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RELATIONSHIPS BETWEEN SUBSTITUENT AND SOLVENT PARAMETERS IN THE SOLVOLYSIS OF ARYLDI-TERT-BUTYLCARBINYL p-NITROBENZOATES. A REPLY TO RECENT CRITICISM.

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Amongst the most frequently used linear free energy relationships are equations such as (1) and (2) for handling substituent[1] and solvent[2] effects upon reaction rates :

$$\log k_X/k_H = \rho\,(\sigma_X^\circ + r\,\Delta\sigma_X^+) \qquad (1)$$

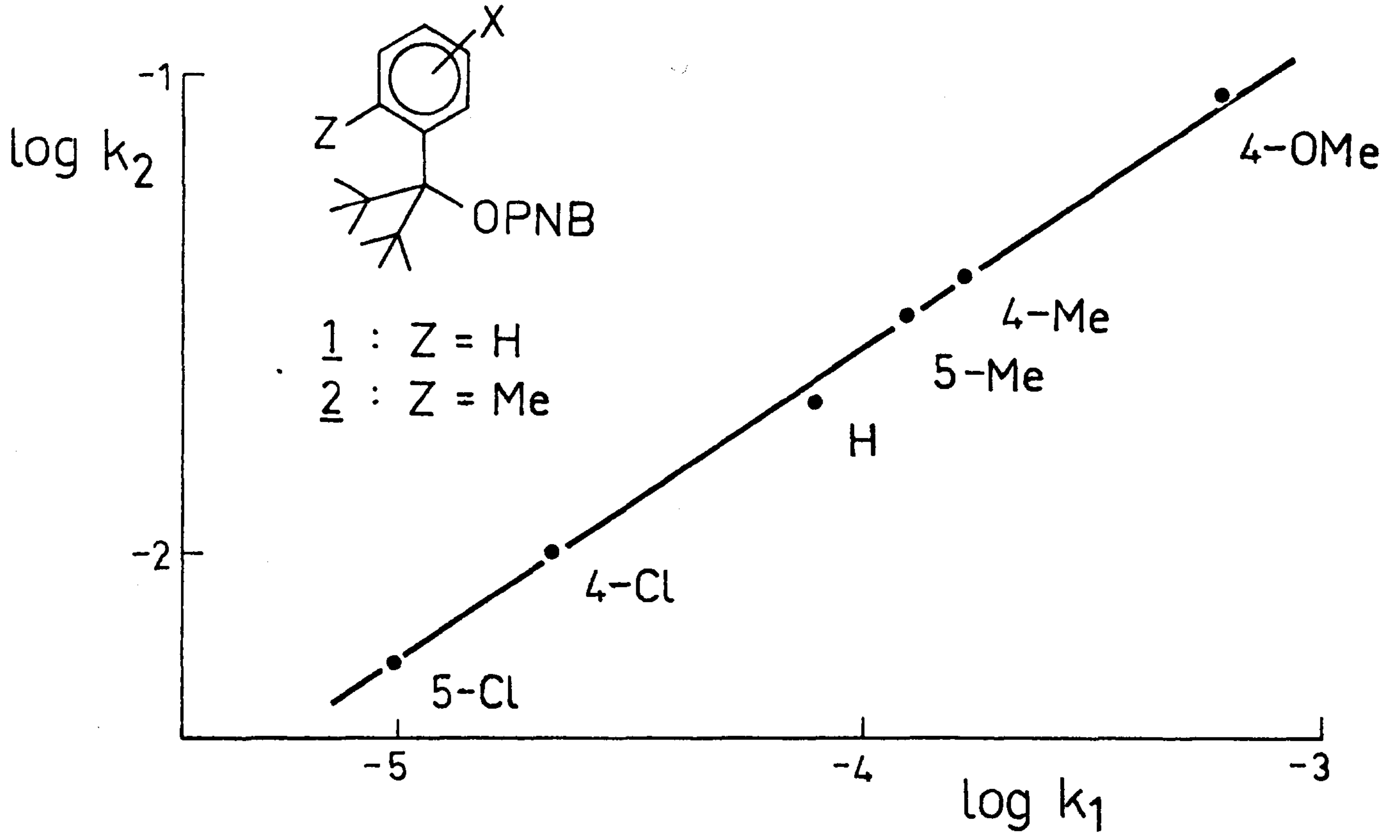
$$\log k_{S_2}/k_{S_1} = m\,(Y_{S_2} - Y_{S_1}) = m\,\Delta Y \qquad (2)$$

Both ρ and m are widely used to measure the ionic character of reaction transition states. In the case of non-assisted (neither by solvent nor by neighbouring group) solvolysis of tertiary carbinyl systems, ρ is concerned with the cationic part of the transition state whereas m depends primarily on the leaving group, and decreases when this latter is able to disperse developing negative charge, in the order : Cl > Br > OTs[3] and Cl > OPNB > thionbenzoate[4]. In the solvolysis of R-L, where L is the leaving group, replacing L by L' should not greatly affect ρ, although m will change. Thus, the ρ value for tert-cumyl chloride solvolysis (-4.4 to -4.8, depending on the solvent)[5] differs insignificantly from that of tert-cumyl PNB solvolysis (-4.6 or -4.7 in aqueous acetone)[6] while m drops from 1.3 to 0.8.

On the other hand, we might anticipate that, since the partial negative and positive charges developed in the transition state are equal, m and ρ would vary in parallel, if at all, when R is replaced by R', provided that this provokes no change in the solvolysis mechanism. Only in certain highly congested systems, where non-assisted solvolysis reaction constants differ markedly from standard values, is it possible to test this hypothesis.

We now report that ρ_2, the reaction constant for the solvolysis of the aryldi-tert-butylcarbinyl p-nitrobenzoates, 2 in 100 % acetic acid at 84.6° is 0.65 times ρ_1, the constant for the solvolysis of 1 (Figure) (-1.62 and -2.48, respectively ; both values calculated by applying eqn. 1; r = 0.41). For the solvolysis of 1 and 2 in acetic acid/water mixtures (84.6°) m_2, the solvent parameter for 2 is again smaller than m_1, by a factor of about 0.70.[7]

Figure : Solvolysis of p-nitrobenzoates 1 and 2 in 100 % acetic acid at 84.6° (k in s^{-1}).



These ratios are sufficiently similar for us to be able to write :

$$m_1/m_2 = \rho_1/\rho_2 \quad \text{or} \quad m_i = A\,\rho_i \qquad (3)$$

for a set of compounds i, where A is a new constant which will depend on the leaving group, the solvent and the temperature. Data for 1 and tert-cumyl PNB also fit eqn. 3 : in aqueous acetone at 100°, m values (X = H) are 0.32 and 0.54[9] (ratio 0.59:1) ; the corresponding ρ values are -2.1[10] and -3.7[9b] (0.57:1).

The diminution of m_i and ρ_i is not compatible with mechanistic change of any sort. It is inconceivable that solvent participation would occur preferentially in the most hindered structure, 2 ; methyl group participation and ion-pair return are unimportant processes in the solvolysis of tertiary carbinyl systems[11] ; neither steric hindrance to solvation nor aryl group rotation[12] can explain the parallel variations of m_i and ρ_i. These results are, however, consistent with the idea that m_i and ρ_i are expressions of the same physical quantity, namely the ionic character of the transition state, although ρ_i for a given series is an averaged measure of a continuously varying quantity.[8]

This last statement has been criticised[14] on the grounds that any pair of linear free energy relationships, such as eqns. 1 and 2, are interrelated.[15] For solvent and substituent parameters :

$$\frac{m_i^{X_1} - m_i^{X_2}}{\sigma_{X_1} - \sigma_{X_2}} = \frac{\rho_i^{S_1} - \rho_i^{S_2}}{Y_{S_1} - Y_{S_2}}$$

or, as it is more usually written :

$$\Delta m_i/\Delta\sigma_X = \Delta\rho_i/\Delta Y = C \qquad (4)$$

where Δm_i and $\Delta\rho_i$ are changes in the solvent parameter and the reaction constant, for a given set of compounds i, associated with $\Delta\sigma_X$ and ΔY, changes in the substituent constant and the solvent ionising power.

The value of C has been measured or can be obtained from published data in only a small number of cases,[8,16] and cannot be estimated a priori. There is no justification for making the assumption, as Johnson does, that ρ_i varies with the solvent without at the same time admitting that the transition state depends on the solvent. Nor, since Δm_i and $\Delta\rho_i$ are related though eqn.4, can one use this assumption as an "explanation" of the m value variation observed in the solvolysis of 1 and 2. To do so is begging the question.

Substituent-dependence of m_i or solvent-dependence of ρ_i can only be understood by going beyond eqn.4 and postulating that the transition state undergoes some sort of modification when the substituent or solvent is changed. For a particular reaction, the sign of C shows whether or not this modification is consistent with the Hammond postulate.[17] In the solvolysis of 1, m decreases as σ_X becomes more negative, suggesting that the transition state is earlier for the more reactive p-nitrobenzoates, i.e. stabilisation of the intermediate carbonium ion favours a more reactant-like transition state, in agreement with this postulate. The same conclusion can obviously be expressed in terms of solvent effects upon reaction constants.

Insofar as m and ρ are "selectivity parameters"[18] and that increase in reactivity leads to their decrease, eqn.4 can be considered to support the much-debated reactivity-selectivity principle (RSP)[19] when C is non-zero and has the correct sign. Nevertheless, selectivity is a concept difficult to apply to unimolecular reactions and is best reserved for situations in which two species react competitively with a common antagonist.[20]

In conclusion, within certain limits eqn.3 validates the use of m and ρ as measures of the degree of transition state charge development ; eqn.4 can therefore be used as test for Hammond behaviour in solvolysis.

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