

THE VIABILITY OF THE TAFT σ^* SCALE FOR ALKYL GROUPS. A REPLY TO RECENT CRITICISM.

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(Received in UK 28 April 1976; accepted for publication 7 June 1976)

In two recent articles^{1a,b} Charton has examined the fundamental assumptions made by Taft in establishing his scales of steric (E_s) and polar effects (σ^*). In the first of these papers he shows that while the basic assumption, that acid catalysed hydrolysis of esters and esterification of carboxylic acids are controlled by steric effects, is valid, the reported values are subject to some errors. Taft² defined the steric constant E_s by the equation

$$(1) \quad E_s = \log (k/k_o)_A$$

where the rate constants could correspond to any one of four closely related reactions involving acid-catalysed hydrolysis or esterification. Taft used average $\log (k/k_o)$ values to calculate his E_s scale, a procedure recognized as faulty by Charton^{1a} and Shorter^{3a,b}.

In the second paper Charton considers the Taft σ^* scale, beginning with the original assumption, that acid catalysed hydrolysis of esters involves only the steric effect while base hydrolysis involves the steric effect to exactly the same extent along with a contribution from the polar effect. This assumption is expressed by well-known equation :

$$(2) \quad \sigma^* = \frac{1}{2.48} \left[\log \left(\frac{k}{k_o} \right)_B - \log \left(\frac{k}{k_o} \right)_A \right] .$$

His analysis leads him to the conclusion that the σ^* scale is invalid and that it results from an incomplete cancellation of steric effects in Equation 2. This is a conclusion which cannot be taken lightly : if it is true a large body of work dealing with the relative importance of steric and polar effects in aliphatic systems is in need of re-examination. We do not feel that Charton's conclusion is justified. In this note we propose to explain why this conclusion is ill-founded and to present several points which indicate that the σ^* scale, in spite of averaging procedures, is fundamentally valid.

Charton's Analysis : a. The σ^* Scale

Proceeding from his elegant demonstration that the Taft E_s values (for symmetrical groups) are linearly related to the Van der Waals radii, Charton has proposed a scale of steric constants,

termed ν values^{1a}. These are defined as the Van der Waals radius relative to hydrogen for symmetrical groups (13 in number) and are calculated directly from the same experimental data as used by Taft for groups that do not have an axis of symmetry.

Charton then proposes to analyse the steric, polar and resonance contribution of alkyl groups to the base catalysed hydrolysis of esters using the ν values and the parameters σ_I and σ_R , i.e. by correlating

$$(3) \quad \log (k_x)_B = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi_B\nu_X + h_B$$

He shows that $\sigma_{I,X}$ and $\sigma_{R,X}$ are not statistically significant and that $\log (k_x)_B$ is a function only of ν_X , a steric parameter. He then correlates the rate data with ν_X alone

$$(4) \quad \log (k_x)_B = \psi_B\nu_X + h_b$$

obtains excellent correlations, and claims, because ψ_B is not identical to ψ_A (obtained for the acid catalysed reactions) to have demolished Taft's original hypothesis and thereby the σ^* scale.

The flaw in Charton's analysis lies in his use of the σ_I scale to assess the contribution of the polar effect in $\log (k_x)_B$. The σ_I values he uses, his own⁴, are determined from the ionization constants of acetic acids. These $\sigma_{I,X}$ constants are, within experimental error, virtually identical for all alkyl groups ($\sigma_{I,Me} = -0.05$, $\sigma_{I,Et} = -0.05$, $\sigma_{I,i-Pr} = -0.03$, $\sigma_{I,s-Bu} = -0.03$, $\sigma_{I,t-Bu} = -0.07$); their use to prove that $\log (k_x)_B$ does not depend on polar effects seems to be begging the question. This is equivalent to stating that because the σ_I scale shows no significant variation for alkyl groups, the σ^* scale, which does show significant variation, must be in error for these same groups. This is opinion rather than established fact. Correlation of $\log (k_x)_B$ as a function of ν_X cannot yield a real value for ψ_B since the polar contribution should be considered. Such a correlation has a deceptively large correlation coefficient since polar effects are of much smaller magnitude than steric effects.

b. Relationship Between ν and σ^*

To support his claim that the σ^* scale for alkyl groups contains principally a contribution from the steric effect Charton shows that there is a vague correlation between σ^* and E_s ($r = 0.732$, $\psi = 0.741$). This correlation is statistically significant but its origin may be other than as suggested by Charton; the fact that both these quantities increase (in absolute value) with increasing substitution is enough to produce such a correlation. This is readily seen by correlating σ^* and ν separately as functions of the number of α and β carbons (Δn) in the alkyl groups considered by Charton (excepting cyclo-C₆H₁₁CH₂ and cyclo-C₆H₁₁) to obtain the following result :

	a	b	r	psi ⁶
$\sigma^* = a\Delta n + b$	0.0469	0.0303	0.772	0.702
$\nu = a\Delta n + b$	0.300	0.271	0.882	0.521

Thus we see that the correlation of ν with σ^* may have a different explanation than that advanced by Charton.

The variation of σ^* and E_s with structure has been studied by us⁵. It appears that the σ^* values, as might be expected, are strictly additive in nature; the behaviour of the E_s 's is more complex and quite different.

Koppel⁷ has analysed the functional relationship between E_s and σ^* , and found that there is a fair correlation of the form

$$(5) \quad E_s = a + b\sigma^* + c(n - 3) \quad r = 0.956$$

where n is the number of α -hydrogen atoms in an alkyl group. He effectively eliminates the "telescopic" effect of the E_s values by dispersing his correlation into straight lines corresponding to primary, secondary, and tertiary alkyl groups. It is this basic behaviour (E_s : Et, -0.07; i-Pr, -0.47; t-Bu, -1.54; σ^* : Et, -0.100; i-Pr, -0.190; t-Bu, -0.300) which distinguishes between these two parameters; its unimportance for the σ^* scale suggests that the separation of polar and steric factors is good. If, as Charton maintains, this is not the case, it becomes rather awkward to explain why data exist² which can be correlated in terms of σ^* but do not depend on E_s .

Two further points argue strongly in favour of the σ^* scale.

Internal Consistency

Any attempt at calculating ψ_B to ascertain whether or not it differs from ψ_A involves one immediately in a vicious circle. One can, however, show that there is internal consistency in the results obtained by Taft and demonstrate that one obtains meaningful results for reaction series not used to define the σ^* scale.

Taft used results reported by Davies and Evans⁸ for alkaline and acid hydrolyses of ethyl esters at 24.8° in 70% v/v aqueous acetone to estimate σ^* for the following alkyl groups: Me, Et, Pr, Bu, n-C₅H₁₁, i-Pr, i-Bu, t-Bu, and Et₂CH. This corresponds to Charton's Set 1. Correlation in terms of Eq. 4 (Charton) and Eq. 6.

$$(6) \quad \log (k_x)_B = \psi_B \nu_X + a\sigma^* + h$$

gives the following results:

	ψ_B	a	h	r	psi ⁶
Eq. 4	2.65	-	0.196	0.987	0.183
Eq. 6	2.17	2.38	0.257	0.997	0.0995

Eq. 6 necessarily gives a better correlation than Eq. 4. What is important to note is that ψ_B

(2.17) calculated from Eq. 6 is not significantly different from Ψ_A (2.06) reported by Charton and that 2.38 is close to the scaling factor (2.48) used by Taft ; this shows internal consistency. We can now use Charton's remaining data sets to demonstrate that the σ^* values attributed using the rate constants of set 1 are not due to random errors. For these 12 sets all except one (set 5, which depends only on steric effects) yield correlations which are more significant in terms of Eq. 6 than Eq. 4. This argues in favour of the σ^* scale, at least for those groups listed above. The ensemble of σ^* values certainly suffers from averaging procedures just as the E_s values do.

Ionization Data

The ionization of acetic acids as well as 4-substituted-(2.2.2)-bicycloöctane-1-carboxylic acids is relatively insensitive to the presence of alkyl groups. A recent study⁹ of the ionization of 4-substituted quinuclidinium perchlorates shows that this is not always the case for equilibria. The pK's of 4-Me, 4-Et, 4-i-Pr, and 4-tBu correlate with Taft's σ^* 's ($\rho^* = 0.664$, $r = 0.994$, $\psi = 0.156$) - a strong point in favour of Taft's values.

Recent work on the ionization potentials of aldehydes and ketones¹⁰, and acetylenes¹¹ indicates a dependence on Taft's σ^* values that is difficult to explain as anything but a polar effect. In particular, for the four aldehydes RCHO (R = Me, Et, i-Pr, and t-Bu) there is an excellent correlation between the first ionization potential and σ^* ($r = 0.995$, $\psi = 0.139$).

In conclusion, we feel that it is important to distinguish between the fundamental hypotheses inherent in the Taft approach and the manner in which they are exploited to obtain substituent parameters. The former have not yet been shown to be unsound while the latter is justifiably subject to some criticism.

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