ELECTRONIC EFFECTS OF ALKYL GROUPS

F. G. Bordwell* and Herbert E. Fried

Department of Chemistry
Northwestern University
Evanston, Illinois 60201

The use of Taft σ^* constants as measures of electronic effects of alkyl groups has been the subject of considerable discussion. In Taft's original analysis, σ^*'s for alkyl groups, R, (and hydrogen) were derived from hydrolyses of esters, such as RCO_2Et, where R is attached to an sp^2 hybridized carbon atom, whereas σ^*'s for heteroatom groups, G, were derived, for the most part, from the hydrolyses of esters, such as GCH_2CO_2Et, where G is attached to an sp^3 hybridized carbon atom.[1] The σ^*_R values obtained appeared to verify and quantify Ingold's earlier suggestion that alkyl groups were electron releasing in the order t-Bu > i-Pr > Et > Me,[2] but Ritchie pointed out a short time later that in many systems Taft correlations are as good when hydrogen and these four alkyl groups (and others) are all assigned $\sigma^* = 0$.[3] Although Hine has accepted Ritchie's analysis,[4] most other authors of recent texts on physical organic chemistry list Taft's original σ^*'s for alkyl groups and hydrogen without critical comment,[5] supporting Shorter's statement that "most physical organic chemists continue to believe that the electron-releasing properties of alkyl groups in aliphatic systems increase with chain length and branching, and continue to use σ^* values as a measure of this".[6,7] Recently, Charton has shown that rate constants for base-catalyzed hydrolyses of esters[8 a, b] and amides,[8 c] RCO_2R' and $RCONH_2$, do not correlate with a modified Taft expression, indicating that the electrical effects of alkyl groups are unimportant in these reactions. On the other hand, satisfactory correlation

of these data with a steric parameter was achieved, and it was concluded, that Taft σ^*_R

values are merely artifacts governed by steric effects.[8] This view is consistent with

recent data obtained in our laboratory using the sterically crowded 9-substituted fluorene

system. Here the effects for the four alkyl groups become progressively more acid

weakening in the order Me < Et < i-Pr < t-Bu, in apparent agreement with Taft σ^*_R's, but

when a sulfur atom, or SO_2 group, or CH_2 group is interposed between the fluorene

nucleus and R the order of effects is reversed.[9]   Both the acid-weakening and the acid-

strengthening effects of the alkyl groups are believed to have a steric, rather than an

electronic, origin.   We now present equilibrium acidity data for carboxamides which

provide further information on alkyl effects.

The carboxamides, $RCONH_2$ and GCH_2CONH_2, are nitrogen acid analogs of the

acetic acids, RCO_2H and GCH_2CO_2H; acidity data for the latter have been used as an

alternative source of σ^* (or σ_I) constants.[1,10] Since the carboxamides resemble the

carboxylic acids closely in structure (compare the geometries in anions 1 and 2) we have

every reason to expect the electronic effects between G and the acidic sites to be similar.

This expectation was realized when G is H, F, PhO, MeO, Ph, α-Nap, PhS, EtS, and

PhSe. Here a reasonably good correlation with $\sigma^*_{CH_2G}$ constants was obtained for

equilibrium acidities measured in dimethyl sulfoxide (DMSO) solution ($\rho^* = 2.8$, $r =$

0.908).[11,12]

$$\underline{1} \qquad\qquad\qquad \underline{2}$$
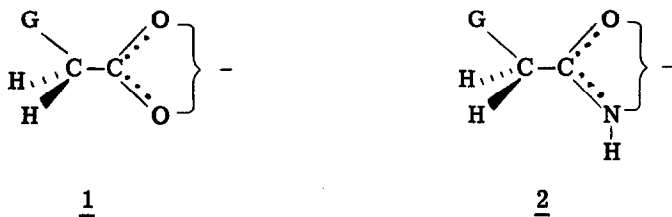
Since ρ^* is larger for the acidities of GCH_2CONH_2 in DMSO than for the acidities

of GCH_2CO_2H in H_2O ($\rho^* = 1.7$), the sensitivity of the acids, $RCONH_2$, to changes in

electronic effects in R should be greater than that of the acids, RCO_2H. Examination of

Table 1 shows that, contrary to expectations from σ^*_R constants, there is very little

change in alkyl effects as the chain is lengthened or branched. The small decreases in acidity observed with increasing alkyl size are probably due to increases in steric inhibition of solvation. Evidently steric inhibition to solvation is greatly exaggerated in the aqueous medium used for measurement of RCO_2H acidities (or RCO_2Et ester hydrolysis rates).

Table 1. Equilibrium Acidities of Carboxamides, $RCONH_2$, in Dimethyl Sulfoxide Solution

R	p$\underline{K}$[a]	R	p$\underline{K}$[a]
Me	25.5[13]	H	23.5
Et	25.7	i-Bu	25.7
i-Pr	25.7	t-BuCH$_2$	26.1
t-Bu	25.7	Et$_3$C	26.0

[a]Measured against two or more standard indicators.[12] The standard deviations in titrations were generally ± 0.05 p$\underline{K}$ unit, or less.

The 2 p$\underline{K}$ unit greater acidity of formamide vs acetamide in DMSO is comparable to the 1 p$\underline{K}$ unit greater acidity of formic acid vs acetic acid in water. These differences can be ascribed to a hyperconjugative (or like[14]) effect of CH_3, and do <u>not</u> constitute a basis for assigning differences in σ^* (or σ_I) constants, to CH_3 and H. The latter should be based on effects at sp^3 carbon atoms.[3,4,10] We conclude that Taft σ^*_H and σ^*_R constants are not valid measures of the electronic effects of hydrogen and alkyl groups.[15]

References and Notes

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6.   J. Shorter, Adv. Linear Free Energy Relat., Chapter 2, 99-100 (1972).

7.   See, for example, A-J. MacPhee and J-E. Dubois, Tetrahedron Lett., 2471 (1976).

8.   (a) M. Charton, J. Am. Chem. Soc., 97, 1552 (1975); (b) M. Charton, ibid., 97,

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9.   F. G. Bordwell, G. E. Drucker, and G. J. McCollum, J. Org. Chem., 41,

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10.   M. Charton, J. Org. Chem., 29, 1222 (1964).

11.   These data will be presented and discussed in a later paper.

12.   W. S. Matthews, et al., J. Am. Chem. Soc., 97, 7006 (1975).

13.   F. G. Bordwell and D. Algrim, J. Org. Chem., 41, 2507 (1976).

14.   See the discussion in ref. 4, pp 92-96; note that "σ_H* is often a poor measure of

      the polar character of the hydrogen substituent".

15.   L. S. Levitt and H. F. Widing, Prog. Phys. Org. Chem., 12, 119 (1976), report

      a statistical analysis of gas phase ionization potential data from which they conclude

      that alkyl groups have an inductive order corresponding to that of Taft σ_R* constants.

      Their data agree well with Taft's σ_I scale, and they recommend use of $\sigma_{I(R)}$ in

      LFER analyses. We advise caution in applying these σ_I's to solution data, since

      it is clear that other factors often overshadow this inherent inductive order.[8,9]