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o-Quinone methide formation from excited state intramolecular proton transfer (ESIPT) in an *o*-hydroxystyrene

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Abstract

The photohydration of *o*-hydroxy-α-phenylstyrene (**7**) has been studied using product studies, laser flash photolysis (LFP), and fluorescence measurements, and shown to react via excited state intramolecular proton transfer (ESIPT), to give the corresponding *o*-quinone methide (**13**) ($\lambda_{max} = 310$, 420 nm in 1 : 1 H_2O–CH_3CN). The same intermediate was also observed on LFP of *o*-hydroxybenzyl alcohol (**10**), a system known to give *o*-quinone methides efficiently, but via a different mechanism. ESIPT of **7** to give **13** is not significantly enhanced by water as the species was also observed in neat CH_3CN; addition of water (up to 1 : 1 H_2O–CH_3CN) did not increase its yield substantially. Efficient ESIPT of **7** in neat CH_3CN is corroborated by its low fluorescence emission quantum yield and subnanosecond fluorescence lifetime. These results provide new insights into ESIPT from phenol to alkene carbon, a process that has not received much attention although **7** is a close relative of *o*-hydroxybenzophenone (**8**), an archetypical system for the illustration of ESIPT. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Quinone methide; Excited state intramolecular proton transfer; Hydroxystyrene; Photohydration

1. Introduction

Excited state intramolecular proton transfer (ESIPT) is a well-known and intensively studied fundamental process in photochemistry and photophysics [1–4]. The energy wasting back proton transfer in these systems is in general very efficient, and as such, many molecules of this type have been used as important UV photostabilizers although more novel applications have been suggested. In general, ESIPT occurs when two functional groups (on the same molecule) which are in reasonable close proximity to each other experience enhancements in both acidity and basicity on photochemical excitation (mostly via the singlet excited state). Much of the literature in this field have been concerned with substituents that are in an *ortho* arrangement, where the presence of a hydrogen bond between the two functional groups assists ESIPT. Moreover, almost all of these ESIPT involve proton transfer between heteroatoms, oxygen being the most common.

The first example of an ESIPT from phenol to carbon (alkene or alkyne) was proposed by Yates and coworkers [5,6] in their study of the photohydrations of *o*-hydroxystyrene (**1**, Eq. (1)) and *o*-hydroxyphenylacetylene. The ESIPT reported was claimed to be the first to be irreversible since the proton transferred to the vinyl carbon (from phenol), to form **2a**, is unlikely to deprotonate fast enough back to the phenolate oxygen to compete with trapping by water. Yates and coworkers [5,6] wrote only species **2a** as the first formed intermediate in the ESIPT, which is subsequently trapped by water to give the final (Markovnikov) photohydration product **3**. However, one would expect that an important resonance contributor to **2a** is the *o*-quinone methide structure **2b**. Our present interest in this reaction is motivated by our general interest in the photogeneration of quinone methides [7,8] as well as our recent demonstration [9] that *m*-hydroxystyrenes **4** and **5** undergo formal ESIPT, to generate the corresponding *m*-quinone methides, e.g., **6** from **4**.

The ESIPT process of **1** would be difficult to study by laser flash photolysis (LFP) since the resulting *o*-quinone methide **2b** (**2a**) would be difficult to detect due to anticipated low ε in the readily accessible wavelengths (>300 nm) for detection [10]. Therefore, we decided to study *o*-hydroxy-α-phenylstyrene (**7**) since the addition of the α-phenyl group will provide the required extended

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conjugation to make the corresponding *o*-quinone methide readily observable by LFP if photogenerated, based on previous work [7,8]. Indeed, **7** may be considered as the 'carbon' analog of *o*-hydroxybenzophenone (**8**), a compound whose ESIPT process has been well-studied [11]. For completeness, the related compounds **9–11** are also studied as well as *o*-hydroxy-*t*-stilbene (**12**), the latter to address the question of whether ESIPT can compete with *trans–cis* photoisomerization, a process known to be very fast from either S_1 or T_1.

2. Experimental details

2.1. General

^{1}H NMR spectra were obtained on a Bruker AC300 (300 MHz) spectrometer in $CDCl_3$. Low resolution mass spectra were obtained on a Finnigan 3300 (CI) and HRMS were obtained on a Kratos Concept H (EI) instrument. UV–Vis spectra were recorded on a Varian Cary 5 instrument.

2.2. Materials

Acetonitrile (HPLC grade) used in fluorescence and LFP experiments was dried with calcium hydride and distilled prior to use. THF used in Grignard reactions was dried with sodium metal and distilled prior to use. Methylene chloride was also distilled prior to use. The starting materials 2-hydroxyacetophenone, 2-methoxyacetophenone, salicylaldehyde, triphenylphosphine, benzyl bromide, ethyl vinyl ether (EVE) and *n*-BuLi were purchased from Aldrich and used as received. Phenylmagnesium bromide was prepared from bromobenzene and magnesium in THF. All alkene products isolated were stored in the refrigerator to minimize decomposition. Preparative thin layer chromatography (TLC) was carried out on 20 cm × 20 cm silca gel GF plates.

2.2.1. α-Methyl-o-hydroxybenzhydrol (10)

2-Hydroxyacetophenone (5.0 g, 36.7 mmol) in 50 ml THF was added dropwise to a THF solution (150 ml) of phenylmagnesium bromide (26.6 g, 147 mmol). The reaction mixture was refluxed overnight under nitrogen. It was quenched with water and ice and the aqueous layer was extracted with 75 ml CH_2Cl_2 (3×). The combined organic layers were washed with saturated $NaHCO_3$, dried and concentrated. The white solid obtained was recrystallized from hot toluene producing the pure product in moderate yield, 4.41 g (56%), m.p. 109–110°C, ^{1}H NMR ($CDCl_3$), δ 1.97 (s, 3H, CH_3), 2.91 (s, 1H, OH), 6.78–7.41 (m, 9H, ArH), 8.37 (s, 1H, OH); mass spectrum (CI) *m*/*z* 197 ($M^+ + 1$); IR (cm^{-1}) 3367, 1585, 1490, 1445, 1237, 1069.

2.2.2. α-Methyl-o-methoxybenzhydrol (11)

2-Methoxyacetophenone (5.0 g, 33.3 mmol) in 50 ml THF was added dropwise to a THF solution (150 ml) of phenylmagnesium bromide (48.3 g, 266 mmol). The reaction mixture was refluxed for 1 h. After work-up as above, the crude white solid was recrystallized from ligroine producing the pure product in moderate yield, 3.98 g (53%), m.p. 71–72°C, ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 3H, CH_3), 3.57 (s, 3H, OCH_3), 4.64 (s, 1H, OH), 6.86–7.31 (m, 9H, ArH); mass spectrum (CI) m/z 229 ($M^+ + 1$); IR (cm^{-1}) 2923, 1601, 1488, 1460, 1236, 1027

2.2.3. o-Hydroxy-α-phenylstyrene (7)

α-Methyl-*o*-hydroxybenzhydrol (10) (1.0 g, 5.14 mmol) was dissolved in 50 ml CH_3CN and a few drops of conc. H_2SO_4 added. The solution was refluxed for 1 h and $NaHCO_3$ was added to the reaction mixture and the product extracted using CH_2Cl_2. The resulting oil was purified using column chromatography (silica gel, 3 : 2 CH_2Cl_2 : hexanes). The product was obtained as a light yellow oil in moderate yield, 0.63 g (63%), ^{1}H NMR ($CDCl_3$) δ 5.16 (s, 1H, OH), 5.42 (s, 1H, =CH), 5.87 (s, 1H, =CH). 6.90–7.40 (m, 9H, ArH); IR (cm^{-1}) 3514, 3056, 1602, 1484, 1458, 1237, 1185, 1026, 781, 759, 702; HRMS (EI) calculated for $C_{14}H_{12}O$, 196.0888, observed 196.0867.

2.2.4. o-Methoxy-α-phenylstyrene (9)

α-Methyl-*o*-methoxybenzhydrol (**11**) (1.0 g, 4.40 mmol) was dehydrated using the above procedure to give a white solid in high yield 0.83 g (90%), m.p. 31.0–33.0, ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 3H, CH_3), 5.32 (s, 1H, =CH), 5.73 (s, 1H, =CH), 6.89–7.30 (m, 9H, ArH); IR (cm^{-1}) 1595, 1265, 1027, 900, 778, 751, 708; HRMS (EI) calculated for $C_{15}H_{14}O$, 210.1045, observed 210.1046.

2.2.5. trans-2-Hydroxystilbene (12)

A solution of benzyl bromide (7.2 g, 41.9 mmol) in 50 ml CH_3CN was added quickly to triphenylphosphine (10.0 g, 38.1 mmol) dissolved in 100 ml CH_3CN. The reaction mixture was stirred for 2 h at room temperature. The benzyltriphenylphosphonium bromide salt was precipitated with the addition of 100 ml of diethyl ether, which was then filtered and dried. The subsequently dried material (16.0 g, 38.2 mmol) was placed in 100 ml THF and *n*-BuLi (in THF, 38.2 mmol) was added dropwise. The solution turned a deep red colour. The reaction mixture was then refluxed for 1 h after which salicylaldehyde (1.7 g, 9.5 mmol) was added dropwise to the cooled mixture. The reaction mixture was again refluxed for 1 h and then quenched with 10% H_2SO_4, extracted with 75 ml CH_2Cl_2(3×) and dried over $MgSO_4$. Upon removal of the solvent, the crude material was separated by column chromatography (silica, 100% CH_2Cl_2). A white solid was obtained in moderate yield, 0.84 g (46%), m.p. 136–138.0°C, ^{1}H NMR ($CDCl_3$) δ 4.99 (s, 1H, O*H*) 6.79 (dd, $J = 8$ Hz, $J = 1.2$ Hz, 1H, *o*-H to OH), 6.95 (td, $J = 7.5$ Hz, $J = 1.2$ Hz, 1H, *m*-H to OH), 7.14 (td, $J = 7.5$ Hz, $J = 1.7$ Hz, 1H, *p*-H to OH), 7.11 (d, $J = 16$ Hz, 1H, =CH *trans*), 7.23–7.28 (m, 1H, ArH), 7.37 (d, $J = 16$ Hz, =CH *trans*), 7.34–7.37 (m, 2H, ArH), 7.51–7.54 (m, 3H, ArH); IR (cm^{-1}) 3528, 2920, 1455, 1376, 977, 755, 724, 692; HRMS (EI) calculated for $C_{14}H_{12}O$, 196.0888, observed 196.0884. The above ^1H NMR was identical to that reported by Delgado et al. [12] for 12.

2.3. Product studies

Product studies were carried out in a Rayonet RPR 100 photochemical reactor using 8 or 16 × 254 nm lamps. Reaction mixtures for the photolysis were contained in a 100 ml quartz tube cooled around 15°C using a cold finger and saturated continuously with argon prior to and during the photolysis. Samples (20 mg) were dissolved in 100 ml of solvent and photolyzed for 1–60 min depending on the desired conversion. After photolysis, the solution was extracted twice with 50 ml CH_2Cl_2. Several runs were performed under identical reaction conditions except in the absence of light which gave no reaction. Representative examples are described below.

2.3.1. Photolysis of **10** *in 1:1 CH_3OH–CH_3CN*

A solution of **10** was photolyzed in a quartz tube for 5 min using the general procedure to give methyl ether product 14 (85%) which was isolated by prep. TLC (CH_2Cl_2), ^1H NMR ($CDCl_3$) δ 1.87 (s, 3H, CH_3), 3.26 (s, 3H, OCH_3), 6.82–7.34 (m, 9H, ArH), 8.46 (s, 1H, OH); HRMS (EI) calculated for $C_{15}H_{16}O_2$, 228.1150, observed 228.1151.

2.3.2. Photolysis of **11** *in 1:1 CH_3OH–CH_3CN*

A solution of **11** photolyzed in a quartz tube for 5 min using the general procedure which gave no reaction. Photolysis for a further 30 min gave 50% conversion to the corresponding methyl ether product, ^1H NMR ($CDCl_3$) δ1.88 (s, 3H, CH_3), 3.06 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 6.77–7.75 (m, 9H, ArH); HRMS (EI) calculated for $C_{16}H_{18}O_2$, 242.1307, observed 242.1304.

2.3.3. Photolysis of **7** *in 1:1 H_2O–CH_3CN*

A solution of **7** was photolyzed for 2 min and gave **10** (27% yield as determined by ^1H NMR).

2.3.4. Photolysis of **7** *in 1:1 CH_3OH–CH_3CN*

A solution of **7** was photolyzed for 15 min and gave 100% conversion to 14.

2.3.5. Photolysis of **9** *in 1:1 H_2O–CH_3CN*

A solution of **9** was photolyzed for 2 min and gave **11** (8% yield)

2.3.6. Photolysis of **10** *in 1:1 H_2O–CH_3CN with added ethyl vinyl ether (EVE)*

To a solution of **10** in 1 : 1 H_2O–CH_3CN EVE was added (1 ml). Photolysis for 60 min gave no significant reaction and the substrate was recovered unchanged.

2.3.7. Photolysis of **7** *in 1:1 CH_3CN–H_2O with added EVE*

To a solution of **7** in 1 : 1 CH_3CN–H_2O EVE was added (0.5–2 ml). Photolysis for 60 min gave only the photohydration product **10** (100% yield)

2.4. Quantum yields

The photohydration quantum yield (Φ_p) of **7** in 1 : 1 H_2O–CH_3CN was measured by comparison of the ^1H NMR yields at low conversion to a reference reaction, the analogous photohydration of *m*-hydroxy-α-phenylstyrene (**4**) in 1 : 1 H_2O–CH_3CN (reported $\Phi_p = 0.22 \pm 0.2$ [9]). Solutions were photolyzed for 1 min to give conversions <30%.

2.5. Fluorescence measurements

Steady state fluorescence spectra were obtained on a Photon Technology International A-1010 (PTI) QuantaMaster Luminescence Spectrometer. Each sample ($OD \leq 0.1$) was prepared in 3.0 ml quartz cuvettes and saturated with argon for 10 min prior to each measurement. The fluorescence quantum yield of **7** was measured using 2-aminopyridine as the reference standard ($\Phi_f = 0.60 \pm 0.05$) [13].

2.6. Laser flash photolysis (LFP)

Nanosecond LFP experiments were carried out using a Nd:YAG laser (Spectra Physics Quanta-Ray GCR, 10-25 mJ) with a pulse width of 10 ns and at an excitation wavelength of 266 nm. Samples were prepared with OD ~ 0.3 in 7 mm × 7 mm quartz flow cells. Flow cells were used to minimize complications from long-lived intermediates. Experiments were carried out with either N_2 or O_2 saturated solutions. In aqueous solution runs, there was little difference in LFP spectra obtained under N_2 or O_2, indicating that T–T absorptions are insignificant in our LFP data under these conditions. Optical densities at 266 nm were kept below 0.3 ensuring that substrate concentrations were $\leq 10^{-5}$ M. In runs for which comparisons of observed signals were required, runs were carried in quick succession with matched solution optical densities.

3. Results and discussion

3.1. Product studies

UV traces taken for the photolysis ($\lambda_{ex} = 254$ nm) of **7** in 1 : 1 H_2O–CH_3CN (Fig. 1) show a clean transformation to a species with much lower in the 230–270 nm region consistent with a photohydration reaction. No changes were observed without photolysis. Preparatory photolysis of **7** in 1 : 1 H_2O–CH_3CN gave cleanly the corresponding Markovnikov hydration product **10** (Scheme 1). The conversion could be taken to 100% if photolysis was carried out for longer

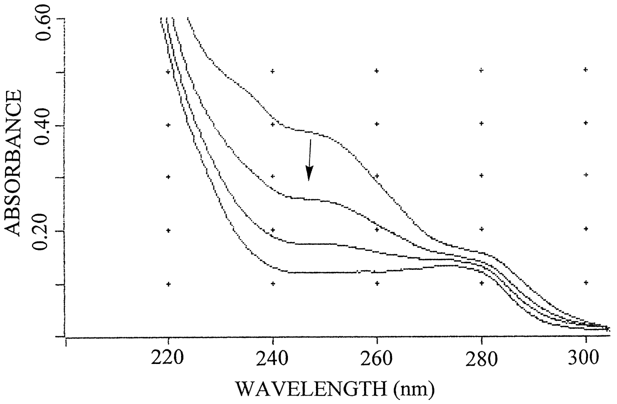


Fig. 1. UV traces for photohydration of **7** in 1 : 1 H_2O–CH_3CN. Each trace represents about 10 s irradiation at 254 nm.

periods. In contrast, photolysis of the methoxy compound **9** gave much lower yields under similar conditions (generally 4–5 fold lower). Similar results were observed on photolysis in 1 : 1 CH_3OH–CH_3CN but in this case the products were the corresponding methyl ethers.

Using the reported quantum for photohydration of **4** reported by Fischer and Wan [9] ($\Phi = 0.22 \pm 0.02$) as secondary reference (using ^1H NMR to follow the reaction), the quantum yield for photohydration of **7** in 1 : 1 H_2O–CH_3CN (water at pH 7) was measured to be 0.13 ± 0.02, indicating that the proposed ESIPT process leads to an intermediate (e.g., *o*-quinone methide (**13**)) which is efficiently trapped by water (unlike the situation for **8** where photoproducts are generally not observable due to the very fast reverse proton transfer in the ground state [11]). When the water portion was adjusted to pH 12, the quantum decreased to 0.08 ± 0.01 suggesting that the phenolate form is somewhat less reactive.

We have recently shown that photolysis of all isomers of hydroxybenzyl alcohols in aqueous solution results in efficient formation of the corresponding quinone methides (via S_1) whereas the corresponding methoxy compounds gave carbocation intermediates but with much lower efficiency [7,8]. In this work, we found that photolysis of *o*-hydroxybenzyl alcohol (**10**) in 1 : 1 H_2O–CH_3OH (water at pH 7) gave high yields of the expected methyl ether product **14** whereas **11** was much less reactive. In addition, photolysis of **10** in 1 : 1 H_2O–CH_3OH (water at pH 12) resulted in a 30% increase in yield of methyl ether. These observations are consistent with formation of *o*-quinone methide **13** from **10** and that the mechanism involves initial formation of the excited state phenolate ion, as suggested previously [7,8]. This is in contrast to the reaction of **7** which reacts with higher hydration yield when the irradiated phenol is initially protonated (in the ground state), consistent with the operation of intramolecular catalysis involving the phenol proton.

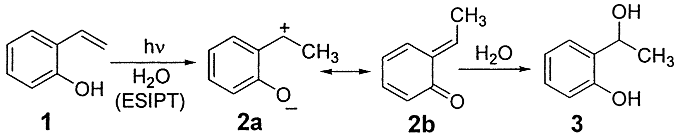
Cis–trans photoisomerization of alkenes (via S_1 or T_1) is known to be very fast. We addressed the question of whether ESIPT (followed by trapping of the quinone methide intermediate by water) could compete with *trans–cis* photoisomerization using 2-hydroxystilbene (**12**). Photolysis of 12 in 1 : 1 H_2O–CH_3CN gave the corresponding *cis* isomer as the major product, as identified by new vinyl signals at δ 6.57 (d, $J = 12$ Hz) and 6.76 (d, $J = 12$ Hz), and only a trace ($\leq 5\%$) of the expected photohydration product **15** (characteristic signals at δ 3.11 (d, $J = 7$ Hz, 2H), 5.02 (t, $J = 7$ Hz, 1H), by comparison with an authentic sample) (Eq. (2)). It seems clear that ESIPT from phenol to an alkene carbon does not compete favourably with isomerization from S_1.

Several photogenerated *o*-quinone methides have been readily trapped with electron rich alkenes such as ethyl vinyl ether (EVE), to give the corresponding chroman adducts in high yields [7,8]. However, photolysis of either **7** or **10** in the presence of EVE (in 1 : 1 H_2O–CH_3CN) under conditions that would have resulted in significant trapping of closely related photogenerated *o*-quinone methides [7,8] resulted only in recovery of substrate for **10** and formation of photohydration product **10** from **7**. Even extended photolysis and use of substantially higher concentrations of EVE failed to produce observable amounts of the expected trapping product. Molecular mechanics calculations (Chem3D, Cambridgesoft Corp.) show that the lowest energy conformation of **13** has the phenyl group in an anti arrangement, as shown in Scheme 1. This implies that the steric hindrance caused by the presence of the syn methyl is sufficient to hinder the approach of the dienophile (EVE). The *o*-quinone methide examples reported previously by Wan and coworkers [7,8] to undergo efficient trapping by EVE all lack this methyl group (it is replaced by hydrogen).

3.2. Fluorescence measurements

The fluorescence emission of **7** was found to be weak in neat CH_3CN ($\Phi_f = 0.020 \pm 0.005$). For comparison, the *meta* isomer **4** was much more fluorescent ($\Phi_f = 0.20$ [9], neat CH_3CN). Not surprisingly, the fluorescence lifetime of **7** was in the subnanosecond range and beyond the scope of the single photon counting instrument used. The *meta* isomer **4** has a singlet lifetime of 5.6 ns in neat CH_3CN [9]. As **4** and **7** are structurally very similar, the above observations suggest that there is an additional deactivational pathway from S_1 available for **7** that is not possible for **4**.

The fluorescence emission of **7** was much more sensitive to the presence of water than observed for **10** (Figs. 2 and 3), an observation that is qualitatively similar to that observed for the corresponding *meta* isomers [9]. For the *meta* isomers, this effect was rationalized [9] as being due to an efficient water-assisted formal ESIPT from the phenol to the alkene moiety from S_1. It would appear that such a mechanism is operative even for the *ortho* isomer **7** where the functional groups are in much closer proximity. A Stern–Volmer plot of water quenching for **7** gave a curved plot which could



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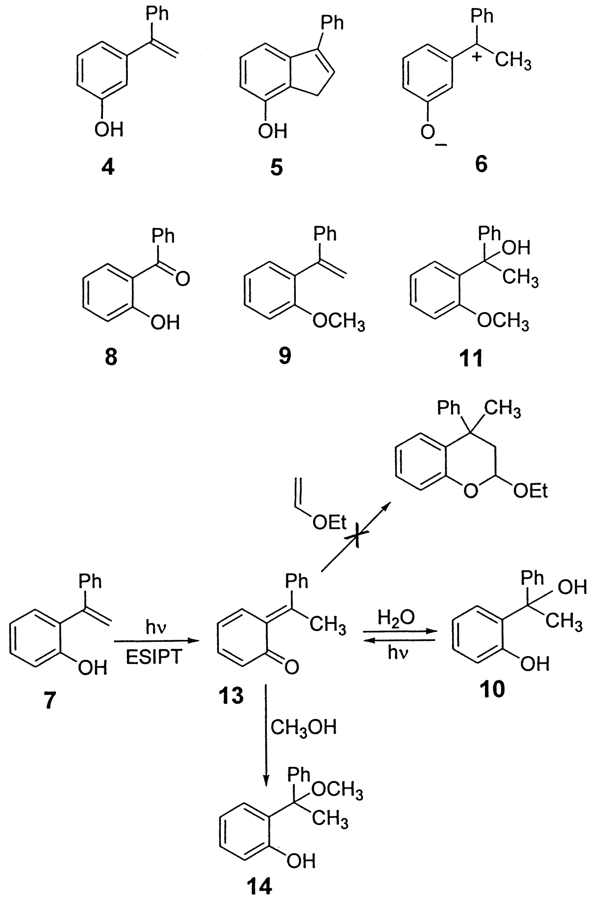
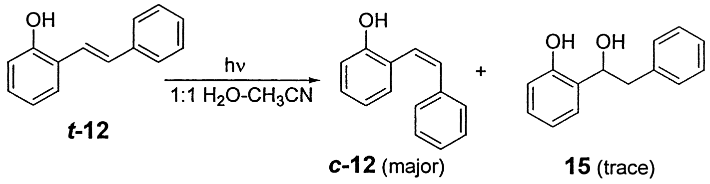


Scheme 1.



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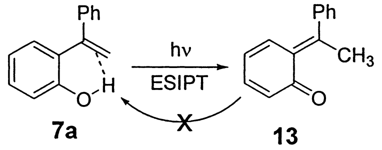

(3)

be fitted to a modified Stern–Volmer equation (Fig. 4) with water to the 1.5 power (i.e., $\Phi^0_f/\Phi_f = 1 + K\,[H_2O]^{1.5}$). Using arguments put forth by us previously [9] for such non-linear plots, one could offer an interpretation where the quenching is assisted by 1–2 molecules of water.

3.3. Laser flash photolysis

Previous work [7–10] have shown that quinone methides (all isomers) are readily detectable in aqueous solution using nanosecond LFP. The *ortho* and *para* isomers were shown to

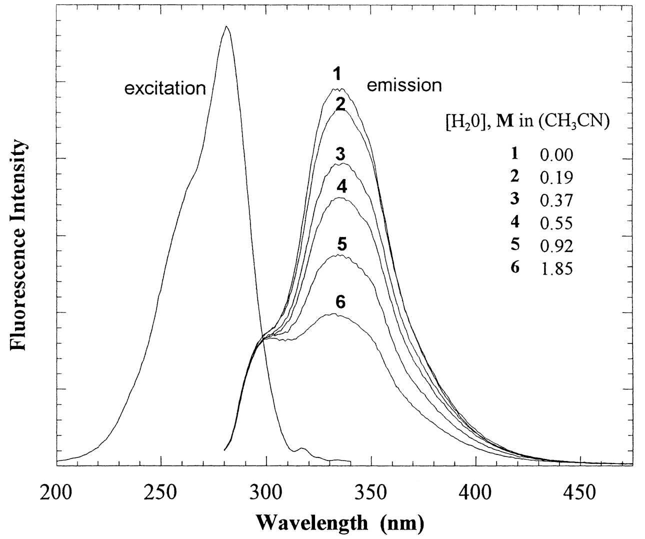

Fig. 2. Fluorescence quenching studies of alkene **7** by water in CH_3CN (λ_{ex} = 275 nm). The shoulder at 300 nm in the emission spectra is due a Raman scattering band from solvent.

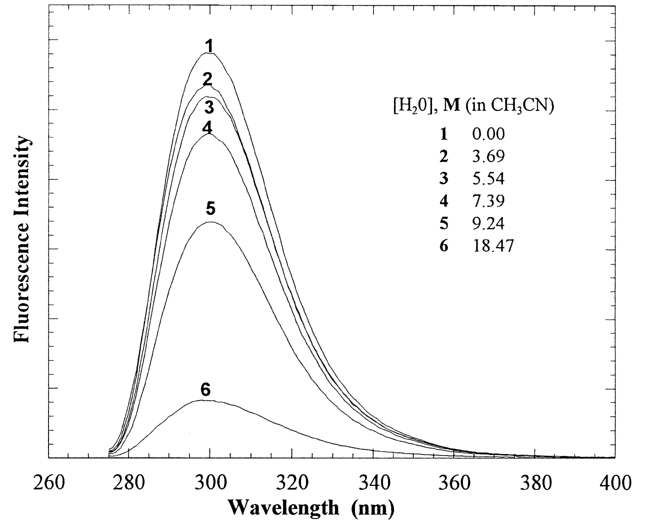

Fig. 3. Fluorescence quenching studies of alcohol **10** by water in CH_3CN (λ_{ex} = 275 nm).

be very long-lived (subsecond or longer lifetimes) in neutral aqueous solution and insensitive to the presence of oxygen. LFP of **7** (O_2 saturated) in neat CH_3CN gave a spectrum (Fig. 5) with λ_{max} = 305 and 400 nm (formed within the laser pulse) and very similar to the reported spectrum for *o*-quinone methides of this type [7]. Essentially no decay was observed to 100 μs consistent with a very long-lived species. LFP in 1 : 1 H_2O–CH_3CN gave essentially the same spectrum buy slightly red-shifted and enhanced in intensity, again with no observable decay. The red-shift observed in aqueous solution is consistent with the π, π* transition assigned to the absorption band of these quinone methides at long wavelength. It should be noted that LFP of the *meta* isomer **4** gave no transient in neat CH_3CN (O_2 saturated) and that strong signals assignable to the corresponding *m*-quinone methide was observable only when water was added [9]. LFP of **9** gave only weak residual signals whereas LFP of **10** (in 1 : 1 H_2O–CH_3CN) gave the same transient shown in Fig. 4. These results are consistent with formation of *o*-quinone methide **13** via ESIPT in **7** which does not require the assistance from water. However, the presence of water does appear to enhance the process marginally.

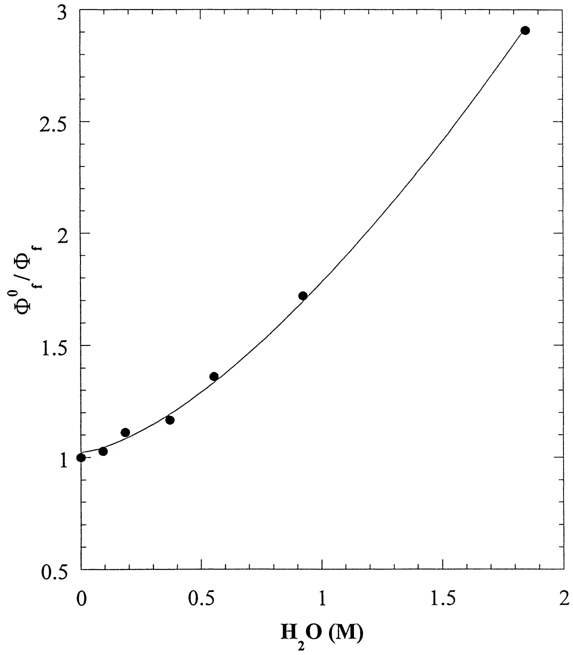

Fig. 4. Modified Stern–Volmer plot ($\Phi_f^0/\Phi_f = 1 + K[H_2O]^{1.5}$) for the fluorescence quenching of **7** by added water (in CH_3CN).

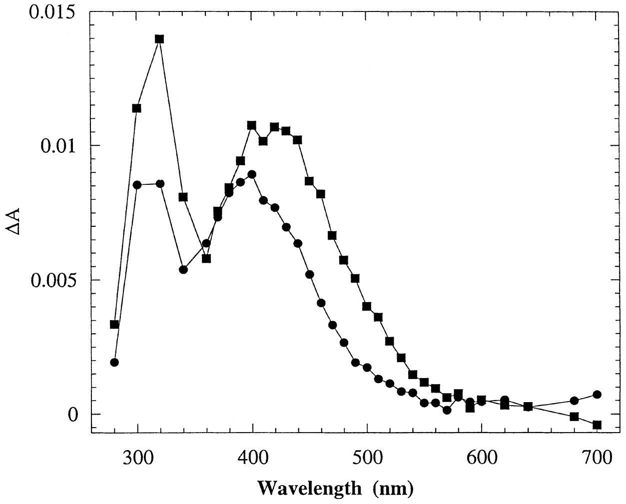

Fig. 5. LFP spectra (100 ns after the laser pulse; oxygen saturated) observed for **7** in neat CH_3CN (circles) and in 1 : 1 H_2O–CH_3CN (squares). No decay was observed to 100–200 μs. The slightly higher signal at 310 nm (relative to the longer wavelength band) in 1 : 1 H_2O–CH_3CN may be due to the formation of a minor unidentified species in aqueous solution.

3.4. Mechanism of photohydration

The initial motivation of this study was to show that the intermediate in the photohydration of *o*-hydroxystyrenes initially reported by Yates and coworkers [5,6] involve an *o*-quinone methide. Our LFP results confirm this. The *o*-quinone methide is generated within the laser pulse (i.e., a fast process) and does not require assistance from water indicating that an intrinsic ESIPT process takes place from the phenol OH to the β carbon of the alkene. This is apparently assisted by the presence of a weak hydrogen bond between the phenol OH and the X system of the alkene [6] (Eq. (3)). We believe the presence of water does assist the ESIPT, however. This is supported by the much more efficient quenching of fluorescence emission by water observed for **7** compared to **10**, and the increase in LFP signal intensity when water was present. In **10**, the primary mechanism for *o*-quinone methide formation requires initial ionization of the phenol proton to solvent water [7,8]. The water dependence of quenching in the modified Stern–Volmer analysis would indicate that between one and two water molecules are involved in the mechanism of assistance although the exact transition state structure for the assistance mechanism is unknown.

The lifetime of **13** was not accurately measurable on our system but it is qualitatively as long as other *o*-quinone methides generated in our laboratory [7,8]. This indicates that reverse proton transfer (from the β methyl group to the carbonyl oxygen) is not an important process for **13**, as would be anticipated since the transfer would require deprotonation of an unexceptional carbon acid, which is known to be intrinsically slow (Eq. (3)).

In summary, we have shown that *o*-hydroxystyrene **7**, the alkene analog of 2-hydroxybenzophenone (**8**), undergoes an intrinsic ESIPT process that is fast on the nanosecond time scale, to generate the correspondiong long-lived *o*-quinone methide. Reverse proton transfer is not an important reaction pathway, unlike the ESIPT process for **8**. Unfortunately, the increased steric bulk at the exocyclic vinyl carbon prevents these *o*-quinone methides from undergoing [4 + 2] cycloaddition with electron rich alkenes.

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