Non-linear Hammett Plots: a Non-traditional Interpretation

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Summary In a two-step reaction, a curvature of the Hammett plot will be observed if one of the sub-rate constants reaches the diffusion-controlled region owing to changes in substituents.

SOME of the most important diagnostic probes for the investigation of reaction mechanisms are undoubtedly the linear free energy relationships (LFER).[1] Since there is an apparent contradiction between the reactivity–selectivity principle and the demand for linearity in LFER, it is debatable whether LFER in general are indeed linear.[2] Nevertheless, the evidence for the linearity of Hammett plots is overwhelming.[1,3] Moreover, in cases where curvature is observed, it usually serves as proof for the existence of specific mechanistic phenomena rather than as a failure of the theory.[1a] (A failure of the theory usually results in scattered data points rather than a non-linear plot.)

Two types of curvature, concave and convex, are well recognized.[4] The concave line reflects the existence of a dual mechanism, in which each mechanism dominates a different portion of the σ-scale. On the other hand, a change in the identity of the rate-determining step, induced by changing the substituents, appears as a convex line in the Hammett plot.

During computer-simulation of reaction profiles and Hammett plots for parallel and consecutive reactions, we observed cases of curvature which could not be attributed to either of these causes. Analysis of the individual rate constants revealed that the curvature appears whenever one of these rate constants reaches the diffusion-controlled limit.

The following two-step mechanism could be used to illustrate this behaviour. The overall rate constant for a reaction of type (1), assuming a steady-state concentration

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{1}$$

for B, is given by equation (2). For $k_{-1} \gg k_2$ equation (2)

$$k_{\mathrm{obs}} = k_1k_2/(k_{-1} + k_2) \tag{2}$$

reduces to equation (3), and thus equation (4) will hold.

$$k_{\mathrm{obs}} = k_1k_2/k_{-1} \tag{3}$$

$$\rho_{\mathrm{obs}} = \rho_1 - \rho_{-1} + \rho_2 \tag{4}$$

Segment a in the Figure demonstrates such a behaviour.

Upon moving along the σ scale k_{-1} increases until it reaches the diffusion-controlled limit rendering $\rho_{-1} = 0$. The observed ρ value under such conditions will be $\rho_1 + \rho_2$ (segment b in the Figure).† The combination of segments a and b gives an upward curvature. It is important to stress that if k_{-1} reaches diffusion control the Hammett plot will always be concave independent of the ρ values of the individual steps.‡

A situation such as this could be encountered when intermediate B, which might be a carbanion, carbocation, radical *etc.*, is sufficiently unstable so that its rate of collapse (k_{-1}) back to starting material can reach the diffusion-controlled region with the proper choice of substituent. A marked effect is expected where a sharp break in k_{-1} is observed upon reaching the diffusion-controlled limit as is typical, for example, with protonation reactions on 'normal acids'. On the other hand, a less pronounced effect is expected when there is a gradual approach to levelling off as in cases of

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† This is for $\rho_{-1} > 0$. For $\rho_{-1} < 0$, the labels a and b should be interchanged.

‡ In cases where one of the rate constants in the forward direction (k_1 or k_2) reaches the diffusion-controlled limit, the Hammett plot will always be convex. Note that in cases of bimolecular reactions, although the rate constant is of the order of 10^{10} l mol^{-1} s^{-1}, the actual reaction rate might in fact be slow since it is governed by the concentration of the other reactant as well. Thus, for example, the second step might still be rate-limiting although k_2 is diffusion-controlled.

protonation on acetylacetonate and other,[5] highly delocalized carbanions.

A more complex pattern (S-shape) might be observed if subsequently the second step ceases to be rate limiting, in which case $\rho_{obs} = \rho_1$ (segment c in the Figure).

A different combination of reaction variables, namely the identity of the rate-determining step, the step whose rate constant reaches the diffusion controlled level, and the general nature of the mechanism (consecutive or parallel reactions or a combination of both) will result in a different and sometimes even a more complex pattern of the Hammett plots.

In conclusion we wish to reaffirm the need for circumspection in interpreting non-linear Hammett plots which may not be derived from the 'traditional' causes but rather arise as a result of the levelling off of one of the individual rate constants approaching diffusion control.

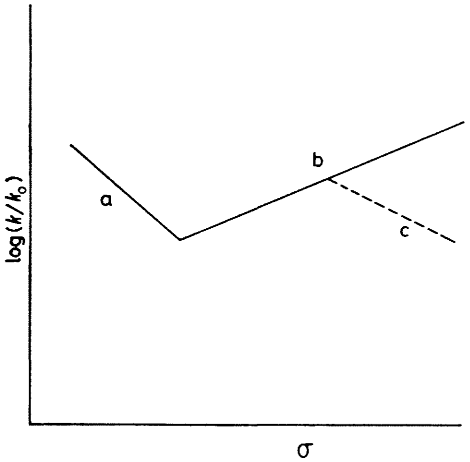

FIGURE. A Hammett plot of a stepwise reaction.

(*Received, 24th January* 1980; *Com.* 085.)

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[1] (a) J. Shorter, 'Correlation Analysis in Organic Chemistry,' Clarendon Press, Oxford, 1973; (b) R. P. Wells, 'Linear Free Energy Relationships,' Academic Press, London, 1968.

[2] A. Pross, *Adv. Phys. Org. Chem.*, 1977, **14**, 69.

[3] H. H. Jaffé, *Chem. Rev.*, 1957, **79**, 1045.

[4] See for example B. M. Anderson and W. P. Jencks, *J. Am. Chem. Soc.*, 1960, **82**, 1773; R. Ta-Shma and Z. Rappoport, *ibid.*, 1977, **99**, 1845.

[5] J. R. Jones, 'The Ionization of Carbon Acids,' Academic Press, London, 1973, ch. 8.