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Ming-De Li  
University of Hong Kong

Toshia Albright  
Iowa State University

Patrick J. Hanway  
Iowa State University

Mingyue Liu  
University of Hong Kong

Xin Li  
University of Hong Kong

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Authors
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Direct Spectroscopic Detection and EPR Investigation of a Ground State Triplet Phenyl Oxenium Ion

Ming-De Li,‡ Toshia R. Albright,‡ Patrick J. Hanway,‡ Mingyue Liu,† Xin Lan,† Songbo Li,† Julie Peterson,† Arthur H. Winter,*‡ and David Lee Phillips*‡

‡Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong, S.A.R., P. R. China
†Department of Chemistry, Iowa State University, 2101d Hach Hall, Ames, Iowa 50011, United States

Supporting Information

ABSTRACT: Oxenium ions are important reactive intermediates in synthetic chemistry and enzymology, but little is known of the reactivity, lifetimes, spectroscopic signatures, and electronic configurations of these unstable species. Recent advances have allowed these short-lived ions to be directly detected in solution from laser flash photolysis of suitable photochemical precursors, but all of the studies to date have focused on aryloxenium ions having closed-shell singlet ground state configurations. To study alternative spin configurations, we synthesized a photoprecursor to the m-dimethylamino phenyloxenium ion, which is predicted by both density functional theory and MRMP2 computations to have a triplet ground state electronic configuration. A combination of femtosecond and nanosecond transient absorption spectroscopy, nanosecond time-resolved Resonance Raman spectroscopy (ns-TR3), cryogenic matrix EPR spectroscopy, computational analysis, and photoproduct studies allowed us to trace essentially the complete arc of the photophysics and photochemistry of this photoprecursor and permitted a first look at a triplet oxenium ion. Ultraviolet photoexcitation of this precursor populates higher singlet excited states, which after internal conversion to S1 over 800 fs are followed by bond heterolysis in ~1 ps, generating a hot closed-shell singlet oxenium ion that undergoes vibrational cooling in ~50 ps followed by intersystem crossing in ~300 ps to generate the triplet ground state oxenium ion. In contrast to the rapid trapping of singlet phenyloxenium ions by nucleophiles seen in prior studies, the triplet oxenium ion reacts via sequential H atom abstractions on the microsecond time domain to ultimately yield the reduced m-dimethylanilinophenol as the only detectable stable photoproduct. Band assignments were made by comparisons to computed spectra of candidate intermediates and comparisons to related known species. The triplet oxenium ion was also detected in the ns-TR3 experiments, permitting a more clear assignment and identifying the triplet state as the a,a,a* triplet configuration. The triplet ground state of this ion was further supported by photolysis of the photoprecursor in an ethanol glass at ~4 K and observing a triplet species by cryogenic EPR spectroscopy.

INTRODUCTION

Oxenium ions are reactive intermediates of formula R−O+. These species are the isoelectronic oxygen analogue of the more familiar nitrene class of intermediates, but bear a formal positive charge on a hypovalent oxygen. Like nitrenes, oxenium ions can be stabilized by transition metals, acting as novel ligands, but in their free form they are short-lived in solution, as might be expected of a species forced to suffer from such an inharmonious electronic arrangement. Of more synthetic relevance, these transient species have often been proposed as intermediates in a number of synthetically useful oxidation reactions of phenols,2−6 including the oxidative Hosomi−Sakurai reaction7−9 and Wagner−Meerwin transposition,9 electrochemical oxidations of phenols and phenolates,6,10,11 and a plethora of other phenolic oxidations and tautomerization reactions. They are also suggested to be key intermediates in the industrial production of materials like poly(phenyl)ether (PPE), an industrial thermoplastic.12−14 In addition, the enzymatic oxidative mechanisms of phenols to quinones are proposed to involve the intermediary of discrete oxenium ions.15 Despite their chemical importance, mechanistic studies of oxenium ions are limited.

Previous experimental studies of aryloxenium ions have been performed by either photochemical or thermal generation methods. In the 1970s and early 1980s, Abramovitch and Okamoto used thermolytic methods to generate aryloxenium ions. Studies of their stable end products permitted indirect characterizations of their reactivity.13,14 Later, Novak and coworkers investigated the reactivities of aryloxenium ions using both thermal and photochemical generation methods.16 Only recently have aryloxenium ions been directly detected by laser flash photolysis in solution. In 2007, Novak, Platz, and coworkers reported the first direct detection of aryloxenium ions in solution (a biphenyl oxenium ion) using laser flash photolysis, providing definitive evidence that these reactive ions are in fact discrete intermediates in solution.17

Like nitrenes, oxenium ions can adopt different electronic configurations. The electronic state energies of phenyl oxenium ions,18...
ions and some simple substituted derivatives have previously been computed using the CASPT2//CASSCF computational method. These computational studies suggested that oxenium ions undergo large changes in the electronic state orderings by changing the substituent attached to the formally positive oxygen. For instance, the simplest oxenium ion, OH+, has degenerate frontier orbitals and a triplet ground state with a gap of 54 kcal/mol to the lowest energy singlet state. Substituting the hydrogen with a phenyl ring leads to the lowest-energy state being a closed-shell singlet ground state by ~20 kcal/mol. Computations suggest most simple aryloxenium ions are closed-shell singlet ground state species, although heteroaryl oxenium ions may adopt alternative electronic states. The singlet ground state of the phenyl oxenium ion is supported by both photoelectron spectroscopy and the results from these high-level computational methods.

Following Novak and Platz’s detection of a substituted biphenyloxenium ion derivative, we used selected protonated hydroxylamine salts as novel photoprecursors to generate both the parent phenyloxenium ion and the biphenyloxenium ion as a product from the photoheterolysis of the aryl hydroxylamine tetrafluoroborate salt. In addition to a concomitant homolytic process, these hydroxylamine salts also undergo heterolytic scission of the O–N bond to lead to the generation of the singlet aryloxenium ion and neutral ammonia. These results allowed comparisons to the neutral photoprecursor studied by Novak, Platz, and co-workers, highlighting the unique differences in the photochemistry/photophysics of the precursors. To summarize the prior results, the aryloxenium ions studied thus far have had closed-shell singlet ground states and lifetimes of a few nanoseconds in solution, typically reacting with nucleophiles (e.g., ammonia, chloride, water) at the ortho and para positions to generate ring-substituted phenols as the ultimate stable photoproducts. See Figure 1. To date, essentially nothing is known about the reactivity of triplet aryloxenium ions.

Here, we report a combined femtosecond transient absorbance (fs-TA), nanosecond transient absorbance (ns-TA), and nanosecond time-resolved resonance Raman (ns-TRr) spectroscopic investigation of the photophysics and photochemistry of m-DMAP 1 that allowed us to directly observe the formation of the ground state triplet phenyloxenium ion after ultraviolet photoexcitation in a MeCN/H2O solution. We also studied the triplet ion by cryogenic matrix photolysis of the photoprecursor in an EtOH glass and observed a triplet species in the electron paramagnetic resonance (EPR) spectrum at 4 K, providing strong evidence for this ion having a triplet ground state. To our knowledge this is the first direct observation and reactivity study of a ground state triplet aryloxenium ion.

### EXPERIMENTAL AND COMPUTATIONAL METHODS

The m-dimethylamino phenylhydroxylamine 1 photoprecursor was synthesized, purified, and characterized via standard methods (see the Supporting Information for synthetic procedures and spectra). Spectroscopic-grade acetonitrile (MeCN) and deionized water were used to prepare the sample solutions for use in the time-resolved spectroscopy experiments. In all of the time-resolved experiments, the sample solutions were purged with argon for 30 min. During the experiments, the sample solutions were also purged with argon.

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![Figure 1](image-url)  
**Figure 1.** Overview of this work and prior work.

![Figure 2](image-url)  
**Figure 2.** Possible schematic electronic configurations considered for the m-dimethylamino phenylhydroxylamine ion. Computations suggest the ground configuration is the π,π* triplet configuration and the lowest energy singlet state is the closed-shell configuration.
Matrix EPR studies were performed using an X-band EPR spectrometer with a temperature control unit capable of achieving near liquid helium temperatures (∼4 K) and equipped with a UV-emitting mercury light source channeled into the cavity using a fiber optic cable. More detailed information on the EPR settings and EPR simulation parameters can be found in the Supporting Information.

5. Computational Studies. We computed the singlet–triplet gap ($\Delta_{ST}$) of the m-dimethylamino phenyloxenium ion 2 using density functional theory (B3LYP/6-31G(d,p)). The $\Delta_{ST}$ at the DFT level of theory was computed to be +12.5 kcal/mol in favor of the triplet state. Because we found a RHF → UHF instability in the singlet state by DFT, for added confidence an MRMP2(8,8)/6-31G(d)//MCSCF-(8,8)/6-31G(d) calculation was also performed using a complete π active space. At this level of theory, the $\Delta_{ST}$ is computed to be +9.3 kcal/mol in favor of the triplet state and the lowest energy singlet state is found to be the closed shell configuration. Thus, the computational studies make a clear prediction that the triplet state is the lowest energy electronic configuration for 2, with the triplet state being a ππ* configuration. This ππ* triplet configuration can be arrived at conceptually by starting with the closed-shell singlet state and transferring an electron from the nitrogen lone pair to the empty π* orbital associated with oxenium ion center. See Figure 2. The TD-DFT methodology was performed to predict the UV–vis absorption spectra of the candidate transient species generated from the photolysis of the photoprecursor (TD-B3LYP/6-31G(d,p)).29 GaussSum software was utilized to simulate the UV–vis spectra.30 To predict the TR3 spectra, second-order Möller–Plesset perturbation theory (MP2) with a 6-311G(d,p) basis set was employed to optimize the structures and predict the Raman spectra of key intermediates. A Lorentzian function with a 15 cm⁻¹ bandwidth for the vibrational frequencies and a frequency scaling factor of 0.974 was used in the comparison of the calculated results with the experimental spectra.31 No imaginary frequency modes were observed at the stationary states of the optimized structures. All of the calculations were done using the Gaussian 03/09 program except for the MRMP2//MCSCF computations, which were computed with the GAMESS software.33

RESULTS AND DISCUSSION

1. Femtosecond Transient Absorption Investigation of m-Dimethylamino Phenylhydroxylamine Hydrochloride 1. Figure 3 shows the evolution of the transient absorption

![Figure 3](image-url)
of m-dimethylamino phenylhydroxylamine (m-DMAP) 1 in an acetonitrile/water (MeCN/H₂O) 1:1 mixed solution from 0.96 to 2990 ps. The spectra at early (Figure 3, top left), middle (Figure 3, top right), and later delay times (Figure 3, bottom left) are given separately to more easily discern the spectral changes that take place on different time scales. First we discuss the observations and our assignments of the transients and then we detail how we made all of the assignments. When using 267 nm as excitation wavelength, the m-DMAP 1 can be excited to higher singlet excited states Sₚ. TD-DFT computations indicate that the predominant absorption of 1 at 267 nm is the Sₗ→Sₚ transition. See the Supporting Information. Over ~800 fs, 1 undergoes internal conversion (IC) and evolves from Sₚ into the S₁ excited state (see Figure 1S and Table 1S for spectra from 450 to 1000 fs). After 1 ps, the absorptions are assigned to the S₁ precursor excited state having an absorption centered at ca. 360 nm. This band rapidly decays over ~1 ps into a new transient having major absorptions at 485 and 627 nm, assigned to the closed-shell singlet oxenium ion ². Similarly, prior studies of the protonated hydroxylamine photoprecursors shown in Figure 1 underwent bond cleavage in ~2 ps. In the top right of Figure 3, it can be seen that the broad bands centered at 485 and 627 nm slightly decayed and noticeably shifted with time toward a shorter wavelength and a longer wavelength, respectively, over ~55 ps, ultimately yielding a sharp band at 476 nm and a broader absorption band centered at ~650 nm. This process is attributed to vibrational cooling as the hot-born oxenium ion sheds heat to solvent, a phenomenon that has also been seen in the prior work following O→N bond cleavage.

Subsequently, the two bands decay over ~550 ps to generate a new band at ~485 nm. This conversion is attributed to intersystem crossing of the singlet oxenium ion ² to the triplet phenyloxenium ion ³. Finally, this band converts to a new band over ~1 μs to a band at 494 nm, attributed to the m-dimethylamino phenol radical cation (see Figure 7), which slowly decays into a final product at 357 nm. An isosbestic point at 394 nm indicates a clean conversion between the latter two species.

2. TD-DFT Calculated Electronic Absorption of Candidate Intermediates after m-DMAP 1 Photolysis

Time-dependent density functional theory (TD-DFT) computations have been previously demonstrated to be useful in estimating the absorption bands for transient species in previous work. For example, they are frequently used for assigning absorption bands for carbenes, nitrenes and oxenium ions. To help assign the transients observed in the fs-TA experiments, we have performed TD-B3LYP/6-311G(2d,p) calculations to estimate the UV–vis absorption for some likely candidate species that could be generated from the excited singlet state of m-DMAP 1. TD-DFT computations were done to estimate the electronic absorption spectra of the m-dimethylamino phenoxyn radical, the triplet m-dimethylamino phenyloxenium ion and the singlet m-dimethylamino phenyloxenium ion. The results using TD-B3LYP/6-311G(2d,p) for these calculations are shown in Figure 4. The computed absorption spectrum for the singlet m-dimethylamino phenyloxenium ion gives a single band at 418 nm in the 300–600 nm region, and this does not agree with the experimental spectra at early delay time (1.6–12 ps) where there are one maximum transient absorptions at about 485 nm and a tailing broad shoulder transient absorption at 627 nm (see Figure 3). We noted that singlet carbenes have been reported to form complexes with solvents such as acetonitrile (and even form ylides in some cases). Thus, we considered the possibility that the singlet oxenium ion was forming a solvent complex, which might alter its absorption profile. Indeed, by adding explicit complexing waters (1, 3, 4 water molecules), the computed TD-DFT absorption spectra of singlet oxenium ion in the absence of water and in the presence of one water molecule did not match with the experimental spectra at early delay time, while the simulated absorption spectra of singlet oxenium ion water adducts in the presence of 3 and 4 water molecules give reasonable agreement with the experimental bands recorded at 19 ps (see Figure 4). At much earlier times, the 476 nm band slightly shifts and decays, and the higher-wavelength 650 nm band becomes relatively smaller. TD-DFT calculation reveals that only water adducts of the singlet oxenium ion rather than the gas phase isolated singlet oxenium ion have the contribution of absorption at around 600 nm (see Figure 4). Therefore, the decay of the 650 nm band is likely associated with the vibrational cooling and the reorientation of the solvent around the singlet oxenium ion.

Figure 4. Shown are the computed electronic spectra of the m-dimethylamino phenoxyn radical (top left), the triplet m-dimethylamino phenyloxenium ion ³ (top right), and the singlet m-dimethylamino phenyloxenium ion ² (bottom left) from TD-B3LYP/6-311G(2d,p) calculations. Bottom right of the figure shows the experimental UV–vis spectrum at 19 ps after the pulse and the computed spectrum of the singlet m-dimethylamino phenyloxenium ion in the presence and absence of explicit solvent waters (note that the simulated spectrum goes to 300 nm to show smaller computed shoulder band).
consistent with the CASSCF calculations described earlier that also indicate that the lowest-energy singlet state is the closed-shell singlet state. Based on our previous study, a ground state singlet aryloxenium ion can be trapped by water molecules or other nucleophiles (chloride, ammonia). In this study, we see no trapping adducts for this oxenium ion, which might be attributed to its short lifetime, decaying into new absorption bands at 357 and 484 nm, which can still be observed at 3 ns. In addition, it should be noted that allylic strain interaction generated by the dimethylamino moiety in the meta position may also prevent nucleophilic additions in para and one ortho position. Although the computed absorption spectrum for the meta-dimethylamino phenoxy radical and triplet meta-dimethylamino phenyloxenium ion have two bands at around 300 and 428 nm, which are in good agreement with the experimental spectra in shape at later delay time (Figure 3), the observation of triplet meta-dimethylamino phenyloxenium ion by ns-TR3 (described later) indicates that this new transient at 357 and 484 nm should be assigned to the triplet meta-dimethylamino phenyloxenium ion, not the meta-dimethylamino phenoxy radical.

3. ns-TR3 Experiments Identify the Transient at 357 nm as the π,π* Triplet meta-Dimethylamino Phenyloxenium Ion. In order to identify the transient species seen at around 3 ns, ns-TR3 experiments for m-DMAP 1 were carried out in an aqueous acetonitrile solution. Figure 5 shows the ns-TR3 spectra obtained with various delay times after 266 nm photoexcitation of meta-dimethylamino phenyloxenium and using a 355 nm as the probe wavelength in a MeCN/H2O 1:1 solution.

The 10 μs spectrum subtracted from it in a MeCN/H2O 1:1 solution and the calculated normal Raman spectrum of the triplet meta-dimethylamino phenyloxenium ion 2 using results from MP2/6-311G(d,p) calculations (blue). (Right) Comparison of the ns-TR3 spectrum obtained at 10 μs in a MeCN/H2O 1:1 solution (red) and the calculated normal Raman spectrum of the meta-dimethylamino phenol radical cation using results from B3LYP/6-311G(d,p) calculations (blue). Asterisks (*) represent solvent subtraction artifacts. See the text for more details.

Figure 6. (Left) Comparison of the ns-TR3 spectrum obtained at 20 ns with an appropriately scaled 10 μs spectrum subtracted from it in a MeCN/H2O 1:1 solution (red) and the calculated normal Raman spectrum of the triplet meta-dimethylamino phenyloxenium ion 2 using results from MP2/6-311G(d,p) calculations (blue). (Right) Comparison of the ns-TR3 spectrum obtained at 10 μs in a MeCN/H2O 1:1 solution (red) and the calculated normal Raman spectrum of the meta-dimethylamino phenol radical cation using results from B3LYP/6-311G(d,p) calculations (blue). Asterisks (*) represent solvent subtraction artifacts. See the text for more details.

4. A ns-TA Experimental Study on the Reactivity of the Triplet meta-Dimethylamino Phenyloxenium Ion. The results from the ns-TR3 study on the meta-dimethylamino phenyloxenium indicated that the triplet meta-dimethylamino phenyloxenium ion is completely consumed within about 10 μs...
to produce the radical cation in an aqueous solution. The ns-TA experiments show that the band at 356 nm continues in intensity while the band at 494 nm decreases in intensity (see Figure 7). There is an isosbestic point at around 396 nm for this process, indicating a clear transformation between a precursor species and a product species. The temporal dependences of the transient absorption intensity of initial compound in a MeCN/H₂O 1:1 mixed solution acquired after 266 nm irradiation of the initial precursor compound. See the text for more details. (Bottom) Temporal dependences of the transient absorption intensity of initial compound in a MeCN/H₂O 1:1 mixed solution at 356 nm (left) and 494 nm (right). Solid red line indicates fittings using a biexponential function.

6. Product Studies from Photolysis of 1. Additional evidence for a triplet ground state for the m-dimethylamino phenyloxenium ion comes from analysis of the photoproducts. The only detectable photoproduct of 1 in water by ¹H NMR is m-dimethylaminophenol. This single photoprodct observed from photolysis is in sharp contrast to photolysis of the unsubstituted phenol hydroxylamine hydrochloride, which gave additional nucleophile trapping adducts (e.g., chlorophenol, hydroquinone, catechol, protonated o/p aminophenols, etc.). In general, one expects nucleophile adducts of a single phenyloxenium ion. Reactivity of a triplet phenyloxenium ion is less certain, but by analogy with related reactive intermediates (e.g., carbenes, nitrenes, etc.), one would expect radical ion chemistry (e.g., H atom abstraction). The parent phenyloxenium ion is a singlet ground state ion, so these nucleophile trapping adducts are not surprising. In contrast, the reduced product found from photolysis of 1 might be expected from a triplet oxenium ion as a result of sequential H atom abstraction processes (followed by loss of a proton) rather than nucleophilic trapping chemistry. Thermolysis studies of 1 led to insoluble tars, likely from oxidation or polymerization (m-dimethylaminophenol itself is an electron-rich species and is unstable to oxidation).

7. Cryogenic EPR Studies from Photolysis of 1 in EtOH Glass Indicates Triplet Ground State for 2. Further evidence for the ground state of the m-dimethylaminophenol being a triplet state comes from low-temperature matrix isolation experiments. A low-temperature EtOH glassy matrix photolysis study of 1 (at 4 K), performed in the cavity of an EPR spectrometer, provided the spectrum shown in Figure 8. The signals in the EPR spectrum are consistent with the formation of a triplet diradical species as well as a monoradical impurity (perhaps arising from a competitive homolysis pathway or from a back electron transfer process). This EPR spectrum provides evidence that the ground state of the oxenium ion is the triplet state, since at 4 K essentially no thermal population of an excited triplet state would be possible outside of having virtually degenerate singlet and triplet energies. The value of the IDI/ℏc parameter (0.026 cm⁻¹) seen here is very close to that of the m-quinone methide IDI/ℏc parameter (0.027 cm⁻¹) reported by Berson and co-workers, perhaps not surprising given the very similar electronic structure.

Figure 7. (Top) ns-TA spectra from 0 to 100 μs produced in a MeCN/H₂O 1:1 solution acquired after 266 nm irradiation of the initial precursor compound. See the text for more details. (Bottom) Temporal dependences of the transient absorption intensity of initial compound in a MeCN/H₂O 1:1 mixed solution at 356 nm (left) and 494 nm (right). Solid red line indicates fittings using a biexponential function.

Figure 8. X-band EPR spectrum of 1 irradiated in EtOH glass at 4 K using a mercury lamp source delivered via a fiber optic cable into the cavity. Triplet simulation parameters: D = 280 G (IDI/ℏc = 0.026 cm⁻¹), E/IDI = 0.075 G (7.0 × 10⁻⁶ cm⁻¹). Inset: Δmₛ = 2 transition.

Scheme 1. Proposed Mechanistic Pathway Based on Piecing Together the Spectroscopic Data
CONCLUSION

In conclusion, using a combination of pulsed laser spectroscopies, we have been able to map out essentially the complete photophysics and photochemistry pathways of 1 in aqueous acetonitrile. This photoprecursor undergoes a photoheterolysis reaction to generate initially the closed-shell singlet oxenium ion and then the triplet oxenium ion after intersystem crossing, which reacts via sequential H atom abstractions to yield a reduced product. One difference between this study and our prior studies with the protonated hydroxylamine photoprecursors is that the photoprecursors for making the phenyloxenium ion and biphenyloxenium ion reported previously gave a mixture of the oxenium ion resulting from a photoheterolysis pathway and the free radical resulting from a photohomolysis pathway of the O–N bond. In this study, we only observe the oxenium ion resulting from the photoheterolysis pathway and do not see transients we can attribute to the free radical. Perhaps the lack of a concomitant homolysis pathway can be attributed to the “meta effect,” a term coined by the late Howard Zimmerman to describe the propensity of the π,π* triplet state of the oxenium ion is longer-lived than the closed-shell singlet state oxenium ions, living for ~1.7 µs in solution. By comparison, singlet aryloxonium ions have lifetimes of a few nanoseconds in solution. The longer lifetime of the triplet state is similar to carbones and nitrenes whose triplet states can be seen with nanosecond spectroscopy, while the singlets often have lifetimes on the order of tens of picoseconds.

In future work, it would be interesting to compare the reactivity and lifetime of this π,π* triplet oxenium ion to an n,π* triplet oxenium ion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06302.

Synthetic procedures and compound characterization data; product studies; absolute energies and Cartesian coordinates; cryogenic EPR details and simulation parameters (PDF)

AUTHOR INFORMATION

Corresponding Authors
*winter@iastate.edu
*phillips@hku.hk

Notes

The authors declare no competing financial interest.

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