for k_- of 10^{10}–1.3×10^{12} s^{-1}, neglecting the pK difference of 0.3 units between phenol and 2-mercaptoethanol. The small sensitivity of k_- to changes in polar effects of substituents suggests that this range is not very different for the pyrazole adduct T$^-$.

(3) Brønsted Plots. Brønsted plots were calculated by using the equations below; the mechanisms and rate constants are defined in eq 2.

(A) For diffusion-controlled trapping (upper path, eq 2), the third-order rate constants, k_B, were obtained from

$$k_B = \frac{K_1 k_2 k_p k_5}{k_p k_5 + k_{-2} k_5 + k_{-2} k_{-p}}$$

using $k_p = 10^{(10 \pm 0.5 \Delta pK_a)}$, in which ΔpK_a refers to the difference between the pK_a values of the catalyst and intermediate.[12]

(B) For preassociation mechanisms with hydrogen bonding (lower path, eq 2), k_B is calculated from

$$k_B = \frac{k_B{}^{DC}(k_{-2} + k_{-4}(10^{\beta(1.74 + pK_{cat})}))k_p k_5 / k_{-2}}{k_5 k_p + (k_{-2} + k_{-4}(10^{\beta(1.74 + pK_{cat})}))(k_5 + k_p)}$$

in which $k_B{}^{DC}$ is the maximal catalytic rate constant calculated for the diffusion-controlled trapping mechanism, when proton transfer between the catalyst and intermediate is thermodynamically favorable, β is the Brønsted slope for hydrogen bonding by basic catalysts, and pK_{cat} is the pK_a of the catalyst.[2]

Registry No. PhOAc, 122-79-2; D^2, 7782-39-0; AcOC$_6$H$_4$-*m*-NO$_2$, 1523-06-4; AcOC$_6$H$_4$-*p*-NO$_2$, 830-03-5; pyrazole, 288-13-1; 4-bromoimidazole, 2302-25-2.

Photohydration of Styrenes and Phenylacetylenes. General Acid Catalysis and Brønsted Relationships

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Abstract: The acid-catalyzed photohydrations of a series of substituted styrenes and phenylacetylenes have been investigated in aqueous buffer solutions. General acid catalysis was clearly detected in five cases with a range of catalysts, and approximately linear Brønsted plots gave α values in the range 0.14–0.18. The rate enhancements caused by excitation from S$_0$ to S$_1$ were estimated from comparisons with thermal hydration data to be in the 10^{11}–10^{15} range. Treatment of the dependence of the rate constants for general acid catalysis (k_{HA}) on the buffer pK_{HA} values with multiple regression analysis suggests that the Brønsted plots are smoothly curved, as predicted by Eigen and by the Marcus equation. However, reliable values of the Brønsted curvature could not be established. The possible catalytic reactivity of analogous triplet states was examined with a series of nitrosubstituted analogues, but no general acid catalysis could be detected. The factors controlling the detection of general acid catalysis in these photoreactions are discussed.

The thermal acid-catalyzed hydrations of styrenes[1] and phenylacetylenes[2] have been studied extensively, and these slow ground-state reactions ($k_{H^+} \sim 10^{-5}$–10^{-7} M^{-1} s^{-1}) have also been shown to be subject to general acid catalysis in a number of cases.[3] Reported values of the Brønsted α exponent are typically in the 0.5–0.85 range. Although the photochemistry of alkenes[4] has been a topic of continuing interest to photochemists, photohydrations in aqueous solution[5] have been much less extensively studied, and this is also the case for the analogous reactions of phenylacetylenes. Previous investigations[5,6] have shown that these reactions are catalyzed by H$_3$O$^+$, and where electron-releasing groups are present in the ring, both styrenes and phenylacetylenes react via their lowest singlet excited states, and the reactions are regiospecific in the Markovnikov direction. Values of the rate constant (k_{H^+}) for proton transfer from H$_3$O$^+$ to S$_1$ show these to be very fast reactions, especially for those involving protonation on carbon. Typical values of k_{H^+} are in the 10^6–10^7 M^{-1} s^{-1} range,[5,6] as determined independently from the pH (or Ho) dependence of fluorescence quenching, fluorescence lifetime, and quantum yield for product formation. The mechanism proposed for these photohydrations, namely rate-determining protonation of S$_1$, followed by rapid attack of H$_2$O on the intermediate carbocation (whether either step is adiabatic or not),[7] is supported by kinetic solvent isotope effects ($k_H/k_D \sim 1.3$–1.8) and the complementary sigmoidal variations of the quantum yields for fluorescence (Φ_F) and product formation (Φ_p).[5,6]

Since Φ_p values do not approach zero at pH 7, the reactions are evidently subject to water catalysis, and this in turn raised the interesting possibility that they might also be subject to detectable general acid catalysis, as are the ground-state analogues. Buffer catalysis was in fact observed for two substituted styrenes in a preliminary study,[6] and plots of the log k_{HA} vs. pK_{HA} for a

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[1] Schubert, W. M.; Keeffe, J. R. *J. Am. Chem. Soc.* **1972**, 94, 559. Koshy, K. M.; Roy, D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1979**, *101*, 357. Nowlan, V.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252. Simandoux, J. C.; Torck, B.; Hellin, M.; Coussemant, F. *Bull. Soc. Chem. Fr.* **1972**, 4402.

[2] Noyce, P. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 1020, 1023. Bott, R. W.; Eaborn, C.; Walton, D. R. M. *J. Chem. Soc.* **1965**, 384. Noyce, D. S.; De Bruin, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 372. Noyce, D. S.; Matesich, M. A.; Schiavelli, M. D.; Peterson, P. E. *J. Am. Chem. Soc.* **1965**, *87*, 2295.

[3] (a) Simandoux, J. C.; Torck, B.; Hellin, M.; Coussemant, F. *Bull. Soc. Chim. Fr.* **1972**, 4410. (b) Chiang, Y.; Chwang, W. K.; Kresge, A. J.; Robinson, L. H.; Sagatys, D. S.; Young, C. I. *Can. J. Chem.* **1978**, *56*, 456. (c) Gold, V.; Kessick, M. A. *J. Chem. Soc.* **1965**, 6718. (d) Salomaa, P.; Kankaanpera, A.; La Junen, M. *Acta Chem. Scand.* **1966**, *20*, 1790. (e) Schubert, W. M.; Jensen, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 566. (f) Stamhuis, E. J.; Drenth, W. *Recl. Trav. Chim. Pays Bas* **1961**, *80*, 797.

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[5] Wan, P.; Culshaw, S. C.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509. Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157.

[6] Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 869.

[7] Although it is inherently unlikely that the attack of water on the intermediate carbocation takes place on the excited state surface, it has recently been shown that carbocations of the type involved here can be generated adiabatically[8] in aqueous solution, so that the proton-transfer step may be adiabatic.

[8] Wan, P.; Yates, K.; Boyd, M. K. *J. Org. Chem.* **1985**, *50*, 2881.

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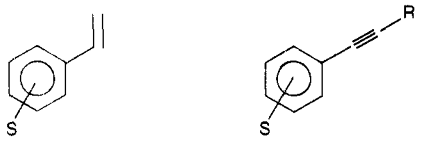
series of acids HA showed these obey the Brønsted relationship[9] approximately, with α values of ~0.15 in each case. These are believed to be the first reported examples of general acid catalysis in a net photochemical transformation,[10] although photochemical general base catalysis has recently been observed by Wubbels and Celander.[12]

It was therefore of interest to investigate general acid catalysis in these reactions more systematically, and particularly to compare them with the reactions of corresponding phenylacetylenes. The subject of acid–base catalysis in photochemistry has recently been reviewed,[13] and it is clear that in this field general catalysis and Brønsted relationships are quite rare, although there is no reason in principle why the Brønsted catalysis law should not be profitably applied to mechanistic investigations in photochemistry, as it has been for ground-state reactions.[9] Brønsted α values and the curvature of Brønsted plots are also of interest in terms of the possible application of Marcus theory[14] to photochemical reactions.

Results and Discussion

General Acid Catalysis and Photoprotonation Rate Constants. The substrates selected for study (**1–12**) were either available commercially or synthesized via dehydration of the corresponding 1-arylethanols (styrenes) or via chlorination of the appropriate acetophenone, followed by dehydrohalogenation with potassium *tert*-butoxide in DMSO (phenylacetylenes).



1: S = H
2: S = *m*-F
3: S = *p*-F
4: S = *p*-CH$_3$
5: S = *p*-OCH$_3$
6: S = 3,4-(C$_4$H$_4$)

7: S = H; R = H
8: S = *p*-CH$_3$; R = H
9: S = *p*-OCH$_3$; R = H
10: S = 2,3-(C$_4$H$_4$); R = H
11: S = 3,4-(C$_4$H$_4$); R = H
12: S = H; R = Ph

With one exception, phosphoric and phosphonic acid derivatives were used as general acid catalysts. These are particularly suitable, since it is essential that the buffer species do not react directly with the substrates during the photohydration reaction and equally importantly that they do not absorb significant radiation in the 254- or 300-nm regions, where the photochemical reactions are run. Since fairly high buffer concentrations are needed (0.1–1.0 M range) this restricts the choice of buffers severely, so that use of a completely uniform[15] set of general acids is out of the question. The buffer pairs used were as follows (with the first named species acting as the general acid catalyst): H_3PO_4–NaH_2PO_4; NaH_2PO_4–Na_2HPO_4; $Na(CH_3)HPO_4$–$Na_2(CH_3)PO_3$; $Na(Cl_2CH)HPO_3$–$Na_2(Cl_2CH)PO_3$; $Na(Cl_3C)HPO_3$–$Na_2(Cl_3C)PO_3$; H_3BO_3–NaH_2BO_3.[16] Total salt concentration was kept constant by the addition of NaCl, although no significant salt effects could be observed as [NaCl] was varied from 0.1 to 1.0 M.

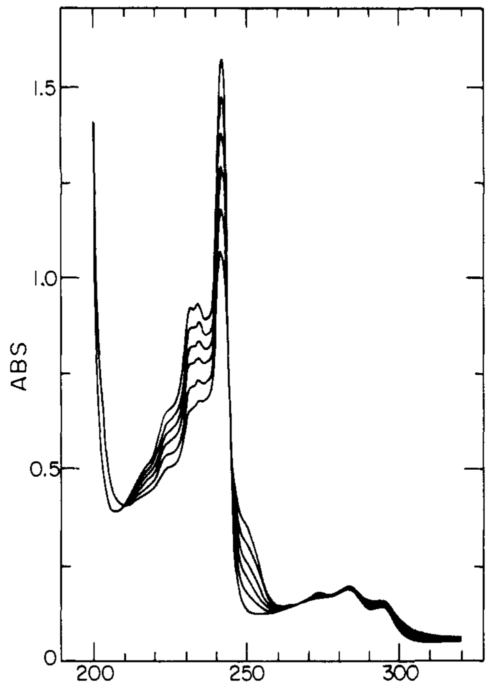
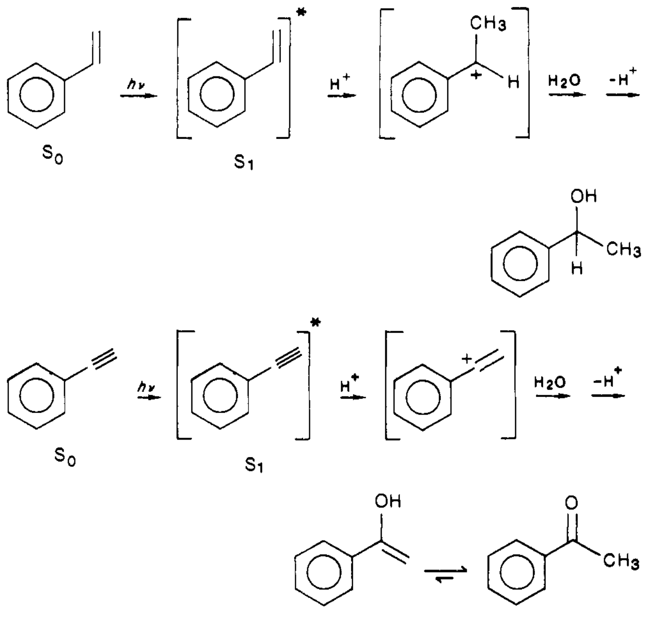


Figure 1. Variation of UV absorption at **11** as a function of (300 nm) irradiation time at pH 2 in aqueous HCl/NaCl solution. (Spectra taken at 10-min intervals from t = 0.)

The reactions were monitored by following the overall change in UV spectrum as the alkene or alkyne is converted into the corresponding 1-arylethanol or acetophenone.[5] An example is shown in Figure 1. In all cases, sharp isosbestic points were observed, showing that the reactions involve simple interconversions of the reactants into the expected hydration products, produced by Markovnikov addition of water across the multiple bond, as observed previously.[5,6]



The relative quantum yield Φ/Φ_0 were obtained by measuring the change in UV spectrum at the appropriate wavelength (for either reactant disappearance or product appearance), where Φ_0 is the quantum yield at the appropriate pH (as determined by the particular buffer pair being used) in the absence of any added general acid. Typical plots of the variation of Φ/Φ_0 with general acid concentration [HA] (at fixed buffer ratio [HA]/[A$^-$]) are shown in Figure 2. The points at zero [HA] were obtained in each case by adjusting the pH of the solution to that of the specific buffer being used by means of added HCl and NaCl the same

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[9] For up-to-date discussions of the Brønsted relationship, see for example: (a) Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic Press: New York, 1985; pp 269–281. (b) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: Oxford, 1985; pp 415–442. (c) Lewis, Hu *J. Am. Chem. Soc.* **1984**, *106*, 3295. Lewis, *J. Phys. Chem.* **1986**, *90*, 3756. Kreevoy, Lee *J. Am. Chem. Soc.* **1984**, *106*, 2550.

[10] However, the Brønsted relationship had previously been shown[11] to be applicable to the rates of quenching of phenol fluorescence by bases in the reversible excited state ionization reaction.

[11] Avigal, I.; Feitelson, J.; Ottolenghi, M. *J. Chem. Phys.* **1969**, *50*, 2614.

[12] Wubbels, G.; Celander, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7669.

[13] Wubbels, G. *Acc. Chem. Res.* **1983**, *16*, 285.

[14] (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891; *J. Am. Chem. Soc.* **1969**, *91*, 7224. (b) For reviews of Marcus theory see: Kresge, A. J. *J. Chem. Soc. Rev.* **1973**, *2*, 475. More O'Ferrall, R. A. In *Proton Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Chapman and Hall: London, 1975. Praso, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69.

[15] See for example the discussion of general catalyst structure in ref 9a, pp 271–274.

[16] Although there is some doubt as to wheter H_3BO_3 functions as a simple Brønsted acid or not, the points obtained with this catalyst fell exactly on a smooth curve defined by the other catalyst points. Therefore retention of H_3BO_3 does not affect any conclusions drawn.

Table I. Rate Constants for General Acid Catalyzed Photohydrations

		k_{HA} (M^{-1} s^{-1})				
catalyst	pK_{HA}	**2**	**4**	**6**	**10**	**11**
H_2O^a	15.7	6.3×10^4	1.5×10^5	6.8×10^3	8.6×10^4	1.0×10^5
$H_3BO_3{}^b$	9.23	1.0×10^6	2.0×10^6		2.0×10^6	5.1×10^6
$(CH_3)HPO_3{}^{-b}$	8.00				2.9×10^6	1.0×10^7
$H_2PO_4{}^{-b}$	7.19	1.8×10^6	3.9×10^6	8.4×10^5	5.0×10^6	1.6×10^7
$(Cl_2CH)HPO_3{}^{-b}$	5.60			2.1×10^6	7.5×10^6	5.1×10^7
$(Cl_3C)HPO_3{}^{-b}$	4.93			4.8×10^6	1.2×10^7	5.75×10^7
$H_3PO_4{}^b$	2.15	1.2×10^7	1.6×10^7	5.25×10^6	3.0×10^7	5.4×10^7
H_3O^{+c}	-1.74	3.4×10^7	3.6×10^7	4.9×10^6	4.6×10^7	1.5×10^7

[a] Rate constants calculated from $k_{H_2O} = \Phi_{pH7}/\tau_{pH7}[H_2O]$. Probable error ± 10%. [b] Rate constants obtained from slopes of Φ/Φ_0 vs. [HA] plots. Probable error ±5%. [c] Rate constants taken from ref 5 and 6.

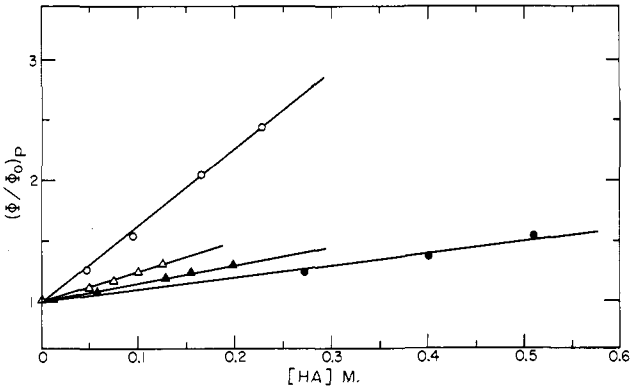


Figure 2. Plots of $(\Phi/\Phi_0)_p$ vs. general acid concentration (HA) for photohydration of **10**. HA = (open circles) H_3PO_4, (open triangles) $CH_3PO_3H^-$, (solid triangles) $CHCl_2PO_3H^-$, and (solid circles) $H_2PO_4^-$.

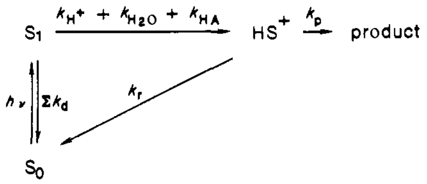
total ionic strength as that of the buffer solutions.

Since in all cases the pH of the buffer solutions used was >2.0, the contribution to Φ from H_3O^+ catalysis is negligible[17] in comparison with that from H_2O and HA. Evidence for this is that previously studied variations of Φ_p (absolute quantum yield) with pH in aqueous sulfuric acid solutions (in the absence of added general acids) have shown[5] that in the pH 7–1 region the reaction is dominated by water catalysis. This is manifested by a flat region in the Φ_p vs. pH profile, where Φ_p remains constant within experimental error. The H_3O^+ catalyzed process is manifested by a sharp increase in Φ_p at acidities greater (more negative) than pH (or Ho) = 0.

Values of the rate constants[18] (k_{HA}) for general acid catalysis were obtained from the data as follows. The previously proposed mechanistic scheme for photohydration of both alkenes and alkynes can be extended to take into account catalysis by H_3O^+, H_2O, and any general acid HA and is shown in Scheme I. Assuming a steady state for HS^+, Φ_p is given by eq 1, where k_{HA} is the photoprotonation rate constant due to any general acid HA, and $\sum k_d$ is the sum of all unimolecular deactivational processes.[19]

$$\Phi_p = \left(\frac{k_p}{k_p + k_r}\right)\left(\frac{k_{H^+}[H^+] + k_{H_2O}[H_2O] + k_{HA}[HA]}{\sum k_d + k_{H^+}[H^+] + k_{H_2O}[H_2O] + k_{HA}[HA]}\right) \tag{1}$$

Scheme I



It has been found that in the ground-state hydration of alkenes,[1] the rate of nucleophilic attack by water on the intermediate carbonium ion is much more rapid than its rate of return to substrate via proton loss. Thus if HS^+ in Scheme I is a ground-state species, $k_p \gg k_r$. However, we have no direct way[21] of determining the exact nature of the intermediate HS^+ in the photohydration reaction, other than to assume that its reactivity is at least equal to (and more likely greater than) that of a ground-state carbonium ion. Therefore we make the reasonable assumption that in eq 1, $k_p \gg k_r$. In the dilute acid region (pH > 2) where all general acid catalysis experiments were carried out, $(k_{H_2O}[H_2O] + k_{HA}[HA]) \gg k_{H^+}[H^+]$.[21] Therefore eq 1 simplifies to eq 2 (assuming only one general acid HA is effective in a given series of experiments).

$$\Phi_p = \frac{k_{H_2O}[H_2O] + k_{HA}[HA]}{\sum k_d + k_{H_2O}[H_2O] + k_{HA}[HA]} \tag{2}$$

It can easily be shown that $(\Phi/\Phi_0)_p$, where Φ_0 is the quantum yield in the absence of HA,[22] is given by eq 3.

$$(\Phi/\Phi_0)_p = \left(1 + \frac{k_{HA}[HA]}{k_{H_2O}[H_2O]}\right)\left(\frac{\sum k_d + k_{H_2O}[H_2O]}{\sum k_d + k_{H_2O}[H_2O] + k_{HA}[HA]}\right) \tag{3}$$

Since under the experimental conditions used $(\Sigma k_d + k_{H_2O}[H_2O]) \gg k_{HA}[HA]$,[23] eq 3 simplifies to eq 4.

$$(\Phi/\Phi_0)_p \cong 1 + \frac{k_{HA}[HA]}{k_{H_2O}[H_2O]} \tag{4}$$

We have already seen that plots of Φ/Φ_0 vs. [HA] are linear (Figure 2). Values of k_{H_2O} can be obtained from eq 2 by setting [HA] = 0 which yields eq 5.

$$k_{H_2O} = \Phi_{pH7}/\tau_{pH7}[H_2O] \tag{5}$$

Absolute values of the quantum yield Φ and singlet state lifetime

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(17) The validity of this assumption was later checked by using the values obtained for k_{H_2O} and k_{HA} and previously determined[5,6] values of k_{H^+}. Even in the most favorable cases for H_3O^+ catalysis, namely where the buffer pH is lowest, contribution of H_3O^+ catalysis to the total reaction rate (and hence Φ/Φ_0) is ≤5%.

(18) These rate constants could probably also have been obtained, for some substrates, from variations in either Φ_F or τ_F as a function of [HA], similarly to previous[5,6] determinations of k_{H^+}. However, it was felt that for correlations of log k_{HA} vs. K_{HA}, it was preferable to use one method consistently for all compounds. The present method has the advantage that it is easier experimentally, and certainly more rapid.

(19) The rate of intersystem crossing (k_{ST}) to T_1 has been included in $\sum k_d$ since it has been shown[5] that triplet sensitization of these substrates does not lead to photohydration. Although k_{ST} is usually assumed to be negligible for hydrocarbons of this type, a recent report[20] suggests that this may not always be the case.

(20) Bonneau, R. *J. Am. Chem. Soc.* **1982**, *104*, 1921.

(21) Work in progress on deuterium incorporation in unreacted starting material shows that k_p must be at least 50 times greater than k_r for styrene and phenylacetylene. (Yates, K.; Boyd, M. K., unpublished results.)

(22) This reference value (Φ_0) was determined in each case at the pH of the particular buffer pair being used.

(23) Maximum [HA] used in these experiments was 1.0 M, and usually lower concentrations were employed. Since $\sum k_d + k_{H_2O}[H_2O] \sim 10^8–10^9$ s^{-1} from lifetime measurements, calculations with observed quantum yields with and without added buffer in the dilute acid region (pH 7–2) show that $(\sum k_d + k_{H_2O}[H_23])/k_{HA}[HA] - 10^1–10^2$.

Table II. Factors Determining Observation of General Acid Catalysis in Photohydration Reactions

	k_{H^+}[a] (M^{-1} s^{-1})	τ_{pH7}[b] (ns)	Φ_{pH7}[c]	$k_{HA}[HA]\tau_{pH7}$[d] Φ_{pH7}	general catalysis detectable	Brønsted plot obtainable
1	2.3×10^6	7.5	0.025	0.02	no	no
2	3.4×10^7	4.3	0.015	0.24	yes	yes
3	8.2×10^5	4.9	0.008	0.01	no	no
4	3.6×10^7	4.5	0.037	0.11	yes	yes
5	$\sim 7 \times 10^7$	~ 1	0.036	~ 0.05	yes	no
6	4.9×10^6	58.2	0.022	0.32	yes	yes
7	1.2×10^7	4.5	0.063	0.02	no	no
8			0.24	<0.05?	no	no
9				$\sim$0.05?	yes	no
10	4.6×10^7	10.0	0.05	0.23	yes	yes
11	1.5×10^7	49.5	0.28	0.07	yes	yes
12		~ 1		<0.05?	no	no

[a] Values taken from ref 5, 6, and 33 or measured from Stern–Volmer plots of Φ/Φ_0 vs. log [H^+] at zero buffer concentration. [b] Values taken from ref 5, 6, and 33. [c] Values taken from ref 5, 6, and 33. [d] Calculated assuming $(k_{HA})_{max} \sim k_{H^+}/4$, and with [HA] = 0.1 M.

τ, both at pH 7 (in the absence of any general acid), were obtained by MGL actinometry[24] and single-photon counting,[25] respectively, and [H_2O] was set equal to 55.5 M. When these values of k_{H_2O} are used, the individual photoprotonation rate constants k_{HA} can be calculated from eq 4 and the slopes of the linear plots of Φ/Φ_0 vs. [HA]. These values are listed in Table I, along with the appropriate k_{HA} values for each catalyst.

It will be noted from Table I that rate constants k_{HA} are only tabulated for five of the twelve substrates studied, namely for compounds **2**, **4**, **6**, **10**, and **11**. The reason for this is that general acid catalysis could not be cleanly detected above the background of H_2O catalysis for several substrates (**1**, **3**, **7**, **8**, and **12**), since Φ did not vary significantly with [HA] for these compounds. For compounds **5** and **9**, general acid catalysis could be detected, but only with the strongest general acid used, i.e., H_3PO_4, and even in these cases the rate constants k_{HA} were not considered as numerically reliable as the ones listed in Table I since the observed variations in Φ/Φ_0 were fairly small.

The reason why the photoprotonation reaction of such closely related substrates showed such variable sensitivity to general acid catalysis was at first puzzling, since there was no obvious reason why the ratio k_{HA}/k_{H_2O} should be so variable. Examination of the individual terms in eq 4 provided an explanation. Substitution of eq 5 into eq 4 yields eq 6. In order to detect catalysis by any general acid HA, the ratio on the right of eq 6 must be significant

$$\Phi/\Phi_0 = 1 + \frac{k_{HA}[HA]\tau_{pH7}}{\Phi_{pH7}} \qquad (6)$$

with respect to unity, otherwise the observable variation in Φ/Φ_0 will be too small to enable the effect of HA to be observed above the background of the water-catalyzed reaction. It is assumed that less than 5% overall variation in Φ/Φ_0 would not be sufficient to give reliable k_{HA} values. Since numerical values of k_{HA} are obviously not available for all substrates (**1–12**), it is assumed that k_{HA} (even for the best general acid used) will in general be no larger than $k_{H^+}/4$ (see later in the discussion of Brønsted α values), where k_{H^+} is the measured rate constant for hydronium ion catalysis. Values of k_{H^+} either were already available[5,6] or were determined in the present study, for most substrates. Values of Φ_{pH7} and τ_{pH7} were also either available[5,6] or determined for most substrates, so that the quantity $k_{HA}[HA]\tau_{pH7}/\Phi_{pH7}$ could be estimated for each substrate, using a value of [HA] = 0.1 M. The relevant data are listed in Table II, from which it can be seen that unless the calculated value of the above ratio is >0.05 it is not likely that general acid catalysis will be easy to detect (from the variation of Φ Φ_0) at this buffer concentration, as was found to be the case for several substrates, and even at higher buffer concentrations it will only be easily detectable for the strongest general acid used (i.e., H_3PO_4). For the five substrates for which catalysis could be measured with a range of buffers, the value of this ratio was found to be between 0.07 and 0.42, at [HA] = 0.1 M, so that values of k_{HA} obtained from slopes of Φ/Φ_0 vs. [HA] should be reliable for buffer concentrations where [HA] > 0.1 M since in all cases the value of $k_{HA}[HA]\tau_{pH7}/\Phi_{pH7}$ will be well above the 0.05 threshold.

Another important factor which governs the ability to detect general acid catalysis experimentally in *either* a photochemical or a thermal reaction of this type, and which is *completely independent* of the relative magnitudes of the rate constants for hydronium ion catalysis for a given substrate, is described in the Appendix.

Photochemical vs. Thermal Reactivity Comparisons. It can be seen from Table I that values of k_{HA} are typically in the 10^6–10^7 M^{-1} s^{-1} range, although the values derived for H_2O acting as a general acid are at least an order of magnitude lower than this. It would be very interesting to compare these rate constants with those for the analogous thermal hydrations, but it is very difficult to do this directly. The reason for this is that general acid catalysis is very hard to detect in thermal hydrations (see Appendix), unless highly activated substrates are used. This is due to competition by hydronium ion catalysis, which swamps any general catalysis for most substrates in the acidity region necessary to follow these slow hydrations, which have Brønsted α values ≥0.5 (see Appendix). In fact general acid catalysis has only been clearly established to date for the thermal hydrations of twelve alkenes and two acetylenes,[3] and of these, the only compound in common with those in the present study is *p*-methylstyrene, which was studied by an indirect method by Jencks and Richard.[26] With use of their value of 1.3×10^{-5} M^{-1} s^{-1} for k_{H^+} (at 22 °C) and their calculated value of α (0.86), values of k°_{HA} for the thermal hydration can be estimated for the general acid catalysis used in the present study. For example, for H_3PO_4 with $pK_{HA} = 2.15$, a value of k_{HA} of 5.9×10^{-9} M^{-1} s^{-1} is obtained. Compared with the photochemical value (k^*_{HA}) from Table I, this gives a ratio of $k_{HA}{}^*/k_{HA}{}^{\circ} \sim 3 \times 10^{15}$. An alternative, perhaps more direct comparison can be made with use of Schubert and Jensen's[3] k_{HA} values for the thermal hydration of *p*-amino- and *p*-(dimethylamino)styrene, which were measured directly. The value of ρ for the thermal hydration of styrenes is known,[1] as are the Brønsted α values for these two styrenes (0.74 and 0.78, respectively).[3] By using a reported value of $\rho = -3.6$ and known[27] σ^+ values for *p*-Me, *p*-NH_2, and *p*-NMe_2, it can be calculated that the thermal hydration of *p*-methylstyrene would have a $k_{H_3PO_4}$ value of 1.3–1.6 $\times 10^{-4}$ M^{-1} s^{-1} at 80 °C. Compared with the value of Table I, this gives a ratio of $k^*_{HA}/k^{\circ}_{HA} \sim 1 \times 10^{11}$. However, since Schubert and Jensen's thermal rate constants were determined at 80 °C,[3] this value is probably a lower limit. Therefore it can be estimated that with H_3PO_4 acting as a general acid, the photochemical reaction of *p*-methylstyrene is between 10^{11} and 10^{15} times as fast as its thermal analogue. The magnitude of this ratio will naturally vary with the structure of the substrate, as well as with the strength of the general acid catalyst, but as will be seen later in the discussion of Brønsted α values, the above estimate of k^*_{HA}/k°_{HA} is probably much too conservative. It is interesting that the previously estimated ratio of photochemical to thermal hydration rate constants, based on directly observed H_3O^+ catalysis in both cases, was in the 10^{11}–10^{14} range.[5] These extremely large rate enhancements on excitation from S_0 to S_1 have been attributed[28] to a high degree of polarization in S_1, which makes protonation of the alkene (and presumably acetylene) group facile even in neutral aqueous solution.

It can also be seen from the values of k_{HA} in Table I that the rate of photochemical proton transfer from HA to phenylacetylenes

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(24) Fischer, G. J.; LeBlanc, J. C.; Johns, H. E. *Photochem. Photobiol.* **1967**, *6*, 757.

(25) Ware, W. R. In *Creation and Detection of the Excited State*; Lamola, A. A., Ed.; Marcel Dekker: New York, 1971; Vol. 1, Part A, p 264.

(26) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373.

(27) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 203.

(28) Kropp, P. *J. Am. Chem. Soc.* **1973**, *95*, 4611. Hixson, S. S. *Tetrahedron Lett.* **1973**, 277.

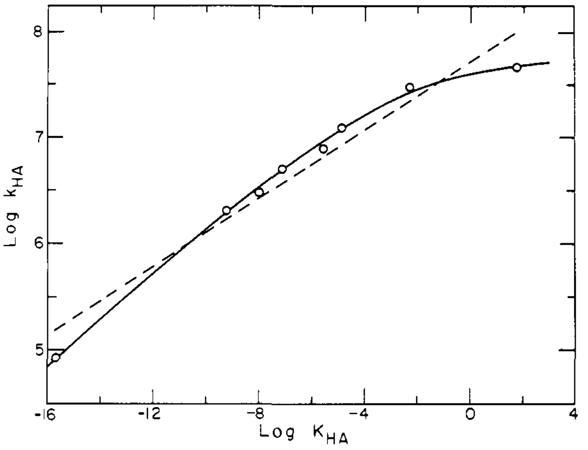

Figure 3. Brønsted plot of log k_{HA} vs. log K_{HA} for **10**. (Dashed lined based on least-squares fit. Solid curves obtained by multiple regression analysis, using a cubic expression.)

is faster than that to styrenes. The most direct comparison can be made between the structurally related 2-vinylnaphthalene (**6**) and β-naphthylacetylene (**11**) where the ratio of k_{HA}(alkyne)/k_{HA}(alkene) varies between 10.0 (H_3PO_4) and 24.3 ($CH_3HPO_3^-$).

A similar observation was made previously for the H_3O^+ catalyzed rates for phenylacetylenes and styrenes[5,6] although the rate ratio k_{H^+}(alkene)/k_{H^+}(alkyne) was somewhat smaller. Why the singlet excited states of phenylacetylenes should be more reactive than those of styrenes is not clear, since in the ground state both react at very similar rates.[29] One possibility is that the actylene group in S_1 is trans-bent as in acetylene itself,[30] which would facilitate proton transfer, since less structural reorganization would be involved in the rate-determining step. This is one factor which makes rates of proton transfer to carbon normally much slower than those to oxygen or nitrogen in ground-state reactions.[31] This argument would imply that excited states of styrenes are protonated in an S_1 configuration in which the ethylene moiety is planar (or nearly so), unlike the lowest singlet state of ethylene itself.[32] This is probably the case, since absorption and emission spectra of styrenes bear a near mirror-image relationship to each other,[5,33] with no pronounced Stokes shift, implying a near Franck–Condon and planar reactive excited state. This behavior is not shown to the same extent by the absorption and emission spectra of corresponding phenylacetylenes,[33] which may relax to trans-bent forms before either fluorescence or proton transfer take place.

Brønsted Relationships. Many general acid (or base) catalyzed ground state reactions are found to obey the Brønsted catalysis law,[9] as expressed in eq 7 and 8, where k_{HA} are the individual

$$k_{HA} = G_A K_{HA} \tag{7}$$

$$\log k_{HA} = \alpha \log K_{HA} + \text{constant} \tag{8}$$

catalytic rate constants, K_{HA} are the corresponding dissociation equilibrium constants for the acid catalysts, and G_A is a constant for the reaction series. The term α is known as the Brønsted coefficient or exponent. In its logarithmic form (eq 8) this predicts a linear relationship between log k_{HA} and log K_{HA}, although it is now generally accepted[34] that truly linear Brønsted plots may be an artefact of the short catalyst pK_{HA} ranges normally used in thermal reactions, and there are strong theoretical reasons[35] to believe that Brønsted relationships should be curved if a wide enough range of reactivity is covered.

Table III. Comparison of Brønsted α Values for Thermal and Photochemical Hydrations

substrate	type of reaction	α[a]	reference
m-fluorostyrene	photochemical	0.16	present work
p-methylstyrene	photochemical	0.14	present work
2-vinylnaphthalene	photochemical	0.18	present work
α-naphthylacetylene	photochemical	0.16	present work
β-naphthylacetylene	photochemical	0.14	present work
α-methyl-*p*-methoxystyrene	thermal	0.47–0.49	3a
p-methoxystyrene	thermal	0.45	3a
methoxyacetylene	thermal	~0.5[b]	3f
ethoxyacetylene	thermal	~0.5[b]	3f
2-chloroethyl vinyl ether	thermal	0.52	3d
α-methoxy-*p*-chlorostyrene	thermal	0.57	3a
α-methylstyrene	thermal	0.57	3a
3-methoxyindene	thermal	0.64–0.78[c]	3b
α-methyl-*m*-methylstyrene	thermal	0.61	3a
α-methyl-*m*-chlorostyrene	thermal	0.71	3a
p-aminostyrene	thermal	0.74[d]	3e
p-(dimethylamino)styrene	thermal	0.78[d]	3e
isobutylene	thermal	0.85	3c
p-methylstyrene	thermal	0.86[e]	26

[a] Based on the original (linear) Brønsted equation in each case. [b] Estimated from reported k_{HA} values. [c] Values based on two different catalyst pK_{HA} ranges. [d] For reaction of neutral form of substrate. [e] Based on β value of 0.14 for deprotonation of carbocation to give *p*-methylstyrene.

When the log k_{HA} values of Table I are plotted against log k_{HA}, the Brønsted relationship in eq 8[36] is only approximately obeyed, since the plots are smoothly curved in every case, if the points for H_2O and H_3O^+ are included. A typical example is shown in Figure 3 for α-naphthylacetylene (**10**). A linear correlation (dashed line in Figure 3) gives an approximate α of 0.16 with a correlation coefficient of only 0.975. In all five cases where general acid catalysis could be clearly observed with a range of catalysts, the approximate Brønsted α values are in the 0.14–0.18 range as shown in Table III. Using the value obtained for α as an approximate measure[37] of the degree of proton transfer in the photoprotonation step of the hydration reaction, we conclude that the proton is much less than half transferred at the transition state. This is in sharp contrast to the situation in the analogous thermal hydrations of carbon–carbon double and triple bonds, where all reported α values are in the 0.5–0.86 range.[3,26] The upper part of this range would be typical of the substrates involved in the present study, since thermal values of α around 0.5 have been reported only for highly activated substrates, as shown in Table III, where a comparison of all available α values for thermal and photochemical hydration is made. Therefore the photochemical hydration reaction involves very "early" transition states, whereas the thermal process involves "midway" to very "late" transition states. This is not unreasonable in terms of the rate ratios pre-

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(29) Modena, G.; Rivetti, F.; Scorrano, F.; Tonellato, U. *J. Am. Chem. Soc.* **1977**, *99*, 3392.

(30) Ingold, C. K. *J. Chem. Soc.* **1954**, 2991.

(31) Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, 1973; Chapter 10. See also ref 9a, p 280.

(32) Dauben, W. G.; Salem, L.; Turro, N. *J. Acc. Chem. Res.* **1975**, *8*, 41.

(33) Wan, P. Ph.D. Thesis, University of Toronto, 1983.

(34) See, for example, the discussion of Brønsted relationships in ref 9b.

(35) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: New York, 1973; p 203. Ahrens, M. L.; Eigen, M.; Kruse, W.; Maass, G. *Ber. Bunsenges. Phys. Chem.* **1970**, *74*, 380. Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(36) Statistical corrections to the Brønsted equation have been ignored in the present study, for several reasons. First, it is not always clear precisely which values should be used, especially in terms of the number of basic sites on species such as H_2O and OH^-, among others. Second, use of such statistical factors, although apparently correct in principle, has never been widely established as being empirically valid. For example, in the discussion of Brønsted relationships in ref 9a and 9b, one author ignores these terms completely and the other concludes "that statistical corrections of this type are seldom critical in determining the slope of a Brønsted correlation".[11] In any event, use of statistical factors in the present study led to worse correlations in every case, at any level of polynomial fitting used.

(37) The magnitude of the Brønsted α is often used as a measure of transition-state development in a proton-transfer reaction.[9] The validity of this interpretation is based on the Hammond postulate.[38]

(38) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. See also ref 37, pp 197–199.

viously discussed, since such unusually fast proton transfers to carbon would be expected to be associated with much lower values of α than the much slower thermal processes (which are known to have activation barriers of ca. 20–25 kcal mol^{-1}).[1,2]

The fact that the Brønsted α values for thermal hydrations are all much greater than those for photohydration means that as the catalyst HA becomes a weaker acid, the previously discussed rate differences expressed by k^*_{HA}/k°_{HA} will increase significantly. This can be seen from a numerical example. Taking average values of $\alpha^* = 0.15$ and $\alpha^\circ = 0.7$ from the data in Table III and the previously estimated range of k_{HA}/k_{HA} for H_3PO_4 ($pK_{HA} = 2.15$), then the change in this ratio produced by a shift to the weaker catalyst methylphosphonate ion ($pK_{HA} = 8.00$) will be given by

$$\log (k^*_{HA})/(k^*_{HA})' = 0.15(-2.15 + 8.00) = 0.88$$

$$\log (k^\circ_{HA})/(k^\circ_{HA})' = 0.7(-2.15 + 8.00) = 4.10$$

$$\text{and } \log \left(\frac{(k^*_{HA})}{(k^\circ_{HA})} \right) = \log \left(\frac{(k^*_{HA})}{(k^\circ_{HA})} \right) + 3.22$$

where the primes refer to methylphosphonate catalysis.

In other words, shifting to the weaker catalyst will increase the relative rate of the photochemical reaction by a factor of 1.7×10^3. Therefore the previously estimated rate factors of 10^{11}–10^{15} in favor of photoprotonation over thermal proton transfer are probably lower limits for the acceleration produced by electronic excitation of these substrates.

It is often found in Brønsted plots that the point for H_3O^+ catalysis falls well below the line through the other points, and the reasons for this deviation have been frequently discussed.[39] It is interesting in the present case that this deviation only occurs for two of the five substrates studied, namely for 2-vinylnaphthalene (**6**) and β-naphthylacetylene (**11**) as shown in Figure 4 where Brønsted plots for all substrates are compared. For the other three substrates, the point for H_3O^+ falls on a smooth curve through all the other points. This may be a consequence of the very low α values involved, since the variation in photochemical rate constant is not as sensitive to the nature or pK value of the catalyst acid involved. Even in the cases of compounds **6** and **11** the deviations of the H_3O^+ points are not that large, being less than an order of magnitude, whereas in thermal acid and base catalyzed reactions, deviations of the usually anomalous H_3O^+ and OH^- points can be as high as several orders of magnitude.[40]

The most important point concerning these Brønsted relationships is their indication of curvature. The solid line drawn through the experimental points in Figure 3 was obtained by multiple regression analysis. The analysis was terminated when the calculated value of the F-statistic no longer increased.[41] This showed that the best statistical fit was obtained with a cubic expression, which improved the correlation coefficient from 0.975 (linear) to 0.999 (cubic) and decreased the root-mean-square error from 0.222 (linear) to 0.057 (cubic). The latter standard error corresponds to the size of the circles in Figure 3, showing that the variation of log k_{HA} with log K_{HA} follows a smooth nonlinear relationship.

Similar behavior was found for the other four substrates (**2**, **4**, **6**, and **11**) as shown in Figure 4. Unfortunately, these curves cannot be used to derive reliable estimates of Brønsted curvature, for several reasons. One is that even ignoring the normally deviant point for H_3O^+ catalysis, the observed curvature is strongly dependent on the location of the point for H_2O. On the basis of the points for the weak acids HA alone, curvature is not clearly established although the Brønsted α values derived are in the same range (0.12–0.17) as those derived from the cubic fit based on all points. Another problem is that for practical reasons, a truly homogeneous set of catalysts could not be used. Work is in progress to attempt to solve these problems, and extend the data on general acid catalysis, in order to examine the possible application[42] of Marcus theory[14] to photochemical proton-transfer reactions.

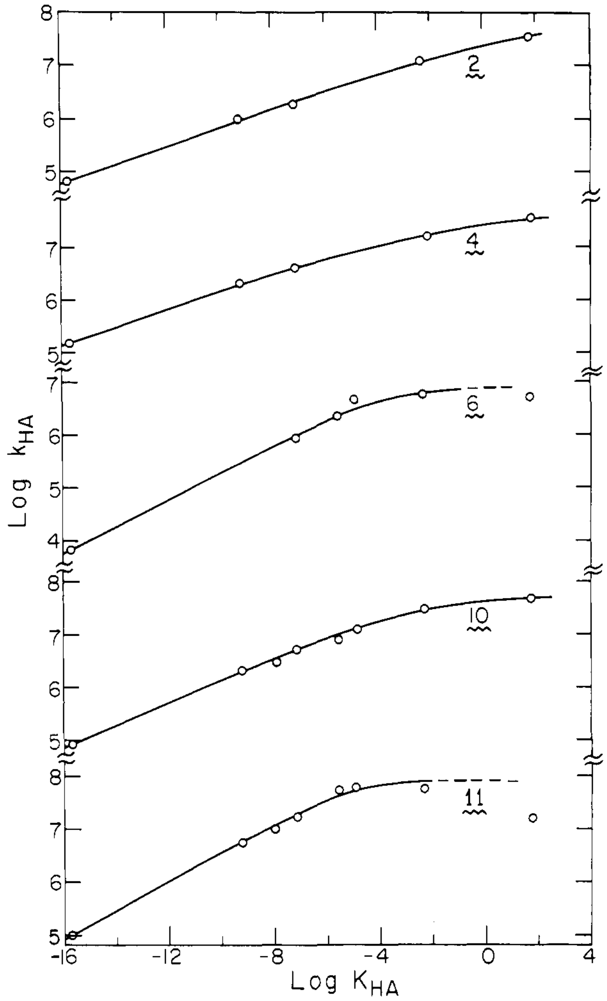

Figure 4. Curved Brønsted type plots for substrates **2**, **4**, **6**, **10**, and **11**. (Solid curves based on multiple regression, using a cubic expression in each case.)

It is interesting, however, that as the acid strength of the catalyst is increased, the slopes or α values appear to decrease and tend toward zero in the limit, as predicted by Eigen.[35] However, the upper limit for log k_{HA} in each case is somewhere in the 10^7–10^8 M^{-1} s^{-1} range, which is considerably lower than the diffusion-controlled limit for thermal proton transfers in aqueous solution involving oxygen atoms, which is around 10^{10} M^{-1} s^{-1}.[43] Thus although these proton transfers on carbon are at least 10^{11}–10^{15} times faster than their ground state analogues, they still do not come within two orders of magnitude of the fastest known thermal proton-transfer reactions. The reason for this is not clear, since in the case of hydronium ion at least, proton transfer to S_1 could occur via a Grotthus chain mechanism[44] involving two or three water molecules. It can be calculated that at concentrations of $[H_3O^+]$ in the 0.1–1.0 M range, there is a very high probability of finding an H_3O^+ ion within the reaction sphere of S_1 at the instant of its creation, taking the radius of the sphere as approximately 0.6–0.75 nm.[45] It has, however, been previously suggested[46] that even the fastest rates of thermal proton transfer involving carbon would have limiting values well below those involving oxygen, due to the different solvent and structural re-

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[39] Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475. See also ref 30.

[40] See, for example: ref 30, p 200.

[41] Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; pp 198–203.

[42] Yates, K. *J. Am. Chem. Soc.* **1986**, *108*, 6511.

[43] See ref 31, Chapter 7.

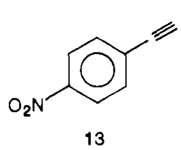
[44] Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117, 7126, 7135.

[45] Huppert, D.; Guttman, M.; Kaufman, K. J. *Adv. Chem. Phys.* **1980**, *47* (*2*), 643.

[46] Kreevoy, M. M.; Konasewich, D. E. *Adv. Chem. Phys.* **1971**, *21*, 243.

organization involved. This may also be true for fast photochemical proton transfer to carbon.

Catalytic Reactivity of Triplet States. Nitroaromatic compounds are well-known[47] to intersystem cross to T_1 with high efficiency, and it has already been shown[5,48] that *m*- and *p*-nitro-substituted styrenes, phenylacetylenes, and phenylallenes all photohydrate cleanly under similar conditions to those presently described. However, these reactions have been shown to proceed via lowest triplet states, from a combination of triplet sensitization and quenching experiments, and to give anti-Markovnikov addition of water across the multiple bonds. Since some of these reactions were found to be subject to specific H_3O^+ catalysis (*m*- and *p*-nitrophenylacetylene, *m*-nitrophenylallene), and in general do not have zero quantum yields in aqueous solution at pH 7, it seemed reasonable that they too would be subject to general acid catalysis, at least in some cases. However, when compounds **13–16** were subjected to the same reaction conditions at **1–12**, with H_3PO_4 as general acid, no variation in Φ/Φ_0 could be detected.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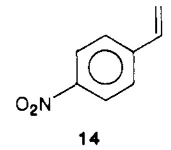
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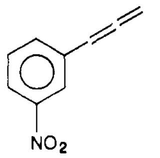
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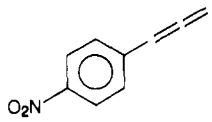
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This was perhaps to be expected for **14**, since it does not show specific H_3O^+ catalysis.[5] However, the lack of triplet reactivity of **15** and **16** was somewhat surprising, since general acid catalysis by H_3PO_4 could easily be detected for phenylallene itself, and its *p*-cyano derivative. Most surprising was the failure of **13** to show any general acid catalysis. On the basis of the previously reported[5] variation of Φ_p with acidity for this compound, a plot of Φ_p vs. $1/[H^+]$ gives a reasonable linear plot with a slope of 4.33 M^{-1}. The triplet lifetimes of **14** and the *m*-nitro isomer of **13** have been estimated[5] as 0.46 and 2.8 μs, respectively, from Stern–Volmer plots based on triplet quenching of photohydration by DTBN in neutral aqueous solution, so that **13** probably has a triplet lifetime in the 1-μs region. Therefore the estimated value of k_{H^+} for specific catalysis of the photohydration of 13 is $\sim 2 \times 10^5$ M^{-1} s^{-1}. This is clearly much lower than k_{H^+} for the other substituted phenylacetylenes, which react via S_1, but this is not really surprising. However, using the above value and the previously reported[5] Φ_{pH7} of 0.045 in eq 6 to estimate whether **13** would show a variation in Φ/Φ_0 with $[H_3PO_4]$ above the threshold (0.05) of water catalysis reveals that it clearly should, if $k_{HA} \sim k_{H^+}/4$ as assumed previously. The fact that there is no detectable catalysis above the background of H_2O catalysis, even with H_3PO_4, must mean that this estimate of k_{HA} is too high, by a considerable margin. It is not very likely that a short T_1 lifetime is solely responsible for the lack of observed reactivity, since these are normally much longer than the S_1 lifetimes previously discussed (Table II). The most likely explanation is that the estimate of $k_{HA} \sim k_{H^+}/4$ as an upper limit is far too high for triplet states, and this in turn can only mean that the Brønsted α of $\sim$0.15 (based on S_1 reactions) used to estimate that $k_{HA} \leq k_{H^+}/4$ is too low. This implies that acid catalyzed triplet state photohydrations would have significantly higher α's and hence less advanced or "early" transition states than analogous singlet state photohydrations. This is reasonable, since as pointed out, k_{H^+} for **13** (2×10^5 M^{-1} s^{-1}) is much lower than k_{H^+} for other phenylacetylenes ($\sim 10^7$ M^{-1} s^{-1}), and from Table III it can be seen that as substrate reactivity decreases α increases. Nonetheless, in view of the factors described in the Appendix it should still be possible to detect general acid catalysis for some of these triplet reactions. At present, attention is being focussed on *m*-nitro derivatives, which it is hoped will show greater reactivity than their para isomers. Work is in progress on these systems.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a Varian T60 spectrometer, using either $CDCl_3$ or acetone-d_6 as solvent, with TMS as internal standard. UV spectra were recorded on a Varian 2300 UV spectrophotometer. Dichloromethane used in extractions was distilled prior to use. All inorganic reagents (phosphoric acid, boric acid, HCl, and NaOH) were of analytical grade (Fisher Scientific or BDH). Diphenylacetylene, 2-vinylnaphthalene, and phenylacetylene were available commercially (Aldrich) and were either sublimed or distilled before use. Lifetimes were obtained by pulsed fluorometry with single-photon counting[25] as described previously.[5,6]

Synthesis. The preparation of methyl phosphonate, dichloromethyl phosphonate, and trichloromethyl phosphonate has been described elsewhere.[52] The phosphonates, once prepared, were dried under vacuum over P_2O_5 to constant melting point, which in all cases corresponded to that of the pure acid. **α-Naphthylacetylene**: A mixture of 15g. (.088 mol) α-naphthylacetophenone in benzene (200 mL) was cooled on ice. To this was added 35g. (.168 mol) PCl_5. The ice bath was removed and the mixture was refluxed for 2 days. The solution was then poured into a saturated NaCl solution and extracted with dichloromethane, followed by evaporation. The resulting oil was purified on a silica gel plate on a Chromatron Model 7924 with 95% pentane/5% dichloromethane as eluent. ^1H NMR δ 3.4 (s, 1 H), δ 7.2–8.4 (m, 7 H). β-Naphthylacetylene was prepared by the above method: mp 39–40 °C (uncorrected) (lit.[53] mp 37–38 °C) after repeated sublimation; ^1H NMR δ 3.1 (s, 1 H), 7.2–8.0 (m, 7 H). 4-Methylphenylacetylene was prepared by the method of Allen and Cook.[54] The final product was purified by vacuum distillation, with the fraction boiling at 58–60 °C (13 mmHg) being collected: ^1H NMR δ 2.17 (s, 3 H), 3.0 (s, 1 H), 7.0–7.45 (dd, 4 H). 4-Methoxyphenylacetylene was prepared by the same method as above[54] and purified by repeated sublimation: mp 26–27 °C (uncorrected) (lit.[54] mp 29 °C); ^1H NMR δ 3.0 (s, 1 H), 3.77 (s, 3 H), 6.7–7.5 (dd, 4 H). Commercial samples of styrene (Fisher), *m*-fluoro-, *p*-fluoro-, and *p*-methylstyrene (Aldrich), and *p*-methoxystyrene (ICN) were purified by distillation before use.

Buffer Solutions. Stock solutions with $H_2PO_4^-$ as general acid were prepared by dissolving monosodium phosphate in distilled water (0.5–1.0 M). Solutions of H_3BO_3 were prepared by dissolving pure boric acid (0.5 M) in distilled water. Stock solutions for the other general acids were prepared as true buffers according to the equation

$$\mathrm{pH} = \mathrm{p}K_{HA} + \log [A^-]/[HA]$$

by adjusting the buffer ratio $[A^-]/[HA]$ to the desired pH by added NaOH or HCl solution. Total buffer concentrations for the phosphonates were limited to the 0.15–0.2 M range because of solubility restrictions. In these cases the concentration of phosphonate dianion was kept at a minimum (ca. 0.01–0.02 M) in order to maximize the concentration of effective general acid. In other cases buffer ratios as close to unity as practicable were used. Blank or reference solutions were prepared for each buffer pair by adjusting the pH of distilled water to match the measured buffer pH and adding NaCl to match the total ionic strength of the buffer solution. Buffer dilutions were carried out by pipetting 0.5–3.0 mL of stock solution into UV cuvettes and adding NaCl of the appropriate ionic strength to bring the total volume to 3.0 mL. Although the ionic strength of the reaction mixture was kept constant, it was found that varying the salt concentration from 0 to 1.0 M had no detectable effect on the photoreaction.

Thermodynamic pK_{HA} values for phosphoric and boric acid are well-known.[55] Values for the phosphonates were taken from the more

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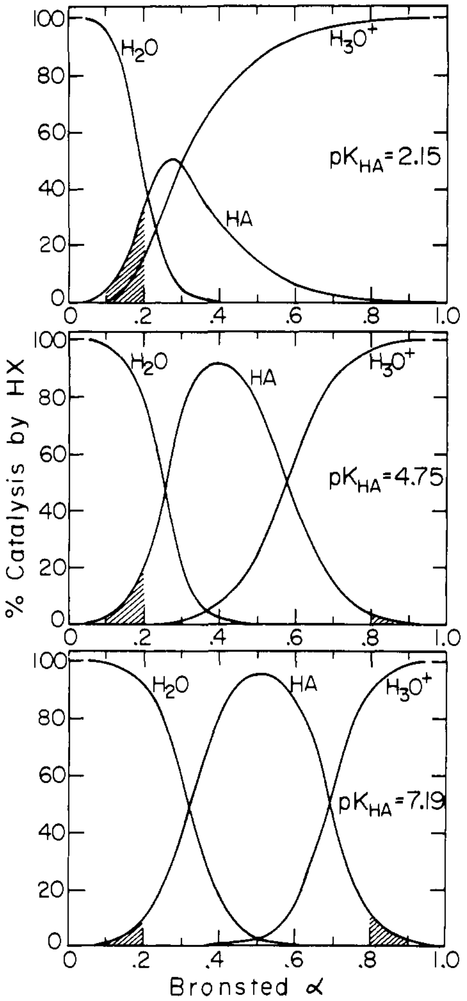

Figure 5. Percentages of acid catalysis by H_2O, HA, and H_3O^+ as a function of Brønsted α, for typical buffer pK_{HA} values, calculated for $[HA] = [A^-] = 0.1$ M. (Shaded areas as described in Appendix.)

recent work of Kresge and Tang.[56]

Quantum Yield Measurements. Irradiations were carried out in a Rayonet RPR-100 reactor with 254- or 300-nm lamps (6 or 12 × 25 W) as appropriate for each substrate. UV cuvettes with various concentrations of general acid HA at fixed buffer ratio $[A^-]/[HA]$ and constant ionic strength were prepared as described above and 20–100 mL of a stock solution of substrate in acetonitrile was injected. The cuvettes were placed in a merry-go-round apparatus during irradiation (5–60 min). In most cases[57] the reference quantum yield Φ_0 was based on the extent of reaction, as determined by the change in UV absorption at the appropriate wavelength for each substrate (see Figure 1), in the absence of general acid. In each case the reference Φ_0 was determined at the same pH and ionic strength as the buffer being used, by means of added HCl and NaCl. The extent of any competing thermal reaction during the time periods normally used for irradiation has been shown[5,6] to be negligible.

The relative quantum yields for product formation $(\Phi/\Phi_0)_p$ were determined by monitoring the UV absorption at the appropriate wavelength for product appearance or substrate disappearance (see Figure 1). Since

$$\Phi_p = \frac{\text{(moles of product formed per unit time)}}{\text{(einsteins of photons absorbed per unit time)}}$$

then for constant irradiation time and light intensity (merry-go-round)

$$(\Phi/\Phi_0)_p = \frac{\text{(moles of product formed)}}{\text{(moles of product formed)}_0}$$

where the subscript zero refers to the reference solution with no added general acid. From the measured UV absorbances (A) in low conversion experiments

$$\Delta A = \Delta c \epsilon l$$

$$\begin{aligned}\Delta A/\Delta A_0 &= \Delta c/\Delta c_0 \\ &= (\Delta \text{ moles of product})/(\Delta \text{ moles of product})_0 \\ &= (\Phi/\Phi_0)_p\end{aligned}$$

Absolute quantum yields Φ_p were determined at pH 7 where necessary (see Tables I and II) by MGL actinometry[24] as described previously.[5,6]

Acknowledgment. The continued financial support of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

Appendix

As first pointed out by Bell,[49] and later commented on by Jencks,[50] whether general acid catalysis can be detected experimentally or not depends on the magnitude of the Brønsted α, as well as on the strength of the acid catalyst. For many reactions, whose α values are in the neighborhood of 0.5, this factor is not too important, but for both thermal and photochemical reactions of the present type, where α values are either less than 0.2 or greater than 0.8, it is critical.

The fraction of total reaction rate of an acid catalyzed reaction which is due to catalysis by hydronium ion, water, and general acid HA, respectively, in a buffer solution of 0.1 M [HA] and 0.1 M $[A^-]$, can easily be calculated for different values of α.[51] The percentage of total reaction due to each catalytic species depends only on the values of α and log K_{HA} and not on the absolute magnitude of the rate constant for $k_{H_3O^+}$, for example. By taking three typical values of buffer pK_{HA} (2.15, 4.75 and 7.19) the percent catalysis due to H_3O^+, H_2O, and HA is shown graphically in Figure 5 as a function of α. The shaded areas under each curve represent the extent of general acid catalysis for reactions either with $0.1 \le \alpha \le 0.2$ (as found for the present photochemical reactions) or with $0.8 \le \alpha \le 0.9$ such as would be expected for the corresponding thermal reactions of the same substrates. In the first case the important competition is between HA and H_2O. In the second, it is between HA and H_3O^+.

It can be seen that as the catalyst becomes a weaker acid, the curve due to HA shifts to the right and the reactions with low α values become more and more dominated by H_2O catalysis. Nevertheless the proportion of catalysis by HA is still significant and should be detectable, providing the pK_{HA} value is not too high. Increasing the buffer concentration can help, and providing the excited state lifetime is not too short and the water catalyzed reaction is not too efficient (see Table III for threshold values), general acid catalysis should be experimentally detectable. It is extremely fortunate in the present case that photohydration reactions have α values of ca. 0.15, since if they had been much smaller, general acid catalysis might not have been detected experimentally.

Comparing this situation with analogous thermal reactions with α values in the 0.8–0.9 range, it can be seen that H_3O^+ catalysis completely dominates the reaction for buffers with low pK_{HA} values, and it is not until $pK_{HA} > 4.75$ that the proportion of catalysis by HA becomes important (see Figure 5). However, increasing the buffer pK does not really help, since as the pH of the solution approaches 7 both the specific and general acid catalyzed reactions would become too slow to follow conveniently. This is why relatively few thermal hydrations have been investigated directly in terms of general acid catalysis and why it has usually been necessary[3] to use highly activated substrates with α values <0.8.

It is therefore very interesting (and somewhat surprising) that in many cases it may be much easier to detect general acid catalysis photochemically, where the competition is with water catalysis, than it is thermally, where the competition is with

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[57] In a few cases, notably with H_3BO_3 as catalyst, a constant and low concentration of general acid ($[HA]_0$) was also used in the reference cell, since this gave the more efficient conversion to photohydration products at high pH values. This necessitated use of a slightly modified version of eq 4 when plotting $(\Phi/\Phi_0)_p$ vs. [HA], where the slope becomes $k_{HA}/k_{H_2O}[H_2O] + k_{HA}\cdot[HA]_0$ rather than $k_{HA}/k_{H_2O}[H_2O]$. It was found that this approach gave smoother plots in these cases.

hydronium ion catalysis. Providing photochemical proton transfer reactions do not have α values much lower than those found here, it should be possible to investigate this phenomenon more widely than has been the case. Another great advantage is that because α values are likely to be smaller in photoreactions, it should be possible to utilize a wider range of catalyst pK_{HA} values than in corresponding thermal reactions. Hence it might well be easier generally to detect and measure Brønsted curvatures photochemically.

In view of the great current interest in proton transfers involving excited states,[13,45,52] such investigations may lead to valuable new insights into the detailed mechanisms of such processes.

Electrochemical and Spectroscopic Analyses of the Thermodynamics of the Reversible Dimerization of Cyanine Radical Dications

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Abstract: Radical dications initially formed during the one-electron oxidation of alkyl-substituted, cationic dicarbocyanine dyes were found to undergo reversible dimerization in acetonitrile at room temperature. The site of radical–radical coupling was determined by NMR spectroscopy to be at an approachable even-methine carbon of the polymethine chain. The $C\cdots C$ bond dissociation energy in the dimer was determined for a series of variously substituted dicarbocyanines from the temperature dependence of UV–vis spectra and was found to range from 12.2 to 16.8 kcal/mol. The corresponding free entropy change involved with the dimer dissociation process ranges from 21 to 32 eu. Upon consideration of the dicarbocyanine structures, the experimental results can be interpreted in terms of steric destabilization of the covalently bonded dimer.

Cyanine dyes have been widely used as spectral sensitizers for silver halide and other inorganic semiconductor materials.[1,2] In silver halide based photographic systems these dyes provide for color separation, in addition to extending the response of silver halide beyond its intrinsic ultraviolet and blue-light photosensitivity. The generic cyanine dye structure involves two heterocyclic nuclei that are linked by a conjugated chain containing an odd number of methine carbon atoms. Dicarbocyanines, which contain five methine carbons, are typically used to impart spectral sensitivity in the red region. Substituent modifications involving either the heterocyclic nuclei or the polymethine chain are the synthetic approaches commonly used to fine-tune dye properties to achieve a desired spectral wavelength response or to gain additional improvements in sensitization efficiency.

Predictions of the efficiency of spectral sensitization of silver halide by cyanine dyes are often based on the electrochemical properties of the particular dye.[3-5] In a recent report describing the measurement of the reversible redox potentials of cationic cyanines it was shown that the stability of the radical dication formed during one-electron oxidation is markedly dependent on the type and extent of substitution in the polymethine chain of the dye.[6] Cyanine radical dication stability was demonstrated to be greatly improved by alkyl substitution at the methine carbons to electronically stabilize the radical and/or sterically inhibit radical–radical coupling reactions. More detailed studies of dye radical stability have since resulted in the discovery of a remarkable collection of chain-substituted dicarbocyanine radical dications that undergo reversible C–C bond formation at room temperature.

This paper reports the results of thermodynamic and kinetic characterization of the reversible dimerization of thiadicarbocyanine and quinodicarbocyanine radical dications in acetonitrile solution. Thermodynamic parameters ΔG, ΔH, and ΔS, describing the dimerization equilibria for a series of variously substituted dyes, are evaluated from temperature-dependent absorption spectra. Complementary information concerning the relative rates of formation and dissociation of the dimers is provided by cyclic voltammetry. Together with product-analysis data, these results indicate that the dicarbocyanine radical/dimer equilibrium is largely controlled by the degree of steric strain in the dimer.

Experimental Section

A. Reagents and Solvents. Dyes were synthesized by previously established procedures,[7,8] and analyzed by thin-layer chromatography, UV–vis spectrophotometry, and ionographic analysis. All dyes were obtained as the *p*-toluenesulfonate (pts) or perchlorate (ClO_4^-) salts for electrochemical studies; however, chemical oxidations were carried out on bromide and iodide salts as well. Ferric chloride hexahydrate ($FeCl_3$, Kodak Laboratory Chemicals) and potassium hexafluorophosphate (Alfa) were used as received. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, Kodak Laboratory Chemicals) was recrystallized three times from ethanol/water mixtures and dried in vacuo. Acetonitrile (CH_3CN, MCB spectrograde) for electrochemistry or radical thermodynamic studies was dried over 4A molecular sieves (Kodak Laboratory Chemicals, baked at 400 °C). Solvents for synthetic use were Kodak reagent grade.

B. Apparatus. Electrochemical measurements were performed with a Princeton Applied Research Corp. (PAR) 173 potentiostat in conjunction with a PAR 175 universal programmer, PAR 179 digital coulometer, and 124A lock-in amplifier. A Hewlett-Packard Model 239A low-distortion oscillator was used in ac measurements. Formal oxidation and reduction potentials were obtained via phase-selective, second-harmonic ac voltammetry or by cyclic voltammetry as described previously.[6] Voltammetric data were obtained at 22 °C at a Pt disk electrode (0.1 cm^2) or a Pt microelectrode (10-μm diameter). Current–voltage curves were recorded on a Hewlett-Packard Model 7045A X–Y recorder or on a Tektronix 5115 storage oscilloscope. All potentials were measured vs. the NaCl saturated calomel electrode and converted to the Ag/AgCl reference by adding 40 mV. Controlled-potential coulometry was performed with a PAR 337A cell system equipped with a Pt gauze working

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