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Deconstruction of Taft's σ^* parameter: QSAR meets QALE

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ABSTRACT: Taft's σ^* parameter has been mostly disregarded in QSAR (quantitative structure–activity relationships) analyses because it appears to reveal only simple field-inductive substituent effects. However, it can be shown that, when a reference reaction different from that adopted by Taft is used, the σ^* values reveal considerably more subtle features. This occurs when a reference reaction parameter, pK'_a, is used that is closely related to the Brønsted basicity of P-donor molecules and that is regarded in QALE (quantitative analyses of ligand effects) analyses as measuring the purely σ-donor properties of the phosphines. Values of Taft's σ^* parameter for alkyl groups show an excellent linear correlation with pK'_a but significant deviations from the correlation increase in the order CH_2Ph (0.19) < Ph (0.46) < *p*-O-*i*-Pr (1.38) < OEt (1.44) < OMe (1.51) < OPh (1.82) < Cl (1.88), and the deviations for the *p*-YC_6H_4 groups increase linearly with decreasing pK'_a as Y changes in the order Me_2N (0.29) < MeO (0.32) < Me (0.39) < F (0.41) < H (0.46) < Cl (0.50) < F_3C (0.60). The new substituent effects for these 'deviant' groups that can be derived from the linear correlations of σ^* with pK'_a are different (even in sign for the *p*-$Me_2NC_6H_4$ group) from the original values of the Taft parameter, and they are much smaller than the additional effects detected here. These results show that σ^* values contain within themselves a variety of new features that should be compared with those shown by parameters used in more recent QSAR analyses, and that might be useful in such analyses. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: QALE; QSAR; LFER; Taft's σ^* parameter; inductive effects; substituent effects

INTRODUCTION

It is 50 years since the formulation of the Taft parameter, σ^*, for substituent effects on aliphatic reaction centers,[1] and the development and application of this parameter have been more recently reviewed by Hansch and Leo.[2] Based originally on relative rates of aliphatic ester hydrolysis, σ^* was believed to reflect simple inductive effects due to the substituents and was given by the equation

$$\sigma^* = (1/2.48)[\log(k_x/k_0)_B - \log(k_x/k_0)_A] \qquad (1)$$

where $(k_x/k_0)_B$ is the rate of base hydrolysis of the compound XCOOR, relative to that of the standard (X = Me), and $(k_x/k_0)_A$ is the relative rate of acid hydrolysis. The latter term was introduced since acid hydrolysis, or the corresponding acid-catalyzed esterification, had been found to be dependent only on the steric effects of substituent X and, with certain necessary assumptions, these could be used to remove steric contributions to the term $\log(k_x/k_0)_B$. The scaling factor1/2.48 was introduced to bring the values of σ^* close to those of comparable Hammett parameters. Other values for Taft parameters were subsequently derived by analysis of different experimental data and an extensive compilation is provided in Vol. 2 of Ref. 2. Even when different methods were used to obtain values of σ^*, the new values are still conceptually related to Taft's original methodology and, therefore, relate to the hydrolysis or esterification kinetics.

The Taft parameter σ^* evolved into the closely correlated σ_I[2], which has been used to correlate diverse molecular properties in organic and biological chemistry using the methodology of quantitative structure–activity relationships (QSAR).[2] Although many prefer to restrict use of the acronym QSAR to biological applications, and use QSRR (quantitative structure-reactivity relationships) for organic reactions, Hansch and Leo included[2] the use of the term QSAR for a large number of applications to purely organic reactions.

Although σ^* and σ_I have been largely replaced by σ_χ (electronegativity), σ_F (field) and σ_α (polarizability) parameters, based partly on theoretical calculations,[3] there is still[4] interest in using values of Taft's parameter. These sometimes even give better correlations than more

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recently introduced parameters,[4c] and there is a tendency to search for correlations with whichever parameters give the best fit.[4b] However, the use of σ^* and σ_I values to correlate closely related kinetic or thermodynamic data means that factors that operate equally in the reference reactions and in the reactions of interest will not be reflected in any observed correlations, which therefore seem deceptively simple. This becomes evident when different set of reference reactions is used.

One such reference set is given by values of pK'_a,[5] which are intimately related to the Brønsted basicity of the P-donor molecules PX_3,[6] and which therefore operate entirely through effects on the σ-bonding strength of the lone pair on the P atom. They are closely related[5] to the parameter χ_d[7] that is derived, for pure σ-donor ligands, from the C—O stretching frequencies shown by the complexes $Ni(CO)_3L$.[8] For P-donor ligands that are also π-acids, such as phosphites, values of pK'_a have to be derived from the rather less precise pK_a values themselves.[5] The parameters pK'_a and χ_d have been extensively used in linear free energy relationships in organometallic chemistry[5,7,9] and the methodology is known as QALE (quantitative analysis of ligand effects).[7]

RESULTS AND DISCUSSION

Values of σ^* are generally the 'preferred values' given by Hansch and Leo in their extensive compilation,[2] and selected by them from among often very similar values derived by as many as five methods that were different from Taft's original one. Values of $\Sigma\sigma^*$ are plotted against corresponding values of pK'_a in Fig. 1. $\Sigma\sigma^*$ represents the sum of the σ^* values for the three, sometimes different, pendant groups on the P-donor atom. (Giering and co-workers originally plotted $\Sigma\sigma^*$ against χ_d for a restricted series of ligands,[10] but their subsequent data analyses of the effects of aryl and other[11] groups were entirely different from those reported here. A similar approach to ours was used some time ago[12] to relate pK_a values for some amines to $\Sigma\sigma^*$.) Values of pK'_a and $\Sigma\sigma^*$ are given in Table 1. The lowest line in Fig. 1 is drawn through the $\Sigma\sigma^*$ data for PR_3 reference bases (R = H or alkyl groups) with pendant groups that are joined to the P atom by pure σ-bonds. This line is made up of 20 points and is defined by the equation 2.

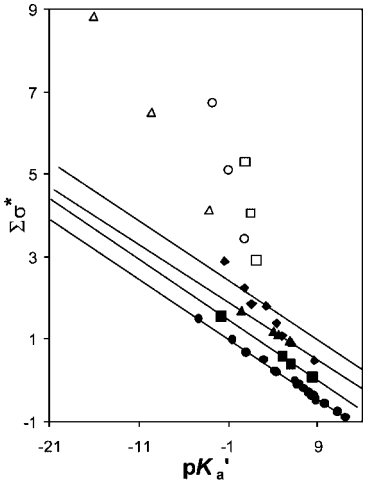

Figure 1. Dependence of $\Sigma\sigma^*$ on pK'_a. ●, PR_3 bases (R = alkyl or H); ■, PR_2Ph; ▲, $PRPh_2$ bases; ◆, $P(p\text{-}YC_6H_4)_3$ bases (Y = Me_2N, MeO, Me, H, F, Cl, F_3C). The upper line is drawn through the data for Y = H, and made to be parallel to the other three lines (see text). □, $P(OMe)_{3-n}Ph_n$; △, $PCl_{3-n}Ph_n$; ○, $P(OPh)_{3-n}Ph_n$ ($n = 0-2$ in all cases)

$$\Sigma\sigma^*_{calc} = 0.87(2) - 0.146(2)pK'_a \quad (r^2 = 0.996,\ s_{\Sigma\sigma^*} = 0.0363) \qquad (2)$$

This excellent correlation of the $\Sigma\sigma^*$ data with the values of pK'_a for a chemically unrelated set of σ-donor bases shows the very high internal self-consistency of changes in both $\Sigma\sigma^*$ and pK'_a. It reflects the additivity of the effects of the different alkyl groups (or hydrogen atoms) on the donor power of the P atom, expressed by the values of pK'_a. This is illustrated by the fact that the effect of replacing a methyl group by an ethyl group is the same (0.5) irrespective of whether there are three, two or one methyl groups to start with. It also suggests that the procedure used in the derivation of the values of σ^* to allow for steric effects was successful.

Although σ^* values were believed at one time to be a function of steric effects,[13] this was later disputed.[14] Steric effects are considered to be absent in χ_d[7] values and have been factored out[5] in the derivation of pK'_a values. Because they vary substantially and irregularly along the series of PR_3 molecules,[8a] they would certainly destroy the excellence of the correlation if they were significant. Although the correlation of the $\Sigma\sigma^*$ values with those of the simple basicity parameter pK'_a is excellent, we do not wish, at this time, to use this empirical observation to imply anything about the *mechanism* by which the effect is transmitted.[15]

The second line up is defined by four points and is drawn through the $\Sigma\sigma^*$ data for PR_2Ph reference bases. The fit is given by the equation

$$\Sigma\sigma^*_{calc} = 1.31(3) - 0.147(5)pK'_a \quad (r^2 = 0.998,\ s_{\Sigma\sigma^*} = 0.0362) \qquad (3)$$

and the gradient is identical with that of the lowest line, but the line is displaced vertically by 0.44 ± 0.04 log units. Although there are only four points, the r^2 value, which depends on the number of points, is still very high. The next line up, for $\Sigma\sigma^*$ data related to the $PRPh_2$ bases, is based on five points and fits the equation

$$\Sigma\sigma^*_{calc} = 1.76(1) - 0.140(3)pK'_a \quad (r^2 = 0.999,\ s_{\Sigma\sigma^*} = 0.0115) \qquad (4)$$

Table 1. Complete listing of values for pK'_a, $\Sigma\sigma^*$ and its constituent contributions

			Contributions to $\Sigma\sigma^*$		
PX_3	pK'_a[a]	$\Sigma\sigma^*$[b]	'σ-Bonding'[c]	Ph in $PX_{3-n}Ph_n$[d]	Non-alkyl X groups in PX_3[d]
$P(t\text{-Bu})_3$	12.2	−0.90	−0.91		
PCy_3	11.26	−0.78	−0.77		
$P(i\text{-Pr})_3$	9.88	−0.57	−0.57		
$P(pentyl)_3$	8.84	−0.48	−0.42		
$P(octyl)_3$	8.84	−0.45	−0.42		
$P(n\text{-Bu})_3$	8.67	−0.39	−0.40		
$P(i\text{-Bu})_3$	8.36	−0.39	−0.35		
PPr_3	8.57	−0.36	−0.38		
PEt_3	7.96	−0.30	−0.29		
PEt_2Me	7.46	−0.20	−0.22		
$PH(t\text{-Bu})_2$	6.68	−0.11	−0.11		
$PEtMe_2$	6.95	−0.10	−0.14		
PMe_3	6.45	0	−0.07		
$PH(octyl)_2$	4.46	0.19	0.22		
$PHBu_2$	4.33	0.23	0.24		
$PH(i\text{-Bu})_2$	4.13	0.23	0.27		
$PHMe_2$	2.98	0.49	0.43		
$PH_2\text{-}t\text{-Bu}$	0.96	0.68	0.73		
PH_2Me	−0.52	0.98	0.95		
PH_3	−4.29	1.47	1.50		
PCy_2Ph	8.4	0.08	−0.36	0.46	
PEt_2Ph	5.94	0.40	0.003	0.46	
PMe_2Ph	5.07	0.60	0.13	0.46	
PH_2Ph	−1.83	1.58	1.14	0.46	
$P(t\text{-Bu})Ph_2$	6.18	0.90	−0.03	0.92	
$PCyPh_2$	5.9	0.94	0.01	0.92	
$PEtPh_2$	4.6	1.1	0.20	0.92	
$PMePh_2$	4.06	1.2	0.28	0.92	
$PHPh_2$	0.53	1.69	0.79	0.92	
PPh_3	3.28	1.8	0.39	1.38	
$P(O\text{-}i\text{-Pr})_3$	3.38	4.53	0.38		4.15[e]
$P(OEt)_3$	1.64	4.92	0.63		4.32
$P(OMe)_3$	0.83	5.19	0.75		4.53
$P(OEt)_2Ph$	1.99	3.88	0.58	0.46	2.88
$P(OMe)_2Ph$	1.48	4.06	0.65	0.46	3.02
$P(OEt)Ph_2$	1.35	2.84	0.67	0.92	1.44
$P(OMe)Ph_2$	2.09	2.93	0.56	0.92	1.51
$P(OPh)_3$	−2.79	6.72	1.28		5.46
$P(OPh)_2Ph$	−0.91	5.08	1.00	0.46	3.64
$P(OPh)Ph_2$	0.87	3.44	0.74	0.92	1.82
PCl_3	−16.1[f]	8.82	3.22		5.64
PCl_2Ph	−9.60[f]	6.48	2.27	0.46	3.76
$PClPh_2$	−3.14[f]	4.14	1.33	0.92	1.88
$P(p\text{-}Me_2NC_6H_4)_3$	8.67	0.48	−0.40		0.88[e]
$P(p\text{-}MeOC_6H_4)_3$	5.13	1.08	0.12		0.96[e]
$P(p\text{-}MeC_6H_4)_3$	4.46	1.38	0.22		1.14[e]
$P(p\text{-}FC_6H_4)_3$	1.63	1.86	0.63		1.23[e]
$P(p\text{-}ClC_6H_4)_3$	0.87	2.25	0.74		1.51
$P(p\text{-}CF_3C_6H_4)_3$	−1.39	2.88	1.07		1.81
$P(CH_2C_6H_5)_3$	5.23	0.66	0.11		0.56
$P(CH_2C_6H_5)Ph_2$	3.92	1.42	0.30	0.92	0.19

[a] pK'_a values taken from Ref. 5b.
[b] σ^* Values are generally Hansch and Leo's 'preferred values' taken from vol. 2 of Ref. 2 and selected by them from among often very similar values derived by as many as five methods that were different from Taft's.
[c] Given by Eqn (2) and so-called because the basicity of each reference P-donor ligand is controlled by the σ-bonding propensities of the pendant groups attached to the P atom.
[d] From Dev vs n plots (see Fig. 2).
[e] Taken from total Dev.
[f] Values given in Ref. 5b are incorrect because they were calculated from Bartik's χ values with the assumption that these ligands are not π-acids. The correct values listed here were calculated from Giering's χ_d values according to the method in Ref. 5b.

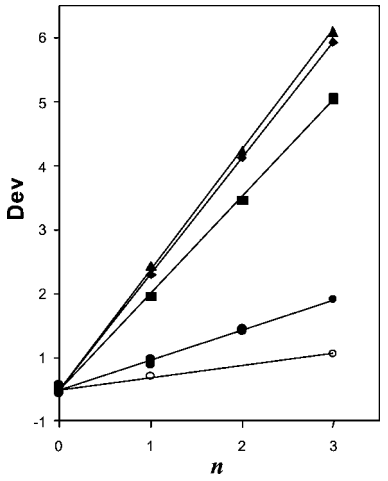

Figure 2. Deviations of $\Sigma\sigma^*$ values from those predicted by using P-donor bases with purely σ-bonding pendant groups. ○, $P(CH_2C_6H_5)_nPh_{3-n}$; Dev = 0.187(7)n; $r^2 = 0.993$; $s_{dev} = 0.0217$. ●, $PR_{3-n}Ph_n$; Dev = 0.460(6)n; $r^2 = 0.994$; $s_{dev} = 0.0323$. ■, $P(OMe)_nPh_{3-n}$; Dev = 1.51(2)n; $r^2 = 0.999$; $s_{dev} = 0.0567$. ◆, $P(OPh)_nPh_{3-n}$; Dev = 1.815(3)n; $r^2 = 1.00$; $s_{dev} = 0.0113$. ▲, PCl_nPh_{3-n}; Dev = 1.88(2)n; $r^2 = 0.999$; $s_{dev} = 0.0442$. The values for the deviations have been adjusted where appropriate for the effects of Ph groups present (see text)

It also has the same gradient but the upward displacement (0.89 ± 0.02) is essentially twice that of the PR_2Ph line. The highest line is drawn through the $\Sigma\sigma^*$ data for PPh_3 but using the gradient common to the three other lines. The vertical displacements of $\Sigma\sigma^*$ from the PR_3 line, referenced to the $PR_{3-n}Ph_n$ ($n = 1$–3) bases, are plotted against n in Fig. 2 and show that the displacements are governed precisely by the number of phenyl groups involved. This linearity has nothing to do with the effects of the phenyl group on the hydrolysis kinetics, which involve only one such group. Rather, it reflects the fact that the effect of the phenyl group on the hydrolysis kinetics is the same regardless of whether it is referenced to the σ basicity changes brought about by replacing one alkyl group by a phenyl group in either PR_3, PR_2Ph or $PRPh_2$, i.e. it reflects the additivity of effects within the PR_nPh_{3-n} bases that are used to correlate the trends in the σ^* values. Hence it is this additivity that leads to the linearity of the plot in Fig. 2, and it is the *gradient* that is a measure of the effects of the phenyl group on σ^* over and above the effect due to the simple change in the basicity effect.

Similar plots derived from data for the $P(CH_2C_6H_5)_{3-n}Ph_n$, $P(OMe)_{3-n}Ph_n$, $P(OPh)_{3-n}Ph_n$ and $PCl_{3-n}Ph_n$ bases ($n = 0$–2), are also given in Fig. 2 and the correlations with n, shown in the caption to Fig. 2, are excellent. In these cases, the deviations from the lowest line that are observed in Fig. 1 for the $PXPh_2$ and PX_2Ph molecules are caused in part by the presence of the Ph groups. Those deviations were, therefore, adjusted according to the deviations expected for the presence of two and one phenyl groups, respectively, before being plotted in Fig. 2.

Each plot shows the strict dependence of the adjusted upward displacement on the number of non-phenyl groups in the reference bases. The gradients of these plots give the contribution to σ^* from each of the X groups over and above the basic contribution from simple basicity effects that is given by

$$\sigma^*(R)_{calc} = 1/3(-0.146)[pK'_a(PR_3) - pK'_a(PMe_3)] - 0.024 \quad (5)$$

where $\sigma^*(R)_{calc}$ is the value of σ^* calculated for R, relative to $\sigma^*(Me) = 0$, from the trend shown in Eqn (1). The term 0.024 is accounted for by the fact that the point for PMe_3 lies slightly above the line of best fit for PR_3 in Fig. 1, although the deviation is small. Finally, the deviations (from the PR_3 line in Fig. 1) of the values of $\Sigma\sigma^*$ that are referenced to the $P(p\text{-}YC_6H_4)_3$ bases must be considered. For the deviations of the aryl group Ph (i.e. Y = H), we have the deviations derived from the use of the $PRPh_2$ and PR_2Ph bases to help construct the plot shown in Fig. 2, but for the other $p\text{-}YC_6H_4$ aryl groups there are no pK'_a data for the corresponding $P(p\text{-}YC_6H_4)Ph_2$ and $P(p\text{-}YC_6H_4)_2Ph$ bases to provide analogous plots. We assume, therefore, that the plots would be similarly linear and that we can estimate their gradients by dividing the value of each deviation, obtained by use of each $P(p\text{-}YC_6H_4)_3$ reference base, by 3. Values of the deviations due to the various $p\text{-}YC_6H_4$ groups involved in Fig. 1 are included in Table 1, and they also vary systematically with pK'_a, according to the equation

$$\Sigma\sigma_{calc} = 2.44(8) - 0.237(18)pK'_a \quad (r^2 = 0.973, \quad s_{\Sigma\sigma^*} = 0.141) \quad (6)$$

It is therefore possible to divide each σ^* parameter into contributions from three distinct effects: (a) those related to the purely σ-bonding properties of the pendant groups in the P-donor molecules and expressed through their effects on the σ basicity of the P atom's lone pair, which can be called the 'σ-bonding effects'; (b) additional effects due to the benzyl and non-alkyl Ph, OR, OPh and Cl groups; and (c) additional effects due to the *para* substituents in the aryl $p\text{-}YC_6H_4$ groups. These contributions are given in Table 2. The fact that the σ-bonding effect of Me on σ^* is no longer zero is unimportant because, in this new approach, no one R group is chosen as a reference standard. Again, we emphasize the empirical nature of these contributions to $\Sigma\sigma^*$ (Table 1) or σ^* (Table 2). The effects of pendant groups such as OR, OPh and Cl on the behavior of P-donor ligands are assumed in QALE chemistry to be due to the generation of π-acidity properties in the ligands. These bring about 'back-bonding' from the reaction center to modify the σ-donor effects, and $pK_a(\pi)'$[16] and π_p[11] parameters have

Table 2. Taft's σ^* parameter and its constituent contributions

X	σ^*[a]	Contributions to σ^*	
		'σ-Bonding'[b]	Non-alkyl X group[c]
t-Bu	−0.30	−0.30	
Cy	−0.26	−0.26	
i-Pr	−0.19	−0.19	
pentyl	0.16	−0.14	
octyl	−0.15	−0.14	
n-Bu	−0.13	−0.13	
Pr	−0.12	−0.13	
i-Bu	−0.13	−0.12	
Et	−0.10	−0.10	
Me	0	−0.02	
H	0.49	0.50	
Ph	0.60	0.13	0.46
O-*i*-Pr	1.51	0.13	1.38[d]
OEt	1.64	0.21	1.44
OMe	1.73	0.25	1.51
OPh	2.24	0.43	1.82
Cl	2.94	1.07	1.88
p-$Me_2NC_6H_4$	0.16	−0.13	0.29[d]
p-$MeOC_6H_4$	0.36	0.04	0.32[d]
p-MeC_6H_4	0.46	0.07	0.39[d]
p-FC_6H_4	0.62	0.21	0.41[d]
p-ClC_6H_4	0.75	0.25	0.50[d]
p-$CF_3C_6H_4$	0.96	0.36	0.60[d]
$CH_2C_6H_5$	0.22	0.04	0.19

[a] σ^* Values taken from Ref. 2. (see footnote b in Table 1).
[b] Given by Eqn (5) (see footnote c in Table 1).
[c] From Dev vs *n* plots (see Fig. 2).
[d] Taken as total Dev/3.

been derived. However, no such physical model is currently available to explain the so-called aryl effect, which can be very prominent in modifying the behavior of P-donors with aryl pendant groups, compared with what would be expected from σ-donor and π-acidity effects.[7b,17]

The gradient of the line for PR_3 bases in Fig. 1 and Eqn (5) essentially provide a measure of the sensitivity to R of the rates of base hydrolysis of RCOOR′, adjusted to remove steric effects, compared with the sensitivity of PR_3 to protonation. Allowing for the arbitrary scaling factor of 2.48 in σ^* [1] [see Eqn (1)], the effect of R on the *partial* formation of the C—OH bond in the transition state for attack by OH^- at C in RCOOR′ is $\sim$36% ($0.146 \times 2.48 = 0.362$) of the effect of R on formation of a *complete* P—H^+ bond with PR_3, and, as expected, in the opposite direction. The correlation shown by this line is excellent [see Eqn (2)] and, when the data for PCl_3 are taken into account, the overall fit extends over a range of 32 orders of magnitude for P-donor basicity and over a comparable range of 25 ($= 10 \times 2.48$) orders of magnitude for rates of base hydrolysis.

Replacing one alkyl group on the P atom with a phenyl group decreases pK'_a in accordance with the electron affinity of the phenyl ring, and the values of $\Sigma\sigma^*$ always increase. It is evident from Fig. 1 that for a unit decrease in pK'_a the value of $\Sigma\sigma^*$ would increase by 0.146 if the phenyl group behaved in the same way as an alkyl group. However, the actual increase is 0.146 *plus* $\sim$0.44 because of the different behavior of the phenyl group, i.e. for a comparable change in basicity the extra effect of the phenyl group on the rates of base hydrolysis is three times that of an alkyl group. This indicates that the extra effect of the phenyl group on the transition state is transmitted about as efficiently as its effect on the basicities, in contrast to the 36% efficiency of transmission of the effects of the alkyl groups estimated above. When the phenyl ring contains substituents in the *para* position, the aryl contribution to $\Sigma\sigma^*$ is greater when the substituents are less π-electron donating. This perturbation of the aryl contribution is not at all negligible, covering a range of $\sim$0.3 (from 0.29 to 0.60) while each phenyl group itself contributes 0.46.

The contribution to σ^* from the simple σ-bonding substituent effects for the non-alkyl groups [designated as effects (a) above] are different from Taft's substituent effects and the extra contribution to σ^* of X are fairly large compared with the much smaller contribution from the σ-bonding effects (Table 2). Replacing Me in (MeO)-COOR with Ph has almost the same extra effect (1.82–1.51 = 0.31; see Table 2) as replacing Me in MeCOOR with Ph (0.46), so the effect is not much attenuated when passed through an oxygen atom. The fact that the effect of the phenyl group is attenuated by a factor of 2.4 when it is transmitted through a CH_2 group is in agreement with observations on other systems.[2]

It should be emphasized that the above observations are not qualitatively dependent on any choices made for the σ^* values, or on the methods used to derive them, and the quantitative effects are not important in this context.

CONCLUSIONS

The use of pK'_a values (closely related to the σ basicity of the lone pairs on the P atoms in P-donor ligands) as a reference for analyzing substituent group effects on aliphatic ester hydrolysis is very successful in deconstructing Taft's σ^* parameter into different constituent contributions.

These contributions can be divided into three groups: (1) those due to substituents such as alkyl groups or hydrogen atoms that bond to the P atoms in the reference P-donor ligands via σ-bonds; (2) those where the bonding of the substituents to the P atoms includes π-acidity and other effects; and (3) those where the additional effect of phenyl groups is modified by *para* substituents on the phenyl ring.

The detection of these different contributions to the Taft parameter is a consequence of using a reference that is not intimately related to ester hydrolysis, as the σ basicity of the lone pair on the P atom is taken to respond simply to the pendant groups on the P atom. The danger

of systematizing effects of substituent groups by reference to their effects on closely related reactions means that factors that operate equally in the reference reactions and the reactions of interest will not be reflected in any observed correlations.

This deconstruction of the Taft parameters is an empirically and precisely observed phenomenon but it is not, at this stage, used to imply anything about the mechanisms whereby these effects are transmitted within the aliphatic esters used in deriving Taft's parameters.

The use of P-atom bases to provide σ basicity data is not a requirement for this analysis of the Taft parameter. Other Brønsted bases that could provide the same range of data would probably also be satisfactory.[12]

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