Communications

Carbon Acids. 11. Acid Strengthening Alkyl Effects and Questionable Applications of the Taft Equation

Summary: Plots of σ^*_R vs. pK (in dimethyl sulfoxide for R = t-Bu, i-Pr, Et, and Me) in 9-R-X-fluorene systems gave ρ^*'s of −7.0, −7.3, and −7.6 for X = S, SO_2, and CH_2, respectively.

Sir: The relative polar effects of the alkyl substituents, Me, Et, i-Pr, and t-Bu have been the subject of considerable discussion. Ingold originally suggested that these groups possess inductive electron-releasing properties in the order t-Bu > i-Pr > Et > Me.[1] This order was later expressed quantitatively in terms of σ^* constants by Taft.[2] However, 15 years ago Ritchie pointed out that alkyl groups behave differently than groups containing heteroatoms with respect to "transmission coefficients", and showed that in many systems Taft correlations work as well when these four alkyl groups (and others) are assigned $\sigma^* = 0$, as when they are given the Taft values (σ^*'s = −0.3, −0.19, −0.1, and 0, respectively[2]).[3] Further doubt concerning the electron-releasing effect of these alkyl groups was raised by the discovery of Brauman and Blair that in the gas phase the acidities of the alcohols, t-BuOH, i-PrOH, EtOH, and MeOH, are in the reverse order to that found in solution.[4] Nevertheless, as pointed out by Shorter in a recent review of the Taft equation, "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".[5] For example, 9-substituted fluorenes have been shown to be particularly sensitive to alkyl effects, and Taft plots have been constructed based upon (a) rates of detritiation by NaOMe in MeOH (Et, Me, $PhCH_2$, CH_3OCH_2),[6] (b) rates of dedeuteration by NaOMe in MeOH (Et, Me, $PhCH_2$, $HOCH_2$, $MeOCH_2$; $\rho^* = 2.25$),[7] (c) equilibrium acidities in Me_2SO–H_2O (t-Bu, i-Pr, Et, Me, $PhCH_2$, Ph, CO_2Me; $\rho^* = 4.6$),[8] and (d) equilibrium acidities in cyclohexylamine (t-Bu, i-Pr, Et, Me, $PhCH_2$; $\rho^* = 4.547$).[9] Conclusions from these studies have been drawn concerning hyperconjugation of the CF_3 group,[6] the concertedness of E_2 eliminations,[7] the extent of carbanion formation in the transition state for detritiation,[8] and the nature of alkyl effects.[7,8] In this paper we present data to show that the order of these alkyl effects in 9-substituted fluorenes can be *reversed* by interposing an additional atom between R and the acidic site.

Examination of the equilibrium acidities in dimethyl sulfoxide of 9-alkylfluorenes gave the expected acidity order,[8,9] i.e., t-Bu < i-Pr < Et < Me, with about an equal sensitivity ($\rho^* = 6.7$, $r = 0.96$) as that observed in Me_2SO–H_2O or cyclohexylamine. On the other hand, for 9-alkylthiofluorenes the acidity increased as the size of the alkyl group increased, i.e., t-BuS > i-PrS > EtS > MeS. Plotting σ^*_R vs. pK for RS-fluorenes gave a better fit ($r = 0.99$) than for 9-alkylfluorenes; the ρ^* was slightly larger in size (7.0), but was, of course, *negative in sign.* Initially, we thought that this order was associated in some way with the high polarizability of the divalent sulfur atom, but further investigation showed that the Taft plots were also negative for 9-alkylsulfonylfluorenes ($\rho^* = -7.3$, $r = 0.98$) and even for 9-alkylmethylenefluorenes ($\rho^* = -7.6$, $r = 0.97$). In other words, by interposing S, SO_2, or CH_2 between R and the acidic site, the effect of increasing the size and branching of R in the fluorenyl anion has changed from deacidifying to acidifying.[10] For 9-R-fluorenes the increase in the destabilizing effect from Me to t-Bu amounts to about 2.7 kcal/mol, and for 9-RCH_2-fluorenes the increase in the stabilizing effect of R from Me to t-Bu is about 3.1 kcal/mol. If we assign the "normal" Taft σ^*'s to the RCH_2 substituents (i.e., Et, −0.10; Pr, −0.115; i-Bu, −0.125; *neo*-Pent, −0.165[2]), we find the correlation coefficient in the Taft plot to be excellent ($r = 0.99$), but ρ^* is ridiculously large and negative ($\rho^* = -36 \pm 4.5$). If all the alkyl points are included (Me, Et, i-Pr, i-Bu, t-Bu, neo-Pent) the Taft plot is chaotic ($\rho^* = 6.2 \pm 5.5$, $r = 0.45$). The pK's are summarized in Table I.

Table I. Equilibrium Acidities in Dimethyl Sulfoxide Solution for 9-R-X- and 9-R-Fluorenes[a]

Alkyl group	pK, 9-substituted fluorene R	RCH_2	RS	RSO_2
Me	22.3_4	22.6	18.0	12.7_5
Et	22.6	22.2	17.5	12.3
i-Pr	23.2	21.6	16.9	11.7
t-Bu	24.3_5	20.3	15.9	10.5_5

[a] Average of values for two or more titrations using at least two indicators [see W. S. Matthews, et al., *J. Am. Chem. Soc.*, **97**, 7006 (1975) for the method used for these measurements]. The values using different indicators generally agreed to within ±0.05 pK units.

The observation of acid-strengthening alkyl effects in solution that increase in magnitude with increased size and branching of the alkyl group appears to be unique. We will reserve detailed comment on the nature of the factors determining alkyl effects pending additional experiments. A progressive increase in the relief of steric strain on forming the carbanion and/or a progressive increase in stabilization of the carbanion by polarization of the alkyl group are potential acid-strengthening effects that are being considered. The primary purpose of this communication, however, is to emphasize the dangers in drawing conclusions concerning polar effects from Taft plots which rely on alkyl points to construct the line.

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References and Notes

(1) See C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1st ed, 1953, Chapter II, and references cited therein.

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