

FACTORS CONTROLLING THE DISSOCIATION OF ALIPHATIC CARBOXYLIC ACIDS IN 80 % METHYLCELLOSOLVE -
20 % WATER. A CASE FOR THE IMPORTANCE OF POLAR EFFECTS

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Abstract : The dissociation constants of a wide range of aliphatic carboxylic acids in 80 % methylcellosolve- 20 % water have been investigated. The pK variation between the limits defined by the acids MeCO_2H and $i\text{-Pr}_3\text{CCO}_2\text{H}$ is controlled principally by polar effects as defined by σ^* .

The dissociation of carboxylic acids in water is a complex phenomenon that has to date received a great deal of attention without producing any real solution. One of the reasons for this is, undoubtedly, the complicated structure of water and its modification in the presence of a dissociation reaction. Subtle structural changes are thereby masked by solvent effects.⁽¹⁻⁴⁾ Studies of large sets of carboxylic acids in water are moreover precluded by solubility problems. One approach to this difficulty has been developed by Simon⁽⁵⁻⁶⁾ who measured the "apparent" dissociation constants of a large number of organic acids in the mixture 80 % methylcellosolve- 20% water. These measurements have the advantage of being simple to perform and requiring only small amounts of compound. Furthermore, solubility is no longer a problem in this solvent system. Pursuing our studies on the nature of the effects of alkyl groups on various systems we decided to investigate the acidities of a wide ranging set of aliphatic carboxylic acids in the solvent system used by Simon. Our continuing interest in the steric and polar effects of alkyl groups has prompted an investigation of the dissociation of aliphatic carboxylic acids in this solvent system.

Table I gives the results (pK's) for a set of aliphatic carboxylic acids RCO_2H . Included in this table for purposes of correlation are our revised Taft steric parameters E_s^+ of the groups, their polar parameters σ^* ,⁽⁷⁾ and the Newman six-number. It should be stated at the outset that two related factors have already been invoked as responsible for the evolution of the pK's of alkyl groups : the first is the more general idea of steric inhibition to solvation and the second, steric as well but more specific, the Newman six-number. Neither idea has been applied quantitatively to the problem of aliphatic acid dissociation due to the lack of suitable parameters.⁽⁸⁾

Table I: pK values for aliphatic carboxylic acids in 80% methylcellosolve
20% water at 25°.

N°	R	pK _{MCS}	-σ*	-E _S ' ^f	Δ6 ^g
1	Me	6.84 ^c	0.0 ^a	0.0	0
2	Et	7.18 ^d	0.1 ^a	0.08	0
3	n-Pr	7.30 ^d	0.115 ^a	0.31	3
4	i-Bu	7.33 ^c	0.125 ^a	0.93	6
5	n-Bu	7.33 ^e	0.13 ^a	0.31	3
6	CH ₃ (CH ₂) ₈ -	7.30 ^c	0.130 ^a	0.31	3
7	i-Pr	7.39 ^d	0.190 ^a	0.48	0
8	s-Bu	7.56 ^e	0.210 ^a	1.00	3
9	Et ₂ CH	7.61 ^c	0.225 ^a	2.00	6
10	i-PrEtCH	7.63 ^e	0.265 ^b	3.23	9
11	t-BuMeCH	7.80 ^e	0.28 ^a	3.21	9
12	t-Bu	7.77 ^e	0.30 ^a	1.43	0
13	EtMe ₂ C-	7.97 ^e	0.31 ^a	2.28	3
14	i-PrMe ₂ C-	8.01 ^e	0.313 ^b	3.54	6
15	Et ₃ C-	8.15 ^e	0.355 ^b	5.29	9
16	t-Bu ₂ CH	8.41 ^e	0.411 ^b	6.97	18
17	t-BuMe ₂ C-	8.38 ^e	0.422 ^b	5.40	9
18	i-PrEt ₂ C-	8.41 ^e	0.435 ^b	6.20	12
19	i-Pr ₃ C-	8.79 ^e	0.518 ^b	6.73	18

a) R.W. Taft, Steric Effects in Organic Chemistry, ch. 13; ed. M.S. Newman, John Wiley, New-York, 1956.

b) Ref. 7.

c) W. Simon, Ref. 6.

d) K. Bowden, M. Hardy, D.C. Parkins, Can.J.Chem., Vol. 46, p. 2929 (1968).

e) Our values.

f) J.A. MacPhee, A. Panaye and J.E. Dubois, Tetrahedron, Vol. 34, p. 3553 (1978).

g) M.S. Newman, J.Am.Chem.Soc., 72, 4783 (1950).

The data in Table I were analysed using a variety of correlation equations as follows :

$$\text{pK} = \sigma^* \sigma^* + a \quad (1)$$

$$\text{pK} = \rho^* \sigma^* + \delta E_S' + a \quad (2)$$

$$\text{pK} = \rho^* \sigma^* + b (\Delta 6) + a \quad (3)$$

$$\text{pK} = \delta E_S' + a \quad (4)$$

$$\text{pK} = b (\Delta 6) + a \quad (5)$$

The results of these correlations are given in Table II. The correlation coefficient r , the ψ parameter of Exner and the standard deviation sd are indicated for each correlation. It is immediately evident from correlation 1 that σ^* is a significant parameter which takes into account 98% (r^2) of the pK variation in the series. This is brought out graphically in the figure where minor deviations from the regression line are portrayed. The importance of the steric effect and the six-number ($\Delta 6$) are assessed by correlations 2 and 3. The improvement

in these correlations with respect to correlation 1 appears to be real since the Student *t* indicates that E'_S and $\Delta 6$ are significant at the 95% and 97.5 % levels respectively. Caution must be exercised in the interpretation of these statistics, however, because of multicollinearity between σ^* and E'_S on the one hand, and σ^* and $\Delta 6$ on the other. σ^* and E'_S correlate as well as the pK's and E'_S so that the improvement noted between

$$\sigma^* = \delta E'_S + a \quad (6)$$

correlations 1 and 2 is simply accounted for by multicollinearity. σ^* and $\Delta 6$ also correlate well but the result of correlation 5 suggests that $\Delta 6$ might be a significant parameter in the corre-

$$\sigma^* = b (\Delta 6) + a \quad (7)$$

lation of pK's and that the improvement noted in correlation 3 is real. This is difficult to affirm with certainty since we are dealing with small differences but it is worth noting that the *i*-Pr and *t*-Bu groups which deviate slightly from the line in the figure are adequately correlated by Equation 3. This point will be considered in more detail in the full article.

In conclusion it may be stated that the dissociation of aliphatic carboxylic acids in 80 % methylcellosolve-20 % water is principally controlled by polar effects even for extremely hindered compounds.

Table II : Correlation of pK values as a function of σ^* , E'_S and $\Delta 6$

Corr.	σ^*	δ	b	a	r	ψ	s.d.
1	-3.715	-	-	6.800	0.990	0.145	0.073
2	-3.097	-0.037	-	6.859	0.993	0.131	0.063
3	-3.381	-	0.010	6.820	0.993	0.129	0.063
4	-	-0.199	-	7.224	0.943	0.350	0.175
5	-	-	0.077	7.273	0.825	0.598	0.299
6	-	0.052	-	-0.118	0.927	0.396	0.053
7	-	-	-0.019	-0.133	0.79	0.648	0.086

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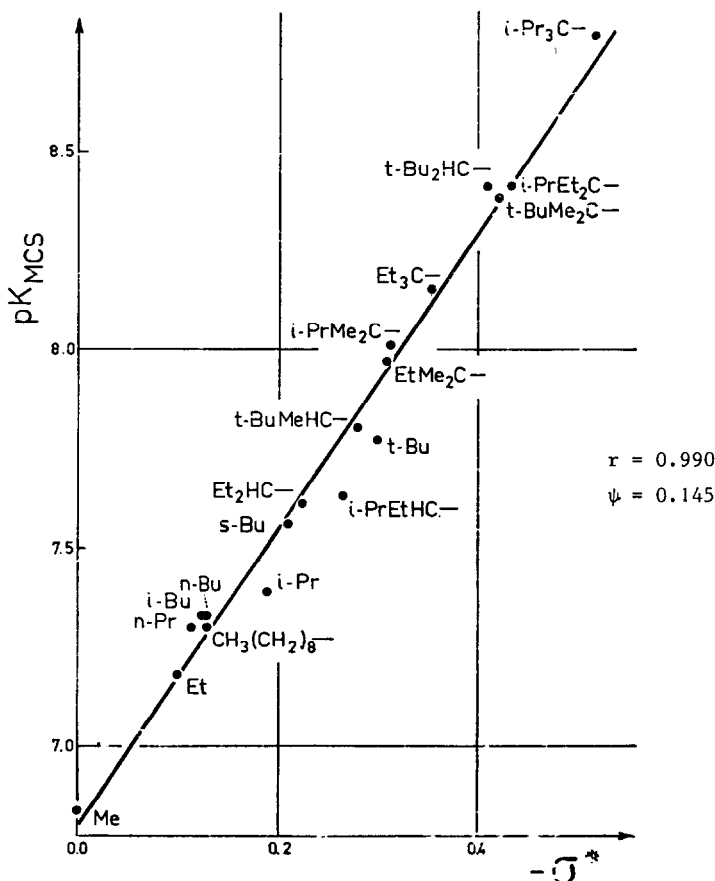


Figure 1. Relationship between dissociation constant and polar effect. The importance of the latter is clearly seen.

- b) P.F. Sommer and W. Simon, Zusammenstellung von Scheinbaren Dissoziationskonstanten im Lösungsmittelsystem Methylcellosolve-Wasser, Vol. 2, Juris-Verlag, Zürich, 1961.
 c) W. Simon and P.F. Sommer, Zusammenstellung von Scheinbaren Dissoziationskonstanten im Lösungsmittelsystem Methylcellosolve-Wasser, Vol. 3, Juris-Verlag, Zürich, 1963.
 7. J.A. MacPhee and J.E. Dubois, Tetrahedron Lett., 2225 (1978).
 The appropriate σ^* values have been estimated from measurements of ν_{CO} on carboxylic acids using the equation :

$$\sigma^* = - (\Delta + 1.45) / 69.73$$

where

$$\Delta = \nu_{\text{CO,Me}}^{\circ} - \nu_{\text{CO,R}}^{\circ}$$

These ν_{CO}° values are obtained by extrapolating values measured in a series of solvents to the vapour phase using the Allerhand and Schleyer equation :

$$\nu_{\text{CO}}^{\text{solv.}} = \alpha G + \nu_{\text{CO}}^{\circ}$$

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