A Hyperbolic Modification of Linear Free Energy Relationships

By **Edward S. Lewis** * and **Celia C. Shen**, Department of Chemistry, Rice University, Houston, Texas 77001, U.S.A.
Rory A. More O'Ferrall,* Department of Chemistry, University College, Belfield, Dublin 4, Ireland

In a one-step reaction the activation energies in either forward or reverse reactions cannot be negative. This limitation specifically excludes very wide-range linear dependences of E_a upon ΔH. Analogously, all rate constants have upper limits (in addition to the diffusion limit), and thus linear free energy relationships such as the Hammett or Brønsted relationships, which when extrapolated lead to absurdly high rate constants, are also impossible. The problem of extrapolation is attacked by using a hyperbolic relationship between the logarithms of rate constants and equilibrium constants. In addition to satisfactory extrapolation, the treatment contains within itself the reactivity–selectivity principle and implies an inverse relationship between the curvature of a free energy plot and reactivity. The hyperbola may be related to a naive pictorial representation of the reaction co-ordinate, from which two measures of product-like character in the transition state ensue; one uses E_a and ΔH, the other compares substituent effects on rate constants and equilibrium constants. The hyperbolic relationship is compared with the equations used by Marcus. The treatments provide a norm for rate–equilibrium correlations of single-step reactions with transition states described as hybrids of reagent and product-like structures; marked deviation from this norm is evidence of contributions of special structures in the transition state.

DISCUSSIONS of the linearity or otherwise of free energy relationships[1] and of alternative formal descriptions[2-4] and causes[5-7] of non-linearity in rate–equilibrium correlations have reached voluminous proportions. The origin of this interest may be traced to Brønsted and Pedersen's demonstration of an empirical linear relationship between logarithms of rate constants and equilibrium constants for general acid and base catalysed reactions,[8] and its interpretation in terms of simple potential energy models by Polanyi and Bell.[9] The impetus for experimental studies of acid–base reactions, one of the few families of reactions for which equilibrium and rate constants are readily available, came from the introduction and application of fast reaction techniques, notably by Eigen,[10] and from the appreciation of the relevance of such studies to enzymatic catalysis. In the gas phase, concern with the position of the activation energy barrier upon a potential surface, indicated by direct computation or by trajectory calculations linked to kinetic measurements with crossed molecular beams or chemiluminescence, stimulated a more theoretical interest[11] and provided a link with the organic chemist's concern with reactivity and selectivity, as expressed in the well known papers of Hammond and Leffler.[12,13] Of special importance, however, has been Marcus' application of his treatment of electron transfer reactions[14] to correlations of rates and equilibria for hydrogen and proton transfer reactions,[15] a treatment now extended to methyl transfer reactions.[16]

In this discussion two quite simple points deserve further consideration. One concerns the influence of limiting values of activation energies and rate constants upon the scope of linear free energy relationships, and the other the analytical form of the simplest treatment of non-linear relationships.

Extrapolation Limits to Linear Free Energy Relationships.—Figures 1 and 2 illustrate a straightforward argument that linear free energy relationships between rate and equilibrium constants or the related linear relationship between activation energies (E_a) and enthalpies of reaction (ΔH), are impossible over a very wide range. Figure 1 shows a plot of E_a *versus* ΔH, with E_a^+ and E_a^- denoting activation energies for forward and reverse reactions, respectively. The requirement that E_a^+ be positive provides a lower limit for E_a^+

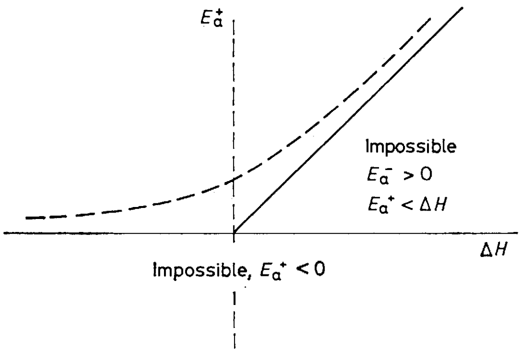

FIGURE 1 A diagram showing the allowed region of a plot of activation energy against overall enthalpy change for a one-step reaction, demonstrating that no straight line can stay everywhere in the allowed region. The curve shown [equation (1)] is a possible relationship

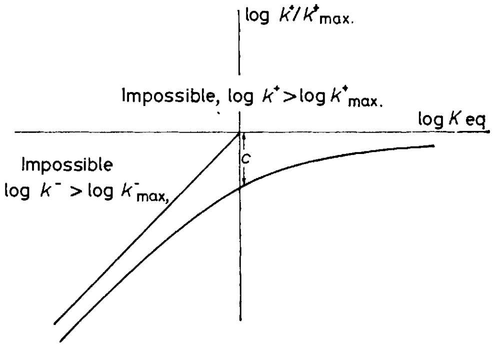

FIGURE 2 A plot of log k^+ *versus* log K_{eq} showing the consequences of the existence of upper limits ($k^+_{max.}$ and $k^-_{max.}$) for rate constants of any order. Straight lines are clearly impossible; a possible relationship is shown

for all values of ΔH, while the similar requirement for E_a^- and the relationship $\Delta H = E_a^+ - E_a^-$ gives the further limit $E_a^+ \geqslant \Delta H$. These limits imply 'impossible' regions for a plot of E_a *versus* ΔH as shown in Figure 1, and it is clear that no infinite straight line dependence of E_a upon ΔH can fit the allowed region.

Figure 2 shows a log–log plot of rate constants (k) *versus* equilibrium constants (K_{eq}) with limits similar to those of Figure 1. Thus the rate constant in the forward direction k^+ cannot exceed some maximum value $k^+_{max.}$, while the other limit is determined by the maximum value of the rate constant in the reverse direction $k^-_{max.}$. Again an infinite straight line must exceed at least one of the limits. The maximum rate constants may be identified with the Arrhenius pre-exponential factors. For each molecularity the pre-exponential factor has an upper limit and no rate constant can be greater than this. If for the series of reactions considered Arrhenius A factors for the forward and reverse reactions are constant we can identify A^+ with $k^+_{max.}$ and A^- with $k^-_{max.}$ and the two representations are readily shown to be equivalent.

A Hyperbolic Free Energy Relationship.—Apparently linear free energy relationships which become nonsense when extrapolated can be made acceptable by introducing a small curvature. Figure 2 illustrates an idealised dependence of log k^+ upon log K_{eq} in which log k^+ varies smoothly between its limits, thus avoiding the impossible extrapolations.

The analytical form of this relationship cannot now be established experimentally;[17] indeed it is a major problem to show that experimental points are better fitted by a curve than a straight line. The commonly used expressions introduced and applied by Marcus to hydrogen atom and proton transfer reactions have been justified by being derived from simple reaction models.[15] By contrast we have chosen a familiar analytical expression consistent with the required limits, and found that it leads to a convenient and plausible formalism usefully compared with that of Marcus. Other approaches to this expression due to Agmon and Miller are noted below.

The curves shown in Figures 1 and 2 are actually hyperbolae[18] ($y^2 - xy - c^2 = 0$). Figure 1 shows the positive branch of the hyperbola of equation (1) with asymptotes $E_a = 0$ and $E_a = \Delta H$. The constant c is the

$$E_a(E_a - \Delta H) = c^2 \qquad (1)$$

activation energy, E_a, when $\Delta H = 0$ and corresponds to Marcus' intrinsic kinetic barrier (Λ) for the reaction series. The equation expresses the combined influence of the kinetic barrier (or inertia[17]) and the thermodynamics of a reaction in determining reactivity. For a nearly thermoneutral reaction the kinetic barrier dominates the activation energy and for a strongly exo- or endo-thermic reaction the barrier approaches the thermodynamic difference between reactants and products in one direction and zero in the other.

In the rate constant form of the relationship the negative branch of the hyperbola of equation (2) is used. In this equation the division by $k^+_{max.}$ makes the first factor independent of the choice of units, as does the $k^-_{max.}/k^+_{max.}$ factor in the second; it also makes the x axis ($y = 0$) an asymptote, in contrast to the simple plot of log k against log K_{eq} in which the asymptote is $y =$ log $k^+_{max.}$. In equation (2) c is dimensionless; it is the

$$\log \frac{k^+}{k^+_{max.}} \left[\log \frac{k^+_{max.}}{k^+} - \log K_{eq} \frac{k^-_{max.}}{k^+_{max.}} \right] = c^2 \qquad (2)$$

counterpart of c in equation (1) but differs in magnitude and sign. The equation may be converted to a free energy form (commonly used in Marcus' equations for solution reactions) by taking $k^+_{max.} = k^-_{max.} = \boldsymbol{k}T/h$ and substituting $\Delta G = -RT\ln K_{eq}$ and $\Delta G^\ddagger = -RT\ln k/(\boldsymbol{k}T/h)$,* to give again the negative branch of the hyperbola. For reactions in solution equation (2) may be extended in the usual way[6] to include diffusion steps and the 'work terms', ω_R and ω_P, introduced by Marcus[14,15] to take account of solvation and other changes preceding or following the proton transfer step.[19]

The curvature of the hyperbola as of the corresponding Marcus equations is controlled by the intrinsic barrier c. To the question, 'why is curvature not seen in ordinary Hammett plots?,' several answers may be given. First, the range of a typical Hammett plot is relatively small. For a variation of σ of one unit the range of equilibrium constants is rarely greater than 10 000 which is usually insufficient to see curvature, especially where the data show experimental and chemical scatter. For larger ranges of equilibrium constant the Hammett correlation may include a second parameter, as in the Yukawa–Tsuno equation, which has the incidental effect of correcting for curvature. Moreover, most reactions listed in compilations (for example that of Jaffé[20]) have rate constants not much larger than the order of 10^{-4} s^{-1} or l mol^{-1} s^{-1}. In terms of the hyperbola this implies large values of c or that the reaction falls far to the left in Figure 2. The curvature of the hyperbola is inversely proportional to c and along a reaction series is maximised for the thermoneutral reaction. Thus detectable curvature is to be expected only for fast reactions that are approximately thermoneutral,[9] or, possibly, for slower reactions combining a low intrinsic barrier with large work terms. There are relatively few examples of these and where they occur the interpretation of curvature may be complicated by the influence of diffusion steps.[6]

Reactivity and Selectivity.—The slope of the hyperbola varies continuously from 0 to 1 between the limits of high and low reactivity. The slope represents the selectivity of the reaction (relative to the 'equilibrium' selectivity), and this behaviour corresponds to the normal inverse relationship between reactivity and selectivity. Differentiation of equation (1) gives the expression for the slope shown in equation (3) which we denote p.[21]

$$\frac{dE_a}{d\Delta H} = p = \frac{E_a}{2E_a - \Delta H} \qquad (3)$$

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* Strictly $k^+_{max.} = k^-_{max.} = e^{\Delta S^\ddagger/R}\,\boldsymbol{k}T/h$. The usual assumption that $\Delta G^\ddagger \rightarrow 0$ in these limits implies the simpler identity given.

For reactions in solution the rate constant expression corresponding to (3) is complicated by limiting rate constants and associated work terms. However in solution the slope may be obtained independently if rate and equilibrium constants can be expressed as linear free energy relationships. For proton transfer reactions it corresponds to the exponent of the Brønsted relationship α and, if $\log k_+$ and $\log K_{eq}$ obey the Hammett relationship, to the ratio of kinetic and equilibrium reaction constants (4). Comparison of these two measures of selectivity is straightforward and of interest.

$$\frac{\mathrm{d}\log k^+}{\mathrm{d}\log K_{eq}} = \frac{\rho^+}{\rho_{eq}} \qquad (4)$$

Identification of p with the progress of bond-making and -breaking at the transition state [13] leads to a simple but plausible dependence of barrier location along a one-dimensional reaction co-ordinate upon activation energy and energy of reaction consistent with Hammond's postulate.[12] The implied energy diagrams can be constructed quite simply in the manner shown in Figure 3.

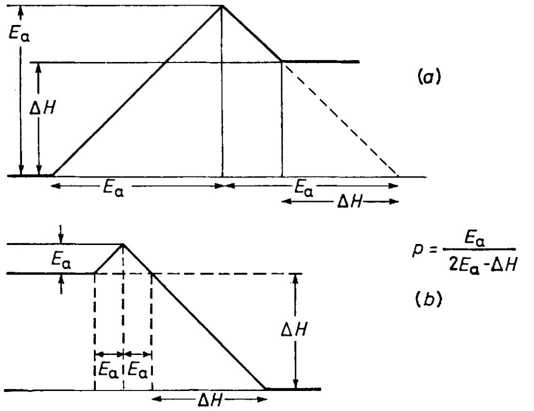

FIGURE 3 The construction of simple energy *versus* reaction co-ordinate diagrams for an endothermic reaction (*a*) and an exothermic reaction (*b*) consistent with $p = E_a/(2E_a - \Delta H)$ as a measure of the position of the transition state along the reaction co-ordinate is obvious

Starting with the reactant at an arbitrary energy and position, a line of slope +1 is drawn until the energy of the transition state is reached (given by E_a). Then another line of slope −1 is drawn until the energy of the product is reached (determined by ΔH). Examples for positive and negative ΔH are shown. The fraction of the distance from reagent to product along the horizontal reaction co-ordinate that the transition state lies is clearly $E_a/(2E_a - \Delta H)$. The diagrams should properly involve potential energies but as usual the experimental quantities are ΔG or ΔH at temperatures near or above 300 K.

Interestingly, equation (3) and the diagrams of Figure 3 have an optical analogue in the application of Fermat's principle [22] to reflection, as has been pointed out by Agmon.[2] With the reactant and products at an arbitrary separation, minimisation of the potential energy path from reactants to transition state to products consistent with E_a and ΔH yields equation (3) directly. This ' derivation ' of (3) has been generalised by Miller to non-linear energy profiles using an arc minimisation theorem.[23] More recently, Agmon and Levine have derived equation (3) by analogy with a resonance combination of valence bond wave functions corresponding to the structures of reactants and products.[24] They also note the previous empirical application of the equation by Rehm and Weller to fluorescence quenching.[25] Thus equation (3) has been used quite extensively, without its connection with the hyperbola generally being noted.

Comparisons with Other Treatments.—Equations (1)—(4) as descriptions of rate–equilibrium relationships are recommended by their correct limits, simplicity, and convenience. Other equations have been proposed, however,[3,4,9,11,15,26] on similar grounds,[26] using alternative analogies,[4] or from relationships to simple reaction models.[9,11,14] Chief among these are Marcus' equations shown as (5) and (6), in their commonly used free energy forms, together with the corresponding hyperbolic expression (7). The quadratic equation (5) comes from

$$\Delta G^\ddagger = c\left(1 + \frac{\Delta G}{4c}\right)^2 \qquad (5)$$

$$\Delta G^\ddagger = c + \frac{\Delta G}{2} + \frac{c}{\ln 2}\ln\cosh\left(\frac{\Delta G \ln 2}{2c}\right) \qquad (6)$$

$$\Delta G^\ddagger = \frac{\Delta G}{2} + \frac{\sqrt{\Delta G^2 + 4c^2}}{2} \qquad (7)$$

Marcus' electrostatic model for electron transfer reactions and (6) is obtained from a simplified BEBO treatment or, as Agmon and Levine suggest,[4] from analogy with the thermodynamics of ' mixing ' of reactants and products. The quadratic equation lacks asymptotic limits and is confined to the range $4c > \Delta G > -4c$ for reactions not subject to diffusion control.[14] Extensive comparison of the hyperbolic equations (1)—(3) with experimental data [24,27] and semi-empirical or *ab initio* calculations of potential energy surfaces [23] testify to their effectiveness, but not to an advantage over alternatives.[15,17,23,24]

A simple comparison of the hyperbolic and Marcus equations is achieved by expanding equations (1) or (6) as polynomials to the second degree about ΔH (ΔG) = 0. The result is shown for the hyperbola and Marcus' quadratic and BEBO expressions in equations (8)—(10), respectively; the kinetic variable (E_a or $\Delta G^\ddagger$) is denoted y and the thermodynamic variable (ΔH or ΔG) is denoted x. It is apparent that the first two terms are the same

$$y = c + \frac{x}{2} + \frac{x^2}{8c} \qquad (8)$$

$$y = c + \frac{x}{2} + \frac{x^2}{16c} \qquad (9)$$

$$y = c + \frac{x}{2} + \frac{x^2}{11.54c} \qquad (10)$$

in each equation, and that the quadratic coefficients, which determine the curvature of the relationships, are all inversely dependent upon the intrinsic barrier c.

However, the magnitudes of the quadratic coefficients differ. Where an intrinsic barrier is determined experimentally from the curvature of a rate–equilibrium relationship, therefore,[19] the value will depend upon the equation used; that from the hyperbola (8) for example being twice that from the usual Marcus equation (9). Differences in coefficients higher than the quadratic are unimportant because the curvature is not well enough defined.

A lower limit can be put on the quadratic coefficients because the plots x *vs.* y should not cross impossible regions of Figures 1 and 2, *i.e.* y must be >0 for all values of x. It is easy to show that this condition is fulfilled when the quadratic coefficient $>1/16c$, and it follows that Marcus' simpler equation (9) provides a lower limit for and indeed must underestimate the barrier.[28,*] In principle the barrier may have any value greater than this limit and less than the measured or extrapolated value of y at $x = 0$ (in solution, work terms may add to the intrinsic barrier). In practice equations (8) and (10) probably provide reasonable values [15,17,18,23,24,27,29] and indeed experimental uncertainties and chemical dispersion make differences between (8)—(10) normally of minor importance in practice,[15] save perhaps in assessing the effect of diffusion steps on curvature.[6]

A further comparison comes from writing $\Delta G^\ddagger$ as a function of α (or p) $= \mathrm{d}\Delta G^\ddagger/\mathrm{d}\Delta G$, the progress variable taken to describe the position of the transition state along the reaction co-ordinate. Equations (11)—(13) show expressions for the hyperbola and for Marcus' quadratic and BEBO equations; between the extremes

$$\Delta G^\ddagger = \alpha\Delta G + 2\alpha^{\frac{1}{2}}(1 - \alpha)^{\frac{1}{2}}c \qquad (11)$$

$$\Delta G^\ddagger = \alpha\Delta G + 4\alpha(1 - \alpha)c \qquad (12)$$

$$\Delta G^\ddagger = \alpha\Delta G - c[\alpha\ln\alpha + (1 - \alpha)\ln(1 - \alpha)]/\ln2 \qquad (13)$$

of exo- and endo-thermic reactions α varies between 0 and 1 and in all cases, $\Delta G^\ddagger = c$, the intrinsic barrier for the reaction, at $\alpha = 0.5$. It may be noted that for a quadratic relationship these conditions are met only for Marcus' choice of quadratic coefficient, *i.e.* $1/16c$ in equation (5). Kurz's recent discussion [3] suggests indeed that the 'correct' behaviour of equation (12) could be regarded as the theoretical basis of equation (5).

A last comparison is between expressions for the progress variables themselves. Here, the hyperbolic equation (3) [rewritten as (14)] shows an advantage. Marcus' quadratic equation leads to incorrect limits

$$\alpha = 1/(2 - \Delta G/\Delta G^\ddagger) \qquad (14)$$

$$\alpha = \tfrac{1}{2} + \Delta G/8c \qquad (15)$$

$$\alpha = 1\Big/\left[1 + \exp\left(\frac{-\Delta G\ln2}{c}\right)\right] \qquad (16)$$

(15), while in contrast to the simplicity of (14), solution of the BEBO expression (16) requires a prior evaluation of c from (6) by iteration. The usefulness of p of equation (3) as a ready reckoner of bond-making and -breaking at the transition state, especially for atom transfer reactions has been emphasised previously.[2,19,21,23]

Scope and Limitations.—A major function of a rate–equilibrium relationship is to describe a normal or ideal behaviour and to identify and estimate deviations from it. Normal behaviour is that expected of a series of reactions with a constant intrinsic barrier and transition states completely describable as hybrids of reagent- and product-like structures (called by Levine a 'Brønsted Series'[17]). Marcus has given reasons for expecting such behaviour for proton transfers between a single carbon base and a series of oxygen and nitrogen bases.[15,30] Thus it appears that normal behaviour is attainable in practice in a commonly studied rate–equilibrium correlation.†

Departures from normal behaviour will occur if the intrinsic barrier itself is a function of structure within a reaction series. Such departures are indicated (i) by a failure of E_a to correlate with ΔH; (ii) by values of α (or ρ^+/ρ_{eq}) that are negative or greater than unity (as in arylnitroethanes [7,31]), or which do not lie between 0 and $\frac{1}{2}$ for thermodynamically favourable reactions or between $\frac{1}{2}$ and 1 for unfavourable reactions;[7] or (iii) when ρ^+ does not lie between zero and ρ_{eq} (as in $E2$ eliminations [32]). These abnormalities may indicate that the reaction has more than one step, but usually they represent variations in intrinsic barrier (or possibly work terms [7]) and have been commonly interpreted as arising from contributions of special structures, *i.e.* other than of reactants and products to the transition state. Such structures, which may be less favourable resonance forms of reactants and products or intermediates of higher energy reaction pathways, have been included on potential energy diagrams using linear,[33] quadratic,[34] or semiempirical multidimensional surfaces.[35]

The diagrams of Figure 3 may similarly be extended to include special transition state structures. Here, however, we wish to emphasise the form of the hyperbola as an intuitively attractive representation of the simplest of non-linear rate–equilibrium relationships. Comparison with the corresponding Marcus formalism indicates the complementary virtues of the treatments. Marcus' quadratic expression (5) offers a compromise between analytical convenience and chemical significance. The hyperbola is arbitrary, but it combines analytical simplicity with a self-consistency deriving from correct handling of rate limits. Where attention to limits is important it offers an attractive alternative to the less straightforward BEBO relationship. In particular, the expression $p = E_a/(2E_a - \Delta H)$ should be useful. In the gas phase or for free radical reactions in solution it provides a measure of the location of an energy barrier along a reaction co-ordinate, and for ionic reactions in solution, where solvation may complicate interpretation,

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[*] Correspondingly for a given barrier Marcus' equation (8) leads to the maximum curvature for a rate–equilibrium relationship.

[†] Practical difficulties of measuring curvature remain, *e.g.* of finding a structurally homogeneous family of O or N acids covering a wide range of pK_a.

it may be compared with the direct measurement of the slope of a rate–equilibrium correlation by the Brønsted coefficient or ρ^+/ρ_{eq}.

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