

perature probe as previously described.<sup>24</sup>

The *infrared spectra* were obtained on a Beckman IR-10 spectrometer and *melting points* (uncorrected) were measured on a Mettler FP-1 melting point apparatus.

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# The Nature of the Electrical Effect of Alkyl Groups.

## 1. The Validity of the $\sigma^*$ Constants

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**Abstract:**  $\sigma^*$  values for alkyl groups are defined from rate constants for the acid- and base-catalyzed hydrolysis of amides, XCONH<sub>2</sub>. These  $\sigma^*$  values show no relationship with those defined by Taft from ester hydrolysis. They also do not show any systematic dependence on alkyl group structure. These results support the conclusion that the Taft  $\sigma^*$  constants for alkyl groups *do not* measure the electrical effects of alkyl groups.

In a recent communication, Macphee and Dubois<sup>1</sup> have presented arguments which they claim refute our conclusions<sup>2</sup> that the electrical effects of alkyl groups are essentially constant and that the  $\sigma^*$  values for alkyl groups are artifacts. These authors very correctly note that if our conclusions are indeed justified, it is necessary to reexamine a large body of published results in which the relative importance of steric and electrical effects of alkyl groups was studied. In this work we present new results which we feel strongly support our view that  $\sigma^*$  values for alkyl groups do not measure the electrical effects of those groups. The question of the significance of the Taft  $\sigma^*$  values for alkyl groups has long been a controversial one. Earlier work in this area has been thoroughly examined in an excellent critical review by Shorter.<sup>3</sup>

To apply the Taft method for separating polar and steric effects we require rate data for substituted compounds undergoing one reaction in which both steric and electrical effects occur and another reaction in which only steric effects occur. It is further necessary that the magnitude of the steric effects be the same in both reactions. We have recently shown<sup>4</sup> that acid-catalyzed hydrolysis of amides is a function only of steric effects, while the base-catalyzed hydrolysis is a function

of both steric and electrical effects. Evidence for this statement is provided by the successful correlation of rate constants for acid hydrolysis of amides XCONH<sub>2</sub> with the modified Taft equation

$$\log k_X = \psi v_X + h \quad (1)$$

whereas rate constants for basic hydrolysis required the LDS equation

$$\log k_X = \alpha \sigma_{1X} + \beta \sigma_{RX} + \psi v_X + h \quad (2)$$

Thus, the acid hydrolyses could be accounted for by a steric term whereas the basic hydrolyses require electrical effect terms as well. It should be noted that the sets studied included groups with a range of electrical effect in both the acid- and base-catalyzed hydrolyses. The data used in the correlations are tabulated in our earlier work.<sup>4</sup> The  $v_X$  values used as steric parameters in eq 2 have been shown to be a linear function of the van der Waals radii in the case of spherically symmetric groups and are independent of electrical effects. Sets of rate constants for basic hydrolysis of amides which contained only alkyl substituents were then shown to be correlated well by the

**Table I.** Results of Correlations with Equation 3

Set <sup>j</sup>	$\rho^*$	$\psi$	$h$	$R^a$	$F^b$	$r_{12}^c$	$s_{\text{est}}^d$	$s_{\rho\psi}^d$	$s_{\psi}^d$	$s_h^d$	$n^e$
4	0.0167	-2.06	2.232	0.981	149.6 <sup>f</sup>	0.418	0.128	0.108 <sup>g</sup>	0.132 <sup>f</sup>	0.115 <sup>f</sup>	15
5	-0.348	-1.99	2.478	0.981	116.9 <sup>f</sup>	0.457	0.126	0.351 <sup>h</sup>	0.142 <sup>f</sup>	0.119 <sup>f</sup>	12
6	-0.631	-2.12	2.931	0.983	71.35 <sup>f</sup>	0.424	0.133	0.379 <sup>i</sup>	0.185 <sup>c</sup>	0.168 <sup>f</sup>	8
7	-0.702	-1.98	2.135	0.981	91.23 <sup>f</sup>	0.408	0.0742	0.416 <sup>i</sup>	0.153 <sup>f</sup>	0.111 <sup>f</sup>	10
8	-0.334	-1.83	2.337	0.990	177.6 <sup>f</sup>	0.408	0.0503	0.282 <sup>h</sup>	0.104 <sup>f</sup>	0.0751 <sup>f</sup>	10
9	-0.499	-1.80	2.555	0.974	70.66 <sup>f</sup>	0.094	0.0693	0.492 <sup>h</sup>	0.152 <sup>f</sup>	0.137 <sup>f</sup>	9

<sup>a</sup> Multiple correlation coefficient. <sup>b</sup>  $F$  test for significance of correlation. Confidence levels are indicated by superscripts. <sup>c</sup> Partial correlation coefficient of  $\sigma^*$  on  $v$ . <sup>d</sup> Standard errors of the estimate,  $\rho^*$ ,  $\psi$ , and  $h$ . Superscripts indicate confidence levels. <sup>e</sup> Number of data points in the set. <sup>f</sup> 99.9% confidence level (CL). <sup>g</sup> < 20.0% CL. <sup>h</sup> 50.0% CL. <sup>i</sup> 80.0% CL. <sup>j</sup> Set numbers refer to ref 3.

**Table II.** Values of for Alkyl Groups

X	Taft <sup>7</sup>	4, 7 <sup>a</sup>	5, 8 <sup>b</sup>	6, 9 <sup>c,d</sup>
Me	0	0	0	0
Et	-0.100	-0.087	-0.078	
Pr	-0.155	-0.053	-0.079	
Bu	-0.130	-0.160		
<i>i</i> -Bu	-0.125	-0.067	0.088	
<i>i</i> -Pr	-0.190	-0.088	-0.154	-0.014
<i>s</i> -Bu	-0.210	-0.087	-0.114	-0.001
<i>c</i> -C <sub>6</sub> H <sub>11</sub> CH <sub>2</sub>	-0.06	0.036	0.075	0.178
<i>c</i> -C <sub>5</sub> H <sub>9</sub>	-0.20	-0.195	0.024	0.138
<i>c</i> -C <sub>6</sub> H <sub>11</sub>	-0.15	-0.096	-0.217	-0.063

<sup>a</sup> From rate constants in water at 75 °C. <sup>b</sup> From rate constants in water at 85 °C. <sup>c</sup> From rate constants in water at 95 °C. <sup>d</sup> Rate constants for the methyl group were calculated from the correlation line. The numbers in the column headings correspond to the numbers of the data sets reported in ref 3.

modified Taft equation. That the magnitude of the steric effect is the same in both reactions, acidic and basic, is shown by  $t$  tests of the significance of the difference between the regression coefficients,  $\psi_A$  and  $\psi_B$  obtained by correlation with eq 1. The subscripts A and B refer to acid- and base-catalyzed hydrolyses, respectively.

As Macphee and Dubois have suggested that alkyl groups do not have constant electrical effects, we have followed their approach and correlated the amide hydrolysis data with the equation

$$\log k_X = \rho^* \sigma_X^* + \psi v_X + h \quad (3)$$

using the  $\sigma^*$  values taken from Taft.<sup>6</sup> The results of these correlations are shown in Table I. The confidence levels of the  $t$  tests for significance of the  $\rho^*$  values shows clearly that there is no dependence on  $\sigma^*$  in either the acidic hydrolysis of all substituent types or the basic hydrolysis of alkyl substituted amides. We therefore conclude that the equality of  $\psi_A$  and  $\psi_B$  is in fact real.

We may now define  $\sigma^*$  constants from these reactions. According to Taft<sup>7</sup>

$$\sigma^* = \rho^{*-1} [\log (k_X/k_{Me})_B - \log (k_X/k_{Me})_A] \quad (4)$$

All that is needed is a value of  $\rho^*$ . We have chosen for  $\rho^*$  the value of 0.969, obtained from the difference  $\rho_B - \rho_A$ , where  $\rho_B$  and  $\rho_A$  are the  $\rho$  values reported by Jaffé<sup>8</sup> for the basic and acidic hydrolyses respectively for 3- and 4-substituted benzamides. This choice was made by analogy with the choice of  $\rho^*$  by Taft<sup>7</sup> which was based on the difference in  $\rho$  values for the acid- and base-catalyzed hydrolysis of amides. In fact *the choice of  $\rho^*$  is not important, as a comparison of the quantities*

*$\rho^* \sigma^*$  for the substituents of interest would have sufficed.* The values of  $\sigma^*$  obtained for alkyl groups are shown in Table II, with the corresponding  $\sigma^*$  values of Taft.<sup>7</sup>

The  $\sigma^*$  values, according to Macphee and Dubois, are "strictly additive in nature." Thus, the validity of the alkyl  $\sigma^*$  values requires that they follow the sequence Me > primary > secondary > tertiary. From the three sets of alkyl  $\sigma^*$  values we have defined, we obtain the sequences:

4,7: *i*-Bu > *c*-C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub> > Me > Pr > Et = *i*-Pr = *s*-Bu > *c*-C<sub>6</sub>H<sub>11</sub> > *c*-C<sub>5</sub>H<sub>9</sub>

5,8: *i*-Bu > *c*-C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub> > *c*-C<sub>5</sub>H<sub>9</sub> > Me > Et = Pr > *s*-Bu > *i*-Pr > *c*-C<sub>6</sub>H<sub>11</sub>

6,9: *c*-C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub> > *c*-C<sub>5</sub>H<sub>9</sub> > Me = *s*-Bu > *i*-Pr > *c*-C<sub>6</sub>H<sub>11</sub>

where the numbers refer to the column headings in Table II. These  $\sigma^*$  values generally bear no relationship to those of Taft. They do not show any discernible pattern of dependence on alkyl group structure. It is particularly significant that although the  $\sigma^*$  constants defined here from amide hydrolysis were obtained for the same reaction in the same solvent by the same laboratory and differ only in temperature, the  $\sigma^*$  values obtained are not well correlated with each other. In fact, they behave like the artifacts they are. They are simply the result of incomplete cancellation of the steric effect due to either experimental error or unknown secondary effects. The failure of the  $\sigma^*$  alkyl values (defined here from pairs of reactions in which the steric effect clearly cancels out) to agree with those of Taft, or to show a simple dependence upon alkyl group structure, seems to us to show clearly and unequivocally that the Taft  $\sigma^*$  values for alkyl groups are artifacts. As was suggested by Macphee and Dubois, it is indeed necessary to reexamine and reinterpret a large part of the literature relating to the effects of alkyl substituents on reactivity and physical properties. A detailed discussion of the arguments of Macphee and Dubois will be presented in a later work together with an explanation of what the Taft  $\sigma^*$  values actually measure and what the significance of a successful correlation with Taft  $\sigma^*$  alkyl values represents.

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