$$Z_N = x_1^N \tag{A16}$$

In order to extract all the information contained in $\Gamma(x)$ about the polymer's properties at any value of N (case 3 in the text), we must also make use of $f(x)$, as well as of $g(x)$'s second root, x_2. This is obtained[17] by developing $f(x)/g(x)$ in a power series in $1/x$, with coefficients that are functions x_1, x_2, $f(x_1)$, and $f(x_2)$, as follows: (1) First, $g(x)$ is factorized as

$$g(x) = (x - x_1)(x - x_2) \tag{A17}$$

and $f(x)/g(x)$ is transformed, by the method of "partial fractions", to

$$\frac{f(x)}{g(x)} = \frac{C_1(x - x_2) + C_2(x - x_1)}{(x - x_1)(x - x_2)} = \frac{C_1}{x - x_1} + \frac{C_2}{x - x_2} \tag{A18}$$

For this transformation to be fulfilled, C_1 and C_2 must satisfy the equation

$$f(x) = C_1(x - x_2) + C_2(x - x_1) \tag{A19}$$

therefore

$$C_1 = f(x_1)/(x_1 - x_2) \qquad C_2 = f(x_2)/(x_2 - x_1) \tag{A20}$$

(2) Next, $1/(x - x_1)$ and $1/(x - x_2)$ are developed in the power series

$$\begin{aligned} 1/(x - x_1) &= (1/x)\sum_{N=0}^{\infty}(x_1/x)^N \\ 1/(x - x_2) &= (1/x)\sum_{N=0}^{\infty}(x_2/x)^N \end{aligned} \tag{A21}$$

(3) Finally, eq A18–A21 are put together into eq A11 for $\Gamma(x)$. The result is

$$\Gamma(x) = \sum_{N=0}^{\infty}[x_1^N f(x)/(x_1 - x_2) + x_2^N f(x_2)/(x_2 - x_1)]x^{-N} \tag{A22}$$

Both eq A22 and A6 express $\Gamma(x)$ as the same power series in x^{-N}. Therefore

$$Z_N = x_1^N f(x_1)/(x_1 - x_2) + x_2^N f(x_2)/(x_2 - x_1) \tag{A23}$$

holds for any value of N. In view of eq A12 and A14

$$f(x_1)/(x_1 - x_2) = (w + v)/w,\ f(x_2)/(x_2 - x_1) = (-w + v)/(-w) \tag{A24}$$

therefore

$$Z_N = x_1^N(1 + v/w) + x_2^N(1 - v/w) \tag{A25}$$

It may be verified by inspection that eq A25 is precisely valid for all N, from monomers and dimers to infinite polymers.

Registry No. Ethyl hexanoate, 123-66-0; 1,1-dideuteriohexanol, 52598-04-6; 1-deuteriohexanal, 55320-52-0; (*S*)-1-deuteriohexanol, 91525-95-0; (*R*)-1-deuterio-1-azidohexanal, 121987-97-1; (*R*)-1-deuterio-1-aminohexanal, 121987-98-2; (*R*)-1-deuterio-1-hexyl isocyanate, 114942-16-4; (*R*)-1-deuterio-1-hexyl isocyanate (homopolymer), 114507-38-9; (*R*)-1-deuterio-1-hexyl isocyanate (SRU), 114507-37-8.

A Laser Flash Photolysis Study of Photodehydroxylation Phenomena of 9-Phenylxanthen-9-ol and Photobehavior of Related Intermediates. Enhanced Electrophilicity of 9-Phenylxanthenium Cation Singlet[1]

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Received April 6, 1989

Abstract: In the course of 248-nm laser flash photolysis, solutions of 9-phenylxanthen-9-ol (**1**) undergo homolytic and heterolytic photodehydroxylation, the relative efficiency of which depends strongly on the solvent nature. Polar/hydroxylic solvents, particularly aqueous mixtures, cause copious formation of 9-phenylxanthenium cation (**2**), the ground- and excited-state properties of which are conveniently studied by single- and double-laser flash photolysis. In 1:1 H_2O/MeCN, the quantum yield of carbenium ion generation is 0.4 ± 0.1; only 1% of photoheterolysis occurs through an adiabatic route. Surprisingly, in polar but nonhydroxylic solvents (e.g., acetonitrile and 1,2-dichloroethane) also, the cation is photogenerated in small but sufficient yields to allow time-resolved spectroscopic detection and study in these relatively neutral and inert media. In relatively nonpolar solvents, e.g., *n*-heptane and benzene, the photolysis of **1** is dominated by homolytic cleavage to 9-phenylxanthenyl radical (**3**). The short-lived triplets of **1** ($\tau_T \leq 0.3\ \mu s$) are also observed in nonaqueous solvents ($\phi_T = 0.05$ in acetonitrile). In comparison to the weak, fast-decaying, doublet–doublet fluorescence of **3** ($\lambda_{max}^F = 590$ nm, $\tau_F \leq 5$ ns), the singlet–singlet fluorescence from **2** is intense and long-lived ($\lambda_{max}^F = 550$ nm, $\tau_F = 25$ ns in acetonitrile in the absence of nucleophilic quenchers) and is almost nonquenchable by oxygen ($k_q \leq 5 \times 10^8\ M^{-1}\ s^{-1}$). The electrophilicity of the lowest excited singlet state of **2**, measured in terms of rate constants (k_q) of bimolecular quenching by anions and lone-pair containing molecules, is considerably more pronounced than that of the ground state (that is, k_q's are higher for the excited state by several orders of magnitude).

The cleavage of a carbon–heteroatom σ-bond as a result of the photoexcitation of a proximal π-system is of interest from several perspectives: First, the study of this photolytic event gives insight into the spatial factors that affect energy migration in the photoexcited state leading to chemical transformations. Second, the charge polarization in the excited-state potential surface, as controlled by intramolecular and environmental factors, manifests itself into heterolytic or homolytic bond cleavage, leading to ions or radicals.[3,4] The relative yields of the ionic and radical type

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(2) (a) Undergraduate research student (fall, 1987) from the University of Waterloo, Canada. (b) Present address: 347 PL, Phillips Research Center, Bartlesville, OK 74004.

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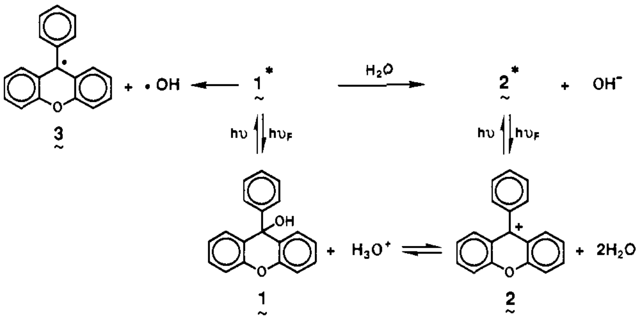
Scheme I



products reflect the electronic makeup of the substrate molecule in its excited state under a given condition. Third, with the use of pulse laser excitation, it is feasible to generate organocations and radicals, the absolute, ground-state reactivity data of which are of relevance to organic reaction mechanisms.[5,6] The excited-state properties of these intermediates, particularly radicals, have also been drawing considerable attention in recent times.[7] Fourth, facile photoinduced heterolysis can be conveniently used in fast-kinetics studies involving the resultant "inorganic" ionic fragments (e.g., pH jump).[8]

Motivated more or less by all of the features or phenomena outlined above, we have undertaken a nanosecond laser flash photolysis study of 9-phenylxanthen-9-ol (**1**) (Scheme I). The time-resolved detail of the primary processes resulting from the photoexcitation of this tertiary alcohol is relevant to the photochemistry (e.g., photosolvolysis) of aromatic alcohols, esters, related compounds,[3,4,9-13] as well as polyene derivatives.[14-16] Specifically, as shown by Wan et al.,[11,12] **1** undergoes adiabatic photodehydroxylation (heterolytic) in aqueous solutions; that is, the photoconversion of **1** to 9-phenylxanthenium cation (**2**; Scheme I) in the singlet manifold takes place on a single excited electronic energy surface.[17-19] We expected to shed light on this interesting photoreaction as well as on the ground and excited states of the resultant photointermediates (carbenium ion and radical), by employing the time-resolved techniques of single- and double-laser flash photolysis.

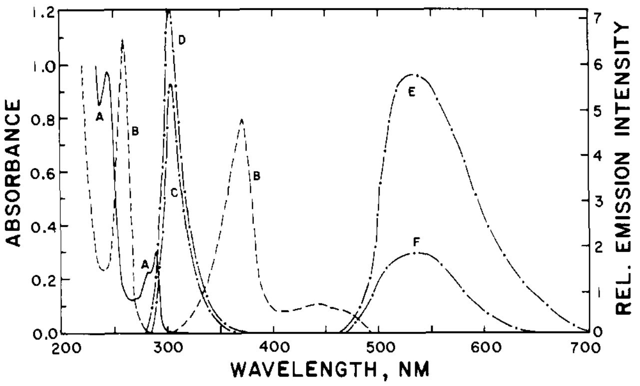


Figure 1. Ground-state absorption spectra (A, B) measured in 2-mm cells and steady-state-corrected fluorescence spectra (C–F) measured in 1 cm × 1 cm cells for 9-phenylxanthen-9-ol (**1**) and 9-phenylxanthenium cation (**2**). Conditions: A, 0.40 mM **1** in MeCN; B, 0.12 mM **2** in 10% H_2SO_4 in MeCN; C, **1** in *n*-heptane (λ_{ex} = 260 nm, OD_{260} = 0.075); D, **1** in 1:1 H_2O/MeCN (λ_{ex} = 260 nm, OD_{260} = 0.100); E, 0.083 mM **2** in 10% H_2SO_4 in MeCN (λ_{ex} = 355 nm); F, **2** produced by adiabatic photodehydroxylation of **1** in 3:1 H_2O/MeCN (λ_{ex} = 280 nm, OD_{280} = 0.520). Band-passes used for emission measurements were 4 nm for C–E and 16 nm for F. The intensities of spectra B–F, as shown, do not reflect their relative quantum yields (see text).

Since the submission of this paper for publication, a detailed report by McClelland et al.[5b] has appeared on electrophilic reactions of xanthylium carbocations, including **2**, produced by laser flash photolysis of 9-xanthenols. The results of laser photolysis of **2** in this work agree very well with those obtained by us. However, it is important to emphasize that while McClelland et al.[5b] investigated the ground-state reactivity of **2** and its analogues, we have focused on the photophysics and excited-state reactivity of **2** and the corresponding radical.

Experimental Section

9-Phenylxanthen-9-ol (Aldrich) and quinine bisulfate (Merck) were recrystallized from benzene and water, respectively. 1,2-Dichloroethane (Eastman, spectral grade) was passed through a silica gel column. Acetonitrile (Aldrich, gold label) was distilled over P_2O_5 in a nitrogen atmosphere. Benzene (Aldrich), methanol (Aldrich), *N*,*N*-dimethylformamide (Fisher), and *n*-heptane (Aldrich) were of ACS or spectral grades and were used without further treatment. Triethylamine, tetraethylammonium chloride, sulfuric acid, trifluoroacetic acid, 2-methyl-2-propanol, and 2-propanol were of best grades available from Aldrich or Eastman and were used as received. 9-Phenylxanthenyl 9-chloride (**4**) was prepared by a method described in the literature[20a] and purified by recrystallization from *n*-heptane.

The ground-state absorption spectra were measured in Suprasil quartz cells of 2-mm and 1-cm path lengths, with Cary 219 and HP8450A spectrophotometers (1-nm band-pass). Steady-state emission spectra were recorded in 1 cm × 1 cm Suprasil quartz cells, with right-angle geometry between the directions of excitation and emission. The description of the SLM photon-counting spectrofluorimeter is given elsewhere,[20b] except that a red-sensitive photomultiplier tube (Hamamatsu R928YG 7006) was used in the present experiments. Fluorescence

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quantum yields were referenced to optically matched solutions of quinine sulfate in 2 N sulfuric acid ($\phi_F = 0.55$)[21] and have estimated experimental errors of ±15%.

For laser flash photolysis, use was made of the following pulsed sources: Lambda-Physik EMG 101 MSC excimer (248 and 308 nm, ~20 ns, 10–50 mJ/pulse), Quanta-Ray DCR-1 Nd-YAG (266 and 355 nm, fourth and third harmonics, 6 ns, 5–30 mJ/pulse), and Molectron UV-400 nitrogen (337.1 nm, ~8 ns, 2–3 mJ/pulse). Quartz cells of 2- or 3-mm path lengths were used in a front-face configuration for laser excitation pulses and light analysis. The kinetic spectrophotometer and the data collection system are described elsewhere.[22a,b] For double-laser flash photolysis, the delay between the photolysis pulse (248 nm, for photogeneration of a transient) and the probe pulse (337.1 or 355 nm, for photoexcitation of the transient) was usually 2–4 μs. For wavelength-by-wavelength transient spectra, a flow cell was used to avoid complications from accumulated photoproducts. Unless otherwise noted, the solutions were deaerated by bubbling oxygen-free argon.

The pulse radiolysis experiments were carried out with 5-ns electron pulses from Notre Dame 7-MeV ARCO LP-7 linear accelerator. Details of the setup are given in earlier publications[22c–e] from the Radiation Laboratory.

Results

(a) Steady-State Absorption and Emission Behaviors. As shown in Figure 1, curve A, the lowest energy absorption band system of 9-phenylxanthen-9-ol (**1**) has its onset at ~300 nm and maximum at ~290 nm (λ_{max} = 288 and 290 nm and $\epsilon_{max} = 3.7 \times 10^3$ and 4.6×10^3 M^{-1} cm^{-1} in acetonitrile and *n*-heptane, respectively). The next higher energy band maximizes at 244 nm ($\epsilon_{max} = 1.20 \times 10^4$ and 1.34×10^4 M^{-1} cm^{-1} in acetonitrile and *n*-heptane, respectively). Most of our laser flash photolysis experiments on **1** were carried out at 248 nm (Kr–F_2, excimer laser) or 266 nm (Nd:YAG, fourth harmonic), causing excitation into the second band system. In several solvents (particularly benzene), the low-energy tail of the band system at ~290 nm extends slightly beyond 300 nm; it was barely possible to do laser flash photolysis on **1** at high concentrations in this solvent with use of 308-nm laser pulses (Xe–HCl, excimer). However, in the latter experiments, aside from the difficulty arising from low achievable ground-state absorbances, caution had to be exercised regarding complications from self-quenching and impurity involvements.

Upon acidification, namely by adding 8–10% concentrated H_2SO_4 in polar and aqueous solvents or by saturation with trifluoroacetic acid in nonpolar solvents (e.g., *n*-heptane), solutions of **1** develop yellow coloration due to dehydroxylation to 9-phenylxanthenium cation (**2**; see Scheme I). By spectrophotometric titration, Wan et al.[12] have measured the ground-state pK_{R^+} of **1** to be 1.0 ± 0.5 in water. The absorption spectrum of **2**, shown in Figure 1, curve B, is characterized by three observable band systems at 220–500 nm (λ_{max} = 445, 373, and 258 nm and the corresponding ϵ_{max} (10^3 M^{-1} cm^{-1}) = 4.90, 33.2, and 44.3 in CH_3CN + 10% H_2SO_4). The absorption spectra obtained in *N*,*N*-dimethylformamide + 10% H_2SO_4 and in *n*-heptane saturated with trifluoroacetic acid are similar except for slight solvent-induced shifts in the maxima (λ_{max} = 373 and 449 nm in *n*-heptane and 379 and 450 nm in DMF).

Under steady-state lamp excitation, both **1** and **2** fluoresce moderately strongly. The fluorescence spectra of **1** exhibit maxima at spectral locations (λ_{max}^F = 306 nm) nearly invariant with respect to solvent nature (Figure 1, curves C and D). The fluorescence quantum yield (ϕ_F) in acetonitrile is measured to be 0.12 (λ_{ex} = 290 nm). The fluorescence intensity (I) in this solvent decreases steadily upon making the solution increasingly aqueous. A Stern–Volmer plot of I_0/I against water concentration (0–8 M) in acetonitrile gave a quenching constant (K_{SV}) of 0.18 M^{-1}. The reported fluorescence lifetime of **1** in water is 1.0 ± 0.5 ns.[12] In the absence of quenching by water, the fluorescence lifetime of **1** in acetonitrile is expected to be longer.[23] Thus, the bimolecular rate constant for the quenching of S_1 of **1** by water is estimated to be $\leq 1.8 \times 10^8$ M^{-1} s^{-1} in acetonitrile.

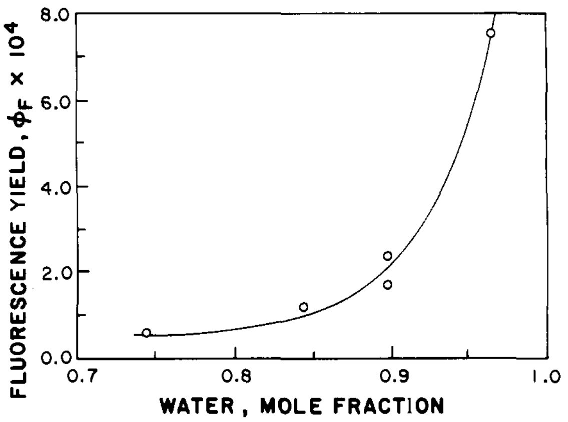

Figure 2. Water content dependence of steady-state fluorescence quantum yield of 9-phenylxanthenium cation **2** produced by adiabatic photodehydroxylation of **1** in aqueous acetonitrile (λ_{ex} = 280 nm).

The steady-state emission spectra of cation **2**, measured in acidified solutions, are broad and structureless, maximize at 540–550 nm (Figure 1, curve E), and display a mirror image relationship with the 450-nm absorption band. The fluorescence quantum yield of this species under 380-nm excitation is 0.42 in acetonitrile + 8% H_2SO_4. As with **1**, the emission intensity of **2** also is sensitive to water content in the solvent. The quenching effect of added water was measured in acetonitrile + 10% H_2SO_4. From the linear Stern–Volmer plot of I_0/I against [H_2O] in the concentration range 0–3.5 M, we obtained a K_{SV} value of 0.37 M^{-1}. With the observed lifetime of 25 ns for S_1 of **2** under the given conditions ([H_2O] = 0) (vide infra), the bimolecular quenching rate constant is calculated to be 1.5×10^7 M^{-1} s^{-1}. More regarding the quenching of S_1 of **2** will be presented later.

In water solution, the adiabatic photogeneration of **2** under steady-state photoexcitation of **1** has been established by Wan et al.[12] by monitoring the weak emission from **2** at long wavelengths. In order to confirm this interesting observation, we carried out similar experiments on **1** in aqueous acetonitrile. With water contents ≥50% (v/v), we were able to observe the weak emission (λ_{max} = 545 nm) due to **2** under 290-nm excitation of **1** (Figure 1, curve F). For these measurements, however, we had to use maximized detection conditions of our spectrofluorimeter, such as 16-nm band-pass for both excitation and emission monochromators and long photon counting times. A 0-52 Corning cutoff filter was placed in the path of emission light (in order to completely exclude the second harmonics of the emission from **1** at 280–380 nm). For every solution in these experiments, emission, if any, was checked under excitation at 450 nm (i.e., the wavelength where **2** is expected to absorb); no long-wavelength emission attributable to the direct excitation of **2** was detectable at 500–600 nm under this condition. This result rules out the possibility that a trace amount of **2** in the ground state is responsible for the yellow emission. Thus, the adiabatic origin of the cation emission under excitation of **1** is established. The dependence of the quantum yield of this cationic emission on the water content in aqueous acetonitrile was studied. As shown in Figure 2, the yield increases sharply with increasing mole fraction of water.

It should be noted that the origin of the yellow emission due to **2** under steady-state photoexcitation of **1** in aqueous solutions could not be due to the reabsorption of the excitation light by the ground state of the photogenerated cation, which happens to be long-lived (see later). As evident from Figure 1 (curve B), relative to **1**, the cation **2** does not absorb at the excitation wavelength (290 nm) used.

(b) Single-Laser Flash Photolysis. **1** was subjected to 248-nm laser flash photolysis in a variety of hydroxylic and nonhydroxylic

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[23] 266-nm laser pulse (fwhm ~ 6 ns) excitation of **1** in acetonitrile gave emission decay traces at 305 nm that nearly followed the laser pulse. τ_F(**1**) in this solvent is estimated at ≤4 ns.

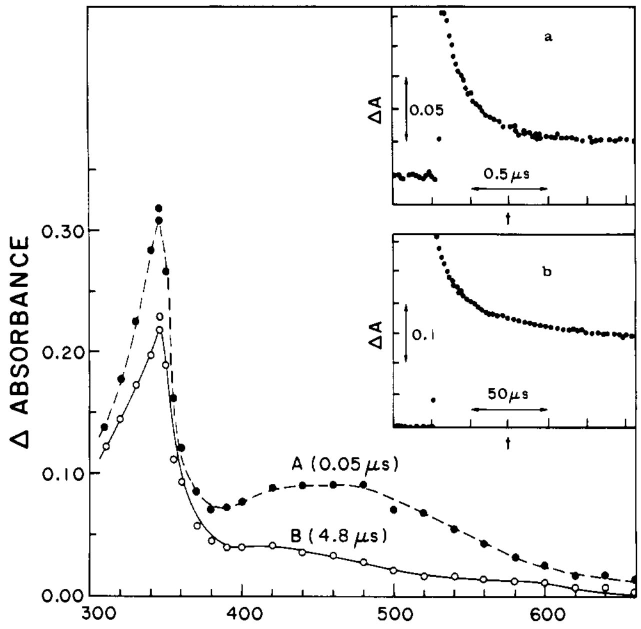

Figure 3. Transient absorption spectra, at times shown, following 248-nm laser flash photolysis of **1** in *n*-heptane (OD_{248} = 0.48 in 2-mm cell). Insets: representative kinetic traces for decay of transient absorption at (a) 480 and (b) 345 nm.

solvents, ranging from nonpolar to polar ones. As illustrated in Figure 3, in *n*-heptane, we observed two transient species, one of which is much longerlived than the other. The short-lived transient contributes to the absorbance change at 320–500 nm (λ_{max} ~ 440 nm) in the microsecond time scale and decays with first-order kinetics (observed lifetime, 0.28 ± 0.05 μs), see curve A and inset a in Figure 3. On the other hand, the longer lived species exhibits its major maximum at 345 nm, along with two minor bands in the visible (λ_{max} ~ 420 and 580 nm), and decays with complex kinetics over a millisecond time scale (curve B and inset b in Figure 3). The fits of the decay profiles of the second transient into second-order equal-concentration kinetics, namely, as a linear plot of $1/\Delta A$ vs t, were not satisfactory.

The quenching effects of oxygen on the decay behavior of both transient species in *n*-heptane (discussed above) were studied. In air-saturated solutions, the decay of the 400-nm species becomes considerably faster (τ_{obsd} = 48 ns); the bimolecular rate constant (k_{q,O_2}) for oxygen quenching is estimated to be 5.4×10^9 M^{-1} s^{-1} (in *n*-heptane, based on $[O_2]$ = 3.09 mM under air saturation, that is, equal to that in hexane[24]). On the other hand, although the decay of the 345-nm species, monitored over ~150 μs, becomes visibly enhanced under air saturation, it still remains too complex to be fitted into pseudo-first-order kinetics. This suggests that this species is only slightly quenchable by oxygen; our best estimate is $k_{q,O_2} \leq 2 \times 10^7$ M^{-1} s^{-1}. On the basis of pronounced oxygen sensitivity, we assign the 440-nm species as the triplet of **1**. This triplet assignment[25] is strongly supported by the fact that the same species produced under 266-nm laser pulse excitation in *n*-heptane is efficiently quenched by 2,5-dimethyl-2,4-hexadiene (k_q = 6.5 $\times 10^9$ M^{-1} s^{-1}) and tetramethylethylene (k_q = 2.2×10^9 M^{-1} s^{-1}). This quenching occurs very probably by an energy-transfer mechanism (also see later text in this section).

In view of the likelihood of homolytic photodissociation of **1** in the nonpolar solvent, *n*-heptane, the most probable assignment of the long-lived, slightly oxygen quenchable, 345-nm species lies in terms of 9-phenylxanthenyl radical (**3**; see Scheme I).[26]

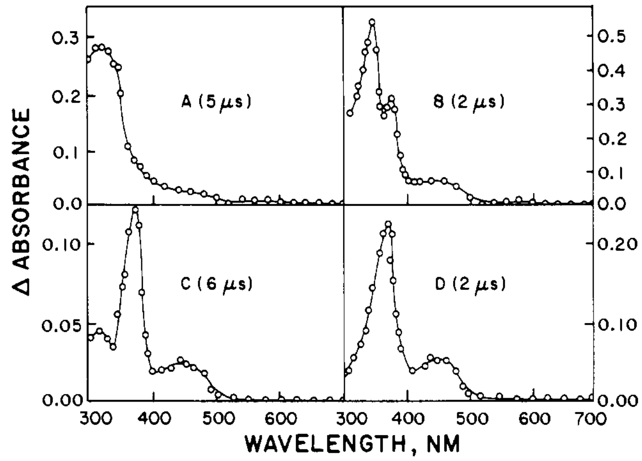

Figure 4. Transient absorption spectra, at times indicated, following 248-nm laser flash photolysis of **1** in (A) MeCN, (B) MeOH, (C) 1:1 MeCN/H_2O, and (D) 1:1 MeOH/H_2O. The ground-state absorbances of the solutions used were ~0.5 at 248 nm. The excitation laser intensities were not the same for experiments in the four solvents.

Photohomolysis of aromatic alcohols is a common phenomenon in relatively nonpolar and nonaqueous solvents.[3,5,10c] To confirm the identity of the 345-nm species, **1** was subjected to pulse radiolysis in methanol. In this solvent, as a result of the reaction of **1** with solvated electron (e^-_{MeOH}), we observed the formation of **3** through dissociative electron attachment:

$$\mathbf{1} + e^-_{MeOH} \rightarrow [\mathbf{1}^{\bullet-}] \rightarrow \mathbf{3} + OH^- \qquad (1)$$

Such reactions of solvated electron with aromatic alcohols and related molecules are well-known.[6,27] The spectral and kinetic similarity of the transient spectrum of pulse radiolytically generated 9-phenylxanthenyl radical (λ_{max} = 345 nm in methanol) with the photolytic 345-nm species in *n*-heptane established the identification of the latter as the radical. Further confirmation for this assignment came from experiments in which *n*-heptane and acetonitrile solutions of 9-phenylxanthenyl-9-chloride (**4**) were flash photolyzed with λ_{ex} = 266 nm. The photolytic transient from the chloride was spectrally and kinetically similar to the long-lived phototransient (λ_{max} = 345 nm) from **1**.

The fact that, when produced in the course of laser flash photolysis in *n*-heptane, the radical decays with complex kinetics rather than with equal-concentration second-order kinetics suggests that the self-coupling reaction (eq 2, **3** ≡ $R^\bullet$) is not dominant

$$R^\bullet + R^\bullet \rightarrow R\text{–}R \qquad (2)$$

$$C_7H_{16} + {}^\bullet OH \rightarrow {}^\bullet C_7H_{15} + H_2O \qquad (3)$$

$$R^\bullet + {}^\bullet C_7H_{15} \rightarrow R\text{–}C_7H_{15} \qquad (4)$$

relative to other possible reaction(s), e.g., reactions of solvent-derived radical(s) with **3** (eq 4). The lack of formation of the cation **2** as a result of the laser photolysis of **1** in *n*-heptane is inferred from the transient spectra (namely, the absence of a peak at 375 nm) as well as from the fact that in double-laser experiments (see later), upon 355-nm photoexcitation of the observed species with microsecond transient absorption, no cationic emission is noted at 500–600 nm.

The situation is dramatically different in the strongly polar/protic solvent, 1:1 H_2O/MeOH. As shown in Figure 4 (curve D), the transient spectrum in this solvent is dominated by a single

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[24] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

[25] An alternative assignment in terms of phenyl radical, $C_6H_5^\bullet$, produced via homolytic photocleavage of the appropriate bond in **1** is ruled out by the fact that this radical does not absorb significantly at the spectral region under consideration. Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609–3614.

[26] (a) The transient absorption spectra of 9-hydroxyxanthenyl radical obtained by laser flash photolysis of xanthone in hydrogen-donating solvents 2-propanol and heptane show double maxima at 400–700 nm; the maximum at 495 nm is ~2 times stronger in intensity that at 610–620 nm.[26b] The lack of this spectral feature in the observed absorbance changes in the case of **1** (Figure 3, curve B) eliminates 9-hydroxyxanthenyl radical as a possible primary photoproduct. (b) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7750.

[27] Bhattacharyya, K.; Bobrowski, K.; Rajadurai, S.; Das, P. K. *Photochem. Photobiol.* **1988**, *47*, 73–83.

Table I. Relative Yields of 9-Phenylxanthenium Cation (**2**) and 9-Phenylxanthenyl Radical (**3**) in the Course of 248-nm Laser Flash Photolysis of **1** in Various Solvents

solvent	rel yield[a] **2**	rel yield[a] **3**
n-heptane	*b*	1.0
acetonitrile	≤0.05	1.0
methanol	0.2	0.5
1:1 H_2O/MeCN	0.5	≤0.1
1:1 H_2O/MeOH	1.0	*b*

[a] ±25%. **2** and **3** were monitored at their respective absorption maxima at 375 and 340–345 nm; corrections were applied for the contribution of **2** at the absorption maximum of **3** and vice versa. [b] The yields are negligible in these cases.

long-lived species; this is assigned as cation **2** on the basis of close spectral similarity to the species (Figure 1, curve B) produced upon acidification of solutions of **1**. In neat methanol (Figure 4, curve B) and 1:1 MeCN/H_2O (Figure 4, curve C), both the cation and the radical are formed. In neat acetonitrile (Figure 4, curve A), however, the 248-nm laser flash photolysis of **1** is dominated by homolytic dissociation, there being little or no hint in transient absorption for the cation formation (see later). The decay of the cation photogenerated in the hydroxylic solvent systems (in the absence of added acids), as monitored at 375 nm over ~150 μs, is found to be complex (rather than pseudo first order). This suggests that the recombination of **2** in the ground state with OH^- competes favorably with its reaction with hydroxylic solvent molecules (nucleophilic).

In acetonitrile and, to a smaller extent in methanol, the triplet of **1** is also observed (τ = 130 and 60 ns in deoxygenated and air-saturated MeCN, respectively). Interestingly, in 1,2-dichloroethane, a nonhydroxylic solvent that is considerably less polar than acetonitrile, the cation photogeneration under both 248- and 308-nm laser flash photolysis is clearly evidenced by a peak at ~370 nm in the transient absorption spectra. In addition, the triplet (τ ~ 0.2 μs) and the radical (λ_{max} = 340 nm) are observed; the total transient absorption observed at the peak of the cation (370 nm) is about 80% of that of the radical at 340 nm. The 308 nm-laser flash photolysis of **1** in benzene leads to the formation of the radical **3** only (λ_{max} = 340 nm); no significant transient absorption ascribable to triplet or cation is observed in this solvent.

Evidence was sought for photoejection of electron from **1** under 248-nm laser flash of **1** in methanol and 1:1 H_2O/MeOH. Transient absorption that could be attributed to solvated electron was looked for over 1–4-μs time domains at 600–700 nm. Although under the conditions of our experiments very weak absorptions (τ ~ 0.5 μs) were barely discernible at the long wavelengths, these were too weak for any practical consideration.

The relative yields of **2** and **3** in the course of 248-nm laser pulse excitation of **1** were estimated in a number of solvents, with the use of solutions that were optically matched with one another at the laser excitation wavelength. The yields, calculated on the basis of the assumption that the ϵ_{max} of **2** and **3** are essentially independent of solvents, are presented in Table I. Because of large uncertainties associated with the relative yield data, these are meant to indicate only the trends.

The absolute quantum yield of heterolysis of **1** was measured in 1:1 MeCN/H_2O under 266-nm laser pulse excitation. Naphthalene triplet formation in cyclohexane (ϕ_T = 0.75, ϵ_T = 2.45 × 10^4 M^{-1} cm^{-1} at 414 nm)[28a] was used for actinometry. With the use of optically matched solutions of **1** and the reference (absorbance 0.5 in 1 cm × 1 cm cells at 266 nm), the maximum laser-photolytic transient absorbances due to cation and reference triplet were measured, respectively, and compared with each other. On the basis of an extinction coefficient of 3.3 × 10^4 M^{-1} cm^{-1} for the cation at 375 nm, we obtained a value of 0.4 ± 0.1 for the quantum yield of formation of **2** from **1** (in 1:1 MeCN/H_2O).

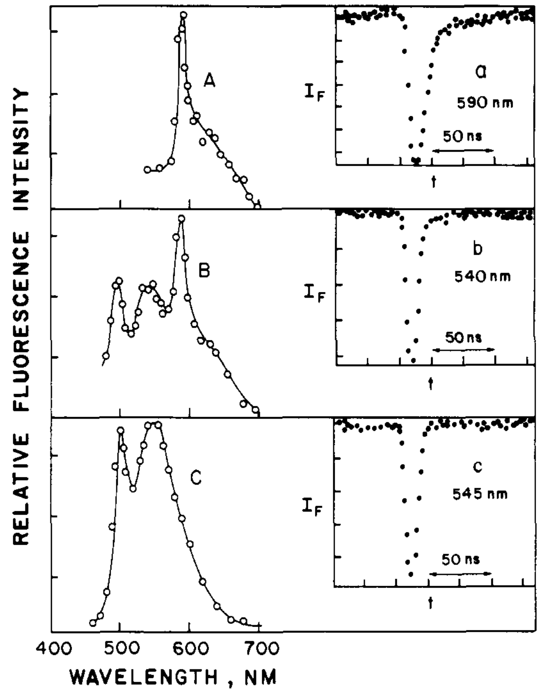

Figure 5. Transient emission spectra, monitored at the maximum of decay traces, following 248-nm laser flash photolysis of **1** and subsequent 355-nm laser flash excitation of the resultant transient(s) in (A) *n*-heptane, (B) methanol, and (C) 1:1 methanol/H_2O. The ground-state absorbances of solutions used were ~0.5 at 248 nm. The delay between the two laser pulses was 2 μs in each experiment. The emission spectra are not corrected for the relative sensitivity of the detector; in particular, the peak at 500 nm is an artifact arising from a corresponding sharp maximum in detector sensitivity. Insets: observed emission decay traces, at indicated wavelengths, in (a) *n*-heptane, (b) methanol, and (c) 1:1 methanol/H_2O.

Subject to uncertainties from the variation of the cation extinction coefficient with solvent conditions and to the excitation wavelength dependence of the quantum yield (248 vs 266 nm), this value of cation yield in aqueous MeCN suggests that the corresponding yield in 1:1 MeOH/H_2O is essentially unity (based on relative yield data in Table I). It should be noted that our value (0.4) of cation yield in 1:1 H_2O/MeCN is in good agreement with that (0.56 ± 0.1) obtained by McClelland et al.[5b] in 4:1 H_2O/MeCN with λ_{ex} = 248 nm and photoejection of e^-_{aq} from aqueous I^- for actinometry.

The formation of triplets from **1** in acetonitrile and 1,2-dichloroethane was confirmed by 308-nm laser flash photolysis of **1** in the presence of biphenyl. In view of the previously noted quenchability of the triplet of **1** by tetramethylethylene (E_T(2-butene) ~ 78 kcal mol^{-1}),[24] we expected the triplet to efficiently transfer energy to biphenyl (E_T ~ 66 kcal mol^{-1}).[24] Experiments with solutions of **1** (absorbances ~0.05 in 2-mm cells at 308 nm) in the presence of 5 mM biphenyl showed the formation of its triplet contributing to a shoulder at 360–365 nm in the transient absorption. Comparison of the portion of the transient absorbance due to the biphenyl triplet sensitized by **1** with that of benzophenone triplet in acetonitrile (ϕ_T = 1, ϵ_T = 6.5 × 10^3 M^{-1} cm^{-1} at 520 nm)[28b] gave an estimate of 0.05 for the intersystem crossing efficiency of **1** (in acetonitrile).[29a]

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(28) (a) Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163–191. (b) Bensasson, R. V.; Gramain, H.-C. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1801–1810.

(29) (a) Experiments to photogenerate the triplet of **1** by energy transfer from a donor are rendered difficult by the facts that the triplet energy of **1** is high (i.e., above that of the olefin tetramethylethylene) and that the ground-state absorption of a possible donor would strongly overlap with that of **1**. The transient phenomena observed upon 308-nm laser flash excitation of acetone in MeCN containing 2 mM **1** were found to be complex, probably owing to exciplex interaction between acetone triplet and **1**. Johnston, J. L.; Scaiano, J. C.; Wilson, T. *J. Am. Chem. Soc.* **1987**, *109*, 1291–1297. (b) The presence of the 500-nm peak in the sensitivity curve of the laser flash detector assembly was shown by comparison of the fluorescence spectra of 1,8-diphenylocta-1,3,5,7-tetraene (in cyclohexane) measured in our laser flash setup and in an SLM spectrofluorimeter.

(c) **Double-Laser Flash Photolysis.** The radiative behavior of the photoexcited states of **2** and **3** was examined by subjecting these species to 355- or 337.1-nm laser pulse excitation following their photogeneration from **1** by 248- or 308-nm laser flash photolysis. In *n*-heptane (Figure 5, curve A and inset a), we observe a fast-decaying red emission ($\tau_F \leq 5$ ns) with a sharp maximum at 590 nm; this is attributable to 9-phenylxanthenyl radical (**3**). The same emission, with maximum at 590 nm, is also observed in methanol (Figure 5, curve B and inset b). In this solvent, a second emission is also noticeable at 480–600 nm; uncorrected for the relative sensitivity of the detector assembly in the laser flash photolysis setup, the second emission displays two maxima at 500 and 550 nm, respectively. Among these, the 500-nm maximum happens to be an artifact arising from a peak in the detector sensitivity at this wavelength.[29b] The second emission arises from cation **2** as shown by experiments in 1:1 MeOH/H_2O (Figure 5, curve C and inset c) wherein the emission due to **3** is absent (because of the lack of formation of **3**). In both neat methanol and 1:1 MeOH/H_2O, the cationic emission decay profile nearly follows the excitation laser pulse (~6-ns fwhm), suggesting that their lifetimes are very short ($\tau_F \leq 1$ ns) in these solvent systems.

The spectrum and decay profiles of cationic emission in 1:1 acetonitrile/H_2O (Figure 6, curve B and inset B) are very similar to those in aqueous methanol (see above). The results in neat acetonitrile, however, are interesting. In this solvent, although the yield of photogenerated cation (as seen in absorption) is insignificant compared to that of the radical, the emission spectrum (λ_{ex} = 355-nm laser) is dominated by contributions from the former (Figure 6, curve A and inset a). There is only a slight indication, at 590 nm, of the red emission from the radical.[30] Furthermore, it is noted that the cationic emission in neat acetonitrile is characterized by a long lifetime ($\tau_F = 25 \pm 2$ ns), indicating that the shortening of τ_F's in hydroxylic solvents is due to the quenching of the singlet of **2** by the hydroxylic molecules (see later). In 1,2-dichloroethane, the single-laser excitation (266 nm) of **2** photogenerated from **1** in the same laser pulse gave τ_F = 18 ns for **2**.

The authenticity of the cation emission in various neutral solvents was established in terms of both spectral shape/location and long lifetime (in acetonitrile) by obtaining emission spectra via single-laser flash photolysis of **2** produced in acidified, nonhydroxylic solvents. The results in MeCN + 8% H_2SO_4, illustrated in Figure 6, curve C and inset c, are similar to those obtained in *n*-heptane saturated with trifluoroacetic acid, except that τ_F in the latter is shorter (10 ns) than that in the former (25 ns). It should be noted that the genuineness of the emission traces attributable to **2** and **3** in the course of double-laser pulse excitations was routinely checked by control experiments using the probe pulse (337.1 of 355 nm) alone (i.e., in the absence of the 248-nm pulse).

To ascertain whether the shortening of the singlet lifetime of **2** in hydroxylic solvents is the manifestation of a chemical interaction, the double-laser experiments (λ_{ex} = 248 and 355 nm) were carried out with **1** in 1:1 MeCN/H_2O in the absorption mode. As shown in Figure 7, part B, the bleaching of the ground-state absorption of **2** (monitored at 375 nm) is prominent, suggesting the loss of the cation as a result of chemical quenching. There was practically no recovery of the absorbance over ~5 μs following the photobleaching. Similar experiments for **3** in *n*-heptane (Figure 7, part A) also indicate a slight bleaching of the radical at 345 nm, although the effect is far less pronounced than in the case of **2** in aqueous MeCN (Figure 7, part B).

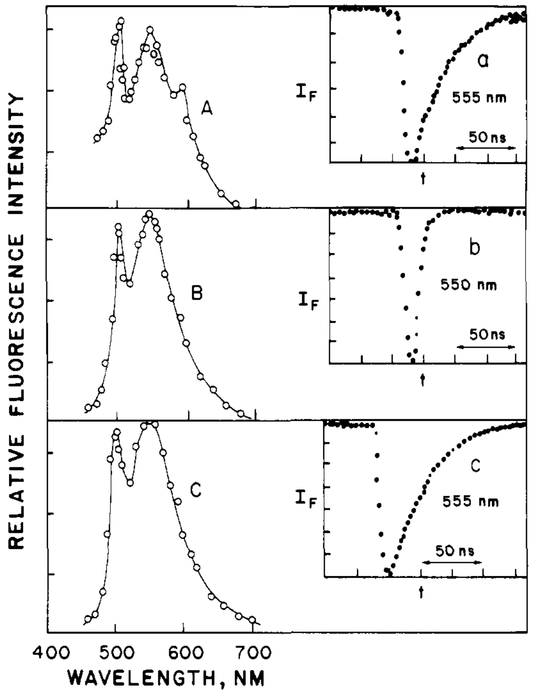

Figure 6. Transient emission spectra monitored at the maximum of decay traces, following 248-nm laser flash photolysis of **1** and subsequent (2 μs later) 355-nm laser flash excitation of the resultant transient(s) in (A) MeCN and (B) 1:1 MeCN/H_2O. The emission spectrum C was obtained by single-laser excitation (355 nm) of 9-phenylxanthenium cation in MeCN + 8% H_2SO_4. The peaks at 500 nm arise from the fact that the spectra are not corrected for the detector sensitivity. The insets show the corresponding emission traces at the indicated wavelengths.

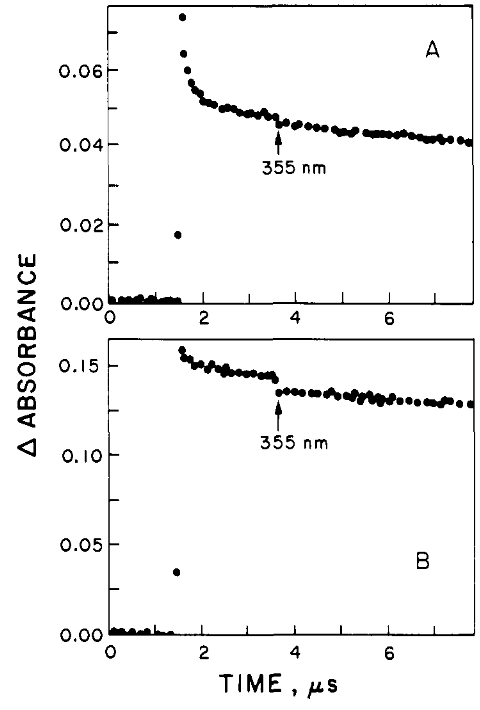

Figure 7. Effect of double-laser flash photolysis (248 and 355 nm, 2 μs apart) on **1** in (A) cyclohexane and (B) 1:1 H_2O/MeCN (both nondegassed). Monitoring wavelengths for transient absorption are 345 and 375 nm for A and B, respectively.

Several double-laser experiments in the absorption mode were also performed with **1** in benzene, 1,2-dichloroethane, and acetonitrile, with 308 and 337.1 nm for photogeneration and pho-

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[30] In acetonitrile, the very weak nature of the emission due to **3** in spite of the fact that **3** was formed in relatively high yiedl and the observation of the prominent emission due to **2** in spite of the fact that the yield of the latter was negligibly small (as seen in absorption) suggested the interesting possibility that the singlet of **2** might be the direct result of an adiabatic process in the course of the photoexcitation of **3** to a relatively high-lying doublet excited state attainable with λ_{ex} = 337.1 or 355 nm (namely, electron transfer to the solvent). In a two-laser experiment in the absorption mode, we did not observe any significant formation of the ground state of **2** (at 375 nm) as a result of 337.1-nm laser pulse excitation of **3** photogenerated from **1** by 308-nm laser flash photolysis in acetonitrile. In view of the less sensitive nature of the detection in the absorbance mode, we however cannot rule out the occurrence of a small extent of the process, $3^* \rightarrow 2^*$, which would possibly be detectable by emission.

Table II. Bimolecular Rate Constants (k_q) for the Quenching of 9-Phenylxanthenium Cation Singlet in Acetonitrile and Stern–Volmer Constants (K_{SV}) for the Quenching of Steady-State Fluorescence due to 9-Phenylxanthenium Cation Adiabatically Photogenerated from 9-Phenylxanthen-9-ol in 3:1 H_2O/Acetonitrile

quencher	k_q,[a] M^{-1} s^{-1}	K_{SV},[b] M^{-1}
triethylamine	$(3.0 \pm 0.5) \times 10^{10}$	24 ± 2
tetraethylammonium chloride	$(3.0 \pm 0.2) \times 10^{10}$	19 ± 2
tetrahydrofuran	$(6.2 \pm 0.6) \times 10^8$	1.2 ± 0.1
2-methyl-2-propanol	$(6.9 \pm 0.9) \times 10^7$	0.082 ± 0.02
2-propanol	$(1.2 \pm 0.1) \times 10^8$	0.62 ± 0.03
methanol	$(9.7 \pm 0.9) \times 10^7$	0.39 ± 0.03
water	$(3.3 \pm 0.4) \times 10^7$	

[a] λ_{ex}(laser) = 355 nm for **2** derived from **1** by 248-nm laser flash photolysis. Solvent acetonitrile. [b] λ_{ex}(steady-state) = 280 nm for **1**. Solvent: 3:1 H_2O/MeCN.

toexcitation of transient intermediates, respectively. To obtain appreciable ground-state absorbances at 308 nm (0.05–0.1 in 2-mm cells), the solutions of **1** had to be almost saturated. A major drawback under this condition was that the cation emission lifetimes were considerably shortened owing to quenching by its parent, that is **1**; the latter, being an ether as well as an alcohol, interacted with **2*** efficiently, vide infra. However, in these experiments, we focused more on the photobehavior of radical **3**, the excitation of which was made relatively exclusive by using the shorter wavelength laser pulse at 337.1 nm (rather than 355 nm) for the phototransient excitation. A minor complication accompanying the use of the 337.1-nm laser pulse on the concentrated solutions was that small, but nonnegligible, absorbance changes were often caused by this laser pulse alone (i.e., in the absence of the 308-nm laser pulse) and had to be corrected for. In 1,2-dichloroethane, we observed pronounced bleaching of **3** throughout its major absorption band system at 340–400 nm, with no concomitant positive absorbance change at longer wavelengths. The bleaching of **3** in this solvent was comparable to that of **2** in aqueous acetonitrile (Figure 7, part B). In benzene and acetonitrile, the absorbance changes as a result of the 337.1-nm excitation of **3** were negligible at or near its principal maximum (340–350 nm) and no positive absorbance changes occurred at longer wavelengths.

Surprisingly, the air saturation of acetonitrile or acetonitrile + 8–10% H_2SO_4 has a negligible effect on the singlet lifetime of **2**. By comparing singlet lifetimes in deoxygenated and oxygen-saturated acetonitrile, the oxygen quenching rate constant for **2*** is estimated to be $\leq 5 \times 10^8$ M^{-1} s^{-1}.

(d) Nucleophilic Quenching of Cation Fluorescence. The facts that the singlet lifetime of **2** is relatively long in acetonitrile (25 ns) and that the corresponding emission can be easily induced and monitored, without requiring a strong acid, by double-laser experiments in this solvent, prompted us to study the kinetics of interactions of **2** in the excited state with various nucleophiles. Thus, the decay rate constant (k_{obs}) of the fluorescence from **2** was measured as a function of the quencher concentration. Figure 8, part A, shows a typical plot of k_{obs} vs [quencher]. The bimolecular rate constants, measured from the slopes of such linear plots, are given in Table II. Notably, k_q for water as the quencher in acetonitrile (3.3×10^7 M^{-1} s^{-1}, Table II) is twice as high as that measured under steady-state excitation of **2** in MeCN + 10% H_2SO_4 (k_q,H_2O = 1.6×10^7 M^{-1} s^{-1}; vide supra). This probably underlines the lowering of the activity of water in the strongly acidified medium. Alternatively, the photoexcited cation in the ion-paired state is less susceptible to electrophilic quenching.

The electrophilic quenching of the steady-state fluorescence of **2** was also examined in a parallel manner under conditions where S_1 of **2** was produced via adiabatic photodehydroxylation (i.e., λ_{ex} = 280 nm for **1** in 3:1 H_2O/MeCN). A typical Stern–Volmer plot, with 2-propanol as the quencher, is shown in Figure 8, part B. The quenching constants (K_{SV}) are given in Table II (column 3). It is gratifying to note that the trend in K_{SV} is similar to that in k_q (column 2, Table II).

(e) Theoretical Calculations. In order to assess the redox behavior of 9-phenylxanthenium cation, this and several related arylcarbenium ions (namely, $PhCH_2^+$, Ph_2CH^+, and Ph_3C^+) were subjected to semiempirical MO calculations based on MNDO, MINDO/3, and AM1 methods.[31] Full structure optimization in all cases led to geometries planar at the cationic centers. For the polyaryl systems, the phenyl groups were twisted from the plane of the cationic center by angles ranging from 22 to 86°.

According to AM1 calculations, relative to Ph_2CH^+ and Ph_3C^+, the HOMO of **2** was higher in energy by 0.6 and 0.2 eV, respectively. The relative lowering of the LUMO of **2** was also of similar magnitude, namely, by 0.5 and 0.2 eV respectively. Qualitatively, these results are taken to suggest that **2** would be slightly more oxidizable than Ph_3C^+ and Ph_2CH^+ and that $E_{1/2}^{ox}$ of **3** is slightly lower (less positive) than that of $Ph_2CH^\bullet$ ($E_{1/2}^{ox}$ = 0.35 V vs SCE in acetonitrile)[32] and $Ph_3C^\bullet$ ($E_{1/2}^{red}(Ph_3C^+)$ = 0.21 V vs SCE in acetonitrile).[33]

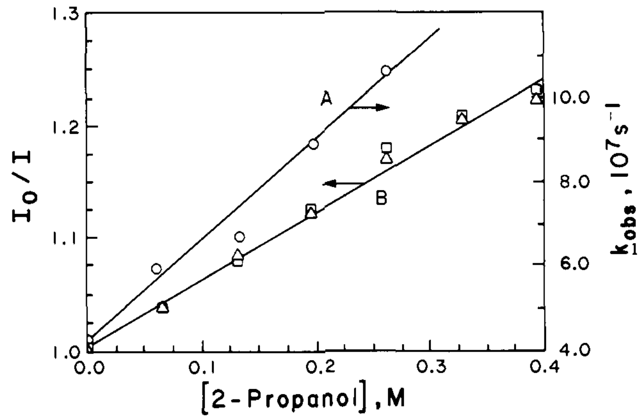

Figure 8. Linear plots vs quencher concentration of (A) observed decay rate constant of emission from 9-phenylxanthenium cation produced by 248-nm laser photolysis of **1** in acetonitrile and subsequently photoexcited by 337.1-nm laser pulses and (B) Stern–Volmer quenching of the steady-state fluorescence of 9-phenylxanthenium cation produced via adiabatic photodehydroxylation of **1** in 3:1 H_2O/MeCN (λ_{ex} = 280 nm).

Discussion

(a) Heterolytic vs Homolytic Photodissociation: Adiabatic Aspects. 9-Phenylxanthen-9-ol (**1**) is a tertiary aryl alcohol, with the oxo bridge rendering the molecule electron rich as well as partially rigid. As first demonstrated by Zimmerman and Sandel,[3] the ortho–meta transmission of electron density in the S_1 state by electron-donating substituents is a characteristic feature of benzyl derivatives and facilitates the photosolvolysis of these compounds via a cationic mechanism. For a series of isomeric methoxybenzyl alcohols, Turro and Wan[4] have shown that an *o*-methoxy group exerts a 3 times greater effect on the photodehydroxylation rate than a *m*-methoxy group. In this context, it is not surprising that in aqueous media **1** is readily photodehydroxylated to cation **2**. The involvement of the cation has been convincingly established by Wan et al.[12] through the observation of its emission of adiabatic origin under steady-state photoexcitation of **1**. In addition to the direct, confirmatory observation of the cation in terms of its time-resolved absorption and emission in hydroxylic solvents, the present laser flash photolysis study has furnished evidence in support of the parallel process of homolytic cleavage leading to radicals in relatively nonpolar solvents and of very small but nonnegligible heterolytic cleavage in nonhydroxylic solvents (namely, 1,2-dichloroethane and acetonitrile). By dint of the latter finding, we could study the reactivity of **2** in its S_1 state toward various nucleophiles in

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(31) QCPE programs (MOPAC and AMPAC) implemented in a DEC microVAX II were run on structures generated by the ChemCore molecular modeling software from Chemical Design, Inc. This work was carried out at the Computational Chemistry Workstation at the Phillips Research Center.

(32) (a) Wayner, D. D. M.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 7764–7765. (b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132–137.

(33) Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222–4229.

a relatively inert solvent (acetonitrile) and under a neutral condition.

In addition to noting the adiabatic character of photogeneration of **2** from the S_1 state of **1**, Wan et al.[12] have shown that the heterolytic photodehydroxylation process is catalyzed by solvent water and not by added hydronium ions (in the range pH 3–12). In support of a mechanism involving product-determining proton transfer from water to the incipient leaving hydroxide ion in the S_1 state of **1**, they observed an isotope effect (H_2O/D_2O) manifested in an increase in the fluorescence yield of **1** by ~16% on going from 20% CH_3CN/H_2O to 20% CH_3CN/D_2O and of a decrease of similar extent in the emission yield of cationic emission (adiabatic) under a similar change in solvent composition. Although we cannot deny the catalytic role of water in the photodehydroxylation process, the findings of the present study show that the presence of water (or a hydroxylic solvent molecule) is not crucial to this process. Interestingly, between 1,2-dichloroethane (ϵ = 10.36 at 25 °C)[24] and acetonitrile (ϵ = 37.5 at 20 °C),[24] the ionic photodissociation of **1** is relatively facile in the former, less polar solvent. It is possible that the chlorinated solvent brings into play a charge-transfer mechanism to produce the cation. This is outlined below:

$$\mathbf{1}^* + S \rightarrow \mathbf{1}^{+\bullet},S^{\bullet-} \rightarrow \mathbf{2} + {}^{\bullet}OH + {}^{\bullet}C_2H_4Cl + Cl^- \qquad (5)$$

Facile cation formation from aryl alcohols has been noted in the course of pulse radiolysis of these compounds in 1,2-dichloroethane.[6a] Also, a previous report from this laboratory has documented efficient ionic photodissociation for *all-trans*-retinol in the same solvent.[16a]

The sharp water content dependence of the intensity of cation fluorescence under steady-state excitation (280 nm) of **1** in aqueous acetonitrile (Figure 2) calls for a close examination. On the basis of the K_{SV} value of 0.18 M^{-1} for the water quenching of the steady-state fluorescence of **1** in acetonitrile, we estimate that the singlet of **1** would be quenched to the extent of 83% in 1:1 H_2O/acetonitrile. Assuming that this water quenching provides the only pathway for the photogeneration of the singlet of **2**, we expect the quantum yield of the latter to increase only marginally on further addition of water. On the other hand, the S_1 of **2** is progressively quenched by water, and hence the quantum yield of the fluorescence of **2** becomes monotonously lower as the water content of the medium is increased. A simplistic but explicit analysis based on K_{SV}'s for water quenching of $^1\mathbf{1}^*$ and $^1\mathbf{2}^*$ and ϕ_F of **2** (in acetonitrile) suggests that as the water concentration is increased, the observed adiabatic fluorescence yield of **2** should attain a maximum value of 0.04 at $[H_2O]$ = 2.6 M and then decrease continuously at higher $[H_2O]$. The trend observed in practice (Figure 2) is very different from this and strongly suggests the involvement of other factors, namely, static interactions between water and **1** in the ground state, inapplicability of K_{SV}'s due to a sharp increase in the polarity of the solvent with increasing water content, and possible changes in photophysical parameters associated with both $^1\mathbf{1}^*$ and $^1\mathbf{2}^*$. Interestingly, the fact that the emission of **2** at low $[H_2O]$ (i.e., ≤25 M) is extremely weak ($\phi_F < 10^{-4}$) suggests that only a small fraction of the singlet of **1** quenched by H_2O results in the formation of the singlet of **2**; that is, the water-catalyzed adiabatic transformation, $^1\mathbf{1}^* \rightarrow {}^1\mathbf{2}^*$, is considerably less than quantitative.

An approximate, but quantitative, assessment is possible for the fraction of the cation produced in the singlet state from $^1\mathbf{1}^*$ in 1:1 H_2O/MeCN. In this solvent mixture, the yield of **2** as measured by 266-nm laser flash photolysis is 0.4. Making allowance for the quenching by water, we estimate the $\phi_F(\mathbf{2}) = 1.8 \times 10^{-2}$. On the basis of these yields as well as the fact that the measured ϕ_F for adiabatic fluorescence is only about 6×10^{-5} (Figure 2), we can easily show that ~99% of the photogenerated cation evolves directly into the ground state (via a diabatic route). Though qualitative, a similar conclusion has also been arrived at by McClelland et al.[5b]

The nearly quantitative yield of photoheterolysis of **1** in aqueous mixtures is potentially utilizable in pH-jump experiments, e.g., to study kinetics of deprotonation of other substrates. Another ramification of this result is that we can now explain why externally added hydronium ions have no apparent effect on the photodehydroxylation process of **1** at pH 12–3 in an aqueous solution,[12] although the situation is otherwise for methoxybenzyl alcohols.[4] Obviously, in the case of **1**, the photodehydroxylation process is overwhelmingly dominated by the interaction with water (leading to a quantum yield of unity), and the quenching interaction with hydronium ions, though existent, remains relatively insignificant.

(b) Excited-State Behavior of Radical and Cation. In spite of the partial rigidity offered by the xanthenyl backbone, the doublet–doublet fluorescence of 9-phenylxanthenyl radical (**3**) is weak and short lived ($\tau_F \leq 5$ ns). The excited-state behavior of arylmethyl radicals has been a subject of several intensive studies[7,34] in recent times. among the series, benzyl, diphenylmethyl, and triphenylmethyl radicals in fluid solution at room temperature, the fluorescence lifetimes are long for $Ph_2CH^{\bullet}$ ($\tau_F \approx 300$ ns), while these are considerably short for the other two radicals ($\tau_F \leq 1$ ns for $PhCH_2$ in hexane and 4.5 ns for $Ph_3C^{\bullet}$ in methylcyclohexane).[34] The lowest doublet excited states of both of the latter radicals enjoy very long lifetimes at low temperatures (e.g., τ_F = 1–1.5 μs for $PhCH_2^{\bullet}$ in glassy matrices at 77 K[31d,e] and 0.14–0.24 μs for $Ph_3C^{\bullet}$ in methylcyclohexane/2-methylpentane glass at 77 K[7g]). The cause of the shortening of the excited-state lifetime of $Ph_3C^{\bullet}$ at room temperature has been described as photochemical in nature (namely, electrocyclic ring closure to a dihydrofluorenyl radical).[7a] Such a photochemical process has been shown to occur in the case of perchlorotriphenylmethyl radical.[7j] On the other hand, for $PhCH_2^{\bullet}$ a photophysical mechanism involving two closely lying doublet excited states has been invoked to explain the strong dependence of the radiationless transition rate on temperature. In analogy to $Ph_3C^{\bullet}$, the short τ_F in the case of **3** may also be thought to arise from photochemistry.[35] However, we observe neither prominent bleaching in the ground state absorption of **3** nor occurrence of transient absorbance attributable to a dihydrofluorenyl-type radical in the course of photoexcitation of **3** by 337.1- or 355-nm laser pulses in *n*-heptane, acetonitrile, and benzene (Figure 7, part A). This testifies against an explanation in terms of photochemistry.

A plausible reason for short τ_F in the case of **3** may be traced to the presence of the heteroatom in this system (oxo bridge). It is recognized that the emission lifetimes of diarylhydroxymethyl radicals are significantly shorter than the corresponding diarylmethyl radicals.[36] For example, at room temperature, $\tau_F(Ph_2\dot{C}OH)$ = 2–5 ns compared to $\tau_F(Ph_2\dot{C}H)$ ~ 300 ns under similar conditions.[36] A simple theoretical basis[37] for this difference has been obtained in terms of heteroatom-related low-energy charge transfer configurations contributing to the D_1 excited state. The presence of these configurations brings into effect relatively nonvanishing one-center terms in the vibronic matrix element for internal conversion and thus causes enhancement of this process. The short τ_F in the case of **3** also can largely be due to this factor.

The pronounced photobleaching of **3** in 1,2-dichloroethane is explainable in terms of chlorine atom transfer from the solvent to the radical. Such a photochemical process in CCl_4 has been

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(35) A definitive evidence for a trityl-type photochemical or a benzyl-type photophysical, mechanism in the case of **3** could be obtained from a study of the temperature dependence of τ_F. However, attempted experiments to observe the fluorescence behavior of **3** at low temperatures via photolysis of **1** were not successful.

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(37) (a) Bhattacharyya, K.; Das, P. K.; Fessenden, R. W.; Hug, G. L. *Abstracts of XI IUPAC Symposium on Photochemistry*; 1986; pp 61–62. (b) See also: Yankov, P.; Nickolov, Zh.; Zhelyaskov, V.; Petkov, I. *J. Photochem. Photobiol.* **1989**, *47*, 155–165.

previously documented for the diphenylmethyl radical.[7b] Electron transfer from a photoexcited state of **3** to the solvent leading to the formation of **2** is ruled out on the basis of the fact that the photobleaching of **3** in 1,2-dichloroethane is not accompanied by an occurrence of transient absorbance at 370–375 nm (i.e., at the absorption maximum of **2**). In any case, as suggested in the case of the diphenylmethyl radical,[7b] the interaction between ^{2}**3*** and the chlorinated solvent is probably of charge-transfer nature (the radical acting as the donor), Cl^- being transferred in the geminate ion pair (**2**$\cdots C_2H_4Cl_2^-$). Assuming that the difference in calculated LUMO energies of structurally related carbenium ions reflects the difference in $E_{1/2}^{ox}$'s of the radicals, we estimate the $E_{1/2}^{ox}$ of **3** to be less positive than that of $Ph_2CH^\bullet$ by 0.5 V. After making allowance for the fact that the lowest excited doublet (D_1) energy of **3** (as seen in doublet–doublet fluorescenc) is lower than that of $Ph_2CH^\bullet$ by 0.2 eV, we note that the free energy change of electron transfer from D_1 of **3** to a given acceptor will be more favorable (more negative) than that from D_1 of $Ph_2CH^\bullet$ by 0.3 V. A similar analysis suggests that the electron transfer from D_1 of **3** to acetonitrile ($E_{1/2}^{red} < -2.5$ V) would be endothermic by ≥ 0.5 eV.

The fluorescence lifetimes of **2** have previously been measured by time-correlated photon counting to be 4.5–9.9 ns in strongly acidified aqueous solutions (2.5–24.2% H_2SO_4). These short τ_F's in aqueous solutions obviously reflect the quenching of ^{1}**2*** by water. On the basis of our measured τ_F of 25 ns in the absence of a quencher in acetonitrile and the value of 3.3×10^7 M^{-1} s^{-1} for k_q by water, we estimate $\tau_F = 0.7$ ns in a solution that is 80% aqueous. The fact that the observed τ_F's in similarly aqueous H_2SO_4 are much longer suggests that the quenching by water is inhibited in the presence of the acid. This conclusion is also arrived at upon comparison of the efficiency of water quenching of steady-state fluorescence of **2** in 10% H_2SO_4 in acetonitrile ($k_{q,H_2O} = 1.6 \times 10^7$ M^{-1} s^{-1}) with that in acetonitrile ($k_{q,H_2O} = 3.3 \times 10^7$ M^{-1} s^{-1}). It is feasible that k_{q,H_2O} is strongly affected by the medium as well as by the presence of the counteranion (as pointed our earlier).

The resistance of the singlet of **2** to oxygen quenching, as evident from a very low k_{q,O_2} ($\leq 5 \times 10^8$ M^{-1} s^{-1}), is surprising. This behavior should be contrasted against the fully diffusion-controlled oxygen quenching of aromatic hydrocarbon and other singlets.[20,38] Charge-transfer interaction between singlets and oxygen has generally been implicated for efficient oxygen quenching.[38] Such an interaction is unfavorable in the case of the cation on the basis of its poor electron-donating capability[39] and appears to constitute the main reason for the inability of O_2 to quench S_1 of **2**.

(c) Reactivity of Cation Singlet toward Nucleophiles. The absolute rates of reactions of many aryl-substituted carbenium ions in the ground state with nucleophiles have been measured primarily by laser flash photolysis and pulse radiolysis techniques.[5,6] For example, the rate constants for the reaction of Ph_2CH^+ with monomeric alcohols are in the range $(2–10) \times 10^7$ M^{-1} s^{-1} in 1,2-dichloroethane.[6b] The decay behavior of **2** in aqueous methanol and in aqueous acetonitrile suggests that this cation is far less reactive in the ground state ($k_q < 10^4$ M^{-1} s^{-1} for **2** with water and methanol). McClelland et al.[5b] measured 23 s^{-1} as the decay rate of **2** in 4:1 H_2O/MeCN and 1.7×10^5 M^{-1} s^{-1} for the bimolecular rate constant for the reaction of **2** with *n*-propylamine (in the same solvent system). In contrast to these, upon photoexcitation to the singlet state, the reactivity of **2** is enormously increased (Table II). Obviously, this is a reflection of the increased exothermicity (by an amount equal to the singlet energy, i.e., ~60 kcal mol^{-1}). Along the alcohol series, methanol, 2-propanol, and 2-methyl-2-propanol, k_q is the highest for 2-propanol (Table II). Evidently, the availability of the lone pair in the nucleophile as augmented by increasing methyl substitution is counterbalanced by a parallel steric effect.

The K_{SV} data in Table II represent the quenching efficiency of adiabatically photogenerated singlet of **2** as it is produced from **1** under steady-state photoexcitation of **1** in 3:1 H_2O/MeCN. The relative quencher dependence of K_{SV} is comparable to that of k_q in MeCN (Table II, column 2). Note that these K_{SV} values incorporate the composite quenching effect on ^{1}**1*** and ^{1}**2***. However, at the high water concentration (~42 M) the decay of ^{1}**1*** is dominated by water quenching and hence should be less susceptible to the quenching (if any) by the specific anionic or nucleophilic quencher. The dominance of a single quenching pathway is also corroborated by the linearity of the experimental Stern–Volmer plots. At ~42 M [H_2O], the extrapolated τ_F(**2**) = 0.7 ns. With this value for τ_F and the K_{SV} data in Table II, we estimate k_q's for triethylamine and tetraethylammonium chloride that are in good agreement with those obtained by direct quenching measurement (Table II, column 2). For other quenchers, namely, tetrahydrofuran and alcohols, the k_q's estimated from K_{SV}'s are 3–7 times higher than those from direct quenching experiments. The difference, understandably noted at the kinetic domain below diffusion control, is probably a manifestation of enhanced reactivity of the singlet in the more polar, aqueous medium used in the steady-state measurement.

Finally, we note that the enhanced electrophilicity of the singlet state of **2** should be utilizable in photoinitiation of organocationic reactions. **2** can be obtained as a stable species in suitable acid matrices (e.g., zeolites and nafion films) or can be photogenerated from **1** as a metastable species in an environment that is relatively nonacidic. The photoexcitation of **2** may be useful in generating various carbenium species and in initiating the chemistry associated with them.[40] The fact that the S_1 of **2** is almost nonquenchable by oxygen should prove advantageous.

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[39] (a) The oxidation potential of **2** is not available.[39b] However, electron transfer from the cation to oxygen would not be favored by the coulombic attraction in the incipient anion–dication pair. (b) Attempted cyclic voltammetry of **2** generated from **1** in acetonitrile acidified with trifluoroacetic acid and containing 0.1 M tetrabutylammonium perchlorate showed an oxidation wave at ~0.9 V (vs SCE), assignable to unchanged **1**. Also, the observed large reduction wave at 0.0 to –1.0 V was shown to be due to the acid. Kamat, P. V. Unpublished results.

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