

## Nature of the Electrical Effect of Alkyl Groups. 2. Significance of the Taft $\sigma^*$ Values for Alkyl Groups

Marvin Charton

Department of Chemistry, Pratt Institute, Brooklyn, New York, 11205

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Values of  $\sigma^*_{\text{rel}}(\sigma^*_{\text{Ak}}/\sigma^*_{\text{Et}})$  for alkyl groups are calculated from rate constants for C-substituted amide hydrolysis in water at three different temperatures for *N*-acylimidazole hydrolysis and imidazole-catalyzed *N*-acylimidazole hydrolysis in water. In all of these cases, the steric effect is the same in both the acid- and the base-catalyzed reactions. The range of  $\sigma^*_{\text{rel}}$  for primary, secondary, and tertiary alkyl groups shows absolutely no dependence on the degree of branching. The corrected or "true"  $\sigma^*_{\text{Ak}}$  constants were calculated from rate constants for C-substituted ester hydrolysis in the same medium at three different temperatures. It has been shown that in this case, steric effects in the acid- and base-catalyzed reactions are not the same. The corrected  $\sigma^*_{\text{Ak}}^t$  constants are well correlated by  $\sigma^*_{\text{Ak}}^t = m\nu_{\text{Ak}} + c$ , which was derived previously. The Taft  $\sigma^*_{\text{Ak}}$  parameters were successfully correlated with the equation  $\sigma^*_{\text{Ak}} = an_{\alpha} + bn_{\beta} + i$ , where  $n_{\alpha}$  and  $n_{\beta}$  are measures of the degree of branching of the  $\alpha$  and  $\beta$  positions of an alkyl group. On the basis of these results it is suggested that the Taft  $\sigma^*$  constants are probably a measure of a steric effect. Thus,  $\log k = \rho^*\sigma^*_{\text{Ak}} + \delta E_{\text{S,Ak}} + h$  (Taft and Pavelich),  $\log k = \rho^*\sigma^*_{\text{Ak}} + \delta E_{\text{S,Ak}} + \Delta G + H$  (Hancock et al.) and  $\log k = \rho^*\Sigma^*_{\text{Ak}} + d(n^*_{\text{H}} - 6)$  (Taft and Kreevoy) can be accounted for in terms of steric effects in reactions which differ in their sensitivity to branching at the  $\alpha$  and  $\beta$  carbon atoms of an alkyl group. The correlations of  $E_{\text{S}}$  and  $E_{\text{S}}^c$  with  $\sigma^*_{\text{Ak}}$  and  $n_{\text{H}}$  by Koppel can be explained in the same manner.

The Taft  $\sigma^*$  values for alkyl groups have frequently been employed in the correlation of physical and chemical data with the Taft equation

$$\log(k_{\text{X}}/k_{\text{Me}}) = \rho^*\sigma^* \quad (1)$$

or the Taft-Pavelich equation

$$\log(k_{\text{X}}/k_{\text{Me}}) = \rho^*\sigma^* + \delta E_{\text{S}} \quad (2)$$

There has been disagreement, however, on the interpretation of  $\sigma^*$  values for alkyl groups. Thus, some authors feel that the  $\sigma^*$  values of alkyl groups do measure the electrical effect of the alkyl group; others feel that alkyl groups all have about the same electrical effect. The problem has been thoroughly examined by Shorter<sup>1a</sup> in an excellent review. More recent papers discussing this problem are those of Adcock and Khor<sup>1b</sup> and of Bordwell and Fried.<sup>1c</sup>

We have previously shown<sup>2</sup> in the first paper of this series that the  $\sigma^*_{\text{Ak}}$  values calculated from rate constants for the acidic and basic hydrolysis of C-substituted amides do not show the variation of  $\sigma^*_{\text{Ak}}$  with structure which is characteristic of the Taft  $\sigma^*_{\text{Ak}}$  values although they were calculated from reactions in which the steric effects were shown to be equivalent.<sup>3</sup> Those observations were limited to amide hydrolysis because of the difficulty in choosing a  $\rho^*$  value, although as was pointed out, it is the product of  $\rho^*\sigma^*_{\text{Ak}}$  which can be compared and the choice of  $\rho^*$  is unimportant. If we write the equation for the definition of  $\sigma^*_{\text{Ak}}$  in the form

$$\rho^*\sigma^*_{\text{Ak}} = \log(k_{\text{X}}/k_{\text{Me}})_{\text{B}} - \log(k_{\text{X}}/k_{\text{Me}})_{\text{A}} \quad (3)$$

and divide it by the same expression written for the particular case of the ethyl group

$$\rho^*\sigma^*_{\text{Et}} = \log(k_{\text{Et}}/k_{\text{Me}})_{\text{B}} - \log(k_{\text{Et}}/k_{\text{Me}})_{\text{A}} \quad (4)$$

we obtain the ratio

$$\frac{\sigma^*_{\text{Ak}}}{\sigma^*_{\text{Et}}} = \frac{\log(k_{\text{X}}/k_{\text{Me}})_{\text{B}} - \log(k_{\text{X}}/k_{\text{Me}})_{\text{A}}}{\log(k_{\text{Et}}/k_{\text{Me}})_{\text{B}} - \log(k_{\text{Et}}/k_{\text{Me}})_{\text{A}}} \equiv \sigma^*_{\text{rel,Ak}} \quad (5)$$

Values of the ratio  $\sigma^*_{\text{Ak}}/\sigma^*_{\text{Et}}$  are presented in Table I. A comparison of these values shows no discernible pattern of behavior with respect to branching. We are forced to the conclusion that the Taft  $\sigma^*_{\text{Ak}}$  values are an artifact. As further evidence we may consider the following.

Our results show a significant correlation of  $\sigma^*$  values with the equation

$$\sigma^*_{\text{Ak}} = m\nu_{\text{Ak}} + c \quad (6)$$

where the  $\nu_{\text{Ak}}$  values are steric parameters.<sup>4,5</sup> Equation 6 was derived from the modified Taft equation and the Taft definition of  $\sigma^*$  values.<sup>6</sup> The value of  $r^2$  obtained for the correlation was only 0.5358, however, thus leaving about 46% of the variation unaccounted for. We explain this by pointing out that Taft had used *average* values of  $\log(k_{\text{X}}/k_{\text{Me}})$  in calculating  $\sigma^*_{\text{Ak}}$  values and came to the conclusion that the  $\sigma^*$  values of alkyl groups depended upon steric factors rather than electrical effects.

To test our explanation of the low  $r^2$  value obtained from correlation with eq 6, we have calculated  $\sigma^*_{\text{Ak}}$  values from the only data available in which rates of acid- and base-catalyzed hydrolysis of esters were measured in the same solvent and at the same temperature. Values of  $\sigma^*$  were calculated from the definition of Taft<sup>7</sup>

$$\sigma^* = (1/2.48)[\log(k_{\text{X}}/k_{\text{Me}})_{\text{B}} - \log(k_{\text{X}}/k_{\text{Me}})_{\text{A}}] \quad (7)$$

using data in 70% v/v MeAc-H<sub>2</sub>O at 24.8, 35, and 44.7 °C (sets 7, 8, and 9 of Table I, ref 6; sets 1, 2, 3 of Table I, ref 4). The  $\sigma^*_{\text{Ak}}^t$  values obtained are set forth in Table II. They have been given the superscript "t" to indicate their origin. They are considered to be "true" or correct  $\sigma^*_{\text{Ak}}$  values which were not obtained from average values. The error in the original Taft  $\sigma^*_{\text{Ak}}$  values arose as follows. It was shown that the *S* values obtained from correlation with the modified Taft equation

$$\log k_{\text{X}} = S\nu_{\text{X}} + h \quad (8)$$

are a function of the solvent. Furthermore, depending on the availability of the data, different sets were used to obtain the averages for different substituents. This would affect most strongly the  $\sigma^*_{\text{Ak}}$  values because, (1) they are much smaller than are values for most other groups; (2) many more different sets of data were available for alkyl groups than for other groups and therefore average values used for alkyl groups should show the most divergence; and (3) the localized (field and/or inductive) effect of alkyl groups is very small, that of most other groups is many times larger, and the  $\sigma^*$  values of other groups should be predominantly determined by the localized electrical effect.

Although  $\sigma^*_{\text{t}}$  values are available for only seven alkyl

Table I. Values of  $\sigma^*_{\text{rel}}$  and  $\sigma^*_{\text{rel}}^{\dagger}$  for Alkyl Groups

X	Taft	4,7	5,8	6,9	10,11	12,27	1,7	2,8	3,9
Me <sup>a</sup>	0	0	0	0	0	0	0	0	0
Et <sup>a</sup>	1	1	1	1	1	1	1	1	1
Pr	1.15	0.605	1.01		1.01	1.90	1.50	1.44	1.64
Bu	1.30	1.84					1.86	1.71	1.63
<i>i</i> -Bu	1.25	-0.765	-1.13				1.80	1.66	1.46
<i>t</i> -BuCH <sub>2</sub>	1.65				1.03	7.53			
<i>c</i> -C <sub>6</sub> H <sub>11</sub> CH <sub>2</sub>	0.60	-0.410	-0.960	3.89					
<i>c</i> -C <sub>5</sub> H <sub>9</sub>	2.0	2.24	-0.303	3.00					
<i>c</i> -C <sub>6</sub> H <sub>11</sub>	1.5	1.10		2.80					
<i>i</i> -Pr	1.90	1.00	1.98	-0.308	0.995	0.843	1.82	1.70	1.62
<i>s</i> -Bu	2.10	0.995	1.47	-0.025					
Et <sub>3</sub> C	3 <sup>b</sup>				0.806	-0.273			
<i>t</i> -Bu	3.00						3.19	3.32	3.82

4,7: hydrolysis of C-substituted amides in water at 75 °C

5,8: hydrolysis of C-substituted amides in water at 85 °C

6,9: hydrolysis of C-substituted amides in water at 95 °C

10,11: hydrolysis of N-acyl imidazoles in water at 30 °C, catalyzed by imidazole

12,27: hydrolysis of N-acyl imidazoles in water at 30 °C, catalyzed by imidazole

1,7: hydrolysis of C-substituted esters in 70% v/v aq acetone at 24.8 °C

2,8: hydrolysis of C-substituted esters in 70% v/v aq acetone at 35.0 °C

3,9: hydrolysis of C-substituted esters in 70% v/v aq acetone at 44.7 °C

<sup>a</sup> Values of  $\sigma^*_{\text{rel}}$  for Me and Et are 0 and 1, respectively, due to the definition of  $\sigma^*_{\text{rel}}$ . <sup>b</sup> Based on the argument that all tertiary alkyl groups have  $\sigma^*$  values  $\sim \sigma^*_{t\text{-Bu}} = 0.30$ . <sup>c</sup> The data used in these sets and their sources are given in ref 3.

groups, this is sufficient to provide some indication of the differences between the  $\sigma^*$  values reported by Taft<sup>7</sup> and the  $\sigma^*_{\text{Ak}}^{\dagger}$  values calculated here. Comparison of the  $\sigma^*_{\text{Ak}}^{\dagger}$  values given in Table I with the average values of  $\sigma^*_{\text{Ak}}^{\dagger}$  shows significant differences for the Pr, Bu, *i*-Pr, and *i*-Bu groups and a small difference for the *t*-Bu group. Furthermore, whereas in the  $\sigma^*_{\text{Ak}}^{\dagger}$  values reported by Taft primary alkyl groups generally have  $\sigma^*$  of about -0.1, secondary alkyl groups have a value of about -0.2, and tertiary groups a value of about -0.3, the  $\sigma^*_{\text{Ak}}^{\dagger}$  values show no significant difference between the values for Bu and *i*-Pr, although the former is a primary and the latter a secondary alkyl group. Thus, we are forced to the conclusion that the  $\sigma^*_{\text{Ak}}^{\dagger}$  values reported by Taft are in fact erroneous.

This point is reinforced by a consideration of the values of  $\sigma^*_{\text{rel}}^{\dagger}$  which are given in Table I. The Bu, Pr, *i*-Bu, and *i*-Pr groups do not differ significantly although three are primary and one secondary. It is instructive to consider the range of  $\sigma^*_{\text{rel}}$  for primary, secondary, and tertiary alkyl groups. We will consider only values of  $\sigma^*_{\text{rel}}$  from sets 4,7; 5,8; 6,9; 10,11; and 12,27 since in these sets we have shown that the steric effect in the acid-catalyzed hydrolysis is in fact equal to that in the base-catalyzed hydrolysis. In the case of the ester hydrolyses (sets 1,7; 2,8; and 3,9) we have shown that this is *not* the case.<sup>4</sup> The ranges obtained are: primary, -1.0 to 7.5; secondary, -1.4 to 3.0; and tertiary, -0.3 to 0.8. Obviously no systematic dependence on branching occurs.

The  $\sigma^*_{\text{Ak}}^{\dagger}$  values we have obtained permit further test of eq 6 and of our explanation of its failure to completely account for the data in the correlation of  $\sigma^*_{\text{Ak}}$  values. We have correlated the three sets of  $\sigma^*_{\text{Ak}}^{\dagger}$  values reported in Table II with eq 6. The results of the correlations are reported in Table III (sets 1, 2, and 3 are the  $\sigma^*_{\text{rel}}$  values at 24.8, 35, and 44.7 °C, respectively). All three sets gave good correlations significant at the 99.0% confidence level (CL), with  $r^2$  values of 0.7754, 0.7973, and 0.7707 thus accounting for about 78% of the variation. This is a considerable improvement over the 54% data accounted for by the correlation of  $\sigma^*_{\text{Ak}}$  values with eq 3. This is in agreement with the explanation we previously proposed. The correlation of  $\sigma^*_{\text{rel}}$  values obtained from sets 4,7; 5,8; 6,9; 10,11; and 12,27 with eq 6 is of course unsuccessful, as would be expected from the derivation of eq 6, based on the

case in which the steric effect in acid-catalyzed and base-catalyzed hydrolysis is *not the same*. As to why the correlations obtained with eq 3 for the  $\sigma^*_{\text{rel}}$  values are not even better, let us consider the following. We have already shown that  $v_{\text{Ak}}$  values are given by the expression

$$v_{\text{Ak}} = an_{\alpha} + bn_{\beta} + cn_{\gamma} + i \quad (9)$$

and have proposed the equation<sup>5</sup>

$$Q = a'n_{\alpha} + b'n_{\beta} + c'n_{\gamma} + d'n_{\delta} + i \quad (10)$$

In eq 9 and 10 then,  $n_{\alpha}$ ,  $n_{\beta}$ , and  $n_{\gamma}$  are the number of  $\alpha$ ,  $\beta$ , and  $\gamma$  carbon atoms, respectively.

Now we may write the definition of  $\sigma^*$  in the form

$$\sigma^* = (1/2.48)[\log k_{\text{X,B}} - \log k_{\text{X,A}} + \log k_{\text{Me,A}} - \log k_{\text{Me,B}}] \quad (11)$$

and as  $\log k_{\text{Me,A}} - \log k_{\text{Me,B}}$  is a constant  $p$ , we obtain

$$\sigma^* = (1/2.48)(\log k_{\text{X,B}} - \log k_{\text{X,A}} + p) \quad (12)$$

Letting  $Q$  in eq 10 be  $\log k_{\text{X,B}}$  or  $\log k_{\text{X,A}}$  gives

$$\sigma^* = (1/2.48)(a'_{\text{B}}n_{\alpha} + b'_{\text{B}}n_{\beta} + c'_{\text{B}}n_{\gamma} + d'_{\text{B}}n_{\delta} + i'_{\text{B}} - a'_{\text{A}}n_{\alpha} - b'_{\text{A}}n_{\beta} - c'_{\text{A}}n_{\gamma} - d'_{\text{A}}n_{\delta} - i'_{\text{A}} + p) \quad (13)$$

or

$$\sigma^* = (1/2.48)(\Delta a n_{\alpha} + \Delta b n_{\beta} - \Delta c n_{\gamma} + \Delta d n_{\delta} + \Delta i + p) \quad (14)$$

where  $\Delta a = a_{\text{B}} - a_{\text{A}}$ , etc., and  $a' = S_{\text{A}}$ , etc. For eq 6 to be rigorously applicable,  $a_{\text{B}} = ma_{\text{A}}$ ,  $b_{\text{B}} = mb_{\text{A}}$ ,  $c_{\text{B}} = mc_{\text{A}}$ , and  $d_{\text{B}} = md_{\text{A}}$ . If there are small differences in the coefficients  $m$  of the terms  $a$ - $d$ , between the acid- and base-catalyzed ester hydrolysis, since  $\sigma^*_{\text{Ak}}$  depends on the difference between these coefficients, these will be significant differences in dependence on alkyl branching between  $\sigma^*_{\text{Ak}}$  and  $v^*_{\text{Ak}}$ . This will be the case even when these differences are too small to interfere with the correlation of the rates of acid- or base-catalyzed ester hydrolysis by the modified Taft equation using the same  $v^*_{\text{Ak}}$  steric parameter.

We may now turn our attention to the significance of the Taft  $\sigma^*_{\text{Ak}}$  values. The successful correlation of many sets of

Table II.  $\sigma^*_{Ak}$  Values

Ak	24.8 °C (1,7)	35 °C (2,8)	44.8 °C (3,9)	average	$\sigma^*_{Ak}$ (Taft)
Me	0.000 <sup>a</sup>	0.000 <sup>a</sup>	0.000 <sup>a</sup>	0.000 <sup>a</sup>	0.000 <sup>a</sup>
Et	-0.0980	-0.0946	-0.0884	-0.0941	-0.100
Pr	-0.147	-0.136	-0.145	-0.143	-0.115
Bu	-0.182	-0.162	-0.144	-0.163	-0.130
<i>i</i> -Pr	-0.178	-0.161	-0.143	-0.161	-0.190
<i>i</i> -Bu	-0.176	-0.157	-0.129	-0.154	-0.125
<i>t</i> -Bu	-0.313	-0.314	-0.338	-0.322	-0.300

<sup>a</sup> By definition

Table III. Results of Correlations of  $\sigma^{*t}$  with  $\nu$ 

set	$m$	$c$	$r^a$	$F^b$	$s_{est}^c$	$s_m^c$	$s_c^c$	$n^d$	$100r^{2e}$
1	-0.329	0.0981	0.881	17.26	0.0492	0.0791	0.0640	7	77.5
2	-0.330	0.109	0.893	19.66	0.0463	0.0744	0.0602	7	79.7
3	-0.350	0.130	0.879	16.81	0.0532	0.0854	0.0691	7	77.1

<sup>a</sup> Correlation coefficient. <sup>b</sup>  $F$  test for significance of correlation. All  $F$  values were significant at the 99.0% CL. <sup>c</sup> Standard errors of estimate,  $m$  and  $c$ . Student  $t$  tests for the significance of  $m$  and  $c$  were significant at the 99.0% CL and 80.0% CL, respectively. <sup>d</sup> Number of points in the set. <sup>e</sup> The percent of the data accounted for by the correlation equation.

data with the Taft  $\sigma^*_{Ak}$  values shows that they must be measuring either electrical effects or steric effects or both. The significant correlation obtained for  $\sigma^*_{Ak}$  values with eq 6 has suggested that they are steric parameters. Further support for this conclusion is the study of  $pK_a$  values of 9-substituted fluorenes carried out by Bordwell and his co-workers.<sup>9</sup> We have been successful in correlating our  $\nu$  steric parameters with eq 9. We have therefore examined the correlation of the Taft  $\sigma^*_{Ak}$  values with the equation

$$\sigma^*_{Ak} = an_\alpha + bn_\beta + cn_\gamma + i \quad (15)$$

The  $\sigma^*_{Ak}$  constants used in the correlation are Me, 0.000; *c*-C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub>, -0.06; Et, -0.100; Pr, -0.115; *i*-Bu, -0.125; Bu, -0.130; *t*-BuCH<sub>2</sub>, -0.165; *i*-Pr, -0.190; *s*-Bu, -0.210; Et<sub>2</sub>CH, -0.225; *t*-BuMeCH, -0.28; *t*-Bu, -0.300; and Me<sub>2</sub>EtC, -0.31.<sup>10</sup> The results of the correlation are reported in Table III (set 4A).  $\sigma^*$  values for the *c*-C<sub>6</sub>H<sub>11</sub> and *c*-C<sub>5</sub>H<sub>9</sub> groups were not included in the correlation as  $\nu_{Ak}$  values for cycloalkyl groups deviated greatly from the correlation line obtained with eq 9. The correlation obtained was significant at the 99.9% CL with an  $r^2$  value of 0.9709, accounting for about 97% of the data. The point for the *c*-C<sub>6</sub>H<sub>11</sub> group deviated significantly from the correlation line, however. On excluding this point, an excellent correlation (set 4B), significant at the 99.9% CL, was obtained. A "Student  $t$ " test indicated that  $c$  was not significant. The data were therefore correlated with

$$\sigma^* = an_\alpha + bn_\beta + i \quad (16)$$

giving an excellent correlation (set 4C) significant at the 99.9% CL with an  $r^2$  value of 0.9982, accounting for about 90.0% of the variation. We conclude from this analysis that the Taft  $\sigma^*_{Ak}$  constants are probably steric effect parameters. Correlations with the Taft equation (eq 1) involving only alkyl substituents are steric in nature, as are correlations with the Taft-Pavelich equation (eq 2) involving only alkyl groups. This is also true of the correlation carried out by Hancock and co-workers<sup>10</sup> who have used the equation

$$\log k = \rho^* \sigma^*_{Ak} + \delta E_{S,Ak} + \Delta 6 \quad (17)$$

to correlate the rates of alkaline hydrolysis of MeCO<sub>2</sub>R<sup>1</sup> in 40% dioxane-water at 35 °C. The parameter  $\Delta 6$  is defined as the difference between the number of atoms in the 6 position (numbering from the carbonyl oxygen) in the alkyl group, Ak, and the 6 number obtained starting from the oxygen atom of the carbonyl group and numbering into the alkyl group, Ak',

of the ester. This is equivalent to

$$\Delta 6 = (n_6 - n_5) \quad (18)$$

where  $n_6$  is the number of atoms in position 6 and  $n_5$  is the number in position 5 of the OR group. We may write for  $\Delta 6$ , from  $n_5 = 3n_\beta$  and  $n_6 = 3n_\gamma$ ,

$$\Delta 6 = 3(n_\gamma - n_\beta) \quad (19)$$

Thus, eq 17 represents a relationship containing three steric parameters.

We have shown that the Taft  $\sigma^*_{Ak}$  is probably a steric parameter. It differs from the  $\nu_{Ak}$  values in two ways: (1) it is on a different scale, and (2) it is dependent on the degree of branching of the alkyl group in a different way. The difference in scale does not make possible a direct comparison of the coefficients  $a$  and  $b$  obtained for  $\nu_{Ak}$  with those obtained for  $\sigma^*_{Ak}$ . We can, however, compare the ratios  $a/b$  obtained for  $\nu_{Ak}$  and  $\sigma^*_{Ak}$ . The values are 1.22 and 4.35, respectively. Thus, while both  $\nu_{Ak}$  and  $\sigma^*_{Ak}$  are steric parameters, the former is not much more sensitive to  $n_\alpha$  than it is to  $n_\beta$ , while the latter is very much more sensitive to  $n_\alpha$  than it is to  $n_\beta$ .

We are now in a position to explain the results of Koppel<sup>11</sup> who reported the successful correlation of  $E_S$  and  $E_{S^0}$  values with  $\sigma^*_{Ak}$  values by means of the equations

$$E_{S,R} = m\sigma^*_{Ak} + a(n_H - 3) + i \quad (20)$$

$$E_{S,R^0} = m'\sigma^*_{Ak} + a'(n_H - 3) + i' \quad (21)$$

As  $(n_H - 3) = n_\alpha$  from our previous work,<sup>8</sup>  $E_S$  is roughly proportional to  $\nu$ , and  $\sigma^*$  is given by eq 15, we obtain from eq 20

$$\nu \sim a''n_\alpha + b'n_\beta + i'' \quad (22)$$

where  $a'' = ma^* - a$  and  $b'' = mb^*$ , the starred coefficients being those obtained for the  $\sigma^*_{Ak}$  values. This equation is equivalent to eq 9 with the omission of the  $n_\gamma$  term. Thus, the results of Koppel are readily understood. We will find it convenient to define a set of  $\nu^*_{Ak}$  constants which will have the same dependence on branching of the alkyl group as the  $\sigma^*_{Ak}$  constants but will be on approximately the same scale as the  $\nu_{Ak}$  constants.

For this purpose, we choose the value of  $\nu^*_{Ak}$  for the *t*-Bu and Me groups to be 1.24 and 0.52, respectively. This choice was made because these values are for symmetric top substituents for which the minimum perpendicular van der Waals

Table IV. Results of Correlations with Equations 15 and 16

set	<i>a</i>	<i>b</i>	<i>c</i>	<i>i</i>	<i>F</i> <sup>a</sup>	<i>R</i> <sup>b</sup>	100 <i>r</i> <sup>2c</sup>	<i>r</i> <sub>12</sub> <sup>d</sup>	<i>r</i> <sub>13</sub> <sup>d</sup>
4A	-0.0974	-0.0209	0.302	-0.00136	99.99	0.985	97.09	0.054	0.256
4B	-0.0990	-0.0227	-0.0135	0.00516	260.4	0.995	98.99	0.015	0.204
4C	-0.0981	-0.0225		0.00243	375.4	0.994	98.82	0.015	
	<i>r</i> <sub>23</sub> <sup>d</sup>	<i>s</i> <sub>est</sub> <sup>e</sup>	<i>s</i> <sub>a</sub> <sup>e</sup>	<i>s</i> <sub>b</sub> <sup>e</sup>	<i>s</i> <sub>c</sub> <sup>e</sup>	<i>s</i> <sub>i</sub> <sup>e</sup>	<i>n</i> <sup>f</sup>		
4A	0.147	0.0941	0.00631	0.00497	0.00936 <sup>g</sup>	0.0131 <sup>h</sup>	13		
4B	0.047	0.0109	0.00372	0.00294	0.0135 <sup>i</sup>	0.00780 <sup>j</sup>	12		
4C		0.0111	0.00371	0.00299		0.00758 <sup>j</sup>	12		

<sup>a</sup> *F* test for significance of regression. CL, 99.9% unless otherwise shown. <sup>b</sup> Multiple correlation coefficient. <sup>c</sup> Percent of data accounted for by regression equation. <sup>d</sup> Partial correlation coefficients of *n*<sub>α</sub> on *n*<sub>β</sub>, *n*<sub>α</sub> on *n*<sub>γ</sub>, *n*<sub>β</sub> on *n*<sub>γ</sub>. <sup>e</sup> Standard errors of the estimate, *a*, *b*, *c*, *i*. CL of "Student *t*" tests for significance of *a*, *b*, *c*, *i* is 99.9% unless otherwise indicated. <sup>f</sup> Number of points in the set. <sup>g</sup> 98.0% CL. <sup>h</sup> <20.0% CL. <sup>i</sup> 50.0% CL. <sup>j</sup> 20.0% CL.

Table V. Values of *v*\*<sub>Ak</sub>

Ak	<i>v</i> * <sub>Ak</sub>	Ak	<i>v</i> * <sub>Ak</sub>	Ak	<i>v</i> * <sub>Ak</sub>
Me	0.52 <sup>a</sup>	<i>i</i> -Bu	0.82	Et <sub>2</sub> CH	1.06
Et	0.76	<i>t</i> -BuCH <sub>2</sub>	0.92	<i>t</i> -BuMeCH	1.19
Pr	0.80	<i>i</i> -Pr	0.98	<i>t</i> -Bu	1.24 <sup>a</sup>
Bu	0.83	<i>s</i> -Bu	1.02	Me <sub>2</sub> EtC	1.26

<sup>a</sup> By definition.

radius is calculable. Then substituting in eq 6 the values of *v*\*<sub>Ak</sub> and *σ*\*<sub>Ak</sub> for *t*-Bu and Me, and calculating values of *m* and *c* of -2.40 and -0.52, respectively, we obtain

$$v^*_{Ak} = -2.40\sigma^*_{Ak} - 0.52 \quad (23)$$

This equation may be used to calculate *v*\*<sub>Ak</sub> values using the Taft *σ*\*<sub>Ak</sub> values listed previously.

The *v*\*<sub>Ak</sub> constants calculated from eq 23 should be used in place of the *σ*\*<sub>Ak</sub> for correlating data as they are on the same scale as the *v*<sub>Ak</sub> values and permit comparisons of *S* and *S*\* to be made. Values of *v*\*<sub>Ak</sub> are listed in Table IV.

Finally, let us consider the correlation of rates of acidic hydrolysis of diethyl acetals of the type R<sup>1</sup>R<sup>2</sup>C(OEt)<sub>2</sub> where R<sup>1</sup> = H or Me, and R<sup>2</sup> is variable, with the equation proposed by Taft and Kreevoy,<sup>12</sup>

$$\log(k_X/k_{Me}) = \rho^* \Sigma \sigma^* + h(n'_H - 6) \quad (24)$$

where *n*'<sub>H</sub> is the total number of α-hydrogen atoms on R<sup>1</sup> and R<sup>2</sup>. Now

$$n'_H = n_{1,H} + n_{2,H} \quad (25)$$

where *n*<sub>1,H</sub> and *n*<sub>2,H</sub> are the numbers of α-hydrogen atoms on R<sup>1</sup> and R<sup>2</sup>, respectively.

However,

$$n_{1,H} = 3 - n_{1\alpha}, \quad n_{2,H} = 3 - n_{2\alpha} \quad (26)$$

where *n*<sub>1α</sub> and *n*<sub>2α</sub> are the number of α-carbon atoms in R<sup>1</sup> and R<sup>2</sup>, respectively. Then

$$(n'_H - 6) = 6 - \Sigma n_{\alpha} - 6 = -\Sigma n_{\alpha} \quad (27)$$

and eq 24 becomes

$$\log(k_X/k_{Me}) = \rho^* \Sigma \sigma^*_{Ak} - h \Sigma n_{\alpha} \quad (28)$$

As we have already shown that *σ*\*<sub>Ak</sub> is probably a steric parameter and *n*<sub>α</sub> is a steric parameter, the Taft-Kreevoy equation is probably a function solely of steric effects as far as alkyl groups are concerned.

### References and Notes

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