17 = $MeCOCH_2$, 18 = $PhOCH_2$, 19 = CF_3CH_2, 20 = ICH_2, 21 = $BrCH_2$, 22 = $ClCH_2$, 23 = $NCCH_2$, 24 = Cl_2CH, 25 = CCl_3.

Table 2. Values of the polar substituent constants σ* for the groups R, calculated from the reaction series 1—6 (Table 1), together with the available literature values

No.	R	σ*(literature)	σ*(1)	σ*(2)	σ*(3)	σ*(4)	σ*(5)	σ*(6)	σ*(recommended)
1	Bu^t	−0.300^a			−0.282		0.089	−0.444	−0.300^a
2	Et_2CH	−0.225^a			−0.103				−0.225^a
3	Bu^s	−0.210^a			−0.110				−0.210^a
4	Pr^i	−0.190^a	−0.121	−0.152	−0.173	−0.131	−0.036	−0.250	−0.190^a
	$Me(CH_2)_4$	−0.1^b					−0.168		−0.17
5	Bu^n	−0.130^a	−0.106		−0.173		−0.147		−0.130^a
6	Bu^i	−0.125^a		−0.110	−0.120		−0.149		−0.125^a
7	Pr^n	−0.115^a	−0.093	−0.124	−0.150	−0.131	−0.174	−0.176	−0.115^a
8	Et	−0.100^a	−0.095	−0.066	−0.183	−0.131	−0.125	−0.189	−0.100^a
9	Me	0	−0.062	−0.015	−0.107	−0.012	−0.172	−0.052	0
10	$Ph(CH_2)_2$	0.080^a			−0.048		0.003	0.048	0.080^a
11	$PhCH_2$	0.215^a			0.181		0.195	0.257	0.215^a
	$CH_2{=}CH$					0.276	0.585		0.28
12	$Cl(CH_2)_2$	0.385^a			0.326			0.365	0.385^a
	$Br(CH_2)_2$	0.25^c			0.371			0.505	0.37
	Ph_2CH	0.405^a			0.416				0.405^a
	Pr^nOCH_2			0.448					0.45
13	H	0.490^a	0.335	0.346	0.545	0.577	−0.192		0.490^a
	$EtOCH_2$			0.500					0.50
14	$MeOCH_2$	0.520^a	0.521	0.517	0.652	0.766		0.679	0.520^a
15	$HOCH_2$	0.555^a			0.485	0.570	0.579	0.623	0.555^a
16	Ph	0.600^a				0.360	0.677		0.600^a
17	$MeCOCH_2$	0.60^a			0.633				0.60^a
	$HSCH_2$							0.632	0.63
18	$PhOCH_2$	0.850^a			0.915	0.570		0.987	0.850^a
19	CF_3CH_2	0.92^a					1.106		0.92^a
20	ICH_2	0.85^a			0.896			0.940	0.85^a
21	$BrCH_2$	1.000^a	1.097	1.101	1.068		1.245	1.076	1.000^a
22	$ClCH_2$	1.050^a	1.047	1.033	1.103	1.124		1.106	1.050^a
	FCH_2	1.10^a			1.196				1.10^a
	MeClCH							1.107	1.11
23	$NCCH_2$	1.300^a			1.356			1.324	1.300^a
	$CH{\equiv}C$					1.657			1.66
	Br_2CH	1.6^b			1.990			1.848	1.99
24	Cl_2CH	1.940^a	(1.59)^d		2.073	2.120		1.905	1.940^a
	F_2CH	2.05^a			2.080				2.05^a
	F_2CHCF_2					2.225			2.22
	CBr_3	2.3^b			2.476			2.390	2.48
	CF_3	2.60^c			2.604	2.471	3.088		2.60
	$CClF_2$				2.643				2.64
25	CCl_3	2.65^a		(1.56)^d	2.609	2.568		2.47	2.65^a

[a] Ref. 3. [b] Ref. 14*a*. [c] Ref. 14*b*. [d] Acid hydrolysis includes the $A\text{–}B_{AC}3$ reaction.

be excellent[13] for series 1, 3, and 6 (correlation coefficient >0.99), satisfactory for series 2 and 4 (correlation coefficient >0.95), but in the case of amine basicities (series 5) the correlation is clearly poorer (correlation coefficient 0.87).

The σ* values, including those for several halogen-substituted groups, are shown in Table 2 together with the available literature data.[3,14] The values obtained by the aid of the reaction series 1—6 (Table 1) are mainly in good agreement with the original values given by Taft.[3] The worst disagreements between the σ* values are those observed in the reaction series 3 and 5 for the smallest group H and for the most crowded groups such as Bu^t (groups 1 and 13, Table 2).

Use of Equations (1) *and* (2) *in predicting Rate and Equilibrium Parameters.*—The prediction of an unknown parameter k on the basis of equation (2) is straightforward if ρ^*, σ^*, and k_0 are known. Equation (1) can also be used for the estimation of rate parameters if, in addition to the ρ^* and σ^* parameters, three of the four rate coefficients are known at same conditions and if all of the reactions follow the $A_{AC}2$ and $B_{AC}2$ mechanisms. The equation may, however, lead to slightly deviating results if the acid- and base-catalysed reactions refer to different temperatures or solvents because it is known that both activation energies and solvent effects depend on the structure of the reacting compound.

Equation (1) is especially useful when estimating the contribution of the $A_{AC}2$ mechanism for electronegatively substituted esters, the acid-catalysed hydrolysis of which is known to take place simultaneously by the $A_{AC}2$ and $A\text{–}B_{AC}3$ mechanisms, because also in these cases the alkaline hydrolyses are known to take place by the $B_{AC}2$ mechanism.

Trichloroacetic Acid System and σ*(CCl_3).—It is known[8–11] that the acid-catalysed hydrolysis of ethyl trichloroacetate in water takes place by the $A\text{–}B_{AC}3$ mechanism. The data for its hydrolysis in 60% aqueous ethanol[15] seem to show that in these conditions normal $A_{AC}2$ hydrolysis is accompanied by neutral $B_{AC}3$ and acid-catalysed $A\text{–}B_{AC}2$ mechanisms. This is concluded on the basis of the data of Timm and Hinshelwood,[15] which show that in the hydrolysis of ethyl esters, RCO_2Et, there is a rate minimum for R = $CHCl_2$ in the series R = Me, CH_2Cl, $CHCl_2$, CCl_3 and that the activation energy continuously decreases in this series.

Although Taft originally included both acid-catalysed ester hydrolysis and esterification of carboxylic acids in the primary reaction series for (k/k_0),[1,2] most standard text books[7] only mention acid-catalysed hydrolysis in this connection. On the basis of this uncertainty as to the origin of the generally accepted value 2.65 for $\sigma^*(CCl_3)$,[3] and to avoid a possible vicious circle, we previously[10] used the value 2.61 when estimating the rate coefficient for the $A_{AC}2$ hydrolysis of ethyl trichloroacetate, this value being calculated from the dissociation constants of carboxylic acids.

It now seems clear that the value 2.65 for $\sigma^*(CCl_3)$ is based[1,2] on the acid-catalysed esterification of trichloroacetic acid in ethanol and on the alkaline hydrolysis of ethyl trichloroacetate in water. This leads to the conclusion that the esterification reactions of trichloroacetic acid and evidently also those of other halogen-substituted carboxylic acids in pure alcohols must take place by the $A_{AC}2$ mechanism, although the acid-catalysed hydrolysis of ethyl trichloroacetate in water proceeds by the A–$B_{AC}3$ mechanism.[9–11] Both these mechanisms have the common tetrahedral intermediate $CCl_3C(OH)_2OEt$, and it has been shown that, in principle, both the hydrolysis and esterification can simultaneously proceed by the $A_{AC}2$ and A–$B_{AC}3$ pathways without violating the principle of detailed balance, the energetically most favourable route being followed.[10,11] The proportion of the $A_{AC}2$ mechanism is found to increase and that of the A–$B_{AC}3$ to decrease with decreasing water concentration.[9,16] Thus the variation in mechanism with reaction medium can be expected.

The value, 3.29×10^{-4} l mol^{-1} s^{-1}, calculated[9] from the data of Kurz and Farrar,[11] for the rate coefficient of the acid-catalysed hydrolysis of ethyl trichloroacetate in 1M-ClO_4^- aqueous solutions at 298 K, is >100 times the value estimated for the $A_{AC}2$ reaction by the above procedure. On the other hand, if the rate coefficients 3.29×10^{-4} and 2 570 l mol^{-1} s^{-1} for the acid- and base-catalysed[17] hydrolyses, respectively, are fitted to equation (1), the wrong value 1.56 for $\sigma^*(CCl_3)$ is obtained.

Other Chloroacetic Acid Systems.—The original $\sigma^*(CHCl_2)$ value, 1.940,[3] based on the acid dissociation constant of dichloroacetic acid, together with the value[17] 1 460 l mol^{-1} s^{-1} for the rate coefficient of the alkaline hydrolysis of methyl dichloroacetate leads to the rate coefficient 1.3×10^{-5} l mol^{-1} s^{-1} for its $A_{AC}2$ hydrolysis. This value, *ca.* 10% of the rate coefficient 12.2×10^{-5} l mol^{-1} s^{-1} obtained for the acid-catalysed hydrolysis of this ester in dilute acid solutions,[9] indicates that the acid-catalysed hydrolysis of methyl dichloroacetate takes place simultaneously by the $A_{AC}2$ and A–$B_{AC}3$ mechanisms, the proportion of the latter being *ca.* 90% in water at 298 K.

When studying the importance of steric effects in acid-catalysed esterification and ester hydrolysis, Charton[5a] employed equation (3). The steric effect substituent constant v_x

$$\log k_{HX} = \Psi v_x + h \qquad (3)$$

for the $CHCl_2$ group, obtained from the esterification of dichloroacetic acid, did not give good results when employed in the acid-catalysed hydrolysis of ethyl dichloroacetate in 60% aqueous acetone. The reason is now clear: the modified Taft equation (3) is valid only for the $A_{AC}2$ hydrolysis. Although the solvent effects are found to be stronger for the A–$B_{AC}3$ than for the $A_{AC}2$ mechanism,[9,16] the contribution of the $A_{AC}2$ hydrolysis under these reaction conditions is still only a minor part of the total reaction.

The acid-catalysed hydrolysis of alkyl monohalogenoacetates probably proceeds by the $A_{AC}2$ mechanism, but additional halogen substituents in the alkyl group may lead to changes in mechanism. For example, it has been estimated using the Bunnett–Olsen method[18] that the acid-catalysed hydrolysis of chloromethyl chloroacetate in water takes place primarily (*ca.* 90%) by the A–$B_{AC}3$ mechanism.[19]

Conclusions

It seems that the Taft σ^* scale in most cases correctly measures the polar effects in aliphatic compounds and is especially useful in the case of electronegatively substituted groups. In such cases, when the acid-catalysed hydrolysis of an ester may take place by several mechanisms, equation (1) can be employed to estimate the contribution of the normal $A_{AC}2$ mechanism. On the basis of the similar values obtained for $\sigma^*(CCl_3)$ from several reactions, it is concluded that the acid-catalysed esterification of trichloroacetic acid takes place by the $A_{AC}2$ mechanism, although the acid-catalysed hydrolyses of halogen-substituted esters have a contribution of the exceptional A–$B_{AC}3$ mechanism.

In spite of their different origins, the calculated σ^* values (Table 2) are usually in good agreement with each other, although the correlation in the case of the amines is essentially poorer than in the other cases considered. We recommend the use of the original σ^* values of Taft[3] when available because of the prevailing practice. For new values, those obtained from the correlation of acid dissociation constants (series 3 in Table 1) are recommended because then the substituent R is attached to an sp^2-hybridised carbon atom as in the original analysis of Taft for ester hydrolysis.[1–3,12]

Owing to some scatter found in different $\rho^*\sigma^*$ correlations in the case of various alkyl groups and to the exceptional behaviour of hydrogen as a substituent, a prediction, based only on these substituents, may lead to highly erroneous results.

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