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LINEAR FREE ENERGY RELATIONSHIPS AND SOLVOLYSIS REACTIONS

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Abstract—The validity of Grunwald-Winstein m values in relation to mechanistic designation of solvolysis reactions is examined. Stability-selectivity relationships in this area are shown to form examples of LFER's and not to emanate from correlations between selectivity and reactivity.

The Grunwald-Winstein equation (eqn 1) has often been employed in solvolysis studies.

$$\log k/k_0 = mY. \qquad (1)$$

Certain misapprehensions appear to arise with regard to the significance of m, exemplified by a recent claim[1] that variation of m in the acetolysis of aryldi-t-butyl-carbinyl p-nitrobenzoates proceeding by an S_N1 route indicates changes in transition state charge separation. *The variation of Hammett ρ values with solvent is however a complete and sufficient condition to produce both m value variation and linear correlation between log k and m.* The connection between m and ρ for solvolyses correlated by the Hammett equation is illustrated in Fig. 1 and defined by eqn (2), one of a family of equations[2] noted by earlier workers and fundamental to the discussion of apparent reactivity-selectivity relationships (RSP's).

$$\Delta m/\Delta\sigma = \Delta\rho/\Delta Y. \qquad (2)$$

Differentiation of eqn (1) leads to:

$$d \log k/dm - d \log k_0/dm = Y \qquad (3)$$

so that a linear relationship between log k and m is solely a mathematical consequence of eqn (1).

Table 1 and Fig. 2 demonstrate these relationships: it will be noted that if the log k or log k_0 values are adjusted to fit onto a perfect σ^+ plot, eqn (3) is followed precisely.

Large ρ values are generally observed for S_N1 processes, and therefore differentials in such values produced by solvent change are likely to be much greater than for S_N2 processes, where ρ values are much smaller. Thus m values can be of some validity in broad differentiation between S_N1 and S_N2 modes of reaction,[3] but they are only alternatives to the use of the Hammett equation, and can afford no information which is not also forthcoming from this latter approach. Moreover reservations attached to the use of ρ values to indicate transition state structure variation within a common mechanistic series are thus equally applicable to m values, and underline the warning previously given that variation of rates by solvent or reagent change cannot be utilised to substantiate RSP's.[4]

This is emphasised by the use of stability-selectivity effects in the designation of reaction mechanisms within the S_N1-S_N2 spectrum. For example, the correlation between log k for solvolysis rates of 2-adamantyl p-X-benzenesulfonates in 70% aq. ethanol[5] and the selectivity factor $\log k_F/k_W$ established by competition between ethanol and water for the intermediate carbonium ion, considered to exist as a solvent separated ion pair, would follow (see eqn 8) from a proportional response of all three quantities k, k_F and k_W to changes in substituent X. Thus if

$$\log k_F = \rho_F\sigma + \log k_{F_0} \qquad (4)$$

$$\log k_W = \rho_W\sigma + \log k_{W_0} \qquad (5)$$

then

$$\log k_F/k_W = (\rho_F - \rho_W)\sigma + \log k_{F_0}/k_{W_0} \qquad (6)$$

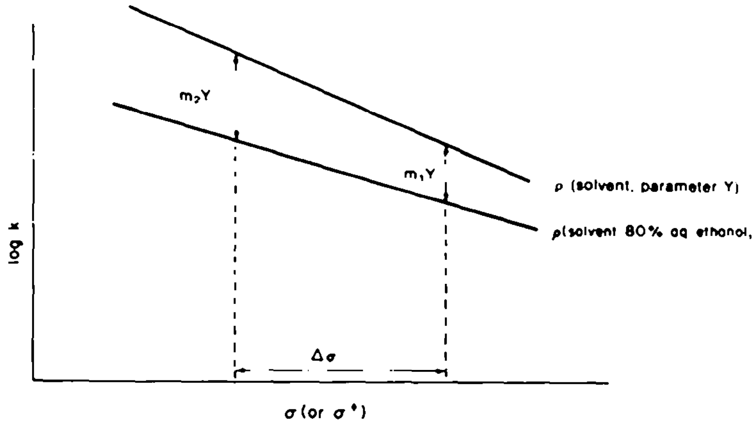

Fig. 1. Relationship between the Grunwald-Winstein equation and the Hammett equation.

Table 1. Variation of m values for the acetolysis of arylidi-*tert*-butylcarbinyl *p*-nitrobenzoates in acetic acid[a] at 85°

Substituent	σ	6 + log k (HOAc)[b]	6 + log k_0[b,c]	m[b,c]
Series 1				
p-OMe	−0.27	2.79, 2.68	3.31, 3.24	0.316, 0.341
p-Me	−0.17	2.24, 2.39	2.87, 2.98	0.384, 0.360
m-Me	−0.07	2.10, 2.11	2.73, 2.71	0.383, 0.366
H	0.00	1.91, 1.92	2.51, 2.53	0.370, 0.372
p-Cl	0.23	1.34, 1.27	1.95, 1.91	0.370, 0.390
m-Cl	0.37	1.00, 0.87	1.66, 1.54	0.402, 0.409
m-CF_3	0.43	0.56, 0.70	1.26, 1.38	0.425, 0.415
Series 2				
o,p-diMe	−0.17	4.59, 4.61	5.02, 5.04	0.259, 0.262
o,m-diMe	−0.07	4.52, 4.47	4.96, 4.91	0.265, 0.268
H	0.00	4.34, 4.37	4.79, 4.82	0.274, 0.274

[a] Y = −1.64, assumed to be temperature invariant. [b] First value is observed, second value is corrected assuming the Hammett equation is followed exactly. [c] Calculated from eqn (1).

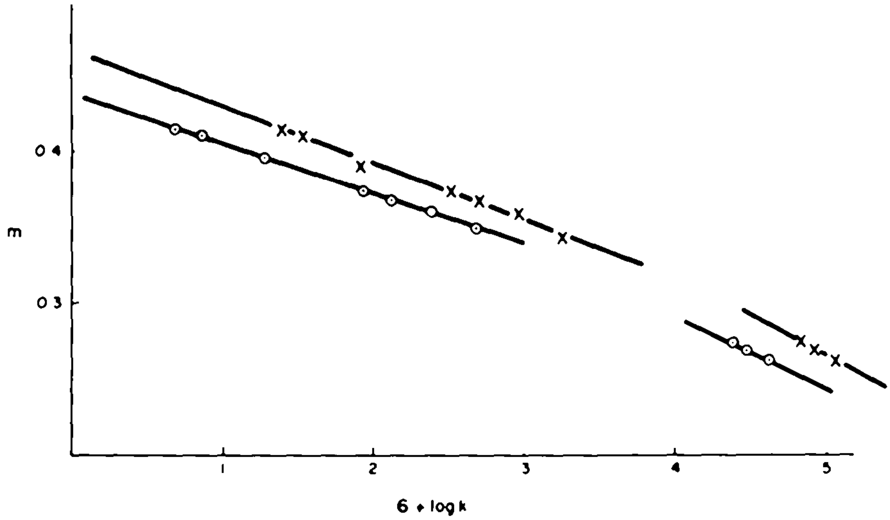

Fig. 2. Log k (reactivity) vs m (solvent-sensitivity) for acetolysis of arydi-t-butyl-*p*-nitrobenzoates. Log k (HOAc) ⊙, log k_0 ×.

and if

$$\log k = \rho\sigma + \log k_0 \tag{7}$$

then

$$\log k = \frac{\rho}{(\rho_E - \rho_W)} \log k_E/k_W + \log k_0 - \frac{\rho}{(\rho_E - \rho_W)} \log k_{E_0}/k_{W_0}. \tag{8}$$

Figure 3 gives the relevant plots of eqns (6) and (7) both for the 2-adamantyl *p*-X-benzenesulfonates and benzhydryl benzoates in 70% aq. ethanol at 75° and 100° respectively.[8] The low ($\rho_E - \rho_W$) values for the log k_E/k_W vs σ correlations are in line with Ritchie's observations of a constant selectivity of nucleophilic systems towards cations,[9] and confirm the contention[7] that for the benzhydryl system product formation is not necessarily by attack on free benzhydryl cations. It may also be noted that the similarity between ρ_E and ρ_W leads to very considerable scatter in the log k vs log k_E/k_W plots unless eqns (4, 5 and 7) are obeyed precisely.

It is also important to notice that the various solvolytic processes need not follow general relationships such as eqn. (4, 5 or 7); a sufficient condition arises from LFER's between the processes concerned. For the solvolysis of alkyl chlorides[10] where a relationship exists between log k (rate of solvolysis in 80% aq. acetone at 25°) and log k_N/k_W (for the competition of the carbonium ion for water and added azide ions), then if eqns (9) and (10) are applicable, eqn (11) follows.

$$\log k_N = \rho_1 \log k_W + C_1 \tag{9}$$

$$\log k = \rho_2 \log k_W + C_2 \tag{10}$$

$$\log k = \frac{\rho_2}{(\rho_1 - 1)} \log k_N/k_W - \frac{C_1}{(\rho_1 - 1)} + C_2. \tag{11}$$

Clearly also if

$$\log k_E = \rho_3 \log k_W + C_3 \tag{12}$$

then a linear relationship holds between log k_E/k_W and log k_N/k_W,[11] from eqn (13).

$$\log k_E/k_W = \frac{(\rho_3 - 1)}{(\rho_1 - 1)} \log k_N/k_W + C_3 - \frac{C_1(\rho_3 - 1)}{(\rho_1 - 1)}. \tag{13}$$

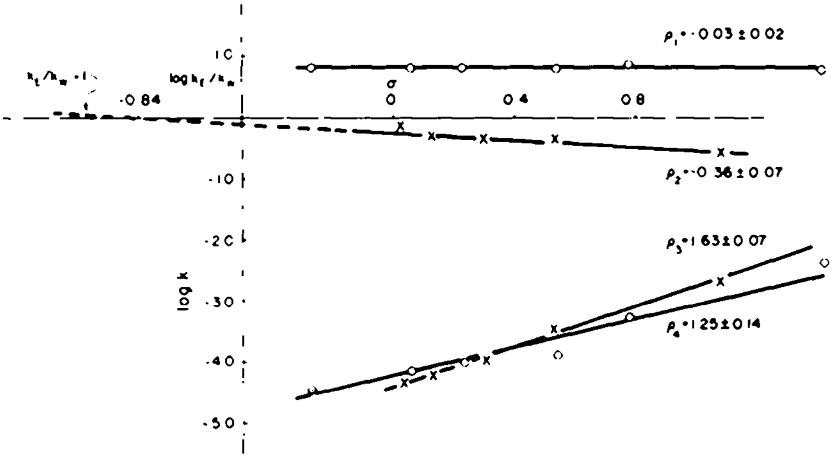

Fig. 3. Log k and log k_E/k_W vs σ for 2-adamantyl *p*-X-benzenesulfonates × and benzhydryl benzoates ○. ρ_1 and ρ_2 are ($\rho_E - \rho_W$), eqn (6); ρ_3 and ρ_4 are ρ, eqn (7).

We would stress that these considerations do not alter the status of such relationships in determing mechanistic routes, involvement of intimate or solvent-separated ion pairs, etc. Indeed, they may enhance the degree of confidence which can be placed in them, and confirm contentions that gross deviations may be indicative of alternative reaction pathways. They do demonstrate however that such relationships are not examples of the RSP, but follow entirely from solvent or reagent induced variation of the slopes of LFER's. Inversion of selectivities can arise from crossover of these LFER's, and there is thus no reason to expect[12] either a limiting value of unity for the selectivity factors, or curvature, at least not until diffusion control is reached.

In conclusion, we note an attempt[13] to accommodate the RSP (considered to exemplify the Hammond postulate) with LFER's, specifically applied to solvolyses of 9-aryl-9-fluorenyl chlorides in 9:1 ethanol water media at 25°, but presumably considered of general applicability. The workers propose the equation

$$\alpha = \Delta G^{\neq}/(2\Delta G^{\neq} - \Delta G^0) \qquad (14)$$

where $\Delta G^{\neq}$ is the free energy change for the S_N1 hydrolyses, ΔG^0 is the free energy change for the corresponding equilibrium between the fluorenols and their cations in water, and α is indicative of the positioning of the transition state of the S_N1 processes along the reaction coordinate.

Rearrangement of eqn (14) gives:

$$\frac{\Delta G^0}{\Delta G^{\neq}} = \frac{(2\alpha - 1)}{\alpha} \qquad (15)$$

whence

$$\Delta\Delta G^0 = \rho^0\sigma^+ = \frac{(2\alpha - 1)}{\alpha}\Delta\Delta G^{\neq} = \frac{(2\alpha - 1)}{\alpha}\rho^{\neq}\sigma^+$$

so that

$$\frac{\rho^0}{\rho^{\neq}} = \frac{(2\alpha - 1)}{\alpha}. \qquad (16)$$

Thus, if both log k and pK_R+ fit a σ^+ correlation, *then α must be constant*; alternatively, if α does vary systematically with reactivity, then there cannot be a *linear* FER between ΔG^0 and $\Delta G^{\neq}$. For the example considered here, Table 2 and Fig. 4 reveal the latter to be the case. This might be a legitimate example of a reactivity-selectivity effect; however, it should be noted that the variation is only very small and over a limited number of substituents.

Table 2. 9-XC_6H_4-9-fluorenyl cation reactivity

X	$\Delta G^{\neq}/4.18^*$	$\Delta G^0/4.18^*$	α
p-OMe	17.7	10.43	0.71
p-Me	20.1	12.87	0.74
H	21.5	14.76	0.76
m-OMe	21.5	15.16	0.77
m-Cl	23.2	17.19	0.79

*kJ mol^{-1}.

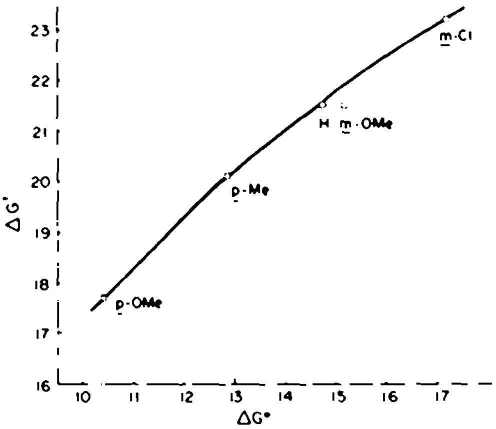

Fig. 4. Curved correlation between $\Delta G^{\neq}$ and ΔG^0 for 9-XC_6H_4-9-fluorenyl cation reactivity, arising from α value variation.

Added in proof: Further claims have appeared that such relationships are examples of the RSP [A. Pross and H. Aronovitch, Chem. Communs., 817 (1976); T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, pp. 231, 232, Harper and Row, New York, N.Y. (1976); B. Giese, *Angew. Chem.* Internat. Edit. **16**, 125 (1977)], although the latter report concedes that correlations between reactivity and selectivity for substituent or solvent variation emanate from variable slopes in LFER's connecting such solvent or substituent effects as we point out here.

rather than any intrinsic relationship between selectivity and reactivity, such as assumed to arise from experimental operation of the Hammond postulate.

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[3] The data in Table 1 for 100% HOAc gives $\rho = -2.82$, r = 0.989, SD = 0.13 for series 1, cf. $\rho = -2.28$, r = 0.988, SD = 0.13 which is obtained using the Yukawa-Tsuno equation. It can be seen that the former treatment gives just as good a correlation despite its greater simplicity, as well as obviating the need for special explanations for conformations in these molecules.[4]
[4] J. S. Lomas and J.-E. Dubois, *Tetrahedron Letters* 407 (1976).
[5] Thus the curved plots denoting changeover from rate limiting S_N2 to S_N1 processes in the hydrolysis of substituted benzyl *p*-toluene sulfonates in aq. acetone and aq. dioxane at 25° give rise to m values for $p-NO_2$ of 0.48, $p-H$ 0.74 and $p-CH_3$ 0.89. The authors would like to thank Prof. J. Milton Harris for drawing their attention to this example.
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