

Notes

Circular Reasoning about Linear Free-Energy Relationships

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Solvolysis rates of aryl-substituted tertiary carbonyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C have been extensively documented.¹ When $\log k_{4\text{-OMe}}/k_{\text{H}}$ (where $k_{4\text{-OMe}}$ is the rate constant of the *p*-anisyl derivative and k_{H} that of the phenyl derivative in a given series) is plotted against the reaction constant, ρ , a straight line results of slope -0.81 closely similar to the σ^+ value of the 4-methoxy substituent.² This correlation is presented as "a critical, sensitive and unequivocal test of the extended selectivity principle³/Yukawa-Tsuno⁴ treatments". We believe it to be simply an example of circular reasoning.

With one exception (see below) the ρ values quoted are Brown's⁵ and are based mainly on four substituents with well-established σ^+ values: 4-OMe, H, 4-CF₃, and 3,5-(CF₃)₂. In some cases, however, the last point is found to deviate from the correlation^{5e} or is inaccessible;^{5d-f} the ρ value is then calculated from the three others.⁶ Consequently, the difference between the *p*-anisyl and the phenyl derivatives weighs heavily in the evaluation of ρ , since it constitutes on average more than 50% of the available information. It is, therefore, inevitable that a straight line of slope $\sigma^+_{4\text{-OMe}}$ will be obtained when $\log k_{4\text{-OMe}}/k_{\text{H}}$ is plotted against ρ .

One point, that for the arylid-*tert*-butylcarbonyl *p*-nitrobenzoates,⁷ lies off the line. The reason for this is simple: the ρ value was calculated from a correlation with Hammett's σ values.⁸ It will therefore lie on a line of slope $\sigma_{4\text{-OMe}}$ not $\sigma^+_{4\text{-OMe}}$. A more appropriate datum, given by extrapolation⁹ of results for 70% aqueous acetone¹⁰ to 25 °C, is situated at $\log k_{4\text{-OMe}}/k_{\text{H}} = 0.88$ and $\rho = -1.51$ (from σ^+ values), i.e., only 0.3 log units below Johnson's line. His approach, if applied consistently, is rather insensitive to even quite large steric effects; deviations only indicate that the rate- σ^+ correlation is less than perfect. A much better procedure for detecting mechanistic variants or steric effects in a particular system is to apply the Yukawa-Tsuno equation first to meta-substituted compounds (to find ρ) and then to para-substituted derivatives (to find r), but this requires more data.

The small values of both ρ and r found in the solvolysis of arylid-*tert*-butylcarbonyl *p*-nitrobenzoates have been discussed in terms of an early transition state and steric hindrance to resonance.^{8,10,11} The two parameters are not necessarily related.⁴ Geometric constraints are known to produce low r values even when ρ is normal,¹² though other factors may be involved.¹³

References and Notes

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On Using the Tool of Increasing Electron Demand to Evaluate the Yukawa-Tsuno Equation and for Identifying Nonclassical Carbocations

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A test of the validity of the Yukawa-Tsuno equation¹ was described very recently by Johnson.² The values of $\log k_{p\text{-OMe}}/k_{\text{H}}$ derived (by Brown and coworkers) from S_N1 solvolyses of compounds of the general type ArCRR'OPNB were plotted against the reaction ρ values; these latter varied from -3.2 to -5.0 .³ This gave a line of slope -0.824 (cf. -0.78 expected) which was interpreted as showing that the Yukawa-Tsuno equation is invalid, i.e., only the Hammett-Brown⁴ equation applies. In principle this test (if carried out over a wide enough ρ range) is a sound one. However, detailed analysis of the manner in which the data were obtained show it in fact to be inapplicable, for in every case the parameter which the analysis was intended to derive was incorporated in the original data. Consequently an excellent fit to the Hammett-Brown equation was unavoidable. The following evidence supports this latter statement.

(i) The data for compounds **19** (the numbers are those used in Johnson's paper) are meaningless. Rate coefficients were obtained only for the *p*-OMe and unsubstituted compound.⁶ A rate coefficient was then created⁶ for the nonexistent *p*-CF₃ compound⁶ and was chosen assuming perfect application of the Hammett-Brown equation. Thus the perfect line through the points for the *p*-OMe, H, and *p*-CF₃ compounds inevitably gives a value of -0.78 for $\sigma^+_{p\text{-OMe}}$ since this value was chosen in the first place. Clearly the data for compounds **19** cannot be included.

(ii) For compounds **1** and **6** in the original paper, the data are barely more meaningful. For these ρ was determined from three compounds only,^{5,6} one of which was the *p*-OMe compound. Consequently ρ was chosen to fit the *p*-OMe point, so again the derived σ^+ value is almost exactly that (-0.78)