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APPLICATION OF MARCUS THEORY TO PHOTOCHEMICAL PROTON TRANSFER REACTIONS. II. MODIFICATIONS BASED ON INTERSECTING STATE MODELS

KEITH YATES
Department of Chemistry, University of Toronto, Toronto M5S 1A1, Canada

ABSTRACT

Various modifications of the Marcus equation have been applied to the problem of photochemical proton transfer, using available data on general acid-catalyzed photohydration reactions. These include incorporation of asymmetry and tightness parameters, as well as distance variation as a function of exo- or endothermicity. The intersecting state model of Formosinho has also been successfully applied to these reactions. The overall conclusion from all of these approaches is that the reactions are characterized by somewhat asymmetric and 'loose' transition states, with a small but significant degree of charge development on the in-flight proton at the transition state. Estimates of the intrinsic barriers and work terms place these in the 5–7 kcal and 2–3 kcal ranges respectively. A simple valence bond configuration mixing model leads to similar qualitative conclusions about the nature of the transition states in these reactions.

INTRODUCTION

Acid–base catalysis of organic photoreactions has been of continuing interest over the past twenty years and the subject has recently been reviewed.[1] Since reversibility of the proton transfer step is unlikely to occur in general, the most probable type of photochemical catalysis is likely to be general acid or general base catalysis, especially where proton transfer to and from carbon is involved. In fact, cases of both general base,[2] and general acid, catalyzed[3] photoreactions have recently been reported, as well as the first examples[3,4] of Brønsted relationships for photochemical processes. Although interest in the detailed nature of proton transfers to electronically excited states is currently very high,[5] it is not yet clear to what extent these processes result in concurrent deactivation to the ground state surface (non-adiabatic proton transfer) or can lead to short-lived electronically excited cationic intermediates (adiabatic proton transfer) which can be attacked in a subsequent step by solvent molecules or other external nucleophiles, then resulting in deactivation. Turro has reviewed the subject of adiabaticity[6] in organic photoreactions and has concluded that although truly adiabatic processes are likely to be rare in photochemistry, proton transfer is one area where such processes are most probable. It has also recently been shown that organic cations of the type involved as intermediates in acid catalyzed photohydration reactions can be generated adiabatically,[7] and under appropriate conditions can have lifetimes of up to 35 ns.[8] This article

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will therefore focus on proton transfers to carbon atoms in photohydration reactions, which either are or can be adiabatic processes, insofar as the cation forming step is concerned.

There are several important differences compared to the well known thermal analogues of these reactions. The rates of reaction are very high[9] ($k_{\mathrm{H}^+} \sim 10^6$–$10^7\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$) indicating rate enhancements on electronic excitation of the order of 10^{11}–10^{14} for typical substrates.[4] The values of the Brønsted α measured to date are very low ($\alpha \approx 0{\cdot}14$–$0{\cdot}18$)[3,4] compared with those reported for the thermal reactions of analogous substrates ($\alpha \approx 0{\cdot}5$–$0{\cdot}9$).[10] Curvature of the Brønsted plots is more clearly detectable in the photochemical reactions, although numerical values of the Brønsted curvature are not yet established very quantitatively.[4] Finally, despite the fact that the excited states of these substrates are obviously very highly activated towards proton transfer, the limiting rates observed in moderately concentrated acid solution tend towards values in the 10^7–$10^8\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$ range, which is well below the diffusion controlled limit ($\approx 10^{10}\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$) observed for the fastest known ground state proton transfers to oxygen or nitrogen. Although values higher than this are known, for the reaction of H_3O^+ with OH^- for example, proton transfer to neutral bases usually has a limiting value of k catalytic of $10^{10}\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$.[11]

An attempt has previously been made[12] to use Marcus theory[13] to determine whether the above general characteristics of Brønsted plots for photohydration reactions could be satisfactorily accounted for, and whether a reasonable description of excited state proton transfer could be arrived at in terms of important quantities such as the intrinsic barrier and extent of proton transfer at the transition state. This involved empirical modification of the Marcus equations by incorporating an asymmetry parameter ε to reflect the inherently different nature of proton transfer from a ground state acid species to an excited state base. This empirical approach suggested that Marcus theory can profitably be used to analyze excited state acid catalyzed reactions, as it has been for many ground state reactions. However the degree of asymmetry obtained implied larger differences between the force constants k_{HX} and k_{HY^*} than seem reasonable[14] in terms of the

$$\mathrm{H{-}X} + (\mathrm{Y})^* \dashrightarrow \mathrm{X}^- + (\mathrm{H{-}Y}^+)^*$$

nature of the excited state bonds involved, and an alternative approach based on the intersecting state model (ISM) was proposed by Formosinho.[15] There is clearly a need to explore these approaches further in terms of both theoretical and experimentally based estimates of the force constants involved in this type of proton transfer reaction.

The central features observed experimentally in these reactions are the very low Brønsted α's obtained in every case so far investigated. There are several obvious ways in which such low values of α (or $\mathrm{d}\Delta G^{\neq}/\mathrm{d}\Delta G^{\circ}$) could arise experimentally (which incidentally also imply low intrinsic barriers and fairly pronounced Brønsted curvature). These include: (i) very strongly exothermic proton transfers (ii) a high degree of asymmetry between the two force constants involved (iii) variations in the 'tightness' or bond order at the transition state for different reactions and (iv) variations in the 'distance' travelled by the in-flight proton as a function of the endo- or exothermicity of the proton transfer step. The basic problem with the original Marcus treatment[13] or any related approach implicitly based on intersecting symmetrical[16] parabolic or other potential energy curves, is that such variations are not explicitly considered. A related and important problem is the extent to which the experimentally observed α value (or $\mathrm{d}\Delta G^{\neq}/\mathrm{d}\Delta G^{\circ}$) correctly reflects the actual extent of proton transfer at the transition state, which has been defined by Kreevoy[17] as χ (or $x_{\neq}/d$ where $x_{\neq}$ is the distance travelled by the proton at the transition state relative to the total distance d between the two sites of the proton in the associated complex leading to proton transfer).

The approaches of Marcus[13], Kreevoy,[17] Kresge and Koeppl[18] will be considered, as well as others not directly based on Marcus theory, such as those of Formosinho,[15] Le Noble,[19] Pross and Shaik,[20] to determine whether any reasonable and consistent picture of proton transfer in these photohydration reactions can be obtained, and hopefully to determine which approaches can best be applied to acid-catalyzed photochemical reactions in general.

RESULTS AND DISCUSSION

Intersecting parabola models

As is well known, the original Marcus equation* can be derived[21] from two intersecting parabolic potential energy curves, where the energies of the two states are given by

$$E_1 = nx^2 \qquad E_2 = n(d - x)^2 + \Delta E^\circ$$

where n is related to the force constant of the X—H bond in a symmetrical proton transfer reaction

$$\text{X—H} + \dashrightarrow [\text{X} --- \text{H} --- \text{X}]^{\neq} \dashrightarrow \text{X} + \text{H—X}$$

where d is defined as the distance between the two minima and x is the distance travelled by the proton from its equilibrium position in the starting X—H molecule. At the transition state, $x = x_{\neq}$ *and* $E_1 = E_2 = \Delta E^{\neq}$ since E_1 at $x = 0$ is defined as the zero reference point, and $\Delta E^\circ = E_2$ at $x = d$. This is illustrated in Figure 1 for subsequent comparison with non-symmetrical analogues. At $x = x_{\neq}$ the above equality yields

$$\Delta E^{\neq} = \lambda/4 + \Delta E^\circ/2 + (\Delta E^\circ)^2/4\lambda$$

where $\Delta E^{\neq}$ at $\Delta E^\circ = 0$ is defined as $\lambda/4$, the intrinsic barrier. If $\Delta E^{\neq}$ in this simple model is equated to $\Delta G^{\neq}$ and ΔE° to ΔG°, this corresponds to the Marcus equation,[14] excluding the work term w^r, i.e.

$$\Delta G^{\neq} = \lambda/4 + \Delta G^\circ/2 + (\Delta G^\circ)^2/4\lambda \tag{1}$$

Evaluation of w^r will be discussed later, but for now this term will be omitted in comparisons of the Marcus equation with other models. Differentiation of (1) with respect to ΔG° yields the well-known expression for α

$$\frac{d\Delta G^{\neq}}{d\Delta G^\circ} = \frac{1}{2} + \frac{\Delta G^\circ}{2\lambda} = \alpha \tag{2}$$

and further differentiation gives the Brønsted curvature c. All derivatives in this paper, such as $d\Delta G^{\neq}/d\Delta G^\circ$ and $d^2\Delta G^{\neq}/d(\Delta G^\circ)^2$ in equations (2), (3), (5) and (6), are really partial derivatives at constant λ. The assumption of constant λ for a given reaction series is generally made in applications of Marcus theory to kinetic data.

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*The original Marcus equations[14] were actually derived as expressions containing hyperbolic functions, rather than the more commonly used simple quadratic expressions. However, as Marcus has pointed out, the two types of equation are essentially equivalent when $|\Delta G^\circ|$ is not large, i.e. when $|\Delta G^\circ|/\lambda \leq 1$. This is the case for the whole range of ΔG° values considered in this paper.

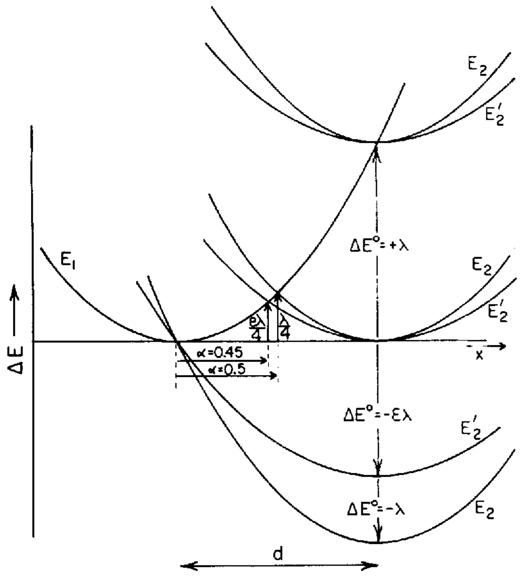

Figure 1. Schematic representation of symmetric and asymmetric (ε = 2/3) intersecting parabolic energy curves

$$\frac{d^2\Delta G^{\neq}}{d(\Delta G^\circ)^2} = \frac{1}{2\lambda} = \frac{d\alpha}{d\Delta G^\circ} = c \qquad (3)$$

The important characteristics of this symmetrical case are that $\alpha = 0{\cdot}5$ at $\Delta G^\circ = 0$, and that the Brønsted plot should be curved, since α depends on ΔG° (equation (2)), and that this curvature should be constant and inversely related to the magnitude of the intrinsic barrier through equation (3). The realistic limits of ΔG° are from $+\lambda$ (endo) to $-\lambda$ (exo) since outside of these limits is the so-called 'anomalous' region,[22] where the intersections of the two curves lie outside the range $0 \leqslant x \leqslant d$, illustrated in Figure 1. It follows that the corresponding limits for $\Delta G^{\neq}$ are from $+\lambda$ to 0. The general dependence of both $\Delta G^{\neq}$ and α on ΔG° are illustrated in Figure 2 which is an Eigen type diagram[11,23] showing how a Brønsted plot should behave ideally for non-diffusion controlled general acid catalyzed reactions. In this diagram the dashed line shown for the variation of α (or Kreevoy's χ)[17] also corresponds to the variation of $x_{\neq}/d$, which can be thought of as the mechanistic α (or χ) as against the experimental or observed α. In this symmetrical case the two are equivalent.

If the situation is changed to the more realistic case

$$\text{X—H} \dashrightarrow [\text{X --- H --- Y}]^{\neq} \dashrightarrow \text{X + H—Y}$$

where the force constants for the X—H and Y—H bonds may be significantly different, as is likely to be the case in general for photochemical reactions[12] and probably also for many thermal reactions,[18] we have

$$E_1 = nx^2 \qquad E_2 = m(d-x)^2 + \Delta E^\circ$$

If we define the ratio of the two force constants m/n to be ε, and make similar correspondences as before between ΔE and ΔG terms, this yields the expression derived by Cannon[24] for the

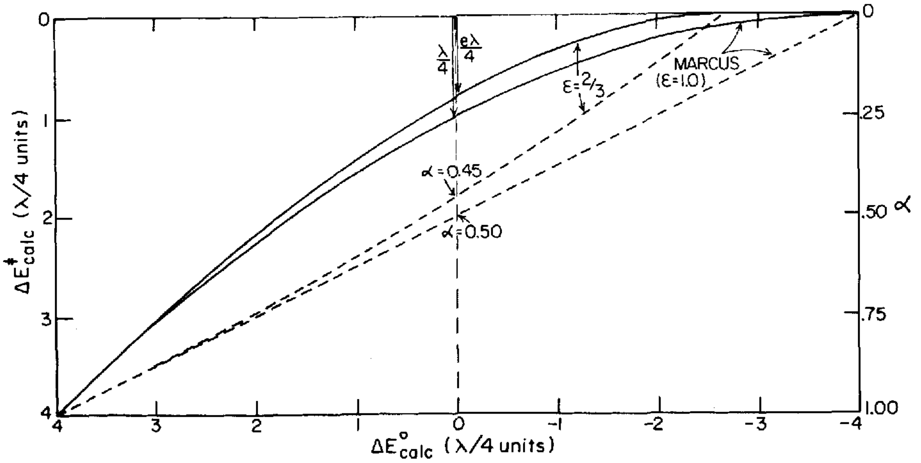

Figure 2. Solid curves—Eigen plots of $\Delta E^{\neq}_{calc}$ versus ΔE°_{calc} (both in units of $\lambda/4$) based on symmetric (Marcus) and asymmetric ($\varepsilon = 2/3$) intersecting parabola expressions (1) and (4). Dashed curves—variation of $\alpha(\mathrm{d}\Delta E^{\neq}/\mathrm{d}\Delta E^{\circ})$ as a function of ΔE°

general case of unsymmetrical intersecting parabolic potential energy surfaces (again omitting any explicit work terms)

$$\Delta G^{\neq} = \frac{\lambda}{(1-\varepsilon)^2}\left\{\varepsilon + \left[\varepsilon + \frac{\Delta G^{\circ}(1-\varepsilon)}{\lambda}\right]^{1/2}\right\}^2 \tag{4}$$

Again differentiating twice with respect to ΔG° yields equations (5) and (6) analogous to the Marcus expressions (2) and (3)

$$\frac{\mathrm{d}\Delta G^{\neq}}{\mathrm{d}\Delta G^{\circ}} = \frac{1}{(1-\varepsilon)} \quad 1 - \frac{\varepsilon}{\left(\varepsilon + \dfrac{\Delta G^{\circ}(1-\varepsilon)}{\lambda}\right)^{1/2}} \tag{5}$$

$$\frac{\mathrm{d}^2\Delta G}{\mathrm{d}(\Delta G^{\circ})^2} = \frac{\varepsilon}{2\lambda\left(\varepsilon + \dfrac{\Delta G^{\circ}(1-\varepsilon)}{\lambda}\right)^{3/2}} \tag{6}$$

The general dependence of $\Delta G^{\neq}$ on ΔG° given by equation (4) for $\varepsilon = 2/3$ is also shown by the Eigen type diagram in Figure 2 for comparison with that predicted by the Marcus equation. There are several important differences. Firstly the realistic limits of ΔG° are now more restricted, since, as illustrated in Figure 1 for the unsymmetrical case, the 'anomalous' region for exothermic reactions would occur at values of $\Delta G^{\circ} < -\varepsilon\lambda$. Thus ΔG° now varies between $+\lambda$ (exo limit) and $-\varepsilon\lambda$ (endo limit), but $\Delta G^{\neq}$ ranges from $+\lambda$ (slow reactions) to 0 (fast reactions) as before. In addition the intrinsic barrier (or $\Delta G^{\neq}$ at $\Delta G^{\circ} = 0$) is now given by $e\lambda/4$ rather than $\lambda/4$ where $e = (1 - (1 - \sqrt{\varepsilon}/1 + \sqrt{\varepsilon}))^2$. In the case where $\varepsilon = 2/3$, $e = 0{\cdot}808$ as shown in Figure 2. Further, the Brønsted α at $\Delta G^{\circ} = 0$ is $\sqrt{e}/2$ (0·45 where $\varepsilon = 2/3$) rather than 1/2, and although a Brønsted type plot would again be curved, the curvature c would not be constant as predicted by the Marcus equation. In addition the variation of $d\Delta G^{\neq}/d\Delta G^{\circ}$ or the observed α is no longer necessarily equal to the variation of $x_{\neq}/d$ or χ over the same range of ΔG°. (This point will be discussed more extensively later.)

Equations (4), (5) and (6) are somewhat unwieldy and are not likely to find practical use as alternatives to the Marcus equations. However, Cannon has shown[24] that equation (4) can be represented approximately in polynomial form, which can be truncated at the quadratic level for more direct comparison with the Marcus equation. Using the present symbolism this yields

$$\Delta G^{\neq} = \frac{e\lambda}{4} + \frac{\sqrt{e}\,\Delta G^{\circ}}{2} + \frac{(\Delta G^{\circ})^2}{4\sqrt{\varepsilon}\,\lambda} \tag{7}$$

$$\frac{d\Delta G^{\neq}}{d\Delta G^{\circ}} = \frac{\sqrt{e}}{2} + \frac{\Delta G^{\circ}}{2\sqrt{\varepsilon}\,\lambda} = \alpha \tag{8}$$

$$\frac{d^2\Delta G^{\neq}}{d(\Delta G^{\circ})^2} = \frac{1}{2\sqrt{\varepsilon}\,\lambda} = c \tag{9}$$

Cannon has pointed out that the quadratic form of equation (3) is valid provided the term $\Delta G^{\circ}(1 - \varepsilon)/\lambda$ is not too large.[24] This is not a problem for the range of ΔG° and ε values considered in the present paper. Figure 3 shows a comparison of the analytical and quadratic forms of these general equations. It is clear that equation (7) is a reasonable approximation to equation (4), and the first derivative form in equation (8) is an even closer approximation to equation (5), providing that $|\Delta G^{\circ}|$ is not greater than about twice the magnitude of the intrinsic barrier. This is not likely to be a serious limitation for photochemical reactions on the exo side, from what is known of the magnitudes of excited state pK shifts,[25] nor on the endo side because of the limitation that bimolecular reactions with $\Delta G^{\neq}$ values approaching ≈10 kcal are not likely to occur within the normally short (1–100 ns) lifetimes of most singlet states.[26]

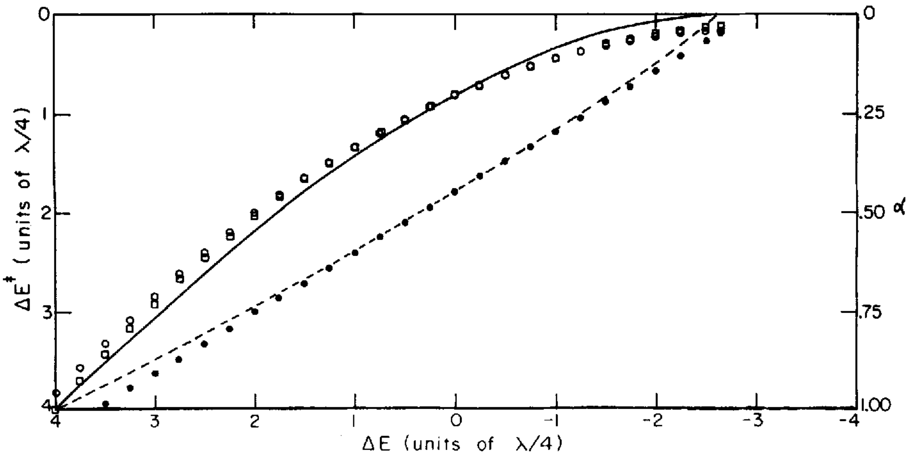

Figure 3. Comparison of calculated $\Delta E^{\neq}$ values as a function of ΔE° (both in units of $\lambda/4$), with $\varepsilon = 2/3$. Solid curve based on equation (4); open circles based on equation (7); squares based on equation (10). Dashed curve—variation of α with ΔE° based on equation (5). Solid circles variation of α with ΔE° based on equation (8)

It can be seen from equation (9) that the Brønsted curvature would still be predicted to be constant, as in the Marcus equations. Truncation of the polynomial expansion of equation (4) at the cubic level, as in equation (10), takes care of this problem,

$$\Delta G^{\neq} = \frac{e\lambda}{4} + \frac{\sqrt{e}\,\Delta G^\circ}{2} + \frac{(\Delta G^\circ)^2}{4\sqrt{\varepsilon}\,\lambda} + \frac{(1-\varepsilon)\,(\Delta G^\circ)^3}{8\lambda^2} \tag{10}$$

and also gives a better fit to the analytical solution from equation (4), as shown in Figure 3. However, it is very doubtful whether inclusion of a cubic term is justified at this stage, in terms of the precision of the data currently available for estimating the magnitude of the Brønsted curvature.

This means that the second derivative expressions, equations (6) and (9), cannot presently be used directly to estimate the possible magnitudes of the intrinsic barrier as a function of the asymmetry parameter ε. Nonetheless the first derivative forms, equations (5) and (8), can be used along with the observed values of α to estimate these barriers. The derived values of $e\lambda/4$ can then be inserted into equations (4) or (7) to estimate values of $\Delta G^{\neq}$, also as a function of ε. This is illustrated in Table 1, where values of both $e\lambda/4$ and $\Delta G^{\neq}$ (exclusive of the work term) have been calculated for a range of possible ε and ΔG° values. Only negative values of ΔG° have been considered, since at the mid-point of the general acid catalyst range previously used[3,4] namely pK_{HA} = 7·0, the value of ΔG° of reaction must be negative. If this were not the case, the ΔG° value for the weakest general acid used, namely H_2O, would have to be significantly greater than 10 kcal, which is impossible for bimolecular reactions of substrates with measured singlet lifetimes in the 1–50 ns range.[9,27] It is clear from Table 1 that in order to explain typical Brønsted α's of ≈0·15 at the mid-point of the general acid catalyst range, the

Table 1. Calculated values of intrinsic barriers and $\Delta G^{\neq}$ as a function of ε

		ΔG° (kcal)		
		−5	−10	−15
$\varepsilon = 1{\cdot}0$[a]	$e\lambda/4$[c]	1·8	3·6	5·4
$e = 1{\cdot}0$[b]	$\Delta G^{\neq}$[e]	0·2	0·3	0·5
$\varepsilon = 2/3$	$e\lambda/4$	2·1	4·1	6·2
$e = 0{\cdot}808$	$\Delta G^{\neq}$	0·6	1·1	1·7
$\varepsilon = 1/2$	$e\lambda/4$	2·3	4·6	6·9
$e = 0{\cdot}686$	$\Delta G^{\neq}$	0·9	1·8	2·7
$\varepsilon = 1/3$	$e\lambda/4$	2·7	5·4	8·1
$e = 0{\cdot}536$	$\Delta G^{\neq}$	1·4	2·8	4·2

[a] $\varepsilon = k_1/k_2$.

[b] $e = \left(1 - \frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right)^2$

[c] Calculated from equation (8) using a typical α value of 0·15[d] for mid-point of catalyst pK_{HA} range used in the Brønsted plots.

[d] Taken from Reference 4.

[e] Calculated from equation (7) using the above values of intrinsic barrier $e\lambda/4$.

Marcus equation must be modified to include a significant degree of asymmetry. Based on the original Marcus equation ($\varepsilon = 1{\cdot}0$) the calculated values of both $e\lambda/4$ and $\Delta G^{\neq}$ are too low for any reasonable value of ΔG°, which based on the range of catalysts used must be somewhere in the 0–(−10)kcal range.* (This point will be addressed more fully later). Since the catalytic rate constants k_{HA} are all approximately in the 10^4–$(5 \times 10^7)\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$ range[4], this corresponds to a $\Delta G^{\neq}$ range of 3·2–8·3 kcal taking a value of $10^{10}\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$ for the diffusion-controlled limit. This means that the intrinsic barriers must also be within this range. Although some of the calculated values for $\varepsilon = 1$ (the Marcus equation) do fall inside this range, the corresponding values of $\Delta G^{\neq}_{\mathrm{calc.}}$ seem far too low for reactions which have limiting rates (for hydronium ion catalysis) of $(1{\cdot}5$–$4{\cdot}9) \times 10^7\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$, even allowing for a significant w^r contribution to $\Delta G^{\neq}_{\mathrm{expt.}}$. Overall the most reasonable values of ΔG°, $e\lambda/4$ and $\Delta G^{\neq}$ are found for $\varepsilon = 1/3$, which is in agreement with the conclusion of a previous exploratory study.[12] However, such a degree of asymmetry implies a reduction of ≈67% in the force constant of the carbon-hydrogen bond in the protonated substrate, compared with that of the oxygen-hydrogen bond in the general acid catalyst. This has been criticized by Formosinho[14] as being an unreasonably large difference, even for electronically excited states, and it seems clear that although some reduction in force constant could be expected for an excited state cation, other factors must be important in producing such low α values, and their implication of very early transition states.

Hyperbolic expressions

One problem inherent in any Marcus type equations based on parabolic potential energy surfaces lies in their limiting behavior at very high endo- or exothermicities. To avoid the so-called 'anomalous' region,[22] there is a cut-off at high endothermicity ($\Delta G^{\circ} = \lambda$) where $\Delta G^{\neq}$ becomes exactly equal to ΔG°, and also at high exothermicity ($\Delta G^{\circ} = -\lambda$ or $-\varepsilon\lambda$) where $\Delta G^{\neq}$ becomes zero. Both forms of limiting behavior have been criticized as being physically unrealistic since it would be expected that although $\Delta G^{\neq}$ might approach these limits, it would never actually attain them. In other words even for the most exothermic proton transfers there should still be a small $\Delta G^{\neq}$ term, which for the endothermic direction means that $\Delta G^{\neq}$ would always be greater than ΔG°. Lewis and More O'Ferrall[28] have proposed an alternative to the Marcus equation based on a hyperbolic expression, given in equation (11).

$$\Delta G^{\neq} = \frac{\Delta G^{\circ}}{2} + \frac{\sqrt{(\Delta G^{\circ})^2 + \lambda^2/4}}{2} \qquad (11)$$

This expression gives more reasonable limiting behavior, since as $\Delta G^{\circ} \rightarrow (+\infty)$, $\Delta G^{\neq}$ approaches ΔG° asymptotically. In the exothermic direction ΔG° approaches zero asymptotically as $\Delta G^{\circ} \rightarrow (-\infty)$. The intrinsic barrier remains $\lambda/4$ as in the Marcus equation, and the Brønsted α is 1/2 at $\Delta G^{\circ} = 0$ as seen from equation (12) which is the first derivative form of equation (11).

$$\frac{\mathrm{d}\Delta G^{\neq}}{\mathrm{d}\Delta G^{\circ}} = 1/2 + \Delta G^{\circ}\left((\Delta G^{\circ})^2 + \lambda^2/4\right)^{-1/2} = \alpha \qquad (12)$$

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*Since the range of catalysts $\mathrm{p}K_{\mathrm{HA}}$ represents 17·4 pK units, this corresponds to a ΔG° range of 24 kcal. For the slowest photochemical reaction to occur, $\Delta G^{\neq}$ must be less than 10 kcal. Therefore the mid-point of the catalyst ΔG° range must be less than −2 kcal.

However the Brønsted curvature c is now predicted to be variable as shown in equation (13) unlike the constant curvature predicted by the Marcus equation.

$$\frac{d^2\Delta G^{\neq}}{d\Delta(G^\circ)^2} = 1/2\left((\Delta G^\circ)^2+\frac{\lambda^2}{4}\right)^{-1/2} - \frac{(\Delta G^\circ)^2}{2}\left((\Delta G^\circ)^2+\frac{\lambda^2}{4}\right)^{-3/2} \tag{13}$$

Similar limiting behavior is predicted by the Marcus BEBO expression,[29] equation (14), as are the values of $\Delta G^{\neq}$, and α at $\Delta G^\circ = 0$, and variable Brønsted curvature as a function of ΔG°.

$$\Delta G^{\neq} = \frac{\lambda}{4} + \frac{\Delta G^\circ}{2} + \frac{\lambda}{4\ln 2}\ln\cosh\left(\frac{\Delta G^\circ \ln 2}{\lambda/2}\right) \tag{14}$$

The variation of $\Delta G^{\neq}$ as a function of ΔG°, based on the Lewis–More O'Ferrall hyperbolic expression is compared with that based on the Marcus equation in the Eigen type diagram shown in Figure 4. Also shown is the variation of α, which has a more compressed range than 0–1, based on the hyperbolic expression, with α being greater than the Marcus α for endo reactions and less than the Marcus α for exo reactions. A similar comparison could be made using the BEBO expression (equation (14)), but this has been omitted for clarity. As Lewis and More O'Ferrall[28] have pointed out, the use of this expression is less simple than that of equation (11) in that it requires evaluation of the intrinsic barrier by iteration. In order to make the two hyperbolic expressions, equations (11) and (14) less unwieldy and to compare them more directly with the Marcus equation, Lewis and More O'Ferrall[28] have proposed approximate forms based on the polynomial expansions of these equations, truncated at the quadratic level. These are shown by equations (15) and (16) respectively.

$$\Delta G^{\neq} = \frac{\lambda}{4} + \frac{\Delta G^\circ}{2} + \frac{(\Delta G^\circ)^2}{2\lambda} \tag{15}$$

$$\Delta G^{\neq} = \frac{\lambda}{4} + \frac{\Delta G^\circ}{2} + \frac{(\Delta G^\circ)^2}{2{\cdot}885\lambda} \tag{16}$$

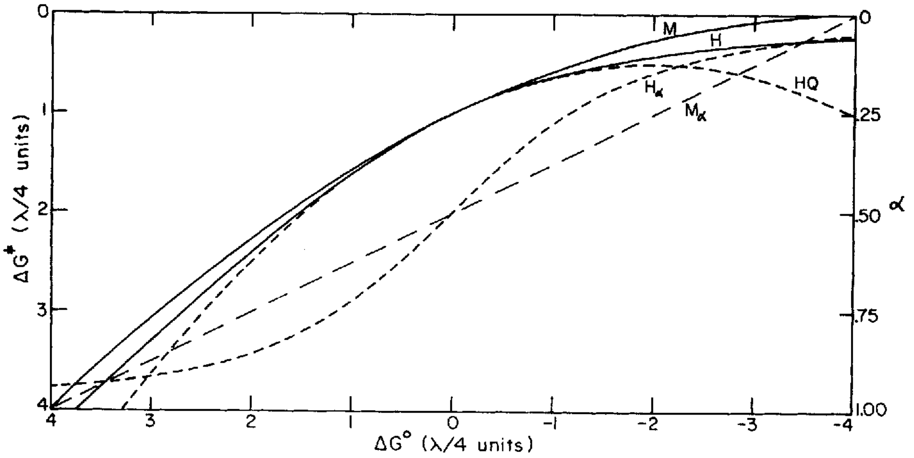

Figure 4. Comparison of $\Delta G^{\neq}$ versus ΔG° based on the Marcus equation (1) (curve M), the Lewis–More O'Ferrall hyperbolic equation (11) (curve H), and the quadratic approximation equation (5) (curve HQ). Curves Mα and Hα represent the variation in α as a function of ΔG° calculated from equations (2) and (12) respectively

Although these two expressions resemble the Marcus equation very closely, they are unfortunately very poor approximations to the hyperbolic expressions originally proposed, except in a very narrow range of ΔG° ($\pm\lambda/4$). This is shown in Figure 4 for the Lewis–More O'Ferrall expressions. (The problem does not lie in the truncation at the quadratic level so much as in the limited range of variables over which the full polynomial expansion is valid.)*

It is now of interest to determine whether the two original hyperbolic expressions (11) and (14) can give a better representation of the observed experimental variation of log k_{HA} versus log K_{HA} (or equivalently of $\Delta G^{\neq}$ versus ΔG°) than the previously discussed Marcus type expressions.

Comparison of Marcus type and Hyperbolic expressions

In order to compare the fit of equations (1), (7), (11) and (14) to the available experimental data, it is necessary to plot $\Delta G^{\neq}$ versus ΔG° in common units of $\lambda/4$ as previously shown in Figures 2 and 3. This requires empirical evaluation of the intrinsic barriers for the reactions in question, which can be obtained from the experimental Brønsted plots, providing the position corresponding to $\Delta G^\circ = 0$ can be located on these plots. This requires a knowledge of $pK_{S_1H^+}$ or the excited state basicities of the substrates in question, since for the proton transfer reaction involving any general acid HA,

$$S_1 + HA \rightarrow S_1H^+ + A^- \qquad \Delta G^\circ_R$$

it can easily be shown that

$$\Delta G^\circ_R = \Delta G^\circ_{HA} - \Delta G^\circ_{S_1H^+} \qquad (17)$$

where $\Delta G^\circ_{HA} = -RT \ln K_{HA}$ and $\Delta G_{S_1H^+} = -RT \ln K_{S_1H^+} = 2{\cdot}303RTpK_{S_1H^+}$. Since the proton transfer to S_1 is not reversible to any significant extent,† this means $pK_{S_1H^+}$ cannot be measured directly,[30] by fluorescence titration for example. One way of estimating $pK_{S_1H^+}$ is via the well-known Förster cycle method[31] which is based on changes in absorption and emission maxima on protonation. Recent measurements of shifts in absorption and emission maxima of styrene type molecules and their cations lead to a value of $\Delta pK^* = pK_{S_1H^+} - pK_{S_0H^+}$ of approximately[8] 22 units, which taken with Jencks and Richards' value of $-11{\cdot}1$ for the ground state of *p*-methyl styrene[32] leads to an estimated $pK_{S_1H^+}$ of about +11. This means that the catalyst pK_{HA} on a Brønsted plot corresponding to an overall ΔG°_R of zero would also be +11, as seen from equation (17).

An alternative approach is to consider that for the weakest acid catalyst used (H_2O) the $\Delta G^{\neq}$ of reaction must be larger than the overall $\Delta G_R{}^\circ$ for that reaction. The $\Delta G^{\neq}$ values for the water reaction can be obtained from the observed k_{H_2O} values,[4] and if $\Delta G_R{}^\circ$ in each case is to be taken to 0·5 kcal less than $\Delta G^{\neq}$, a limiting value of $\Delta G^\circ_{S_1H^+}$ can be obtained, knowing ΔG°_{HA} for water. For the five substrates whose Brønsted plots have been established, this leads to estimated values of $pK_{S_1H^+}$ of 10·9, 11·3, 9·9, 11·0 and 11·3, which are reassuringly close to the value for typical styrenes of 11·0 estimated via the Förster cycle method. The average value of 10·9 can then be used to estimate log k_{HA} ($\Delta G_R{}^\circ = 0$) from the Brønsted

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*In the present case this corresponds to the range $-\lambda < \Delta G^\circ < +\lambda$.

†All singlet state lifetime measurements based on the single photon counting method showed single exponential decay for these substrates[3,4,9] at all acidities used.

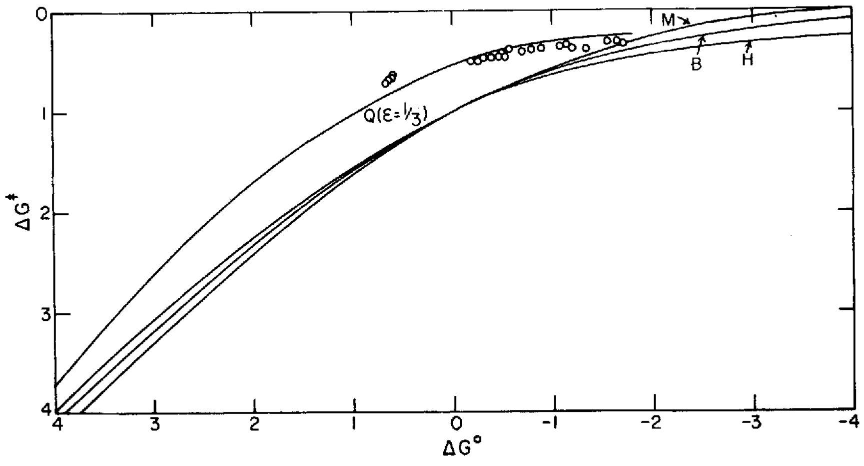

Figure 5. Comparison of the fit of the experimental data, open circles, (see text), to the calculated $\Delta G^{\neq}$ curves based on equation (1) (curve M); equation (7) with ε = 1/3 (curve Q); equation (11) (curve H) and equation (14) (curve B)

plots, which in turn leads to estimated intrinsic barriers for these reactions of 5·2–6·5 kcal depending on the individual substrate.

Plots of $\Delta G^{\neq}$ versus ΔG° (both in units of $\lambda/4$) are shown in Figure 5, based on the Marcus type equations with $\varepsilon = 1{\cdot}0$ and $\varepsilon = 1/3$, and on the Lewis–More O'Ferrall[28] and Marcus BEBO equations,[29] with experimental points[3,4] (also reduced to units of $\lambda/4$) for comparison. It can be seen that the only expression giving a reasonable fit to the experimental points, both in terms of the shapes of the curves and their limiting behavior at high acidity (i.e. high exothermicity) is the Marcus equation modified to include an asymmetry parameter of $\varepsilon = 1/3$. It may be that modifying the hyperbolic expressions to include some form of asymmetry could improve their fit, but it is not easy to see how this could be done realistically. Attempts have been made to do this, for example by replacing ΔG° in equation (11) by $e\Delta G^{\circ}$ and replacing λ by $e\lambda$, but this unfortunately leads to unrealistic behavior for positive ΔG° values i.e. where $\Delta G^{\neq}$ becomes less than ΔG°, which is physically impossible, It should be pointed out that this is also a problem for the approximate quadratic form of the asymmetric parabolic equation (7), but only at very high positive ΔG° values. However, as pointed out previously, photochemical reactions with very high ΔG° values are not likely to occur anyway, so that this region is of no practical importance.

Despite the excellent fit of equation (7) (with $\varepsilon = 1/3$) to the experimental data, the implied high degree of asymmetry is again subject to the same criticism as made previously by Formosinho.[14] It seems therefore that although some degree of asymmetry may be required to explain both the shapes of the Brønsted plots and low overall α values found for these photohydration reactions, other important factors must be operative.

Kreevoy τ parameter approach

Kreevoy[17] has proposed a modification of the Marcus equation which attempts to take into account the variability of the 'tightness' of the transition state via a parameter τ, as in equations (18) and (19). It should be noted that these expressions have been simplified[17] by dropping higher order terms which are expected to be small in most cases. The quantity τ is related to the charge δ

$$\Delta G^{\neq} = \frac{\lambda}{4} + \frac{\Delta G^\circ}{2} + \frac{(\Delta G^\circ)^2}{4\lambda} + \frac{(\tau - 1)}{2} \Delta G^\circ \tag{18}$$

$$\frac{d\Delta G^{\neq}}{d\Delta G^\circ} = \frac{1}{2} + \frac{(\tau - 1)}{2} + \frac{\Delta G^\circ}{2\lambda} = \alpha \tag{19}$$

on the in-flight atom at the transition state. In the case of proton transfer this is given by $(1 - \tau) = \delta$. (The definition of δ differs in sign from that given in the original paper,[17] since proton rather than hydride transfers are involved here.) The quantity $(1/2 + \Delta G^\circ/2\lambda)$ on the right hand side of equation (19) is defined by Kreevoy as χ and corresponds to α in the original Marcus expression (equation (2)). Since

$$\frac{d\Delta G^{\neq}}{d\Delta G^\circ} = \chi + \frac{\tau - 1}{2} = \alpha$$

the observed values of $d\Delta G^{\neq}/d\Delta G^\circ$, or its equivalent $d\ln k/d\ln K$, corresponds to the 'experimental' Brønsted α, whereas χ represents the 'mechanistic' α, or the degree of proton transfer at the transition state along the diagonal of Albery–Jencks–More O'Ferrall diagram,[33] as illustrated in Figure 6. The term involving τ represents the orthogonal distance of the transition state from this diagonal in terms of the 'tightness' ($\tau > 1$) or 'looseness' ($\tau < 1$) of the transition state relative to so-called 'normal' transition states where the actual degree of proton transfer is equivalent to $d\Delta G^{\neq}/d\Delta G^\circ$. Kreevoy has applied this approach successfully to hydride transfer reactions[17,34] and has evaluated τ independently from symmetrical reactions which can be studied in both directions. Unfortunately this cannot be done for irreversible photochemical proton transfer reactions, but trial values of τ can be used with

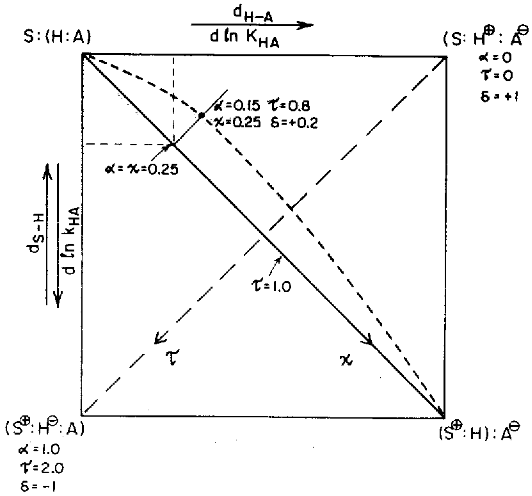

Figure 6. Two-dimensional transition state map for proton transfer from a general acid HA to an excited state substrate S as a function of the Kreevoy tightness parameter τ and the charge on the in-flight proton δ. Note that α (or $d\ln k_{HA}/d\ln K_{HA}$) is only equal to the progress variable χ in the solid diagonal where $\tau = 1$. Dashed line represents the reaction pathway for $\tau = 0{\cdot}8$

Table 2. Calculated values of intrinsic barrier and $\Delta G^{\neq}$ as a function of τ

		ΔG° (kcal)		
		−5	−10	−15
τ = 0·6[a]	$\lambda/4$[b]	4·17	8·33	12·5
(χ = 0·35)	$\Delta G^{\neq}$[d]	3·05	6·08	9·13
τ = 0·7	$\lambda/4$	3·13	6·25	9·38
(χ = 0·30)	$\Delta G^{\neq}$	1·88	3·75	5·63
τ = 0·8	$\lambda/4$	2·5	5·0	7·5
(χ = 0·25)	$\Delta G^{\neq}$	1·13	2·25	3·38

[a] 'Tightness' parameter,[17] as defined in equation (18).

[b] Calculated from equation (19) using a typical value of α = 0·15[c] for mid-point of catalyst pK_{HA} range in Brønsted plots.

[c] Taken from Reference 4.

[d] Calculated from equation (18) using above values of intrinsic barrier $\lambda/4$.

observed Brønsted α values using equation (19) to evaluate possible $\lambda/4$ values, and then by substituting these values into equation (18) corresponding $\Delta G^{\neq}$ values can be evaluated. It turns out that only a certain range of τ is feasible, given the low observed α values in the 0·15 region. Values of $\tau > 1$ give small positive $\lambda/4$ values but negative $\Delta G^{\neq}$. Values of $\tau < 0·3$ give negative $\lambda/4$ values. Although some values of $\tau \leqslant 0·5$ give positive $\lambda/4$ values, the calculated $\Delta G^{\neq}$ values are smaller than observed $\Delta G^{\neq}$ values. It therefore appears that τ must be in the 0·5–1·0 range for the photohydration reactions. The most reasonable values of $\lambda/4$ and $\Delta G^{\neq}$ are obtained for τ in the 0·6–0·8 range, when compared with the previously described experimental values of these two quantities, based on experimental Brønsted plots. These are shown in Table 2, for the same range of ΔG° as in Table 1.

This strongly suggests that these photochemical proton transfer reactions are characterized by somewhat 'loose' transition states in which the in-flight proton bears a significant positive charge at the transition state. Based on the previous estimate of ΔG°_{R} for the mid-point of the catalyst pK_{HA} range used to construct the Brønsted plots, the values in Table 2 at $\Delta G^{\circ} = -5$ kcal are the most reasonable. It should be noted that a τ value in the 0·6–0·8 range implies a value of χ (the extent of proton transfer at the transition state) which is significantly greater than that indicated by the experimental value of α. As shown in Table 2, χ would be in the 0·25–0·35 range for the mid-point of the Brønsted curve where $\alpha \simeq 0·15$. This is illustrated in Figure 6 where the dashed line on the Albery–Jencks–More O'Ferrall diagram is based on a τ value of 0·7. This is a physically more reasonable situation than that indicated by the Brønsted α values themselves, which vary between about 0·3 (for the weakest catalysts used) to effectively zero (for H_3O^+). Inclusion of the τ term leads to extents of proton transfer at the transition state which would vary between 45% for the slowest reactions at pH 7 and 15% for the limiting rates observed at high acidity ($H_o \approx -2$). Since the various forms of the Marcus equation used so far completely neglect the work term, the Kreevoy expression gives an opportunity to estimate typical values of w^r for photohydration reactions. This is illustrated in Figure 7 where Brønsted plots are shown in terms of both experimental and calculated values

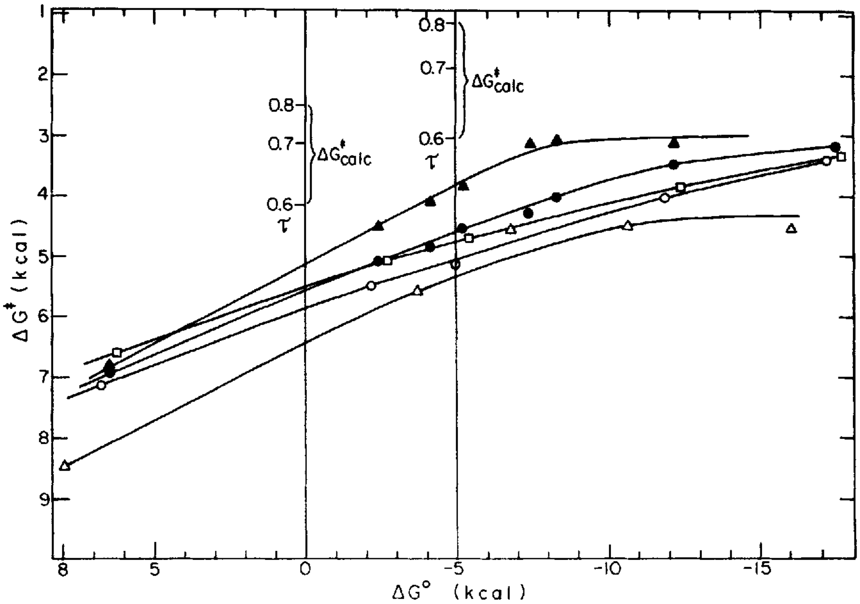

Figure 7. Experimental curves (see text) showing variation of $\Delta G^{\neq}$ (from log k_{HA}) for photohydration as a function of ΔG° (from log K_{HA}). Open circles—*m*-fluorostyrene; closed circles—α-naphthylacetylene; open triangles—2-vinylnaphthalene, closed triangles—β-naphthylacetylene; open squares—methylstyrene. Vertical lines represent calculated $\Delta G^{\neq}$ values at selected τ for $\Delta G^{\circ} = 0$ and -5 kcal respectively

of $\Delta G^{\neq}$ as a function of ΔG°. Since the calculated values $\Delta G^{\neq}$ ignore w^r, the difference between $\Delta G^{\neq}{}_{\text{calc}}$ and $\Delta G^{\neq}{}_{\text{obs}}$ for different possible τ values gives an estimate of the range of reasonable w^r values. For τ in the 0·6–0·8 range this gives w^r values in the 2·5 ± 1·0 kcal range. There is good agreement between the average values of w^r obtained, whether $\Delta G^{\neq}{}_{\text{calc}}$ is based on equation (18) at $\Delta G^{\circ} = -5$ kcal, or on equation (19) with $\Delta G^{\circ} = 0$. For an intermediate value of $\tau = 0{\cdot}7$ the average values of w^r are 2·6 and 2·8 kcal respectively. This is similar to the conclusion reached previously,[12] namely that work terms for excited state proton transfers are likely to be smaller than those found for analogous thermal reactions ($w^r \approx$ 4–11 kcal). It is reasonable that during the fast process of internal conversion to the vibrationally and geometrically relaxed form of S_1, which occurs before any chemical reaction takes place, there would be similar solvent relaxation which could reduce the extent of solvent reorganization needed in the reactive complex leading to proton transfer. This would be particularly important if catalyst acid species were within the reaction sphere[35] of the excited state species at the time of its creation, and could transfer a proton to it via a Grotthus chain mechanism. Although Jencks and Bednar[36] have demonstrated that this mechanism is probably not operative for proton transfers to carbon in the ground state, it does not follow that the more highly polarized* and reactive species involved in photohydration reactions will behave similarly. Although their limiting rate constants are lower than for very fast proton transfers to

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*The idea that the S_1 states of phenylacetylenes and styrenes are strongly polarized is supported experimentally by their large p*K* shifts and the regiospecificity of their photohydration reactions, as well as by theoretical calculations on a variety of simple model systems.[37]

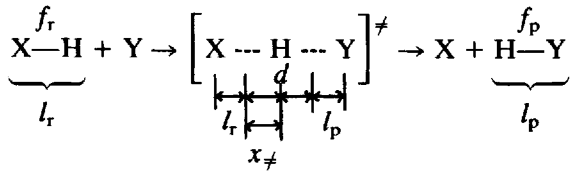
oxygen or nitrogen, where the Grotthus mechanism does operate, they are still much faster (by 10^{11}–10^{14}) than analogous ground state proton transfer reactions.

It is probable that some combination of transition state asymmetry (as expressed by an ε term) and 'looseness' (as expressed by τ) could give a more satisfactory and complete description of these excited state proton transfers than either approach alone. Unfortunately this is not feasible at present since there is no satisfactory way of evaluating either ε or τ independently. It would therefore be futile to try to modify the Kreevoy equation by incorporating an asymmetry parameter, although it seems clear that any degree of 'looseness' incorporated into the model would require a lower and therefore more reasonable degree asymmetry than previously indicated by an ε of 0·33. For example, introduction of a Kreevoy τ parameter term into equation (7), with an arbitrary value $\tau = 0{\cdot}7$, leads to a calculated $\Delta G^{\neq}$ versus ΔG° curve which only gives a good correspondence with the experimental variation of log k_{HA} versus K_{HA} when an asymmetry parameter of $\varepsilon \approx 0{\cdot}66$ is used, rather than the physically less realistic value of 0·33 discussed previously.

It must be concluded that although Marcus theory can be applied, with suitable modifications, to excited state proton transfers to yield reasonable qualitative conclusions, the overall situation is somewhat unsatisfactory in a quantitative sense.

Intersecting state model

Formosinho has developed an interesting model, originally based on intersecting Morse curves,[15] and later modified this to include intersecting harmonic oscillators,[38] which give essentially the same results. The model differs from Marcus theory in taking specific account of stretching force constants and entropy of mixing terms, following the proposals of Agmon and Levine.[39] The idea of an intrinsic barrier is not explicitly included in Formosinho's equations, although obviously $\Delta G^{\neq}$ at $\Delta G^{\circ} = 0$ can be calculated. He has successfully applied this ISM model to a wide variety of thermal reactions,[40] mainly hydrogen atom and proton transfers, and more recently to some photochemical reactions.[14] The ISM model has been described in detail elsewhere[38] and can be summarized as:



$$\underbrace{\overset{f_r}{X{-}H}}_{l_r} + Y \rightarrow \left[X \cdots H \cdots Y\right]^{\neq} \rightarrow X + \underbrace{\overset{f_p}{H{-}Y}}_{l_p}$$

where d is the variable distance travelled by the in-flight proton, l_r and l_p are the equilibrium bond lengths of the bound hydrogen in the reactant and product states, and f_r and f_p are the corresponding stretching force constants. In this model d is defined by

$$d = \eta l = \eta(l_r + l_p) \qquad (20)$$

where the parameter η is the reduced distance given by

$$\eta = \frac{a' \ln 2}{n^{\neq}} + \frac{a'}{2\lambda^2}(\Delta G^{\circ})^2 \qquad (21)$$

In equation (21), a' is a constant, $n^{\neq}$ is the total bond order at the transition state and λ is the entropy of mixing term as defined by Agmon and Levine.[39] 'Loose' transition states are characterized by high values of λ, corresponding to a greater degree of freedom in distributing excess energy, and vice versa. Formosinho has described methods[38,40] of evaluating η from experimental data and its variation with $\Delta G°$, and has concluded that more ionic processes ('normal' acids) will have values of $n^{\neq} \approx 1$ and $\lambda < 24$ kcal, whereas more covalent processes, such as with 'pseudo-acids' and hydrogen atom transfers should have $n^{\neq}$ values closer to 0·5 and $\lambda > 24$ kcal. Values of $\Delta G^{\neq}$ can be calculated from the expression

$$1/2\, f_r\, x_{\neq}^2 = 1/2\, f_p(d - x_{\neq})^2 + \Delta G°$$

where $x_{\neq}$ corresponds to the extent of proton transfer at the transition state, and hence $x_{\neq}/d$ corresponds to χ or the 'mechanistic' α. Rate constants can be calculated from $k_r = (kt/h)\, e^{-\Delta G_{\neq}/RT}$ taking the limiting value of k_r for diffusion-controlled reactions to be $10^{10}\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$. Formosinho[14] has used a higher value than this, but his calculations on the photohydration of *p*-methylstyrene lead to the unrealistically high value of 12·8 kcal for $\Delta G^{\neq}$, given that the S_1 lifetime of this substrate is only 4·5 ns.[4] Values of f_r are typically in the range 6·97–7·36 mdyne Å^{-1} for ground state oxygen acids,[40] and values of f_p for ground state carbonium ions can be estimated from observed vibrational spectra[41] in the C—H stretching region to be in the 4·05–4·37 mdyne Å^{-1} region. Corresponding values of f_p for excited state carbocations are not yet available, but it can be safely assumed that these would be no greater than the value of 4·82 mdyne Å^{-1} used by Formosinho[14] in his recent calculations on the photohydration of *p*-methylstyrene. Both ground and excited state force constants can also be calculated by *ab initio* LCAO-SCF methods based on simple model systems,[42] and the ratio f_p/f_r compares reasonably with that used by Formosinho for *p*-methylstyrene photohydration. The values of k_r (6·97 mdyne Å^{-1}) and k_p (4·82 mdyne Å^{-1}) used by Formosinho,[14] give a ratio of k_p/k_f = 0·7, whereas the values calculated by *ab initio* methods[42] give a ratio of 0·77, based on the protonation of acetylene to give the vinyl cation. Although the two excited state carbocations are of different types, the general agreement emphasizes the asymmetry of the proton transfer step.

Using values of k_r = 6·97 mdyne Å^{-1} and k_f = 4·82 mdyne Å^{-1} and various trial values of λ and $n^{\neq}$, the variation of log k can be calculated as a function of $\Delta G°$ via the Formosinho equations. In these calculations l_r was taken as 0·98Å, and l_p as 1·08Å, based on recent *ab initio* LCAO-SCF calculations[42] on model systems of the type of involved in photohydration. The results of the Formosinho type calculations are plotted as Brønsted type curves in Figure 8 for the $\Delta G°$ range +10 to −20 kcal. It can be seen that log k_{calc} varies over the range 10^{-10} to $10^{10}\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$ depending on the assumed values of $n^{\neq}$ and λ. The values used in Figure 8 are typical of those used by Formosinho in treating a wide variety of reactions.[40] The vertical location of the curve (or overall rate range covered by the Brønsted plot) is largely controlled by $n^{\neq}$, whereas the shapes of the curve (Brønsted α and curvature) are largely controlled by λ and the ratio of k_p to k_r. The experimental catalytic rate constants (log k_{HA}) are superimposed on the plot as ranges of values for different substrates at a given catalyst pK_{HA}.

The best fit is obtained for a value of $n^{\neq}$ = 0·82 and λ = 30·4 kcal, both of which imply a somewhat 'looser' transition state than that normally found for typical ionic reactions ($n^{\neq}$ = 1·0 λ = 20·7 kcal). It should also be pointed out that such an excellent fit could not have been achieved without the significant degree of asymmetry implied by the different values of the two force constants used. (In this case they correspond to a value of ε, as previously defined in the modified Marcus treatment, of 0·69).

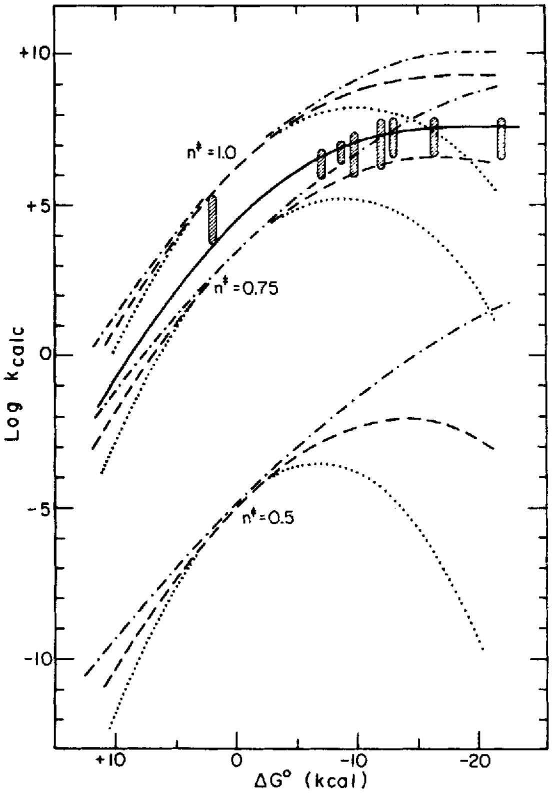


Figure 8. Calculated values of log k as a function of log K for different $n^{\neq}$, based on Formosinho's intersecting state model. Broken curves with λ = 71·7 kcal; dashed curves, λ = 30·4 kcal; dotted curves, λ = 20·7 kcal. Solid curve, λ = 30·4 kcal and $n^{\neq}$ = 0·82. Shaded enclosed areas—range of experimental log k values for different substrates at particular catalyst pK_{HA} values

Considering the possible vertical range involved in Figure 8 and the different possible shapes or curvatures, the fit to the experimental data which can actually be obtained must be considered remarkable. It is very interesting and reassuring that the nature of the proton transfer process implicit in the calculated bond lengths and force constants and selected values of $n^{\neq}$ and λ required to give such a fit is in very good qualitative agreement with that previously deduced from the various modified Marcus treatments, namely a significantly asymmetric process with a somewhat 'looser' transition state than for 'normal' ground state acid–base reactions.

It must be noted that despite the excellent fit obtained in Figure 8 the value of $\Delta G^{\neq}$ at $\Delta G^{\circ} = 0$ which comes from the calculated curve (+7·5 kcal) does not correspond very precisely with the experimentally derived intrinsic barriers discussed previously, which were in the 5·2–6·5 kcal range. This can be seen from the poorer correspondence between the calculated curve with the experimental points data in the $\Delta G^{\circ} > 0$ region. In addition the location of the ΔG° value corresponding to the water catalyzed rate constants, implies excited states which are somewhat more basic than previously estimated by either Förster cycle calculations or by the limiting rate assumptions. Part of the problem is that the generally accepted pK_{HA} value for water of 15·7 is not as well-defined as that for typical general acids, and that water as a catalytic species probably cannot be treated with respect to its stoicheometric concentration of 55·5 M in the same way as other catalyst species, due to its much greater self-association. It is difficult to know what if anything can be done to improve this situation quantitatively, but despite the possible anomalous behavior of H_2O as a general acid catalyst, the overall agreement shown between the conclusions based on Formosinho's treatment and modified Marcus treatments must be considered very satisfactory in terms of a general description of these excited state proton transfer reactions. Attempts are currently under way to increase the range and uniformity of the general acid catalysts used, partly in order to deemphasize the influence of the K_{H_2O} term on the shape of the Brønsted plots.

It is interesting that the distance variation involved in equations (20) and (21) as a function of ΔG°, is similar in form to that proposed by Kresge and Koeppl,[18] who modified the Marcus equation to include an increase in distance travelled by the proton (or increase in looseness of the transition state) as reactions become either more endo- or more exothermic. Indeed if Kresge and Koeppl's calculations of $\Delta G^{\neq}$ are repeated, allowing up to a 25% increase in d as ΔG° approaches $\pm\lambda$, an excellent 1:1 correspondence with the results of the Formosinho approach is obtained, as shown in Figure 9. The correspondence of the asymmetric quadratic modification of the Marcus equation (equation (7) with $\varepsilon = 2/3$) with either the Formosinho or Kresge and Koeppl $\Delta G^{\neq}$ values is not as good, since although the plot is linear, the slope is greater than unity, and the correlation does not quite pass through the origin, as shown in Figure 9. This emphasizes that transition state asymmetry is not the only important factor in determining the observed Brønsted α values and curvature.

It is again the case with the Formosinho calculations that $d\Delta G^{\neq}/d\Delta G^\circ$ or α is not equivalent to $x_{\neq}/d$ or χ. For endothermic reactions $\alpha > \chi$ and for exothermic reactions with $\Delta G^\circ \leq -5$ kcal, $\chi > \alpha$. In other words, as before, the observed Brønsted α does not accurately reflect

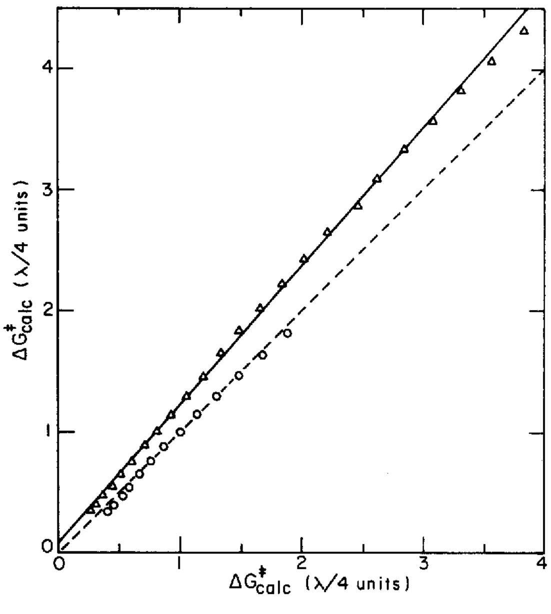


Figure 9. Relationship of $\Delta G^{\neq}$ calculated from Formosinho's equation (open circles) and from asymmetric Marcus expression, equation (7) with $\varepsilon = 2/3$ (open triangles), to $\Delta G^{\neq}$ values calculated from Koeppl and Kresge's expression (see text). Dashed line represents 1:1 correspondence

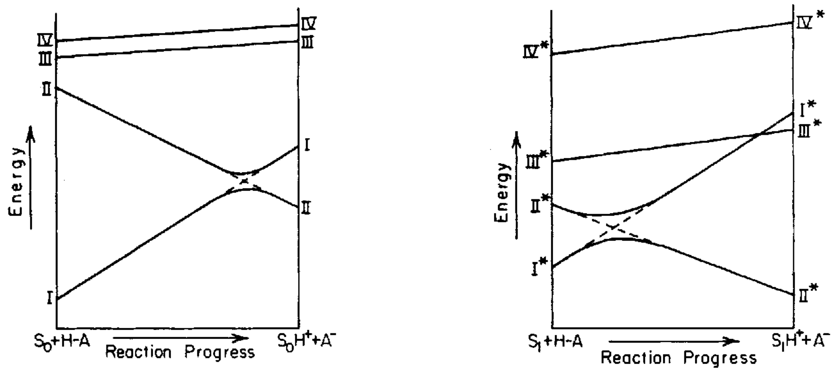


Figure 10. Schematic representations of variation of energy with reaction progress, based on Valence Bond Configuration Mixing model, for proton transfer reactions of ground (S_0) and excited state (S_1) styrenes (see text for description of configurations I–IV)

the extent of proton transfer at the transition state. At the mid-point of the catalyst range used experimentally, where $\alpha \approx 0{\cdot}14$–$0{\cdot}18$, χ is $0{\cdot}28$–$0{\cdot}30$, which is similar to the conclusion reached via the Kreevoy approach. It is interesting that a similar conclusion is also reached using Le Noble's approach,[19] which is based on a quartic equation as being the simplest representation of a two dimensional potential energy surface with two minima and one maximum, corresponding to a typical reaction profile. Le Noble has successfully applied this simple approach to the interpretation of pressure effects on reaction rates.[19] Although the overall variation of $\Delta E^{\neq}$ and ΔE° calculated from the Le Noble equations is very similar to that obtained via the Marcus equation, the first derivative behavior is different, and depends on how it is defined. For cases where $E_1 < 0$, Le Noble's equation gives $dE^{\neq}/dE_1$ (or α) less than $dx_{\neq}/d\Delta E^\circ$ (or χ), and for cases where $E_1 > 0$, $d\Delta E^{\neq}/d\Delta E^\circ$, is greater than $dx_{\neq}/d\Delta E^\circ$. It appears that for any approach other than a simple intersecting parabola model, with surfaces of equal curvature, $d\Delta E^{\neq}/d\Delta E^\circ$ is not in general equal to the variation of the intersection point $x^{\neq}$, or transition state position, with ΔE° If this is correct in practice, this means that for endothermic reactions, the measured Brønsted α implies a later transition state than is really the case, and for exothermic reactions one which is not as early as indicated by α. In other words, while the observed α may possibly vary between zero and 1·0 (and even lie outside these limits in anomalous cases)[43] the actual extents of proton transfer corresponding to these limits are more compressed than this. It is also worth pointing out that the variation of d as a function of $|\Delta G^\circ|$, whether via the Formosinho or Kresge and Koeppl approach, automatically leads to flattening out of the $\Delta G^{\neq}$ versus ΔG° curve at high exothermicities (as observed experimentally)[4] and to asymptotic behavior at high endothermicities. In other words the basic Marcus approach leads to more realistic limiting behavior, if distance variation is taken into account, without the need to propose hyperbolic modifications of the Lewis and More O'Ferrall type.[28] Even with modest distance variation, the so-called 'anomalous' regions can be avoided for any realistic ΔG° range, so that $\Delta G^{\neq}$ is always either greater than zero or greater than ΔG° as the two limits are approached.

A final point with regard to the Formosinho calculations is that the Brønsted curvature c can be calculated from the second derivative of $\Delta G^{\neq}_{\text{calc}}$ with respect to ΔG°, for the range +10 to −20cal. Values of c ranging from 0·005 to 0·05 are obtained, with an average value over the whole ΔG° range of 0·031. Although an experimental value of c has not yet been firmly established for photohydration reactions, treatment of the experimental Brønsted plots using a cubic expression[4] yields estimates of c for the five substrates involved that are in the 0·005 to 0·033 range at the mid-point of the pK_{HA} range.[44] Based on the empirical values of $\lambda/4$, the Marcus, Kreevoy, and Cannon asymmetric expressions yield c values in the 0·019 to 0·042 range. It therefore seems reasonable that if the Brønsted curvature for these reactions has values in the 0·01–0·05 range, as indicated above, it should be easily possible once larger and more uniform sets of acid catalysts and reactions are studied, to measure these c values accurately and hence provide further tests for the various types of treatment described in this paper.

Configuration mixing model

Pross and Shaik[20] have proposed a qualitative valence-bond configuration mixing (VBCM) model to describe how reaction profiles can be built up from constituent VB configurations. This approach can be used to compare the major characteristics of the rate profiles for the ground and excited state hydrations of typical styrenes (or phenyacetylenes). If we examine first the initial S_0 and S_1 states of the substrate, the major VB contributors to each are

$$\text{Ar CH}{=}\text{CH}_2 \leftrightarrow \text{AR}{-}\overset{\oplus}{\text{C}}\text{H}{-}\overset{\ominus}{\text{C}}\text{H}_2 \leftrightarrow \overset{\oplus}{\text{A}}\text{r}{=}\text{CH}{-}\overset{\ominus}{\text{C}}\text{H}_2$$

Omitting the third structure for simplicity, these two states can be represented as

$$\psi(\text{Ar CH}{=}\text{CH}_2)S_0 = (\text{Ar CH}{=}\text{CH}_2) + \lambda(\text{Ar }\overset{\oplus}{\text{C}}\text{H}{-}\overset{\ominus}{\text{C}}\text{H}_2)$$

$$\psi(\text{Ar CH}{=}\text{CH}_2)S_1 = (\text{Ar}{-}\overset{\oplus}{\text{C}}\text{H}{-}\overset{\ominus}{\text{C}}\text{H}_2) - \lambda(\text{Ar CH}{=}\text{CH}_2)$$

where the first structure in each case is the major contributor to that state. If we now consider the general acid catalyzed ground state reaction:

$$(\text{A}{-}\text{H})S_0 \rightarrow [\text{A}\text{---}\text{H}\text{---}S_0]^{\neq} \rightarrow \overset{\ominus}{\text{A}}{:}(\text{H}{-}S_0{}^{\oplus})$$

then in terms of the VBCM model the major reactant and product configurations will be I and II respectively

$(\text{A}{:}\text{H}){:}S_0$
I

$\text{A}{:}^{\ominus}(\text{H}{:}S_0{}^{\oplus})$
II

$\overset{\ominus}{\text{A}}{:}\text{H}^{\oplus}{:}S_0$
III

$\overset{\oplus}{\text{A}}{:}\overset{\ominus}{\text{H}}{:}S_0$
IV

Configurations III and IV can be effectively neglected for the ground state reaction as being too high in energy. As the reaction proceeds from left to right I will increase steeply in energy as the A—H bond is stretched. Proceeding from right to left the energy of II will also increase steeply for similar reasons, but II will clearly start off from a much higher energy position than I. Styrenes are known to be very weak bases in their ground state.[32] Although similar estimates of pK_{BH^+} for phenylacetylene have not been made, it is presumably a weaker base than benzonitrile, which has a ground state pK_{BH^+} of -10.[45] Both III and IV will increase in energy from right to left for electrostatic reasons, but less steeply. These are only included for completeness. The overall energy diagram is represented by Figure 10 where as the two major curves start to cross, configuration mixing lowers the energy of the system at the transition state. The overall qualitative conclusions are that the reaction will be a distinctly endothermic process with a late transition state. The charge on the in-flight hydrogen will be effectively zero, since contributions from III or IV will be very small and an effective bond order of one will be maintained throughout the reaction. Thus $\delta = 0$, and therefore τ should be unity in Kreevoy's terms, or $n^{\neq} = 1{\cdot}0$ in Formosinho's terms.

For the excited state analogue, we have similarly

$$A{:}S_1 \rightarrow [A\text{---}\ H\ \text{---}S_1]^{\neq} \rightarrow A{:}^{\ominus}(H{:}S^{\oplus}{}_1H)$$

and the reactant and product configurations are given by I*–IV*. However

$$\begin{array}{cc} (A{:}H)\ S_1 & A{:}^{\ominus}(H{:}S^{\oplus}{}_1) \\ \text{I}^* & \text{II}^* \\ A{:}^{\ominus}H^{\oplus}{:}S_1 & A^{\oplus}{:}H^{\ominus}S_1 \\ \text{III}^* & \text{IV}^* \end{array}$$

in this case the two major reactant and product configurations I* and II* will initially be more nearly equal in energy,† and configuration III*, although a minor one, will no longer be negligible, since the more highly dipolar nature of S_1 (as shown previously) will lower its energy, while at the same time increasing that of IV*. These changes could be either due to electrostatic or hydrogen-bonding effects. The overall energy changes in each of the various configurations as the reaction proceeds will be similar to those described for the ground state reaction, but the configuration mixing near the transition state will be different, due to both the different initial positions of I* and II* and to the increased contribution from III*. This is shown in Figure 10. The overall conclusion is that the excited state reaction will be much faster and will have a much earlier transition state than the thermal reaction. In addition there will be a small positive charge δ on the in-flight hydrogen due to the contribution of III*, or a Kreevoy τ value of less than unity. In bond order terms, this corresponds to an overall Formosinho $n^{\neq}$ value of less than unity.

Although this is a very qualitative, descriptive approach it is in general accord with the results of recent *ab initio* LCAO-SCF calculations on simple but related model systems, insofar as the increased polarization of S_1 is concerned, and the basicity and rate enhancements occurring on electronic excitation of S_0.[46] In addition, the overall picture which emerges is in very satisfactory agreement with the conclusions reached previously by analyzing the experimental data by either the Marcus–Kreevoy or Formosinho approaches.

Conclusions

Marcus theory can be applied to photochemical proton transfer reactions providing a significant degree of asymmetry is introduced via a parameter ε. The unmodified Marcus equations do not give realistic results for these fast reactions which have very low α values. However the degree of asymmetry implied by this simple approach seems too high ($\varepsilon \approx 0{\cdot}33$) and there is also a need to take into account possible variations in transition state 'tightness' which can be done via Kreevoy's τ parameter. In the present case this leads to a restricted range of possible τ values and to the conclusion that the transition state is somewhat 'looser' ($\tau \approx 0{\cdot}6$–$0{\cdot}8$) than in normal ground state proton transfer reactions. The Kreevoy approach can

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†Although excited state pK values for styrenes and phenylacetylenes are not known, approximate estimates based on fluorescence titration[3,4,12] and the Förster cycle method[8] place these in the 0–10 region. Therefore proton transfer to S_1 must be much less endothermic than to S_0, and is almost certainly exothermic where H_3O^+ is the catalytic species.

be used in these cases to estimate a reasonable range for the work term w^r, which is lower (≈2–3 kcal) than typical values found for ground state reactions ($w^r \approx 4$–11 kcal). Due to the difficulty of simultaneously incorporating asymmetry (ε) and 'tightness' (τ) in the Marcus equation, the Formosinho intersecting state model is preferred, since this simultaneously takes into account differences in force constants (asymmetry), transition state bond order $n^{\neq}$ (tightness) as well as variations in the distance traversed by the proton as a function of ΔG°. This gives a remarkable fit to available experimental data, leading to the conclusions that for photohydration the transition state is asymmetric ($\varepsilon \approx 0{\cdot}69$, which is a more reasonable value), somewhat 'loose' ($n \approx 0{\cdot}8$) compared with typical ground state reactions ($n^{\neq} \approx 1{\cdot}0$), and that the distance parameter varies by approximately ±25% from the value at $\Delta G^\circ = 0$ over the experimental range of ΔG° values.

An important conclusion from all the approaches used is that except for highly symmetric proton transfer reactions, the experimental Brønsted α or $\mathrm{d}\Delta G^{\neq}/\mathrm{d}\Delta G^\circ$ does not correctly reflect the degree of advancement of proton transfer at the transition state (χ). In general, for endothermic processes $\alpha > \chi$ and for exothermic processes $\chi > \alpha$. This means that for photohydrations with very low α's at the mid-point of the catalyst range used, of ≈0·15, the actual extent of proton transfer is probably closer to 30% at this point.

The Kresge and Koeppl approach to the Marcus equation, which also takes account of both force constant asymmetry and distance variation, leads to very similar conclusions to those obtained from the Formosinho model, and is a very useful and simple alternative, providing reasonable estimates for force constants and bond length variation can be made.

Application of the qualitative configuration mixing model of Pross and Shaik to this type of excited state reaction, also leads to conclusions which are of a very similar nature to those obtained by the Kreevoy and Formosinho approaches, namely that the transition states are 'loose'.

Finally, estimates of the Brønsted curvature c using the various Marcus type modifications, are in the same range as those estimated approximately from Brønsted plots.

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