Photophysics and Photochemistry of Carbocations

Maria R. Valentino
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PHOTOPHYSICS AND PHOTOCHEMISTRY OF CARBOCATIONS

A DISSERTATION SUBMITTED TO
THE FACULTY OF THE GRADUATE SCHOOL OF
LOYOLA UNIVERSITY OF CHICAGO
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

MARIA R. VALENTINO

CHICAGO, ILLINOIS
JANUARY, 1996
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My sincere thanks to my research advisor, Professor Mary K. Boyd, for all her help and patience. She has helped me mature as a scientist and a person.

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# TABLE OF CONTENTS

ACKNOWLEDGEMENT ............................................................... iii  
LIST OF TABLES ................................................................. v  
LIST OF FIGURES ............................................................... vi  
LIST OF ABBREVIATIONS ....................................................... ix  
ABSTRACT ........................................................................ xii

Chapter

I.  INTRODUCTION ........................................................................ 1  
II. RESULTS
    Substrate synthesis and characterization ........................................ 20  
    Measurement of quenching rate constants ..................................... 28  
    Photoproduct studies .................................................................. 51  
III. DISCUSSION
    Substituent effects on quenching rate constants .............................. 60  
    Relative quenching order ........................................................... 83  
    Quenching mechanism ............................................................... 88  
    Photoproduct studies ................................................................. 91  
    Photophysical properties of the 9-aryl substituted cations ............. 100

IV. CONCLUSIONS ....................................................................... 106  
V.  EXPERIMENTAL ..................................................................... 110  
SPECTRA .................................................................................. 127  
REFERENCES .......................................................................... 171  
VITAE ...................................................................................... 177
LIST OF TABLES

Table

1. Rate constants for fluorescence quenching of the xanthyl I, 9-phenylxanthyl II, and dibenzosubereryl III cations with aromatic donors in TFE ........................................... 11

2. fluorescence lifetimes, $\tau_f$, of 9-arylxanthyl cations 20a-f and 9-arylthioxanthyl cations 21a-e ........................................... 23

3. Fluorescence quantum yields, $\Phi_f$, of 9-arylxanthyl cations 20a-f and 9-arylthioxanthyl cations 21a-e ........................................... 25

4. Photophysical data for 9-arylxanthyl cations 20a-f and 9-arylthioxanthyl cations 21a-e ........................................... 27

5. Excited-state rate constants (M$^{-1}$ s$^{-1}$) for quenching of 9-arylxanthyl cations 20a-f by water and alcohols ........................................... 48

6. Excited-state rate constants (M$^{-1}$ s$^{-1}$) for quenching of 9-arylxanthyl cations 20a-f by ethers ........................................... 49

7. Excited-state rate constants (M$^{-1}$ s$^{-1}$) for quenching of 9-arylthioxanthyl cations 21a-e by water and alcohols ........................................... 54

8. Correlation of $\log[k_q(X)/k_q(H)]$ versus $\sigma^h$ for quenching of the 9-arylxanthyl cations 20a-f by water and alcohols ........................................... 81

9. Correlation of $\log[k_q(X)/k_q(H)]$ versus $\sigma^h$ for quenching of the 9-arylxanthyl cations 20a-f by ethers ........................................... 82

10. Reduction potentials for 9-arylxanthyl cations ........................................... 92
LIST OF FIGURES

Figure

1. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_p$, versus $H_2O$ concentration for quenching of 9-phenylxanthylium tetrafluoroborate 20a .............................................. 30

2. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_p$, versus MeOH concentration for quenching of 9-(4-fluorophenyl)-xanthylium tetrafluoroborate 20b .............................................. 32

3. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_p$, versus i-PrOH concentration for quenching of 9-(3-methylphenyl)-xanthylium tetrafluoroborate 20e .............................................. 34

4. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_p$, versus $t$-BuOH concentration for quenching of 9-(4-methylphenyl)-xanthylium tetrafluoroborate 20d .............................................. 36

5. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_p$, versus i-Pr$_2$O concentration for quenching of 9-(3-fluorophenyl)-xanthylium tetrafluoroborate 20c .............................................. 38

6. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_p$, versus Et$_2$O concentration for quenching of 9-(4-fluorophenyl)-xanthylium tetrafluoroborate 20b .............................................. 40

7. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_p$, versus $t$-BuOMe concentration for quenching of 9-phenylxanthylium tetrafluoroborate 20a ..................................................... 42

8. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_p$, versus $t$-BuOEt concentration for quenching of 9-(3-methoxyphenyl)-xanthylium tetrafluoroborate 20a ..................................................... 44
9. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_r/\Phi_f$, versus THF concentration for quenching of 9-(3-methylphenyl)-xanthylum tetrafluoroborate 20e ................................. 46

10. Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_r/\Phi_f$, versus MeOH concentration for quenching of 9-(4-fluorophenyl)-thioxanthylum tetrafluoroborate 21b .............................. 52

11. Plot of the percent composition of photoproducts 22 and 24-27 versus time for the irradiation of 20a in acetonitrile in the presence of i-Pr$_2$O ........................................ 57

12. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by H$_2$O .................................................. 62

13. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by MeOH .................................................. 64

14. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by i-PrOH .................................................. 66

15. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by t-BuOH .................................................. 68

16. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by Et$_2$O .................................................. 71

17. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by i-Pr$_2$O .................................................. 73

18. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by t-BuOMe .................................................. 75

19. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by t-BuOEt .................................................. 77

20. Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^h$ for quenching of 20a-f by THF .................................................. 79
LIST OF FIGURES (Continued)

21. Plot of the $\log[k_q(X)/k_q(H)]$ versus $\sigma^{lv}$ for quenching of 21a-e by $\text{H}_2\text{O}$ ........................................... 84

22. Plot of the $\log[k_q(X)/k_q(H)]$ versus $\sigma^{lv}$ for quenching of 21a-e by $\text{MeOH}$ .................................................. 86
LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>c</td>
<td>cyclo</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>$E_{1/2}^{ox}$</td>
<td>oxidation potential</td>
</tr>
<tr>
<td>$E_{1/2}^{red}$</td>
<td>reduction potential</td>
</tr>
<tr>
<td>$E_s$</td>
<td>singlet energy</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>i</td>
<td>iso</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>kcal/mol</td>
<td>kilocalories per mole</td>
</tr>
<tr>
<td>m</td>
<td>meta</td>
</tr>
<tr>
<td>Me</td>
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</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>ns</td>
<td>nanosecond</td>
</tr>
<tr>
<td>o</td>
<td>ortho</td>
</tr>
<tr>
<td>p</td>
<td>para</td>
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ix
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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</thead>
<tbody>
<tr>
<td>Pr</td>
<td>propyl</td>
</tr>
<tr>
<td>s</td>
<td>seconds</td>
</tr>
<tr>
<td>t</td>
<td>tertiary</td>
</tr>
<tr>
<td>TFA/TFE</td>
<td>trifluoroacetic acid/trifluoroethanol</td>
</tr>
<tr>
<td>TFE</td>
<td>trifluoroethanol</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>volts</td>
</tr>
<tr>
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ABSTRACT

Several 9-arylxanthyl and 9-arylthioxanthyl tetrafluoroborate salts (Ar = H, p,m-F, p,m-Me, m-OMe) have been synthesized by reaction of the corresponding 9-arylxanthen-9-ol or 9-arylthioxanthen-9-ol with fluoroboric acid in propionic anhydride.

Fluorescence from the 9-arylxanthyl cations was quenched by the addition of H$_2$O, alcohols and ethers. Stern-Volmer analysis of the fluorescence quenching gave excited-state bimolecular rate constants ranging from $10^7$-10$^{10}$ M$^{-1}$s$^{-1}$. The larger rate constants were associated with the electron donating substituents. Hammett plots of log[$k_q(X)/k_q(H)$] versus $\sigma^e$ gave negative \( \rho \) values for each quencher. This substituent dependence is opposite to that observed for the corresponding ground-state reaction. The relative alcohol quenching order (i-PrOH>MeOH>t-BuOH>H$_2$O) also differs from the order observed for ground-state cation reactivity.

Preparative photolysis of the 9-phenylxanthyl cation in the presence of i-Pr$_2$O resulted in the formation of unique photoproducts not produced in the corresponding dark reaction. The photoproducts suggest the intermediacy of the 9-phenylxanthyl radical. An electron-transfer mechanism to form the 9-phenylxanthyl radical was ruled out based on the reduction potentials of the 9-arylxanthyl cations and quenching rate constants. Instead, the excited-state mechanism is proposed to proceed via
nucleophilic attack of the ether on the 9-phenylxanthyl cation to form an oxonium ion intermediate. Homolytic cleavage generates the resonance-stabilized 9-phenylxanthyl radical and the corresponding ether radical cation.

Fluorescence from the 9-arylthioxanthyl cations was also quenched by H$_2$O and alcohols. In contrast to the 9-arylxanthyl cations, no substituent dependence is observed in the rate constants for quenching of the 9-arylthioxanthyl cations by H$_2$O and MeOH.

Photophysical properties of the 9-arylxanthyl cations exhibit a substantial substituent dependence in the lifetimes, fluorescence quantum yields, total decay rate constants and non-radiative rate constants. In contrast, no substituent effect was observed on the same photophysical properties in the 9-arylthioxanthyl cations. No substituent dependence was observed on the position of the absorbance or fluorescence maxima for either the 9-arylxanthyl or 9-arylthioxanthyl cations.
CHAPTER I

INTRODUCTION

Carbocations are organic molecules containing a positive charge centered on a carbon atom. The positive charge makes these species inherently reactive, and therefore particularly interesting from both fundamental and practical viewpoints. While ground-state carbocations have been extensively investigated (Olah, 1970), much less is known about the photochemistry of these species. Excited-state cations possess different electronic distributions and higher energies compared to ground-state species. The excited-state reactivity of carbocations may lead to the formation of unique products formed only through an excited state.

Early studies on carbocation photochemistry focused primarily on photoproduct determination following irradiation of cations thermally generated in acidic media (Cabell-Whiting, 1973 and Childs, 1991). The first carbocation photolysis to be investigated was that of the tropylium ion (van Tamelen, 1968). In 5% aqueous sulfuric acid solution, the tropylium ion 1 rearranged to bicyclo[3.2.0]-hepta-3,6-dien-2-ol 3 and the corresponding ether 4 shown in Scheme 1.
These photoproducts were proposed to have formed via a reactive valence-bond isomer, the "Dewar tropylium ion" 2 (van Tamelen, 1968 and van Tamelen, 1971b). Irradiation of the tropylium ion in ethanol in the absence of acid gave tropyl ethyl ether. With additional irradiation, tropyl ethyl ether continued to react with formation of ditropyl and its photoisomer, hexaene (van Tamelen, 1968 and 1971b). Upon irradiation in stronger acid (FHSO₃) the tropylium and methyltropylium ions isomerized to form the 7-norbornadienyl and 2-methyl-7-norbornadienyl cations, respectively (Child, 1970 and Hogeveen, 1970). The phenyltropylium ion is photochemically stable when irradiated in FHSO₃ (Childs, 1970) or aqueous sulfuric acid (van Tamelen, 1971b) under anaerobic conditions. When irradiated in aqueous sulfuric acid in the presence of oxygen, the phenyltropylium ion was converted to biphenyl, known to form by the action of hydrogen peroxide (Jutz, 1964). Photolysis of the phenyltropylium ion in acetonitrile gives ortho- and para-phenylbenzaldehydes as well as the coupling products cis- and trans-diphenylstilbenes (van Tamelen, 1971b). The mechanism by which these compounds are produced is not clear, but may involve a norcaradiene valence isomer as a precursor.
Irradiation of azulene in 50% aqueous sulfuric acid resulted in formation of dimeric and trimeric azulene-type products in addition to polymeric material. It was proposed that the isopropylidene unit in these products was derived from the azulene moiety, however, a mechanism was not proposed (van Tamelen, 1971b).

The stable triphenylcyclopropenyl cation undergoes an electron-transfer reaction when irradiated in aqueous acid solution, giving hexaphenylbenzene. The reaction is proposed to proceed via an initial charge transfer from an unspecified donor to produce the cyclopropenyl radical which then coupled to give hexaphenylbenzene (van Tamelen, 1968 and 1971b).

Irradiation of the cation produced by the protonation of 1,1-di-p-anisylethylene in equilibrium with the alkene in benzene/trifluoroacetic acid solution resulted in a single electron transfer (SET) from the neutral alkene to the electronically excited cation. The electron transfer product pair of radical 6 and radical cation 7 leads to the formation of 8-11 shown in Scheme 2 (Al-Ekabi, 1988).
Photoprodus formed following irradiation of the extensively delocalized triphenylmethyl cation have also been investigated. Product formation depended on numerous variables including solvent, pH of the medium and the presence or absence of oxygen. Initial work involved irradiation of the triphenylmethyl cation in
concentrated aqueous H$_2$SO$_4$ solution (96%) with the formation of 9-phenylfluoren-9-ol (van Tamelen, 1968). At lower H$_2$SO$_4$ concentrations (72%) and the absence of oxygen, irradiation of the triphenylmethyl cation 12 yielded dimeric products 13, 14, and 15 which are shown in Scheme 3, formed by the interaction of an excited triplet triphenylmethyl cation with a ground-state triphenylmethyl cation.

Scheme 3

\[
\begin{align*}
\text{hv} & \quad (\text{Ph})_2\text{C} - \text{H(Ph)}_2 \\
\text{72\% H}_2\text{SO}_4 & \quad (\text{Ph})_2\text{CH} - \text{CH(Ph)}_2 \\
\text{12} & \quad 13 \\
\text{12} & \quad 14 \\
\text{12} & \quad 15
\end{align*}
\]

In weaker acid systems and with the addition of benzene or toluene, irradiation of the triphenylmethyl cation produced 9-phenylfluorenyl type compounds such as triphenylmethane, 9-phenylfluorene, bis-9-phenylfluorenylperoxide and tetraphenylmethane. The mechanism was proposed to proceed via a radical intermediate (van Tamelen, 1971a).

In the presence of oxygen and weakly acidic media, irradiation of a 10$^{-3}$ M solution of the triphenylmethyl cation yielded benzophenone and 2,2-diphenylmethylenedioxybenzene as major photoproducts. It was proposed that direct
combination of an excited triplet triphenylmethyl cation and ground-state molecular oxygen were involved in the mechanism. Irradiation of a $10^{-5}$ M solution of triphenylmethyl cation in 99% H$_2$SO$_4$ yielded 9-phenylfluoren-9-ol as the major photoproduct and upon addition of oxygen, fluoren-9-one was detected (Allen, 1971 and Owen, 1973). An excited triplet cation was again proposed to be involved in the mechanism.

Irradiation of xanthodyl 16, triphenylmethyl 12 or 5H-dibenzosuberenyl 17 cation in the presence of triphenylmethane in trifluoroacetic acid solution led to the quantitative formation of the triphenylmethyl cation. Results indicated that the triplet excited cation, acting as a sensitizer, was responsible for the photo-oxidation of the hydrocarbon (Bethell, 1972).

There has been considerable recent attention given to the characterization, properties and reactivity of excited-state carbocations (Das, 1993). The photophysical properties of resonance-stabilized carbocations have been characterized by UV/Vis and fluorescence emission spectroscopies. Spectral data for carbocations are usually
obtained on stabilized species in strongly acidic solutions and are only slightly red-shifted compared to those observed by laser flash photolysis in neutral solvents.

Diarylmethyl and trityl cations have been characterized and show absorption bands in the 400-500 nm region with molar extinction coefficients generally greater than 40,000 (Das, 1993 and Azarani, 1991). The trityl cation has been reported to give a fluorescence band in acidified solvents centered at 530 nm (Samanta, 1993) and 475 nm (Azarani, 1991). The diarylmethyl cations \((4-\text{MeO-Ph})_2\text{C(CH}_3\text{)}^+\) and \((4-\text{MeO-Ph})_2\text{CH}^+\) fluoresce at 535 nm and 600 nm, respectively. The singlet lifetimes of these compounds have been measured by a number of groups. Samanta and co-workers and Azarani and co-workers report a fluorescence lifetime for the trityl cation in acidified solvents of <1.0 ns. Singlet lifetimes for \((4-\text{MeO-Ph})_2\text{C(CH}_3\text{)}^+\) and \((4-\text{MeO-Ph})_2\text{CH}^+\) were reported as 6 ns and 3 ns, respectively (Azarani, 1991). A fluorescence quantum yield of 0.001 has been reported for the trityl cation (Samanta, 1993).

Cations containing the xanthyl backbone have a strong absorption maximum around 370 nm and a weaker absorption in the visible range at about 450 nm. In comparison, thioxanthyl cations have absorbance maxima in the 380 nm (strong) and 480 nm (weak) regions (Samanta, 1993). The fluorescence emission of the xanthyl and thioxanthyl cations show broad emission bands with maxima between 500 and 600 nm (Azarani, 1991; Boyd, 1985 and 1991; Samanta, 1990 and 1993). The singlet lifetimes of a variety of xanthyl compounds have been measured, with the 9-phenylxanthyl cation being the most widely studied. The singlet lifetime of the 9-
phenylxanthyl cation has been reported as 24.2 to 36 ns, depending upon the solvent system (Azarani, 1991; Boyd, 1991; Das, 1993; Johnston, 1993; Minto, 1989; Samanta, 1990 and 1993). A lifetime of 37 ns has also been reported for the 9-phenylxanthyl cation generated on silica-gel surfaces (Berger, 1990). Fluorescence quantum yields have also been reported for this cation in acidified solvents and range from 0.33 to 0.48 (Azarani, 1991; Samanta, 1990 and 1993; Minto, 1989). Fluorescence quantum yields of 0.80 for the 9-phenylxanthyl cation and 0.55 for the 9-(4-fluorophenyl)xanthyl cation generated by laser flash photolysis in 1% TFA/TFE solution have been reported (Johnston, 1993). The higher values obtained in primarily TFE solvent were attributed to the absence of water, which is known to quench the singlet excited state of these cations (Boyd, 1991; Wan, 1985). Substituents on the 9-phenyl ring apparently have a dramatic effect on the lifetimes as the values range from approximately 28 ns for the $p$-CF$_3$ substituted cation to subnanosecond values for the $m$- and $p$-OMe substituted cations (Boyd, 1991).

The singlet lifetimes of the xanthyl cation and alkyl substituted xanthyl cations have also been measured. The parent xanthyl cation in acidified solvents has been reported as having a singlet lifetime ranging from 17.5 to 31 ns (Azarani, 1991; Boyd, 1991 and Samanta, 1993) with a fluorescence quantum yield of 0.16 (Samanta, 1993) and 0.12 (Azarani, 1991). The wide variation seen in the lifetimes may also be due to the water present in the solvent medium. Alkyl substitution (Me, i-Pr, c-Pr) on the 9-position of the xanthyl cation does not cause as dramatic an effect on the lifetime
as seen with the 9-arylxanthyl cations. Lifetimes for the 9-alkylxanthyl cations ranged from only 32.6 to 41 ns (Azarani, 1991 and Boyd, 1991).

Measured fluorescence lifetimes and quantum yields for the thioxanthyl and 9-phenylthioxanthyl cations in acidified solvents differ greatly. A lifetime of 22.8 ns and quantum yield of 0.24 have been reported for the thioxanthyl cation compared to a lifetime of <2 ns and a quantum yield value of 0.025 and 0.031 for the 9-phenyl substituted thioxanthyl cation (Samanta, 1993).

Dibenzosubereryl cations have characteristic absorption maxima between 370 and 556 nm with a fluorescence emission band between 550 and 580 nm (Azarani, 1991). The same group reports a measured fluorescence lifetime of <1 ns for the phenyl-substituted dibenzosubereryl cation.

The triplet excited state of 9-arylxanthyl (H, p-F, p-OMe) and 9-arylthioxanthyl (H, p-F) cations have also been characterized (Johnston, 1992 and 1993). Using luminescence and transient absorption techniques, the triplet excited states of these cations were found to have absorption bands in the 300 nm region. At room temperature and in the absence of quenchers, these species are relatively long lived (5-10 µs) in TFE/TFA solution. A weak phosphorescence emission between 600 and 700 nm at 77 K was detected for these cations. Triplet energies were estimated at ~48 kcal/mol for the 9-arylxanthyl cations and at ~41 kcal/mol for the 9-arylthioxanthyl cations based on the onset of phosphorescence.

Singlet excited 9-arylxanthyl cations possess relatively long excited-state
lifetimes making them excellent candidates for the study of bimolecular reactions such as nucleophilic and electron transfer processes. In one particular reactivity study, the 9-phenylxanthyl cation was thermally generated from 9-phenylxanthen-9-ol in trifluoroacetic acid/acetonitrile (Samanta, 1990). The solution was irradiated and the fluorescence of the 9-phenylxanthyl cation was found to decrease in the presence of aromatic donors, such as substituted benzenes and polycyclic aromatic compounds. Bimolecular rate constants for the steady-state fluorescence quenching of the cation were determined using the Stern-Volmer method (Stern, 1919) and ranged from 4.5x10^9 M\(^{-1}\) s\(^{-1}\) (benzene) to 2.6x10^10 M\(^{-1}\) s\(^{-1}\) (anthracene). An electron-transfer quenching mechanism was proposed based upon transient absorption detection of the 9-phenylxanthyl radical and the radical cation of the aromatic donor. Further evidence in support of the electron-transfer quenching mechanism came from correlation of the quenching rate constants with the oxidation potential of the aromatic donor.

Similarly, the fluorescence from xanthyl, 9-phenylxanthyl and dibenzosuberenyl cations produced in trifluoroacetic acid/trifluoroethanol from their corresponding alcohols was quenched upon the addition of aromatic donors (Azarani, 1991). Singlet excited quenching rate constants were determined by monitoring the fluorescence decay of the cation as a function of the concentration of added aromatic donor (substituted benzenes). Table 1 lists the data obtained for reaction of the singlet excited xanthyl, 9-phenylxanthyl and dibenzosuberenyl cations with a variety of substituted aromatic compounds. Again, a correlation was seen between the observed
TABLE 1
RATE CONSTANTS FOR FLUORESCENCE QUenching OF THE
XANTHYL I, 9-PHENYLXANTHYL II, AND DIBENZOSUBERENYL III
CATIONS WITH AROMATIC DONORS IN TFE.\(^a\)

<table>
<thead>
<tr>
<th>Quencher</th>
<th>(E_{\text{ox}})(^b) (V)</th>
<th>(k_q) ((\times)(10^9) M(^{-1}) s(^{-1}))</th>
</tr>
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<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>1,2,4,-Trimethoxybenzene</td>
<td>1.12</td>
<td>7.4</td>
</tr>
<tr>
<td>Anisole</td>
<td>1.76</td>
<td>7.6</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>1.80</td>
<td>-</td>
</tr>
<tr>
<td>(o)-Xylene</td>
<td>1.89</td>
<td>-</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.98</td>
<td>5.5</td>
</tr>
<tr>
<td>Cumene</td>
<td>2.07</td>
<td>5.3</td>
</tr>
<tr>
<td>Benzyltrimethylsilane</td>
<td>2.09</td>
<td>4.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.30</td>
<td>4.2</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.42</td>
<td>4.9</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td>Cyanobenzene</td>
<td>-</td>
<td>&lt;0.001</td>
</tr>
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</table>


\(^b\)In acetonitrile versus saturated calomel electrode (SCE).
rate constant and the oxidation potential of the quencher suggesting an electron-transfer quenching mechanism.

To further investigate the excited-state mechanism, product studies were undertaken. Irradiation of the dibenzosubereryl cation in the presence of benzyltrimethylsilane produced 5-benzodibenzocycloheptene. This product is proposed to arise from either coupling of the benzyl radical to the dibenzosubereryl radical or the dibenzosubereryl cation. With either intermediate, electron transfer is proposed as the initial step of the quenching mechanism.

More recently, Das and co-workers (Samanta, 1993) studied the excited-state reactivity of the 9-phenylxanthyl and 9-phenylthioxanthyl cations in the presence of aromatic donors. These cations were thermally generated from the corresponding alcohols using trifluoroacetic acid or H₂SO₄ in acetonitrile, followed by irradiation. The reactivity of the singlet excited cations with substituted benzenes and polycyclic aromatics was studied using laser flash photolysis. A representative case was reported for the transient absorption changes following laser excitation of the 9-phenylxanthyl cation in the presence of 1-methylnaphthalene. Transient absorption bands corresponding to the 9-phenylxanthyl radical and the 1-methylnaphthalene radical cation were observed.

The magnitude of the steady-state rate constants for quenching of the xanthyl cations by the aromatic donors varied, but were in the diffusion controlled region. The authors also investigated quenching of the singlet excited cations by oxygen. Results
indicate the cations are resistant to quenching by oxygen. An unfavorable charge-transfer interaction and poor capability as an electron-donor were proposed as reasons for the inability of oxygen to quench the singlet cations.

The xanthyl rate constants are generally lower than those for the thioxanthyl carbocations. This is a reflection of the fact that the singlet energy of the thioxanthyl cation is about 5 kcal/mol lower than the xanthyl cation. The rate constants for quenching of the xanthyl cation are 2-3 times larger than for quenching the 9-phenylxanthyl cation. Since the singlet energies ($E_s$) and reduction potentials ($E_{1/2}^{\text{red}}$) for these two cations are nearly equal, the lower rate constants for the 9-phenylxanthyl cation is proposed to be due to steric hindrance of the phenyl ring. Additionally, estimated electron-transfer quantum yields for quenching of the xanthyl and 9-phenylxanthyl singlet cations by biphenyl were 0.01-0.02. This suggests that back electron transfer dominates over the dissociation of the generated radical and radical cation pair.

Another recent study investigated the products formed from reaction of the photoexcited 9-phenylxanthyl cation with aromatic donors (Shukla, 1993). Here, the cation was thermally produced from its alcohol precursor in acidic acetonitrile. Excited-state quenching rate constants were determined using the Stern-Volmer method upon addition of methyl-substituted benzenes. Quenching rate constants were in the range of 5-7.9x10^9 M^-1 s^-1. A solution of the 9-phenylxanthyl cation was irradiated in the presence of 1,3-dimethoxybenzene and photoproducts isolated.
identification of the radical derived photoproduct, bis(9-phenylxanthen-9-yl) peroxide, provided further evidence for an electron-transfer mechanism.

The triplet state of some 9-arylxanthyl cations were similarly found to undergo electron-transfer reactions with aromatic donors (Johnston, 1992 and Johnston, 1993). The 9-phenylxanthyl, 9-(4-fluorophenyl)xanthyl and 9-phenylthioxanthyl cations were thermally generated in trifluoroacetic acid/trifluoroethanol solution from their respective alcohol precursors. The triplet excited state of these cations were directly observed using transient absorption techniques. The triplet cations were found to undergo efficient electron-transfer reactions in the presence of substituted benzenes, naphthalenes and the precursor alcohols. For example, addition of biphenyl resulted in quenching of the 9-phenylxanthyl triplet cation. The 9-phenylxanthyl radical and the biphenyl radical cation were detected via transient techniques. The quenching rate constants measured in TFE ranged from lower than $10^7 \text{ M}^{-1} \text{ s}^{-1}$ to nearly the diffusion controlled limit. The triplet cations are proposed to be poorer oxidizing agents than the singlet excited state of the same cations due to the lower excitation energy of the triplet cations (Azarani, 1991).

Measured electron-transfer yields for quenching of the triplet 9-phenylxanthyl cation by biphenyl was 0.04, based on biphenyl radical cation formation. Triplet cations are proposed to be potentially useful as sensitizers since they give substantially higher yields of cage escape from the initial pair than the corresponding singlet compounds.
The reactivity of singlet 9-arylxanthyl cations with species other than aromatic donors has also been studied. Minto and Das (Minto, 1989) used a two-laser flash photolysis technique to generate the 9-phenylxanthyl cation from 9-phenylxanthen-9-ol in acetonitrile. This photolytic technique also resulted in the generation of the 9-phenylxanthyl radical. Fluorescence from the 9-phenylxanthyl cation was quenched by water, alkyl alcohols and amines. The Stern-Volmer method was used to determine the excited-state quenching rate constants which ranged from $3.3 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$ for quenching of the cation by water to $3.0 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ for quenching by triethylamine. Rate constants for quenching of the singlet 9-phenylxanthyl cation by H$_2$O and amines were several orders of magnitude larger than those measured for the corresponding ground-state reaction (McClelland, 1989). It was suggested that the increased reactivity of the singlet excited cation was due to the increased exothermicity by an amount equal to the singlet energy (~60 kcal/mol). The observed relative order for the quenching of the excited-state cation by water and the alcohols was $i$-PrOH$>$MeOH$>t$-BuOH$>\text{H}_2\text{O}$. This does not follow the steric order of the quenchers. The excited-state quenching of the 9-phenylxanthyl cation by these species was proposed to proceed via nucleophilic attack, with the observed alcohol quenching order rationalized by the steric effect of increasing methyl substitution counter balancing the increase in lone pair availability of the nucleophile. This study also reports that the fluorescence of the 9-phenylxanthyl cation decreased in the presence of tetrahydrofuran. An excited-state rate constant of $6.2 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ was determined
using time-resolved measurements.

The water quenching behavior of singlet excited xanthyl cations in aqueous sulfuric acid solution was also studied (Boyd, 1991). 9-Alkyl (H, Me, i-Pr) and 9-aryl (H, p-CF₃, p-Me, m-Me, p-OMe, m-OMe) substituted xanthyl cations were generated in the ground state by reaction of the corresponding alcohols with aqueous sulfuric acid. The ground state cations were then irradiated, and the fluorescence intensity and measured fluorescence lifetimes of the cations were found to increase as the percent acid increased. This was found not to be due to the formation of additional cation, as absorption spectra showed the alcohol to be completely ionized. Rather it was proposed that the cations were quenched by the water available in the aqueous acid solution. Excited-state quenching rate constants were determined by the Stern-Volmer method. For the 9-alkyl substituted xanthyl cations, \( k_q \) values were in the range of 2-9\( \times 10^6 \) M\(^{-1}\) s\(^{-1}\), depending on the size of the alkyl group. With the small variance in the rate constants measured for the 9-alkyl substituted cations, a steric effect rather than an electronic effect was proposed to be the controlling factor.

The rate constants determined for water quenching of the singlet excited 9-aryl xanthyl cations varied over a much larger range. Rate constants varied from \( 10^6 \) to \( 10^9 \) M\(^{-1}\) s\(^{-1}\), a three order of magnitude difference. Also, the rate constant for quenching of the 9-phenyl xanthyl cation by water is higher than the rate constant associated with the xanthyl cation. This result is opposite that seen for quenching of these same cations by aromatic donors (Samanta, 1993). The result suggests a special
electronic effect operating for quenching of the 9-arylxanthyl cations by water. Additionally, the excited-state rate constants were found to increase as the electron donating ability of the substituent increased.

An excited-state Hammett plot was constructed using the $\sigma^{\text{hv}}$ substituent parameter scale (McEwen, 1991). The $\sigma^{\text{hv}}$ scale is appropriate for 9-arylxanthyl cation reactivity since it is based on formation of structurally similar benzyl cations in photoprotonation reactions of ring-substituted styrenes and phenylacetylenes. Plots of the relative rate constants versus either the $\sigma$ or $\sigma^+$ substituent parameters (Murov, 1973) gave poor correlation. The poor correlations were primarily due to scatter from the meta-substituted cations, whose points fell above the correlation line, indicative of an increased reactivity of these cations. Meta-substituents are known to exhibit an enhanced conjugative effect in the excited-state compared to the corresponding ground-state compounds (Zimmerman and Somasekhara, 1963; Zimmerman and Sandel, 1963 and Havinga, 1956).

Plots of $\log[k_q(X)/k_q(H)]$ versus $\sigma^{\text{hv}}$ gave a negative $\rho$ value, again indicating that electron-donating substituents increase the rate of reaction. This negative $\rho$ value is opposite in sign to that observed for reaction of ground-state 9-arylxanthyl cations with water (McClelland, 1989). In the ground-state study, the cations were photolytically produced from their corresponding alcohols. The rate constants for the reaction of the cations with water decreased as the electron-donating ability of the substituent increased. A Hammett plot was constructed using the $\sigma$ substituent scale,
resulting in a $p$ value of +0.5. This result is consistent with ground-state theory where carbocation molecules are stabilized through inductive effects by electron donating substituents, making them less reactive toward species such as nucleophiles. This stabilization of the cations by electron donating substituents is presumably somewhat attenuated due to twisting of the 9-aryl group away from planarity with the xanthyl backbone.

The results obtained by Boyd and co-workers cannot be explained by invoking conventional ground-state theory (Boyd, 1991). Hückel MO calculations provided a possible explanation for the observed substituent dependence. The calculations showed that the size of the lobe and MO coefficient increased as the substituents became more strongly electron donating. The larger $k_q$ values can then be explained by invoking frontier orbital theory (Fleming, 1976), as the larger lobe would provide better overlap with the incoming nucleophile lone pair.

In order to further investigate the photophysics and photochemistry of excited state cations an alternate method for generating excited-state cations is necessary. In the previous studies where the cations were generated in aqueous sulfuric acid solution, the choice of quencher was limited to water. Furthermore, photoproducts from the reaction of the cation could not be isolated. The alternative two-laser flash photolysis method employed by Das successfully generated the 9-phenylxanthyl cation in acetonitrile from its alcohol precursor (Minto, 1989). Unfortunately, cation formation was accompanied by the generation of the 9-phenylxanthyl radical. Xanthyl
cations have also been generated in Nafion matrices (Minto, 1989) and on silica gel surfaces (Berger, 1990), however for these studies we are interested in solution-phase generation of the cations.

The goal of this research is to explore all aspects of carbocation photochemistry, and in particular, understand the fundamental chemical principles leading to the unusual excited-state substituent effects. Classical physical organic chemical methodology will be used, focusing on substituent effects on cation reactivity and the identification of photoproducts. Comparison of our results on excited-state cations to the ground-state results, will indicate whether different mechanisms are operating in the ground state and excited state.
CHAPTER II
RESULTS

Substrate Synthesis and Characterization

9-Arylxanthen-9-ols 18b-f and 9-arylthioxanthen-9-ols 19a-e were synthesized via a Grignard reaction of the appropriate arylmagnesium bromide with xanthone.

\[
\begin{align*}
18a-f & \quad X = O \\
19a-e & \quad X = S
\end{align*}
\]

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

Reaction of 18a-f and 19a-e with fluoroboric acid in propionic anhydride (Dauben, 1960) gave 9-arylxanthylum tetrafluoroborate salts 20a-f and 9-arylthioxanthylum tetrafluoroborate salts 21a-e as crystalline solids. The cations were stable indefinitely both in the solid phase and dissolved in dry acetonitrile.
Aryl substituent: a=H, b=p-F, c=m-F, d=p-\text{CH}_3, e=m-\text{CH}_3, f=m-\text{OCH}_3

UV/Visible spectra of 20a-f in acetonitrile were identical to the spectra reported for the same cations generated in acidified organic solvents (Azarani, 1991; Johnston, 1992 and 1993; Minto, 1989; Samanta, 1990 and 1993) or aqueous acidic solutions (Boyd, 1985 and 1991) with absorption maxima at 260, 374 and 450 nm. UV/visible spectra of 21a-e in acetonitrile exhibit absorption maxima at 246, 280, 386 and 492 nm, identical to the spectra reported for the 9-phenylthioxanthyl cation in acidified organic solvents (Samanta, 1993) and the 9-phenylthioxanthyl and 9-(4-fluorophenyl)thioxanthyl cations generated by laser flash photolysis in 1% TFA in TFE (Johnston, 1993). There is no substituent dependence on the position of the absorbance maxima for 20a-f or 21a-e.

Excitation of 20a-f at 374 nm in acetonitrile gave steady-state fluorescence spectra that were identical to the emission spectra previously reported, with a broad band centered at 540 nm (Azarani, 1991; Boyd, 1991; Minto, 1989; Samanta, 1990 and 1993; Wan, 1985). Excitation of 21a-e at 386 nm in acetonitrile gave steady-state fluorescence spectra that were also identical to emission spectra previously
reported, with a band centered at 580 nm (Johnston, 1992 and 1993). There is no substituent effect observed on the position of the fluorescence maxima for 20a-f or 21a-e.

Fluorescence lifetimes, $\tau_i$, for 20a-e and 21a-e were measured in acetonitrile and are listed in Table 2. The measured lifetimes were obtained from primarily single exponential decays. The lifetime of compound 20f was below the range of our instrument and was estimated from relative fluorescence quantum yields according to the method previously described for weakly fluorescent compounds (Boyd, 1991).

Substituents apparently have a dramatic effect on the lifetimes of 20a-f with values ranging from 28 ns for 20a to a subnanosecond value for 20f. The lifetime for 20a is in excellent agreement with a previous measurements of 25 ns for the cation generated in acetonitrile using a double-laser photolysis technique (Minto, 1989) and 28.5 ns for the cation generated in 1:1 TFA-acetonitrile (Samanta, 1993). Lifetimes of 20a, 20b and 20e are also in very good agreement with the values obtained for the same cations generated in strongly acidic aqueous media (Boyd, 1991). Lifetime values for 20a and 20b agree reasonably well with those measured in trifluoroethanol acidified with trifluoroacetic acid, after making allowance for possible solvent effects (Azarani, 1991).

In contrast to the measured lifetimes for 20a-f, there is no substituent effect on the lifetimes of 21a-e with all $\tau_i$ values about 1 ns. The measured lifetimes were obtained from single exponential decays. The lifetimes for 21a and 21b are in excel-
### TABLE 2

**FLUORESCENCE LIFETIMES, $\tau_0$, OF 9-ARYLXANTHYL CATIONS 20a-f AND 9-ARYLTHIOXANTHYL CATIONS 21a-e**

<table>
<thead>
<tr>
<th>Compound</th>
<th>9-Aryl Substituent</th>
<th>$\tau_0$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20a</td>
<td>H</td>
<td>27.6</td>
</tr>
<tr>
<td>20b</td>
<td>$p$-F</td>
<td>18.8</td>
</tr>
<tr>
<td>20c</td>
<td>$m$-F</td>
<td>14.0</td>
</tr>
<tr>
<td>20d</td>
<td>$p$-Me</td>
<td>2.1</td>
</tr>
<tr>
<td>20e</td>
<td>$m$-Me</td>
<td>2.0</td>
</tr>
<tr>
<td>20f</td>
<td>$m$-OMe</td>
<td>0.028</td>
</tr>
<tr>
<td>21a</td>
<td>H</td>
<td>1.0</td>
</tr>
<tr>
<td>21b</td>
<td>$p$-F</td>
<td>1.0</td>
</tr>
<tr>
<td>21c</td>
<td>$m$-F</td>
<td>1.3</td>
</tr>
<tr>
<td>21d</td>
<td>$p$-Me</td>
<td>1.0</td>
</tr>
<tr>
<td>21e</td>
<td>$m$-Me</td>
<td>1.0</td>
</tr>
</tbody>
</table>
lent agreement with a previous measurement of <2 ns for the cations generated from
the corresponding alcohols via laser flash photolysis in 1% TFA in TFE (Johnston,
1993). The lifetime of 21a is also in excellent agreement with the values of 1.0 ns
for the cation generated in acidified acetonitrile (Samanta, 1993) and <1 ns for the

Fluorescence quantum yields relative to quinine sulfate, \( \Phi_F \), for 20a-f and 21a,
21b and 21d were measured in acetonitrile and are listed in Table 3. As seen with the
fluorescence lifetimes of 20a-f, there is a significant substituent effect on the
fluorescence quantum yields of the xanthyl cations with values ranging from 0.47 for
20a down to 6.6x10^{-4} for 20f. The fluorescence quantum yield of 0.47 measured for
20a is in excellent agreement with values of 0.48 and 0.45 for the same cation
generated in TFA-acetonitrile (Samanta, 1990 and 1993) and 0.42 for the cation
generated in 8% H_2SO_4 in acetonitrile (Minto, 1989). The value is in good agreement
with the fluorescence quantum yield reported by Johnston and co-workers of 0.33 for
the cation generated in TFA-TFE (Azarani, 1991). However, the value is somewhat
lower than the reported value of 0.80 for the 9-phenylxanthyl cation in 1% TFA in
TFE (Johnston, 1993). Since the 9-phenylxanthyl cation is quenched by water with a
rate constant of 3.3x10^7 M^{-1} s^{-1} (Minto, 1989), the lower quantum yield value may be
explained by traces of water in the solvent, although it is remarkable that three
separate measurements would give such consistent results. Similarly, the quantum
yield for 20b is lower than the reported value of 0.55 for the 9-(4-fluorophenyl)xanthyl
## TABLE 3

**FLUORESCENCE QUANTUM YIELDS, \( \Phi_F \), OF 9-ARYLXANTHYL CATIONS 20a-f AND 9-ARYLTHIOXANTHYL CATIONS 21a-e**

<table>
<thead>
<tr>
<th>Compound</th>
<th>9-Aryl Substituent</th>
<th>( \Phi_F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20a</td>
<td>H</td>
<td>0.47</td>
</tr>
<tr>
<td>20b</td>
<td>p-F</td>
<td>0.28</td>
</tr>
<tr>
<td>20c</td>
<td>m-F</td>
<td>0.18</td>
</tr>
<tr>
<td>20d</td>
<td>p-Me</td>
<td>0.014</td>
</tr>
<tr>
<td>20e</td>
<td>m-Me</td>
<td>0.084</td>
</tr>
<tr>
<td>20f</td>
<td>m-OMe</td>
<td>( 6.6 \times 10^{-4} )</td>
</tr>
<tr>
<td>21a</td>
<td>H</td>
<td>0.020</td>
</tr>
<tr>
<td>21b</td>
<td>p-F</td>
<td>0.018</td>
</tr>
<tr>
<td>21d</td>
<td>p-Me</td>
<td>0.011</td>
</tr>
</tbody>
</table>
cation in 1% TFA in TFE (Johnston, 1993). Again it is possible that trace amounts of water may be responsible for the lower value reported here.

In contrast to the measured fluorescence quantum yields for 20a-f, there is little to no substituent effect observed in the measured fluorescence quantum yield for 21a, 21b and 21d. A fluorescence quantum yield of 0.020 for 21a was measured and is in very good agreement with a value of 0.025 measured for the cation generated in TFA-acetonitrile (Samanta, 1993). The quantum yields measured for 21a and 21b are in very good agreement with the values of 0.031 and 0.020, respectively, for these cations generated in 1% TFA in TFE (Johnston, 1993).

Total decay rate constants, $k_d$, were calculated from the measured lifetimes of 20a-f and 21a-e and are listed in Table 4. As indicated by the lifetimes, a dramatic substituent effect is observed in the $k_d$ values for the 9-arylxanthyl cations. Total decay rate constants range from $3.6 \times 10^7$ s$^{-1}$ for 20a up to $3.6 \times 10^9$ s$^{-1}$ for 20f. In contrast to the decay rate constants for the xanthyl cations, there is no substituent effect observed on the $k_d$ values for the 9-arylthioxanthyl cations, where all total decay rate constants are about $1 \times 10^9$ s$^{-1}$.

Fluorescence rate constants, $k_f$, and non-radiative rate constants, $k_{nr}$, were calculated from the fluorescence quantum yields and lifetimes for 20a-f and 21a, 19b and 21d and are listed in Table 4. The $k_f$ values of $1.7 \times 10^7$ s$^{-1}$ for 20a and $2.0 \times 10^7$ s$^{-1}$ for 21a are in excellent agreement with the $k_f$ values of $1.7 \times 10^7$ s$^{-1}$ and $2.5 \times 10^7$ s$^{-1}$, respectively, determined by Das from fluorescence quantum yield and lifetime measurements.
TABLE 4

PHOTOPHYSICAL DATA FOR 9-ARYLXANTHYL CATIONS 20a-f
AND 9-ARYLTHIOXANTHYL CATIONS 21a-e

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{at}$ (s$^{-1}$)</th>
<th>$k_r$ (s$^{-1}$)</th>
<th>$k_{ar}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20a</td>
<td>3.6x10$^7$</td>
<td>1.7x10$^7$</td>
<td>1.9x10$^7$</td>
</tr>
<tr>
<td>20b</td>
<td>5.3x10$^7$</td>
<td>1.5x10$^7$</td>
<td>3.8x10$^7$</td>
</tr>
<tr>
<td>20c</td>
<td>7.1x10$^7$</td>
<td>1.3x10$^7$</td>
<td>5.8x10$^7$</td>
</tr>
<tr>
<td>20d</td>
<td>4.8x10$^8$</td>
<td>6.6x10$^6$</td>
<td>4.6x10$^8$</td>
</tr>
<tr>
<td>20e</td>
<td>5.0x10$^8$</td>
<td>4.2x10$^7$</td>
<td>4.6x10$^8$</td>
</tr>
<tr>
<td>20f</td>
<td>3.6x10$^9$</td>
<td>2.4x10$^7$</td>
<td>3.6x10$^9$</td>
</tr>
<tr>
<td>21a</td>
<td>1.0x10$^9$</td>
<td>2.0x10$^7$</td>
<td>9.8x10$^9$</td>
</tr>
<tr>
<td>21b</td>
<td>1.0x10$^9$</td>
<td>1.8x10$^7$</td>
<td>9.8x10$^9$</td>
</tr>
<tr>
<td>21c</td>
<td>7.8x10$^8$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21d</td>
<td>1.0x10$^9$</td>
<td>1.1x10$^7$</td>
<td>9.9x10$^9$</td>
</tr>
<tr>
<td>21e</td>
<td>1.0x10$^9$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Das also used the Strickler-Berg formula (Strickler, 1962) to calculate $k_r$ values of $2.5 \times 10^7 \text{s}^{-1}$ for the 9-phenylxanthyl cation and $2.4 \times 10^7 \text{s}^{-1}$ for the 9-phenylthioxanthyl cation which are also in very good agreement with our fluorescence rate constants.

The fluorescence rate constants show a modest substituent effect in both the xanthyl and thioxanthyl series, ranging from a low value of $6.6 \times 10^6 \text{s}^{-1}$ for 20d to a high value of $4.2 \times 10^7 \text{s}^{-1}$ for 20e, and ranging from a low of $1.1 \times 10^7 \text{s}^{-1}$ for 21a to a high of $2.0 \times 10^7 \text{s}^{-1}$ for 21d. A significant substituent effect is observed on the non-radiative decay rate constants for the 9-arylxanthyl cations, ranging from $1.9 \times 10^7$ for 20a to $3.6 \times 10^9 \text{s}^{-1}$ for 20f. As observed in the $k_{dr}$ values, the larger values for $k_m$ are associated with the xanthyl cations substituted with the more strongly electron donating substituents. In contrast to the xanthyl cations, no substituent effect is observed for $k_m$ with the thioxanthyl cations, where $k_m$ values vary slightly from $9.8 \times 10^8 \text{s}^{-1}$ for 21a and 21b to $9.9 \times 10^8 \text{s}^{-1}$ for 21d.

**Measurement of Quenching Rate Constants**

The fluorescence of 20a-f in acetonitrile was quenched by the addition of water, alcohols (MeOH, i-PrOH, t-BuOH) and ethers (Et₂O, i-Pr₂O, t-BuOMe, t-BuOEt, THF). Relative fluorescence quantum yields ($\Phi_0/\Phi_d$) were measured for all cations and plotted versus the quencher concentration. Excellent linear plots ($r > 0.98$) were obtained in each case. Stern-Volmer analysis gave excited state bimolecular rate
constants, \( k_q \), for the reaction of the singlet excited cations with the quenchers. Representative Stern-Volmer plots for each quencher (\( \text{H}_2\text{O}, \) three alcohols and five ethers) are illustrated in Figures 1-9. The rate constants for quenching of singlet excited \( 20a-f \) by \( \text{H}_2\text{O}, \) MeOH, \( \text{i-PrOH} \) and \( \text{t-BuOH} \) are listed in Table 5. Excited-state rate constants for quenching of \( 20a-f \) by \( \text{Et}_2\text{O}, \) \( \text{i-Pr}_2\text{O} \), \( \text{t-BuOMe}, \) \( \text{t-BuOEt} \) and THF are listed in Table 6. For each quencher, the excited-state rate constants show a substantial substituent dependence, with the larger \( k_q \) values associated with the electron-donating substituents.

For quenching of singlet excited \( 20a-f \) by water and alcohols, the rate constants vary from about \( 10^6-10^7 \, \text{M}^{-1} \, \text{s}^{-1} \) for \( 20b \) up to the diffusion-controlled limit for \( 20f \). Each substituent exhibits a much smaller \( k_q \) range along the quencher series. Using \( 20a \) as an example, \( k_q \) values range from \( 2.02 \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1} \) for quenching by \( \text{H}_2\text{O} \), to \( 8.94 \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1} \) for quenching by \( \text{i-PrOH} \). The rate constants vary on average by a factor of 4-6, and for \( 20b \), by a factor of 9.

The excited-state rate constant of \( 2.02 \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1} \) for quenching of \( 20a \) by water, is in very good agreement with a rate constant of \( 1.5 \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1} \) obtained by steady-state measurement for the 9-phenylxanthyl cation generated in strongly acidic aqueous solution (Boyd, 1991) and with the value of \( 1.6 \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1} \) obtained by time-resolved measurement of the fluorescence decay for the cation generated in acidic acetonitrile (Minto, 1989). The slightly lower values obtained in acidic media can be attributed to a lowering of the water activity. A rate constant of \( 3.3 \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1} \) was
Figure 1

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_r/\Phi_0$, versus H$_2$O concentration for quenching of 9-phenylxanthylum tetrafluoroborate 20a.
Figure 2

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_r/\Phi_b$, versus MeOH concentration for quenching of 9-(4-fluorophenyl)xanthylum tetrafluoroborate 20b.
Figure 3

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_b$ versus i-PrOH concentration for quenching of 9-(3-methylphenyl)xanthylum tetrafluoroborate 20e.
Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_t/\Phi_b$, versus $t$-BuOH concentration for quenching of 9-(4-methylphenyl)xanthyl xanthium tetrafluoroborate 20d.
Figure 5

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_e/\Phi_0$, versus $i$-$Pr_2O$ concentration for quenching of 9-(3-fluorophenyl)xanthylum tetrafluoroborate 20c.
Figure 6

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_r/\Phi_0$, versus Et$_2$O concentration for quenching of 9-(4-fluorophenyl)xanthylum tetrafluoroborate 20b.
Figure 7

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_f / \Phi_i$, versus $t$-BuOMe concentration for quenching of 9-phenylxanthylum tetrafluoroborate 20a.
Figure 8

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_r/\Phi_0$, versus $t$-BuOEt concentration for quenching of 9-(3-methoxyphenyl)xanthylum tetrafluoroborate 20f.
Figure 9

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_i/\Phi_0$, versus THF concentration for quenching of 9-(3-methylphenyl)xanthylum tetrafluoroborate 20e.
### Table 5

**Excited-State Rate Constants (M⁻¹s⁻¹)** for Quenching of 20a-f by Water and Alcohols

<table>
<thead>
<tr>
<th>Substituent</th>
<th>H₂O</th>
<th>MeOH</th>
<th>i-PrOH</th>
<th>t-BuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>(2.02±0.02)×10⁷</td>
<td>(4.56±0.52)×10⁷</td>
<td>(8.94±0.23)×10⁷</td>
<td>(3.33±0.54)×10⁷</td>
</tr>
<tr>
<td>m-F</td>
<td>(1.20±0.01)×10⁸</td>
<td>(8.10±0.02)×10⁷</td>
<td>(1.05±0.05)×10⁸</td>
<td>(2.34±0.03)×10⁷</td>
</tr>
<tr>
<td>p-F</td>
<td>(8.88±0.11)×10⁶</td>
<td>(4.11±0.27)×10⁷</td>
<td>(8.05±0.69)×10⁷</td>
<td>(1.80±0.02)×10⁷</td>
</tr>
<tr>
<td>m-CH₃</td>
<td>(2.16±0.30)×10⁹</td>
<td>(8.03±0.25)×10⁹</td>
<td>(1.02±0.02)×10¹⁰</td>
<td>(3.36±0.14)×10⁹</td>
</tr>
<tr>
<td>p-CH₃</td>
<td>(6.23±0.66)×10⁸</td>
<td>(2.06±0.26)×10⁹</td>
<td>(3.28±0.38)×10⁹</td>
<td>(1.02±0.16)×10⁹</td>
</tr>
<tr>
<td>m-OCH₃</td>
<td>(1.76±0.34)×10¹⁰</td>
<td>(4.97±0.02)×10¹⁰</td>
<td>(6.14±0.30)×10¹⁰</td>
<td>(3.12±0.27)×10¹⁰</td>
</tr>
</tbody>
</table>

*Errors quoted are the standard deviations obtained from repeated measurements.*
TABLE 6

EXCITED-STATE RATE CONSTANTS (M^{-1}s^{-1})* FOR QUENCHING OF 20a-f

BY ETHERS

<table>
<thead>
<tr>
<th>Quencher</th>
<th>i-Pr,O</th>
<th>Et,O</th>
<th>t-BuOMe</th>
<th>t-BuOEt</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>(2.28±0.02)x10^7</td>
<td>(2.35±0.09)x10^7</td>
<td>(6.94±0.46)x10^6</td>
<td>(5.71±0.09)x10^7</td>
<td>(4.86±0.01)x10^8</td>
</tr>
<tr>
<td>p-F</td>
<td>(1.91±0.14)x10^7</td>
<td>(1.34±0.01)x10^7</td>
<td>(4.90±0.52)x10^6</td>
<td>(5.17±0.07)x10^7</td>
<td>(5.02±0.04)x10^8</td>
</tr>
<tr>
<td>m-F</td>
<td>(2.80±0.04)x10^7</td>
<td>(2.24±0.03)x10^7</td>
<td>(6.22±0.06)x10^6</td>
<td>(6.72±0.42)x10^7</td>
<td>(7.60±0.10)x10^8</td>
</tr>
<tr>
<td>p-Me</td>
<td>(1.70±0.01)x10^8</td>
<td>(1.88±0.12)x10^8</td>
<td>(7.42±0.76)x10^7</td>
<td>(7.76±0.52)x10^8</td>
<td>(2.28±0.14)x10^9</td>
</tr>
<tr>
<td>m-Me</td>
<td>(4.40±0.06)x10^8</td>
<td>(3.77±0.22)x10^8</td>
<td>(2.01±0.09)x10^7</td>
<td>(1.22±0.04)x10^9</td>
<td>(8.88±0.42)x10^8</td>
</tr>
<tr>
<td>m-OMe</td>
<td>(2.11±0.22)x10^{10}</td>
<td>(1.88±0.06)x10^{10}</td>
<td>(5.86±0.28)x10^9</td>
<td>(4.59±0.02)x10^{10}</td>
<td></td>
</tr>
</tbody>
</table>

*Errors quoted are the standard deviations obtained from repeated measurements.
obtained using time-resolved measurements for the 9-phenylxanthyl cation generated in acetonitrile by a two-laser flash photolysis technique (Minto, 1989). The slightly higher value obtained using laser flash photolysis agrees with an earlier suggestion that ion-paired photoexcited cations are less susceptible to quenching (Minto, 1989).

For quenching of the singlet excited 20a-f by the acyclic ethers (Et₂O, i-Pr₂O, t-BuOMe and t-BuOEt), the kₚ values range from 10⁶ to 10¹⁰ M⁻¹ s⁻¹ and are similar in magnitude to the rate constants determined for quenching of 20a-f by H₂O and alcohols. Excited-state rate constants for quenching of 20a-e by THF range from 4.9x10⁸ M⁻¹ s⁻¹ for 20a to 8.9x10⁹ M⁻¹ s⁻¹ for 20e.

The rate constant of 4.86x10⁸ M⁻¹ s⁻¹ for quenching of singlet excited 20a by THF is in very good agreement with the value of 6.2x10⁸ M⁻¹ s⁻¹ determined by Das using time-resolved measurements for the 9-phenylxanthyl cation generated via a two-laser flash photolysis technique (Minto, 1989). As with quenching of the 9-phenylxanthyl cation by water using this photolysis technique, the slightly higher value obtained suggests that ion-paired photoexcited cations are less susceptible to quenching (Minto, 1989).

The excited-state quenching of 21a-e by H₂O and MeOH in acetonitrile was also investigated. The excited-state quenching of two 9-arylthioxanthyl cations 21a and 21d by the alcohol series (MeOH, i-PrOH, t-BuOH) was also studied. Relative fluorescence quantum yields (Φᵣ/Φ₀) were measured for 21a-e and plotted versus the quencher concentration. Excellent linear plots (r>0.98) were obtained in each case.
Stern-Volmer analysis gave excited state bimolecular rate constants, \( k_q \), for the reaction of the singlet excited 9-arylthioxanthyl cations with the quenchers. A representative Stern-Volmer plot for quenching of the \( p\)-F cation by MeOH is illustrated in Figure 10. The quenching rate constants are listed in Table 7 for quenching of singlet excited 9-arylthioxanthyl cations 21a-e by water and alcohols.

In contrast to the substituent effect observed in the \( k_q \) values for quenching of the 9-aryl xanthyl cations, there is no substituent dependence observed in the rate constants for quenching of 21a-e by water and methanol. The \( k_q \) values for quenching of singlet excited 21a-e by H\(_2\)O vary only over a small range, with a low \( k_q \) value of 3.9x10\(^8\) M\(^{-1}\) s\(^{-1}\) (21a) to an upper \( k_q \) value of 6.9x10\(^8\) M\(^{-1}\) s\(^{-1}\) (21d). Additionally, a small \( k_q \) range is observed for quenching of 21a-e by MeOH where \( k_q \) values vary from 1.6x10\(^9\) M\(^{-1}\) s\(^{-1}\) for 21d to 5.4x10\(^9\) M\(^{-1}\) s\(^{-1}\) for 21b.

For quenching of singlet excited 21a and 21d by water and alcohols, the rate constants vary from about 10\(^8\)-10\(^9\) M\(^{-1}\) s\(^{-1}\). The unsubstituted cation 21a and the \( p\)-Me compound 21d exhibit a very small \( k_q \) range along the quencher series. For 21a, \( k_q \) values range from 3.92x10\(^8\) M\(^{-1}\) s\(^{-1}\) for quenching by H\(_2\)O up to 1.39x10\(^9\) M\(^{-1}\) s\(^{-1}\) for quenching by i-PrOH, differing by a factor of only 1.2. For 21d, \( k_q \) values range from 6.92x10\(^8\) M\(^{-1}\) s\(^{-1}\) for quenching by H\(_2\)O up to 4.80x10\(^9\) M\(^{-1}\) s\(^{-1}\) for quenching by i-PrOH, a factor of only 0.7.
Figure 10

Stern-Volmer plot of the relative fluorescence quantum yield, $\Phi_0/\Phi$, versus MeOH concentration for quenching of 9-(4-fluorophenyl)thioxanthylum tetrafluoroborate 21b.
TABLE 7
EXCITED-STATE RATE CONSTANTS (M⁻¹ s⁻¹) FOR QUENCHING OF 21a-e
BY WATER AND ALCOHOLS

<table>
<thead>
<tr>
<th>Substituent</th>
<th>H₂O</th>
<th>MeOH</th>
<th>i-PrOH</th>
<th>t-BuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>(3.92±0.16) x 10⁸</td>
<td>(4.12±0.29) x 10⁹</td>
<td>(4.74±0.16) x 10⁹</td>
<td>(1.42±0.04) x 10⁹</td>
</tr>
<tr>
<td>p-F</td>
<td>(6.70±0.68) x 10⁸</td>
<td>(5.39±0.87) x 10⁹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-F</td>
<td>(4.58±0.44) x 10⁸</td>
<td>(3.54±0.14) x 10⁹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Me</td>
<td>(6.92±0.31) x 10⁸</td>
<td>(1.65±0.04) x 10⁹</td>
<td>(4.80±0.29) x 10⁹</td>
<td>(1.20±0.02) x 10⁹</td>
</tr>
<tr>
<td>m-Me</td>
<td>(4.36±0.20) x 10⁸</td>
<td>(2.26±0.36) x 10⁹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Errors quoted are the standard deviations obtained from repeated measurements.
Photoproduct Studies

Photoproducts from the reaction of the 9-aryl xanthyl cations with H₂O or alcohols could not be isolated due to the competing thermal reaction at the high concentration of reactants necessary for preparative photolysis. Instead, a solution of 20a (0.001 M) in acetonitrile was irradiated in the presence of i-Pr₂O (1 M). Unique photoproducts 22 and 24-27 have been identified by HPLC and are shown in Scheme 4. Independent synthesis and characterization of 9-hydroperoxy-9-phenyl xanthene 22 and 9-phenyl xanthene 24 confirmed the structures of isolated compounds 22 and 24. Spectral analysis confirmed the structures of xanthone 26 and o-hydroxy benzophenone 27 by comparison to authentic samples. A precipitate 23 formed upon irradiation and was identified as bis(9-phenyl xanthen-9-yl) peroxide 22 by melting point comparison to an authentic sample.
The major photoproduct 25 was isolated and characterized via spectral analysis. An independent synthesis and characterization of 2-(o-hydroxyphenoxy)benzophenone confirmed the structure of photoproduct 25. Irradiation of 20a in the absence of ether shows no reaction.

Percent conversion of 20a over the irradiation time (40 minutes) was also monitored by HPLC. The relative amounts of photoproducts 22 and 24-27 resulting from the irradiation of oxygen saturated or argon purged solutions of 20a were identical. Time profiles for the formation of photoproducts 22 and 24-27 are shown in Figure 11. The amount of unreacted cation 20a was represented by the amount of
Figure 11

Plot of the percent composition of photoproducts 22 and 24-27 versus time for the irradiation of 20a in acetonitrile in the presence of i-Pr₂O: ○ = 20a; ★ = 25; ▲ = 26; ■ = 27; ☆ = 24; ○ = 22.
9-methoxy-9-phenyl xanthene 28 present after quenching each photolysis solution with methanol.

Compounds 22-25 and 27 were not produced in a "dark" reaction under the same conditions with only trace amounts of xanthone 26 produced. Irradiation of 9-phenylxanthan-9-ol 18a, xanthone 26 and 9-phenylxanthene 24 in acetonitrile in the presence or absence of ether showed no reaction. Irradiation of 9-hydroperoxide-9-phenylxanthene 22 in the presence or absence of ether showed no reaction. Irradiation of 9-hydroperoxide-9-phenylxanthene 22 in the presence of ether and a trace of acid resulted in formation of 25-27.
CHAPTER III
DISCUSSION

Substituent Effects on Quenching Rate Constants

Singlet excited 9-arylxanthyl cations 20a-f are quenched by H₂O, alcohols and ethers with excited-state bimolecular rate constants ranging from 10⁷-10¹⁰ M⁻¹ s⁻¹. A substantial substituent dependence is observed in the kₚ values, with the larger rate constants associated with the electron-donating substituted cations. This substituent dependence can be further examined by construction of Hammett plots. Correlation was first attempted with plots of \( \log[k_p(X)/k_p(H)] \) versus the \( \sigma \) and \( \sigma^+ \) substituent parameters (Murov, 1973), with very poor results for each of the quenchers. The poor correlation was largely due to scatter of the meta-substituted cations, whose points fell above the correlation line, indicating an enhanced reactivity of these cations. This behavior by excited-state meta-substituted compounds was first reported by Havinga (1956) and later by Zimmerman (1963), where substituents in the meta position exhibit greater conjugative effects than those in the para position. Further support for the meta effect is also obtained through comparison of the kₚ values in Tables 5 and 6 obtained for the same substituent in the meta or para position. For both the fluoro and methyl substituted cations, the larger kₚ value is associated with the meta
substituted cations, 20c and 20e, compared to the para substituted cations, 20b and 20d.

Excellent correlation was obtained with a plot of log\([k_q(X)/k_q(H)]\) versus \(\sigma^\text{bw}\), an excited-state substituent parameter (McEwen, 1991). This scale is appropriate for singlet excited xanthyl cations since it is based on the photoprotonation reaction of ring-substituted styrenes and phenylacetylenes to give the structurally similar benzyl cation. A plot of log\([k_q(X)/k_q(H)]\) versus \(\sigma^\text{bw}\) for H\(_2\)O quenching gave a \(\rho\) value of -2.07 and excellent correlation with a correlation coefficient of 0.98. Figure 12 illustrates the Hammett plot obtained for quenching of singlet excited cations 20a-f by water. This \(\rho\) value is in very good agreement with a \(\rho\) value of -1.45 determined for H\(_2\)O quenching of the excited state 9-aryl xanthyl cations in strongly acidic aqueous media (Boyd, 1991).

Plots of log\([k_q(X)/k_q(H)]\) versus \(\sigma^\text{bw}\) for quenching by MeOH, i-PrOH and t-BuOH also gave excellent correlation (\(r>0.98\)), with the exception of the point corresponding to 20c, the \(m\)-F substituted cation. This point fell below the correlation line, with the extent of deviation from the line increasing with increasing steric bulk of the alkyl portion of the alcohol. That is, the \(m\)-F point is only slightly below the line for MeOH quenching, somewhat further from the line for i-PrOH quenching and furthest from the correlation line for t-BuOH quenching. Figures 13-15 illustrate the excited state Hammett plots obtained for quenching of 20a-f by the alcohols.

Plots of log\([k_q(X)/k_q(H)]\) versus \(\sigma^\text{bw}\) for quenching by Et\(_2\)O, i-Pr\(_2\)O, t-BuOMe,
Plot of the log\[k_q(X)/k_q(H)\] versus $\sigma^{hv}$ for quenching of 20a-f by H$_2$O.
\[
\log \left[ \frac{k_q(X)}{k_q(H)} \right]
\]
Plot of the log\([k_q(X)/k_q(H)]\) versus \(\sigma^h\) for quenching of 20a-f by MeOH.
Plot of the log\([k_q(X)/k_q(H)]\) versus \(\sigma^h\) for quenching of 20a-f by \(i\)-PrOH.
Figure 15

Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^{bw}$ for quenching of 20a-f by $t$-BuOH.
\( t\text{-BuOEt} \) and THF also gave excellent correlation \((r>0.98)\), again with the exception of the point corresponding to the \( m\text{-F} \) substituted cation. In contrast to the increasing deviation of the point from the line with increasing steric bulk of the alcohol, the \( m\text{-F} \) point shows approximately the same deviation from the line for each of the ether quenchers. Figures 16-19 illustrate the excited-state Hammett plots obtained for quenching of 20a-f by Et\(_2\)O, i-Pr\(_2\)O, t-BuOMe and t-BuOEt. Figure 20 illustrates the excited-state Hammett plot obtained for quenching of 20a-e by THF.

Values of \( \rho \) were calculated from the excited-state Hammett plots for quenching of 20a-f by the three alcohols and are listed in Table 8 for water and the alcohols and in Table 9 for the ethers. These calculations of \( \rho \) exclude the points corresponding to the \( m\text{-F} \) substituted cation. It is worth noting however, that the calculated \( \rho \) values were not greatly different if the \( m\text{-F} \) data were included or excluded. For each of the alcohol and ether quenchers a negative \( \rho \) value was obtained, showing that the substituent dependence observed for quenching of the singlet excited 9-arylxanthyl cations is not unique for quenching by water. Hammett plots for nucleophilic reactions of ground state 9-arylxanthyl cations with water and anionic species gave weakly positive \( \rho \) values \((\rho=0.4-1.1)\) in every case (McClelland, 1989). The ground-state substituent effect can be rationalized by weak electronic stabilization of the positively charged species by electron-donating substituents, with the effect somewhat attenuated due to the twisting of the 9-aryl ring out of planarity of the xanthyl backbone.
Figure 16

Plot of the log$[k_q(X)/k_q(H)]$ versus $\sigma^h$ for quenching of 20a-f by Et$_2$O.
Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^b$ for quenching of 20a-f by i-Pr$_2$O.
Figure 18

Plot of the $\log[k_q(X)/k_q(H)]$ versus $\sigma^{hv}$ for quenching of 20a-f by t-BuOMe.
Figure 19

Plot of the $\log[k_q(X)/k_q(H)]$ versus $\sigma^{bw}$ for quenching of 20a-f by $t$-BuOEt.
Figure 20

Plot of the log[$k_q(X)/k_q(H)$] versus $\sigma^{hv}$ for quenching of 20a-f by THF.
### TABLE 8
CORRELATION OF $\log[k_q(X)/k_q(H)]$ VERSUS $\sigma^v$
FOR QUENCHING OF 20a-f

<table>
<thead>
<tr>
<th>quencher</th>
<th>H$_2$O</th>
<th>MeOH$^a$</th>
<th>i-PrOH$^a$</th>
<th>t-BuOH$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope (ρ)</td>
<td>-2.07</td>
<td>-2.02</td>
<td>-1.88</td>
<td>-2.03</td>
</tr>
</tbody>
</table>
r$^b$      | 0.98   | 0.98     | 0.98       | 0.99       |
|intercept$^c$ | 0.11 | 0.32     | 0.30       | 0.17       |
|σ$_y$$^d$ | 0.14   | 0.20     | 0.19       | 0.15       |
|σ$_{slope}$$^e$ | 0.19 | 0.26     | 0.24       | 0.19       |

$^a$The data corresponding to 20c were omitted from the linear regression analysis (see Discussion 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.
TABLE 9
CORRELATION OF log[k_q(X)/k_q(H)] VERSUS $\sigma^b$
FOR QUENCHING OF 20a-f

<table>
<thead>
<tr>
<th>quencher</th>
<th>$i$-Pr_2O</th>
<th>Et_2O</th>
<th>t-BuOMe</th>
<th>t-BuOEt</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope ($p$)</td>
<td>-1.84</td>
<td>-1.86</td>
<td>-1.87</td>
<td>-1.80</td>
<td>-1.30</td>
</tr>
<tr>
<td>$r^b$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>intercept$^c$</td>
<td>-0.04</td>
<td>-0.23</td>
<td>0.07</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>$\sigma_y^d$</td>
<td>0.14</td>
<td>0.11</td>
<td>0.06</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>$\sigma_{slope}^e$</td>
<td>0.17</td>
<td>0.14</td>
<td>0.08</td>
<td>0.14</td>
<td>0.23</td>
</tr>
</tbody>
</table>

$^a$The data corresponding to 20c were omitted from the linear regression analysis (see Discussion 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.
In contrast to the large substituent effect observed in the excited-state quenching rate constants for the 9-arylxanthyl cations 20a-f, there is apparently no substituent effect observed for quenching of the 9-arylthioxanthyl cations 21a-e. Plots of $\log[k(q(X)/k(q(H))]$ versus $\sigma^{hv}$ for H$_2$O and MeOH were constructed and are shown in Figures 21 and 22.

Values of $\rho$ were calculated from the excited-state Hammett plots for quenching of 21a-e by H$_2$O and MeOH and are 0.04 and 0.45, respectively. A $\rho$ value of 0.04 clearly indicates no substituent effect for quenching of the thioxanthyl cations. Although the $\rho$ value determined for quenching by MeOH is slightly positive, a correlation line with zero slope can visually be drawn on the MeOH Hammett plot in Figure 22.

**Relative Quenching Order**

The relative order for quenching of 20a-b and 20d-f by water and the alcohols is i-PrOH>MeOH>t-BuOH>H$_2$O although the effect is modest, with the $k_q$ values varying by a factor of 4-6 and in one case (20b) by a factor of 9. This order was previously observed for quenching of the 9-phenylxanthyl cation generated in acetonitrile by two-laser flash photolysis, with the observed alcohol quenching order rationalized by the steric effect of increasing methyl substitution counter balancing the increase in lone pair availability of the nucleophile (Minto, 1989). The $m$-F substituted cation 20c exhibits a quenching order different than the other cations:
Figure 21

Plot of the log\(k_q(X)/k_q(H)\) versus \(\sigma^b\) for quenching of 21a-e by H₂O.
Figure 22

Plot of the log\( k_q(X)/k_q(H) \) versus \( \sigma^h \) for quenching of 21a-e by MeOH.
\[ \log \left[ \frac{k_q(X)}{k_q(H)} \right] \]
The different behavior of the \( m \)-F substituted cation 20c was also observed in the alcohol-quenching Hammett plots, where the \( m \)-F points fell below the correlation line, indicating a decreased reactivity with alcohols in comparison to the other substituted cations. A steric effect is suggested since the decrease in the reactivity of 20c (relative to the other substituted cations) correlates with an increase in the steric bulk of the alcohol. However, it seems unlikely that this behavior of 20c is due to a steric effect of the substituent. A fluoro substituent would not exhibit a greater steric influence compared to either a methyl or methoxy substituent in the \textit{meta} position. Furthermore, any excited-state electronic effects associated with the \( m \)-F substituent should already be accounted for by use of the \( \sigma^\text{by} \) substituent parameter scale.

The relative order for quenching of 20a-f by the ethers is THF\( >t\)-BuOEt\( >\text{Et}_2\text{O} \rightarrow i\)-Pr\(_2\)O\( >t\)-BuOMe. For each substituent, the variation in the quenching rate constants is small, with the \( k_q \) values varying by a factor of 6 for 20e up to 11 for 20c. The rate constants do not appear to depend solely on steric factors, as the rate constants for quenching of 20a-f by \( t\)-BuOEt are larger than for quenching by \text{Et}_2\text{O}.

The relative order for quenching of 21a and 21d by water and the alcohols is \( i\)-PrOH\( >\text{MeOH} \rightarrow t\)-BuOH\( >\text{H}_2\text{O} \). This is the same relative quenching order observed for quenching of the 9-aryl)xanthyl cations 20a-f by water and the alcohols.
**Quenching Mechanism**

Quenching of the singlet excited 9-arylxanthyl cations by water and alcohols was previously suggested to occur via a nucleophilic mechanism (Boyd, 1991 and Minto, 1989). The substituent effects for quenching of these cations by H₂O and alcohols in the excited state are opposite that seen in the ground state reactivities. In order to examine the possibility of a nucleophilic mechanism, it would be advantageous to analyze the water and alcohol reactivity data using one of the nucleophilicity parameters (Ritchie, 1975 and 1978). The N⁺ scale would be particularly appropriate since it is based on the reactivity of structurally similar triarylmethyl cations (Ritchie, 1975). Unfortunately, N⁺ values are not available for these four quenchers in acetonitrile.

Instead we compared the excited-state relative quenching order to the quenching order observed for the reaction of ground-state cations with nucleophiles. Rate constants have been measured for reaction of vinyl (Kobayashi, 1983 and 1987), diarylmethyl (Bartl, 1991) and cyclopropyl radical (Dinnocenzo, 1990) cations with H₂O and alcohols in acetonitrile. Although these cations are less stable than the 9-arylxanthyl cations, their bimolecular rate constants with these nucleophiles are of a similar magnitude (≈10⁷ M⁻¹ s⁻¹). The observed trend followed the order MeOH>EtOH>i-PrOH>H₂O>t-BuOH for quenching of these ground-state cations. Additionally, rate constants have been measured for reaction of 9-carbomethoxyfluoren-9-yl and diphenylmethyl cations with H₂O and alcohols in
acetonitrile (Johnston, 1993). The quenching order observed for these ground-state cations was MeOH\(\rightarrow\)EtOH\(\rightarrow\)i-PrOH\(\rightarrow\)H\(_2\)O (quenching by t-BuOH was not studied). 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 the steric size of alkyl group. In contrast to the relative quenching order of these ground-state cations, the excited-state quenching order does not depend solely on steric considerations of the alcohols, since the \(k_q\) values for quenching by i-PrOH is larger than the \(k_q\) values for quenching by MeOH for 20a-f.

Both the quenching reactivity order and substituent effects in the excited state reaction differ compared to the ground-state cation-nucleophile reactions. We considered the possibility of a different mechanism operating in the excited-state, namely electron transfer. The Rehm-Weller equation (Rehm, 1969 and 1970) can be used to determine the free energy change for electron transfer to the singlet excited cations.

\[
\Delta G_{ET} = E_{1/2}^{ox} - E_{1/2}^{red} - E_s
\]

\(E_{1/2}^{ox}\) is the oxidation potential of the electron donor (water, alcohol or ether), \(E_{1/2}^{red}\) is the reduction potential of the electron acceptor (9-arylxanthyl cations) and \(E_s\) is the excited singlet energy of the cations. For any particular quencher, \(E_{1/2}^{ox}\) will remain constant for all 9-arylxanthyl cations. \(E_s\) is \(-60\) kcal/mol for each 9-arylxanthyl cation, based on the wavelength for onset of fluorescence (Johnston, 1992 and 1993).
must then account for the reactivity difference of the cations should an electron transfer process be operating. In qualitative terms, the ease of reduction of the cations should parallel an increase in the quenching rate constants.

The reduction potentials for the 9-arylxanthyl cations 20a, 20b, 20d and 20f have been reported and are listed in Table 10 (Arnett, 1993 and Flowers II, 1994). These $E_{1/2}^{red}$ values were measured in sulfolane against a ferrocene/ferrocenium couple. Although the electrochemical measurements were performed in a solvent system different from the acetonitrile used for measurements of the $k_q$ values, the reduction potentials will nevertheless indicate the substituent effect for the 9-arylxanthyl cations. The $E_{1/2}^{red}$ values (Table 10) and $k_q$ values (Table 5 for H$_2$O and alcohols and Table 6 for ethers) for quenching of 20a-f by H$_2$O, alcohols and ethers 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 the singlet excited 9-arylxanthyl cations 20a-f by water, alcohols or ethers.

**Photoproduct Studies**

Photoproducts from the reaction of the 9-arylxanthyl cations with water or alcohols could not be isolated due to the competing thermal reaction at the high concentration of reactants necessary for preparative photolysis. Instead, preparative
### TABLE 10

REDUCTION POTENTIALS FOR 9-ARYLXANTHYL CATIONS

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^{\text{red}}_{1/2}$(V)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>20a</td>
<td>-0.356\textsuperscript{b}</td>
</tr>
<tr>
<td>20b</td>
<td>-0.323\textsuperscript{b}</td>
</tr>
<tr>
<td>20d</td>
<td>-0.363\textsuperscript{b}</td>
</tr>
<tr>
<td>20f</td>
<td>-0.387\textsuperscript{c}</td>
</tr>
</tbody>
</table>

*In sulfolane versus a ferrocene/ferrocenium couple.


\textsuperscript{c}Source: R.A. Flowers, private communication.
photolyses were conducted for the reaction of 20a with i-Pr\textsubscript{2}O. Unique photoproducts 22-25 and 27 were produced upon irradiation of 20a in acetonitrile in the presence of i-Pr\textsubscript{2}O that were not formed in a "dark" reaction under the same reaction conditions. The photoproducts are shown in Scheme 4 (Results chapter). Photoproduct 26 was also produced upon irradiation, in addition to trace amounts in the corresponding "dark" reaction. Irradiation of 9-phenylxanthen-9-ol and xanthone in the absence and presence of i-Pr\textsubscript{2}O was also investigated as a possible source of the photoproducts (see Experimental chapter). Both the alcohol and xanthone were unreactive.

The percent conversion of 20a over time was monitored by HPLC (see Figure 11, Results chapter) and indicates that 2-(o-hydroxyphenoxy)benzophenone 25 is the major photoproduct and 22, 24 and 26 are produced in minor amounts. Bis(9-phenylxanthen-9-yl) peroxide 23 was not included in this time-conversion study due to its insolubility in the acetonitrile solvent. o-Hydroxybenzophenone 27 is a secondary photoproduct generated upon the irradiation of 2-(o-hydroxyphenoxy)-benzophenone 25.

There is literature precedence to account for two of our observed photoproducts. It has been established that the ground-state hydroperoxide 22 can rapidly rearrange in the presence of acid to form 2-(o-hydroxyphenoxy)benzophenone 25 or xanthone 26 and phenol (Koorts, 1987). Phenol could not be detected using our experimental procedure. This mechanism is proposed to proceed by protonation of the hydroperoxide terminal oxygen, followed by rearrangement, and is shown in Scheme
5. Irradiation of 9-hydroperoxy-9-phenylxanthene 22 in acetonitrile in the presence of acid (see Experimental chapter) produced 2-(o-hydroxyphenoxy)benzophenone 25, xanthone 26 and o-hydroxybenzophenone 27. Compounds 25-27 were also generated in the corresponding thermal reaction, but in lesser amounts. Thus, this rearrangement is suggested to be photocatalyzed.
Photoproduts 22-27 suggest the intermediacy of the 9-phenylxanthyl radical. However, an electron-transfer mechanism to form the 9-phenylxanthyl radical was ruled out based on the reduction potentials of the 9-arylxanthyl cations and quenching rate constants. Instead, we propose that the excited-state mechanism proceeds via
nucleophilic attack of the ether on 20a to form the intermediate oxonium ion 29. Homolytic cleavage of the bond between the C(9) and oxygen generates the resonance-stabilized 9-phenylxanthyl radical 30 and the corresponding ether radical cation 31 shown in Scheme 6.

Scheme 6

With the formation of the 9-phenylxanthyl radical 30, the remaining photoproducts can be accounted for, with a mechanism shown in Scheme 7. The 9-phenylxanthyl radical 30 can partition between being trapped by O₂ to produce the 9-phenylxanthene-9-peroxyl radical 32 followed by hydrogen atom abstraction to form 9-hydroperoxy-9-phenylxanthene 22. Alternatively, radical 30 can undergo hydrogen-atom abstraction to form 9-phenylxanthene 24. Benzophenone-sensitized (Glover, 1984) as well as unsensitized (Taljaard, 1986) irradiation of 9-phenylxanthene in benzene produced 9-hydroperoxy-9-phenylxanthene. The hydroperoxide was proposed to be generated via initial formation of the 9-phenylxanthyl radical and subsequent trapping by O₂ generating the 9-phenylxanthene-9-peroxyl radical (Glover, 1985).
Once formed, the 9-phenylxanthene-9-peroxyl radical 32 can couple with a 9-phenylxanthyl radical 30 to form bis(9-phenylxanthen-9-yl) peroxide 23, accounting for the remaining observed photoproducts.
Scheme 7

The photoproducts 22-27 formed via our proposed mechanism indicate that both
proton and hydrogen-atom sources are necessary. The ether radical cation 31 can act as a source of both, in a cascade process with a proposed mechanism shown in Scheme 8. The ether radical cation 31 is an excellent proton source yielding radical 33. Subsequently, radical 33 is an excellent hydrogen-atom donor to form alkene 34.

Scheme 8

\[
\begin{align*}
(Me)_2CH-O-CH(Me)_2 & \quad 31^+ \\
\downarrow & \\
(Me)_2CH-O-C(Me)_2 & \quad 33 \\
\downarrow & \\
(Me)_2CH-O-C\equiv CH_2 & \quad 34
\end{align*}
\]

It might be expected that the relative amounts of the oxygen trapping products 9-hydroperoxy-9-phenylxanthene 22, 2-(o-hydroxyphenoxy)benzophenone 25 and xanthone 26 should increase compared to the amount of hydrogen-atom abstraction
product 9-phenylxanthene 24 if photolysis solutions are purged with oxygen. Conversely, the relative amounts of hydrogen-atom abstraction product 24 should increase, compared to the amounts of hydroperoxide 22, 2-(o-hydroxyphenoxy)benzophenone 25 and xanthone 26 produced if photolysis solutions are purged with argon. Contrary to this hypothesis, solutions purged with O₂ or argon show no difference in the photoproducts produced or their relative amounts.

A rate constant of 3.42 x 10⁹ M⁻¹ s⁻¹ has been obtained for the reaction of the benzyl radical with O₂ in acetonitrile (Maillard, 1983). This kₒ(O₂) value is several orders of magnitude larger than the rate constant of 3.13 x 10⁵ M⁻¹ s⁻¹ obtained for the reaction of the benzyl radical with the very efficient hydrogen-atom donor, PhSH, in hexane or cyclohexane (Franz, 1986). We can use these kₒ(O₂) and kₒ(H•) values obtained for the benzyl radical as a model to explain the data obtained for our structurally similar 9-phenylxanthyl radical 30. Since kₒ(O₂)>>kₒ(H•), the 9-phenylxanthyl radical 30 can be trapped by small amounts of adventitious oxygen in the argon purged photolysis solution to form the hydroperoxide 22 and subsequent rearrangement products 2-(o-hydroxyphenoxy)benzophenone 25 and xanthone 26 much faster than radical 30 can abstract a hydrogen to form 9-phenylxanthene 24. Therefore, lack of an increase in the amount of 9-phenylxanthene 24 compared to 9-hydroperoxy-9-phenylxanthene 22 with argon purging is rationalized based on the kₒ(O₂) and kₒ(H•) values.
Photophysical Properties of the Aryl Substituted Cations

The observed substituent effects on the photophysical properties of the 9-aryl xanthyl cations 20a-f indicate that an increase in the electron donating ability of the 9-aryl substituent results in a decrease in fluorescence lifetimes and quantum yields and an increase in the non-radiative rate constants. A study of 9-arylfluorenyl anions by Tolbert and co-workers (1992) show that both meta-withdrawing and para-donating substituents result in shorter fluorescence lifetimes and lower fluorescence quantum yields. These substituent effects on the photophysical properties of the fluorenyl anions were rationalized using the energy gap law, relating the nonradiative decay rates to the energy difference between the first excited state and ground state, \( \Delta E \). \( \Delta E \) was chosen to be the difference between the lowest vibronic levels of the ground and excited states, \( E_{0,0} \), estimated from the energy of lowest wavelength emission maximum, due to the presence of well-resolved vibronic structure. A plot of \( \ln(k_{nr}) \) versus \( \Delta E \) gave very good correlation, providing a rationalization of the photophysical properties by intrinsic properties. This approach can not be applied to the 9-aryl xanthyl cations 20a-f, as they exhibit no substituent effect on either the absorption or emission spectra.

Another possibility which may account for the observed photophysical properties of the 9-aryl xanthyl cations is a substituent effect on the rates of intersystem crossing of the cation from the singlet excited state to the triplet state. The triplet excited state of the 9-phenyl xanthyl and 9-(4-fluorophenyl)xanthyl cations have been
characterized using transient absorption techniques (Johnston, 1993). The 9-(4-methoxyphenyl)xanthyl cation exhibits behavior different from that of the parent and \( p-F \) substituted cations. The \( p\text{-}\text{OMe} \) substituted cation exhibits a short fluorescence lifetime, and no phosphorescence could be detected at room temperature. A large rate constant for intersystem crossing thus was ruled out to account for the short fluorescence lifetime. Instead, a rapid intramolecular charge transfer quenching mechanism was proposed as a possible deactivational mode, consistent with the previous observation of efficient quenching of the 9-phenylxanthyl cation by anisole \((k_q = 4.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})\) (Azarani, 1991). The \( p\text{-}\text{OMe} \) substituted xanthyl cation exhibits an absorption spectrum different than each of the other 9-aryl xanthyl cations. In contrast to \( 20\text{a-f} \) which exhibit an absorption band centered at about 450 nm, the longest wavelength absorption band for the \( p\text{-}\text{OMe} \) substituted cation is shifted to 500 nm. Xanthyl cations \( 20\text{a-f} \) give absorption spectra which are virtually superimposable, ruling out intramolecular charge transfer as an explanation for the short lifetimes and low fluorescence quantum yield for the stronger electron-donating substituted 9-aryl xanthyl cations. A substituent effect on the rate constant for intersystem crossing may account for the substituent dependence on the fluorescence lifetimes and other photophysical parameters for \( 20\text{a-f} \). However, it can not account for the observed substituent effect on the quenching of the singlet excited 9-aryl xanthyl cations by water, alcohols and ethers, in which the magnitude of the quenching rate constants increases as the electron donating ability of 9-aryl substituent increases.
The 9-arylxanthyl cations 20a-f exhibit a dramatic substituent effect on the fluorescence quantum yields, lifetimes and excited-state quenching rate constants but no substituent effect on the absorption or emission spectra. We speculate that the 9-arylxanthyl fluorescent species may be different than the species which is quenched, with a possible mechanism shown in Scheme 9.

Scheme 9

A structure in which the 9-aryl ring is twisted out of planarity (relative to the xanthyl backbone) may exhibit less conjugative effects from the 9-aryl ring on the cation, thus
not effecting the position of the absorption and fluorescence maxima. This twisted
cation may be in equilibrium with a (partially) planar species where the substituents
may exert a greater conjugative effect during the quenching. Substituent effects are
observed on the quenching rate constants, fluorescence lifetimes and quantum yields
for the 9-arylxanthyl cations, in support of the mechanism outlined in Scheme 9.

In contrast to the substantial substituent effect seen in the photophysical
properties of the xanthyl cations 20a-f, there is little or no substituent effect exhibited
on the photophysical properties of the 9-arylthioxanthyl cations 21a-e. One
explanation for the absence of a substituent effect is the sulfur atom in the thioxanthyl
backbone causing an enhanced intersystem crossing of the singlet excited cation to the
triplet state, an influence which might overwhelm any effects due to the 9-aryl
substituent.

Another possibility to explain the lack of substituent effect on the thioxanthyl
cations is that structural changes due to the presence of the sulfur atom could result
in a greater twisting of the 9-aryl ring out of planarity (relative to the xanthyl
backbone), decreasing the conjugative interactions from the 9-aryl ring. To investigate
this possibility, geometry optimization calculations were carried out on the 9-
phenylxanthyl and 9-phenylthioxanthyl cations at the AM1 level. The minimized
structures show that the 9-phenyl ring is twisted 59° out of planarity (where a 90°
degree twist represents the structure with the 9-phenyl ring perpendicular to the
xanthyl portion of the molecule). The 9-phenyl ring in the thioxanthyl cation has a
twist angle of $68^\circ$. Thus, less conjugative interactions are suggested in the thioxanthyl system, in accord with our experimental results.
CHAPTER IV

CONCLUSIONS

9-Arylxanthyl and 9-arylthioxanthyl tetrafluoroborate salts have been synthesized and prove to be excellent substrates for the study of carbocation photochemistry and photophysics. The fluorescence intensity of the 9-arylxanthyl cations in acetonitrile decreased upon addition of water, alcohols and ethers. Relative fluorescence quantum yields were measured for these cations and plotted versus the quencher concentration. Stern-Volmer analyses gave excited-state bimolecular rate constants. A substantial substituent dependence is observed in each case, with the larger rate constants associated with the electron-donating substituted cations.

The substituent effect was further examined through Hammett analyses. Excited-state Hammett plots, were constructed and resulted in negative $\rho$ values in every case. This negative $\rho$ value is opposite in sign to the $\rho$ value obtained for the nucleophilic reaction of the ground-state 9-arylxanthyl cations with water.

The relative order for quenching of the 9-arylxanthyl cations by water and the alcohols is different compared to the ground-state quenching order for similarly reactive cations with H$_2$O and alcohols. The relative quenching order of the ground-state cations by the alcohols is strictly steric dependent. This is in contrast to the excited-state quenching order for the excited-state cations which is not based solely on steric considerations. Since both the relative reactivity order and the substituent
dependence are different between the excited-state and ground-state, a mechanism other than nucleophilic attack is suggested. The possibility of an excited-state electron transfer mechanism was considered and eliminated through application of the Rehm-Weller equation using the reduction potentials of the 9-aryl xanthyl cations and the excited-state quenching rate constants.

To further study the excited-state quenching mechanism, photoproducts for the reaction of the 9-phenyl xanthyl cation with i-Pr₂O were isolated. Unique photoproducts were isolated and identified that were not produced in the corresponding "dark" reaction. The photoproducts formed suggest the intermediacy of the 9-phenyl xanthyl radical. Because an electron-transfer mechanism was ruled out, we propose that the excited-state mechanism proceeds via nucleophilic attack of the ether on the 9-phenyl xanthyl cation to form an oxonium ion intermediate. Homolytic cleavage generates the resonance-stabilized 9-phenyl xanthyl radical and the corresponding ether radical cation.

The effect of the heteroatom in the xanthyl backbone on the cation was also investigated. The fluorescence intensity of the 9-aryl thioxanthyl cations in acetonitrile decreased upon addition of water and alcohols. Relative fluorescence quantum yields were measured for these cations and plotted versus the quencher concentration. Stern-Volmer analyses gave excited-state bimolecular rate constants. In contrast to the 9-aryl xanthyl cations, there is no substituent effect observed for quenching of the 9-aryl thioxanthyl cations by H₂O and MeOH. The excited-state quenching of two 9-
arylthioxanthyl cations by the alcohol series was also investigated. The same relative quenching order for quenching of the 9-aryl xanthyl cations was observed for quenching of the 9-arylthioxanthyl cations.

Photophysical properties of the 9-aryl xanthyl and 9-arylthioxanthyl cations were investigated. For the xanthyl series, there is a substantial substituent dependence observed in the lifetimes, fluorescence quantum yields, total decay rate constants and non-radiative rate constants. In contrast, no substituent effect was observed on the same photophysical properties in the 9-arylthioxanthyl series. The calculated fluorescence rate constants for the xanthyl and thioxanthyl cations show only a modest substituent effect. Additionally, there is no substituent dependence observed on the position of the absorbance or fluorescence maxima for either the 9-aryl xanthyl or 9-arylthio-xanthyl cations.

In order to account for the substituent dependence observed on the $t_t^*$, $\Phi_t$ and $k_q$ values but no substituent effect observed on the absorption or emission spectra, we speculate that the 9-aryl xanthyl fluorescent species may be different than the species being quenched. This may be due to the twisting of the 9-aryl ring out of planarity. A structure in which the 9-aryl ring is twisted out of planarity may exhibit less conjugative effects from the 9-aryl ring on the cation.

Another possibility to explain the lack of substituent effect observed on the thioxanthyl cations is that structural changes, due to the presence of the sulfur atom, may result in a greater twisting of the 9-aryl ring out of planarity. Again, this twisting
out of planarity would decrease the conjugative interactions from the 9-aryl ring on
the cation.
CHAPTER V

EXPERIMENTAL

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 measurements were obtained on a Photon Technology International LS-100 spectrophotometer. NMR spectra were obtained on a Varian VXR300 instrument operating at 300Hz for $^1$H and 75Hz 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$_3$. GC analyses were conducted on a Hewlett-Packard 5890 Series II gas chromatograph equipped with an FID detector and a 25 m x 0.2 mm x 0.33 μm film thickness HP-1 polymethylsiloxane capillary column operated at 200 °C for 0 minutes and raised at 3 °C/min to 225 °C, and held there for 10 minutes. Injector and detector temperatures were held at 250 °C. HPLC analyses were obtained with a Beckman Model 334 Liquid Chromatograph equipped with a Beckman Model 210 injector under isocratic conditions with a flow rate of 1 mL/min using a Beckman ODS column (Ultrasphere, 5 μm packing, 4.6 mm x 25 cm) using 1:1 2% aqueous TEA:acetonitrile. A Beckman Model 153 variable wavelength detector was used for detection, monitored at 254 nm.
Fluorescence Measurements

Fluorescence quantum yields for both the 9-arylxanthyl 20a-f and 9-arylthioxanthyl 21a-e cations in dry acetonitrile were measured versus quinine sulfate monohydrate in 0.1 N H$_2$SO$_4$ (Φ$_\text{f}$=0.52) (Weber, 1957). Fluorescence lifetimes of 20a-e and 21a-e were measured in dry acetonitrile using a nanosecond flash lamp filled with nitrogen. Excitation of 20a-e and 21a-e was at 381 nm (N$_2$), and emission monitored at 540 nm for the xanthyl cations 20a-e and 573 nm for the thioxanthyl cations 21a-e, with a 350 nm cut-off filter placed before the emission monochromator to eliminate excitation and Raman scattering. All lifetimes measured were independent of cation concentration below 5.0x10$^{-5}$M. The fluorescence lifetime of 20f was estimated according to the method used by Boyd (1991) for weakly fluorescent compounds. The lifetime of 20f was assumed to be proportional to its maximum fluorescence intensity and equal to the same proportion of 20e. By measuring the fluorescence intensity of both compounds and the lifetime of 20e, the lifetime of 20f was calculated. An internal check of this method estimated the lifetime of 20c to be 12.6 ns, relative to 20b, and consistent with the measured value of 20c. Steady state fluorescence emission was measured using a pulsed Xe lamp apparatus and the 350 nm cut-off filter previously described. Stern-Volmer quenching of the 9-arylxanthyl and 9-arylthioxanthyl cations in dry acetonitrile was conducted at a cation concentration of 5.0x10$^{-5}$M. Quencher solutions in acetonitrile were prepared below the concentration that might permit ground state quenching to occur.
Solvents

All $^1$H and $^{13}$C NMR spectra were taken in CDCl$_3$ solvent obtained from Aldrich Chemical Company, unless otherwise specified. Anhydrous tetrahydrofuran used in Grignard syntheses was dried over calcium hydride and then freshly distilled. Arylbromides were obtained from Aldrich and distilled prior to use. Spectroscopic grade acetonitrile used in UV, steady state and fluorescence lifetime measurements was obtained from Mallinckrodt. Residual water was removed by passing the acetonitrile through a column of neutral aluminum oxide obtained from Aldrich. Propionic anhydride and fluoroboric acid used in the syntheses of xanthylum tetrafluoroborate salts were obtained from Aldrich and used as received. Alcoholic quenchers were obtained from Fisher and Aldrich and used without further purification. Water used as quencher was doubly distilled. Diethyl ether, isopropyl ether, tert-butyl methyl ether and tert-butyl ethyl ether (>99%) used as quenchers were obtained from Aldrich and distilled from sodium metal prior to use. Tetrahydrofuran (>99%) used as a quencher was obtained from Aldrich and distilled from CaH$_2$ prior to use. Isopropyl ether used in irradiation experiments was distilled from CaH$_2$ prior to use.

9-Phenylxanthen-9-ol (18a)

9-Phenylxanthen-9-ol was obtained from the Aldrich Chemical Company as an off-white solid. Recrystallization from 95% ethanol yielded white crystals, mp 158-161°C
Synthesis of 9-Arylxanthen-9-ols

A Grignard reagent was prepared from the appropriate arylbromide (5.8 mmol) and magnesium turnings (5.8 mmol) in anhydrous tetrahydrofuran (30mL). Recrystallized xanthone (5.0 mmol) was added and the mixture heated at reflux temperature until no more alcohol was being produced, determined by thin layer chromatography (1-4 hours). The mixture was quenched by the addition of aqueous ammonium chloride. The organic layer was washed with water and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporation yielding a yellow solid. The solid was identified as two components by thin layer chromatography, where methylene chloride was used as the eluant. One component corresponded to unreacted xanthone and was removed by column chromatography. The desired alcohol was obtained as an off-white solid. Recrystallization from 95% ethanol yielded a white solid.

9-(4’-Fluorophenyl)xanthen-9-ol (18b)

Yield 0.71g (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=4,300).
9-(3'-Fluorophenyl)xanthen-9-ol (18c)
Yield 0.21g (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=5,100).

9-(4'-Methylphenyl)xanthen-9-ol (18d)
Yield 0.99g (69%); mp 146-148 °C (lit. mp 150 °C (Gomberg, 1909), lit. mp 141-142 °C (Gaffney, 1991)); $^1$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=4,900).

9-(3'-Methylphenyl)xanthen-9-ol (18e)
Yield 0.34g (24%); mp 144-146 °C (lit. mp 149 °C (Schonberg, 1947)); $^1$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=5,600).

9-(3'-Methoxyphenyl)xanthen-9-ol (18f)
Yield 0.57g (38%); mp 120-123 °C (lit. mp 112-113 °C (Hori, 1973)); $^1$H NMR δ 3.81 (s, 3H), 2.85 (br, 1H), 6.73-7.45 (m, 12H); UV at 244 nm (ε =13,000), 282 nm (ε=5,900).
Synthesis of 9-Arylxanthylium Tetrafluoroborate Salts

The tetrafluoroborate salts were prepared following the method of Dauben, *et al.* (1960). The corresponding 9-arylxanthen-9-ol (1.7 mmol) was dissolved in propionic anhydride (34.9 mmol) at room temperature or slightly higher, where heat was provided by a warm water bath. This temperature was maintained as fluoroboric acid (3.8 mmol) was added to immediately yield a yellow solution. The xanthylium tetrafluoroborate salt was allowed to crystallize, whereafter, cold dry ethyl ether (5mL) was added to the solution and the supernatant discarded. This washing procedure was repeated five times to remove residual starting material. The precipitate was suction filtered and washed with cold, dry ethyl ether (10mL) to yield a bright yellow solid in every case except the $m$-OCH$_3$ cation salt which was dark orange.

**9-Phenylxanthylium Tetrafluoroborate (20a)**

Yield 0.46g (76%); mp 228 °C dec; $^1$H NMR $\delta$ 7.75-8.52 (m, 13H); $^{13}$C NMR $\delta$ 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 ($\varepsilon$=38,700), 372 nm ($\varepsilon$=29,400), and 446 nm ($\varepsilon$=4,900).

**9-(4'-Fluorophenyl)xanthylium Tetrafluoroborate (20b)**

Yield 0.14g (78%); mp 216°C dec; $^1$H NMR $\delta$ 7.44-8.50 (m, 12H); $^{13}$C NMR $\delta$ 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 ($\varepsilon$=42,300), 374 nm...
(ε=36,200), and 450 nm (ε=5,600).

9-(3'-Fluorophenyl)xanthylum Tetrafluoroborate (20c)
Yield 0.06g (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=3,900).

9-(4'-Methylphenyl)xanthylum Tetrafluoroborate (20d)
Yield 0.06g (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=6,300).

9-(3'-Methylphenyl)xanthylum Tetrafluoroborate (20e)
Yield 0.06g (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=6,300).

9-(3'-Methoxyphenyl)xanthylum Tetrafluoroborate (20f)
Yield 0.09g (50%); mp 204 °C dec; \(^1\)H NMR \(\delta\) 3.97 (s, 3H), 7.27-8.58 (m, 12H); \(^{13}\)C NMR \(\delta\) 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 (\(\varepsilon=34,000\)), 372 nm (\(\varepsilon=29,000\)), and 452 nm (\(\varepsilon=4,400\)).

**Synthesis of 9-Arylthioxanthen-9-ols**

A Grignard reagent was prepared from the appropriate arylmagnesium bromide (8.7 mmol) and recrystallized thioxanthone (4.4 mmol) in anhydrous tetrahydrofuran. The reaction mixture was heated at reflux temperature for 1 h. Aqueous workup followed by purification with silica gel chromatography using methylene chloride as eluant, and subsequent recrystallization from 95% ethanol gave the pure 9-arylthioxanthenols as white solids.

**9-Phenylthioxanthen-9-ol (19a)**

Yield 0.50 g (39%); mp 103-107 °C (lit. mp 106 °C (Gomberg, 1910)); \(^1\)H NMR \(\delta\) 2.76 (s, 1H), 7.00-8.05 (m, 13H); UV at 200 nm (\(\varepsilon=50,900\)), 216 nm (\(\varepsilon=29,700\)), 268 nm (\(\varepsilon=11,000\)).

**9-(4'-Fluorophenyl)thioxanthen-9-ol (19b)**

Yield 23 mg (17%); mp 140-142 °C (lit. mp 141-142 °C (Ahn, 1982)); \(^1\)H NMR \(\delta\) 2.79 (s, 1H), 6.86-8.08 (m, 12H); UV at 200 nm (\(\varepsilon=48,500\)), 216 nm (\(\varepsilon=30,000\)), 266
9-(3'-Fluorophenyl)thioxanthen-9-ol (19c)

Yield 53 mg (2.2%); mp 123-125 °C. $^1$H NMR δ 2.78 (s, 1H), 6.74-8.02 (m, 12H); $^{13}$C NMR δ 164.09, 160.83, 146.21, 146.12, 139.29, 131.29, 129.49, 129.38, 127.55, 127.29, 126.60, 126.40, 126.11, 122.49, 114.78, 114.48, 114.20, 113.90, 73.37; UV at 200 nm (ε=44,600), 216 nm (ε=28,200), 266 nm (ε=12,000).

9-(4'-Methylphenyl)thioxanthen-9-ol (19d)

Yield 46 mg (7%); mp 161-163 °C (lit. mp 164-165 °C (Nagao, 1987)); $^1$H NMR δ 2.29 (s, 3H), 2.81 (s, 1H), 6.88-8.11 (m, 12H); UV at 200 nm (ε=47,800), 216 nm (ε=26,600), 266 nm (ε=9,400).

9-(3'-Methylphenyl)thioxanthen-9-ol (19e)

Yield oil, 56 mg (8.4%); $^1$H NMR δ 2.19 (s, 3H), 2.74 (s, 1H), 6.71-8.02 (m, 12H); $^{13}$C NMR δ 143.38, 140.05, 137.74, 131.58, 128.63, 127.90, 127.56, 127.26, 126.66, 126.48, 126.17, 124.04, 53.32, 21.57.

9-Arylthioxanthylium Tetrafluoroborate Salts

Tetrafluoroborate salts 21a-e were prepared following the method of Dauben, et al. (1960). The corresponding 9-arylthioxanthen-9-ol (0.1 mmol) was dissolved in
propionic anhydride (0.27 mL) at room temperature or slightly higher, where heat was provided by a warm water bath. This temperature was maintained upon the addition of fluoboric acid (19 mg, 0.22 mmol), which immediately gave a red solution. The thioxanthylum tetrafluoroborate salt precipitated and was collected by suction filtration. The salts were washed repeatedly with cold, anhydrous diethyl ether to yield a bright red solid in every case.

9-Phenylthioxanthylum Tetrafluoroborate (21a)
Yield 10 mg (27%); mp 194-196 °C dec; \(^1\)H NMR δ 7.00-8.88 (m, 13H); \(^13\)C NMR δ 170.72, 146.60, 137.56, 135.40, 134.40, 131.13, 130.98, 130.21, 129.56, 129.07, 128.23; UV at 192 nm (ε=42,000), 218 nm (ε=22,500), 246 nm (ε=14,000), 278 nm (ε=39,700), 384 nm (ε=17,400), and 494 nm (ε=5,600).

9-(4'-Fluorophenyl)thioxanthylum Tetrafluoroborate (21b)
Yield 48 mg (49%); mp 218-220°C dec; \(^1\)H NMR δ 6.88-9.09 (m, 12H); \(^13\)C NMR δ 141.72, 138.72, 138.53, 133.08, 132.3, 132.15, 130.02, 129.91, 128.16, 127.39, 127.35, 127.25, 116.95, 115.16, 114.88; UV at 194 nm (ε=43,400), 220 nm (ε=22,400), 246 nm (ε=12,400), 278 nm (ε=38,900), 384 nm (ε=18,100), and 496 nm (ε=4,800).

9-(3'-Fluorophenyl)thioxanthylum Tetrafluoroborate (21c)
Yield 9.9 mg (17%); mp 208-210 °C dec; \(^1\)H NMR δ 7.28-8.88 (m, 12H); \(^13\)C NMR
δ 164.07, 160.74, 148.79, 137.37, 136.17, 136.07, 134.87, 131.16, 131.03, 130.92, 129.97, 128.20, 126.63, 125.54, 125.49, 118.10, 117.82, 117.04, 116.72; UV at 192 nm (ε=43,400), 220 nm (ε=18,500), 246 nm (ε=10,000), 280 nm (ε=40,200), 386 nm (ε=12,400), and 494 nm (ε=3,800).

9-(4’-Methylphenyl)thioxanthylum Tetrafluoroborate (21d)
Yield 11 mg (49%); mp 134-136 °C dec; ¹H NMR δ 2.63 (s, 3H), 7.30-8.86 (m, 12H); ¹³C NMR δ 141.72, 138.72, 138.53, 133.08, 132.30, 132.15, 130.02, 129.91, 128.16, 127.39, 127.35, 127.25, 116.95, 115.16, 114.88; UV at 200 nm (ε=49,800), 180 nm (ε=25,400), 246 nm (ε=11,800), 282 nm (ε=38,900), 382 nm (ε=11,800), and 496 nm (ε=5,200).

9-(3’-Methylphenyl)thioxanthylum Tetrafluoroborate (21e)
Yield 0.10 g (12%), mp 173-175 °C dec; ¹H NMR δ 2.57 (s, 3H), 7.29-8.88 (m, 12H); ¹³C NMR δ 171.02, 148.54, 139.15, 137.48, 135.47, 134.37, 131.70, 131.02, 130.18, 129.95, 128.89, 128.23, 126.75, 21.50; UV at 198 nm (ε=43,600), 218 nm (ε=23,200), 248 nm (ε=10,600), 282 nm (ε=39,000), 378 nm (ε=10,200), and 494 nm (ε=3,900).

Preparative Irradiations (GC Analysis)
Irradiations were performed in a Rayonet reactor equipped with fifteen 350-nm lamps (RPR 3500). A merry-go-round apparatus was used to insure even irradiation of
multiple samples. After irradiation, the samples were rotary evaporated to dryness. To each sample, acetonitrile (0.5 mL) and MeOH (2 drops) were added to quench any unreacted cation, followed by GC analysis.

Irradiation of 9-Phenylxanthen-9-ol (18a) in the Absence and Presence of \( i-\text{Pr}_2\text{O} \)
A solution of 9-phenylxanthen-9-ol in acetonitrile (0.001 M) was purged with argon for 30 minutes. The sample was divided and diisopropyl ether (1 M) was added to one of these alcohol solutions and both were irradiated for 10 minutes in quartz tubes. Identical "dark" irradiations were performed simultaneously by wrapping tubes in aluminum foil.

Irradiation of Xanthone (24) in the Absence and Presence of \( i-\text{Pr}_2\text{O} \)
A solution of xanthone in acetonitrile (0.001 M) was purged with argon for 30 minutes. The sample was divided and diisopropyl ether (1 M) was added to one of the xanthone solutions and both were irradiated for 10 minutes in quartz tubes. Identical "dark" irradiations were performed simultaneously.

Irradiation of 9-Phenylxanthylium Tetrafluoroborate (20a)
A solution of 9-phenylxanthylium tetrafluoroborate in acetonitrile (0.0024 M) was purged with argon for 30 minutes. The sample was placed in a quartz vessel equipped with a cold finger apparatus and irradiated for 10 minutes. Identical "dark"
irradiations were performed simultaneously.

Irradiation of 9-Phenylxanthylum Tetrafluoroborrate (20a) in the Presence of i-Pr₂O
A solution of 9-phenylxanthylum tetrafluoroborrate in acetonitrile (0.0024 M) was
purged with argon for 30 minutes. The sample was placed in a quartz vessel equipped
with a cold finger apparatus along with diisopropyl ether (25 mL) and irradiated for
10 minutes. The products of this irradiation were separated by column
chromatography and identified by spectroscopic methods. Identical "dark" irradiations
were performed simultaneously.

2-(o-Hydroxyphenoxy)benzophenone (25)
Prepared as described in the literature (Quint, 1931): yield 0.011 g (66%); mp 196-
198 °C (lit. mp 104 °C (Quint, 1931) and 103-104 °C (Glover, 1984)); 1H NMR δ
6.88-800 (m, 13H), 8.16 (s,1H); 13C NMR δ 196.88, 156.65, 149.29, 142.98, 136.77,
133.86, 132.68, 130.56, 128.78, 128.55, 126.32, 122.56, 122.32, 119.62, 117.61; UV
at 204 nm (ε=48,000), 252 nm (ε=9,900), and 276 nm (ε=7,9400).

9-Phenylxanthene (24)
Prepared as described in the literature (Ullmann, 1904): yield 0.12g (13%); mp 137-
139 °C (lit. mp 145 °C (Ullmann, 1904) and 148-150 °C (Glover, 1984)); 1H NMR δ
5.28 (s, 1H), 7.00-7.30 (m, 13H); UV at 202 nm (ε=44,000), 248 nm (ε=8,300), and
282 nm (ε=3,300).

**9-Hydroperoxy-9-phenylxanthene (22)**

Prepared as described in the literature (Glover, 1984): yield 0.39 g (30%); double mp 126-127 and 225-226 °C (lit. double mp 134 and 208 °C (Glover, 1984)); $^1$H NMR δ 7.10-7.40 (m, 13H), 7.43 (s, 1H, OOH); UV at 204 nm (ε=46,000), 244 nm (ε=16,000), and 292 nm (ε=5,600).

**Di-(9-phenylxanthen-9-yl) Peroxide (23)**

Prepared as described in the literature (Glover, 1984): yield 18 mg (77%); mp 214-215 °C turns brown and 222-223 liquid °C dec. (lit. mp 212-214 °C (Glover, 1984), 232 °C (Wan, 1993), 215-219 °C (Gomberg, 1909) and 230 °C (Schönberg, 1945)); $^1$H NMR δ 6.72-7.30 (m, 26H).

**9-Methoxy-9-phenylxanthene (28)**

Prepared as described in the literature (Llama, 1989): yield 12 mg (47%); mp 90-92 °C (lit. mp 142-144 °C (Llama, 1989)); $^1$H NMR δ 2.95 (s, 3H), 7.05-7.41 (m, 13H); $^{13}$C NMR δ 151.54, 148.97, 129.53, 129.00, 127.78, 126.50, 126.44, 123.42, 123.04, 116.18, 75.91, 51.03; UV at 202 nm (ε=44,000), 244 nm (ε=14,000), and 290 nm (ε=5,300).
Quantitative Irradiations (HPLC Analysis)

Irradiations were performed in a Rayonet reactor equipped with fifteen 350-nm lamps (RPR 3500). Irradiations took place at 4 °C. A merry-go-round apparatus was used to insure even irradiation of multiple samples. Irradiations were done to quantify the amount of photoproducts present in the reaction mixture. Photoproduct 22 was not stable for GC analysis and therefore analyzed by HPLC. Standard solutions of each photoproduct were prepared to determine the yields of the photoproducts for the irradiation. The irradiated samples and the standard solutions were analyzed by HPLC. The integrated areas for the standards containing a known amount of photoproduct were compared to the integrated areas of the photoproducts.

Irradiation of 9-Phenylxanthylum Tetrafluoroborate (20a)

A solution of 9-phenylxanthylum tetrafluoroborate in acetonitrile (.001 M) was purged with O₂ for 30 minutes. To 4 small quartz tubes, 8 mL of the cation solution was added. The total time of irradiation varied, with one tube removed from the merry-go-round apparatus every ten minutes. After irradiation, the samples were rotary evaporated to dryness. To each sample, 0.8 mL of acetonitrile and 0.6 mL of methanol were added, followed by HPLC analysis.

Irradiation of 9-Phenylxanthylum Tetrafluoroborate (20a) in the Presence of i-Pr₂O

A solution of 9-phenylxanthylum tetrafluoroborate in acetonitrile (.001 M) was purged
with O₂ for 30 minutes. To 4 small quartz tubes, 8 mL of the cation solution was added along with 1.13 mL of i-Pr₂O. The total time of irradiation varied, with one tube removed from the merry-go-round apparatus every ten minutes. After irradiation, the samples were rotary evaporated to dryness. To each sample, 0.8 mL of acetonitrile and 0.6 mL of methanol were added, followed by HPLC analysis.

Irradiation of 9-Phenylxanthylum Tetrafluoroborate (20a) in the Presence of i-Pr₂O
A solution of 9-phenylxanthylum tetrafluoroborate in acetonitrile (0.001 M) was purged with argon for 30 minutes. To 4 small quartz tubes, 8 mL of the cation solution was added along with 1.13 mL of i-Pr₂O. The total time of irradiation varied, with one tube removed from the merry-go-round apparatus every ten minutes. After irradiation, the samples were rotary evaporated to dryness. To each sample, 0.8 mL of acetonitrile and 0.6 mL of methanol were added, followed by HPLC analysis.

Irradiation of 9-Hydroperoxy-9-phenylxanthene (22)
A solution of 9-hydroperoxy-9-phenylxanthene in acetonitrile (0.001 M) was purged with O₂ for 30 minutes. To 4 small quartz tubes, 8 mL of the hydroperoxide solution was added. The total time of irradiation varied, with one tube removed from the merry-go-round apparatus every five minutes. After irradiation, the samples were rotary evaporated to dryness. To each sample, 0.8 mL of acetonitrile and 0.6 mL of methanol were added, followed by HPLC analysis.
Irradiation of 9-Hydroperoxy-9-phenylxanthene (22) in the Presence of Acid

A solution of 9-hydroperoxy-9-phenylxanthene in acetonitrile (0.001 M) was purged with O₂ for 30 minutes. To 4 small quartz tubes, 8 mL of the hydroperoxide solution was added along with 72 µL of a 1.87% (w/w) H₂SO₄ solution. The total time of irradiation varied, with one tube removed from the merry-go-round apparatus every five minutes. After irradiation, the samples were rotary evaporated to dryness. To each sample, 0.8 mL of acetonitrile and 0.6 mL of methanol were added, followed by HPLC analysis.
SPECTRA
$^1$H NMR of 9-(4-fluorophenyl)xanthen-9-ol, (18b)
$^{13}$C NMR of 9-(4-fluorophenyl)xanthene-9-ol, (18b)
$^1$H NMR of 9-(3-fluorophenyl)xanthene-9-ol, (18c)
$^{13}$C NMR of 9-(3-fluorophenyl)xanthene-9-ol, (18c)
$^1$H NMR of 9-(3-methylphenyl)xanthen-9-ol, (18e)
\(^1\)H NMR of 9-(3-methoxyphenyl)xanthen-9-ol, (18f)
$^1$H NMR of 9-phenylxanthen-9-ol, (19a)
$^1$H NMR of 9-(4-fluorophenyl)thioxanthen-9-ol, (19b)
$^{13}$C NMR of 9-(3-fluorophenyl)thioxanthen-9-ol, (19c)
$^1$H NMR of 9-(4-methylphenyl)thioxanthren-9-ol, (19d)
$^1$H NMR of 9-(3-methylphenyl)thioxanthen-9-ol, (19e)
$^1$H NMR of 9-(3-methylphenyl)thioxanthene-9-ol, (19e)
$^1$H NMR of 9-phenylxanthylum tetrafluoroborate, (20a)
$^{13}$C NMR of 9-phenylxanthylum tetrafluoroborate, (20a)
$^1$H NMR of 9-(4-fluorophenyl)xanthylum tetrafluoroborate, (20b)
$^{13}$C NMR of 9-(4-fluorophenyl)carbazole tetrafluoroborate, (20b)
$^1$H NMR of 9-(3-fluorophenyl)xanthylum tetrafluoroborate, (20c)
$^{13}$C NMR of 9-(3-fluorophenyl)xanthylum tetrafluoroborate, (20c)
$^{13}$C NMR of 9-(4-methylphenyl)xanthylum tetrafluoroborate, (20d)
$^1$H NMR of 9-(3-methylphenyl)xanthylum tetrafluoroborate, (20e)
$^{13}$C NMR of 9-(3-methylphenyl)xanthium tetrafluoroborate, (20e)
$^1$H NMR of 9-(3-methoxyphenyl)xanthium tetrafluoroborate, (20f)
$^{13}$C NMR of 9-(3-methoxyphenyl)xantylum tetrafluoroborate, (20f)
$^1$H NMR of 9-phenylthioxanthylum tetrafluoroborate, (21a)
$^{13}$C NMR of 9-phenylthioxanthylum tetrafluoroborate, (21a)
$^1$H NMR of 9-(4-fluorophenyl)thioxanthylum tetrafluoroborate, (21b)
$^{13}$C NMR of 9-(4-fluorophenyl)thioxanthylum tetrafluoroborate, (21b)
$^1$H NMR of 9-(3-fluorophenyl)thioxanthylum tetrafluoroborate, (21e)
$^{13}$C NMR of 9-(3-fluorophenyl)thioxanthylum tetrafluoroborate, (21c)
$^1$H NMR of 9-(4-methylphenyl)thioxanthylum tetrafluoroborate, (21d)
$^{13}$C NMR of 9-(4-methylphenyl)thioxanthylum tetrafluoroborate, (21d)
$^1$H NMR of 9-(3-methylphenyl)thioxanthylum tetrafluoroborate, (21e)
$^1$C NMR of 9-(3-methylphenyl)thioxanthylum tetrafluoroborate, (21e)
$^1$H NMR of 9-hydroperoxo-9-phenylxanthen, (22)
$^1$H NMR of dl-(9-phenylxanthene-9-yl) peroxide, (23)
$^1$H NMR of 9-phenylxanthene, (24)
$^1$H NMR of 2-(o-hydroxyphenoxy)benzophenone, (25)
$^{13}$C NMR of 2-(o-hydroxyphenoxy)benzophenone, (25)
$^1$H NMR of 9-methoxy-9-phenylxanthene, (28)
$^{13}$C NMR of 9-methoxy-9-phenylxanthene, (28)
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VITAE

The author, Maria R. Valentino, was born on September 15, 1962 in Evergreen Park, Illinois. In September, 1980 she entered DePaul University and received a B.S. degree in Chemistry in May, 1985. During her last year as an undergraduate at DePaul, she started her master’s project under the guidance of Professor Avrom A. Blumberg. She obtained her M.S. degree in Chemistry in May, 1986.

After graduation she obtained employment at Service Coatings, Inc. in Harvey, Illinois as a Research and Development Chemist. After 1.5 years in the coatings industry, Ms. Valentino obtained employment with Nalco Chemical Company as a Development Chemist where she remained for 1 year prior to pursuing her doctoral studies.

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The dissertation is, therefore, accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Date

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11/29/95