

Intramolecular Proton Transfer in Photohydration Reactions

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Abstract: The photohydration by intramolecular proton transfer of compounds 1-12 has been studied. The non-nitro-substituted *o*-hydroxystyrenes photohydrate cleanly via the Markovnikov addition of water to afford the 1-arylethanol. The nitro-substituted *o*-hydroxystyrenes showed no dependence of product quantum yield with change in pH. The products isolated and identified in this case were the corresponding 2-(2-hydroxyphenyl)ethanols. Compounds with α substituents showed evidence of an increased interaction between the hydroxyl group and the π orbitals of the vinyl moiety. The absolute quantum yields for 1 and 9 at pH 2 are 0.19 and 0.41, respectively. The intra- and intermolecular proton transfer rate constants for 1 and 9 were estimated and used to calculate the effective molarities, EM = 10^{-2} and 2.6, respectively.

The possibility of intramolecular proton transfer (ipt) in photohydration reactions was investigated primarily as a result of Weller's classic work on salicylic acid derivatives.¹ Preliminary work involved the study of irreversible intramolecular proton transfer in the photohydration of *o*-hydroxystyrene and *o*-hydroxyphenylacetylene.² This type of reaction, as well as the thermal analogue, involves Markovnikov addition of a proton in the rate-limiting step followed by the attack of water to afford the corresponding 1-arylethanol and acetophenones.

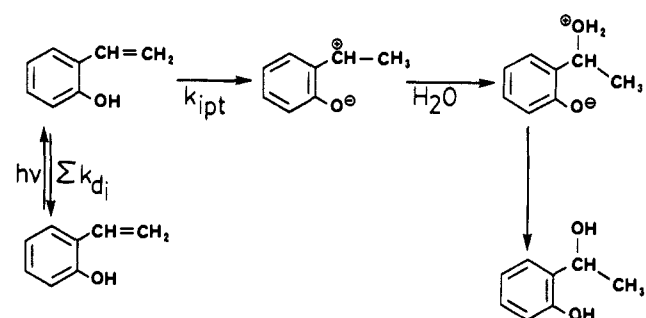
In the ground state, the electrophilic addition reactions are very slow³ ($t_{1/2}$ is typically of the order of several hours to several days). A means of enhancing the observed rate is by increasing the basicity of the substrate, thus making the protonation step more facile. This can in principle be achieved by photochemical excitation to the singlet or triplet excited states.⁴ The enhanced basicity of numerous aromatic chromophores on excitation is well known.⁵

Wooldridge and Roberts⁶ took advantage of this phenomenon when they reported the facile photoprotonation of several aromatic alkynes in either dilute acid solution or water. The products obtained were the corresponding ketones, as observed in the ground-state reactions.^{3a} This use of enhanced basicity was confirmed and extended to the photohydration of variously substituted aromatic alkenes, which produced the corresponding 1-phenylethanol.^{4,7}

The photohydrations of *o*-hydroxystyrene and *o*-hydroxyphenylacetylene are the first clear photochemical examples of irreversible intramolecular proton transfer.² Essentially the reaction involves the transfer of a proton in the Markovnikov sense from the phenolic OH group to the unsaturated side chain of the compound. Photoprotonation produces a zwitterionic intermediate which is trapped by water or other nucleophiles present to form the observed alcohol or ether (Scheme I). Various substituents have now been investigated in order to test the quantum efficiency, acid catalysis, geometric requirements, and regioselectivity of the photohydration reaction in question.

This paper deals with the study of the photohydration reactions of a number of *o*-hydroxy- and *o*-methoxystyrenes. The results obtained should help broaden our understanding of the structural

Scheme I



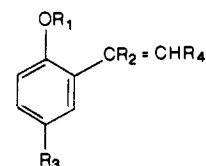
$$\Phi_{\text{intermolec}} = \frac{k_{\text{H}}[\text{H}^+]}{\sum k_{\text{d}_i} + k_{\text{H}}[\text{H}^+] + k_{\text{i.p.t.}}} \quad (1)$$

$$\Phi_{\text{intramolec}} = \frac{k_{\text{i.p.t.}}}{\sum k_{\text{d}_i} + k_{\text{H}}[\text{H}^+] + k_{\text{i.p.t.}}} \quad (2)$$

requirements and effective molarities necessary for such intramolecular reactions to occur efficiently.

Results

Product Studies. The *o*-hydroxy- and *o*-methoxystyrenes (1-10)



	R ₁	R ₂	R ₃	R ₄
1	H	H	H	H
2	CH ₃	H	H	H
3	H	H	H	CH ₃
4	CH ₃	H	H	CH ₃
5	H	H	NO ₂	H
6	CH ₃	H	NO ₂	H
7	H	H	NO ₂	CH ₃
8	CH ₃	H	NO ₂	CH ₃
9	H	CH ₃	H	H
10	CH ₃	CH ₃	H	H

are listed below. Also investigated for comparison purposes were *p*-hydroxy- (11) and *p*-methoxystyrene (12). The quantum yield dependences on pH for compounds 1, 2, 11, and 12 are shown in Figure 1a and for compounds 9 and 10 in Figure 1b (all compounds were irradiated at 300 nm). In general, the *o*-hydroxy derivatives with no nitro substituents show intramolecular proton transfer behavior in the region pH 8 to 1. Above pH 8 the reaction is less efficient, presumably owing to prior deprotonation of the

(1) (a) Weller, A. Z. *Elektrochem.* **1956**, *60*, 1144. (b) Weller, A. *Prog. React. Kinet.* **1961**, *1*, 188.

(2) Isaks, M.; Yates, K.; Kalanderopoulos, P. *J. Am. Chem. Soc.* **1984**, *106*, 2728.

(3) (a) Phenylacetylenes: Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 1020. (b) Styrenes: Schubert, W. M.; Keefe, J. R. *Ibid.* **1972**, *94*, 559, and references therein.

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

(5) (a) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131. (b) Lahiri, S. C. *J. Sci. Ind. Res.* **1979**, *38*, 492. (c) Martynov, I. Yu.; Demyashkevich, A. B.; Uzhinov, B. M.; Kuz'min, M. G. *Russ. Chem. Rev.* **1977**, *46*, 1.

(6) Wooldridge, T.; Roberts, T. D. *Tetrahedron Lett.* **1973**, *41*, 4007.

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

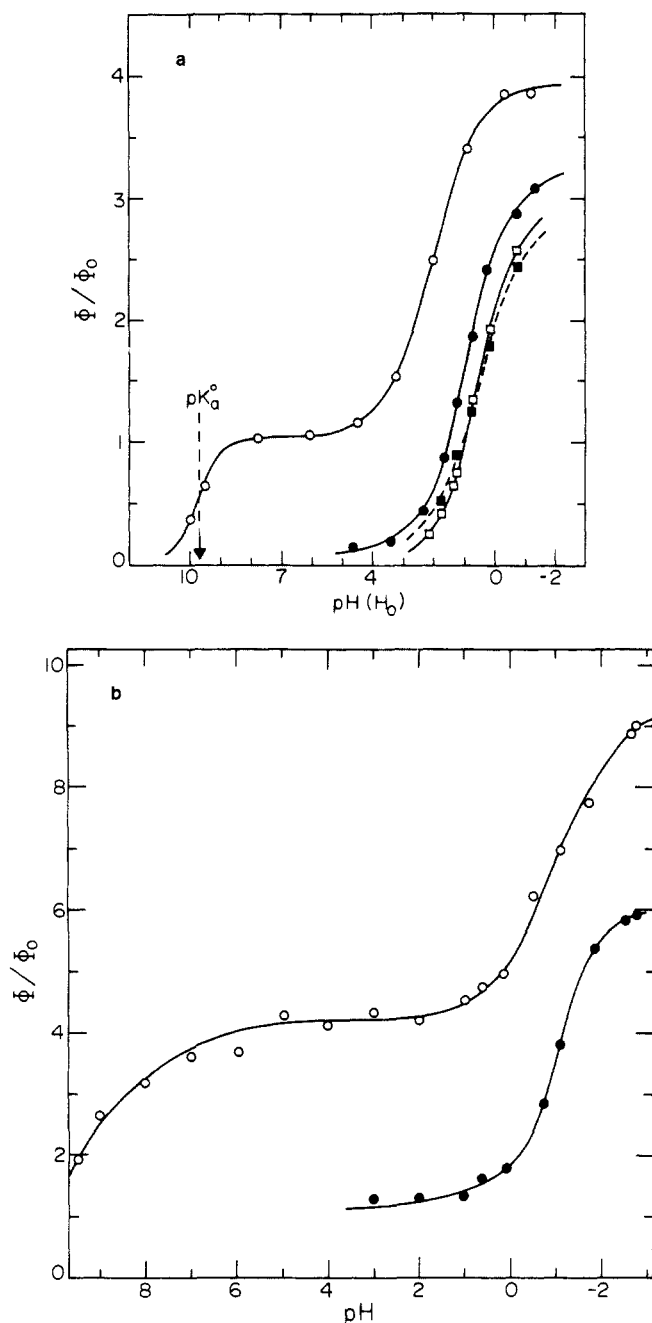


Figure 1. Relative product quantum yields (Φ/Φ_0) as a function of acidity for (a) hydroxy- and methoxystyrenes **1**, (open circles), **2** (closed circles), **11** (open squares), and **12** (closed squares) ($\text{p}K_a^0$ refers to ground-state ionization constant for **1**); (b) α -substituted *o*-hydroxy- (**9**, open circles) and *o*-methoxystyrene (**10**, closed circles).

ground-state phenolic OH (see later). At higher acidities, the relative quantum yield increases and external acid catalysis eventually dominates the reaction mechanism. The sigmoidal increase in the relative quantum yield and the concurrent sigmoidal fluorescence quenching at higher acidities support the assumption of competing intermolecular proton transfer.

The quantum yield dependence on pH for the corresponding nonnitro *o*-methoxy and para-substituted (**11** and **12**) derivatives show they also photohydrate but with quite a different dependence on acidity (Figure 1). Their behavior is very similar to that of the meta- and para-substituted derivatives previously investigated.⁴

The nitro-substituted *o*-hydroxy and *o*-methoxy compounds react via the triplet state as shown by sensitization and quenching experiments, rather than via the singlet state as in the case of the nonnitro compounds. The quantum yield for product formation is independent of medium acidity over the entire range studied (pH 10 to $H_0 = -1.5$). The products obtained are the corre-

sponding 2-(2-hydroxyphenyl)ethanols which are produced via anti-Markovnikov addition to the alkene moiety, as previously found for other nitro-substituted styrenes and phenylacetylenes.⁴

Compounds **9** and **10** were studied because of data reported by Oki and Iwamura⁸ indicating that the interaction of the hydroxyl group and the vinyl moiety can be increased by increasing the size of the α substituent on the vinyl group from hydrogen to methyl to *tert*-butyl. This was based on analysis of the IR and UV spectra of the compounds in question.

In the IR, **1** has a doublet stretching vibration (3611 and 3557 cm^{-1}) associated with the hydroxyl group. The 3611- cm^{-1} band is assigned to free hydroxyl by direct comparison to phenol which has a 3610- cm^{-1} band. The lower frequency band is associated with the intramolecular interaction of the hydroxy group with the π electrons on the vinyl group. (The interaction does not involve the oxygen lone pair as a H^+ acceptor. However, the polarizable π electrons play the role of electron donor.) The intensity of the free hydroxyl band decreases as the intensity of the "H-bonding" band increases with the increasing size of the α substituent. Electron-releasing groups tend to shift the H-bonding band to lower frequency. The results from the unsubstituted and α -substituted styrenes are discussed later.

In the UV, **1** has two absorption bands: one at 295 nm and the other at 325 nm. As the pH is increased, the 295-nm band decreases in intensity while the 325-nm band begins to dominate the spectrum. The 325-nm band is the absorption associated with the phenolate ion. A similar result is observed in the fluorescence spectrum (346 and 420 nm). The 420-nm band corresponds to the phenolate. By comparing the UV and the fluorescence spectra at 295 and 346 nm, a mirror-image relationship is observed which is indicative of a near-Franck-Condon excited state for the unionized form and implies that only minor changes in geometry occur upon excitation.

In contrast, the UV and fluorescence spectra of **2**, **4**, **10**, and **12** have only one band each (294 and 342 nm, respectively) as expected.

Product Quantum Yields. The product quantum yields for the compounds **1**–**12** were measured as a function of the medium acidity at a substrate concentration of 10^{-5} M. The photochemical reactions were followed by observing the changes in the UV spectra (Figure 2), since the substrate and product absorption characteristics were quite different. Two clean isosbestic points were observed in the UV spectra for most compounds studied, which indicated that only two interconvertible absorbing species were present: reactant and product. The time of irradiation (RPR-100 Rayonet Reactor; 200 W) for the example in Figure 2 is a total of 2 min at 300 nm in water. The reaction is obviously very fast.

The sigmoidal-type quantum yield curves strongly suggest that the protonation is the rate-determining step in these photohydration reactions. In the region of pH 8–1, not enhancement in the quantum yield for compound **9** is observed even though the acidity changes by seven orders of magnitude. This is explained by very rapid intramolecular photoprotonation of the vinyl moiety followed by attack of water. External protonation in this region does not compete to any significant extent. All *o*-hydroxystyrenes studied showed a flat, pH-independent, quantum yield region of at least 5 units from pH 8 down, showing that intramolecular proton transfer is an important process, before external catalysis takes over.

In the case of the nitro-substituted *o*-hydroxy- and *o*-methoxystyrenes, the product quantum yields are not dependent on the medium acidity over a wide range (pH 10 to $H_0 = -1.5$). However, efficient photohydration is observed, which suggests that a different photohydration mechanism from the non-nitro-substituted styrenes is operative, as previously reported.⁴ The products isolated and identified are the 2-nitroaryl ethanols arising from anti-Markovnikov addition of water to the double bond.

Fluorescence Quenching Studies. Fluorescence of all non-nitro-substituted styrenes could be quenched at low pH by the addition of sulfuric acid (Figure 3). Plots of the relative

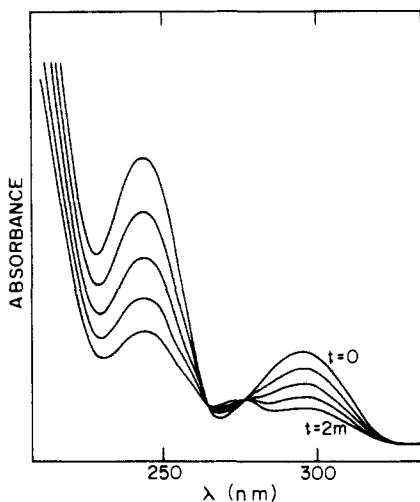


Figure 2. Ultraviolet spectra of *o*-hydroxystyrene in water as a function of irradiation time ($t = 0$ – 2 min at 300 nm.)

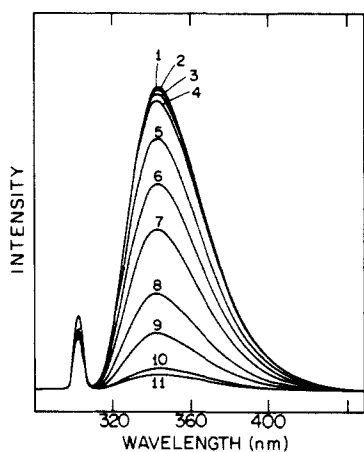


Figure 3. Quenching of fluorescence in aqueous sulfuric acid for *o*-methoxystyrene (**2**). Fluorescence spectra 1–11 measured at pH (H_0) values of 5.01, 4.03, 2.98, 2.07, 1.81, 1.22, 0.97, 0.61, 0.11, -0.54 , and -0.69 , respectively.

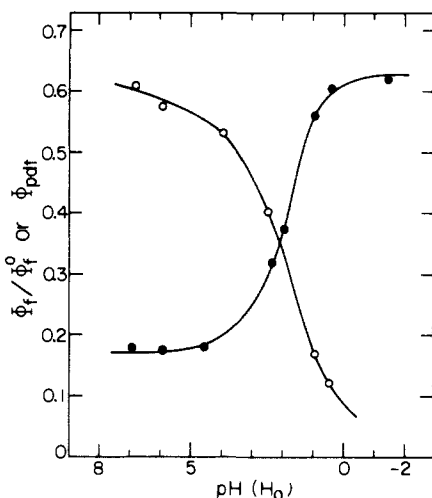
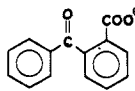


Figure 4. Complementary product quantum yield and fluorescence quenching curves at 346 nm for *o*-hydroxystyrene, as a function of pH: open circles, Φ_t/Φ_t^0 ; closed circles, Φ_{pdt} .

fluorescence quantum yield (at 346 nm) vs. pH have an inverse relation to the product quantum yield vs. pH dependence. That is, concurrent with the increased product formation, the fluorescence intensity (at 346 nm) decreases (Figure 4). This behavior strongly suggests that proton transfer is the single most important step in the photohydration reaction. From these ob-

Table I

Sensitizers	E_t (kcal/mol)	λ_{ex} (nm)
acetone 13	79	300
 14	68	350

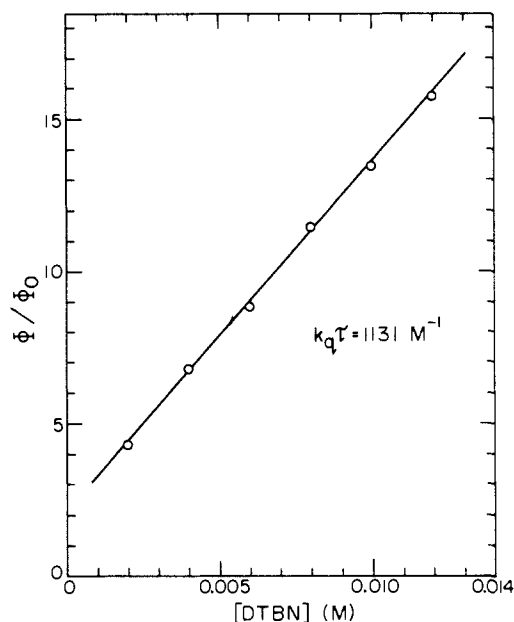


Figure 5. Quenching of photohydration of 2-methoxy-5-nitrostyrene by DTBN.

servations, it is probable that all non-nitro-substituted compounds studied react via the lowest singlet excited state. The nitro-substituted compounds exhibited no observable fluorescence.

Triplet Sensitization and Quenching Studies. In order to determine whether or not the triplet state is involved, sensitization experiments were carried out. Two of the sensitizers used are shown in Table I along with the triplet energies⁹ and the wavelength of irradiation. Enough water-soluble triplet sensitizer was added to an aqueous solution of substrate to ensure that the sensitizer absorbed at least 95% of the incident light. The nitro-substituted styrenes when sensitized afforded the expected anti-Markovnikov products which were identified by ¹H NMR and mass spectrometry. (In the case of non-nitro-substituted styrenes, only starting material was recovered, thus indicating these compounds react only via the singlet excited state.)

The photohydration for compounds **5**–**8** was sensitized by both **13** and **14**. Based on this information, the triplet-state energy is less than 65 kcal mol⁻¹ which is in the range of the known triplet energy of phenylacetylene (ca. 72 kcal mol⁻¹) and that of nitrobenzene (ca. 60 kcal mol⁻¹).⁹

Quenching of **6** was effected by using di-*tert*-butyl nitroxide (DTBN), a known quencher of triplet states with energies greater than ca. 55 kcal mol⁻¹.¹⁰ The quantum yield was determined as a function of [DTBN] and produced a linear Stern–Volmer-type

(9) (a) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973. (b) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.

(10) Schwerzel, R. E.; Caldwell, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 1382.

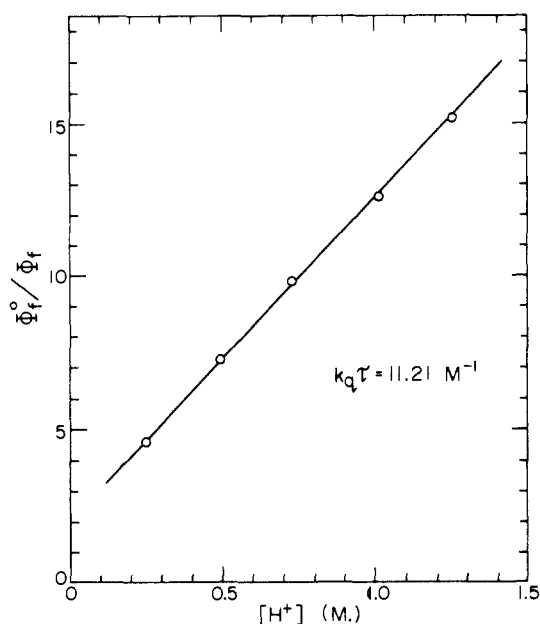


Figure 6. Plot of Φ_f^0/Φ_f vs. $[H^+]$ for *o*-hydroxystyrene.

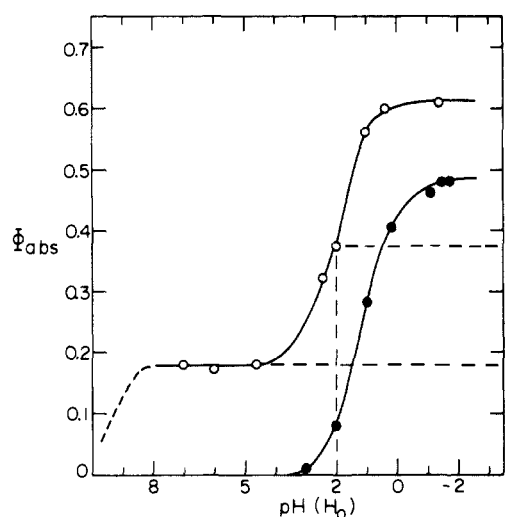


Figure 7. Absolute quantum yields vs. pH for the photohydration of *o*-hydroxy- (open circles) and *o*-methoxystyrene (closed circles).

plot (Figure 5). Using a value of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_q , the triplet lifetime for **6** was estimated to be $1.13 \mu\text{s}$ in 4% acetonitrile-water. This is very similar to the values previously obtained for *m*-nitrostyrene, and *m*-nitrophenylacetylene.⁴ A comparable lifetime would be expected for **8** due to the structural similarity to **6**.

Photoprotonation Rate Constants. A similar quenching study of **2** at higher acidities, where $[H^+]$ is the quencher, is shown in Figure 6. From this linear Stern-Volmer plot and the singlet lifetime of **2** determined by single photon counting (3.62 ns), k_H was calculated to be $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The relationship between **1** and **2** can be seen in Figure 7 to be very similar at low pH where external proton transfer is dominant in both cases. The near parallelism of the curves in the pH 3 to $H_0 = -2$ region indicates that k_H for **1** is probably very similar to the above value for **2**. Using eq 1 and 2 derived from Scheme I, the following equality can be derived at pH 2 where the efficiencies of photohydration for the intra- and intermolecular processes are approximately equal:

$$\frac{k_H[H^+]}{\sum k_d + k_H[H^+] + k_{ipt}} = \frac{k_{ipt}}{\sum k_d + k_H[H^+] + k_{ipt}}$$

Making the reasonable assumption that $\sum k_d$ is the same in both cases the value of k_{ipt} can be estimated to be $3 \times 10^7 \text{ s}^{-1}$. Compounds **9** and **10** were studied using the same types of experiment.

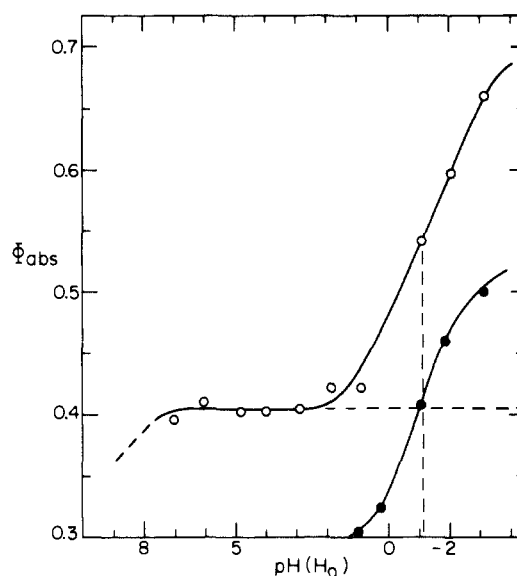


Figure 8. Absolute quantum yields vs. pH for the photohydration of α -methyl-*o*-hydroxy- (open circles) and α -methyl-*o*-methoxystyrene (closed circles).

Single photon counting determined the excited-state lifetime of **10** to be 5.20 ns. The slopes of the Stern-Volmer plot for **10** was found to be 16.1 M^{-1} . The inflection point (Figure 8) for both **9** and **10** occurs at $H_0 = -1.15$ (or $[H^+] = 2.6 \text{ M}$). The rate constant for intramolecular proton transfer for **9** was thus estimated to be $8.05 \times 10^9 \text{ s}^{-1}$. It should be noted that in this treatment (Scheme I) it is assumed that the product of protonation (whether internal or external) goes to form product with unit efficiency.

Effective Concentration or Molarity. A comparison of the inter- and intramolecular reaction rates gives the effective concentration or molarity (EM). Kirby has reviewed the topic of effective molarities and compiled some 400 EM's in various structural categories.¹¹ The EM's for **1** and **9** were calculated to be 10^{-2} and 2.6 M, respectively.

Discussion

The rate-limiting step for photohydration of aromatic alkenes and alkynes is protonation of the singlet excited state.^{4,12} The excited molecules probably have a high degree of charge transfer, with the transition dipole being toward the side chain. This type of intermediate has been postulated by a number of previous workers in their study of photoprotonation reactions.¹³⁻¹⁵ Styrenes are also known to be able to undergo stabilizing twisting motions upon excitation.¹⁶ Trapping of the protonated excited state by water molecules from the solvation shell must be very rapid in the subsequent step, which leads to only one hydration product. This step could occur before or after electronic deactivation of the polarized S_1 species, depending on whether protonation is adiabatic or not.

The nitro-substituted *o*-hydroxystyrenes undergo reaction by a different mechanism characterized by the rate-limiting attack of water at the β carbon of a highly polarized triplet excited state, with the transition dipole being oriented toward the nitro group. The result of such a reaction is overall anti-Markovnikov addition of water. The reverse polarized intermediate is consistent with the powerful electron-withdrawing character of the nitro group in the excited state.¹⁸

- (11) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.
- (12) Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 869.
- (13) Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1.
- (14) Kropp, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 4611.
- (15) Hixson, S. S. *Tetrahedron Lett.* **1973**, 277.
- (16) (a) Salem, L.; Stohrer, W.-D. *J. Chem. Soc., Chem. Commun.* **1975**, 140. (b) Salem, L.; Rowland, C. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 92.
- (c) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.
- (17) Wan, P.; Boyd, M.; Yates, K. *J. Org. Chem.* **1985**, *50*, 2881.

The acid-catalyzed photohydration of substituted aromatic alkenes and alkynes appears to be a general reaction^{4,7,13} even though different pathways are involved for singlet and triplet state reactions. The photohydration of *o*-hydroxystyrenes presents a new reaction pathway, which gives some insight into rate constants for intramolecular proton transfer in the excited state and geometrical requirements for more efficient transfer. This is in contrast to the ground-state reaction in which all aromatic alkenes and alkynes afford Markovnikov addition products by rate-limiting external protonation.^{3,4}

Comparing the absolute quantum yields for other styrenes to those for *o*-hydroxystyrenes (including those with α -methyl substituents), it can be seen how markedly the efficiency of the photohydration reaction is improved in neutral aqueous solution. Styrene has an absolute quantum yield of 0.02 at pH 7.¹⁹ Figures 7 and 8 show that the absolute quantum yields for **1** and **9** at this pH are 0.19 and 0.41, respectively. Infrared and ultraviolet data have been used to predict the intramolecular "H-bonding" nature of **9**.⁸ The hydroxy group- π interaction is enhanced by substituting a methyl group for hydrogen in the α position on **1**. The substituent exerts an electronic and steric effect which forces the vinyl group out-of-plane with the benzene ring. The rotation around the carbon-carbon bond will result in the loss of some resonance stabilization energy but will allow overlap between the hydroxyl group and the π orbitals. Theoretical calculations indicate that the minimum energy gauche cis conformation has an angle of about 45° between the vinyl moiety and the benzene ring.²⁰

In order to examine how catalytic efficiency depends on structure, a comparison between the intra- and intermolecular reaction rate can be made. The most commonly used comparison method is that of effective molarity. Effective molarity is formally the concentration of the catalytic species required to make the intermolecular reaction go at the observed rate of the corresponding intramolecular process.¹¹ From the reported results, a seemingly small structural change has caused the intramolecular reaction to be much faster than the intermolecular reaction at pH 7. In addition the photohydration reaction is probably general acid catalyzed. These conclusions are based on compiled data in a review by Kirby¹¹ and a study of substituted aromatic alkenes.¹²

Schubert and Keefe determined the protonation rate constants for thermal hydration of monosubstituted styrenes to be in the range 10^{-5} to 10^{-7} M⁻¹ s⁻¹.^{3b} The excited states of these molecules are therefore approximately 10^{11} – 10^{14} times more reactive toward protonation (and hydration) than their ground states. Proton transfer to ground-state neutral carbon bases is normally very slow,²¹ especially in comparison to protonation rates for oxygen and nitrogen bases. The reasons for this are believed to lie in the electronic distributions and geometries involved. Rehybridization at carbon is required for efficient proton transfer. In the excited states of molecules of the present type, both requirements can be met, that is, highly developed charge-transfer character and twisted or bent geometries.

The enhanced rate of intramolecular proton transfer, observed for *o*-hydroxystyrene, and for *o*-hydroxyphenylacetylene,² is attributed to the increased acidity of the phenolic OH group and the simultaneous increase in basicity of the vinyl or acetylenic group, on electronic excitation.⁵ The quantum yields for photohydration are acidity independent over wide ranges of pH, although in the case of *o*-hydroxystyrenes external protonation begins to compete at low pH and eventually becomes dominant. For those substrates with no nitro groups, the quantum yield dependence on pH becomes sigmoidal at higher acidities with inflection points coinciding reasonably well with those for fluorescence quenching

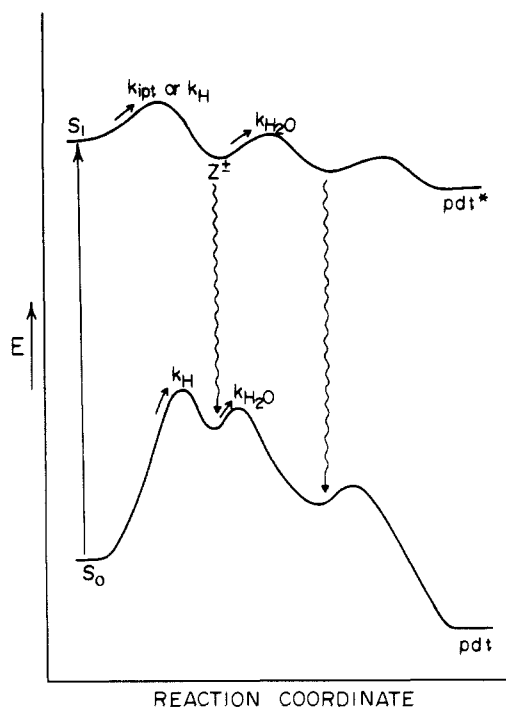


Figure 9. Schematic comparison of excited- and ground-state reaction coordinate diagrams for the hydration of *o*-hydroxystyrenes. Relative energy levels are not drawn to scale.

between pH (H_0) 2 to -1. This suggests that these compounds have pK^* values which are shifted many orders of magnitude from their ground-state values.²² Such large shifts in acidity and basicity ($\Delta pK = pK^* - pK$) are well documented for conjugated aromatic systems.⁵

The decrease in quantum yield observed at high pH for the *o*-hydroxystyrenes and phenylacetylenes is attributed to ground-state deprotonation of the phenolic OH group before irradiation takes place. The ground-state pK^* s for **1** and **9** were determined by spectroscopic and potentiometric methods to be 9.65 and 9.71, respectively, which correspond reasonably well with the high pH inflection points in Figure 1a,b.

An attempt to compare the potential energy surfaces for the ground- and excited-state reactions is made in Figure 9. From all available evidence proton transfer is the rate-determining step in both cases. The ground-state energy barrier is about 20 kcal mol⁻¹, as estimated by Noyce and Schiavelli,^{3a} which means the thermal process is slow, even at high acidities. Excitation (at 254 and 300 nm) provides 95–110 kcal of excess energy, which is more than enough to pass the high thermal barrier, providing proton transfer can compete with fluorescence and other nonproductive deactivation processes. All k_H or k_{ipt} values estimated or measured so far for substituted styrenes and phenylacetylenes are in the 10^6 – 10^9 s⁻¹ range,⁴ showing that proton transfer can compete efficiently. Deactivation of the protonated excited state (or zwitterion in the case of k_{ipt}) could occur at several points on the excited-state surface, and it is most unlikely that the reaction is adiabatic over the entire surface. Proton transfer could result in immediate deactivation, but there is evidence¹⁷ that cations of the

(18) (a) Zimmerman, H. E.; Somasekhara, S. J. *J. Am. Chem. Soc.* **1963**, *85*, 922. (b) Havinga, E.; Kronenberg, M. E. *Pure Appl. Chem.* **1968**, *16*, 137. (c) Dopp, D. *Top. Curr. Chem.* **1975**, *55*, 49.

(19) The reaction of styrene is, however, much more efficient than this in acid solution.⁴

(20) Trinquier, G.; Malrieu, J.-P. *J. Mol. Struct.* **1978**, *49*, 155.

(21) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 131.

(22) Substituted phenols have ground-state pK values around 9 to 10, while pK^* values have been estimated by Forster cycle calculations and fluorescence titrations to be in the 3–4 range. Ground-state pK_{BH^+} values for styrenes cannot be measured directly,²³ but it is reasonable to assume they are weaker bases than benzonitrile ($pK_{BH^+} = -10$).²⁴ If the inflection points of the sigmoidal fluorescence quenching curves vs. pH are used as a crude²⁵ estimate of $pK^*_{BH^+}$, these are in the 0 to -2 range.⁴

(23) Jencks and Richard, however, have estimated that *p*-methylstyrene has $pK_{BH^+} = -11$.²⁶

(24) Liler, M. *Reaction Mechanisms in Sulfuric Acid*; Academic Press: London, 1971; p 103.

(25) Schulman, S. G.; Capomacchia, A. C. *Spectrochim. Acta, Part A* **1972**, *28*, 1.

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present type can be formed adiabatically in aqueous solution. Nucleophilic attack of water on the ion would almost certainly deactivate the molecule to a vibrationally excited ground state, or equally via multiple collisions before nucleophilic attack actually takes place. In either event, the reaction can proceed along the ground-state surface toward completion. The use of electronic excitation to overcome the large thermal barrier to reaction thus eliminates the need for concentrated acid solutions or elevated temperatures in this type of reaction.

One important and puzzling question remaining is why external protonation can obviously compete with fast intramolecular proton transfer at low pH in the case of the *o*-hydroxystyrenes, but apparently does not in the case of *o*-hydroxyphenylacetylene. As reported previously,² the quantum yield for photohydration in the latter case is independent of acidity from pH 8 down to $H_0 = 0$, and there is no indication of a subsequent increase in quantum yield as in the case of **1** and **9**. Since external acid catalysis (as measured by k_H) is at least as effective for meta- and para-substituted phenylacetylenes as for analogous styrenes,^{4,12} this is puzzling. It does not seem likely that k_{ip} for *o*-hydroxyphenylacetylenes could be that much greater than the values of 10^7 – 10^9 s⁻¹ estimated for **1** and **9**. One plausible explanation is that the hydrogen-bonded conformations^{3,20} (*gauche*–*cis*) required for efficient intramolecular proton transfer in the styrene case, would not sterically prevent external attack by H_3O^+ on the opposite face of the vinyl group, whereas the corresponding conformation of *o*-hydroxyphenylacetylenes, with the acetylenic group bent in an *s-trans* configuration could prevent intermolecular attack by H_3O^+ from either side due to the steric effect of the C–H bond or a hydrogen bond. Additional work is in progress on phenylacetylene systems to answer this question.

Experimental Section

General Procedures. The ¹H NMR spectra were recorded on a Varian T-60 spectrometer using CDCl₃ with Me₄Si as internal standard. The UV spectra were obtained with a Varian 2300 (UV-VIS-NIR) spectrometer. The IR spectra were recorded using a Nicolet 5DX FTIR spectrometer. Fluorescence spectra were obtained from a Perkin-Elmer MPF-44B spectrometer.

Irradiation Procedures. Preparatory scale irradiations were performed in a Rayonet RPR-100 reactor. The wavelengths for the irradiation available were 254, 300, and 350 nm. Approximately 150–300 mg of substrate as dissolved in ca. 600 mL of acetonitrile–water (minimum amount of acetonitrile was used). The solution was purged with nitrogen or argon gas for 20 min. The solution was stirred continuously with a magnetic stirring bar.

For absolute quantum yield determinations, a GE 250-W medium-pressure lamp was used. The monochromatic light obtained from the Bausch and Lomb high-intensity monochromator (blaze 250 nm; dispersion 3.2 nm/mm) with variable slits was passed through a Corning 7-54 band-pass filter, a variable iris, a series of focusing lens, and a beam splitter to two cuvette cells containing a sample and a chemical actinometer.

Product Isolation. A typical experiment involved the following procedure. A solution of 200 mg of *o*-hydroxystyrene (**1**) in 25 mL of acetonitrile was added to 550 mL of water. Additional acetonitrile was added until the opaqueness of the solution just disappeared (usually 25–50 mL). The solution once prepared was purged with argon for 20 min in a quartz tube vessel. A cold finger (circulating water) was used to prevent any thermal reaction during the irradiation. The reaction was followed by UV spectroscopy. After 1 h the solution was saturated with NaCl and extracted with 100 mL of dichloromethane, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator. A slightly yellow (190 mg) oil was recovered. Analysis and comparison with an authentic sample (prepared by NaBH₄ reduction of acetophenone in

ethanol) proved the product to be 1-(2'-hydroxyphenyl)ethanol in good yield (>85%). Product mixtures were analyzed using a combination of GC, NMR, and UV techniques.

Product Quantum Yield. Malachite green leucocyanide²⁶ (MGL) in acidic ethanol solution was used as the chemical actinometer. It was found that this was much more suitable than potassium ferrioxalate for the short irradiation times used (≤4 min), since the absorption changes obtained using potassium ferrioxalate were too small to give reliable quantum yields, whereas under the present conditions MGL reacts at a rate more comparable with those of the *o*-hydroxy- and *o*-methoxystyrenes. MGL was synthesized according to the method of Calvert and Rechen,²⁸ mp 174–176 °C (lit.²⁸ mp 176–177 °C). The actinometer solution was prepared by mixing 0.5 mL of a 10⁻³ M HCl in ethanol with 2.5 mL of 10⁻³ M stock solution of MGL in ethanol in a quartz cuvette. The optical density (OD) of MGL was measured at 622 nm. The OD of the substrate to be studied was also measured at its λ_{max} . The change in OD (ΔA) was then used to calculate the light intensity of the source by the equation:

$$I [\text{in einsteins}/(\text{min}\cdot\text{cm}^2)] = 10^3 \Delta A / \epsilon_{622} \Phi_{MGL} \Delta t$$

where ϵ_{622} is the extinction coefficient of the blue dye produced at 622 nm (1.063×10^5 cm²/M),²⁷ Φ_{MGL} is the quantum yield for dye formation (0.91),²⁰ and Δt is the elapsed time for the irradiation in minutes.

Lifetimes. The lifetimes were measured using pulsed fluorometry and single photon-counting technique.²⁹ Excitation was through a Jarrell-Ash monochromator (250–330 nm) and the emission was isolated by a combination of band-pass and cutoff filters. The substrate concentrations were 10⁻⁵ M in doubly distilled water.

Sensitization and Quenching Experiments. To the solution in the product isolation section, 15 g of sensitizer **14** was added. The irradiation time was doubled and the same work-up procedure was followed.

For the triplet quenching experiments, the substrate and a known amount of DTBN were dissolved in 10% acetonitrile–water and irradiated after purging with argon. After workup, the amount of product was determined.

Synthesis of Substrates. *o*-Hydroxystyrene (**1**), β -methyl-2-hydroxystyrene (**3**), β -methyl-2-hydroxy-5-nitrostyrene (**7**), 2-hydroxy-5-nitrostyrene (**5**), and α -methyl-2-hydroxystyrene (**9**) were prepared according to the methods of Dale and Hennis,³⁰ Vogel,³¹ modified Vogel procedure,³¹ Surpateanu et al.,³² and Oki and Iwamura,⁸ respectively.

The methyl ethers were all prepared in the same way. To a solution of substrate (1.5 g) in acetone (25 mL), a twofold excess of methyl iodide and a 15% solution of sodium hydroxide (25 mL) are added. The mixture was stirred overnight. Workup consisted of adding water (50 mL) and extracting with dichloromethane. The organic layer was dried and concentrated. The yields varied between 45 and 85% depending on the nature of the starting material.

Compounds **11** and **12** were obtained from commercial sources and distilled before use.

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Registry No. **1**, 695-84-1; **2**, 612-15-7; **3**, 6380-21-8; **4**, 10577-44-3; **5**, 3179-08-6; **6**, 103851-61-2; **7**, 103851-62-3; **8**, 103851-63-4; **9**, 10277-93-7; **10**, 10278-02-1; **11**, 2628-17-3; **12**, 637-69-4.

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