

Ether quenching of singlet excited 9-arylxanthyl cations

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Abstract

Fluorescence from a series of 9-arylxanthyl cations (Ar=H, *p*-, *m*-F, *p*-, *m*-Me, *m*-OMe) is quenched by the addition of dialkylethers (Et₂O, *i*-Pr₂O, *t*-BuOMe and *t*-BuOEt). Stern–Volmer analysis of the fluorescence quenching gave bimolecular excited state rate constants ranging from 10⁶ to 10¹⁰ M⁻¹ s⁻¹, with the larger rate constants associated with electron-donating substituents. Hammett plots of log[k_q(X)/k_q(H)] vs. σ^{hv} gave negative ρ values for each ether quencher. This substituent effect is identical to that seen with quenching of these singlet excited cations by water and simple alkyl alcohols. In contrast, ground state xanthyl cations reacting with nucleophilic species exhibit the opposite substituent effect. Using the Rehm–Weller equation and $E_{1/2}^{red}$ values for the 9-arylxanthyl cations, the possibility of an electron transfer mechanism is ruled out for quenching of the singlet excited cations by ethers, alcohols and water. The mechanism for quenching of the singlet excited 9-arylxanthylum cations by these species is evaluated in terms of nucleophilic attack.

Keywords: Carbocations; Substituent effects; Fluorescence quenching; Xanthylum ions; Nucleophilic quenching

1. Introduction

Early studies on carbocation photochemistry focused primarily on photoproduct determination following irradiation of cations thermally generated in acidic media (for reviews on carbocation chemistry see Ref. [1]). The observed photoproducts resulted from intramolecular rearrangements, photoisomerization or photoinduced electron transfer [2–6]. Recently, attention has been focused on the characterization, properties and reactivity of excited state carbocations [7], complementing the extensive studies on these species in their ground states [8]. Both singlet and triplet excited carbocations have been characterized through use of fluorescence, phosphorescence and laser flash photolysis techniques [9–18].

Singlet and triplet excited xanthyl, thioxanthyl and dibenzosuberonyl cations undergo electron transfer reactions with aromatic donors to generate the corresponding xanthyl radicals and the radical cation of the aromatic donor [15–17, 19]. Both the radicals and the radical cations were detected by laser flash photolysis transient techniques. Further evidence for an electron transfer mechanism came from correlation of the rate constants for quenching of the excited state cations with the ionization potential of the aromatic donor [15–17], as well as the isolation of radical-derived photoproducts [19].

The singlet excited 9-phenylxanthyl cation is also quenched by water, alcohols and amines, suggested to be acting as nucleophiles [10,12,18]. Rate constants for reaction of the excited state cation with these quenchers were several orders of magnitude larger than the corresponding ground state values, suggesting an enhanced cation electrophilicity in the excited state [10]. Substituent effects on the quenching of 9-arylxanthyl cations by water and alcohols demonstrate that the magnitude of the quenching rate constants increases as the electron donating ability of the substituent increases [12,18]. Excited state Hammett plots using the σ^{hv} substituent parameter scale [20] gave negative ρ values, opposite to the substituent effect observed for the corresponding ground state reactions of the 9-arylxanthyl cations with nucleophiles [21]. The relative quenching order for the excited state reaction, *i*-PrOH > MeOH > H₂O > *t*-BuOH, also differs from the reactivity order observed for reaction of ground state carbocations with alcohols in acetonitrile [22–24].

Both the substituent dependence and the relative reactivity order differed between reactions of ground and excited state carbocations with water and alcohols, suggesting that a mechanism other than nucleophilic attack might be operating in the excited state [18]. The possibility of an excited state electron transfer mechanism was considered and eliminated through application of the Rehm–Weller equation [25], although

with the use of reduction potentials of structurally similar diarylmethyl carbocations as model compounds [26]. Shukla and Wan ruled out electron transfer as the mechanism for quenching of thioxanthyl cations by water, owing to the absence of radical coupling products and the inability to trap any putative radicals [19].

Minto and Das have reported that fluorescence from the 9-phenylxanthyl cation was quenched by the addition of tetrahydrofuran [10]. As part of our mechanistic studies on the reactivity of excited state carbocations, we wished to explore the nature of substituent effects on cation quenching with a variety of quenchers. In this way we hoped to determine the generality of the observed substituent effects, namely whether electron-donating substituents increase the rate constants for reaction of excited state carbocations with other quenchers likely to act as nucleophiles. Herein we report results of our studies on the quenching of several 9-arylxanthyl cations by dialkyl ethers and consider the mechanistic implications.

2. Experimental details

2.1. Materials

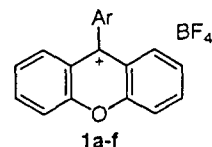
Spectroscopic grade acetonitrile used in the fluorescence quenching experiments was obtained from Mallinckrodt and dried by passage through a column of neutral aluminum oxide. Diethyl ether, isopropyl ether, *tert*-butyl methyl ether and *tert*-butyl ethyl ether (better than 99%) used as quenchers were obtained from Aldrich and distilled from sodium metal prior to use. Tetrahydrofuran (better than 99%) used as a quencher was obtained from Aldrich and distilled from CaH₂ prior to use.

2.2. Fluorescence measurements

Steady state fluorescence emission was measured on a Photon Technology International LS-100 spectrophotometer equipped with a pulsed Xe lamp apparatus. Excitation of the cations was at 374 nm and emission monitored at 540 nm, with a 350 nm cut-off 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.

2.3. 9-Arylxanthylum tetrafluoroborate salts

Tetrafluoroborate salts **1a–1f** were prepared according to a literature procedure [18]. Their spectral data (¹H and ¹³C nuclear magnetic resonance, absorption and fluorescence spectra) were consistent with those previously reported [18].



Aryl substituent: a=H, b=*p*-F, c=*m*-F, d=*p*-CH₃, e=*m*-CH₃, f=*m*-OCH₃

3. Results and discussion

We chose the 9-arylxanthylum tetrafluoroborate salts **1a–1f** as our substrates. The preparation and characterization of these compounds have been previously described [18]. There is no substituent effect on the absorption or fluorescence spectral characteristics, with solutions of each cation salt in acetonitrile exhibiting absorption maxima at 260, 374 and 450 nm, and a broad fluorescence emission centered at 540 nm. A dramatic substituent effect is observed on the fluorescence lifetimes of the cations (Table 1), which range from 27.8 ns for the parent 9-phenylxanthyl cation, to a subnanosecond value for the *m*-OCH₃ cation [18].

3.1. Measurement of ether quenching rate constants

Salts **1a–1f** are soluble in neutral, inert solvents such as acetonitrile, allowing the addition of a wide range of quenchers and use of the Stern–Volmer method [28] of fluorescence quenching analysis for determination of quenching rate constants. Rate constants for quenching of excited state 9-arylxanthyl cations by water and alcohols were obtained in earlier work using tetrafluoroborate salts and fluorescence quenching techniques [18]. The singlet excited cations are not quenched by acetonitrile, as evidenced by the excellent agreement for the water and alcohol quenching rate constants measured for the cation salts in acetonitrile with added quencher, compared with the values obtained in aqueous acidic media [12,18].

Substrates **1a–1f** were dissolved in acetonitrile and their fluorescence intensity measured upon addition of four dialkyl ethers: diethyl ether (Et₂O), isopropyl ether (*i*-Pr₂O), *tert*-butyl methyl ether (*t*-BuOMe), and *tert*-butyl ethyl ether (*t*-BuOEt). Addition of the ethers resulted in quenching of the fluorescence from **1a–1f**. Relative fluorescence quantum yields Φ_F^0/Φ_F were measured for **1a–1f** for addition of each ether and plotted vs. the ether concentration. Excellent linear plots ($r > 0.99$) were obtained in every case, as shown in Fig. 1 for quenching of **1b** by *i*-Pr₂O. Stern–Volmer analysis of the fluorescence quenching data with the measured cation fluorescence lifetimes gave values for k_q , the bimolecular excited state quenching rate constants (Table 1). The k_q values range from 10⁶ to 10¹⁰ M⁻¹

Table 1
Rate constants for quenching of **1a–1f** by ethers ^a

Compound	τ_F^0 (ns) ^b	$E_{1/2}^{red}$ (V)	Rate constants ($M^{-1} s^{-1}$) for the following ether quenchers			
			<i>i</i> -Pr ₂ O	Et ₂ O	<i>t</i> -BuOMe	<i>t</i> -BuOEt
1a (H)	27.6	-0.356 ^c	$(2.28 \pm 0.02) \times 10^7$	$(2.35 \pm 0.09) \times 10^7$	$(6.94 \pm 0.46) \times 10^6$	$(5.71 \pm 0.09) \times 10^7$
1b (<i>p</i> -F)	18.8	-0.323 ^c	$(1.91 \pm 0.14) \times 10^7$	$(1.34 \pm 0.01) \times 10^7$	$(4.90 \pm 0.52) \times 10^6$	$(5.17 \pm 0.07) \times 10^7$
1c (<i>m</i> -F)	14.0		$(2.80 \pm 0.04) \times 10^7$	$(2.24 \pm 0.03) \times 10^7$	$(6.22 \pm 0.06) \times 10^6$	$(6.72 \pm 0.42) \times 10^7$
1d (<i>p</i> -Me)	2.1	-0.363 ^c	$(1.70 \pm 0.01) \times 10^8$	$(1.88 \pm 0.12) \times 10^8$	$(7.42 \pm 0.76) \times 10^7$	$(7.76 \pm 0.52) \times 10^8$
1e (<i>m</i> -Me)	2.0		$(4.40 \pm 0.06) \times 10^8$	$(3.77 \pm 0.22) \times 10^8$	$(2.01 \pm 0.09) \times 10^8$	$(1.22 \pm 0.04) \times 10^9$
1f (<i>m</i> -OMe)	0.028	-0.387	$(2.11 \pm 0.22) \times 10^{10}$	$(1.88 \pm 0.06) \times 10^{10}$	$(5.86 \pm 0.28) \times 10^9$	$(4.59 \pm 0.02) \times 10^{10}$

^a Errors quoted are the standard deviations obtained from repeated measurements.

^b Taken from Ref. [18].

^c Taken from Ref. [27].

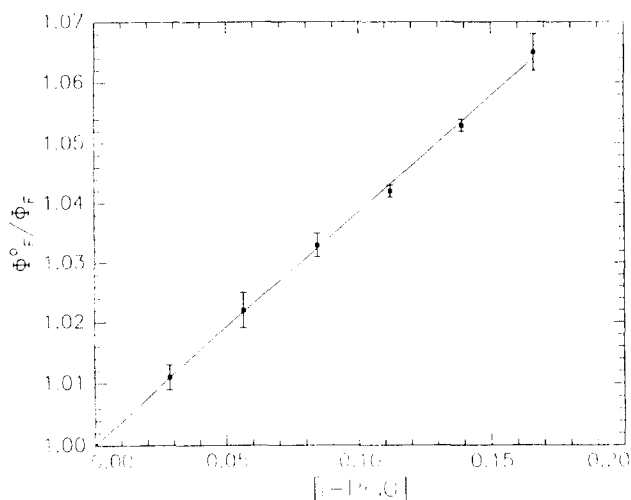


Fig. 1. Stern–Volmer plot of Φ_0^b/Φ^b for **1b** vs. *i*-Pr₂O concentration.

s^{-1} and are similar in magnitude to the rate constants determined for quenching of these singlet excited cations by water and alcohols.

We also used Stern–Volmer fluorescence quenching methods to obtain a k_q value of $4.86 \times 10^8 M^{-1} s^{-1}$ for quenching of **1a** by THF. This value is in very good agreement with the rate constant of $6.2 \times 10^8 M^{-1} s^{-1}$ determined with time-resolved measurements, for the 9-phenylxanthyl cation generated in acetonitrile by a two-laser flash photolysis method [10]. The slightly lower value we determined is in accord with the previous suggestion that ion-paired species are less susceptible to quenching [10]. A similar trend was previously observed in measurements of water and alcohol quenching rate constants [18], in which the 9-phenylxanthylum ion tetrafluoroborate salt gave k_q values slightly lower than the rate constants obtained for the same cation generated in acetonitrile by the two-laser flash photolysis technique [10].

3.2. Substituent effects on the quenching rate constants

For each of the ether quenchers, the k_q values for **1a–1f** listed in Table 1 increase in magnitude as the

electron-donating ability of the substituent increases. The substituent effects can be further examined by means of an excited state Hammett plot. Plots of $\log[k_q(X)/k_q(H)]$ vs. either σ or σ^+ substituent parameters [29] gave poor correlation, as previously observed with correlations of the rate constants for water and alcohol quenching of the singlet excited 9-arylxanthyl cations [18]. This poor correlation is due mainly to scatter from the *meta*-substituted cations, whose points fall above the line indicating a greater reactivity than predicted from the ground-state substituent parameters. *Meta* substituents are known to exhibit an enhanced conjugation in the excited state compared with corresponding ground state compounds, as first reported by Zimmerman, Havinga and coworkers [30]. This effect of enhanced reactivity of *meta* substituents can also be observed by comparison of the k_q values in Table 1 obtained for the same substituent in the *meta* or *para* position. For both the fluoro and the methyl substituents, larger ether quenching rate constants are observed for the *meta*-substituted cations, **1c** and **1e**, compared with the corresponding *para*-substituted cations, **1b** and **1d** respectively.

To examine the excited-state substituent behavior, we plotted $\log[k_q(X)/k_q(H)]$ vs. σ^{hr} , an excited state substituent parameter [20]. The σ^{hr} scale is particularly appropriate for correlation of excited state xanthyl cation reactivity, since it is based on the formation of structurally similar benzyl cations from the photoprotonation of ring-substituted styrenes and phenylacetylenes. Excellent linear correlation was observed in the excited state Hammett plots for each of the ether quenchers, with the exception of the point corresponding to **1c**, the *m*-F substituted cation, which falls below the line in each case. Fig. 2 illustrates the Hammett plot obtained for quenching of **1a–1f** by *t*-BuOMe. Excited state Hammett plots for quenching of the 9-arylxanthyl cations by alcohols similarly showed the *m*-F point falling below the line [18]. However, in the alcohol quenching plots, the extent of deviation from the line increased as the steric bulk of the alkyl group increased. Thus the point

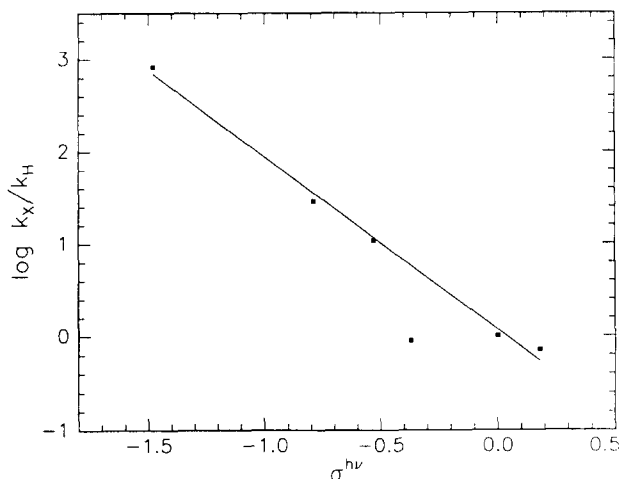


Fig. 2. Excited state Hammett plot ($\log[k_q(X)/k_q(H)]$ vs. σ^{hv}) for quenching of **1a–1f** by *t*-BuOMe.

Table 2
Correlation of $\log[k_q(X)/k_q(H)]$ vs. σ^{hv} for ether quenching of **1a–1f**

	Quencher			
	<i>i</i> -Pr ₂ O	Et ₂ O	<i>t</i> -BuOMe	<i>t</i> -BuOEt
Slope ρ^a	-1.84	-1.86	-1.87	-1.80
r^b	0.987	0.991	0.997	0.991
Intercept c	-0.04	-0.23	0.07	0.12
σ_y^d	0.14	0.11	0.06	0.11
σ_{slope}^e	0.17	0.14	0.08	0.14

^a The data corresponding to **1c** 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.

^e Standard deviation in the slope.

corresponding to the *m*-F cation fell furthest from the line for quenching of the 9-arylxanthyl cations by *t*-BuOH, with only a modest deviation for MeOH quenching of the cations. In contrast, the point corresponding to **1c** exhibits approximately the same deviation for each of the ether quenchers. As noted earlier, the anomalous behavior exhibited by **1c** cannot be attributed solely to steric effects, since the steric effect of an *m*-F substituent must be less than those of either an *m*-Me or an *m*-OMe substituent [18]. Furthermore, use of the σ^{hv} substituent parameter scale should account for any unusual excited state electronic effects associated with the *m*-F substituent.

Values of ρ were calculated from the excited state Hammett plots for each of the ethers (Table 2). We excluded the point corresponding to **1c** from the linear regression analysis because of its apparently anomalous behavior. These ρ values were not greatly different, however, if the point corresponding to **1c** was either included or excluded. Negative ρ values were obtained in each case, showing that electron-donating substituents

increase the rate constant for quenching of the singlet excited cations by ethers. In contrast, small positive ρ values are obtained for quenching of ground state 9-arylxanthyl cations by nucleophilic species such as water and alcohols [21]. The ground state substituent effect can be explained by electronic stabilization of the positively charged species by electron-donating substituents, with the effect somewhat attenuated owing to twisting of the 9-aryl group away from the planarity of the xanthyl backbone. The ether quenching results demonstrate the generality of the substituent effect reversal between the ground and excited states, as the effect had been observed previously only for quenching by water and alcohols [12,18].

3.3. Quenching mechanism

Since the substituent dependence on the reactivity of **1a–1f** with nucleophilic species (water, alcohols and ethers) is opposite to that seen in the reaction of ground state cations, the likelihood of an alternative mechanism operating in the excited state must be considered. We had previously considered the possibility of an electron transfer mechanism in the quenching of 9-arylxanthyl cations by water and alcohols [18]. We used the Rehm–Weller [25] equation (Eq. (1)) to determine the free energy ΔG_{ET} for electron transfer, where $E_{1/2}^{red}$ is the reduction potential of the xanthyl cation, $E_{1/2}^{ox}$ is the oxidation potential of the electron donor and E_s is the excited singlet energy of the cation:

$$\Delta G_{ET} = E_{1/2}^{ox} - E_{1/2}^{red} - E_s \quad (1)$$

For any single given quencher (water, alcohol or ether) $E_{1/2}^{ox}$ is the same, while E_s is approximately 60 kcal mol⁻¹ for each of **1a–1f**, based on the onset of fluorescence [12,18]. Thus for an electron transfer mechanism to be operating, $E_{1/2}^{red}$ must account for the observed substituent effect on reactivity. For example, the k_q value for quenching of the *m*-OMe substituted cation by ethers, alcohols or water is nearly three orders of magnitude greater than the corresponding k_q value for quenching of the parent 9-phenylxanthyl cation. In our prior studies employing the Rehm–Weller equation, we used values of $E_{1/2}^{red}$ for diarylmethyl cations as a model system because of their structural similarity to the xanthyl cations [18]. $E_{1/2}^{red}$ values for the parent diphenylmethyl cation and the *m*-OMe substituted cation exhibit a difference of only 0.03 V [26]. This extremely small difference in reduction potential cannot account for the nearly three order of magnitude difference between the quenching rate constants determined for those two cations. Thus an electron transfer mechanism was ruled out, although based on redox potentials for the diarylmethyl model compounds.

Reduction potentials for 9-arylxanthyl cations have been recently reported [27], permitting a more conclusive test of an electron transfer mechanism. $E_{1/2}^{\text{red}}$ values for **1a–1f** are listed in Table 1. These $E_{1/2}^{\text{red}}$ values were measured in sulfolane against a ferrocene–ferrocenium couple. Although the electrochemical measurements were performed in a solvent system different from the acetonitrile we used for measurement of the k_q values, the reduction potentials will indicate the substituent effect for the 9-arylxanthyl cations. As described above, for an electron transfer mechanism to be operating, the substituent effect on the reduction potentials must account for the observed substituent effect on the k_q values. In qualitative terms, the ease of reduction of the cations should parallel an increase in the quenching rate constants. The $E_{1/2}^{\text{red}}$ values and k_q values in Table 1 demonstrate that the trend for ease of reduction decreases with a concomitant increase in the magnitude of the quenching rate constants. This trend is opposite to that predicted should an electron transfer mechanism be operating in the quenching of excited state 9-arylxanthyl cations **1a–1f** by ethers, alcohols or water. Since an electron transfer mechanism is thus ruled out, and we can conceive of no other likely mechanism, we conclude that the mechanism must involve nucleophilic attack by the quencher on the excited state xanthyl cations.

The rate constants for **1a–1f** listed in Table 1 demonstrate a relative quenching order of $t\text{-BuOEt} > \text{Et}_2\text{O} \sim i\text{-Pr}_2\text{O} > t\text{-BuOMe}$, although the differences between the quenchers are not very large, varying by a factor of only 6–11. The k_q values do not exhibit a large steric effect as might be predicted for nucleophilic attack by the ethers. The largest k_q value is seen with the $t\text{-BuOEt}$ quencher, demonstrating that the relative quenching order does not depend solely on steric factors. The relative order for quenching of 9-arylxanthyl cations by alcohols, $i\text{-PrOH} > \text{MeOH} > t\text{-BuOH}$, similarly does not follow the steric trend [10,18]. Minto and Das rationalized the non-steric order for quenching of the singlet excited 9-phenylxanthyl cation by alcohols, with the availability of the lone pairs counterbalanced by the steric effect of increasing methyl substitution [10].

A possible explanation for the observed substituent dependence was previously suggested invoking Hückel molecular orbital calculations [12]. The calculations showed that the size of the lobe at C_9 (i.e. the coefficient of the p-orbital) in the singlet excited state of the xanthyl cation increases as the substituents become more strongly electron donating. The larger k_q values can then be explained by invoking frontier orbital theory [31], as the larger lobes would provide better overlap with the incoming nucleophile lone pair.

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