Excited-State Behavior of Thermally Stable Radical Ions

David T. Breslin and Marye Anne Fox*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712 Received: October 12, 1993; In Final Form: November 30, 1993[®]

The excited states of several families of thermally stable radical ions in solution are surveyed by transient absorption and steady-state fluorescence spectroscopy to determine prevalent deactivation mode(s). Of the species investigated, weak fluorescence can be observed only for substituted triarylamine radical cations, presumably from their lowest excited doublet states. The primary excited-state deactivation pathway for radical anions of the quinones, aryl ketones, and cyanoarene hydrocarbons examined here is internal conversion from the lowest excited doublet state to the ground-state doublet. The efficiency of this deactivation mode arises typically from a low D_0 - D_1 energy gap, as demonstrated by near-infrared absorbance in each species. Contrary to a prior literature report, the 9,10-anthraquinone radical anion and the 9,10-dicyanoanthracene radical anion are nonluminescent in solution. Luminescent side products generated in ground-state reactions of these radical anions are identified as 9,9-bianthrone dianion (from the dimerization and deoxygenation of the anthraquinone radical anion) and 10-cyanoanthrolate (from the reaction of dicyanoanthracene radical anion with molecular oxygen).

Introduction

Photocatalysis via electron transfer has gained considerable attention because of the widespread applicability for chemical synthesis^{1,2} and in imaging technologies.³ As such, the introduction of novel photoinduced electron-transfer agents with desirable photochemical and photophysical properties is of primary importance. We have been interested in the identification and the development of open-shell organic molecules, specifically organic neutral free radicals or radical ions, as novel electron donor or acceptor photocatalysts. A major focus of this research effort has been the investigation of the photophysics and photochemistry of stable neutral free radicals.4-6 Organic stable free radicals, by virtue of their oxidation level intermediate between that of a cation and an anion, can interact by electron exchange with energetically suitable electron donors or acceptors. For example, electron-transfer fluorescence quenching of the lowest excited doublet state of perchlorotriphenylmethyl and perchlorodiphenylmethyl radicals takes place upon interaction with either electron donors or acceptors.⁴ Although these excited radicals can catalyze one-electron reduction or oxidation, the accompanying photoinduced cyclization reaction precludes their use as efficient photocatalysts.

As with closed-shell molecules, the redox potentials of radical ions are expected to be substantially changed upon photoexcitation compared from those attained in the ground state (Figure 1). For example, ground-state 9,10-anthraquinone radical anion (AQ⁺⁻), already a potent electron donor with a single electron residing in π^* orbital at -0.86 V vs SCE in DMF,⁷ has enhanced electrondonating ability compared with the ground state since excitation promotes a single electron into a higher-energy antibonding orbital (-2.1 V).^{8,9} Similarly, radical cations are transformed into stronger electron acceptors in the excited state, since the lowestenergy transition involves promotion of an electron from a lowenergy filled molecular orbital to the singly occupied molecular orbital (SOMO), thus creating an electron vacancy at a higher oxidation potential.¹⁰

Chemical reactions catalyzed by excited radical ions at electrode surfaces^{11,12} and in solution¹³⁻¹⁹ have been the topic of several studies. In pioneering work, Reverdy and Moutet have shown that photoexcited radical cations can be employed in catalytic



Anthraquinone Radical Anion

Figure 1. Molecular orbital energy diagram depicting excitation of AQ*-.

cycles as single-electron oxidants.¹³⁻¹⁷ However, the nature of this excited-state electron transfer is still not clear since no data on the excited-state characteristics of the radical ion were presented. More recently, Shine and co-workers have shown that the weakly luminescent excited state of N-methylphenothiazine radical cation can also catalyze one-electron oxidation,¹⁹ specifically for the activation of phenylacetylenes.

A prerequisite for understanding the photochemistry of a radical ion is a thorough characterization of its photophysics. Examples of luminescence from radical ion excited states in the gas phase and frozen matrices are numerous, 20,21 whereas fluorescence from these species is rare in solution.²²⁻²⁵ Electron-transfer fluorescence quenchings of the 9,10-anthraquinone radical anion (AQ*-), 9,10-dicyanoanthracene radical anion (DCA*-), and thianthrene radical cation (TA*+) have been reported^{23,24} and are suggestive of photocatalytic activity. The rates of electron-transfer quenching of the excited states of these radical ions were unusually slow when analyzed using the Rehm-Weller equation, and abnormally high bond reorganization energies were invoked to explain this phenomenon. We have reinvestigated the spectroscopy of these radical ions, along with several others, seeking to explore the utility of these species as novel photoinduced electron-transfer catalysts by examining their photophysical properties.

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Figure 2. Absorption spectra of a 10^{-4} M solution of 9,10-anthraquinone radical anion before photolysis (AQ⁻⁻) and after (BA²⁻) in deareated DMF containing 0.1 M TBAPF₆ at 25 °C.

Results and Discussion

Quinone Radical Anions. The half-lives of simple benzoquinone and naphthaquinone radical anions are approximately minutes.⁷ Therefore, these species cannot be investigated without taking into account potential complications arising from ground-state products. The analysis is greatly simplified by using a more stable radical anion, as is achieved by extending the π -system as in 9,10-anthraquinone (AQ^{*-}).⁷

The bulk electrolysis of a 1×10^{-4} M solution of AQ at -1.0 V (vs SCE) in DMF/TBAPF₆ electrolyte solution produces an intense fuchsia color attributable to anthraquinone radical anion.²⁶ The D₀-D₁ transition is located in the near-infrared (NIR) region with λ_{max} at 1050 nm in DMF solution. The D₀-D₂ and D₀-D₃ transitions have maxima in the visible at 570 and 413 nm, respectively. Because of the D₀-D₁ NIR transition, luminescence reported at 580 nm,^{23,24} if correctly assigned to AQ^{•-} would require fluorescence from the second excited state, an improbable but not impossible event. Alternatively, this blue-shifted luminescence could be the result of intersystem crossing to the quartet manifold, since the lowest quartet state must be of higher energy than the first excited doublet.¹⁰

Freshly prepared AQ radical anion solutions are nonluminescent and remain so when stored in the dark for as long as 15 h. However, under photolytic conditions (room light is sufficient), changes in the visible absorption spectra are observed, as shown in Figure 2, along with simultaneous bleaching of the D_0-D_1 NIR band. The 570-nm absorption band (D_0-D_2) exhibits noticeable change, the absorption at λ_{max} being decreased more than one-half, while the shoulder at 525 nm remains relatively unchanged. At shorter wavelengths, the lower vibrational energy component of the D_0-D_3 transition at 430 nm is increased to approximately twice its original intensity. The absorption and emission spectra of this photoproduct are identical with those of an authentic sample of 9,9'-bianthrone dianion (BA²⁻).²⁷ Furthermore, an excitation spectrum of the luminescence at 580 nm corresponds exactly to the absorption spectrum of BA²⁻, thus demonstrating that luminescence is a consequence of a photochemically generated fluorescent product.

A proposed reaction scheme for this transformation is shown in Scheme 1 in which photolysis induces coupling not observed with the ground-state radical. Details of the chemical sequence ultimately leading to formation of 9,9'-bianthrone dianion are not yet clearly understood, but a series of steps that may include sequential proton transfers and dehydrations are probably involved. Photolysis of a 1:1 reaction mixture of AQ⁻⁻ and AQ with light of wavelength longer than 500 nm, where only AQ⁺⁻ SCHEME 1: Proposed Mechanism of Photochemical Conversion of Anthraquinone Radical Anion to Bianthrone Dianion



absorbs, did not result in observable coupling. However, the photochemical conversion to bianthrone dianion was efficiently induced with 350–500-nm light, suggesting that the reaction is the result of excitation of AQ itself or of a thermally reversible intermediate. The quantum yield for conversion of AQ radical anion into BA^{2-} in this wavelength region is approximately 0.3 in DMF containing 0.1 M TBAPF₆ electrolyte. This highly efficient bimolecular photochemical transformation is suggestive of trapping of a long-lived triplet excited state, produced in high yield by intersystem crossing of the neutral quinone. AQ efficiently intersystem crosses to its lowest triplet state with quantum yield of 0.9;²⁸ the triplet state lifetime is approximately 3 ms in solution.²⁹

The lack of any observable nonemissive transients with nanosecond lifetimes upon excitation at wavelengths longer than 500 nm and the absence of steady-state fluorescence in carefully prepared reductive bulk electrolyses of AQ indicate efficient nonradiative decay of the excited state of AQ^{•-}. The NIR absorption band is predictive of efficient internal conversion, because of the low energy gap between D_0 and D_1 .

If the bianthrone dianion rather than AQ^{-} is responsible for the observed fluorescence, the anomalous electron-transfer quenching rates obtained in a Rehm–Weller plot of excited AQ radical anion^{23,24} can be resolved. Substituting the oxidation potential of BA²⁻ (-0.30 V vs SCE)³⁰ into Rehm–Weller equation results in excellent agreement for observed electron-transfer quenching rates with theory and obviates the need to postulate unusual reorganization energies associated with electron-transfer quenching.

Metal Ketyl Radical Anions. In the absence of molecular oxygen and proton sources, solutions of metal diarylketal radical anions are sufficiently stable for ground-state characterization by absorption and ESR spectroscopy.³¹⁻³³ The absence of any reports of luminescence from ketyl radical ions stands in striking contrast to that from the corresponding neutral ketyl radicals, which are highly fluorescent.^{34,35}

The radical anions of benzophenone, fluorenone, and xanthone, produced either electrochemically (in DMF or THF) or by direct reduction with sodium metal (THF), are highly colored.²⁶ Benzophenone radical anion ($\lambda_{max} = 800$ nm) exhibits neither measurable fluorescence ($\phi < 10^{-5}$) nor any nonemissive transient excited state living for nanoseconds or longer. The absence of fluorescence is anticipated because of the low energy of the D₀-D₁ electronic transition, which can easily couple with available vibronic modes, leading to excited-state deactivation. Searching for fluorescence or transient absorptive excited states in a solid 3-methyltetrahydrofuran glass at 77 K, where vibrational and rotational freedom are restricted, was also unsuccessful. Covalent linking of the phenyl groups in fluorenone and xanthone enhances the structural rigidity, but this shifts the D₀-D₁ absorption band to even lower energies (1020 and 1300 nm, respectively). Attempts to observe transients by excitation of these radical ions were also unsuccessful, either in solution or in a 3-methyltetrahydrofuran glass at 77 K.

Radical Anions of Cyanoarenes. The radical anions of 9,10dicyanoanthracene (DCA) and 1,2,4,5-tetracyanobenzene (TCB) are thermally stable.³⁶ Electrochemical reduction of DCA in DMF containing 0.1 M TBAPF₆ supporting electrolyte results in a distinctively purple colored solution, with a lowest-energy absorption maxima at 708 nm.²⁶ Any emissive state would be expected to be red-shifted from this band, and luminescence was not observable upon excitation at 600 nm. However, an emission identical to that reported for DCA⁻⁻ ($\lambda_{max} = 530$ nm) is observed upon excitation at 450 nm.²³ Luminescence could potentially arise from fluorescence from an upper excited state or quartet phosphorescence, as discussed for AQ*-. However, when the purple color of DCA^{•-} is completely discharged upon exposure to air, the emission still remains intact. As with AQ⁻⁻, this fluorescence can be assigned to a side product, 10-cyanoanthrolate, initially observed by Janzen in the chemiluminescent oxygenation of DCA^{--,37} We have more thoroughly described elsewhere this chemiluminescent reaction, which takes place by fragmentation of an intermediate dioxetanimine dianion.³⁸ As with the Rehm-Weller analysis of AQ*-, substitution of -0.2 V, the oxidation potential measured for 10-cyanoanthrolate in DMF, for the reduction potential of DCA leads to good correspondence between published experimental rate constants^{23,24} and theory, without the need to invoke unusual reorganization energies for the electrontransfer quenching.

A yellow solution whose absorption spectrum identically matches that reported for TCB radical anion²⁶ results from the bulk electrolysis of TCB at -0.5 V (vs SCE) in a 0.1 M TBAPF₆/ DMF electrolyte. The absorbance spectrum of TCB^{•-} is a broad structureless band centered at 460 nm. Steady-state fluorescence measurements showed emission at 420 nm, blue-shifted from the absorption band. The excitation spectrum obtained by monitoring fluorescence at 420 nm did not match the absorption spectrum of TCB⁻⁻. The introduction of molecular oxygen by exposure to air resulted in immediate bleaching of the TCB⁻⁻, with a simultaneous increase in the fluorescence intensity at 420 nm. Oxygenation of TCB⁻⁻ produces a fluorescent species, presumably 2,4,5-tricyanophenolate anion, in an analogous reaction to DCA. with O₂. Addition of an aqueous HCl solution, sufficient to completely protonate this product, led to quantitative fluorescence quenching. Luminescence was fully restored when the acidic solution was made basic by titrating with aqueous KOH, demonstrating that 2,4,5-tricyanophenolate ion is the luminescent product. Attempts to detect transients from excited TCB⁻⁻ by nanosecond laser flash photolysis were ambiguous, because even low concentrations of the highly fluorescent 2,4,5-tricyanophenolate anion product interfered.

Radical Cations of Substituted Triarylamines. The thermal stability of substituted triarylamine radical cations is exemplified by their use as single electron oxidants for the catalysis of Diels-Alder reactions.³⁹ This class of radical ions is known to be photoactive, since their solutions bleach when exposed to light,⁴⁰ although products and mechanism of the photochemical transformation(s) have not been fully explored.

 TABLE 1: Absorption and Emission Data for Substituted

 Triarylamines in CH2Cl2

compd	absorbance (max), nm	emission (max), nm	fluorescence quantum yield
TBA	716	790	~10-5
TMA	726	803	~10-5

The excited states of the radical cations of tris(4-bromophenyl)amine (TBA) and tris(4-methoxyphenyl)amine (TMA) were studied in methylene chloride solution. The TBA and TMA radical cations are dark blue, and extremely weak fluorescence is observed upon excitation into this broad visible absorption band (Table 1). The emission maxima and fluorescence quantum yields for TBA and TMA radical cation are also compiled in this table. Emission is expected in this spectral region since there are no observable lower-energy electronic transitions.²⁶

Preliminary investigation of the photolysis mixture shows that photocyclization competes with fluorescence in these radical cations, since GC mass spectrometry reveals a product with two fewer protons (eq 1).



Photocyclizations of this type are well-documented for the lowest excited triplet state of di- and triarylamines,⁴¹ as well as for the lowest excited states of isoelectronic transient and stable diphenylmethyl radicals.^{4,42} Photocyclization appears to be facile, since bleaching of the ground-state absorption (650 nm) takes place during the 10-ns excitation pulse and never recovers. The low quantum yield for fluorescence in TBA and TMA radical cations can presumably be assigned to thermal relaxation and this competing photochemical process.

Conclusions

Extreme caution is needed when assigning luminescence from species with reactive ground states such as radical ions. AQ⁻ and DCA⁻ are not luminescent in solution, the observed luminescence being instead assigned to side products. The lack of luminescence in most radical ions presumably arises from the small energy gaps between the ground and excited states, evidenced by strong absorption bands in the NIR. Because the excitedstate lifetimes of typical radical ions are short, they are poor candidates for use as efficient photosensitizers. Although substituted triarylamines could potentially be used as mechanistic probes for photoinduced electron transfer since they fluoresce weakly, a competing photochemical cyclization is a potential drawback.

Experimental Section

Reagents. 9,10-Anthraquinone (Aldrich) was recrystallized twice from acetic acid. 9,10-Dicyanoanthracene (Kodak) was recrystallized twice from nitromethane. Fluorenone and xanthone (Aldrich) were recrystallized from ethanol. 1,2,4,5-Tetracy-anobenzene (Pfaltz and Bauer), tetrabutylammonium hexafluorophosphate (Southwestern Analytical), and bianthrone (Aldrich) were used without further purification. Dimethylformamide (Baker) was dried over molecular sieves prior to use. 3-Methyltetrahydrofuran (Aldrich) was purified by simple distillation. Tris(4-bromophenyl)aminium hexafluoroantimonate was purified by a literature method.⁴³

Letters

Electrochemical Measurements. A Bioanalytical Systems 100 potentiostat equipped with a Houston Instruments DMP-40 plotter was used for bulk electrolyses and cyclic voltammetry. A three-electrode cell configuration, consisting of a platinum working electrode, a Ag/AgCl quasi-reference electrode, and a platinum auxiliary electrode, was used. Typically, bulk electrolyses were performed on 10⁻⁴ M solutions in the appropriate solvent containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte. Oxygen was removed by an argon purge.

Spectral Measurements. Fluorescence spectra were recorded on a SLM Aminco SPF-500 spectrofluorimeter equipped with an IBM 6180 plotter. Absorption spectra were recorded on a Hewlett-Packard 8451-A diode array spectrophotometer equipped with a Hewlett-Packard 7470 plotter. NIR absorption spectra were recorded on a Cary 7 instrument.

Transient Absorption Spectroscopy. Time-resolved flash photolysis experiments were conducted on a Q-switched Nd:YAG laser (Continuum Surelite Model 30A-P). Absorptive transients were monitored with a conventional 150-W Xe lamp, PTI monochromator, and Hamamatsu R928 photomultiplier arrangement. Signals were passed to a Tektronix Model 540 digitizing oscilloscope interfaced to a personal computer.

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