Direct Observation of Styrylfluorenone Radical Cations Formed by Photoionization in Acetonitrile

Z. Wang, W. G. McGimpsey,* Y. Ren, and S. J. Weininger*

Department of Chemistry
Worcester Polytechnic Institute
Worcester, Massachusetts 01609-2280

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Accounts of the generation and study of radical cations of carbonyl compounds in the gas phase by way of various mass spectrometric techniques are numerous.[1] However, descriptions of carbonyl radical cations in condensed phases are much less abundant and are confined mainly to frozen matrices. Both ESR[2] and absorption[3] spectra have been measured in these media. We describe the generation and observation on a microsecond time scale of carbonyl-substituted radical cations in solution.

In view of the high ionization potentials of most carbonyl compounds and the expected high reactivity of their derived cations, the paucity of direct observations of carbonyl cations in the liquid phase is not surprising. In solution, polycyclic alphatic ketone radical cations fragment rapidly by C(O)–C cleavage.[4,5] Biphotonic ionization of benzophenone by laser flash photolysis (LFP) at 248 nm in H_2O produces the radical cation, which does not fragment but reacts with solvent in a time span shorter than the pulse width.[6–8]

We report 308-nm photolyses[9] of several isomeric styrylfluorenones in acetonitrile (MeCN) that give rise to radical cations, and the effect of changing wavelength, solvent, and additives on their formation and quenching. The compounds used are shown in Chart 1.[10]

Like fluorenone itself, derivatives with substituents at the 2- and 4-positions have ground-state absorption spectra with broad, shallow bands between 400 and 500 nm,[11] but with greater intensity due probably to charge transfer.[12] At shorter wavelengths new bands arise from fluorenone/styrene interactions. A relatively clear separation between short- and long-wavelength absorptions is not observable in 1-substituted fluorenones.

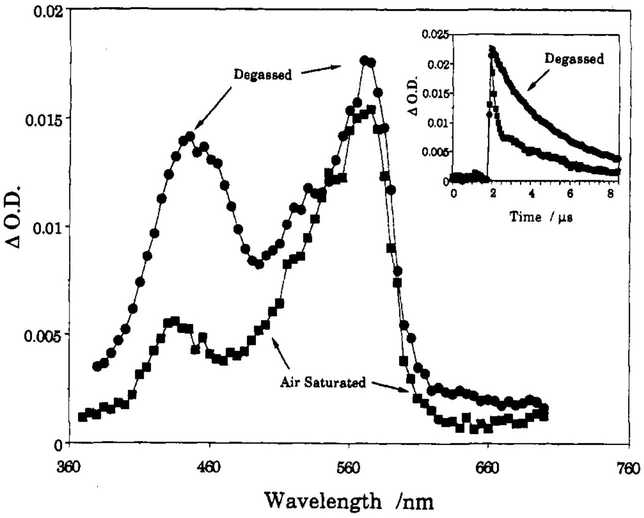
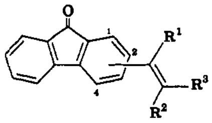
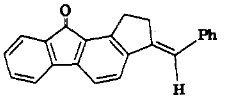


Figure 1. Transient absorption spectra obtained 2 μs following 308-nm laser photolysis of ***trans*-2** in degassed (●) and air saturated (■) MeCN. Inset: Decay kinetics obtained at 440 nm under degassed and air-saturated conditions (same symbols).

Chart 1



$R^1 = R^2 = H$, $R^3 = Ph$: *trans-1, trans-2, trans-4*
$R^1 = Me$, $R^2 = H$, $R^3 = Ph$: *β-Me-2*
$R^1 = R^2 = H$, $R^3 = 3,4\text{-}(MeO)_2Ph$: *MeO-2, MeO-4*
$R^1 = R^2 = $ —, $R^3 = Ph$: *yne-1, yne-2, yne-4*



cyclo - 2

LFP of ***trans*-2** in cyclohexane (308 nm, 3 × 10^{-5} M, N_2) produces a transient (λ_{max} 460 nm, $\tau \sim 2$ μs) that is strongly quenched by air saturation ($\tau \sim 200$ ns). On the basis of its lifetime, air quenchability, and absorption characteristics[13] we conclude that it is the triplet of ***trans*-2**, (^{3}***trans*-2***).[10] The same spectrum is obtained in $PhCH_3$ and CH_2Cl_2 under N_2 whether irradiation is carried out at 308 nm (excitation to S_n) or at 445 nm (excitation to S_1).

Most derivatives substituted at C-2 give rise to similar transient spectra in nonpolar solvents, which we assign to the planar triplet. The exceptions are ***β-Me*-2** and ***cyclo*-2**, which we believe give perpendicular triplets with shorter lifetimes and shorter wavelength maxima.[10] Similarly, ***trans*-1** and ***trans*-4** do not give rise to absorptions attributable to planar triplets; however, all alkynyl derivatives do.

By contrast, irradiation of ***trans*-2** (308 nm, 3 × 10^{-5} M, N_2) in MeCN generates a spectrum showing a major peak at 580 nm ($\tau \sim 4$ μs; first-order decay), a weaker one at 440 nm, and a shoulder at 450–460 nm (Figure 1). The peaks at 580 and 440 are unaffected by air while the shoulder (^{3}***trans*-2***) is quenched. The following evidence indicates that the air-insensitive transient is a *radical cation* (***trans*-2**$^{\bullet+}$) produced by monophotonic ionization from an upper singlet state of ***trans*-2**:

(i) The transient is generated in MeCN and MeOH but not in less polar solvents; air saturation increases its lifetime in MeOH.

(ii) Addition of $Bu_4N^+Br^-$ to the MeCN efficiently quenches the transient (k_q = 3.9 × 10^9 M^{-1} s^{-1}), while addition of $Bu_4N^+ClO_4^-$ increases its lifetime.

(iii) Photolysis under air at either 308 or 355 nm produces the transient, although with equal absorbed laser dose the yield is greater at 308 nm. The OD at 580 nm is linearly dependent on incident laser energy. However, photolysis at 445 nm yields *no*

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(7) Radical cations of acetophenones and benzophenones generated by oxidation of their triplets with paraquat in aqueous MeCN also decompose too rapidly to be detected: Baral-Tosh, S.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 1404–1408.

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(9) Our experimental setup and procedures have been described previously: Wang, Z.; Weininger, S. J.; McGimpsey, W. G. *J. Phys. Chem.* **1993**, *97*, 374–378.

(10) We use the term *trans* to refer to the relative positions of the fluorenone ring and the styryl aromatic ring. The syntheses, fluorescence behavior, cis–trans isomerization, and triplet spectra of these compounds will be described in our full paper (in preparation).

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(12) AM1 calculations for ***trans*-2** indicate that the HOMO has considerable electron density in the side chain while the electron density in the LUMO is concentrated in the fluorenone ring. Solvatochromic studies give a value of 15–16 D for S_1.

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Table 1. Absorption Maxima of Regioisomeric Styryl- and (Phenylethynyl)fluorenone Radical Cations[a]

compd	λ_{max} (nm)	compd	λ_{max} (nm)
***trans*-1**	500	***MeO*-2**	545, 565
***trans*-2**	580	***yne*-2**	530
***β-Me*-2**	570	***trans*-4**	500
***cyclo*-2**	570	***MeO*-4**	490

[a] Generated by photolysis of the precursor in air-saturated MeCN at 308 nm.

transient in air-saturated solution, while under N_2 only (^{3}***trans*-2***) is observed.

(iv) Addition of 0.1 M 1,4-dicyanobenzene (DCNB) does not increase the transient yield upon 308-nm irradiation, nor does further photolysis of (^{3}***trans*-2***) in MeCN with a second laser in either the absence or presence of DCNB.

(v) Photolysis of 2-styryl-9-fluorenol (***2-trans*-ol**) gives a spectrum with a peak at λ_{max} 545 nm, ruling out the possibility that our transient is a fluorenyl radical cation or fluorene cation derived from a ***2-trans*-ol** impurity.[14]

All styryl derivatives substituted at C-2 give very similar transient spectra in air-saturated MeCN (Table 1). Their similarity suggests that the transients have similar conformations, probably trans planar. Styryl derivatives substituted at C-1 and C-4 also produce air-insensitive transients after 308-nm irradiation in MeCN. However, their λ_{max} values are blue-shifted by 60–70 nm compared to those found for the 2-substituted regioisomers (Table 1).

The behavior of ***yne*-2** was very sensitive to precise photolysis conditions. In MeCN containing $\approx 1\%$ CF_3COOH a weak spectrum was generated that contained an air-stable peak at 530 nm tentatively assigned to (***yne*-2**$^{\bullet+}$). No air-stable transients could be generated from ***yne*-1** or ***yne*-4**.

Two characteristics of all styrylfluorenone radical cations that merit attention are their mode of formation and their anomalously long lifetimes. Numerous styrylarenes photoionize in polar solvents. Styrylnaphthalenes,[15] (pyridylethenyl)naphthalenes,[15] and styrylphenanthrenes[16] all undergo monophotonic ionization in MeCN when irradiated at ~350 nm; styrylanthracenes undergo biphotonic ionization under the same conditions.[17] None of them show the striking dependence of cation yield on excitation wavelength displayed by the styrylfluorenones. Furthermore, DCNB enhances the radical ion yield from the styrylarenes but fails to do so for the styrylfluorenones. Taken together these results indicate that styrylfluorenone radical cations are formed via short-lived upper excited states. Our results rule out radical cation formation by either T–T annihilation[6] or re-excitation of the triplet.[18,19]

The long lifetimes of the styrylfluorenone cations are likely related to their ground-state electronic configuration. Recent ground-state calculations for several carbonyl radical cations predict a Π rather than Σ ground state for cyclopentadienone,[20] of which fluorenone is the dibenzannelated derivative. Furthermore, AM1 calculations show that the HOMO of ***trans*-2** has considerable electron density in the side chain and a node at the carbonyl group.[10] The charge must be substantially delocalized throughout the entire π-system since λ_{max} for the cations is a function of positional isomerism and differs from the values found for styryl cations.[21] This delocalization should reduce the electrophilic reactivity of the radical cation.

Finally, we note the unusual behavior of ***trans*-2** in trifluoroethanol (TFE), normally a favorable medium for generating and stabilizing radical cations.[22] Photolysis of ***trans*-2** in TFE at 308 nm under N_2 gives *only* the spectrum of (^{3}***trans*-2***); under air no transient at all was detectable. Hydrogen bonding would raise the ionization potential of ***trans*-2** and increase the electrophilicity of (***trans*-2**$^{\bullet+}$); either or both effects could account for the failure to observe the radical cation in this solvent.[23]

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