

In Figure 13 the δ_2 value increases from C_6H_5Cl to C_6H_5I , which corresponds to the decrease in the halogen p_y character for the π_1 orbital. The fact that the relative intensity of the π_1 band in Figure 13 decreases from C_6H_5Cl to C_6H_5I despite the increase in the size of the p_y orbital shows that the effect of the p_y mixing is stronger than that of the size of the p_y orbital on the reactivity of the π_1 orbitals.

Conclusions

Penning ionization electron spectroscopy (PIES) provides direct information on the spatial distribution of individual molecular orbitals. On the basis of this unique feature of PIES, all the bands in the He I spectra of monohalobenzenes, C_6H_5F , C_6H_5Cl , C_6H_5Br , and C_6H_5I , have been assigned. Since Penning ionization can be interpreted as an electrophilic reaction in which an electron in an occupied orbital is extracted into the vacant orbital of the metastable atom, the relative reactivity of electrons in a particular orbital upon electrophilic attacks can be probed by PIES. By the

use of this character of PIES, the relative reactivities of the n and π orbitals of monohalobenzenes have been studied. It is found that the orbital reactivity depends on the electronic factor due to the size of the halogen p orbitals and the conjugation between the benzene ring and the halogen atoms, and also on the steric factor due to the benzene ring shielding some orbitals from the impact of metastable atoms. Although we have selected a series of halobenzenes as an example, the present results are of general importance and demonstrate that PIES is a powerful technique for studying the stereochemical property and the reactivity of individual molecular orbitals.

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Registry No. C_6H_5F , 462-06-6; C_6H_5Cl , 108-90-7; C_6H_5Br , 108-86-1; C_6H_5I , 591-50-4.

Application of Marcus Theory to Photochemical Proton-Transfer Reactions. 1. An Exploratory Study of Empirical Modifications of the Basic Equations

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Abstract: Marcus theory has been applied empirically to photochemical proton-transfer reactions by the inclusion of an asymmetry parameter ϵ or ϵ' which is allowed to vary between 0 and 1, to reflect the fact that excited-state potential energy wells will generally be shallower than analogous ground-state surfaces. It is found that experimentally observed Brønsted α values and the curvature of the Brønsted plots can only be reasonably explained by using ϵ' values in the neighborhood of 0.3. Such values give reasonable estimates of the "intrinsic" barrier for proton transfer and probable ΔG° ranges for these reactions. Various forms of modified Marcus equations, and their relationship to intersecting parabolas of different curvature, are discussed.

Marcus theory, which was originally developed to interpret the rates of electron-transfer reactions,¹ has also been successfully applied to proton-transfer reactions.² It has apparently not yet been applied to any photochemical proton-transfer reactions, although there is no reason in principle why it should not be, at least for simple proton transfers involving singlet excited states. We have recently³ reported the first examples of general acid catalysis in photochemical reactions, and the values of the Brønsted α found for these reactions, as well as the observed curvature in the Brønsted plots, can be used to test the applicability of the Marcus equations.

The theory⁴ relates the free energy of activation ΔG^\ddagger to the standard free energy of the overall reaction ΔG° via the equation:

$$\begin{aligned} \Delta G^\ddagger &= w^r + \lambda(1 + \Delta G^\circ/\lambda)^2/4 \\ &= w^r + \lambda/4 + \Delta G^\circ/2 + (\Delta G^\circ)^2/4\lambda \end{aligned} \quad (1)$$

where w^r is the work required for solvent reorganization to form the encounter complex between substrate and catalyst, ΔG° is the actual free-energy change in the proton-transfer step itself, and

$\lambda/4$ is the "intrinsic" barrier to reaction, for the case in a reaction series where $\Delta G^\circ = 0$. Thus ΔG^\ddagger and ΔG° are connected for a reaction series which shares a common intrinsic barrier.

Since the Brønsted α coefficient is defined as $d\Delta G^\ddagger/d\Delta G^\circ$, then as pointed out previously,^{1,5} differentiation of (1) gives the equation:

$$d\Delta G^\ddagger/d\Delta G^\circ = 1/2 + \Delta G^\circ/2\lambda = \alpha \quad (2)$$

The extent of curvature in a Brønsted plot can be obtained by differentiating eq 2 to give eq 3. Therefore, any observed cur-

$$d\alpha/d\Delta G^\circ = 1/2\lambda \quad (3)$$

vature will depend on the magnitude of the intrinsic barrier for the reaction series. Slow reactions with large intrinsic barrier should show essentially linear Brønsted plots (especially over the short catalyst pK ranges normally employed), while fast reactions such as photochemical proton transfers, with low values of $\lambda/4$, should yield distinct curvature. Rates of proton transfer (k_{HA}) have been previously reported⁶ for the photohydration of substituted styrenes and phenylacetylenes. Independent measurements of k_{HA} based on the pH dependences of fluorescence quenching, singlet-state lifetimes, and observed quantum yields for overall reaction gave consistent results, with k_{HA} values for these substrates being in the 1.0×10^6 to 5×10^7 $M^{-1} s^{-1}$ range. Values of k_{HA}

(1) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891; *J. Am. Chem. Soc.* **1969**, *91*, 7224.

(2) See, for example, several excellent reviews: Kresge, A. *J. Chem. Soc. Rev.* **1973**, *2*, 475; *Acc. Chem. Res.* **1975**, *8*, 354. More O'Ferrall, R. A. In *Proton Transfer Reactions* Caldin E. F., Gold, V., Eds.; Chapman and Hall: London, 1975.

(3) Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 869.

(4) This presentation of Marcus theory follows the discussion of: Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69.

(5) Albery, W. J.; Campbell-Crawford, A. N.; Curran, J. S. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2206.

(6) Wan, P.; Culshaw, S. C.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509.

Table I

catalyst	pK_{HA}	rate constants ($M^{-1} s^{-1}$)			
		<i>p</i> -methylstyrene (1)	<i>m</i> -fluorostyrene (2)	2-vinylnaphthalene (3)	β -naphthylacetylene (4)
H ₂ O	15.7	1.5×10^5	6.3×10^4	6.8×10^3	1.0×10^5
H ₃ BO ₃	9.23	2.0×10^6	1.0×10^6		
H ₂ PO ₄ ⁻	7.19	3.9×10^6	1.8×10^6	1.1×10^6	3.7×10^6
H ₃ PO ₄	2.15	1.6×10^7	1.2×10^7	1.4×10^6	
H ₃ O ⁺	-1.74	3.6×10^7	3.4×10^7	4.9×10^6	1.5×10^7
α^a		0.14	0.15	0.12	~0.16
$d\alpha/d\Delta G^\circ$		0.0048	0.0045	0.0057	

^a Average or least-squares value of slope of $\log k_{HA}$ vs. pK_{HA} . ^b Average value of $\Delta\alpha/\Delta\Delta G^\circ$ based on pairwise comparisons of $\Delta \log k_{HA}$ vs. ΔpK_{HA} .

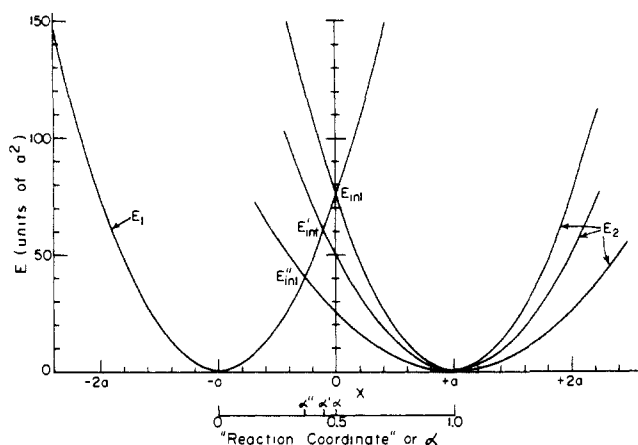


Figure 1. Variation of intrinsic barrier height (ΔE_{int}) and extent of reaction at the transition state (α) as a function of changing parabolic curvature of one of the reactants.

have also been obtained for general acid catalysis^{3,7} using Stern-Volmer plots of φ/φ_0 vs. catalyst (HA) concentration. Plots of $\log k_{HA}$ vs. pK_{HA} give Brønsted α values around 0.15,⁸ implying very early transition states in comparison with the analogous thermal hydrations which have α in the 0.5–0.85 range.⁹ However, these plots of $\log k_{HA}$ vs. catalyst pK_{HA} show significant curvature. The rate constants^{3,7} given in Table I yield overall α values in the 0.12–0.16 range, and in two cases there are sufficient data to make reliable estimates of the curvature $d\alpha/d\Delta G^\circ$.¹⁰

Equation 3 can be used to estimate the intrinsic barrier $\lambda/4$ from the observed values of $d\alpha/d\Delta G^\circ$, and this value can then be used in eq 2, along with the overall α value, to estimate ΔG° for the reaction of substrate with hydronium ion (and hence provide an estimate of the excited-state pK^* value). It is immediately clear from these calculations that the unmodified Marcus equation (eq 3) gives values of $\lambda/4$ which are much too high for such fast reactions. For *p*-methylstyrene and *m*-fluorostyrene respectively these are $\lambda/4 = 26.0$ and 28.1 kcal. Also the values of ΔG° obtained from eq 2 are unreasonably exothermic (-72.8 and -77.7 kcal, respectively) even allowing for the well-known and often large effects of electronic excitation on pK values.¹¹

(7) Yates, K.; McEwen, J., unpublished results.

(8) In all cases of general acid catalysis found so far for the photo-protonation of styrenes and phenylacetylenes,^{3,7} the Brønsted α values are in the 0.12–0.18 range.

(9) Schubert, W. M.; Keeffe, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 559. Simandoux, J. C.; Torck, B.; Hellin, M.; Coussemant, F. *Tetrahedron Lett.* **1967**, 2971. Gold, V.; Kessick, M. A. *J. Chem. Soc.* **1965**, 6718.

(10) It is unfortunate that a more uniform set of general acid catalysts could not be used to obtain the Brønsted α and curvature values, but there are two experimental restrictions inherent in these photochemical reactions which prevent this. One is that the buffer solutions must not have significant UV absorption in the region of the spectrum (254 or 300 nm) where kinetic measurements are made, and secondly that the buffer species must not react independently with the substrates, as we have found to be the case for typical carboxylic acids. Work is currently in progress⁷ to extend the range of suitable catalysts available by using structurally related phosphonates. So far this has shown that even with catalysts of mixed type, smooth Brønsted curves are obtained (see Figure 4, for example), with both α and Brønsted curvature values falling within narrow ranges for these closely related photoreactions.

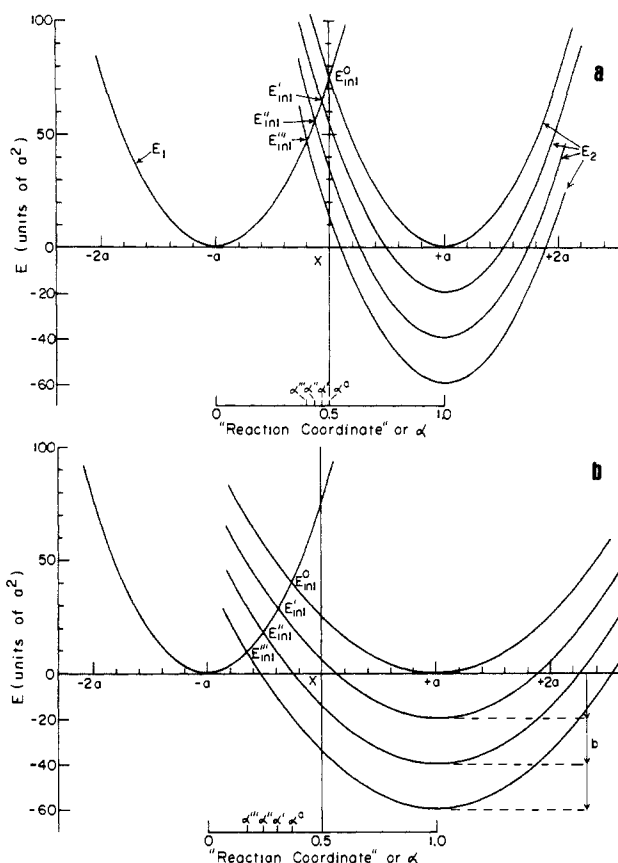


Figure 2. Comparison of barrier heights and Brønsted α values as a function of the exothermicity of reaction b for symmetrical (a) and unsymmetrical (b) intersecting parabola models.

The problem lies in the fact that these equations, derived from the basic Marcus equation (eq 1), imply a more or less symmetrical proton-transfer process at $\Delta G^\circ = 0$, between two steep ground-state potential energy wells, which in turn requires α for a degenerate proton transfer $XH^+ + X \rightarrow X + XH^+$ to be 0.5. Recognizing that excited-state potential energy surfaces are much shallower because of the presence of electrons in antibonding orbitals,¹² then even for an isoenergetic proton transfer from XH^+ to X^* , the transition state would lie distinctly to the left of that in the thermal analogue, and α should be significantly less than 0.5. This is shown in Figure 1, where simple parabolic curves have been constructed for illustrative purposes. Also the rate of change of α with respect to ΔG° (shown in the exothermic sense only in Figure 2) would clearly be different for analogous thermal and photochemical proton transfers. The question is how to modify

(11) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131. Klopffer, W. *Adv. Photochem.* **1977**, *10*, 311. Martinov, I. Y.; Demyashkevich, A. B.; Uzhinov, B. M.; Kuzmin, M. G. *Russ. Chem. Rev. (Engl. Trans.)* **1977**, *46* (1), 1.

(12) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 4, p 68.

Table II. Calculated Values^a of the "Intrinsic" Barrier and ΔG° as a Function of ϵ

ϵ	substrate					
	1		2		3	
	$\lambda/4$	ΔG°	$\lambda/4$	ΔG°	$\lambda/4$	ΔG°
0.1	0.26	+18.7	0.28	+22.2	0.22	+12.3
0.2	1.04	+8.34	1.11	+11.1	0.88	+3.51
0.25	1.63	+3.12	1.74	+5.55	1.39	-0.88
0.3	2.37	-2.09	2.50	0	1.97	-5.26
0.33	2.89	-5.64	3.09	-3.78	2.44	-8.25
0.4	4.17	-12.5	4.44	-11.1	3.51	-14.0
0.5	6.51	-22.9	6.94	-22.2	5.48	-22.8
0.75	14.7	-49.0	15.6	-50.0	12.5	-44.7
0.9	21.1	-64.0	22.5	-66.7	17.8	-57.9
1.0	26.1	-75.0	27.8	-77.8	21.9	-68.4

^aThe same numerical values are obtained using eq 18–20 for the given values of ϵ' ($=\epsilon$), except that the $\lambda/4$ values above become $\epsilon'\lambda/4$.

the basic Marcus equations to take account of this asymmetry in proton transfers from ground-state acids to excited-state bases. A simple first approach is to modify the Marcus equations by selecting some arbitrary value of α , say 0.25 rather than 0.5, for a $\Delta G^\circ = 0$ process and see how reasonable the calculated results are in terms of the observed rate constants and estimated⁶ pK^* values for the substrates, based on fluorescence titration curves. This could be done either by changing the divisor in eq 1 from 4 to 8 or by changing the denominator of the bracketed ΔG° term from λ to 2λ . As it turns out, these two changes give the same result, given that the intrinsic barrier in one case is $\lambda/8$ rather than $\lambda/4$ as in (1). For *p*-methylstyrene, with $\alpha = 0.14$ and $d\alpha/d\Delta G^\circ = 0.0048$, we obtain a value of 6.5 kcal for the intrinsic barrier, which, although much more reasonable for observed proton-transfer rates in the 10^4 – 10^7 $M^{-1} s^{-1}$ range, still seems much too high given the observed S_1 lifetimes of these substrates (typically 3–50 ns).⁶ The calculated value of ΔG° from either modification is -20.8 kcal, which is still unreasonably exothermic. Although excited-state pK^* shifts for typical aromatic molecules can be quite large¹¹ (up to 15 log units), and would be expected to involve generally low and quite possibly significantly negative ΔG° values, a value of $\Delta pK^* = pK_{S_1} - pK_{S_0}$ based on the above estimated ΔG° value would imply an enormous ΔpK^* shift of 26 log units, based on the recently estimated¹³ pK_{S_0} value for *p*-methylstyrene (-11.1). Although the estimate of pK^* based on fluorescence titration of this substrate is only very approximate (ca. 0–(-1)⁶), there are good reasons to believe such estimates are not out by more than ± 3 units (see later), and a ΔpK^* of 10 ± 3 is much more in line with the large number of previously reported ΔpK^* values.¹¹

It is thus clear that the Marcus equations need to be modified in some more general way to determine whether they can give reasonable estimates of intrinsic barriers and typical ΔG° values for photochemical proton-transfer reactions, which are consistent with all experimental observations. It is proposed that Marcus theory be modified by introducing an eccentricity or asymmetry parameter ϵ , which can vary between 0 and 1 ($0 < \epsilon \leq 1$) and determine how $\lambda/4$ and ΔG° vary as a function of ϵ . Rewriting eq 1 as

$$\Delta G^\ddagger = w^\ddagger + \lambda(1 + \epsilon\Delta G^\circ/\lambda)^2/4 = w^\ddagger + \lambda/4 + \epsilon\Delta G^\circ/2 + [\epsilon^2(\Delta G^\circ)^2/4\lambda] \quad (4)$$

we obtain

$$d\Delta G^\ddagger/d\Delta G^\circ = \epsilon/2 + \epsilon^2(\Delta G^\circ)/2\lambda = \alpha \quad (5)$$

and

$$d\alpha/d\Delta G^\circ = \epsilon^2/2\lambda \quad (6)$$

Using the values of α and $d\alpha/d\Delta G^\circ$ from Table I for the three substituted styrenes (1–3), the calculated values of $\lambda/4$ and ΔG°

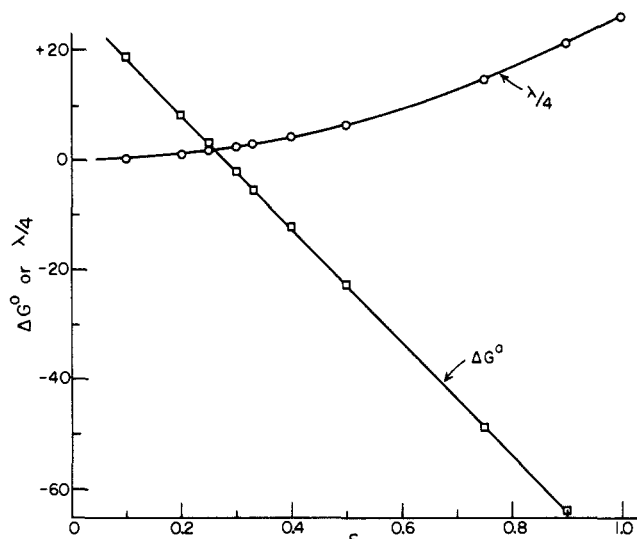


Figure 3. Calculated dependence of intrinsic barrier height ($\lambda/4$) and ΔG° on the magnitude of selected asymmetry parameter (ϵ) values.

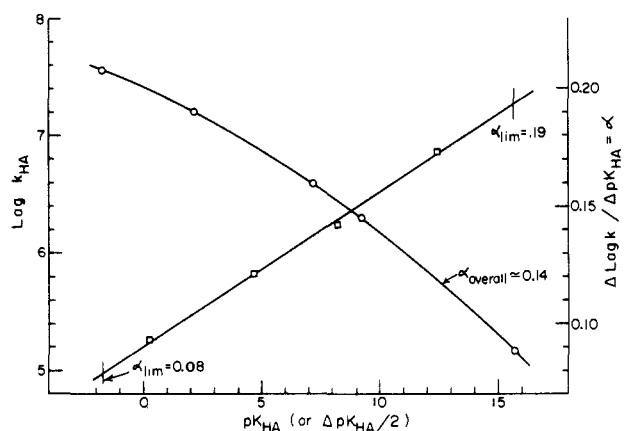


Figure 4. Brønsted plot of k_{HA} vs. catalyst pK_{HA} (circles) illustrating curvature, and plot of $\Delta\alpha/\Delta pK_{HA}$ (squares) vs. midpoints of catalyst pK_{HA} ranges giving limiting values of Brønsted α at low and high acidity.

using eq 4–6¹⁴ are as shown in Table II.

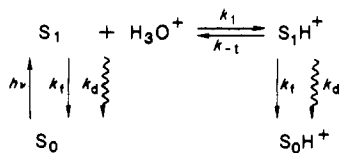
The values for 1 and 2 in Table II are more reliable than those for 3, but in any event all three substrates give very similar dependence of $\lambda/4$ and ΔG° on ϵ . This is shown graphically for 1 in Figure 3. The two curves intersect at $\epsilon = 0.26$, but this is not in itself significant since it is simply the point where the calculated intrinsic barrier is equal in magnitude to the calculated ΔG° value. However, if the experimental value of ΔG° were actually zero for overall proton transfer to *p*-methylstyrene, this would give a value of $\lambda/4 = 2.04$ kcal (at $\epsilon = 0.28$), which is not an unreasonable value for such fast excited-state reactions.

As a check on the internal consistency of these calculations, the range of pK_{HA} values¹⁵ used in the Brønsted plots is 17.44 (i.e., from $pK_{H_2O} = 15.7$ to $pK_{H_3O^+} = -1.74$), and it should therefore be possible to calculate the range of ΔG° values using

(14) A referee has pointed out that the original Marcus equations (eq 1 and 2), on which eq 4 and 6 are based, were actually derived¹ as expressions containing hyperbolic functions rather than as 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 $|\Delta G^\circ|/\lambda \leq 1$. Calculation shows this to be the case for all the values of ϵ shown in Table III, and for all values of ϵ in Table II except where $\epsilon = 0.1$, which is probably an unrealistically high degree of asymmetry, even for photochemical reactions. In fact, most of the values of $|\Delta G^\circ|/\lambda$ in the present paper are ≤ 0.25 , so that the modified quadratic expressions should be applicable in the present case and yield the same Brønsted α values as the hyperbolic tangent expression given in ref 1.

(15) Meites, L. *Handbook of Analytical Chemistry*; McGraw-Hill: New York, 1963; pp 1–21. For the pK_{HA} of H_2O and H_3O^+ see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; pp 264, 280.

Scheme I



eq 5 and 6 from the limiting values of α at the high and low acidity ends. In Figure 4 are plotted values of $\alpha = \Delta \log k / \Delta pK_{HA}$ for each successive pair of catalysts, as a function of "pK_{HA}" for the midpoints of each pair of pK_{HA} values. This gives a reasonable straight line with limiting values of α of 0.08 (at pK_{HA} = -1.74) and 0.19 (at pK_{HA} = 15.7). For any value of ϵ one obtains a calculated value of $\Delta \Delta G^\circ = 23.0$ kcal which since

$$\Delta G^\circ_{1,2} = -RT \ln K_{1,2}$$

and

$$\Delta \Delta pK = \frac{1}{2.303RT} (\Delta G^\circ_2 - \Delta G^\circ_1)$$

gives

$$\Delta \Delta pK = 23.0 / 1.372 = 16.8$$

which is fairly close to the actual range of pK_{HA} values used for the experimental Brønsted plots over the range, pH 7 to H₀ (-2).

An estimate of the possible range of ΔG° for this type of reaction is needed in order to determine what range of ϵ values is appropriate for excited-state proton transfers and the types of $\lambda/4$ values these generate, and whether these are reasonable. Following Weller's¹⁶ original treatment of excited-state proton transfers, Scheme I can be written, where S₁ is the lowest singlet state of a typical substituted styrene.

This yields an expression for the fluorescence quantum yield of S₁ as a function of acidity, as follows:

$$\varphi/\varphi_0 = \frac{1 + k_{-1}\tau_0'}{1 + k_{-1}\tau_0' + k_1\tau_0[H_3O^+]} \quad (7)$$

where τ_0 is the lifetime of S₁ in neutral solution (where no S₁H⁺ is present) and τ_0' is the lifetime of S₁H⁺ in an acid solution where no S₁ is present. At the inflection point of fluorescence titration curves based on S₁ we have for [H₃O⁺] = [H₃O⁺]_{1/2}

$$\varphi/\varphi_0 = \frac{1}{2} \sum (\varphi_0 + \varphi_{im})$$

where φ_{im} is the limiting value observed in strongly acid solution. Since S₁ fluorescence is completely quenched in strong acid

$$\varphi/\varphi_0 = 1/2\varphi_0$$

Therefore from eq 7

$$\frac{1}{2} = \frac{1 + k_{-1}\tau_0'}{1 + k_{-1}\tau_0' + k_1\tau_0[H_3O^+]_{1/2}}$$

or

$$2 = 1 + \frac{k_1\tau_0[H_3O^+]_{1/2}}{1 + k_{-1}\tau_0'}$$

If $k_{-1}\tau_0' \ll 1$, which is probably the case since there is no observable fluorescence from S₁H⁺ at any acidity, then

$$1 = k_1\tau_0[H_3O^+]_{1/2}$$

and

$$[H_3O^+]_{1/2} = 1/k_1\tau_0$$

or

$$pH_{1/2} = \log k_1\tau_0 \quad (8)$$

Table III. Calculated "Intrinsic" Barriers for Probable Range of ΔG° Values

ΔG°	1		2		3	
	ϵ	$\lambda/4$	ϵ	$\lambda/4$	ϵ	$\lambda/4$
+4.1	0.24	1.5	0.265	1.95	0.19	0.8
0	0.28	2.0	0.3	2.5	0.24	1.3
-4.1	0.32	2.7	0.34	3.2	0.29	1.8

Therefore, what is being measured at the inflection point of the S₁ fluorescence quenching curve is $\log k_1\tau_0$, not $pK^*_{S_1H^+}$. For all compounds previously studied pH_{1/2} corresponds to an H₀ value of 0 to -2, which is reasonable in terms of eq 8 since for both substituted styrenes and phenylacetylenes τ_1 is in the 3-50-ns range and k_H values are in the $10^6 - 5 \times 10^7$ M⁻¹ s⁻¹ range.⁶

However, if it is assumed that the true $pK^*_{S_1H^+}$ value is several units more negative (i.e., S₁ is a weaker base) than indicated by the pH_{1/2} value, say $pK_{S_1H^+} = -4$, then from

$$K^*_{S_1H^+} = 10^4 = k_{-1}/k_1$$

and the average value of k_1 for these substrates of $\sim 10^7$ M⁻¹ s⁻¹, k_{-1} , the deprotonation rate, would have to be 10^{11} s⁻¹, which is too fast to be possible even if deprotonation were diffusion-controlled. This suggests the upper limit on $K_{S_1H^+}$ is 10^3 or $pK_{S_1H^+} = -3$.

On the other hand, if the estimate of $pK_{S_1H^+}$ based on fluorescence titration were smaller than indicated by the pH_{1/2} value (i.e., S₁ is a stronger base), this would place no limitation on the magnitude of k_{-1} . However, as shown by Weller¹⁶

$$pH_{1/2} = -\log K_{S_1H^+} + \log \tau_0/\tau_0' \quad (9)$$

All values of τ_0 measured for these substrates are in the $10^{-8} - 10^{-9}$ -s range. Although τ_0' (for S₁H⁺) cannot be measured experimentally, since rapid nucleophilic attack by H₂O to give product effectively quenches fluorescence, S₁H⁺ is a singlet state and under nonnucleophilic conditions must have an intrinsic lifetime in the 1-1000-ns range.¹⁷ If extreme examples are chosen ($\tau_0 = 1$ ns; $\tau_0' = 1000$ ns) eq 9 gives

$$pH_{1/2} = -\log K_{S_1H^+} + \log 1/1000 = pK_{S_1H^+} - 3$$

This strongly suggests that estimates of $pK_{S_1H^+}$ based on fluorescence titration of S₁ are not likely to be out by more than ± 3 units, or $pK_{S_1H^+} \approx 0 \pm 3$. Taking these limits, a reasonable range of ΔG° values can be calculated from which $\Delta G^\circ = 0 \pm 4.1$ kcal. From the curves in Figure 3 this gives $\epsilon = 0.24-0.32$ and $\lambda/4 = 1.5-2.7$ kcal for 1. Based on the data for all three substrates, as shown in Table III, these values are typical of this type of proton transfer.

From eq 4 it is now possible to make estimates of ΔG^\ddagger (excluding the unknown w^\ddagger term) for the possible range of ΔG° values. Because of the functional dependence of ΔG° and $\lambda/4$ on ϵ , as shown in Figure 3, each pair of values in Table III yields the same values for $(\Delta G^\ddagger - w^\ddagger)$ which are +2.04, 2.52, and 1.26 kcal for 1, 2, and 3, respectively. These values are quite reasonable for such fast proton transfers, assuming the w^\ddagger term is not large,¹ but only for processes in which an overall $\Delta G \lesssim 0$. It seems improbable that if ΔG° were as high as +4.1, the calculated value of ΔG^\ddagger would be sufficient to achieve reaction at the observed rates ($\sim 10^7$ M⁻¹ s⁻¹ in H₃O⁺ solutions), even if the w^\ddagger were comparable in magnitude to the values in Table III. For example, if $(\Delta G^\ddagger - w^\ddagger) = 2.04$ for 1, and $w^\ddagger \sim \Delta G^\ddagger_{\text{calcd}}$, then $\Delta G^\ddagger = 2.04 + w^\ddagger \approx 4.1$ which seems unlikely for a reaction with an overall ΔG° of similar magnitude.

The most reasonable combinations of ϵ , $\lambda/4$, and ΔG° which fit the observed or estimated magnitudes of k_H , $pK^*_{S_1H^+}$, α , and $d\alpha/d\Delta G^\circ$ are therefore $\epsilon \approx 0.3$, $\lambda/4 \approx 2-3$ kcal, and $\Delta G^\circ \sim 0-(-4)$ kcal. It thus appears that the Marcus equations can be modified empirically as in eq 4-6 to account for the observed behavior of these types of substrate in photoprotonation (or photohydration) reactions, and can perhaps be applied in a similar

(16) Weller, A. Z. *Elektrochem.* 1952, 56, 662.

(17) See ref 12, Chapter 1, p 7.

way to other primary photochemical processes.

An important question at this point is what is the physical significance of an eccentricity or asymmetry parameter of 0.3 or some similar magnitude. A partial answer to this question can be obtained from an examination of the simple parabolic expressions represented in Figure 2 and their relationship to the basic Marcus equations. The intersecting curves in Figure 2a (symmetrical case) were constructed from the general expression

$$E_{1,2} = n\epsilon'(x \pm a)^2 + b\epsilon$$

where n gives the parabolic curvature, ϵ and ϵ' are asymmetry parameters which have initially been set equal to unity in Figure 2a, $\pm a$ gives the locus of each parabola, and b is an adjustable parameter which gives the exo- or endothermicity of the overall process (only cases where $b \leq 0$ are shown, for simplicity).¹⁸ For the simplest case, where $b = 0$, $\epsilon = \epsilon' = 1$, we have

$$E_1 = n(x + a)^2$$

$$E_2 = n(x - a)^2$$

The minimum values of E_1 and E_2 occur at $x = \pm a$, i.e.

$$E_1 = 0 \text{ at } x = -a$$

$$E_2 = 0 \text{ at } x = +a$$

The intersection of the two curves occurs at ΔE_{int} , or at x_{int} where $E_1 = E_2$. In general x_{int} can be obtained from the equality

$$n(x + a)^2 = n(x - a)^2$$

or where $4ax = 0$, i.e., $x_{\text{int}} = 0$. Therefore, ΔE_{int} is given by $E_1 = E_2 = na^2$ at x_{int} . Since the minimum value of E_1 is 0 at $x = -a$, the quantity na^2 is analogous to the intrinsic barrier $\lambda/4$ in the unmodified Marcus equations 1–3. Also since the distance between the two minima is $2a$, the value of the Brønsted " α " corresponds to $\alpha = 0.5 + x_{\text{int}}/2a = 0.5$ at $x_{\text{int}} = 0$.

If the parameter b , which represents the overall ΔG° (i.e., $E_1^{\text{min}} - E_2^{\text{min}}$) for the process, is now included we have

$$E_1 = n(x + a)^2$$

$$E_2 = n(x - a)^2 + b$$

and the intersection of the two curves now occurs where $E_1 = E_2$ or where $4anx = b$. Thus from $x_{\text{int}} = b/4na$ the value of ΔE_{int} ($= E_1 - E_1^{\text{min}}$, which crudely represents the height of the "transition state" or ΔG^\ddagger) is found to be

$$\begin{aligned} \Delta E_{\text{int}} &= n(b/4na + a)^2 \\ &= na^2 + b/2 + b^2/16na^2 \end{aligned} \quad (10)$$

which, neglecting the w^2 term in this simple treatment, corresponds exactly to the form of the basic Marcus equation

$$\Delta G^\ddagger = \lambda/4 + \Delta G^\circ/2 + (\Delta G^\circ)^2/16(\lambda/4)$$

in other words, where ΔE_{int} corresponds to ΔG^\ddagger and b corresponds to ΔG° . Differentiating eq 10 with respect to b therefore gives equations analogous to the basic Marcus equations 2 and 3, i.e.

$$dE_{\text{int}}/db = 1/2 + b/8na^2 = \alpha \quad (11)$$

and

$$d\alpha/db = 1/8na^2 \quad (12)$$

If one of the asymmetry parameters is now included, for example, by setting $\epsilon \neq 1$ and leaving $\epsilon' = 1$, this leaves E_1 unchanged, and we have initially

$$E_1 = n(a + a)^2$$

$$E_2 = n(x - a)^2 + b\epsilon$$

For the isoenergetic case, where $b = 0$, $\Delta E_{\text{int}} = E_1 = E_2$ at $x = 0$ and ΔE_{int} remains at na^2 as before (or $\lambda/4$). Where $b \neq 0$ we have x_{int} where $E_1 = E_2$ which gives

$$x_{\text{int}} = b\epsilon/4na$$

Thus at x_{int} , $\Delta E_{\text{int}} = E_1 = n(x + a)^2 = \Delta E^\ddagger$ (or ΔG^\ddagger), or

$$\begin{aligned} \Delta E_{\text{int}} &= n(b/4na + a)^2 \\ &= na^2 + \epsilon b/2 + \epsilon^2 b^2/16na^2 \end{aligned} \quad (13)$$

which again corresponds to the basic Marcus equation, as modified in eq 4 by the inclusion of an eccentricity parameter ϵ . Also, by differentiation with respect to b we naturally obtain

$$dE_{\text{int}}/db = \epsilon/2 + \epsilon^2 b/8na^2 = \alpha \quad (14)$$

and

$$d\alpha/db = \epsilon^2/8na^2 \quad (15)$$

which correspond to eq 5 and 6.

In this way ϵ introduces a different effect on ΔE_{int} (or ΔG^\ddagger) of changing b (or ΔG°), but retains the intersection point ΔE_{int} or the intrinsic barrier at $\lambda/4$, and also introduces a different effect on α of changing b .

However, the inclusion of $\epsilon \neq 1$, does not change the parabolic curvature of E_2 , since both curves have the same value of n . Thus, although the form of both the original (eq 1–3) and modified (eq 4–6) Marcus equations can be developed from these crude parabolic expressions, the situation represented in Figure 2b, which led to the proposal that consideration of photochemical proton transfers such as $\text{H}^+ + \text{S}_1 \rightarrow \text{S}_1\text{H}^+$ should be based on potential surfaces of different steepness, is not satisfactorily represented by including ϵ in this way. This is merely an artificial way of changing the effect of b (or ΔG°) on ΔE_{int} (or ΔG^\ddagger). An alternative is to include $\epsilon' \neq 1$ instead of $\epsilon \neq 1$, which is the situation represented in Figure 2b, where the curves were constructed from parabolas of the form $n(x + a)^2$ and $m(x - a)^2 + b$.

Thus if $\epsilon' = m/n$ where $n > m$, ϵ' can be varied from $0 < \epsilon' \leq 1$ to reflect the shallowness of the excited-state potential surface (E_2) as shown in Figure 2b where m/n was arbitrarily set at 0.333. Thus

$$E_1 = n(x + a)^2$$

$$E_2 = m(x - a)^2 + b$$

Setting b initially = 0 (isoenergetic process), E_1^{min} is still at $-a$, and the distance¹⁹ between the two minima remains at $2a$. However, even for $b = 0$, the position of x_{int} is significantly changed since for $E_1 = E_2 = \Delta E_{\text{int}}$, we have

$$(n - m)x^2 + 2(n + m)ax + (n - m)a^2 = 0$$

which yields

$$\begin{aligned} x_{\text{int}} &= \frac{-a}{(n - m)}(\sqrt{n} - \sqrt{m})^2 \\ &= -a \left(\frac{1 - \sqrt{\epsilon'}}{1 + \sqrt{\epsilon'}} \right) \end{aligned}$$

so that x_{int} is shifted to left of $x = 0$, or α becomes less than 0.5, even for $b = 0$, as shown in Figure 2b. Substitution into the expression for E_1 gives

$$\Delta E_{\text{int}} = na^2 \left[1 - \frac{(\sqrt{n} - \sqrt{m})^2}{(n - m)} \right]^2 \quad (16)$$

$$\Delta E_{\text{int}} = na^2 \left[1 - \frac{(1 - \sqrt{\epsilon'})}{(1 + \sqrt{\epsilon'})} \right]^2 = na^2 \left(1 + \frac{x_{\text{int}}^2}{a^2} \right) \quad (17)$$

Although these expressions are somewhat intractable in terms of

(18) Koepl, G. W., and Kresge, A. J., (*J. Chem. Soc., Chem. Commun.*, 371 (1973)) have reported a similar study of an intersecting parabola model using estimated force constants for ground-state species. The terms n and m in the present paper are clearly proportional to the force constants for both ground- and excited-state species. Since the latter are much less well known, the present treatment has been kept very general.

(19) Koepl and Kresge¹⁸ have discussed the effect of varying the distance between the minima of the two potential wells, as the exo- or endothermicity of the reaction is changed. The effects of their proposal on intersecting parabolas of widely different curvature is currently under systematic investigation. In the present empirical treatment the distance between the two minima has been assumed to be constant for the sake of simplicity.

any simple mathematical correspondence to the Marcus equations,²⁰ it is clear that the intrinsic barrier is now significantly less than na^2 (or $\lambda/4$), since for any reasonable value of ϵ' , such as $1/3$ for example, the difference $(m - n)$ is such that the first and second terms in brackets in eq 16 will be much larger than the third term. Therefore, truncating this expression gives

$$\Delta E_{\text{int}} = na^2 \left[1 - \frac{2}{(n-m)} (\sqrt{n} - \sqrt{m})^2 \right]$$

and means that incorporation of asymmetry, as shown in Figure 2b, automatically lowers the intrinsic barrier to some fraction of the value it would have in a thermal reaction. As an illustration, where $m/n = \epsilon' = 1/3$, ΔE_{int} is reduced from na^2 to $0.536na^2$.

Although eq 16 and 17 cannot be as simply related to the original Marcus equations²⁰ as can the expressions 10–12, where $\epsilon \neq 1$, this method of introducing asymmetry is much more conceptually satisfactory. If the term b is now introduced, so that

$$E_1 = n(x+a)^2 \\ E_2 = m(x-a)^2 + b$$

where as before $\epsilon' = m/n$, the resulting expressions for x_{int} and ΔE_{int} become even more intractable than eq 16 and 17, in terms of relating them directly to the Marcus equations,²⁰ but the basic point still remains that they are theoretically more attractive for photochemical proton transfers. It is very interesting that if the Marcus equations 1–3 are modified in a form which corresponds more closely to the introduction of asymmetry via the ϵ' parameter, as in Figure 2b, the experimental values of α and $d\alpha/d\Delta G^\circ$ can be explained equally well as by using eq 4–6. For example, if we write

$$\Delta G^\ddagger = w^\ddagger + \epsilon'\lambda(1 + \Delta G^\circ/\lambda)^2/4 = \\ w^\ddagger + \epsilon'\lambda/4 + \epsilon'\Delta G^\circ/2 + \epsilon'(\Delta G^\circ)^2/4\lambda \quad (18)$$

$$d\Delta G^\ddagger/d\Delta G^\circ = \epsilon'/2 + \epsilon'\Delta G^\circ/2\lambda = \alpha \quad (19)$$

$$d\alpha/d\Delta G^\circ = \epsilon'/2\lambda \quad (20)$$

then the intrinsic barrier now becomes $\epsilon'\lambda/4$ as in eq 4, which is more in accord with the idea that the intersection of the two surfaces should be automatically reduced in a photochemical reaction compared with that in the analogous thermal process (see Figure 2a,b). However, for a $\Delta G^\circ = 0$ process, α remains at $\epsilon'/2$ in eq 19 as in eq 5, or less than 0.5 since $\epsilon' < 1$.

Also, taking any experimental values of α and of the curvature of the Brønsted plot, $C = d\alpha/d\Delta G^\circ$, we have from eq 19 and 20

$$C = \epsilon'/2\lambda \text{ or } \lambda = \epsilon'/2C$$

therefore the intrinsic barrier in this case will be

$$\epsilon'\lambda/4 = (\epsilon')^2/8C$$

which gives the same numerical result for any given ϵ' as does eq 6 for the same numerical value of ϵ where the intrinsic barrier is

$$\lambda/4 = \epsilon^2/8C$$

Similarly from eq 19

$$\Delta G^\circ = \frac{2\lambda}{\epsilon'}(\alpha - \epsilon'/2) \\ = \frac{1}{C}(\alpha - \epsilon'/2)$$

which for a given numerical value of ϵ' will give the same result as from eq 5 with $\epsilon = \epsilon'$, where

$$\Delta G^\circ = (2\lambda/\epsilon^2)(\alpha - \epsilon/2) \\ = (1/C)(\alpha - \epsilon/2)$$

Since eq 18–20 give the same numerical results as in Table II, with the only difference being that the listed $\lambda/4$ values now become $\epsilon'\lambda/4$ values for a given ϵ' , it seems preferable to adopt this approach in general. It is more in accord with the basic idea of asymmetrical intersections for photochemical proton transfers and lower intrinsic barriers. Also, since eq 4–6 can be directly related to the parabolic expressions in Figure 2a (as can the original Marcus equations 1–3), then the fact that eq 18–20 give the same results as eq 4–6 for any given value of ϵ' or ϵ suggests that these equations can also be related²⁰ to the parabolic expressions in Figure 2b.

However, there is still a problem with both of the present empirical modifications of the original Marcus expression, whether eq 4 or eq 18 is used, in that they do not meet the constraint that $(\Delta G^\ddagger - w^\ddagger)$ for the forward reaction minus a similar quantity for the reverse reaction should equal ΔG° .²¹ Although this constraint is met by the initial equations which lead to eq 17, it is not met by the proposed modification in eq 18. This is due to the non-cancellation of the quadratic terms in ΔG° . Fortunately, the numerical magnitude of the discrepancy involved is not large, provided the reactions are neither very endothermic nor very exothermic, as is likely to be the case for photochemical reactions, which either are or can be adiabatic, as is implicit in the present treatment. For example, for the range of endo- and exothermicities involved in Table III ($\Delta G^\circ = \pm 4.1$ kcal), the discrepancy in most cases would be less than 1 kcal. It is highly probable that any photochemical proton transfer more endothermic than this could not take place within the lifetime of the excited state in any event, and any proton transfer more exothermic than this probably would not occur adiabatically. Despite the apparent seriousness of this discrepancy, it is clear that use of the unmodified Marcus equations for photochemical proton transfers presents even more serious problems. The intent of the present paper was to arrive at reasonable estimates of ΔG° and $\lambda/4$ for these photoreactions (not necessarily precise values), and more importantly to illustrate the differences involved between them and their thermal analogues and demonstrate the need to introduce some form of asymmetry in the proton-transfer process. Work in progress to extend and improve the present exploratory approach will obviously need to meet the above constraint if it is to be more generally useful.

It is instructive at this point to construct approximate free-energy profiles for the thermal and photochemical acid-catalyzed hydrations of *p*-methylstyrene, and to compare the general characteristics of the two reactions, insofar as the proton-transfer step to form the intermediate carbocation is concerned. This is shown schematically in Figure 5 where Richard and Jencks¹³ estimate of pK_{S_0} has been used to obtain ΔG° for the ground-state process and the value of $\Delta G^\circ = -4$ kcal has been taken from the earlier discussion for the excited-state process. It is more difficult to assign individual ΔG^\ddagger values, but since the rate constants for H_3O^+ catalysis have been determined^{6,13} in each case, $\Delta\Delta G^\ddagger$ can be calculated to be 16 kcal ($k_{S_1}/k_{S_0} \approx 10^{12}$), and values of $\Delta G^\ddagger_{S_0} = 18^{22}$ and $\Delta G^\ddagger_{S_1} = 2$ kcal have been chosen. Values of the intrinsic barrier and α shown in Figure 5 are based on the unmodified Marcus equations 1 and 2 for the S_0 profile, and on eq 18 and 19 for the S_1 profile. For the slow thermal hydration, there is a high intrinsic barrier even through the proton transfer is a strongly uphill process, and a late transition state, with $\alpha \sim 0.7$ (which is in the range found experimentally⁹ for this type of reaction). For the very fast photochemical reaction, there is still a very low intrinsic barrier, even though it is a downhill process, and a very early transition state, with $\alpha \sim 0.15$. Although the expected curvature of a Brønsted plot for the thermal reaction would be somewhat higher in this case ($C = 0.014$ based on eq 3), then it is for the photochemical reaction ($C = 0.0048$), as is

(21) We are grateful to a referee for pointing this out.

(22) Noyce and Schiavelli²³ have estimated that the ground-state free-energy barrier for this type of reaction to be in the 20-kcal region.

(23) Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 120.

(20) Cannon, R. D. (*Electron Transfer Reactions*; Butterworths; London, 1980; pp 179–182), has derived a general analytical expression for the variation of ΔG^\ddagger as a function of ΔG° , for intersecting parabolas of different curvature, based on a study of electron-transfer reactions. The question of whether equations of the form of the original Marcus equations can be used to simulate the behavior of such analytical expressions, particularly with respect to their first and second derivatives, is currently being investigated systematically.

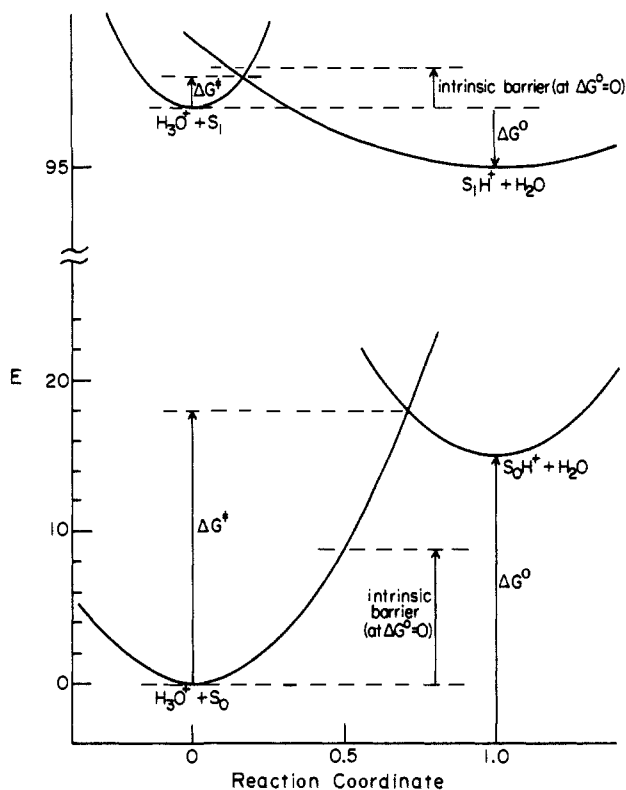


Figure 5. Schematic comparison of energy profiles for thermal (lower curve) and photochemical (upper curve) proton transfers to *p*-methylstyrene.

evident from Figure 5 by comparing the change in α as $\Delta G^\circ = 0$ is approached in each case, this will not be true in general. However, for thermal and photochemical processes of comparable rates and exothermicities, $d\Delta G^\ddagger/d\Delta G^\circ$ will always be smaller for the photochemical process,²⁰ using any reasonable value of ϵ or ϵ' . The general consequences of introducing asymmetry into the Marcus equations for photochemical proton transfers will therefore be lower intrinsic barriers, lower values of α or earlier transition states, and different curvature in Brønsted plots.

Conclusions

Although obviously much further investigation and testing with additional experimental data needs to be done, it is clear from

this exploratory investigation that the Marcus equations can profitably be applied to photochemical reactions, if they are modified empirically to include transition-state asymmetry via an eccentricity parameter ϵ or ϵ' . Therefore, it should be possible to use Marcus theory to interpret the rates of proton transfers involving excited states in a similar way²⁴ to the extensive applications of this theory to ground-state proton-transfer reactions.

For the types of photoprotonation involved in the photohydration reactions of styrenes and phenylacetylenes, only a value of the eccentricity parameter in the neighborhood 0.3 gives reasonable estimates of the "intrinsic" barrier and reasonable or probable ΔG° ranges for such reactions. For proton transfers to excited states, which actually have an overall ΔG° close to zero, typical values of the intrinsic barrier are calculated to be in the 1–3-kcal range.²⁵ From an examination of the parabolic energy curves represented in Figure 2a,b, and their relationship to the Marcus equations, it seems clear that the Brønsted α values in photochemical reactions should be significantly less than 0.5, even for isoenergetic proton transfers, and for downhill proton transfers should give very low values of this parameter. It may be that values of $\epsilon' \approx 0.3$ are typical of photochemical reactions in general, particularly those involving proton transfer in the primary step, but this conclusion is tentative and must await further experimental work. Finally, it will be very interesting to see whether these ideas can also be applied to base-catalyzed photochemical reactions. The first examples of general base catalysis in photochemical reactions were recently reported by Wubbels.²⁶ However, as yet no Brønsted relationships have been established for this type of reaction, and hence their extent of curvature is unknown. It is predicted that these reactions also will show different Brønsted curvature from that found for typical base-catalyzed thermal reactions, and that their overall Brønsted β values will be significantly *greater* than 0.5, if proton transfer is rate determining.

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(24) Because of the often wide range of rate constants and catalysts experimentally accessible in photochemical reactions, via Stern–Volmer plots, it may be easier to measure curvature in Brønsted plots over a wider range than in analogous thermal reactions. Therefore it should be easier in most cases to test Marcus theory by using photochemical proton-transfer reactions.

(25) However, any uncertainty in the numerical values obtained for the Brønsted curvature due to the use of nonuniform catalyst types¹⁰ would result in a corresponding uncertainty in the derived values of any Marcus-type parameters, such as the intrinsic barriers.

(26) Wubbels, G. G. *Acc. Chem. Res.* **1983**, *16*, 285. Wubbels, G. G.; Celandier, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7669.

The Ground-State Oxygen–Benzophenone Complex

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Abstract: In studies of the photoproduction of triplet excited benzophenone in cyclohexane by picosecond absorption spectroscopy (266-nm pump), it is shown that the presence of dissolved oxygen at 1 atm of pressure decreases the triplet–triplet 347-nm transition by 50% in less than 25 ps, indicating the presence of a stable ground-state oxygen–benzophenone complex. This work suggests that there may be a need to reevaluate any triplet risetime and quantum yield experiments performed on aromatic/carbonyl compounds in nondeoxygenated solutions.

When a solution to be used in a spectroscopic experiment is prepared in the presence of air, it often contains enough dissolved oxygen to affect the photophysics of the solute under investigation. In such cases one is concerned with molecular reactions which

usually involve the production of transient species that are extremely sensitive to the presence of such dissolved oxygen. For example, if one were to generate by flash photolysis a population of triplet molecules in solution, the high mobility of molecular