Tetrahedron Letters No. 25, pp 2225 - 2228, 1978.
©Pergamon Press Ltd. Printed in Great Briton.

0040-4039/78/0615-2225$02.00/0

THE INFRARED CARBONYL GROUP FREQUENCY OF ALIPHATIC CARBOXYLIC ACIDS. A PROBE FOR THE POLAR EFFECTS OF ALKYL GROUPS.

By John Anthony MacPhee and Jacques-Emile Dubois*
Institut de Topologie et de Dynamique des Systèmes de l'Université Paris VII,
associé au C.N.R.S., 1, rue Guy de la Brosse 75005 PARIS.

(Received in UK 11 April 1978; accepted for publication 27 April 1978)

Despite the fact that the first quantitative estimate of the polar effects of alkyl groups (the Taft σ^* scale) was published some 25 year ago (1), the very existence of differences between the polar effects of such groups with chain lengthening and branching continues to be questioned (2,3). This is due to the particular difficulty of the separation of polar and steric effects for alkyl groups; these groups have steric effects which increase rapidly with substitution and tend to mask all other effects. Taft's approach to solving this problem by taking differences between the relative rates of acid and base hydrolysis of carboxylic esters gave the well-known equation:

$$\sigma^* = \frac{1}{2.48}\left[\ \log\left(\frac{k}{k_o}\right)_B - \log\left(\frac{k}{k_o}\right)_A\ \right] \qquad (1)$$

the first term of which ($\log (k/k_o)_B$) is assumed to be a function of polar and steric effects, and the second a function of steric effects only.

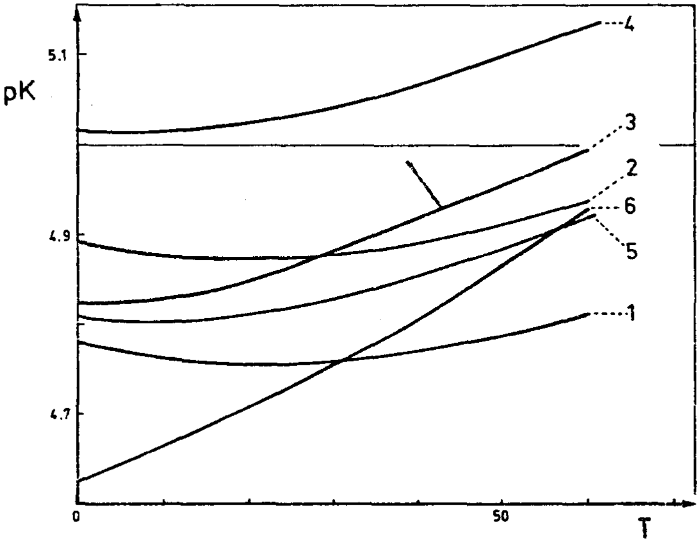
The assumption that $\log (k/k_o)_B$ is a function of steric and polar effects has recently been challenged by Charton (2) who analysed the data by a multiple correlation equation:

$$\log (k)_B = \alpha\sigma_I + \beta\sigma_R + \psi_B\nu + h_B \qquad (2)$$

The parameters in eq. 2 (σ_I,σ_R and ν) are assumed to reflect inductive, resonance, and steric effects. It was found that the parameters σ_I and σ_R (for alkyl groups) are not statistically significant and it was concluded that $\log (k)_B$ is a function of the steric effect only. The validity of this conclusion depends on the aptitude of σ_I to reflect the inductive nature of alkyl groups. In view of our own interest (4) in this matter we propose to examine in this note the reason why Charton's conclusions are not definitive and to present new experimental evidence in support of our own position.

The σ_I parameter (Charton's own) is measured from the pK's of substituted acetic acids in water. Fig.1 shows the behaviour of the pK's of a number of alkyl substituted acetic acids in water as a function of temperature (5). It is evident that the pK's are extremely temperature dependent and that in several cases there are inversions of acidity order with temperature. It has been reported that the ionization of acetic and trimethylacetic acids in water at 25° is entropy controlled, contrary to expectation (6). This overall behaviour is indeed not well understood but it is generally accepted that solvation changes are extremely important (7). The use of these pK values to calculate σ_I's which are assumed to reflect the inductive character of alkyl groups seems rather drastic since the σ_I values could even change sign with temperature. For this reason we feel that the contribution of the polar effect to the variation of log $(k)_B$ in eq.2 cannot adequately be assessed by σ_I and that the validity of Taft's σ^* scale for alkyl groups has therefore not been undermined. The ionization of acetic acids in water constitutes a much too complicated and poorly understood system to be used in estimating the polar effects of alkyl groups. Recently Grob et al. (8) have shown that the ionization of 4-substituted quinuclidinium perchlorates in water has a much simpler temperature dependence. He has, in addition, shown that these ionizations are enthalpy and not entropy, controlled. It is noteworthy that the measured pK_s' follow closely the Taft σ^*'s for Me, Et, i-Pr and t-Bu. Presumably solvation effects remain constant in the quinuclidinium series in water for structural reasons and not in the case of aliphatic carboxylic acids.

Fig.1- Dissociation constants of aliphatic carboxylic acids, RCO_2H, in water as a function of temperature. R = 1. Me; 2. Et; 3. i-Pr, 4. t-Bu; 5. n-Bu; 6. Et_2CH.



Substituent dependence of infrared frequencies is well-documented (9a,b). Excellent correlations between the ν_{CO} of meta- and para-substituted benzoic acids and the corresponding Hammett σ constants have been demonstrated. In some cases, when the frequency changes are small (i.e. ν_{OH}), integrated band intensities have been used with some success (10). In most cases excellent ν-σ correlations are obtained with small sets of closely related compounds. Our own extensive work on the ν_{CO} of aliphatic ketones (11) shows that polar effects are operating to some extent in determining frequency variation. However, the simultaneous intervention of other effects (opening of the C-CO-C angle, specific solvent effects) do not make this a simple procedure for determining the polar effects of alkyl groups.

A preliminary study of the ν_{CO} of carboxylic acids demonstrated that this is a much simpler system than ketones. Accordingly, the ν_{CO} corresponding to the monomeric form of 9 substituted acetic acids with an R group of known σ^* have been measured in four solvents of differing polarity (Table I) (hexane, CCl_4, CH_2Cl_2, $CHBr_3$). The groups measured include Me, n-Pr, i-Pr, s-Bu, Et_2CH, t-Bu, $EtMe_2C$, t-BuMeCH, and cyclo-C_5H_9. Table II shows the result of correlating the measured frequencies as a function of σ^* in various solvents. It is seen that satisfactory correlations are obtained in CCl_4 and hexane. The last row of Table I reports the result of correlating the vapour phase frequencies as a function of σ^*. These frequencies were not measured directly but extrapolated from the frequencies measured in the four solvents using the Allerhand and Schleyer G parameter (12).

$$\nu_{CO}^{solv.} = \alpha G + \nu_{CO}^{o} \tag{3}$$

These extrapolated frequencies correlate slightly better than those measured in solution, providing a justification of the extrapolation procedure.

TABLE I : ν_{CO} (cm^{-1}) Corresponding to Monomeric RCO_2H)

R \ Solv.	$CHBr_3$	CH_2Cl_2	CCl_4	Hexane	Vap. (Ext)
Me	1752.5	1757.7	1767.3	1775.0	1788.4
n-Pr	1742.0	1746.8	1758.5	1766.9	1782.0
i-Pr	1740.0	1746.5	1755.2	1764.0	1777.7
s-Bu	1737.5	1743.8	1754.0	1763.0	1777.9
Et_2CH	1738.0	1743.0	1753.0	1760.0	1773.4
t-Bu	1737.5	1742.0	1751.0	1758.0	1770.2
$EtMe_2C$	1734.2	1740.0	1749.0	1755.3	1768.2
t-BuMeCH	1738.0	1741.0	1751.0	1756.8	1768.6
cyclo-C_5H_{11}	1736.5	1741.5	1752.5	1760.0	1774.4

TABLE II : Correlation of ν_{CO} vs. σ^* in Various Solvents by Means of the Equation $\nu_{CO}^{solv.} = a\sigma^* + b$.

Solvent	a	b	r	F	ψ[13]
$CHBr_3$	49.45	1749.6	0.911	34.3	0.467
CH_2Cl_2	51.42	1755.2	0.930	44.9	0.416
CCl_4	54.78	1765.7	0.975	133.1	0.253
Hexane	62.72	1775.1	0.974	127.9	0.258
Vapour	66.35	1789.1	0.976	137.5	0.250

A correlation of σ^* as a function of Δ (the vapour phase frequency shift in cm^{-1} of a group with respect to methyl) yields the following equation

$$\sigma^* = -(\Delta + 1.45)/69.73, \quad r = 0.976, \quad \Psi = 0.250, \quad s = 0.023 \qquad (4)$$

which may be used to estimate σ^* values for alkyl groups. A good example of this is a rectification of the reported σ^* value for cyclo-C_6H_{11} (-0.150) which appears anomalous when compared with cyclo-C_5H_9 ($\sigma^* = -0.200$) and Et_2CH ($\sigma^* = -0.225$). The extrapolated ν_{CO} is 1775.4 cm^{-1} ($\Delta = 13.0$ cm^{-1}); equation 4 then gives $\sigma^* = -0.207$, which is a more plausible value for this group.

A demonstration that the steric effect does not seriously interfere with the measured σ^* values comes from a comparison of the ν_{CO} for the groups Et_3C- and 1-adamantyl. These two groups have very different steric effects but are expected to have similar polar effects. The extrapolated ν_{CO} values are 1765.1 and 1764.0 cm^{-1} respectively, giving the σ^* values of -0.355 and -0.370 which differ by less than the standard error of eq.4. Indeed, the σ^* calculated for Et_3C on the basis of strict additivity (14) and the σ^* for the n-Pr group is -0.345. This is good evidence in support of the unimportance of steric effects in determining the frequency shifts for carboxylic acids and for the use of these frequencies as a probe for the polar effects of alkyl groups.

Furthermore, it supports the widely held view that the polar effect of alkyl group is adequately reflected by the Taft σ^* and refutes recent criticism (2).

REFERENCES

(1) R.W. Taft, Jr., in "Steric Effects in Organic Chemistry", ed. M.S. Newman, John Wiley, New York, 1956.

(2) M. Charton, J.Amer.Chem.Soc., 97, 3691 (1975).

(3) F.G. Bordwell and J.E. Fried, Tetrahedron Lett., 1121 (1977).

(4) J.A. MacPhee and J.E. Dubois, Tetrahedron Lett., 2471 (1976).

(5) G. Kortüm, W. Vogel and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solutions", Butterworths, London, 1961.

(6) G.V. Calder and T.J. Barton, J.Chem.Educ., 48, 338 (1971).

(7) E.K. Euranto, in "The Chemistry of Carboxylic Acids and Esters", ed. S. Patai, Interscience, London, 1969, ch. 11.

(8) C.A. Grob and M.G. Schlageter, Helv. Chim. Acta, 59, 264 (1976).

(9) a) A.R. Katritzky and R.D. Topsom, in "Advances in Linear Free Energy Relationships", eds. N.B. Chapman and J. Shorter, Plenum Press, London, 1972.
b) C.N.R. Rao, in "Chemical Applications of Infrared Spectroscopy" Academic Press, London, 1963.

(10) T.L. Brown, J.Amer.Chem.Soc., 80, 3513 (1958).

(11) J.E. Dubois, Pure Appl. Chem., 49, 1029 (1977).

(12) A. Allerhand and P. von R. Schleyer, J.Amer.Chem.Soc., 85, 374 (1963).

(13) Ψ is Exner's parameter which takes into account the number of data points and the number of parameters. O. Exner, Collect. Czech. Chem. Commun., 31, 3222 (1966).

(14) J.E. Dubois, A. Panaye and J. MacPhee, C.R.Acad.Sci. Paris, 280C, 411 (1975).