

ANALYSIS OF SPECTRAL AND REACTIVITY DATA
USING HAMMETT SUBSTITUENT CONSTANTS

By R.T.C. Brownlee and R.D. Topsom*

Department of Organic Chemistry, La Trobe University,
Victoria, 3083, Australia

(Received in UK 31 October 1972; accepted for publication 15 November 1972)

It is now well understood that there are two basic mechanisms of electronic transmission by which a substituent can affect a system to which it is bonded. The inductive effect is predominantly^{1,2} a through space electrostatic interaction (field effect) while resonance effects occur in systems where the substituent is joined directly to a pi-electron system. These effects are quantitatively assessed by the Hammett substituent constants σ_I and σ_R^O . In most systems, chemists examine the variation of some particular group or chromophoric property resulting from variations in a second substituent. This "probe" may cause additional and variable interactions with substituents resulting in exalted substituent constants.³

Thus although the use of the Hammett analysis has been extremely successful in the correlation of a vast amount of substituent data in benzoic acid type reactivity series, there appear to us to be two reasons why the original analysis fails in other systems.

A When the electron demand caused by the probe studied is substantially different from that in the benzoic acid series ($\sigma_{(BA)}$, $\sigma_R(BA)$), or ground state (σ^O , σ_R^O), then enhanced parameters (σ^+ , σ_R^+);

σ^- , σ_R^-) are required. The conditions for these are well understood^{3,4} and σ_R^+ and σ_R^- are not proportional^{4,5} to σ_R^0 .

B The field effect depends on the electronic distribution and geometry about the probe. Clearly as one changes from one system to another, there cannot be a constant relation between the transmission of this effect and of the resonance effect. Thus instead of the Hammett relationship (equation 1), a multiparameter equation⁶ (equation 2) must be used where P is the property of interest expressed in energy units.

$$P - P_0 = \rho(\sigma_I + \sigma_R) \quad 1$$

$$P - P_0 = \rho_I \sigma_I + \rho_R \sigma_R \quad 2$$

These two conditions for the non-operation of equation 1 can occur separately or together. We feel that the failure of some authors to appreciate this has resulted in yet more substituent parameters being developed and in data being used to draw invalid conclusions. We give three examples of this.

In a recent paper,⁷ it was suggested that the ¹³C NMR shifts of the para carbon atom in monosubstituted benzenes follow σ^+ (that is $\sigma_I + \sigma_R^+$) allowing values of σ^+ to be derived for some additional substituents. An analysis of the data given in that paper using equation 2 and a standard set⁴ of σ_I , σ_R^0 , σ_R^+ and σ_R^- values shows the expected correlation with the ground state parameter (σ_R^0)

$$\int_H^{P-X} = 4.08\sigma_I + 19.72\sigma_R^0$$

with a standard deviation of 0.52. The best correlation with σ_R^+ was

$$\int_H^{P-X} = 4.44\sigma_I + 7.86\sigma_R^+$$

with a standard deviation almost three times higher. The constraining of ρ_I and ρ_R to be the same led to the erroneous correlation with σ_R^+ . The ¹³C shifts are known^{7,8} to follow theoretically calculated ground state electron densities in monosubstituted benzenes in agreement with our analysis.

As a second example, various authors^{9,10} have correlated the ultraviolet absorption frequencies of the band occurring at about 203 nm in monosubstituted benzenes with various substituent parameters including some of their own origin.¹⁰ An analysis¹¹ of these results by equation 2 shows no meaningful relation between the data and substituent constants. This is expected since the substituent orbitals can interact with the chromophore in the excited state.

Finally in the reactivity field. It has been suggested that the basicity of para substituted pyridines follows the σ values of the substituents derived from benzoic acid acidities resulting in special explanations¹² for this correlation since a relationship with σ^+ would be more realistic. Analysis⁴ of the data by equation 2 gives the identity of best fit as

$$\Delta pK = 5.15\sigma_I + 2.69\sigma_R^+$$

with a standard deviation of 0.14. The best fit using $\sigma_R(\text{BA})$ was

$$\Delta pK = 4.86\sigma_I + 4.16\sigma_R(\text{BA})$$

with a standard deviation of 0.28. The high inductive component in the better correlation is to be expected as a result of the shorter distance in the pyridine compared with benzene series.

We appreciate that single parameter treatment has the merit of simplicity but where this suggests correlations which are unrealistic in terms of chemical experience, then a dual parameter approach is certainly necessary.

Acknowledgement. We thank La Trobe University Computer Centre for computing time.

REFERENCES

1. L.M. Stock, *J. Chem. Educ.*, 49, 400 (1972).
2. C.L. Liotta, W.F. Fisher, E.L. Slighton, and C.L. Harris, *J. Amer. Chem. Soc.*, 94, 2129 (1972); R. Golden and L.M. Stock, *ibid*, 94, 3080 (1972).
3. C.D. Ritchie and W.F. Sager, *Progr. Phys. Org. Chem.*, 2, 323 (1964); A.R. Katritzky and R.D. Topsom, *Angew. Chem. (Int. Ed.)*, 9, 87 (1970); O. Exner in "Advances in Linear Free Energy Relationships", Ed. N.B. Chapman and J. Shorter, Plenum, London, 1972.
4. S. Ehrenson, R.T.C. Brownlee, and R.W. Taft, *Progr. Phys. Org. Chem.*, 10, in press.
5. A.R. Katritzky and R.D. Topsom, *J. Chem. Educ.*, 48, 471 (1971).
6. P.R. Wells, S. Ehrenson, and R.W. Taft, *Progr. Phys. Org. Chem.*, 6, 147 (1968).
7. G.L. Nelson, G.C. Levy, and J.D. Cargioli, *J. Chem. Soc. D*, 506 (1971); *ibid*, *J. Amer. Chem. Soc.*, 94, 3089 (1972).
8. J.E. Bloor and D.L. Breen, *J. Phys. Chem.*, 72, 716 (1968).
9. C.N.R. Rao, "Ultraviolet and Visible Spectroscopy: Chemical Applications", 2nd edn., Butterworths, London, 1967; H.H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, 1962.
10. E.C. Lim, *Spectrochim. Acta*, 19, 1967 (1963).
11. R.T.C. Brownlee and R.D. Topsom, *Spectrochim. Acta*, in press.
12. G.B. Ellam and C.D. Johnson, *J. Org. Chem.*, 36, 2284 (1971).