# *m*-Quinone Methides from *m*-Hydroxy-1,1-Diaryl Alkenes via Excited-State (Formal) Intramolecular Proton Transfer Mediated by a Water Trimer

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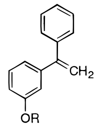
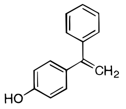
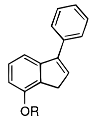
Excited-state intramolecular proton transfer (ESIPT) reactions are of fundamental interest.[1] ESIPT generally occurs when both basic and acidic groups are present on the same molecule and when excitation leads to enhancement of their basicity and acidity, respectively. The most commonly observed examples are when the basic and acid groups share a hydrogen bond,[1] which facilitates the proton transfer, although in many of these cases one may view these reactions as hydrogen transfers or the tunneling of a proton.[1] Although much less common and restricted to only a few molecular systems, examples in which one or more water (or alcohol) molecules or substrate mediates the ESIPT (via a "proton relay" mechanism resulting in *formal* intramolecular proton transfer) are also known.[1,2] In continuing work[3] on the use of hydroxybenzyl alcohols and related compounds as precursors for the photogeneration of quinone methides (QMs), we came upon the opportunity of studying the photochemistry of *m*- and *p*-hydroxy-substituted 1,1-diaryl alkenes **1**−**3** in aqueous solution.



**1** R = H
**4** R = $CH_3$

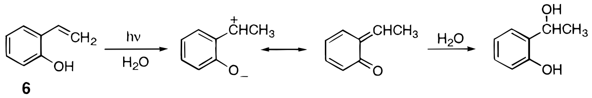


**2**



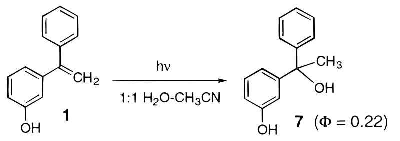
**3** R = H
**5** R = $CH_3$

Kalanderopoulos and Yates[4] reported the efficient photohydration of *o*-hydroxystyrenes via ESIPT from the phenol to the $\beta$-carbon of the alkene moiety, to generate proposed *o*-QMs,[5] resulting in $\beta$-arylethanol products, as shown in eq 1 for the parent *o*-hydroxystyrene (**6**). We decided to test whether ESIPT can operate for *m*- and *p*-hydroxy-substituted styryl systems **1**−**3** (which would give rise to *m*- and *p*-QMs, respectively) where the acid/base moieties are distal from each other. We find that all of **1**−**3** react efficiently in aqueous solution, to give the corresponding photohydration product, and show that the mechanism involves proton transfer (formally intramolecular) requiring a "proton relay" mechanism assisted by solvent water.



(1)

The photohydration of hydroxy-substituted styryl compounds **1**−**3** were initially studied, chosen such that if the corresponding QM were photogenerated, its UV−vis absorption spectra would be readily detected by nanosecond laser flash photolysis (LFP), based on results of earlier work.[3,6] Photolysis of **1** in 1:1 $H_2O/CH_3CN$ (~$10^{-3}$ M; Rayonet RPR-100 photochemical reactor; 254 nm lamps; <15 °C; argon-purged solutions; 2−10 min) gave diarylmethanol **7** cleanly with high quantum yield (> 40%; $\Phi = 0.22$) (eq 2), whereas photolysis of *m*-methoxy-substituted derivative **4** gave a residual amount of the corresponding photohydration product only after extended photolysis ($\Phi \leq 0.02$). Photolysis of 1,1-diphenylethylene even under extended photolysis times resulted in no reaction. Photolysis of the *p*-isomer **2** also yielded the corresponding photohydration product cleanly ($\Phi \approx 0.1$). Similar photohydration chemistry was observed for indene **3** ($\Phi = 0.24$). In this case, the photohydration product was found to be thermally labile and readily dehydrated back to **3** on workup. However, photolysis in an NMR tube in $D_2O/CD_3CN$ showed clean formation of the expected alcohol. All of these results indicate that the hydroxyl group is necessary for efficient photohydration in these compounds suggesting the possibility of ESIPT as the primary photochemical step.[7]



(2)

Steady-state fluorescence studies provided additional details with respect to the photohydration mechanism. As shown in Figure 1, addition of small amounts of $H_2O$ to a $CH_3CN$ solution of **1** (or **3** but not **4**, **5**, or 1,1′-diphenylethylene) efficiently quenched the fluorescence emission. $CH_3OH$ quenches to a much lesser extent, and THF quenches not at all. However, the Stern−Volmer plots are not linear and are curved upward. This curved dependence on $H_2O$ concentration in Stern−Volmer analysis has been previously observed for several other excited-state proton transfer systems where a modified plot using higher order dependence on water concentration was used to linearize such plots thus providing information with regard to the molecularity of the quencher.[8] The fluorescence quenching data for **1** and **3** fit the modified Stern−Volmer plot with a cubed quencher concentration dependence (Figure 2). This is consistent with an ESIPT mechanism in which water in the form of a trimer is involved in the deactivation of the singlet state and responsible for the reaction. The rate constants for quenching of **1** and **3** by $H_2O$ were $3.2 \times 10^8$ $M^{-3}$ $s^{-1}$ and $1.5 \times 10^8$ $M^{-3}$ $s^{-1}$, respectively. Use of $D_2O$ resulted in ~50% less efficient quenching for both **1** and **3**, again consistent with proton transfer as the primary photochemical

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(1) (a) Formosinho, S. J.; Arnaut, L. G. *J. Photochem. Photobiol. A* **1993**, *75*, 21. (b) Kasha, M. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2379. (c) Heldt, J.; Gormin, D.; Kasha, M. *Chem. Phys.* **1989**, *136*, 321. (d) Le Gourrierec, D.; Ormson, S. M.; Brown, R. G. *Prog. React. Kinet.* **1994**, *19*, 211. (e) Hibbert, F. *Adv. Phys. Org. Chem.* **1986**, *22*, 113.

(2) Selected references: (a) Chou, P.-T.; Wei, C.-Y.; Chang, C.-P.; Chiu, C.-H. *J. Am. Chem. Soc.* **1995**, *117*, 7259. (b) Chen, Y.; Gai, F.; Petrich, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 10158. (c) Suzuki, T.; Okuyama, U.; Ichimura, T. *J. Phys. Chem. A* **1997**, *101*, 7047. (d) Herbich, J.; Hung, C.-Y.; Thummel, R. P.; Waluk, J. *J. Am. Chem. Soc.* **1996**, *118*, 3508. (e) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1984**, *106*, 850. (f) Konijnenberg, J.; Ekelmans, G. B.; Huizer, A. H.; Varma, C. A. G. O. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 39. (g) Itoh, M.; Yoshida, N.; Takashima, M. *J. Am. Chem. Soc.* **1985**, *107*, 4819. (h) Itoh, M.; Adachi, T. *J. Am. Chem. Soc.* **1984**, *106*, 4320. (i) Nimbos, M. R.; Kelly, D. F.; Bernstein, E. R. *J. Phys. Chem.* **1989**, *93*, 643. (j) Choi, J. D. C.; Fugate, R. D.; Song, P.-S. *J. Am. Chem. Soc.* **1980**, *102*, 5293.

(3) (a) Diao, L.; Yang, C.; Wan, P. *J. Am. Chem. Soc.* **1995**, *117*, 5369. (b) Wan, P.; Barker, B.; Diao, L.; Fischer, M.; Shi, Y.; Yang, C. *Can. J. Chem.* **1996**, *74*, 465. (c) Shi, Y.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1217. (d) Shi, Y.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1997**, 273.

(4) Kalanderopoulos, P.; Yates, K. *J. Am. Chem. Soc.* **1986**, *108*, 6290.

(5) The authors did not explicitly state that an *o*-QM intermediate is formed in their photohydration reactions, although the structure drawn for their zwitterionic intermediate is the commonly accepted important resonance form for such a species.

(6) The lifetime for the *m*-QM from *m*-hydroxystyrene is expected to be much less than 20 ns in aqueous solution and hence undetectable by nanosecond LFP.[3] For this reason, we have studied only *m*-hydroxystyryl system possessing an $\alpha$-phenyl group (**1** and **3**).

(7) Photolysis of **1** or **3** at pH 13 (excitation of the phenolate) gave essentially no reaction under similar photolysis times consistent with the requirement of the phenol proton in the reaction mechanism. It also rules out a stepwise mechanism in which the phenol dissociates adiabatically on excitation, to generate an excited phenolate, which then reacts by protonation (by water or hydronium ion) at the $\beta$-carbon.

(8) (a) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 10593. (b) Moore, R. A.; Lee. J.; Robinson, G. W. *J. Chem. Phys.* **1985**, *89*, 3648. (c) Lee, J.; Robinson, G. W.; Webb, S. P.; Philips, L. A.; Clark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 6538.

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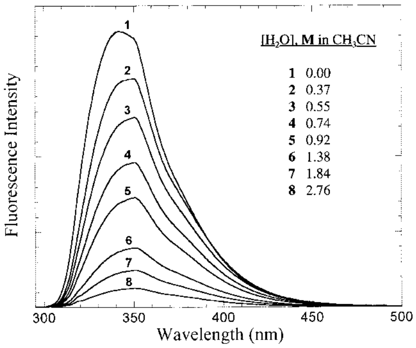


**Figure 1.** Fluorescence quenching of **1** by added $H_2O$ in $CH_3CN$ ($\lambda_{excit}$ = 290 nm; $\Phi_f$ (100% $CH_3CN$) = 0.20; $\tau$ (100% $CH_3CN$) = 5.5 ns). The fluorescence observed is that of the phenol (ArOH); emission from $ArO^-$ is not observed.

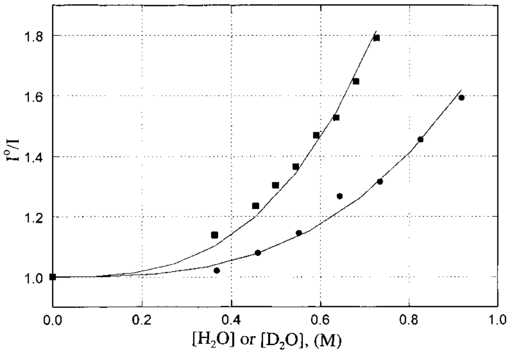


**Figure 2.** Modified Stern−Volmer plots for fluorescence quenching by $H_2O$ and $D_2O$ (in $CH_3CN$) for **1** (● $D_2O$; ■ $H_2O$). The points represent experimental data and the lines are fits to the modified Stern−Volmer equation, $I°/I = 1 + k_q[Q]^3$.

step responsible for the quenching of fluorescence.[9] Fluorescence emission from the *p*-isomer **2** was too weak for reliable quenching studies.[10] These $H_2O$-mediated ESIPTs are irreversible since photolysis of **3** in $D_2O/CD_3CN$ did not result in formation of any deuterium label at the $\beta$-carbon in substrate, which would be expected if back proton transfer was significant. Instead, these photogenerated *m*-QMs are completely trapped by $H_2O$.

Nanosecond laser flash photolysis (LFP) studies provided evidence that the primary photochemical step responsible for fluorescence quenching of **1** and **3** results in the formation of the corresponding *m*-QMs. Thus, LFP of **1**-**3** (Nd:YAG laser; 266 nm; <30 mJ/pulse; oxygen-purged and flowing solutions) in aqueous solution gave strongly absorbing long wavelength transients centered at 425, 350, and 415 nm, respectively (Figure 3), similar to those observed and assigned to *m*- and *p*-QMs reported recently.[3] The transients are produced within the laser pulse (~10 ns) and undergo clean single-exponential decay back to baseline. No transients were observed on photolysis in 100% $CH_3CN$ but addition of a small amount of $H_2O$ (<3 M) to the $CH_3CN$ solution produced increasing amounts of the above transients which corroborates the interpretation of the fluorescence quenching results. In addition, the observed lifetimes decreased with increasing water concentration consistent with nucleophilic quenching (probably concerted with proton transfer to the phenolate) by water as the main mode of reaction. LFP of **4** and **5** gave weaker signals probably assignable to radical cations (and to a minor amount of the corresponding diarylmethyl cation for **5**). These results indicate that the transients shown in Figure 3 are *m*-QMs **8** and **9**, formed from water-trimer-mediated ESIPT of **1** and **3** (in $S_1$), respectively (Scheme 1).[12,13]

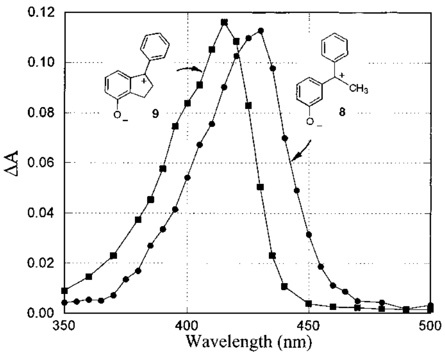
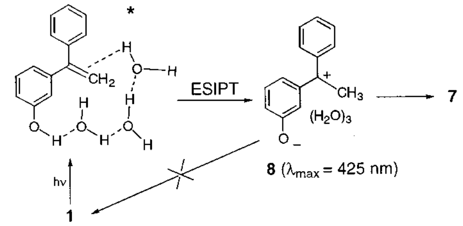


**Figure 3.** LFP transients (taken 50−60 ns after the pulse) assigned to the corresponding *m*-QMs ($\lambda_{excit}$ = 266 nm) of **1** and **3** in aqueous solution. All transient spectra are observed within the laser pulse (~10 ns). ● *m*-QM **8** from **1** (in 100% $H_2O$), $\tau$ = 47 ns; ■ *m*-QM **9** from **3** (in 9:1 $H_2O/CH_3CN$), $\tau$ = 5.0 $\mu$s.

**Scheme 1**



In summary, ESIPT from the phenol moiety to the $\beta$-carbon of a conjugated alkene is a general reaction for all *o*-, *m*-, and *p*-isomers, giving rise to the corresponding QM intermediates. For the *m*-isomers, we have shown that the ESIPT is unique in that a very small amount of water acting in the form of a water trimer is able to catalyze the reaction in a pool of solvent $CH_3CN$. We envision that these systems may provide a new and valuable probe of the dynamics of solvent-mediated reactions. Coupled with the high quantum yields observed for these isomers, this is another example of Zimmerman's "meta-ortho effect"[14] manifesting in the hydroxy substituent.

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(9) Fluorescence quenching data from lifetime measurements also show a cubed dependence on water concentration (in the same concentration range used for the steady-state measurements) in the modified Stern−Volmer plot but the quenching effect is less than observed from steady-state measurements suggestive of both static and dynamic components in the quenching mechanism, the details of which will be reported in the full paper. Preliminary data indicate the formation of a weak substrate−water-trimer complex in the ground state which is responsible for the static component.

(10) Lewis and Yang[11] have observed that *p*-substituted amino styryl systems are only weakly fluorescent, in contrast to the much more emissive *m*-isomers. They suggested that differences in the ability to twist about the Ar−CH bond between the *m*- and *p*-isomers (the *m*-isomers being more twisted) might offer a possible explanation for the difference in fluorescence quantum yields (and lifetimes) for these isomers. In our systems, essentially no difference in fluorescence characteristics was observed between alkenes **1** and **3** although **3** is an indene where twisting about the Ar−CH bond would be prohibitive. This clearly suggests that twisting about this bond is not required for charge-transfer character in our system. Our results suggest that these reactions proceed via planar, highly polarized (charge transfer) singlet states. A study of the corresponding *p*-hydroxy-substituted indene derivative might provide more information as to why the *p*-isomer is much less fluorescent.

(11) Lewis, F. D.; Yang, J.-S. *J. Am. Chem. Soc.* **1997**, *119*, 3834.

(12) Only singlet state reactivity (for ESIPT) of these compounds is studied in this work. The corresponding triplet states are not expected to undergo ESIPT due to their expected diradicaloid character. In addition, it is well-known that triplet excited phenols have similar p$K_a$ values as in the ground state and would not provide a driving force for the proton transfer.

(13) There is no evidence to indicate that the ESIPT of these compounds is adiabatic. Indeed, even if the *m*-QMs were photogenerated adiabatically, they would be very short-lived due to their high intrinsic reactivity (carbocationic species), resulting in negligible fluorescence emission, if any. In addition, fast radiationless deactivation to the ground state would be expected due to the inherent conformational flexibility of these carbocation-like structures.

(14) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1995**, *117*, 8988. (b) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915.