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Water Quenching Behavior of Excited 9-Xanthylium Cations in Aqueous Sulfuric Acid Solutions

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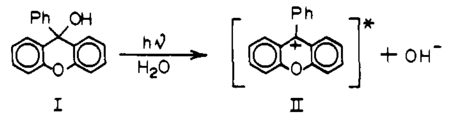
Abstract: A series of 9-alkyl- and 9-aryl-substituted xanthylium cations (H, Me, *i*-Pr, c-Pr, *t*-Bu; Ph, *p*-CF_3, *p*-Me, *m*-Me, *p*-OMe, *m*-OMe) were generated from the corresponding 9-xanthenols in strongly acidic aqueous acetonitrile (2:1) solutions (39–78% H_2SO_4). Steady-state irradiation at 370 nm produced the excited cations, all of which were fluorescent in the 520-nm region. Fluorescence lifetimes varied considerably with acid concentration, from subnanosecond values at low acidity to 20–35 ns at high acidity. Stern–Volmer plots of $\Phi_F{}^\circ/\Phi_F$ versus the "free" water concentration in these acid solutions gave linear plots in all cases, yielding k_q values in the 10^6–10^9 M^{-1} s^{-1} range, depending on substituents. For the 9-aryl systems, a plot of log k_q versus a recently determined $\sigma^{h\nu}$ scale was reasonably linear ($r = 0.974$) with a ρ value of -1.5, which is opposite in sign to that recently determined for H_2O quenching of the same cations in their ground states. Possible explanations for this surprising result are considered.

Introduction

The ground-state behavior of carbocations generated in strong or superacid media has been the subject of considerable investigation.[1] The excited-state behavior of thermally generated carbocations has also been studied, in terms of both reaction products and mechanisms,[2] but much less extensively. Electron-transfer reactions of excited-state carbocations have also been studied, for example, with triphenylmethyl[3] and aryltropylium systems.[4] The cations were irradiated in the presence of electron donors, such as amines and aromatic hydrocarbons. A correlation was found between the rate constant for quenching of the excited cation and the ionization potential of the donor.

More recently, 9-substituted xanthyl cations have been studied by both steady-state and flash photolytic methods. We have shown previously[5] that 9-phenyl-9-xanthenol (I) undergoes adiabatic photodehydroxylation in aqueous solution, to give the 9-phenylxanthylium cation (II), via steady-state irradiation of I at 290 nm.



The fluorescence of II at 520 nm was shown to be identical with that of the same cation, formed via thermal ionization of I in strong acid (H_2SO_4) solutions, followed by irradiation at 370 nm. Similar adiabatic heterolysis occurs with other xanthenols and related compounds, to give xanthylium-type cations, including the parent (unsubstituted) 9-xanthylium cation.[6] Thus, excited-state xanthylium cations can be generated and studied either via photodehydroxylation in neutral solution or via thermal ionization in acid solution, followed by excitation.

Recently McClelland et al.[7] have generated a series of 9-arylxanthylium cations via laser flash photolysis of 9-aryl-9-xanthenols in 1:4 acetonitrile/water. These researchers studied the nucleophilic trapping of the cations with a variety of nucleophiles, and measured the rate constants for these electrophilic reactions of 9-arylxanthylium cations. It is important to emphasize however that while the cations in this study were generated flash photolytically, the subsequent reactions of cations such as II with water or other nucleophiles were those of ground-state species, formed after decay of the initially formed excited-state cations.

More recently, Minto and Das[8] have reported a thorough investigation of the photodehydroxylation of I itself and have obtained detailed information concerning the photophysics and photochemistry of II. In this work, II was produced under nonsteady-state conditions by using a two-pulsed laser system. Bimolecular quenching rate constants were obtained by monitoring the decay of fluorescence of II as a function of the quencher concentration or by following the quenching of steady-state fluorescence of II produced adiabatically via irradiation of I in 3:1 water/acetonitrile.

Following our earlier work[5] on the adiabatic generation of 9-substituted xanthylium cations, we had decided to conduct a further study of these excited cations by a different approach, namely, via their thermal generation from the corresponding 9-xanthenols in sufficiently strong H_2SO_4 solutions (in 2:1 water/acetonitrile) to ionize the alcohols completely, followed by steady-state irradiation. In this way, we could more conveniently measure their lifetimes via single photon counting methods and their fluorescence quenching behavior by the Stern–Volmer approach. We now report on the effects of structure on both the singlet lifetimes and k_q values, for a series of 9-substituted and 9-aryl-substituted xanthylium cations.

Results

The systems chosen for study were the 9-substituted 9-xanthenols **1–5** and the substituted 9-aryl-9-xanthenols **6–11**. The corresponding xanthylium cations were first formed thermally through dehydroxylation of the 9-substituted 9-xanthenols in aqueous sulfuric acid, containing acetonitrile for solubility reasons (H_2O/acetonitrile, 2:1 by volume). The extent of ionization could be followed by measuring changes in UV spectra as a function of acid concentration. The absorbance maxima of the xanthenols (ca. 280 nm) and cations (ca. 375 nm) are quite well separated. A typical UV titration curve is shown in Figure 1 for **3**. The

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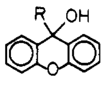

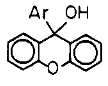

R		Ar aryl substituent	
H	**1**	H	**6**
Me	**2**	*p*-CF_3	**7**
i-Pr	**3**	*p*-Me	**8**
c-Pr	**4**	*m*-Me	**9**
t-Bu	**5**	*p*-OMe	**10**
		m-OMe	**11**

sigmoidal change in absorbance at 374 nm (cation) as a function of pH (or H_0)[9] shows that thermal dehydroxylation is essentially complete at an acid concentration of ca. 35%. The H_0 values in Figure 1 have not been corrected for the 33% (v/v) acetonitrile cosolvent, since we are only interested in determining the percent acid region where ionization is complete. Therefore, only apparent pK_{R^+} values can be estimated from the half-ionization points of these curves. These are in the range −0.50 to −2.0 for substrates **1–4** and **6**, which compares with a reported value for pK_{R^+} of +0.1[10] for similar substrates obtained in purely aqueous solution. Substrate **5** behaved quite differently from the rest. No trace of cation could be detected at acidities lower than 67% H_2SO_4. Further, the cation absorbance was not stable in acid solution (as found for all other substrates), indicating other reactions than simple dehydroxylation were occurring. It had been previously reported[11] that the 9-*tert*-butylfluorenyl cation, generated in superacid media undergoes a methyl 1,2-shift, followed by various other processes, to give a mixture of products. It seems likely that similar decomposition of **5** is occurring in our system; therefore, the 9-*tert*-butylxanthylium cation was not studied further.

Since compounds **1–4** and **6–11** all showed similar sigmoidal behavior in terms of their UV absorption at ca. 370 nm, as a function of acid concentration, and give a plateau region at or above 39% H_2SO_4 (H_0(uncorrected) ≤ −3), where ionization is presumably complete, we expected that the cation fluorescence would show similar behavior. The corresponding cation fluorescence (at 520 nm) did indeed show sigmoidal behavior as a function of acid concentration, as shown for **3** in Figure 2. However, no plateau region was observed, and the fluorescence intensity continued to increase steadily as a function of acidity up to the highest concentrations used (77% H_2SO_4). The increase in fluorescence intensity well beyond $H_0 = -3$ cannot be due to the formation of more cation, since the UV absorption curves show that the substrates are present completely in their cationic form by this acidity. This disparity between the ground-state cation results (absorption) and excited-state cation (emission) can best be illustrated by plotting the UV absorption data versus the fluorescence data for each compound, as shown in Figure 3, for compound **3**. A good linear correlation is found up to the acid region where the absorption reaches a plateau (ionization complete), as would be expected, but the fluorescence intensity continues to increase sharply after this point. A straight line has been drawn through the data points to emphasize the dramatic change in behavior at the break point; we do not mean to imply a linear dependence.

Since the fluorescence quantum yield is related to the excited-state lifetime, it was decided to test whether the above increases in fluorescence efficiency were matched by a concomitant increase in singlet lifetime. It should be noted that while the fluorescence quantum yield and the excited-state lifetime are not directly related, if the fluorescence quantum yield increases, an increase in the lifetime is likely to occur. Lifetimes were measured (by single photon counting methods)[12] for the cations of xanthenols **1–6** in 39–77% H_2SO_4, as well as for the xanthenols themselves

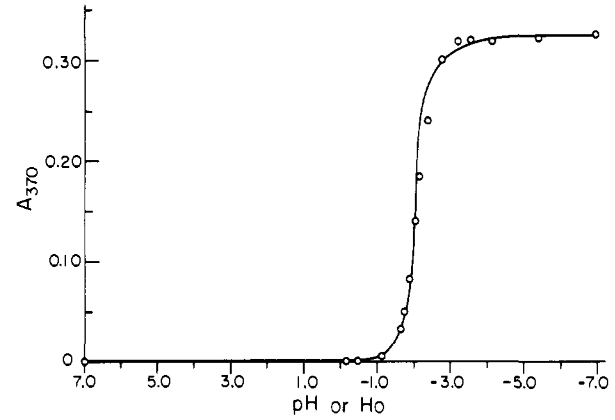

Figure 1. Absorbance at 370 nm of 9-isopropyl-9-xanthylium cation in H_2SO_4 solutions, from pH 7 to $H_0 = -7$.

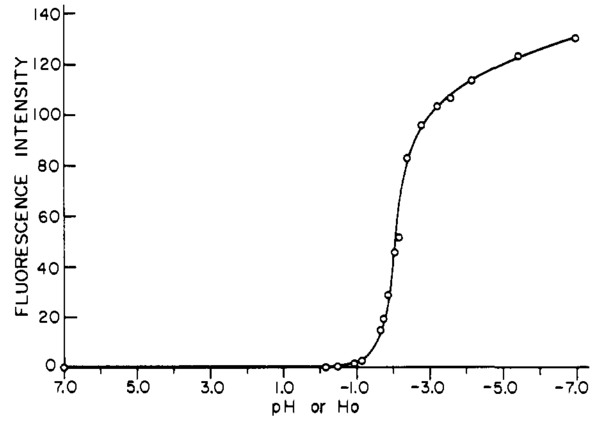

Figure 2. Fluorescence intensity (arbitrary units) at 520 nm of 9-isopropyl-9-xanthylium cation in H_2SO_4 solutions, from pH 7 to $H_0 = -7$.

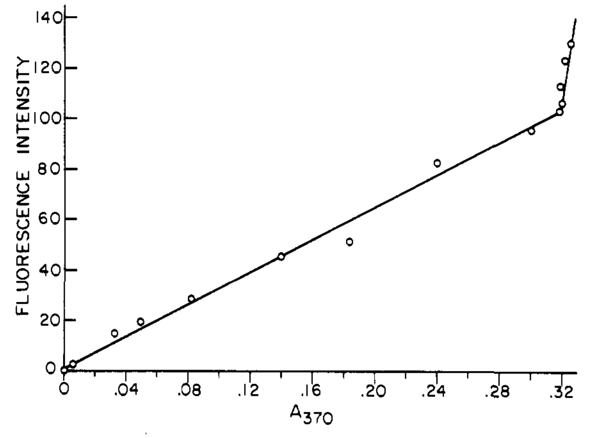

Figure 3. Fluorescence intensity at 520 nm versus absorbance at 370 nm for 9-isopropyl-9-xanthylium cation.

Table I. Fluorescence Lifetimes[a] of Xanthenols **1–6** and Corresponding Xanthylium Cations

	solvent			
		aqueous sulfuric acid[b]		
substrate	pH 7[c]	39.4%[d]	52.7%[d]	76.9%[d]
1	0.47	10.8	13.6	19.4
2	~0.9			35.0
3	3.4	27.3	30.7	35.4
4				32.6
5	3.5			10.9
6	1.2	8.0	15.8	26.6

[a] All lifetimes given in nanoseconds, estimated error ±10%. [b] Acid percentages are not corrected for acetonitrile cosolvent present. [c] Lifetimes measured in neutral solution correspond to parent xanthenols. [d] Lifetimes in acid solutions are for corresponding 9-xanthylium cation.

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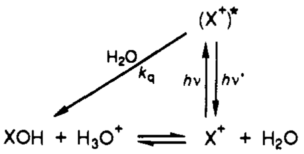
Scheme I



in neutral solution. The results are given in Table I. All measured lifetimes are based on clean single-exponential decays. Table I shows that, in every case, the cation has a much longer lifetime than the neutral alcohol. Furthermore, the results show that the cation lifetimes increase dramatically as the acid concentration is increased. For example, the lifetime of the 9-phenyl-9-xanthylium cation doubles in going from 39% to 53% H_2SO_4, and in 78% acid it is three times that in the lowest acid concentration used. It should be noted that the *tert*-butyl derivative **5** has a shorter lifetime than the other cations in 77% acid, presumably due to the decomposition discussed earlier. Alternatively, products from the decomposition could be acting as quenchers for the excited singlet **5**.

These medium effects on fluorescence lifetimes and intensities were proposed to arise from differential quenching of the excited-state cations. It has been previously suggested[5,7,8] that the cation would be quenched by water in a deactivational step competitive with fluorescence, regenerating the starting xanthenol, as shown in Scheme I. As the acidity of the solution increases, the amount of water decreases and the resulting decrease in quenching of the excited-state carbocation results in longer fluorescence lifetimes and a larger fluorescent intensity.

Quenching experiments were performed only in the plateau region (39–77% H_2SO_4), where the above equilibrium is shifted completely over to the cation side. The highest acid concentration used (77%) is defined as the $\Phi_F{}^0$ situation, and measurements at lower acidities are used for Φ_F. In this way a modified Stern–Volmer[13] approach can be used, as shown below.

$$\Phi_F{}^0 = \frac{k_F{}^0}{k_F{}^0 + \sum k_d + k_q[H_2O]^0} = k_F{}^0\tau_F{}^0$$

$$\Phi_F = \frac{k_F{}^0}{k_F{}^0 + \sum k_d + k_q[H_2O]}$$

$$\Phi_F{}^0/\Phi_F = (k_F{}^0 + \sum k_d)\tau_F{}^0 + k_q[H_2O]\tau_F{}^0$$

In these expressions, $\sum k_d$ is the sum of all other deactivational processes, $\tau_F{}^0$ is the observed lifetime in 77% H_2SO_4, and $[H_2O]$ is the "free" water concentration (see Experimental Section) in the acid solution in question. In this way, $[H_2O]^0$ is the lowest quencher concentration used, but unlike the standard Stern–Volmer situation this is not exactly zero. However, a plot of $a[H_2O]$(molar) versus $\%H_2SO_4$ for purely aqueous acid[14] shows that water acitivity in this medium effectively approaches zero at about 80% acid. Unfortunately our use of acetonitrile as cosolvent precludes use of reported water activities, but the calculated "free" water concentrations used in the present treatment correlate against $a[H_2O]$(aqueous) with an r value of 0.995 and a slope significantly less than unity, as would be expected due to the dilution of our aqueous acids by 33% by volume of acetonitrile.

Relative fluorescence quantum yields ($\Phi_F{}^0/\Phi_F$) were measured for all cations (except that derived from **5**) and plotted against the "free" water concentration. Excellent linear plots were obtained, as shown in Figure 4 for the cation from **1**, the parent 9-xanthylium ion. In Table II are collected the Stern–Volmer slopes and derived k_q values for the 9-substituted xanthyl cations **1**–**4**, which are all in the range (2–9) × 10^6 M^{-1} s^{-1}. Correlation coefficients are all >0.99 and σ_y values are all low.

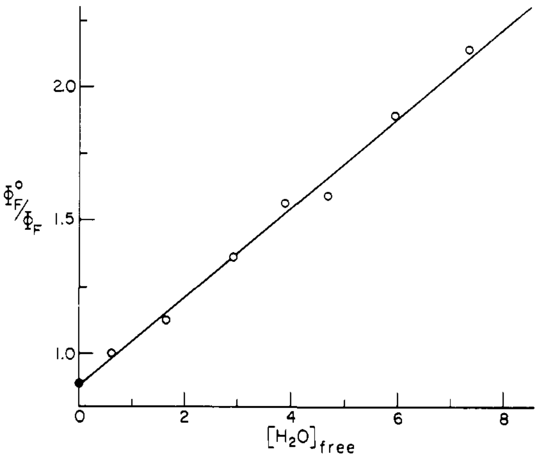


Figure 4. Stern–Volmer plot of $\Phi_F{}^0/\Phi_F$ versus free water concentration in H_2O/acetonitrile H_2SO_4 for 9-xanthylium cation: experimental points, open circles; intercept calculated from K_{SV}, solid circle.

Table II. Stern–Volmer Quenching of 9-Substituted Xanthylium Cations

	9-substituent			
	H (**1**)	Me (**2**)	*i*-Pr (**3**)	c-Pr (**4**)
K_{sv}[a]	0.171	0.073	0.066	0.067
τ^0 (ns)[b]	19.4	35.0	35.4	32.6
k_q (M^{-1} s^{-1})[c]	8.81 × 10^6	2.09 × 10^6	1.86 × 10^6	2.04 × 10^6
r[d]	0.996	0.993	0.998	0.996
int[e]	0.862	0.937	0.956	0.968
(int calcd)[f]	(0.891)	(0.953)	(0.958)	(0.957)
σ_y[g]	0.042	0.023	0.027	0.013

[a] Slope of Stern–Volmer plot of $\Phi_F{}^0/\Phi_F$ versus $[H_2O]_{free}$, error in slope ±5% based on standard deviation. [b] Fluorescence lifetime in 77% H_2SO_4 in 1:2 acetonitrile/H_2O, measured by single photon counting, estimated error ±10%. [c] Error is ±10%. [d] Correlation coefficient. [e] Intercept obtained from linear regression. [f] Intercept calculated from observed slope and lifetime. [g] Standard deviation on Φ_F axis.

Since the Stern–Volmer approach has been modified as described above, this means that the intercepts of the plots will no longer be unity, as in the standard Stern–Volmer approach. However, the intercepts obtained can easily be checked for internal consistency, in two ways. Since the intercept is given by $(k_F{}^0 + \sum k_d)\tau_F{}^0$, this term can be calculated from the Stern–Volmer slope (K_{SV}) and the measured lifetime, since it is equal to $1 - k_q[H_2O]^0\tau_F{}^0$. This gives the calculated intercept values listed in Table II, which are all close to those obtained from the Stern–Volmer plots. Alternatively, it is easy to show that the ratio of intercept to slope should be given by

$$I/S = \frac{1 - K_{SV}[H_2O]^0}{K_{SV}}$$

The calculated I/S values are in all cases close to those observed, showing that the intercepts obtained are consistent with the Stern–Volmer slopes, and hence that the modified approach is internally consistent.

Similar results were obtained for the substituted 9-aryl-9-xanthylium cations as shown in Table III, except that the k_q values have a much wider range (6 × 10^6 to 3 × 10^9 M^{-1} s^{-1}) than that for the 9-alkyl systems. The correlations are again excellent (r > 0.99), with one exception (r = 0.981), and the calculated intercepts agree well with those observed, in all cases but one.

The modified Stern–Volmer equations can be expressed in terms of lifetimes, as shown below. Thus, the more limited lifetime data in Table I can be used to check some of the k_q reported in Tables III and IV, since

$$1/\tau_F = 1/\tau_F{}^0 + k_q([H_2O] - [H_2O]^0)$$

The values obtained for the cations from xanthenols **1**, **3**, and **6** by using the lifetime data in Table I are 6.4 × 10^6, 1.3 × 10^6,

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Table III. Stern–Volmer Quenching of 9-Aryl-Substituted Xanthylium Cations

	aryl substituent					
	p-CF_3 (**7**)	H (**6**)	*p*-Me (**8**)	*m*-Me (**9**)	*p*-OMe (**10**)	*m*-OMe (**11**)
K_{sv}[a]	0.155	0.397	0.844	0.627	0.428	0.451
τ^0[b] (ns)	24.1	19.4	3.2[c]	2.1[c]	0.14[d]	0.18[d]
k_q ($M^{-1}\ s^{-1}$)[e]	6.42×10^6	1.49×10^7	2.64×10^8	2.99×10^8	3.06×10^8	2.51×10^9
r[f]	0.998	0.981	0.998	0.989	0.993	0.989
int[g]	0.908	0.479	0.511	0.792	0.816	0.734
(int calcd)[h]	(0.901)	(0.747)	(0.462)	(0.600)	(0.727)	(0.712)
σ_y[i]	0.026	0.203	0.118	0.231	0.260	0.292

[a] Slope of Stern–Volmer plot of Φ_F^0/Φ_F versus $[H_2O]_{free}$, error in slope ±5% based on standard deviation. [b] Fluorescence lifetime measured by single photon counting, estimated error ±10%. [c] Fluorescence too weak to give reliable τ values. Single photon counting method gave estimated τ's in 2–3-ns range. Values quoted obtained from relative Φ_F's (see text). [d] Lifetimes too short for instrumental range. Values quoted obtained from relative Φ_F's (see text). [e] Error is ±10%. [f] Correlation coefficient. [g] Intercept obtained from linear regression. [h] Calculated from observed slope and lifetime. [i] Standard deviation on Φ_F axis.

Table IV. Correlations of log k_q Values for 9-Arylxanthylium Ion Quenching versus Substituent Constants

9-aryl substituent	τ_F^0 (ns)	log k_q	$\sigma^{h\nu}$	σ^+	σ	σ_{ex}[d]
p-CF_3	26.6	6.81	+0.56[a]	+0.58	+0.54	+0.58
H	24.1	7.17	0	0	0	0
p-Me	3.2	8.42	−0.53	−0.26	−0.17	−0.13
m-Me	2.1	8.52	−0.79	−0.065	−0.069	−0.1
p-OMe	0.14	9.49	−1.17	−0.65	−0.27	−0.1
m-OMe	0.18	9.40	−1.48	+0.05	+0.12	−0.49
slope (ρ)			−1.44	−2.00	−2.52	−2.50
intercept (log k_q^H)			7.48	8.19	8.37	8.2
r[b]			0.975	0.726	0.648	0.807
σ_y[c]			0.276	0.856	0.948	0.735

[a] No value available for $\sigma^{h\nu}$. Value used is average of σ^+ and σ. [b] Correlation coefficient. [c] Standard deviation on log k_q axis. [d] Taken from ref 18b.

and $1.05 \times 10^7\ M^{-1}\ s^{-1}$, respectively, which are in reasonable agreement with those reported in Tables II and III. This supports the idea expressed earlier that the increases in fluorescence and lifetime observed in acid solutions are both due to the same quenching phenomenon.

Discussion

Quenching of 9-Alkyl Cations. The values of k_q obtained for the cations of **1–4** show the order of reactivity with respect to 9-substitution: H > Me > *i*-Pr ≈ c-Pr although the relative rate differences are not very large ($k_q \approx (2–9) \times 10^6\ M^{-1}\ s^{-1}$), especially for the three alkyl-substituted cations. This at first sight appeared to be due to stabilization of the cation by an inductive effect, thereby lowering its k_q. However, the fact that the 9-phenyl cation, and the 9-aryl cations with electron-donating substituents, all react *faster* ($k_q \approx 10^7–10^9\ M^{-1}\ s^{-1}$) than the parent 9-xanthylium cation ($k_q = 8.8 \times 10^6$) does not support this idea. Similarly, the 9-isopropyl and 9-cyclopropyl cations are both quenched at approximately the same rate, again suggesting that the electronic effects of alkyl groups are not the controlling factor. A similar lack of cyclopropyl stabilization[15] was found for the 9-cyclopropylxanthylium cation in its ground state, and was attributed to the inherent stability of the xanthylium system through charge delocalization into the aromatic rings. The simplest explanation for the differences in reactivity of cations **1–4** is that there is a small steric effect toward attack by H_2O on the cationic center at position 9. This is consistent with the order H > Me > *i*-Pr, as well as with the fact that **3** and **4** do not react at very different rates. Unfortunately, k_q for the 9-*tert*-butyl cation could not be measured, for the reasons mentioned earlier, since this would have given a clearer indication of the importance of steric effects. However, the fact that the *tert*-butyl cation decomposes by other pathways faster than it is quenched by H_2O is at least consistent with the above proposal.

Quenching of 9-Aryl Cations. Turning to the 9-aryl-substituted systems **6–11**, the results are quite surprising, in two respects.

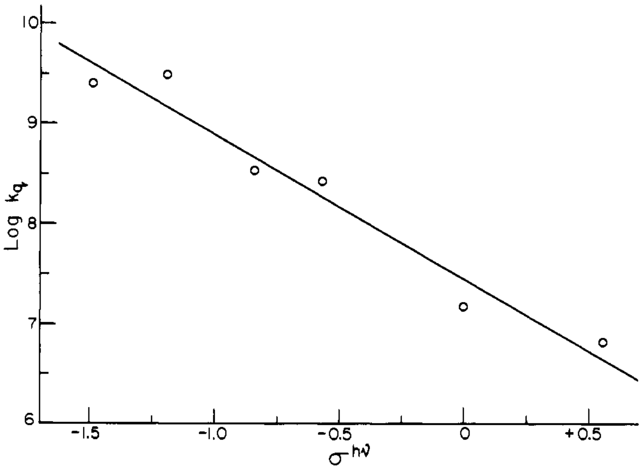

Figure 5. log k_q for 9-aryl-substituted-9-xanthylium cations versus $\sigma^{h\nu}$.

Firstly, the parent 9-phenylxanthylium cation reacts faster than the 9-xanthylium ion itself, although clearly the steric effect of 9-phenyl, however rotated, can not be less than that of 9-H. Secondly, it is clear that increasingly electron donating groups at the meta or para positions of the 9-aryl group cause a marked increase in k_q from about 10^7 to greater than $10^9\ M^{-1}\ s^{-1}$. Before these substituent effects are discussed in detail, it should be pointed out that the value obtained for k_q for the cation from 9-phenyl-9-xanthenol, $1.5 \times 10^7\ M^{-1}\ s^{-1}$, is in excellent agreement with the values reported by Minto and Das,[8] when the difference in solvent systems is taken into account. Their value for H_2O as the quencher in acetonitrile as solvent was $3.3 \times 10^7\ M^{-1}\ s^{-1}$. However, in acetonitrile with 10% aqueous H_2SO_4 added, they observed $k_q = 1.6 \times 10^7\ M^{-1}\ s^{-1}$ for quenching by H_2O, and suggested this difference was probably due to the lowering of the water activity in the strongly acidified medium. This is similar to our proposal, on which the present modified Stern–Volmer treatment is based, and the agreement between the two values of k_q obtained further justifies the present approach.

Correlation of log k_q with Substituent Constants. For **6–11**, values of log k_q were plotted against a recently determined $\sigma^{h\nu}$ scale,[16] based on the photohydration reactions of substituted styrenes and phenylacetylenes. This σ scale should be appropriate for the excited states of 9-arylxanthylium cations since it is based on formation of related aryl-substituted carbocations formed via rate-determining protonation of S_1 states (possibly adiabatically).[17] The results are shown in Figure 5, where a reasonable linear correlation is obtained ($r = 0.977$, $\sigma_y = 0.267$). Correlations were also attempted versus both σ^+ [18a] and σ [18a] as shown in Table IV.

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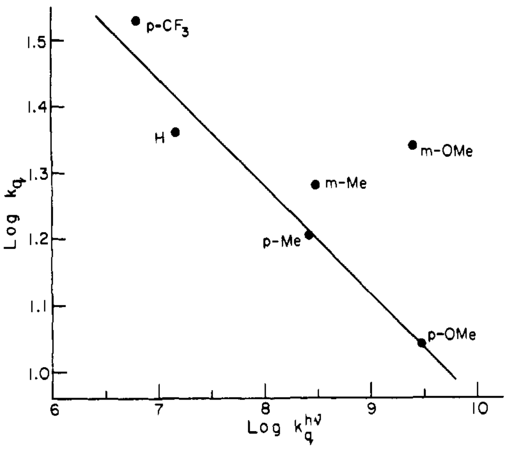


Figure 6. Water quenching rates for ground-state xanthylium cations (log k_q^{Δ}) versus quenching rates for corresponding excited states (log $k_q^{h\nu}$).

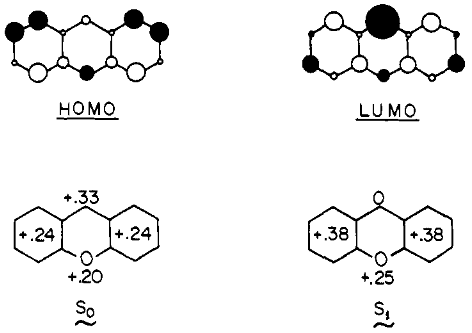
Although the σ^+ might have seemed most appropriate for these cations, correlations against both ground-state substituent parameters are very poor (r = 0.726 (σ^+), 0.648 (σ)). Correlation versus σ_{ex}, an excited-state substituent constant scale determined by Baldry,[18b] gave similarly poor results (r = 0.807). Thus, despite the fact that the correlation in Figure 5 is by no means ideal, it is much better than those obtained by using conventional σ scales.

The most surprising result is that ρ for the quenching of excited 9-aryl-9-xanthylium ions is negative (−1.5). This is also clear from the fact that the τ values in the reference medium (77% H_2SO_4) become distinctly shorter as electron-donating substituents are introduced. This substituent dependence is exactly opposite to that found for the ground states of similar cations as determined by McClelland et al.[7] ($\rho[H_2O]$(versus σ) = +0.5). The difference in excited- versus ground-state cation quenching is illustrated most clearly by plotting log k_q(excited) versus log k_q(ground), as shown in Figure 6. Two things are evident from this plot. One is that, independent of the particular σ scale chosen, the response of the two types of cation toward electron-donating substituents is opposite. Secondly, although the points for para substituents fall close to the line, those for meta substituents fall above the line (i.e., excited-state cations are relatively more reactive with meta substitution). This is again suggestive of the so-called "meta effect" in photochemical systems, first reported by Zimmerman[19] and Havinga,[20] where meta substituents of a given type (electron-donating or electron-withdrawing) show greater conjugative effects in excited states than do the same substituents in the para position.

The small positive ρ values reported for quenching of the ground-state xanthylium cations by various anionic and neutral nucleophiles have been explained[7] quite straightforwardly in terms of weak cation stabilization via electronic effects of the 9-aryl group, and thus lowering of k_q values. However, an explanation for the substituent effects found here for their excited-state analogues is anything but straightforward. Why strongly electron donating substituents such as methoxy should strongly *increase* the rate of quenching by H_2O, and greatly decrease τ_F, even in strongly acidic solutions where effective nucleophilic trapping species are very low in concentration, is not at all clear.

We had hoped to explain these trends by means of semiempirical MO calculations (MNDO, MINDO/3, and AM1 methods),[21] as employed by Minto and Das[8] to rationalize the redox behavior of xanthylium and related carbenium ions. However, in order to explain the present effects, it would be necessary to carry out open-shell MO calculations on the xanthylium cation excited states. Although this could be done in principle by using the LCAO-SCF-RHF[22] approach, SCF methods, whether semiempirical or ab initio, would not give valid results in the present case, for the following reasons. Whatever the geometry of the cations with respect to 9-aryl rotation, and whatever the pattern of 9-aryl substitution, the symmetries of these systems would necessarily place them in either the C_s, or most probably the C_2, point group.[23] The electronic transitions involved are all (π,π^*) type, and since both the HOMO(π) and LUMO(π^*) would belong to the same representation (A″ or B) as each other, because of the nodal plane of all π-type orbitals, the S_1 states involved would necessarily belong to the totally symmetric representation, as do all closed-shell ground states, S_0. Since the SCF approach can only be used for the lowest energy electronic state of a given symmetry,[24] the AM1 method for example would not give valid results for S_1. This problem could be avoided by doing MCSCF-CI calculations, but this is not presently feasible for molecules of this size.

Chart I



One alternative is to examine the HOMO–LUMO pattern, which can easily be done by using simple HMO calculations,[25] without the attendant problems described above. The HMO calculations took into account the substituent effect by using standard heteroatom parameters for the various substituents used. While the *overall* charge density distribution does not change very much, the main difference between the HOMO and LUMO is the very large increase in the MO coefficient at C_9 (see Chart I). The main result of this is that while the cationic charge is well delocalized in S_0, a considerable fractional positive charge remains at C_9. In S_1, after promotion of an electron to the LUMO, the surprising result is that there is very little residual charge at C_9. (It should be pointed out that a MINDO3[26] calculation on the ground-state cation gave essentially the same HOMO–LUMO pattern.) The lobe and MO coefficient at C_9 upon going from the HOMO to the LUMO increase with electron-donating substituents. These changes are small; however, the change does seem to parallel the trend observed in k_q.

If the lobe of the π-orbital at C_9 in the LUMO is dominant, in comparison to that in the HOMO, it may be that frontier-orbital theory[27] can be invoked to explain why k_q for the excited xanthylium cations is so much larger than that for the ground-state cations ($k_q^{h\nu} \approx 10^6 - 10^9$ M^{-1} s^{-1}; $k_q^{\Delta} \approx 10^4$ M^{-1} s^{-1}), in terms of better overlap with the incoming nucleophile lone pair. However, at the moment, we are at a complete loss as to how to explain the large substituent effects observed.

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(23) The only possible exception to this could be the parent 9-phenyl system, which if completely planar would be in the C_{2v} point group. In such a case, S_1 *could* belong to the B_1 representation if the HOMO and LUMO belonged to different symmetry species. However, it is much more likely that the 9-phenyl group would be out of the plane of the xanthyl group, placing it in the C_2 point group, in which case the HOMO and LUMO would both be of B symmetry and hence S_1 would belong to A_1 (totally symmetric representation) as does S_0.

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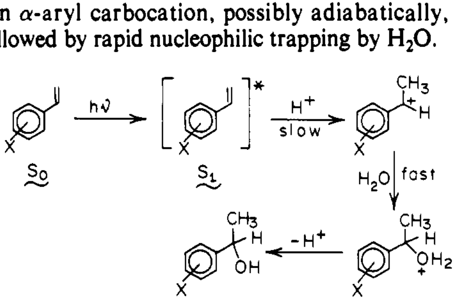
Relationship of Xanthylium Cation Behavior to Photohydration Intermediates. It is interesting that the present results can be used to throw light on the detailed mechanism of acid-catalyzed photohydration.[17] In the reaction of styrenes for example, it has been proposed that the rate-determining step is protonation of S_1 to give an α-aryl carbocation, possibly adiabatically, as shown below, followed by rapid nucleophilic trapping by H_2O. However,



although fluorescence is observed from S_1, no intermediate cation fluorescence has ever been detected. This could be explained by immediate deactivation at the proton-transfer step, leading to ground-state cation, but results of trapping experiments on photochemically and thermally generated intermediates do not support this.[28] The other alternative is that trapping of excited-state cation is so fast that its concentration and lifetime would be too low to allow any significant fluorescence to be detected. Estimates of the lifetimes of the xanthylium cations studied here can be made for the region of acidity typically used in photohydration studies, namely, pH 7 to $H_0 = -2$. For these estimates, it is assumed that $k_F{}^0$ and $\sum k_d$ are essentially medium independent over this acid range, which seems reasonable; i.e.

$$\tau_F(\text{calcd}) = \frac{1}{k_F{}^0 + \sum k_d + k_q[H_2O]}$$

On the basis of known $[H_2O]$ values for the above aqueous pH-H_0 range, the aryl-substituted xanthylium ions (**6**–**11**) would be expected to have τ values in the range 1.5–0.006 ns at pH 7 and the range 7.4–0.03 ns at $H_0 = -2$. Since the related cations involved in photohydration are much less rigid than the xanthylium ion systems, these estimated τ's must represent upper limits on the expected lifetimes of photohydration intermediates, and hence it is not surprising that no cation fluorescence can be detected.

A second area where the proposed mechanism of photohydration can be tested is in terms of observed general-acid catalysis.[29] This phenomenon has been observed in several, but not all, photohydration reactions of styrenes and phenylacetylenes, and implies that proton transfer to S_1 is always slower than subsequent nucleophilic trapping by H_2O. Since k_{H^+} values are available for the proton-transfer step, and k_q values are now available for nucleophilic attack by H_2O on similar types of cation, estimates can be made of the relative rates of these two processes. For styrenes substituted with electron-donor groups (from H through *p*-OMe), values of $k_{H^+}[H^+]$ are in the range 8×10^6 to 7×10^8 s^{-1} [17c,29] for pH 0 (intermediate acidity for photohydration). For xanthylium ions with the same range of substituents and at the same acidity, calculated $k_q[H_2O]$ values are in the range 1.0×10^8 to 1.7×10^{11} s^{-1}. This large difference is consistent with the general mechanism proposed for photohydration and with a recent observation[30] that photohydration is not accompanied by any deuterium incorporation in unreacted starting material, showing that the proton-transfer step is irreversible.

Experimental Section

Instrumentation. UV and visible absorption spectra were measured on a Varian 2300 UV-VIS-NIR spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer MPF66 instrument. All fluorescence spectra were corrected for wavelength response of the instrument. Sulfuric acid densities were determined at 25.0 °C with an Anton-Paar DMA02C digital precision density meter.

Materials. Mallinckrodt spectroscopic-grade acetonitrile was used as cosolvent for all UV absorption measurements, steady-state fluorescence experiments, and lifetime measurements. Sulfuric acid solutions were prepared from distilled water and Canlab reagent-grade acid. Solution densities were determined precisely, and the weight percentage acid determined from literature tables. H_0 values were obtained from these weight percentages and reported H_0 values at 25.0 °C.[31]

Xanthenols. Xanthydrol (9-xanthenol) was obtained from Aldrich as a yellow solid. Recrystallization (ethanol) gave white needles, mp 122–123 °C (lit.[32] mp 121–123 °C). 9-Methyl-9-xanthenol was prepared by the method of Alam and MacLean,[33] in an argon atmosphere. The crude product was recrystallized (hexane/ether) to yield a white solid, mp 96–99 °C (lit.[33] mp 95–99 °C; lit.[34] mp 96–99 °C). 9-Isopropylxanthenol was also prepared by the method of Alam and MacLean.[33] Recrystallization (pentane) gave a white solid, mp 64–66 °C. No mp was listed in the literature. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.80 (d, 6 H, J = 8 Hz), 2.05 (m, 1 H, J = 8 Hz), 2.40 (s, 1 H), 6.90–7.62 (m, 8 H). UV (33% acetonitrile in H_2O) λ_{max} 237 nm (ϵ = 16 000), 280 (ϵ = 3700). 9-Phenylxanthenol was obtained (Aldrich) as an off-white solid. Recrystallization (ethanol) gave white needles, mp 155–156 °C (lit.[34] mp 158.5–159 °C). 9-*tert*-Butylxanthenol was prepared by the method of Looker et al.[35] A pale yellow solid was obtained. Recrystallization (methylcyclohexane) gave a white solid, mp 105–107 °C (lit.[35] mp 106–107 °C). All other substituted xanthenols were supplied by Professor R. A. McClelland and N. Banait, to whom we are very grateful.

Fluorescence Measurements. Lifetimes were measured by using a Photochemical Research Associates apparatus, which has been described previously.[36] For the neutral 9-xanthenols, measurements were carried out in 2:1 H_2O/acetonitrile. For the xanthylium cations, 40–77% aqueous H_2SO_4 was diluted 2:1 with acetonitrile. Substrate concentrations were varied to maximize fluorescence at the wavelength chosen (300 nm for xanthenols; 520 nm for xanthylium cations). Clean single-exponential decays were obtained in every case, and accurate τ values could be obtained for **1**–**4** and **6**–**7**. In two cases (**8** and **9**), emission was found to be too weak to give accurate and reliable $\tau_F{}^0$ values. These were estimated by single photon counting to be roughly 3 and 2 ns, respectively. Their lifetimes were estimated as follows. The relative fluorescence intensities of cations **6**–**11**, corrected for sample concentration, were determined in 77% H_2SO_4 (2:1 H_2O/acetonitrile). The fluorescence lifetime was assumed to be inversely related to the fluorescence intensity (i.e., $k_F{}^0$, the intrinsic fluorescence rate constant, was taken to be effectively constant for all the 9-arylxanthylium cations). With the lifetime for **6** and **7** known, the values for **8** and **9** were scaled to these values, on the basis of relative fluorescence intensities. This method gave $\tau_F{}^0$ values of 3.2 and 2.1 ns for **8** and **9**, respectively. The same approach was used for the most weakly emitting cations **10** and **11**. Fluorescence quenching of cation fluorescence by water was carried out as follows for **1**–**4** and **6**–**11**. A 10^{-2} M stock solution (10 μL) was syringed into a mixture of 1 mL of acetonitrile and 2 mL of aqueous H_2SO_4 and the fluorescence intensity (Φ_F) measured at 520 nm. All quenching was determined relative to the intensity of cation fluorescence in 76.9% H_2SO_4 ($\Phi_F{}^0$). Values of $\Phi_F{}^0/\Phi_F$ were measured at six different acid concentrations from 76.9% H_2SO_4 down to 39.4% acid, which corresponds to the plateau region for xanthenol–xanthylium ion ionization (see next section). Values of the "free" H_2O concentration were obtained from the expression $[H_2O]_{free} = (M[H_2O] - M[H_2SO_4])/(M[H_2SO_4])$, to allow for complete ionization of H_2SO_4. All concentrations were corrected for dilution by the acetonitrile cosolvent. Stern–Volmer determinations were repeated at least once for each substrate. Plots of $\Phi_F{}^0/\Phi_F$ versus $[H_2O]_{free}$ were all linear, with $r \geq 0.99$ for all cases but one.

Titration Curves. To determine the acid concentration region where the xanthenols are fully ionized to xanthylium cations, acid titration curves were determined by monitoring both UV absorption and fluorescence. A 10^{-2} M stock solution of xanthenol (10 μL) was syringed into a mixture of 1 mL of acetonitrile and 2 mL of aqueous H_2SO_4. Absorption and fluorescence spectra were recorded for each solution. From the former spectra, the extent of cation formation was determined

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by monitoring the growth in absorption of the peak at ~370 nm. Fluorescence spectra were measured with an excitation wavelength of 370 nm and scanned between 450 and 700 nm. The extent of cation formation was calculated either from the area under the fluorescence curve or from the height of the peak. Both methods of calculation gave identical results.

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Registry No. 1, 90-46-0; **1** cation, 261-23-4; **2**, 5569-25-5; **2** cation, 46406-21-7; **3**, 101169-00-0; **3** cation, 135074-99-6; **4**, 4127-29-1; **4** cation, 135075-00-2; **5**, 35666-57-0; **5** cation, 135075-01-3; **6**, 596-38-3; **6** cation, 20460-07-5; **7**, 112305-07-4; **7** cation, 112305-04-1; **8**, 29903-57-9; **8** cation, 112304-98-0; **9**, 29903-56-8; **9** cation, 119681-16-2; **10**, 94465-25-5; **10** cation, 112305-00-7; **11**, 42960-05-4; **11** cation, 119681-18-4.

Photochemistry of Phenyl Thioethers and Phenyl Selenoethers. Radical vs Ionic Behavior

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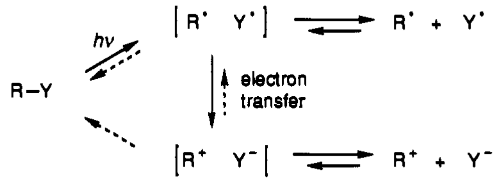
Abstract: In analogy with alkyl iodides and bromides, the phenyl thio- and selenoethers **2a,b**, **13a**, **21b,c** and **35** displayed competing radical and ionic photobehavior on irradiation in solution, via a mechanism thought to involve initial homolytic cleavage of the alkyl C–S or C–Se bond followed by electron transfer within the resulting radical pair cage (Scheme I). These are the first examples of ionic photobehavior to be recognized for the C–SAr and C–SeAr chromophores. The electronegatively substituted pentafluorophenyl analogues **2c**, **13b**, and **21d** displayed enhanced ionic photobehavior. By contrast, the 4-methoxyphenyl derivative **21a** exhibited almost exclusively radical behavior. The sulfoxide ($2R^*,R^*_S$)-**21f** displayed principally radical behavior, accompanied by epimerization at sulfur. The quantum yields for the disappearance of the 2-norbornyl ethers **21b** and **21c** were 0.53–0.64 in solution and rose to 0.89–0.95 in the presence of suspended fumed silica. Irradiation of the phenyl thioether **21b** on silica gel resulted in nucleophilic trapping by surface silanol groups to afford covalently bound material (**33**), which afforded chloride **34** on treatment with $SOCl_2$. Irradiation of phenyl thioethers **2a** and **35**, phenyl selenoether **2b**, or C_6H_5SH in allyl alcohol solution afforded acetal **11**, apparently via isomerization of some of the solvent to propanal (**44**) followed by acetalization. Irradiation of alcoholic solutions of aldehydes containing C_6H_5SH is a useful means of generating acetals under neutral conditions.

Extensive studies from these laboratories and those of others have shown that alkyl iodides and bromides, which had traditionally been thought to exhibit only radical photobehavior,[1] in fact afford mixtures of radical and ionic products on irradiation in solution.[2,3] We have proposed that the latter products arise via a previously unrecognized electron transfer within an initially formed radical pair cage (Scheme I, Y = I).[4] This photobehavior is of both synthetic and mechanistic interest. Synthetically, it has proven to be a convenient and powerful method for the generation of a wide variety of carbocations, including many that are not readily available by classical, ground-state procedures, such as bridgehead cations,[5] the 7-norbornyl cation,[6] and small-ring cyclic and α-unsubstituted vinyl cations.[7] Mechanistically, it represents one of the first, and most general, examples of electron transfer within a radical pair to be recognized.[4,8] We wish now to extend our studies to two additional systems that have traditionally been thought to exhibit only radical photobehavior, the C–SAr and C–SeAr chromophores.[9,10]

Scheme I



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