Quenching Behavior of Singlet Excited 9-Arylxanthylium Cations

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Several 9-arylxanthylium tetrafluoroborate salts (Ar = H, *p,m*-F, *p,m*-Me, *m*-OMe) were synthesized by reaction of the corresponding 9-arylxanthen-9-ol with fluoroboric acid. Spectral characteristics of the xanthyl cations were identical to those previously reported for the cations generated by alternate methods. The 9-arylxanthyl cation fluorescence was quenched by the addition of H_2O, MeOH, *i*-PrOH, and *t*-BuOH. Stern–Volmer analysis of the fluorescence quenching gave bimolecular excited-state rate constants ranging from 10^6 to 10^{10} M^{-1} s^{-1}, with the larger rate constants associated with electron-donating substituents. Hammett plots of $\log[k_q(X)/k_q(H)]$ versus $\sigma^{h\nu}$ gave negative ρ values for each quencher, opposite to the substituent dependence observed for ground-state cations reacting with nucleophiles. The relative quenching order also differs from the order observed for ground-state cation reactions. The mechanism for quenching of the singlet excited 9-arylxanthylium cations is evaluated in terms of nucleophilic attack. The possibility of an electron-transfer mechanism is considered and eliminated.

Introduction

The ground-state chemistry of carbocations has been extensively investigated, including reactivity, structure, and product studies.[1] The excited-state behavior of carbocations has also been studied, but much less extensively. Early studies of the photochemistry of carbocations focused predominantly on the determination of photoproducts,[2] with considerable recent interest in the photophysics, intermolecular reactivity, and excited state characterization.[3] Singlet excited xanthylium cations have been the subject of several of these studies due to their relatively long excited-state lifetimes and strong emission.[4-8] These singlet excited cations were shown to undergo electron-transfer reactions with several aromatic donors to give aromatic radical cations and the corresponding xanthyl radical.[4,6,7] The triplet excited states of some 9-arylxanthylium cations have also been characterized.[9] These excited triplet cations were similarly found to undergo electron-transfer reactions with aromatic donors.

The reactivity of xanthylium ions with species other than aromatics has also been studied.[5,8] Fluorescence from the 9-phenylxanthylium ion was quenched by amines, water, and alcohols, suggested to be acting as nucleophiles.[8] Rate constants for quenching of this excited-state carbocation by water and triethylamine were several orders of magnitude higher than those measured for the corresponding ground-state reaction.[10] It was suggested that the larger excited-state rate constants reflect an enhanced electrophilicity of the singlet excited species, due to the increased exothermicity of the excited-state cation by an amount equal to the singlet energy (~60 kcal mol^{-1}).[8]

The substituent dependence on the water quenching of excited-state xanthylium ions was determined.[5] Bimolecular rate constants were obtained from Stern–Volmer analyses of the fluorescence quenching of several 9-arylxanthylium ions as a function of water concentration. Rate constants ranging from 10^7 to 10^{10} M^{-1} s^{-1} were measured, with the values at the higher end of the range associated with aryl ring substitution by groups known to act as electron donors in ground-state reactions. The substituent dependence on the water quenching rate constants was further analyzed with an excited-state Hammett plot. A ρ value of −1.45 was obtained, again indicating that electron-donating substituents increase the reaction rate. This ρ value is opposite in sign to that obtained for the ground-state reaction, where electron-donating groups decrease the reaction rate.[10]

In order to determine whether this unusual substituent dependence and ρ reversal are general phenomena with other quenchers, and to examine the quenching mechanism, a new procedure for generation of the cations was required. In previous studies xanthylium cations were generated from their corresponding 9-xanthenol by acid-catalyzed dehydration.[4-8] We wished to avoid the use of acidic media as those conditions limit the range of potential quenchers or nucleophiles. An alternative two-laser flash photolysis technique has been successfully employed to generate the 9-phenylxanthylium cation from its alcohol precursor, although cation formation was accompanied by the generation of the 9-phenylxanthyl radical.[8] Xanthylium ions have also been generated in Nafion matrices[4] and on silica gel surfaces,[11] however for these studies we are interested in solution-phase generation of the cations.

We chose instead to thermally generate the 9-arylxanthylium ions as stable tetrafluoroborate salts. These cation salts are soluble in neutral, inert media such as acetonitrile, permitting us to measure their singlet excited lifetimes in

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Table I. Fluorescence Lifetimes and Excited-State Quenching Rate Constants (M^{-1} s^{-1})[a] for 2a–f

		quencher			
compound	$\tau_F°$ (ns)	H_2O	MeOH	*i*-PrOH	*t*-BuOH
2a (H)	27.6	$(2.02 \pm 0.02) \times 10^7$	$(4.56 \pm 0.52) \times 10^7$	$(8.94 \pm 0.23) \times 10^7$	$(3.33 \pm 0.54) \times 10^7$
2b (*p*-F)	18.8	$(8.88 \pm 0.11) \times 10^6$	$(4.11 \pm 0.27) \times 10^7$	$(8.05 \pm 0.69) \times 10^7$	$(1.80 \pm 0.02) \times 10^7$
2c (*m*-F)	14.0	$(1.20 \pm 0.01) \times 10^8$	$(8.10 \pm 0.02) \times 10^7$	$(1.05 \pm 0.05) \times 10^8$	$(2.34 \pm 0.03) \times 10^7$
2d (*p*-CH_3)	2.1	$(6.23 \pm 0.66) \times 10^8$	$(2.06 \pm 0.26) \times 10^9$	$(3.28 \pm 0.38) \times 10^9$	$(1.02 \pm 0.16) \times 10^9$
2e (*m*-CH_3)	2.0	$(2.16 \pm 0.30) \times 10^9$	$(8.03 \pm 0.25) \times 10^9$	$(1.02 \pm 0.02) \times 10^{10}$	$(3.36 \pm 0.14) \times 10^9$
2f (*m*-OCH_3)	0.028[b]	$(1.76 \pm 0.34) \times 10^{10}$	$(4.97 \pm 0.02) \times 10^{10}$	$(6.14 \pm 0.30) \times 10^{10}$	$(3.12 \pm 0.27) \times 10^{10}$

[a] Errors quoted are the standard deviations obtained from repeated measurements. [b] Lifetime determined by relative fluorescence quantum yields.

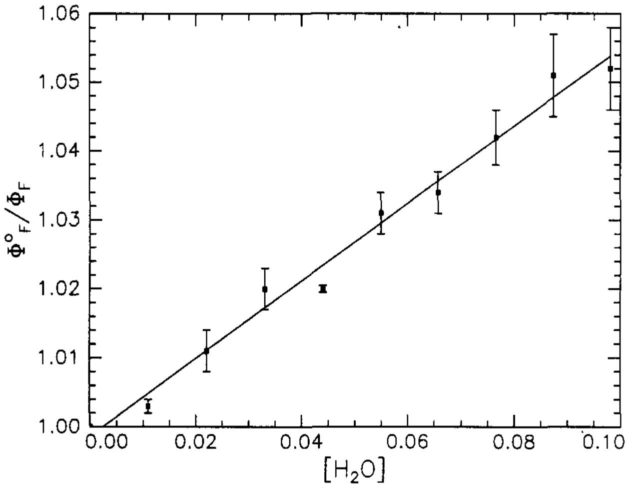
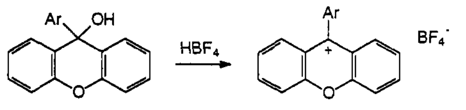


Figure 1. Stern–Volmer plot of $\Phi_F°/\Phi_F$ for **2a** versus H_2O concentration.

the absence of quenchers and study their fluorescence quenching behavior using the Stern–Volmer approach. We now report on the quenching behavior and substituent dependence for a series of 9-arylxanthylium ions with water and several alcohols.

Results

9-Arylxanthen-9-ols **1b–f** were synthesized via a Grignard reaction of the appropriate arylmagnesium bromide with xanthone. Reaction of **1a–f** with fluoroboric acid in propionic anhydride[12] gave xanthylium salts **2a–f** as crystalline solids. The cations were stable indefinitely both in the solid phase and dissolved in dry acetonitrile.



1a-f **2a-f**
aryl substituent: a=H, b=*p*-F, c=*m*-F, d=*p*-CH_3, e=*m*-CH_3, f=*m*-OCH_3

UV/visible spectra of **2a–f** in acetonitrile were identical to the spectra reported for the same cations generated in aqueous acidic solution[5,13] or acidified organic solvents[4,6-9] with absorption maxima at 260, 374, and 450 nm. Excitation at 374 nm of **2a–f** in acetonitrile gave steady-state fluorescence spectra that were also identical to emission spectra previously reported, with a broad unstructured band centered near 540 nm.[4-8,13] Fluorescence lifetimes were measured for **2a–e** in acetonitrile solvent. The lifetimes are listed in Table I, with all measured lifetimes obtained from primarily single exponential decays. The lifetime of compound **2f** was below the range of our instrument and was estimated instead from relative fluorescence quantum yields (see Experimental Section). The fluorescence lifetime of **2a** was unchanged upon oxygen saturation of the acetonitrile solution. It has been previously noted that the singlet excited xanthyl cations exhibit resistance to quenching by oxygen.[4,8]

Substituents apparently have a dramatic effect on the lifetime as the lifetimes range from approximately 28 ns for the parent cation **2a** to a subnanosecond value for **2f**. The lifetime for **2a** is in excellent agreement with previous measurements of 25 and 28.5 ns for the cation generated in acetonitrile[8] and 1:1 trifluoroacetic acid–acetonitrile,[4] respectively. The lifetimes of **2a**, **2d**, and **2e** are also in very good agreement with the values obtained for the same cations generated in strongly acidic aqueous media.[5] Lifetime values for **2a** and **2b** agree reasonably well with those measured in trifluoroethanol acidified with trifluoroacetic acid, after making allowance for possible solvent effects.[6]

The fluorescence of **2a–f** in acetonitrile solvent was quenched by the addition of H_2O, MeOH, *i*-PrOH, and *t*-BuOH. Relative fluorescence quantum yields ($\Phi_F°/\Phi_F$) were measured for all cations and plotted versus the quencher concentration. Excellent linear plots ($r > 0.98$) were obtained in each case, as shown in Figure 1 for quenching of **2a** by H_2O. Stern–Volmer analysis[14] gave excited-state bimolecular rate constants k_q for reaction of the singlet excited cations with the quenchers. The k_q values are listed in Table I. The rate constant for quenching of **2a** by water can be compared to values previously obtained both by steady-state quenching and time-resolved measurements. The k_q value reported here (2.02×10^7 M^{-1} s^{-1}) is in very good agreement with the rate constant of 1.5×10^7 M^{-1} s^{-1} obtained by steady-state measurement for the cation generated in strongly acidic aqueous solution[5] and with the value of 1.6×10^7 M^{-1} s^{-1} reported from time-resolved measurement of the fluorescence decay when the cation was generated in acidic acetonitrile.[8] The slightly lower values obtained in the acidic media can be attributed to a lowering of the water activity. A rate constant of 3.3×10^7 M^{-1} s^{-1} was obtained using time-resolved measurements for the 9-phenylxanthyl cation generated in acetonitrile by a two-laser flash photolysis technique.[8] This value is in very good agreement with our result as well, with the difference in rate constants in accord with the earlier suggestion that ion-paired photoexcited cations are less susceptible to quenching.[8]

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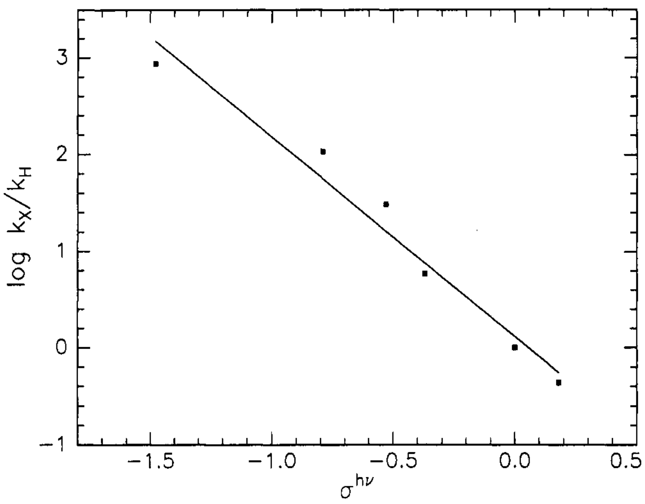

Figure 2. Excited-state Hammett plot (log[k_q(X)/k_q(H)] versus $\sigma^{h\nu}$) for quenching of **2a–f** by water.

The quenching rate constants in Table I also show a substantial substituent dependence, with larger k_q values associated with the electron-donating substituents. For each of the four quenchers the rate constants vary from a low of ~10^6–10^7 M^{-1} s^{-1} (for **2b**) up to the diffusion limit (for **2f**). Each substituent exhibits a much smaller range of rate constants along the quencher series. Using **2a** as an example, the k_q values range from 2.02 × 10^7 M^{-1} s^{-1} (quenching by water) to 8.94 × 10^7 M^{-1} s^{-1} (quenching by *i*-PrOH). The rate constants vary on average by a factor of 4–6, and in one case (compound **2b**) by a factor of 9.

Discussion

Substituent Effects on Quenching Rate Constants. The quenching rate constant dependence on the 9-aryl substituent is interesting, in two respects. First, the results provide further support for the meta/para dichotomy of excited-state substituent effects, where substituents in the meta position exhibit greater conjugative effects than those in the para position.[15] For each of the four quenchers used here, larger rate constants were observed for the methyl and fluoro meta-substituted cations (**2c** and **2e**), compared to the same substituents in the para position (**2b** and **2d**). Second, for each quencher the rate constants increase (up to the diffusion limit) as the substituents become more strongly electron donating.

The substituent effects were further examined through a Hammett analysis. Correlations were first attempted versus the σ and σ^+ substituent parameters,[16] with very poor results for each of the quenchers. For quenching by *i*-PrOH, for example, correlation coefficients of 0.44 and 0.32 were obtained for σ and σ^+, respectively. The poor correlations were due mainly to scatter from the meta-substituted cations whose points fall above the line, again indicating their enhanced excited-state reactivity. Excellent correlation was obtained with $\sigma^{h\nu}$, a substituent parameter for excited-state reactivity.[17] The $\sigma^{h\nu}$ scale is appropriate for xanthylium ion reactivity since it is based on formation of structurally similar benzyl cations in photoprotonation reactions of ring-substituted styrenes and phenylacetylenes. A plot of log[k_q(X)/k_q(H)] versus $\sigma^{h\nu}$ for H_2O quenching gave an excellent linear plot with a correlation coefficient of 0.98 and a ρ value of −2.07 (see Figure 2). This substituent dependence and ρ value are in agreement with those determined for water quenching of singlet excited 9-arylxanthyl cations, when the cations were generated in strongly acidic aqueous media.[5]

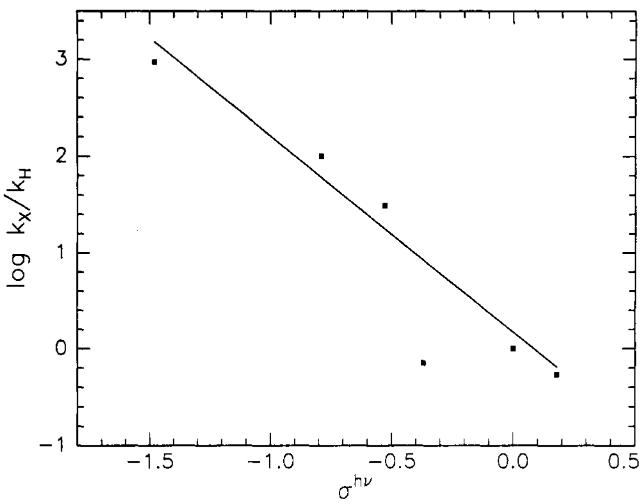

Figure 3.

Table II. Correlation of log[k_q(X)/k_q(H)] versus $\sigma^{h\nu}$ for Quenching of 2a–f

	quencher			
	H_2O	MeOH[a]	*i*-PrOH[a]	*t*-BuOH[a]
slope (ρ)	−2.07	−2.02	−1.88	−2.03
r^b	0.98	0.98	0.98	0.99
intercept[c]	0.11	0.32	0.30	0.17
$\sigma_y{}^d$	0.14	0.20	0.19	0.15

[a] The data corresponding to **2c** were omitted from the linear regression analysis (see text for details). [b] Correlation coefficient. [c] Intercept obtained from linear regression. [d] Standard deviation on log[k_q(X)/k_q(H)] axis.

Plots of log[k_q(X)/k_q(H)] versus $\sigma^{h\nu}$ for the three alcohol quenchers also give excellent linear plots, with the exception of the point corresponding to **2c**, the *m*-F substituted cation. The *m*-F point falls below the line, with the extent of the deviation from the line increasing with the steric bulk of the alcohol alkyl groups, that is, the excited-state Hammett plot for MeOH quenching shows the *m*-F point only slightly below the slope, somewhat further below the slope for quenching by *i*-PrOH, and substantially below the slope for *t*-BuOH quenching (Figure 3). These results indicate that the rate constants for quenching of **2c** by alcohols decrease with respect to rate constants for the other cations, although this effect is not seen in the water-quenching rate constants.

Values of ρ were calculated for quenching by the three alcohols and are listed in Table II. These ρ values were calculated by excluding the point corresponding to **2c**, the *m*-F cation. We chose to exclude the **2c** point from the linear regression analysis for the alcohol-quenching Hammett plots due to the apparently anomalous behavior of this cation. It is worth noting, however, that the calculated slopes were not greatly different if the point corresponding to **2c** was either excluded or included. For each of the quenchers a negative ρ value was obtained, showing that the substituent dependence observed for quenching of the

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singlet excited 9-arylxanthylium ions is not unique for quenching by water, that is, as the 9-aryl substituent becomes more strongly electron donating, the rate constant for water or alcohol quenching of the 9-arylxanthylium cations increases.

Hammett plots for nucleophilic reaction of ground-state 9-arylxanthylium ions with water and anionic species gave small positive ρ values in every case (ρ = 0.4–1.1).[10] This substituent dependence was explained as weak electronic stabilization of the cation by the 9-aryl substituents, with the magnitude of the effect somewhat attenuated due to the twisting of the 9-aryl ring away from planarity, decreasing the conjugative interaction. Electron-donating substituents stabilize the cations, thereby decreasing its rate of reaction. This substituent dependence is opposite that reported here for reaction of the singlet excited 9-arylxanthylium ions.

Relative Quenching Order. 9-Arylxanthylium cations **2a,b** and **2d–f** follow the relative quenching order *i*-PrOH > MeOH > *t*-BuOH > H_2O, although the differences between the quenching rate constants for each cation are not very large. This quenching order was previously observed for reactivities of the parent 9-phenylxanthylium ion generated in acetonitrile by double laser flash photolysis and monitored by time-resolved techniques.[8] Steady-state fluorescence quenching measurements on the same cation also indicated the same relative order for quenching by the three alcohols. In those experiments the cation was adiabatically photogenerated in 3:1 H_2O/acetonitrile, with the quenching order implied from the Stern–Volmer constants obtained from alcohol quenching.[8]

The *m*-F-substituted cation **2c** behaves differently than the other 9-arylxanthylium cations in the quenching order. **2c** follows the order H_2O > *i*-PrOH > MeOH > *t*-BuOH. This effect was also seen in the alcohol-quenching Hammett plots where the points corresponding to **2c** fell below the slope, indicating a decreased reactivity with alcohols in comparison to the other substituted cations. This behavior was not observed for water quenching of **2c**, suggesting that the effect is not due to an increase in the water-quenching rate constant but rather is a result of a decrease in the rate constants for quenching by the alcohols. A steric effect is suggested since the decrease in reactivity of **2c** (compared to the other cations) correlates with an increase in the steric bulk of the alcohol. It seems unlikely that this anomalous behavior of **2c** is due to a steric effect of the substituent, since a fluoro substituent would not be expected to exhibit a greater steric influence than either a methyl or methoxy substituent in the meta position. Excited-state electronic effects of the *m*-F substituent should already be accounted for by use of the $\sigma^{h\nu}$ substituent parameter scale.

Quenching Mechanism. Quenching of singlet excited xanthylium cations by water was previously proposed to occur by a nucleophilic mechanism.[5] Quenching of the 9-phenylxanthylium cation by alcohols was similarly proposed to proceed via nucleophilic attack with the observed alcohol quenching order rationalized by the steric effect of increasing methyl substitution counterbalancing the increase in lone pair availability of the nucleophile.[8] We had hoped to pursue the possibility that the water and alcohol quenchers of **2a–f** were acting as nucleophiles by analyzing the reactivity as a function of nucleophilicity, for example, by using one of the nucleophilicity parameter scales.[18] The N^+ scale would be particularly appropriate since it is based on the reactivity of structurally similar triarylmethyl cations.[18b] Unfortunately N^+ values are not available for the four quenchers used here. N^+ values are available for water reacting in aqueous media and methanol in methanol solvent. The difference between those solvent systems and the acetonitrile used here makes it impossible to attempt correlations with our data.

Instead we compared our excited-state quenching order to relative reactivity orders for nucleophilic reactions of ground-state cations in acetonitrile solvent. Rate constants have been measured for reaction of water and alcohols with aryl- and alkyl-substituted vinyl cations,[19] diarylmethyl cations,[20] and arylcyclopropyl radical cations.[21] Although these cations are less stable than the xanthylium ions, their bimolecular rate constants with these nucleophiles are of a similar magnitude ($\sim 10^7$ M^{-1} s^{-1}). The ground-state reactivities of these cations in acetonitrile also show an insensitivity to the nucleophile, exhibiting similar small differences in rate constants. The observed trend in the alcohol reactivity order is completely dependent on steric effects of the alkyl group (MeOH > EtOH > *i*-PrOH > *t*-BuOH). The water-quenching rate constants fall between the rate constants for *i*-PrOH and *t*-BuOH. This reactivity order obtained for ground-state cation–nucleophile reactions is different than the order we observe for quenching of the singlet excited 9-arylxanthylium cations. The excited-state order does not depend solely on steric considerations of the alcohol quencher, since k_q for quenching by *i*-PrOH is larger than the k_q value for MeOH quenching for each of **2a–f**.

The substituent dependence and relative reactivity order are different for quenching of singlet excited **2a–f** as compared to reactions of ground-state carbocations with nucleophiles. This suggests either that nucleophilic mechanisms operate quite differently in excited-state reactions or that nucleophilic attack is not the excited-state quenching mechanism. We first considered the possibility that a different mechanism might be operating in the excited-state reaction by probing the likelihood of an electron-transfer process. Singlet excited carbocations, including xanthylium ions, are known to undergo electron-transfer reactions with aromatic donors.[3] The Rehm–Weller[22] equation can be used to determine the free energy change for electron transfer to singlet excited **2a–f**.

$$\Delta G_{ET} = E_{1/2}^{ox} - E_{1/2}^{red} - E_S$$

$E_{1/2}^{ox}$ is the oxidation potential of the electron donor (water or alcohol quencher in this case), $E_{1/2}^{red}$ is the reduction potential of the electron acceptor (**2a–f**), and E_S is the singlet energy of the carbocation acceptor. For any given quencher acting as the putative electron donor, $E_{1/2}^{ox}$ will remain constant for all aryl-substituted carbocations. The singlet energies are the same ($\sim$60 kcal mol^{-1}) for each of **2a–f**, based on the wavelength for onset of the fluorescence.

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For an electron-transfer mechanism to be operating, the very different reactivities of the substituted cations with a particular quencher must then be rationalized on the basis of the carbocation $E_{1/2}^{\text{red}}$ values.

$E_{1/2}^{\text{red}}$ potentials of 0.002 and 0.01 V vs SCE have been measured for the parent and *p*-F arylxanthylium cations, respectively, showing little effect due to *p*-F substitution.[9a] These potentials provide little evidence for or against an electron-transfer mechanism, since their rate constants with the four quenchers are very similar. It seems unlikely that the aryl substituents would have a significant effect on the $E_{1/2}^{\text{red}}$ potentials, since oxidation potentials measured for the xanthylium radicals differed by only 0.005 V for hydrogen or phenyl substitution at the 9-position.[23] Nevertheless, potentials measured for the diarylmethyl system can be used to approximate substituent effects in the xanthylium system. While the parent diphenylmethyl and 9-phenylxanthylium compounds have different redox potentials (0.35V and 0.002 V vs SCE in acetonitrile, respectively),[9a,24] due to the extra phenyl ring and the electron-donating oxo bridge of the xanthyl system, these differences remain constant and the effect of the aryl substituent can be evaluated. In the diphenylmethyl series the parent (unsubstituted), *m*-OMe, and *p*-Me compounds have redox potentials of 0.35, 0.38, and 0.32 V vs SCE in acetonitrile, showing essentially no effect due to the substituent, with a difference of only 0.03 V between the unsubstituted and *m*-OMe compounds.[24] For a given quencher the Rehm–Weller equation would predict nearly identical reactivity for **2a** and **2f**. We observe a nearly 3 order of magnitude difference in the rate constants between **2a** and **2f** for each of the four quenchers, and thus an electron-transfer mechanism can be ruled out.

The absence of curvature in the Hammett plots rules out the possibility of a change in mechanism over the substituent range. Since we can conceive of no other likely mechanism, we are then left with the conclusion that nucleophilic attack is the most probable quenching mechanism of the singlet excited carbocations. Huckel MO calculations provided a possible explanation for the excited-state substituent dependence.[5] The calculations showed that in S_1 there is negligible positive charge at C_9, and the lobe and MO coefficient at C_9 in S_1 increase as the substituents become more strongly electron donating. The larger k_q values can then be explained by invoking frontier orbital theory,[25] as the larger lobes would provide better overlap with the incoming nucleophile lone pair. Nucleophilic reactions with excited-state carbocations apparently differ greatly from their ground-state counterparts. We are continuing our studies on related systems.

Experimental Section

Instrumentation. Melting points were taken on a Mel-Temp melting point apparatus and are uncorrected. UV and visible absorption spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer. Fluorescence lifetimes and steady-state measurements were obtained on a Photon Technology International LS-100 spectrophotometer. NMR spectra were obtained on a Varian VXR300 instrument operating at 300 Hz for ^{1}H and 75 Hz for ^{13}C. ^{1}H NMR signals are reported in parts per million (δ) from TMS as an internal standard. ^{13}C NMR chemical shifts (δ) were reported in reference to the 77.0 ppm NMR peak for $CDCl_3$.

Materials. Anhydrous tetrahydrofuran used in Grignard syntheses was dried over calcium hydride and freshly distilled. Aryl bromides were obtained from Aldrich and distilled prior to use. Spectroscopic grade acetonitrile used in absorption and fluorescence measurements was obtained from Mallinckrodt and dried by being passed through a column of neutral aluminum oxide. Propionic anhydride and fluoroboric acid used in the syntheses of xanthylium tetrafluoroborate salts were obtained from Aldrich and used as received. MeOH, *i*-PrOH, and *t*-BuOH (>99%) used as quenchers were obtained from Fisher or Aldrich and used without further purification. Doubly distilled water was used in the quenching experiments. All ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ solvent obtained from Aldrich Chemical Company, unless otherwise specified. All absorption spectra were taken in acetonitrile solvent.

Fluorescence Measurements. Fluorescence lifetimes of **2a–e** were measured in dry acetonitrile using a PTI stroboscopic lifetime system with a nitrogen-filled gas thyratron lamp. Excitation of the cations was at 381 nm and emission monitored at 540 nm, with a 350-nm cutoff filter placed before the emission monochromator. All measured lifetimes were independent of cation concentration below 5.0×10^{-5} M. The fluorescence lifetime of **2f** was estimated from relative fluorescence intensities according to the method previously described for weakly fluorescent compounds.[5] Steady-state fluorescence emission was measured using a pulsed Xe lamp apparatus, an excitation wavelength of 374 nm, and a 350-nm cutoff filter before the emission monochromator. Stern–Volmer quenching of the cations in dry acetonitrile was conducted at a cation concentration of 5.0×10^{-5} M. No ground-state quenching of the cations occurred under these experimental conditions.

9-Arylxanthen-9-ols. 9-Phenylxanthen-9-ol (**1a**) was obtained from the Aldrich Chemical Company as an off-white solid. Recrystallization from 95% ethanol yielded white crystals, mp 158–161 °C (lit.[26] mp 158.5–159 °C). Alcohols **1b–f** were prepared by Grignard reaction. The Grignard reagent was formed by reaction of the appropriate aryl bromide (5.8 mmmol) and magnesium turnings (5.8 mmol) in anhydrous tetrahydrofuran. Xanthone (5.0 mmol) was added and the reaction mixture heated at reflux temperature for 1 h. Aqueous workup followed by purification by silica gel chromatography with methylene chloride as eluant and recrystallization from 95% ethanol gave the pure 9-arylxanthenols as white solids.

9-(4-Fluorophenyl)xanthen-9-ol (1b): yield 0.71 g (49%); mp 152–154 °C; ^{1}H NMR 2.77 (s, 1H), 7.10–7.59 (m, 12H); ^{13}C NMR δ 163.18, 159.92, 149.62, 143.87, 143.83 129.22, 128.87, 128.00, 127.89, 126.95, 123.63, 116.50, 114.90, 114.61, 70.12; UV at 244 nm (ε = 13 600), 290 nm (ε = 4300).

9-(3-Fluorophenyl)xanthen-9-ol (1c): yield 0.21 g (18%); mp 95–96 °C; ^{1}H NMR δ 2.77 (s, 1H), 7.10–7.96 (m, 12H); ^{13}C NMR δ 154.69, 151.17, 129.34, 129.28, 129.20, 129.18, 129.08, 128.86, 123.67, 123.44, 123.28, 122.51, 122.47, 116.54, 116.32, 113.41, 113.37, 113.09, 58.92; UV at 244 nm (ε = 12 300), 290 nm (ε = 5100).

9-(4-Methylphenyl)xanthen-9-ol (1d): yield 0.99 g (69%); mp 146–148 °C (lit.[27a] mp 150 °C, lit.[27b] mp 141–142 °C); ^{1}H NMR δ 2.28 (s, 3H), 2.66 (s, 1H), 7.00–7.36 (m, 12H); UV at 226 nm (ε = 28 000), 244 nm (ε = 15 000), 290 nm (ε = 4900).

9-(3-Methylphenyl)xanthen-9-ol (1e): yield 0.34 g (24%); mp 144–146 °C (lit.[28] mp 149 °C); ^{1}H NMR δ 2.39 (s, 3H), 2.76 (s, 1H), 7.09–7.46 (m, 12H); UV at 244 nm (ε = 13 000), 290 nm (ε = 5600).

9-(3-Methoxyphenyl)xanthen-9-ol (1f): yield 0.57 g (38%); mp 120–123 °C (lit.[29] mp 112–113 °C); ^{1}H NMR δ 3.81 (s, 3H),

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2.85 (br, 1H), 6.73–7.45 (m, 12H); UV at 244 nm (ϵ = 13 000), 282 nm (ϵ = 5900).

9-Arylxanthylium Tetrafluoroborate Salts. Tetrafluoroborate salts **2a–f** were prepared following the method of Dauben *et al.*[12] The corresponding 9-arylxanthen-9-ol (1.7 mmol) was dissolved in propionic anhydride (4.5 mL) at room temperature or slightly higher, where heat was provided by a warm water bath. This temperature was maintained upon addition of fluoroboric acid (0.33 g, 3.8 mmol), which immediately gave a yellow solution. The xanthylium tetrafluoroborate salt precipitated and was collected by suction filtration. The salts were washed repeatedly with cold, anhydrous diethyl ether to yield a bright yellow solid in every case except the m-OCH$_3$ cation salt (**2f**) which was dark orange.

9-Phenylxanthylium tetrafluoroborate (2a): yield 0.46 g (76%); mp 228 °C dec; ^{1}H NMR δ 7.75–8.52 (m, 13H); ^{13}C NMR δ 156.60, 143.80, 132.26, 131.72, 130.81, 130.57, 129.13, 123.93, 123.51, 120.18, 116.37; UV at 260 nm (ϵ = 38 700), 372 nm (ϵ = 29 400), and 446 nm (ϵ = 4900).

9-(4-Fluorophenyl)xanthylium tetrafluoroborate (2b): yield 0.14 g (78%); mp 216 °C dec; ^{1}H NMR δ 7.44–8.50 (m, 12H); ^{13}C NMR δ 159.28, 158.76, 143.83, 133.38, 133.26, 131.68, 129.28, 128.93, 128.05, 124.20, 123.89, 120.20, 117.05, 116.75, 116.56; UV at 260 nm (ϵ = 42 300), 374 nm (ϵ = 36 200), and 450 nm (ϵ = 5600).

9-(3-Fluorophenyl)xanthylium tetrafluoroborate (2c): yield 0.06 g (86%); mp 200 °C dec; ^{1}H NMR δ 7.04–8.49 (m, 12H); ^{13}C NMR (acetone-d_6) δ 164.99, 161.74, 159.83, 145.79, 132.60, 130.60, 129.76, 128.67, 128.57, 127.41, 125.15, 124.29, 123.19, 120.77, 119.91, 119.63, 118.50, 118.18, 116.96; UV at 260 nm (ϵ = 37 500), 376 nm (ϵ = 27 500), and 448 nm (ϵ = 3900).

9-(4-Methylphenyl)xanthylium tetrafluoroborate (2d): yield 0.06 g (100%); mp 200 °C dec; ^{1}H NMR δ 2.57 (s, 3H), 7.56–8.50 (m, 12H); ^{13}C NMR δ 158.53, 143.83, 143.76, 132.04, 131.96, 131.16, 130.02, 129.16, 128.07, 123.83, 120.22, 21.78; UV at 260 nm (ϵ = 31 000), 370 nm (ϵ = 25 000), and 454 nm (ϵ = 6300).

9-(3-Methylphenyl)xanthylium tetrafluoroborate (2e): yield 0.06 g (43%), mp 185 °C dec; ^{1}H NMR δ 2.59 (s, 3H), 7.57–8.54 (m, 12H); ^{13}C NMR δ 158.61, 143.86, 139.40, 133.16, 131.84, 131.32, 130.95, 130.82, 129.15, 129.03, 127.65, 123.90, 120.22, 21.48; UV at 260 nm (ϵ = 31 000), 370 nm (ϵ = 25 000), and 454 nm (ϵ = 6300).

9-(3-Methoxyphenyl)xanthylium tetrafluoroborate (2f): yield 0.09 g (50%); mp 204 °C dec; ^{1}H NMR δ 3.97 (s, 3H), 7.27–8.58 (m, 12H); ^{13}C NMR δ 159.89, 158.63, 143.78, 131.85, 130.23, 129.09, 128.92, 124.06, 123.55, 122.55, 120.11, 118.36, 115.72, 55.93; UV at 260 nm (ϵ = 34 000), 372 nm (ϵ = 29 000), and 452 nm (ϵ = 4400).

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Supplementary Material Available: ^{1}H NMR spectra for compounds **1d–f** and ^{1}H and ^{13}C NMR spectra for compounds **1b,c** and **2a–f** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.