

2012

Theoretical and Experimental Studies of Oxenium Ions

Patrick James Hanway
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Theoretical and experimental studies of oxenium ions

by

Patrick James Hanway

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Organic Chemistry

Program of Study Committee
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Ames, Iowa

2012

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Chapter 1

Introduction

Oxanium ions are hypovalent species of formula $R-O^+$. These reactive intermediates are isoelectronic with nitrenes, with a formally monovalent oxygen containing two non-bonding electron pairs. Like nitrenes, the electron-deficient nature of these intermediates makes them powerful electrophiles, further amplified by the formal positive charge on the electronegative oxygen. These species are increasingly being proposed as intermediates in useful *umpolung* synthetic transformations, such as the oxidative Hosomi-Sakurai reaction,^{1,2} the oxidative Wagner-Meerwin transposition,³ electrochemical oxidations of phenols and phenolates,^{4,5} alkane oxidations,⁶ and a wide variety of other phenolic oxidations and tautomerization reactions.⁷⁻¹¹ These reactions convert phenols and alkanes, many of which are derived from petrochemical feedstocks, into value-added products such as cyclohexadienones, substituted phenols, oxidized alkanes, as well as petrochemicals like poly(1,4-phenylene ether) (PPE), a high-value industrial thermoplastic.¹²⁻¹⁴ They are also formed from exposing phenols, anisoles, and nitrobenzenes to ionizing radiation,¹⁵⁻¹⁷ are reactive intermediates in iron-mediated enzymatic oxidations of phenols into quinone compounds,¹⁸ and persist in interstellar clouds and planet atmospheres.^{19,20} Like nitrenes and carbenes, oxanium ions are short-lived in solution, but can form stable complexes with transition metals, acting as novel ligands.²¹ Given the importance of these species to such a diverse range of chemists, it is surprising how little basic science is known of this class of reactive intermediates.

Chapter 2

Phenyl oxenium Ions: More like phenylnitrenium than isoelectronic phenylnitrenes?

Taken in part or whole from: Hanway, P. J.; Winter, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 5086.

INTRODUCTION

This paper attempts to answer two fundamental questions to further the understanding of these reactive intermediates: 1) What is the nature and quantitative energetic orderings of the chemically relevant electronic states of the phenyl oxenium ion **1** (Ph-O⁺)?; and 2) How do simple substituents perturb these electronic state orderings? The parent oxenium ion, the hydroxy cation (OH⁺), is a ground-state triplet ion (³Σ⁻) with a large adiabatic energy gap of 54 kcal/mol to the lowest-energy singlet state (¹Δ).²² This favoring of the triplet state in this ion results from a degeneracy in the *p* orbitals, leading to adoption of a lowest energy spin unpaired state following a molecular orbital extension of Hund's rule. The lowest energy singlet state can also be nominally described as open-shell.

The ground state of aryloxenium ions, in contrast, is far less certain due to a breaking of the degeneracy of the frontier oxygen *p* orbitals from mixing of the ring π orbitals with the out-of-plane *p* orbital on the oxenium center. Indeed, in contrast to the parent hydroxy cation, experimental work thus far on aryloxenium ions has tended to implicate two-electron (closed-shell singlet) chemistry for aryloxenium ions rather than diradical chemistry.^{1,23-28} It should be noted, however, that since most thermal and photochemical methods generate the nascent oxenium ion in the singlet state irrespective

of whether this is the ground state, the observation of singlet reactivity is not conclusive evidence for the ion being a ground-state singlet. For instance, under certain conditions, triplet ground-state nitrenes decay via singlet channels because the reactions of the singlet nitrene occur faster than intersystem crossing;^{29,30} for carbenes, dynamic equilibria between a low-energy singlet and a triplet ground-state configuration can lead to predominantly singlet products under Curtin-Hammett conditions.^{31,32} Consequently, computation is a crucial partner with experiment in establishing the nature and quantitative orderings of the electronic states of these ions, particularly when experimental methods to obtain values for the singlet-triplet gap (such as ultraviolet photoelectron spectroscopy) are by no means straightforward.

Previous experimental studies of aryloxenium ions have been performed by either photochemical or thermal generation methods. In the 1970s and early 1980s, the labs of Abramovitch and Okamoto used thermolytic methods to generate aryloxenium ions.^{23-25,33,34} Product studies were subsequently used to indirectly characterize their reactivity. More recently, the lab of Novak has studied the reactivities of aryloxenium ions using both thermal and photochemical generation methods.²⁶ Only recently have oxenium ions been directly detected by solution-phase laser flash photolysis. In a noteworthy study in 2007, the groups of Novak and Platz reported the first direct detection of a discrete aryloxenium ion in solution (biphenyl oxenium ion) using laser flash photolysis; this transient species has a lifetime of 170 ns in water.³⁵

Some computational studies of aryloxenium ions have also been reported. In 1989, a study by Houk and Abramovitch (HF/STO-3G) was performed on the phenyloxenium ion **1** and meta-substituted derivatives.³⁶ A more recent computational

study by Glover and Novak (employing the pBP/DN**//HF/6-31G* level of theory) found that the closed-shell configuration (1A_1) of phenyloxenium ion **1** (Ph-O⁺) has more quinoidal character than the phenylnitrenium ion **2** (Ph-NH⁺).³⁷ Additionally, this study computed the singlet-triplet gaps (ΔE_{ST}) of several phenyloxenium ions at this level of theory, and rationalized the difference in lifetimes between the *p*-methylphenyloxenium ion and the *p*-biphenyl oxenium ion using thermodynamic arguments from computed isodesmic hydration reactions. A recent study on the effect of meta substitution on the ΔE_{ST} of phenyloxenium ions found that substituting the meta positions of phenyloxenium ions with pi donors (e.g. NMe₂) stabilizes an *m*-xylylene-like π,π^* triplet state in preference to the singlet state.³⁸

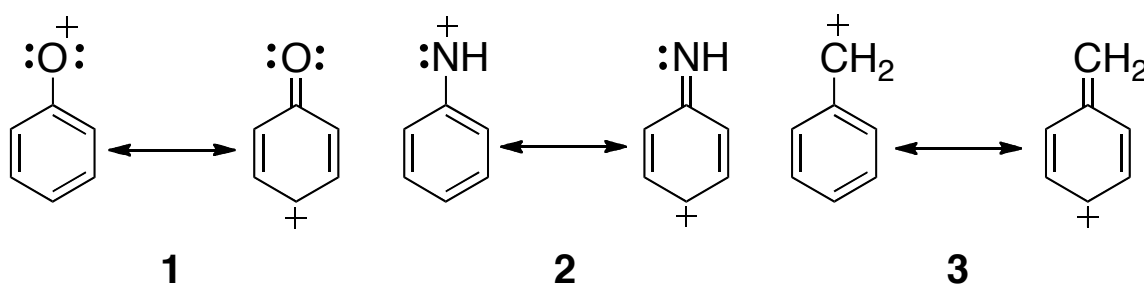


Figure 1. Important canonical forms of the closed-shell singlet phenyloxenium ion **1** (1A_1), phenylnitrenium ion **2** ($^1A'$), and benzyl cation **3** (1A_1).

However, the properties and electronic states of oxenium ions still remain poorly understood. In particular, the relevance of open-shell singlet states and triplet states to the chemistry of aryloxenium ions has to our knowledge not been rigorously addressed. Given that phenyloxenium ion **1** is isoelectronic to phenylnitrene **4**, and given the importance of open-shell electronic states to the reactivity of aryl nitrenes,³⁹ it is critical to similarly characterize the electronic states of aryloxenium ions if their reactivity is to be fully understood.

The results from this computational study indicate that, in contrast to the parent hydroxy cation, phenyloxenium ions generally have lowest-energy states that are closed-shell singlet states. The singlet-triplet gap (ΔE_{ST}) can be manipulated by the para substituent. Meta-donor substituted phenyloxenium ions have low-energy open-shell diradical states; however, for the parent phenyloxenium ion and para-substituted derivatives, open-shell states are significantly higher in energy. Consequently, reactions of phenyloxenium ions are expected to be more similar to phenylnitrenium ions than their isoelectronic phenylnitrene counterparts.

COMPUTATIONAL METHODS

All the molecular geometries of the electronic states of the phenyloxenium ion were optimized at the CASSCF(8,8) level of theory under C_{2v} symmetry constraints.⁴⁰ The stationary points were found to have zero imaginary frequencies, and all energies contain a correction for the zero-point energy (unscaled). For the phenyloxenium ion **1**, the active space electrons included the six benzene pi electrons and two oxygen non-bonding electrons. The active space orbitals included the six benzene π orbitals (4 b_1 and 2 a_2 orbitals), the oxygen out-of-plane p orbital (b_1) and the oxygen in-plane p orbital (b_2). CASPT2 single point energy corrections (using the same active space) were computed at the CASSCF geometries, using a level shift to eliminate intruder states and reduce a systematic bias in the method favoring high spin states.⁴¹ The basis set employed was the flexible ANO-L basis set of Widmark et al., of polarized valence triple zeta (pVTZ) quality.⁴² All the CASPT2/CASSCF calculations were performed using the Molcas 6.2 software suite.⁴³ All the single-reference computations (G3, CBS, and DFT)

computations were computed with Gaussian03/09.⁴⁴ Principally, the hybrid B3LYP functional was used, which consists of the Becke 3-parameter exchange^{45,46} functional with the correlation functional of Lee, Yang, and Parr⁴⁷. This and related DFT functionals have been shown to give quite reasonable agreement with experiment for related reactive intermediates such as carbenes and nitrenium ions.⁴⁸⁻⁵⁰

RESULTS/DISCUSSION.

Electronic state orderings of the phenyloxenium ion. As shown in Table 1, the singlet-triplet gap (ΔE_{ST}) of the phenyloxenium ion **1** is computed to be 22.1 kcal/mol (1A_1 - 3A_2). Thus, there can be little doubt that the ground state of phenyloxenium ion **1** is the singlet state. Also noteworthy is that prior DFT estimates of the ΔE_{ST} computed the singlet state to be the ground state.^{26,27,37} Open-shell singlet states (e.g. 1A_2) are significantly higher in energy than the closed-shell singlet state (1A_1), with the lowest open-shell singlet state (1A_2) being 30.8 kcal/mol higher in energy than the closed-shell singlet state (see Table 1).

Table 1. Adiabatic and Vertical Energies (kcal/mol) of Phenyloxenium Ion 1 Electronic States (CASPT2(8,8)/pVTZ//CASSCF(8,8)/pVTZ, C_{2v} symmetry). Refer to Figure 2 for schematic state configurations.

Irrep. (C_{2v})	Principle Determinant(s) (C_i , weight)	Relative Energy Adiabatic (Vertical)	Exptl. ^{a, 51}
1A_1	$(1b_1^2)(2b_1^2)(1a_2^2)(1b_2^2)$ (0.927, 85.9%)	0 (0)	0
1A_2	$(1b_1^2)(2b_1^2)(1a_2^2)(1b_2^1)(3b_1^1)$ (0.948, 89.9%)	30.8 (34.8)	30.9
1B_1	$(1b_1^2)(2b_1^2)(1a_2^1)(1b_2^2)(3b_1^1)$	48.3 (66.6)	

	(0.944, 89.1%)		
1^1B_2	$(1b_1^2)(2b_1^2)(1a_2^1)(1b_2^1)(3b_1^2)$ (0.945, 89.3%)	48.0 (58.1)	
2^1A_1	$(1b_1^2)(2b_1^2)(1a_2^2)(1b_2^1)(3b_1^1)$ (0.502, 25.2%) $(1b_1^0)(2b_1^2)(1a_2^2)(1b_2^2)(3b_1^2)$ (0.613, 37.5%)	89.0 (102.1)	
1^3A_2	$(1b_1^2)(2b_1^2)(1a_2^2)(1b_2^1)(3b_1^1)$ (0.941, 88.7%)	22.1 (26.1)	19.8
1^3B_1	$(1b_1^2)(2b_1^2)(1a_2^1)(1b_2^1)(3b_1^2)$ (0.938, 87.9%)	47.0 (65.7)	
1^3B_2	$(1b_1^2)(2b_1^2)(1a_2^1)(1b_2^2)(3b_1^1)$ (0.946, 89.4%)	29.9 (38.7)	27.7

a. Revised assignments. See discussion in text.

Revision to band assignments from photoelectron spectroscopy of the phenoxy radical. The ultraviolet photoelectron (UPE) spectrum of the phenoxy radical was the first UPE spectrum of a complex organic radical assigned in detail.⁵¹ In light of the present study, these computational data suggest that the assignments of the singlet/triplet pairs corresponding to ionization of an n and π electron of the phenoxy radical may have been switched. According to the original assignments, the lowest energy triplet state is the 3B_2 (π, π^*) state with the 3A_2 (n, π^*) state 7.8 kcal/mol higher in energy (see Figure 2 for a schematic representations of these states). This assignment was based on the reasonable assumption that since the π -bonding a_2 orbital is the highest energy doubly occupied orbital for the phenoxy radical (using MNDO) that the 3B_2 state derived from

ejection of one of these a_2 electrons from the phenoxy radical would yield a triplet oxenium ion lower in energy than the 3A_2 state derived from ejection of an n (b_2) electron, which is a lower-energy orbital in the phenoxy radical.

These CASPT2 computations favor reassignment of these bands. As shown in Table 1, the CASPT2 method computes the 3A_2 state to be lower in energy than the 3B_2 state by 7.9 kcal/mol. If the currently accepted assignments are correct, the CASPT2 calculations are in error by 15.7 kcal/mol for the relative energy between these two states. Alternatively, if the pairs of band assignments were switched, the CASPT2 calculations are in error by 0.1 kcal/mol for the relative energy between the two triplet states. Typically, one obtains accurate results for CASPT2 with an appropriate space and a flexible basis set (errors < 5 kcal/mol for relative energies are typical). An error of ca. 15 kcal/mol for CASPT2 would be remarkable. We note that our benchmarks of the same computational method (CASPT2(8,8)/pVTZ//CASSCF(8,8)/pVTZ) for the isoelectronic phenylnitrene **4** gives energy differences of 17.2 kcal/mol (3A_2 to 1A_2) and 31.4 kcal/mol (3A_2 to 1A_1). These are close to the experimental values of 18 and 30 kcal/mol derived from photoelectron spectroscopy.^{30,52,53} Finally, every theoretical level we used here (see Table 4)—including CCSD(T)/cc-pVTZ—indicates the lowest energy triplet state is 3A_2 , not 3B_2 . We note that switching the assignments of these two pairs of bands gives good quantitative agreement with theory with the computed relative energies (< 2.5 kcal/mol relative error).

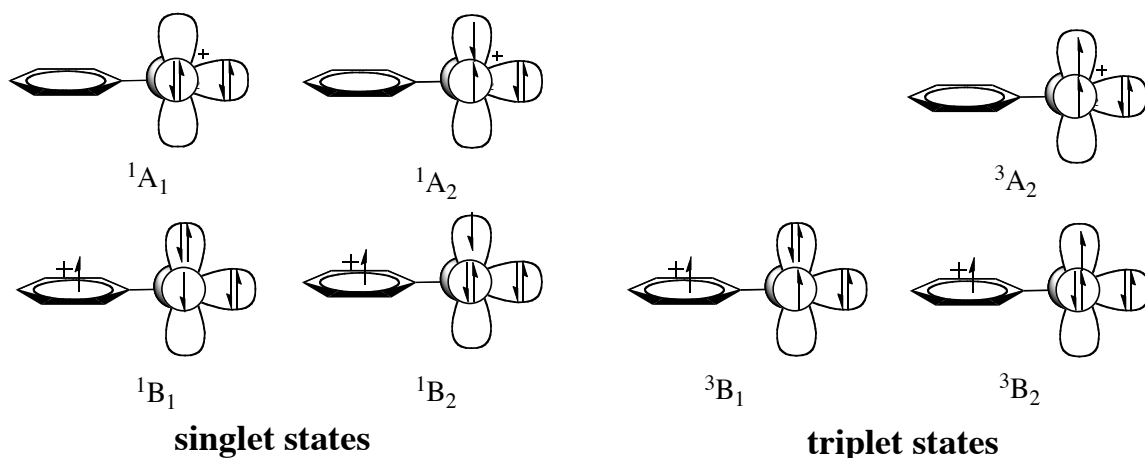


Figure 2. Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of phenyloxenium ion **1**.

Comparison of the electronic states of phenyloxenium ion to phenylnitrenium

ion and isoelectronic phenylnitrene. The phenyloxenium ion **1** is isoelectronic to phenylnitrene **4**; it is thus interesting to contrast the relative orderings of the electronic states between the phenyloxenium ion **1** (${}^1A_1 < {}^3A_2 < {}^1A_2$) and its more highly studied isoelectronic nitrogen counterpart (${}^3A_2 < {}^1A_2 < {}^1A_1$).^{30,39,54} The ground state of phenylnitrene is the 3A_2 state, with a gap of ca. 18 kcal/mol to an open-shell 1A_2 singlet state, and a gap of 33 kcal/mol to the 1A_1 state. The energetic orderings of these states are shuffled in the phenyloxenium ion **1**, with the 1A_1 state being the ground state with an adiabatic energy gap of ca. 20 kcal/mol to the 3A_2 state and a gap of 30 kcal/mol to the open-shell 1A_2 state. The gaps and orderings of these electronic states in the phenylnitrene **4** have been established by both experimental and computational studies. Moreover, while the 1A_1 state of the phenyloxenium ion **1** can be well described by a single closed-shell determinant (closed-shell reference weight = 86%), the 1A_1 state of the phenylnitrene **4** must be described as a linear combination of two closed-shell determinants (Figure 3). This suggests that the degeneracy of the orthogonal p orbitals

on the electron-deficient heteroatom is much more strongly broken in phenyloxenium ion than phenylnitrene.

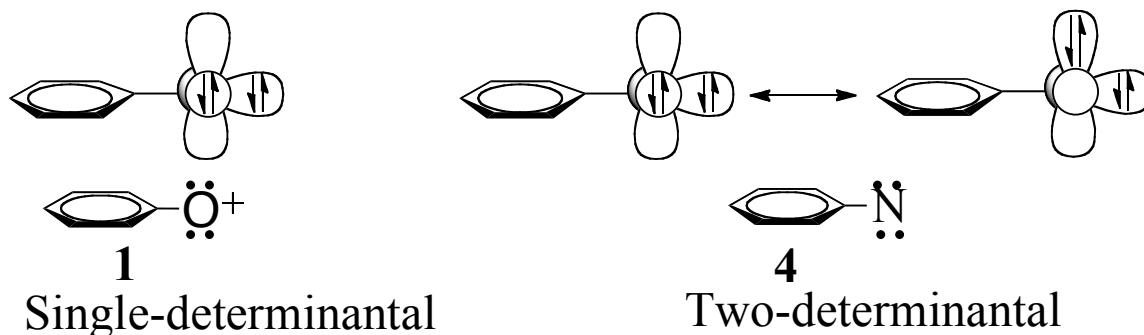


Figure 3. Comparison of the 1A_1 state of the phenyloxenium ion **1** and phenylnitrene **4**.

Why such a remarkable change in state orderings for isoelectronic species? Both resonance/valence bond and MO arguments suggest themselves. First, a closed-shell singlet state for the phenyloxenium ion **1** allows the positive charge on the oxenium ion to delocalize off the oxygen and onto the more electropositive ring carbons. In fact, these and prior calculations³⁷ show that the equilibrium geometry of the 1A_1 irreducible representation of the phenyloxenium ion **1** can be reasonably described as a cyclohexadienonyl cation **1** (right resonance structure in Figure 1), in spite of the significant loss of the benzene aromatization energy that is probably inherent to this geometry. This ‘carbocation-like’ structure is also supported experimentally, since nucleophiles add predominantly to the ring carbons rather than to the oxygen. In contrast, in open-shell configurations (open-shell singlet, triplet) the positive charge is formally restricted³⁷ to the oxygen, which disfavors these configurations. From an MO perspective, the switch from a nitrogen in a nitrene to a more electronegative (and positively charged) oxygen atom in an oxenium ion acts to contract and lower the energy of the p orbitals on the reactive heteroatom. This brings the out-of-plane p orbital on the

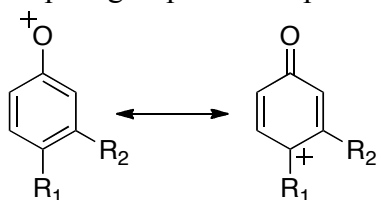
oxygen closer in energy to the ring π orbitals, allowing the orbitals to mix more strongly. This mixing acts to raise the energy of the MO containing the out-of-plane p orbital on the phenyloxenium ion **1** much more than the same MO on the phenylnitrene **4**. Therefore, the degeneracy of the orthogonal p orbitals is more strongly broken in the phenyloxenium ion **1** than the phenylnitrene **4**, and the energetic penalty of placing an electron into this π^* orbital—required for open-shell singlet and triplet configurations—is larger for the phenyloxenium ion **1** than the phenylnitrene **4**. Thus, while the ground state of the phenylnitrene **4** is a triplet state (3A_2), the ground state of the phenyloxenium ion **4** is the closed-shell singlet state (1A_1).

Taken in whole, these data appear to be consistent with the solution-phase experiments that have been performed to date. For example, the experimental studies of Abramovitch and Novak on the phenyloxenium ion **1** and its simple derivatives suggest the intermediacy of a closed-shell intermediate that reacts via standard two-electron electrophile chemistry (e.g. rapid nucleophilic additions).^{15-20,23-25,33,37,55} To the best of our knowledge, chemical reactions that would implicate an open-shell singlet or triplet electronic state (such as hydrogen atom transfer reactions) have not been reported for the phenyloxenium ion **1** or simple analogs.

Effect of para substituents on the ΔE_{ST} of phenyloxenium ion. This MO analysis suggests that, all things being equal, any substituents on the phenyl ring that act to raise the energy of the out-of-plane p orbital on oxygen (e.g. π -donors) will more strongly favor the closed-shell singlet state relative to open-shell configurations. Conversely, substituents that act to lower the energy of this orbital (π -withdrawers) will lead to lowered-energy open-shell (e.g. triplet) states. This is indeed the case. For these

larger systems, we used DFT to compute the ΔE_{ST} of a number of para-substituted phenyloxenium ions. We note that while the quantitative accuracy of these DFT calculations are likely to underestimate the singlet stability (described *vide infra*), the trends predicted by this method are likely to be qualitatively valid. From these calculations, a linear free energy relationship (LFER) of the ΔE_{ST} with the Hammett-like $\sigma^{+56,57}$ and σ_R^{+58} substituent parameters is observed (squared correlation coefficients values, R^2 , of 0.89 and 0.91, respectively). Additionally, the C-O bond length, which we take as a rough diagnostic of the contribution of the two resonance forms depicted in Table 2, also shows a reasonable, albeit small in magnitude, correlation with these two parameters. (The plots of the σ_R^+ vs. the C-O bond length and vs. the ΔE_{ST} can be found in Figure 4; plots of the C-O bond length and ΔE_{ST} vs. σ^+ can be found in the Supporting Information). This geometrical correlation is interpreted to indicate that phenyloxenium ions with π donors in the para position have equilibrium geometries that are more quinoidal than those substituted with electron-withdrawing groups. These LFERs and geometrical changes as a function of the para substituent is remarkably similar to those observed for phenylnitrenium ions.⁵⁹

Table 2. Changes in the ΔE_{ST} (kcal/mol) and singlet C-O bond length as a function of the para group's σ^+ / σ_R parameter as computed by DFT (B3LYP/cc-pVTZ).



Compound Number	R ₁	R ₂	ΔE_{ST} (kcal/mol)	C-O (Å)	$\sigma^+_{25,26}$	σ_{R^+}
5	NH ₂	H	-28.6	1.210	-1.3	-0.5
6	OH	H	-24.1	1.209	-0.92	--
7	OMe	H	-25.6	1.210	-0.78	-0.42
8	CH ₃	H	-18.3	1.211	-0.31	-0.13
9	F	H	-19.1	1.209	-0.07	-0.31
1	H	H	-13.4	1.211	0	0
10	CN	H	-12.3	1.212	0.66	0.08
11	NO ₂	H	-13.4	1.211	0.79	0.15
12	H	NH ₂	4.9	1.220	-1.3	-0.5
13	H	OH	-7.2	1.215	-0.92	--
14	H	OMe	-4.8	1.216	-0.78	-0.42
15	H	CH ₃	-13.0	1.213	-0.31	-0.13
16	H	F	-12.4	1.211	-0.07	-0.31
1	H	H	-13.4	1.211	0	0
17	H	CN	-12.3	1.211	0.66	0.08
18	H	NO ₂	-12.0	1.209	0.79	0.15

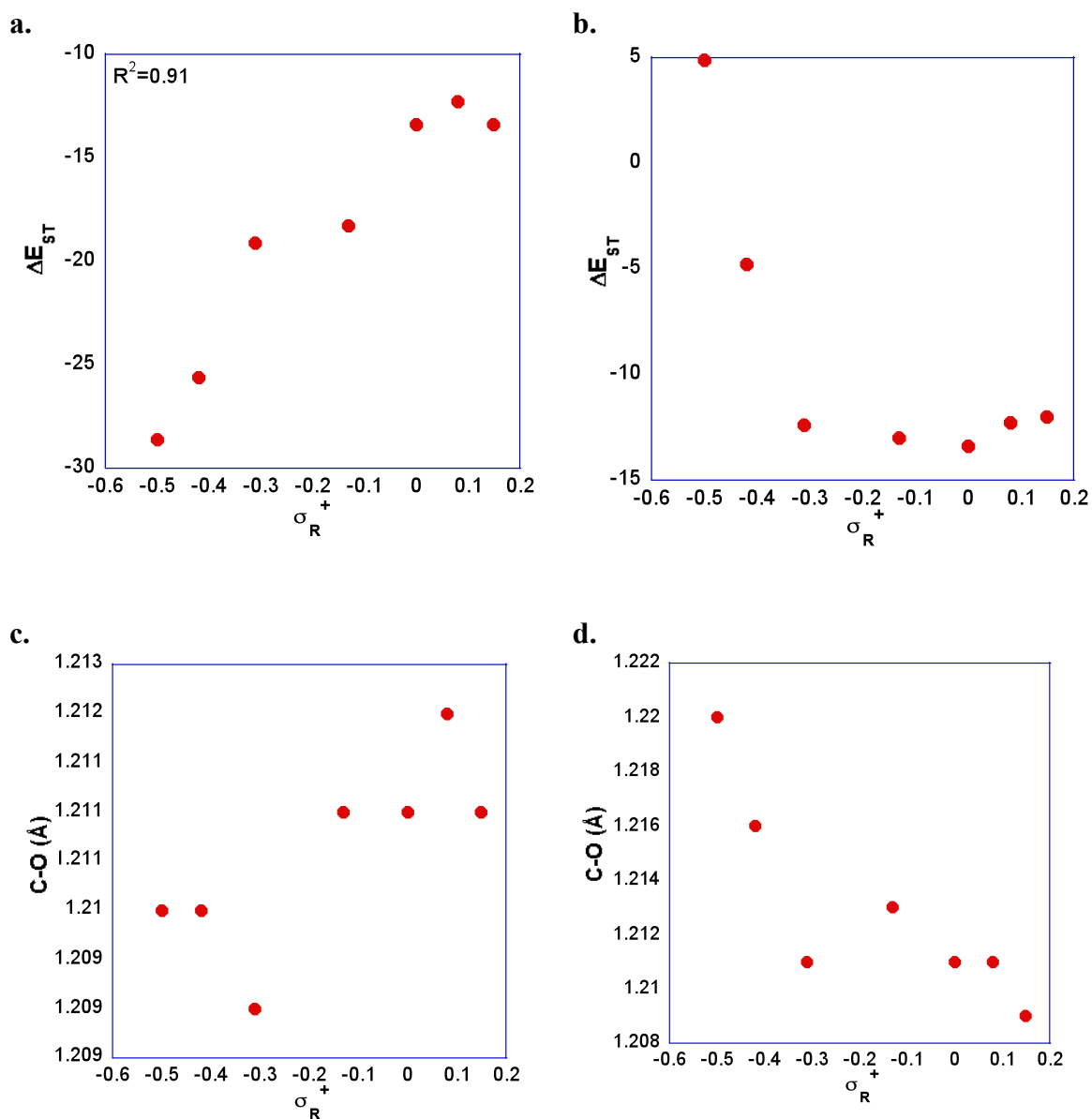


Figure 4. ΔE_{ST} vs σ_R^+ for a) para and b) meta substituents, and singlet C-O bond length vs σ_R^+ for c) para and d) meta substituents. A negative value for ΔE_{ST} indicates a singlet ground state.

Effect of meta and para substituents on the electronic state orderings of **1**.

We also considered the possibility that the open-shell singlet state could become chemically relevant by simple substitutions. We chose the *p*-amino phenyloxenium ion **5** and the *p*-cyano phenyloxenium ion **10**. Both remain in the C_{2v} point group and are

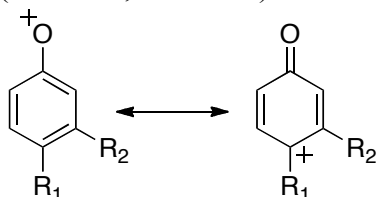
expected to be fairly representative of both a π -donor-substituted and π -withdrawer-substituted phenyloxenium ion. For these species, the active space was increased to include the additional π orbitals and electrons. As seen in Table 3, however, the perturbation in the relative energies of the electronic states is small, and the ordering of the electronic states remains unchanged by the para substitutions.

For meta-substituted phenyloxenium ions, one expects to see little perturbation on the electronic states since this position cannot communicate with the oxenium center through resonance. As expected, the singlet-triplet gap for withdrawing and weakly donating substituents (Figure 4b) remains largely unperturbed. However, for donating substituents, there is a sharp inflection point at $\sigma_R^+ -0.3$, where better donors cause a sharp increase in the singlet-triplet gap in favor of the triplet. This can be explained by a stabilization of a π, π^* triplet state by the meta donor substituent, as can be seen in Table 3. While the parent phenyloxenium ion has a lowest energy triplet state that can be described as n, π^* , the m-amino phenyloxenium ion has a lowest energy triplet state that is described as π, π^* (this is the $^3A'$ state under Cs symmetry). The inflection point in the graph marks the switch from the n, π^* state ($^1A''$) being the lowest energy configuration to the π, π^* state ($^1A'$) being the lowest energy configuration. The meta substituent σ_R^+ value is also correlated with bond length, wherein better meta pi donors increase the C-O bond length. For the m-amino phenyloxenium ion, the ground state is computed to be the triplet state at the DFT level of theory by ca. 5 kcal/mol, but is computed to have essentially degenerate singlet and triplet energies at the CASPT2/pVTZ level of theory. Consequently, the ground state of the m-amino phenyloxenium ion cannot be predicted with certainty. Reactivity may be possible from both the singlet and triplet state. Also of

note is that a further consequence of the narrowing of the frontier orbital energies for the meta-amino phenyloxenium ion is that the open-shell singlet state is low in energy.

While for the parent phenyloxenium ion the adiabatic energy gap from the closed-shell singlet ground state (1A_1) to the open-shell singlet state (1A_2) is 30.8 kcal/mol, for the *m*-amino phenyloxenium ion, the vertical gap from the closed-shell singlet state ($^1A'$) to the open-shell singlet state ($2^1A'$) is 6.6 kcal/mol.

Table 3. Effect of para (C_{2v}) and meta (C_s) substituents on electronic state energies (adiabatic, Kcal/mol) and orderings (CASPT2/pVTZ).



Compound Number	R1	R2	Active Space	1A_1	1A_2	3A_2
1	H	H	(8,8)	0	30.8	22.1
5	NH ₂	H	(10,9)	0	28.8	23.6
10	CN	H	(12,12)	0	23.7	19.4

Compound Number	R1	R2	Active Space	$^1A'$	$2^1A''$	$^3A''$	$^1A''$	$^3A'$
12	H	NH ₂	(10,9)	0	6.6 ^a	12.6	15.4	1.0
17	H	CN	(12,12)	0	53.6 ^a	17.6	28.2	29.5

a. vertical energies

Molecular geometries. The molecular geometries, computed at the CASSCF(8,8)/pVTZ level, are depicted in Figure 5. The heavy atom—heavy atom bond lengths (Å) are shown for the lowest energy configuration of each irreducible representation. As seen in Figure 5, the C-O bond length is shortest in the closed-shell singlet irreducible representation (1A_1). Additionally, there is significant bond length

alternation in the ring carbons in this electronic state, as well as in the other A_1 and A_2 configurations, suggesting significant quinoidal character. Conversely, the B configurations— 1B_2 , 3B_2 , 1B_1 —which involve promotion of a ring π electron rather than an oxygen n electron, show less bond length alternation. However, these states are significantly higher than the A states.

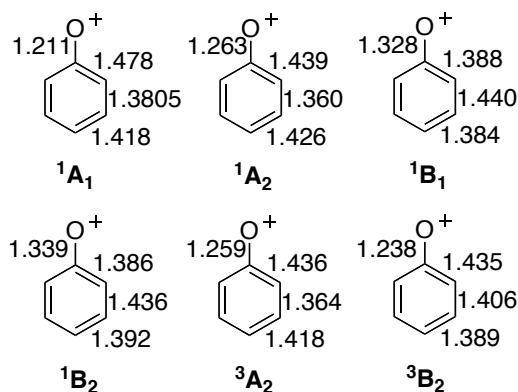


Figure 5. Heavy atom-heavy atom bond lengths (Å) for irreducible representations of **1** (C_{2v} , CASSCF(8,8)/pVTZ).

Larger aryloxenium ions. Larger aryloxenium ions than phenyloxenium ions tend to show an increased preference for the singlet state relative to the triplet. At the DFT level, the ΔE_{ST} of 1- and 2- naphthyl oxenium ion **20** and **19**, and the 9-anthryloxenium ion **21** (Figure 6), are -23.2, -15.2, and -33.5 kcal/mol, respectively. These ions have larger singlet-triplet splittings in favor of the singlet relative to phenyloxenium ion **1** (-13.5 kcal/mol at this level of theory). To ensure that the lowest-energy singlet state remained closed-shell, stability calculations were performed on the singlet states, and the ‘wavefunctions’ were found to be stable to an RHF->UHF perturbation. Inspection of the Kohn-Sham SOMOs indicates that, like the phenyloxenium ion, the lowest energy triplet state is n,π^* for these larger aryloxenium

ions, with the exception of the 2-naphthyloxenium ion, which can be described as a π, π^* triplet state ($^3A'$; see Supporting Information for plots of the Kohn-Sham SOMOs).

Performance of density functional theory. We also examined the ΔE_{ST} by density functional theory (DFT) and other computational methods (See Table 4). While CASPT2 is a rigorous methodology, it is only computationally tractable for small systems, and it would be useful to have a DFT functional that could give reasonable results. DFT, which is relatively inexpensive and easily implemented, has been shown to give quite reasonable values for the ΔE_{ST} of carbenes, nitrenium ions, and related species.^{38,60,61} Given that the phenyloxenium ion **1** does not appear to present a pathological case for theory (e.g. an open-shell singlet state), the somewhat disappointing performance of DFT compared to CASPT2 or the compound extrapolation methods (G3, CBS) is somewhat surprising—but not without precedent.

Table 4. Computed adiabatic singlet-triplet energy gaps [$\Delta E_{ST} = E(^1A_1) - E(^3A_2)$] of the phenyloxenium ion **1** by different methods. A negative value for ΔE_{ST} indicates a singlet ground state. Geometries were optimized at the same level unless otherwise indicated.

Computational Method	ΔE_{ST} (kcal/mol)
CASPT2/pVTZ//CASSCF/pVTZ	-22.1
G3	-20.6
CBS-Q	-20.5
CCSD(T)/cc-pVTZ	-20.0
Experimental value	-19.8
CBS-QB3	-18.2
BVWN/cc-pVTZ	-18.2
B3LYP/cc-pVTZ	-13.5
BLYP/cc-pVTZ	-12.3
MPW1PW91/cc-pVTZ	-10.5
BH&HLYP/cc-pVTZ	-10.0
TPSSTPSS/cc-pVTZ	-9.5

Typically, DFT systematically underestimates the singlet stability of carbenes and related hypovalent species by about 5 kcal/mol because non-dynamical correlation is generally more important for singlet states than triplet states.⁶² However, in this case, all the DFT functionals we tested except BVWN underestimate the singlet stability by a somewhat larger 5-10 kcal/mol compared to the experimental value or values computed by G3, CBS-Q, or CASPT2. Some of the blame for this relatively poor performance appears to be assignable to poor singlet state geometries at the DFT level of theory. For example, B3LYP/cc-pVTZ single-point energy differences of the singlet and triplet states at the CASSCF geometries changed from -13.5 to -15.5 kcal/mol—an improvement of 2.0 kcal/mol. A likely origin of the poor singlet geometries is the tendency of DFT functionals to overestimate aromatization. Thus, one obtains geometries that have too much Ph-O⁺ character (left resonance structure **1** in Figure 1) relative to cyclohexadienonyl cation character (right resonance structure **1** in Figure 1) using B3LYP, as shown by the longer C-O bond lengths using DFT compared to the CASSCF geometries (1.227 Å rather than 1.211 Å). Since CBS-QB3 employs a B3LYP optimization step, and since we estimate the error introduced by using a B3LYP geometry to be ca. 2 kcal/mol, it is not unexpected that the CBS-QB3 value of the ΔE_{ST} is lower than G3, CQS-Q, and CCSD(T) by ca. 2 kcal/mol. Multireference computations are needed for species with significant non-dynamic correlation; however, for species that do not have significant non-dynamical correlation (such as the phenyloxenium ion), single reference methods that better capture dynamical correlation than CASPT2/CASSCF may give better quantitative accuracy. Indeed, it is notable from Table 4 that the most rigorous single-reference computational methodologies predict a

ΔE_{ST} value for the phenyloxenium ion **1** close to the experimental value derived from photoelectron spectroscopy of -19.8 kcal/mol.

CONCLUSIONS

The singlet-triplet gap of the phenyloxenium ion **1** is ca. 20 kcal/mol, which represents the adiabatic energy difference between the 1A_1 state and the 3A_2 state. While the parent oxenium ion, hydroxy cation OH^+ , has a triplet ground state with a very large energy gap to the lowest energy singlet state, substituting the hydrogen with a phenyl ring strongly breaks the degeneracy between the frontier p orbitals and leads to a closed-shell singlet state (1A_1) being the lowest energy configuration. Open-shell singlet states do not appear to be chemically relevant for the parent phenyloxenium ion and para-substituted aryloxenium ions studied here, having energies 20 kcal/mol or higher than their closed-shell counterparts. This stands in contrast to the isoelectronic aryl nitrenes, which often have open-shell singlet states lower in energy than the closed-shell singlet states, and more in line with aryl nitrenium ions, which are generally closed-shell singlet ground state species. These aryloxenium ions have two low-energy types of triplet states, n,π^* or π,π^* . The n,π^* triplet is computed to be lower in energy for the parent phenyloxenium ion **1** at the CASPT2 level of theory, but the π,π^* triplet becomes lower in energy for the 2-naphthyl oxenium ion. Meta-donor-substituted aryloxenium ions have low-energy open-shell states due to a stabilization of a π,π^* configuration by the meta donor substituent. The ΔE_{ST} of para-substituted phenyloxenium ions correlates with the σ^+_{R/O^+} Hammett substituent parameter, with strong para donors increasing the gap in favor of the singlet and electron-withdrawing substituents decreasing the gap. Experimental studies

to generate and characterize these species are needed to fully characterize their properties and reactivity.

Acknowledgements. We thank the Ohio Supercomputing Center for computational resources, and Christopher Hadad for helpful discussions.

Supporting Information. Plots of σ^+ and σ^+_R values versus ΔE_{ST} and C-O bond length for meta and para-substituted systems. Absolute energies and Cartesian coordinates. Full citation for reference 43b, 44. Kohn-Sham SOMO plots for the triplet states of **1**, **19-21**.

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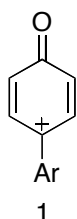
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Chapter 3

Experimental Studies of Oxenium Ions

INTRODUCTION

Oxenium ions are proposed intermediates for a number of important reactions, and understanding the physical properties and reactivity of oxenium ions could lead to improved reactions involving these intermediates. Although oxenium ions are poorly understood intermediates, they are proposed to be formed in numerous reactions that yield value-added products from petrochemical feedstocks.¹⁻³ A better understanding of these species may lead to new and improved reactions.



Computational studies have suggested that the phenyloxenium ion has a singlet ground state.⁴ However, experimentally oxenium ions have received little attention. Abramovitch and Okamoto used thermolytic methods to generate aryloxenium ions,⁵⁻⁹ and the reactivities of aryloxenium ions were determined using thermal and photochemical generation methods.¹⁰ The only direct detection of an oxenium ion in solution was reported by Platz and Novak for the biphenyl oxenium ion **1**.¹¹ This species has a lifetime of 170 ns in water. One major problem with the photoprecursor of Platz and Novak was that, along with heterolytic scission to form the biphenyl oxenium ion, the precursor underwent competitive homolytic scission leading to the phenoxy radical. The lack of clean photoprecursors to generate oxenium ions has thwarted studies of their reactivity.

Improved oxenium ion photoprecursors should be designed to disfavor the radical pathway and favor the formation of the oxenium ion. We considered the possibility that

positively charged ammonium ion leaving groups would discourage this competitive homolytic scission channel. Homolytic scission of these precursors would result in the formation of a high-energy ammonium radical cation. For example, we considered that precursor **2a** might be a good source for phenyloxenium ions since the formation of the ammonium radical cation may be disfavored due to the instability of this species.

EXPERIMENTAL:

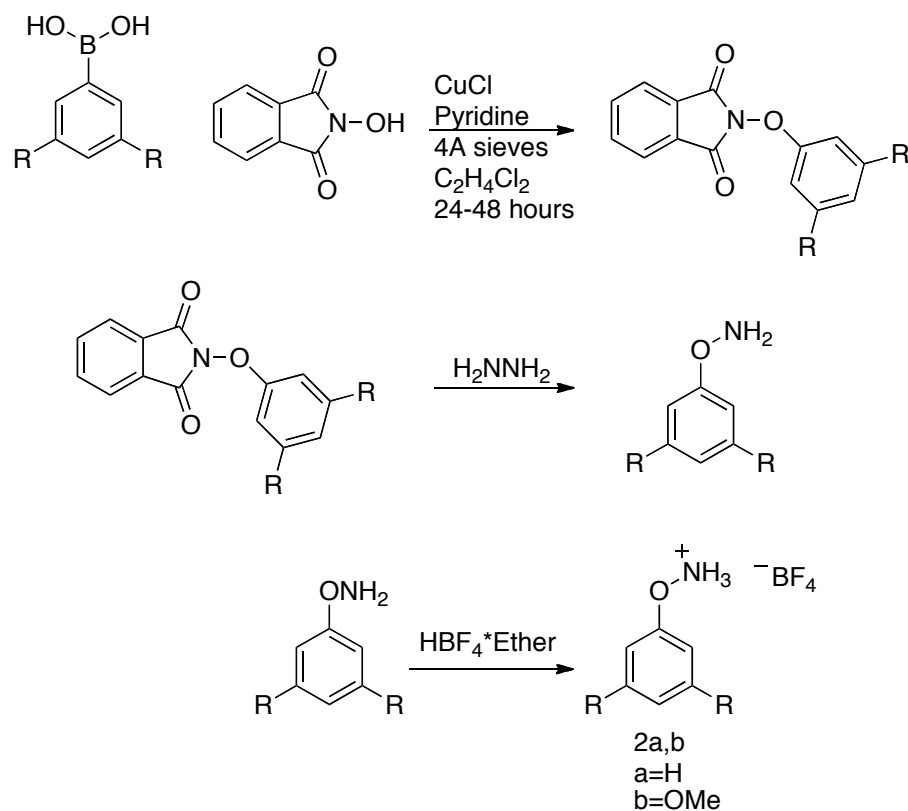


Figure 1: Synthetic pathway for the formation of the tetrafluoroborate salts used for photolysis studies

The synthesis of O-linked phenylhydroxylammonium cations was carried out as shown in Figure 1. The tetrafluoroborate salt **2a** was substituted for the chloride to have a non-nucleophilic counterion.

Product Studies

Product studies were then performed in different solvents. The results of these studies can be seen in Figures 4-7 at the end of the chapter.

Figure 4 shows the NMR of the products after the photolysis of the chloride salt of the O-phenylhydroxylamine hydrochloride precursor. Here it is easy to see that the major product is phenol, with only a slight amount of ortho and para aminophenol salts. Ammonium chloride is also visible as a byproduct of the reaction.

In contrast, for the photolysis of the tetrafluoroborate salt in acetonitrile, it can be seen in Figure 5 that the major product is phenol along with some of the ortho and para aminophenol salts. Peak integration suggests that there is approximately equal amounts of the amino phenol salts and phenol. Thus, with the tetrafluoroborate precursor there is a substantially larger amount of the ortho and para amino phenols that are being formed as compared to when the reaction was run in the chloride salt. This result suggests that chloride favors the pathway leading to the phenol formation.

The photolysis of the tetrafluoroborate salt was also carried out in methanol. Figure 6 shows that phenol, along with ortho and para aminophenol salts, was formed here as well. Like the run in acetonitrile with the tetrafluoroborate salt, the products favor the formation of the ortho and para aminophenol along with phenol, but form more of the phenol in comparison to the run in acetonitrile.

The photolysis was then run on the tetrafluoroborate salt in water, and as can be seen this is a very interesting case. Figure 7 shows that the only major products are the ortho and para aminophenol. There is a small amount of hydroquinone that is formed as well. Conceivably, this product forms from the water solvent reacting as a nucleophile.

The photolysis of the tetrafluoroborate salt was run in an 80:20 Benzene:Acetonitrile mixture. Preliminary studies show that while the traditional products form, a significant amount of the benzene adducts formed as well. Since this is a relatively weak π nucleophile, it makes sense that potentially stronger π nucleophiles would lead to more substitution, and this could potentially lead to getting rates of the reaction. These experiments are currently being undertaken.

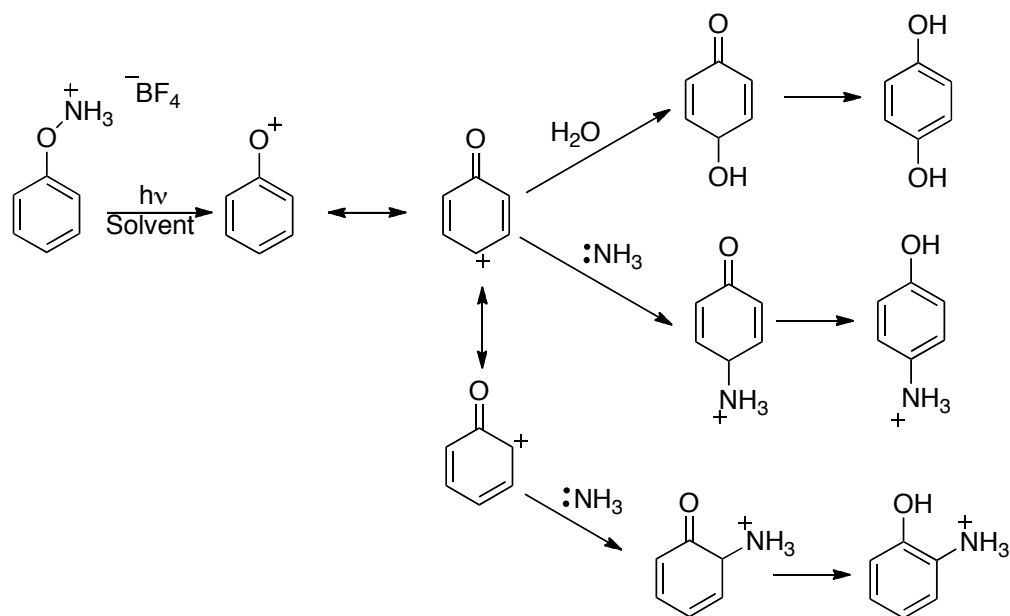


Figure 3: Potential mechanistic pathways that lead to the formation of the photolysis products.

So do these product formations follow typical singlet oxenium ion chemistry? It is reasonable that the ortho and para aminophenol salts would be formed from the release of the NH_3 , which would form a positive charge on the oxygen, as shown in Figure 3. This

positive charge would then be delocalized to the ortho and para positions on the ring. The lone pair on the NH_3 would then attack the partially positive ortho or para position of the ring and would form the two products. The formation of hydroquinone is also easy to explain. This would be a similar route in which the water (or adventitious water in CH_3CN) would react with the para cation to form the hydroquinone. The phenol on the other hand is less easy to explain. The phenol could come from a variety of mechanisms. It could be formed from formation of the phenyloxenium ion, followed by hydride transfer or by an electron transfer. Following electron transfer, the phenoxy radical could abstract a hydrogen to form phenol. The ammonium chloride and ammonium tetrafluoroborate salts were formed due to the solution being acidic and the residual ammonium forming an ion pair with the excess chloride or boron ions to form the salts. The most likely path of formation of all or most of these products is through the phenyloxenium ion.

Why do we obtain such varying results and product quantities in different solvents? Since in water a large amount of the ortho and para aminophenol salts are formed at the exclusion of phenol, it is possible that water stabilizes the oxenium ion intermediate, leading to the formation of more of the typical singlet phenyloxenium chemistry. All of the products observed in the photolysis of water (ortho and para aminophenol salts and hydroquinone) have been very easily explained to potentially run through the phenyloxenium ion intermediate. Whenever the solvent was switched to acetonitrile, a slightly less polar and therefore less stabilizing solvent, some phenol starts to form. Perhaps this is from the loss of stability of the phenyloxenium ion in solution, which is then leading to other unknown and complicated pathways. Methanol continues

this trend by being slightly less polar than acetonitrile and leading to slightly more phenol and less of the amino salts.

LFP Studies:

The laser flash photolysis studies were attempted with an excitation wavelength of 266 nm, and a pulse time of 5 ns. As shown in Figure 3 a peak was observed.

Unfortunately as can be seen the peak that was observed was a broad peak that increased in intensity as time went on. Steady-state UV-Vis performed after the photolysis showed identical peaks. Therefore it was determined that this peak was a photoproduct instead of a transient species. Many attempts were made in order to reduce the background or increase the signal but identical results were obtained.

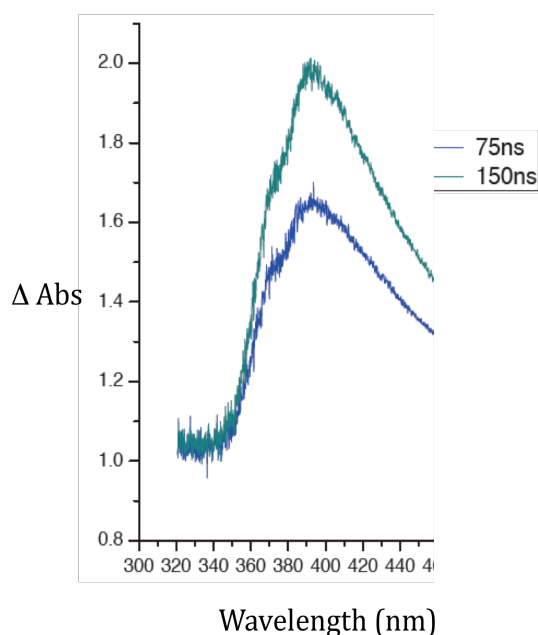


Figure 3: LFP of tetrafluoroborate salt **2a**

Our inability to detect the oxenium ion by laser flash photolysis is not terribly surprising, since the reported value for species **1** has a lifetime of 170 ns. Since the parent phenyloxenium ion has less conjugation it seems reasonable to anticipate that the parent phenyloxenium ion would have a shorter lifetime. How much shorter is unclear, but our laser flash photolysis instrument has a practical limit of detecting species with longer lifetimes than 50 ns due to the pulse time of the laser being 5 ns. Further, it is

conceivable that the nucleophilicity of the ammonia leaving group could trap the oxenium ion faster than the detection limit of our laser flash system.

CONCLUSIONS

These experimental studies provide insight into the chemistry that is occurring through the photolysis of the tetrafluoroborate salt **2a**. The products are consistent with the formation of the phenyloxenium ion and the nucleophilic attack of the water or ammonia group on the singlet ion. The exclusive formation of the amino adducts and hydroquinone in water suggests clean generation of the oxenium ion. However, the minimal amount of solvent adducts suggests that the ammonia leaving group is an excellent trap for the oxenium ion, possibly leading to very short lifetimes of the intermediate. Two differing paths should be taken to further this study. The first is to form the dimethoxy phenyloxenium ion and see if a triplet forms as would be expected by computations. The chemistry for the photolysis of **2b** should be more diradical-like if that is indeed what occurs. If this does form a different intermediate, it may have a long enough lifetime to be viewed by LFP.

The other direction that should be taken with this is to form a less nucleophilic leaving group. This could be done by adding a protecting group to the nitrogen or any other hindered group, or it could be done by forming a different leaving group entirely, which would be less nucleophilic when displaced. In any case, there is much to be done in order to further understand these intermediates, and the better we can tune the starting materials, the better results and understanding we will gain from these studies.

Synthesis

Procedure for formation of N-aryloxyphthalimide.¹² 163 mg (1mmol, 1eq) of N-hydroxyphthalimide, 99mg (1mmol, 1equiv) of CuCl, 244 mg (X mmol, X equiv) of phenylboronic acid, and ~250 mg of 4Å molecular sieves were added to a round bottom flask. 5 mL of 1,2-dichloroethane followed by 90 µL (1.1 mmol, 1.1 equiv) of pyridine were added to the flask. The reaction was stirred overnight under air at ambient temperature. The reaction was monitored by TLC (75:25 Hexanes:Ethyl Acetate). The reaction was allowed to react for 24 hours and then the solvent was evaporated under reduced pressure. The product was separated by column chromatography (75:25 Hexanes:Ethyl Acetate). A white solid (N-aryloxyphthalimide) was collected and dried by high vacuum, to give 70% yield (168 mg), of the desired product. This product was then used for the next step in the synthesis. When this reaction was scaled up, the reaction took substantially longer. For example, whenever the reaction was run on 3 times the scale, the reaction time was typically around 5 days before workup.

Procedure for the formation of O-Phenylhydroxylamine tetrafluoroborate. 652 mg (2.73 mmol, 1 equiv) of N-aryloxyphthalimide was added to a flask containing 25 mL of 10% MeOH in CHCl₃ and 0.401 mL (8.2 mmol, 3 equiv) of hydrazine monohydrate. A colorless solution was formed, which yielded a white precipitate over time. The reaction was monitored by TLC (75:25 Hexanes:Ethyl Acetate) and allowed to react overnight (12 hours). The filtered solid was then purified by column chromatography (75:25 Hexanes:Ethyl Acetate).¹² The resulting product was dissolved in ether, to which HBF₄*OEt₂ (ca. 0.2 mL) was added until the TLC spot no longer moved. This signified the protonation of the hydroxylamine to the hydroxylamine

tetrafluoroborate salt. This solution was then dried under reduced pressure to yield 155 mg, 29% yield of the desired product. (155 mg, 29% yield) and was used for identification purposes as well as the product studies.

Supplemental Information provides ^1H NMR spectra for synthetic analysis.

Special thanks to the labs of Dr. Jenks and Dr. Petrich, specifically Matthew Sherman and Ujjal Bhattacharjee.

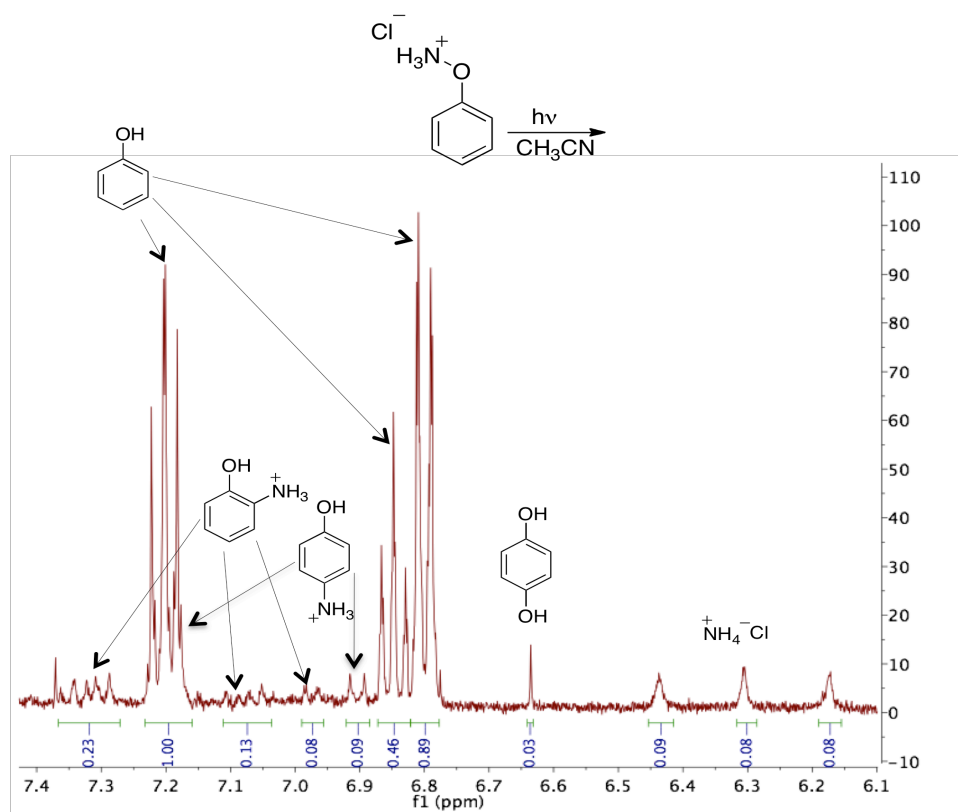


Figure 4: ^1H NMR of the photolysis of O-phenylhydroxyl hydrochloride in acetonitrile

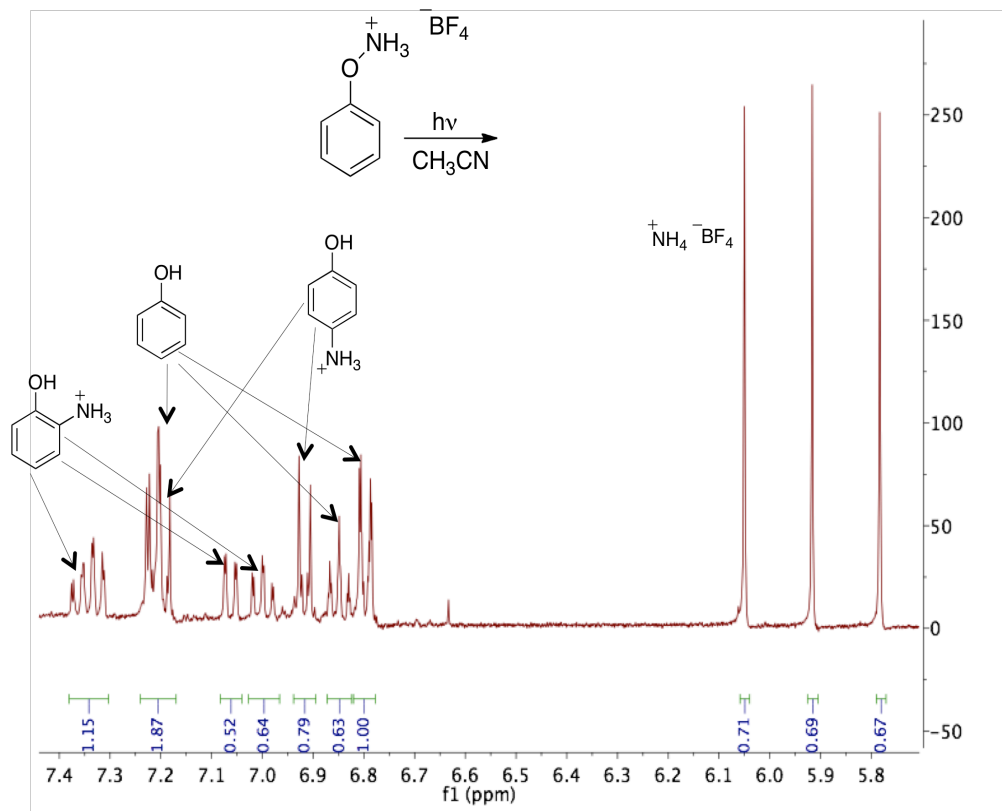


Figure 5: ^1H NMR of the photolysis of O-phenylhydroxyl tetrafluoroborate in acetonitrile

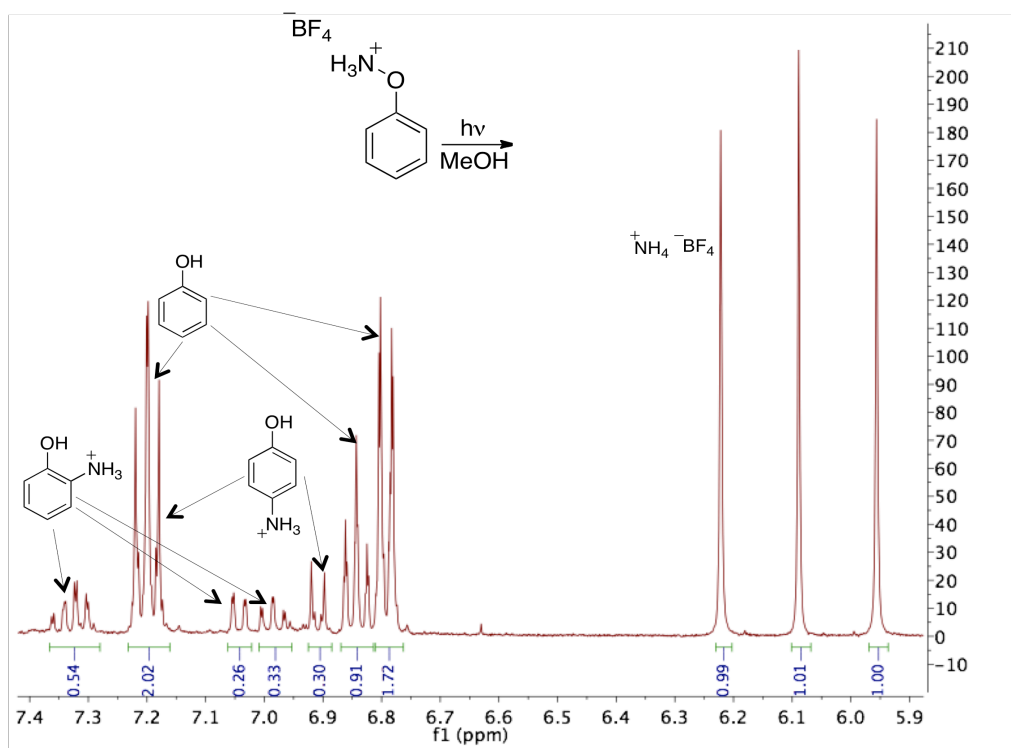


Figure 6: ^1H NMR of the photolysis of O-phenylhydroxyl tetrafluoroborate in methanol

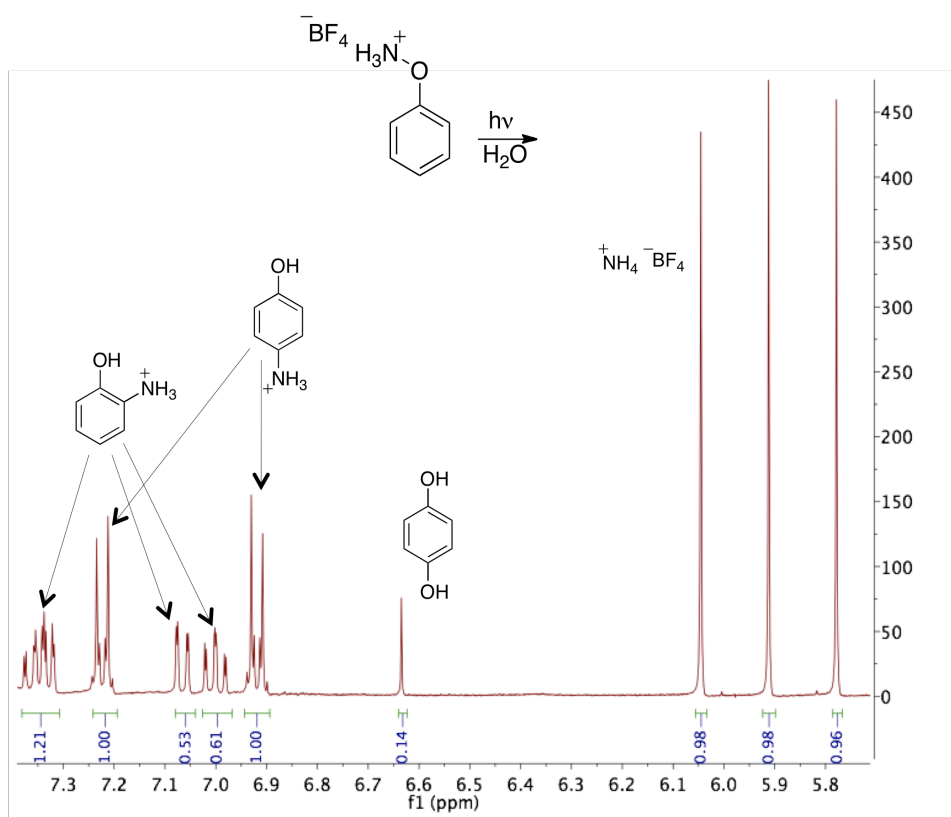


Figure 7: ^1H NMR of the photolysis of O-phenylhydroxyl tetrafluoroborate in acetonitrile

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Chapter 4

Heteroaryl oxenium ions have diverse and unusual low-energy electronic states

† indicates an imaginary frequency at the geometry and energy displayed

INTRODUCTION

Recently, the electronic state energies of phenyloxenium ions and simple derivatives were computed using high-level multireference computational methods.¹ These computational studies suggested that oxenium ions have large swings in the lowest-energy electronic states by changing the substituent attached to the formally positive oxygen. For instance, the simplest oxenium ion OH^+ has a triplet ground-state with a gap of 54 kcal/mol to the lowest energy singlet state.² Substituting the hydrogen with a phenyl ring leads to the lowest-energy state being the closed-shell singlet ground state.¹ The singlet ground state of phenyloxenium ion is supported both by photoelectron spectroscopy and high-level computational methods. In particular, the parent phenyloxenium ion (Ph-O^+) was computed to have a ΔE_{ST} of -22.1 kcal/mol (CASPT2/pVTZ, a negative value indicates a singlet ground state).¹ This study also provided evidence that simple ring substituents could lead to significant changes in the ΔE_{ST} .¹ While oxenium ions are common reactive intermediates that are important to a diverse groups of chemists, the properties, electronic states, and reactivities of these species are poorly understood. Further, the exuberant swing of ca. 70 kcal/mol in the ΔE_{ST} on substituting hydrogen for phenyl on the oxenium center suggests that the ground state configurations of these ions are highly sensitive to the substituent.

In this study, we computed the electronic states of heteroaryl oxenium ions using CASPT2/CASSCF computations. We find that heteroaryl oxenium ions have a number of low-energy electronic states. The lowest energy configuration of these heteroaryl oxenium ions can be the open-shell singlet, closed-shell singlet, or the triplet ground state. Thus, a variety of different spin-selective reactivities may be expected for these heteroaryl oxenium ions.

COMPUTATIONAL METHODS

All the molecular geometries of the electronic states of 2-, 3-, and 4-pyridinyloxenium ions were optimized at the CASSCF (10,9) and the pyrimidinyl and pyridinyloxenium ions were calculated under the CASSCF (12,10) level of theory under C_{2v}/C_s (whichever appropriate) symmetry constraints.³ Pyrimidinyl oxenium ion 3B_1 used CASSCF (12,12) due to convergence problems. All of these optimized structures were found to have zero imaginary frequencies except for the ones denoted in the tables. All of these energies contained a correction for the zero-point energy (unscaled). The energies that were obtained with an imaginary frequency are recorded in the tables as well. For the C_{2v}/C_s symmetry calculations that did have imaginary frequencies, optimizations were performed that broke symmetry, and if successful, the unsymmetrical optimizations were used and the energies were reported. For the optimizations that failed, vertical energies were calculated with CASSCF/CASPT2 from the ground state structure. The only exception was pyridinyloxenium $^1A''$ and here the ground state geometry for the calculation was the $^3A''$ instead of the $^1A'$ due to the $^1A'$ state being out of plane. Active spaces include all π electrons and all π orbitals, as well as

chemically relevant lone pairs and orbitals, such as nitrogen or oxygen lone pairs. In the few cases where the lone pair of electrons did not contribute significantly to the overall wave function (e.g. electron population > 1.98), the orbital containing the lone pair was replaced with a sigma orbital by the MOLCAS program. The basis set employed was the flexible ANO-L basis set of Widmark et al., consisting of polarized valence triple- ζ (pVTZ) quality.⁴ All the CASPT2/CASSCF calculations were performed using the MOLCAS 7.4 software suite.⁵ All the CBS-Q calculations were done using Gaussian 09.⁶

RESULTS/DISCUSSION

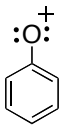
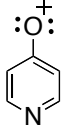
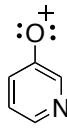
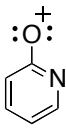
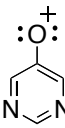
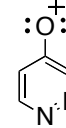
						
Compound Number	1	2	3	4	5	6
ΔE_{ST} (B3LYP/cc-PVTZ)	-13.5	+0.9	-3.8	-1.4	+4.1	+28.0
ΔE_{ST} (CASPT2/pVTZ)	-22.1	-3.4	-19.2	-16.4	~ 0	-1.34
ΔE_{ST} (CBS-Q)	-20.5	-6.5	-15.6	-14.1	-8.7	--

Figure 1: Calculated ΔE_{ST} of the phenyloxenium ion and some nitrogen-based aromatic oxenium ions

The hydroxy cation (OH^+), which is the parent oxenium ion, is a ground state triplet with an adiabatic energy gap of 54 kcal/mol as found by photoelectron spectroscopy.² The degenerate p orbitals on OH^+ lead to the triplet being the ground state following a molecular orbital extension of Hund's rule. In contrast, substituting the hydrogen for a phenyl ring strongly breaks the degeneracy of the frontier orbitals in the phenyloxenium ion and leads to the ground state being a singlet (1A_1) with the lowest triplet (3A_2) being ca. 20 kcal/mol higher in energy.

Figure 1 depicts the overall ΔE_{ST} of a number of nitrogen based aromatic compounds and compares them to the parent phenyloxenium ion. In general, the results show that the addition of nitrogen into the ring favors the triplet and open-shell singlet states when compared to the phenyloxenium ion.

Table 1. Energies of the lowest irreducible representations of the 2-pyridinyloxenium ion.

Irreducible Representation (C_s)	Relative energy adiabatic (vertical), kcal/mol
$1^1A'$	0
$1^1A''$	23.8
$1^3A'$	36.3 [†] (49.0)
$1^3A''$	16.4

The 2-pyridinyloxenium ion and 3-pyridinyloxenium ion have only slightly perturbed energetic orderings from the phenyloxenium ion. For each ion, the lowest energy configuration for each irreducible representation was computed. Most of these states can be reasonably well represented as a single-determinant, and thus each electronic configuration is depicted in Figure 2 to help guide the discussion. As shown in Table 1, the ΔE_{ST} ($1^1A'-3^3A''$) of the 2-pyridinyloxenium ion **4** is computed to have a gap of 16.4 kcal/mol between the closed-shell singlet and an n,π^* triplet state. Thus, there can be little doubt that the ground state of the 2-pyridinyloxenium ion is the closed shell singlet state. A very short C-O bond length of 1.205 Å for the ground singlet state implicates a highly quinoidal structure with significant charge on the carbon para to the oxygen (e.g. a structure resembling an azacyclohexadienonyl cation). These two states are identical to the lowest energy states for the phenyloxenium ion, but with a smaller gap (the ΔE_{ST} of phenyloxenium ion is 22 kcal/mol between 1^1A_1 and 3^3A_2 at the same level of theory).

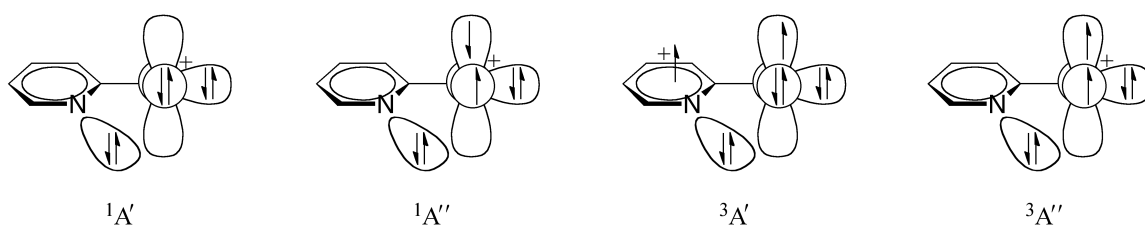


Figure 2: Approximate schematic configurations of the singlet and triplet irreducible representations (C_s) of the 2-pyridinyloxenium ion **4**.

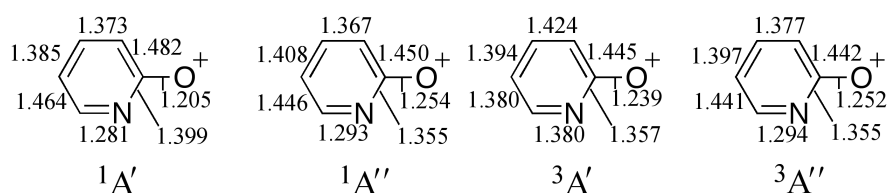


Figure 3: Heavy atom-heavy atom bond lengths (\AA) for irreducible representations of **4** (C_{2v} , CASSCF(10,9)/pVTZ).

Table 2. Energy of the irreducible representations of the 3-pyridinyloxenium ion.

Irreducible Representation (C_s)	Relative energy adiabatic
$1^1A'$	0
$1^1A''$	22.8
$1^3A'$	41.9
$1^3A''$	19.2

As shown in Table 2, the ΔE_{ST} of the 2-pyridinyloxenium ion **3** is computed to be 19.2 kcal/mol ($1^1A' - 1^3A''$). This value leaves little doubt that the singlet state is the ground state. The $1^3A''$ state derives from promoting an electron from the oxygen lone pair to the oxygen-centered π^* . Since 3-pyridinyloxenium has the nitrogen in the meta position to the oxenium center, it would be expected that this heteroaryloxenium ion would vary the least from the phenyloxenium ion, since it lacks a resonance structure which would formally place the positive charge on the nitrogen. Indeed, the ordering of the three

lowest electronic states are the same at the phenyloxenium ion (ground state singlet < triplet < open-shell singlet), and even the energy gaps are very similar.

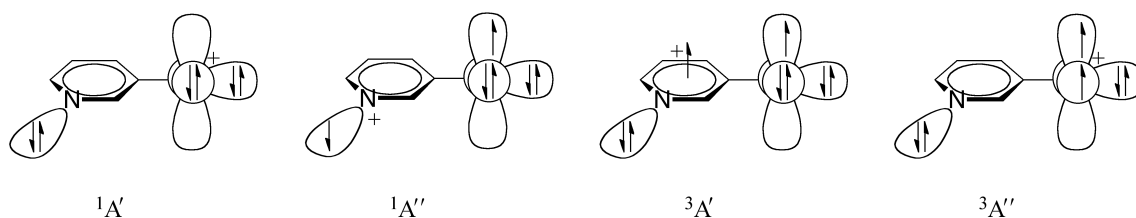


Figure 4: Approximate schematic configurations of the singlet and triplet irreducible representations (C_s) of the 3-pyridinyloxenium ion **3**.

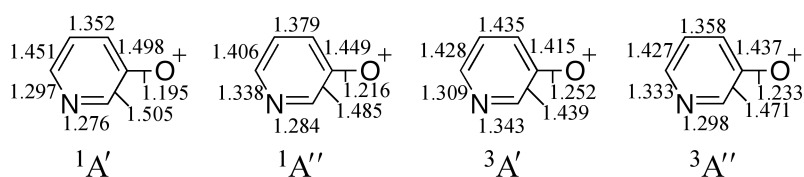


Figure 5: Heavy atom-heavy atom bond lengths (Å) for irreducible representations of **3** (C_s , CASSCF(10,9)/pVTZ).

Table 3. Energies of the lowest irreducible representations of the 4-pyridinyloxenium ion.

Irreducible Representation (C_{2v})	Relative energy adiabatic (vertical)
1^1A_1	0
1^1A_2	22.36† (24.78)
1^1B_1	10.59† (9.67)
1^1B_2	33.52
1^3A_1	60.08
1^3A_2	13.43
1^3B_1	3.41
1^3B_2	15.07

The 4-pyridinyloxenium ion has a low energy triplet state. As shown in Table 3, the singlet-triplet gap of the 4-pyridinyloxenium ion **2** is computed to be 3.4 kcal/mol

(1A_1 - 3B_1). Interestingly, the lowest energy triplet state for this ion is not the typical n,π^* triplet state seen with the 2- and 3-pyridinyloxenium ion, but is better described as a triplet nitrenium ion. Indeed, for both the closed-shell singlet and the lowest energy triplet state, the C-O bond length is very short (1.216 and 1.234 Å respectively), suggesting quinoidal nitrenium ion character for both states.

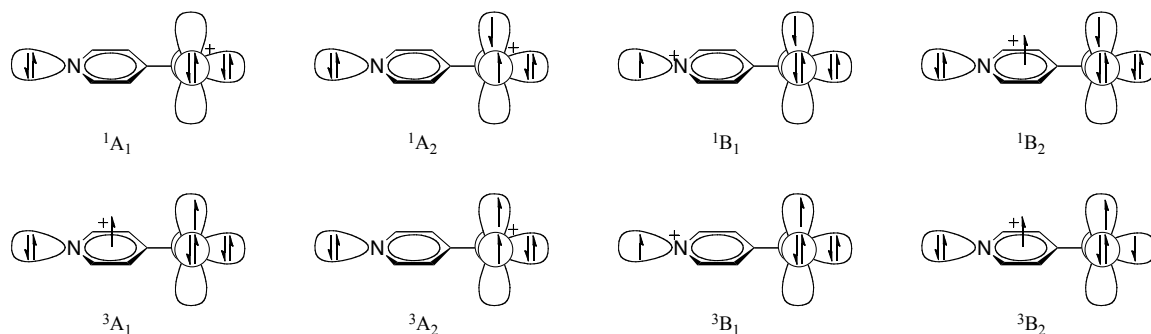


Figure 6: Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of 4-pyridinyloxenium ion **4**.

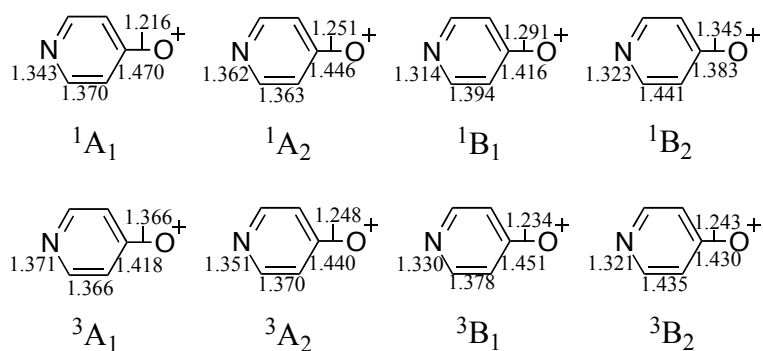


Figure 7: Heavy atom-heavy atom bond lengths (Å) for irreducible representations of **4** (C_{2v} , CASSCF(10,9)/pVTZ).

Table 4. Energies of the lowest irreducible representations of the pyrimidinyloxenium ion.

Irreducible Representation (C_{2v})	Relative energy adiabatic (vertical)
1^1A_1	5.42
1^1A_2	-.35† (0.98)
1^1B_1	56.97
1^1B_2	77.31
1^3A_1	73.73
1^3A_2	0
1^3B_1	56.66† (62.60)
1^3B_2	64.73

Electronic State Orderings of the pyrimidinyloxenium ion. As shown in Table 4, the ΔE_{ST} of the pyrimidinyloxenium ion **5** is essentially zero. Thus, there is little certainty as to whether the 1^1A_2 or the 3^3A_2 state is the ground state of the pyrimidinyloxenium ion. Unfortunately, we were not able to obtain the optimized structure of the 1^1A_2 state. Optimization under symmetry leads to an imaginary frequency. In a broken symmetry calculation of this state, CASPT2 theory places the 1^1A_2 state as the ground state, but it is an excited state at the CASSCF level of theory, leading to intractable problems involving root switching. While the energy from the 1^1A_2 state was unable to be obtained without an imaginary frequency, by looking at this energy as well as the vertical energy, it can be reasonably concluded that the energy is similar to the 3^3A_2 state, although the open-shell singlet state is likely to be lower in energy since it is computed to be lower even without a fully optimized geometry. Also interesting is that the 1^1A_2 has a lower calculated energy than that of the 1^1A_1 state. Both the 1^1A_1 and 1^1A_2 states are close in energy, and both have non-planar geometries.

The significance of having the 1^1A_2 state lower than the 1^1A_1 state suggests that this ion could have an open-shell singlet ground state—quite unusual indeed. In most cases

ground state singlets are closed shell, but if the frontier orbitals approach each other in energy, then either the triplet state or an open-shell singlet can be the ground state. Thus, it makes sense that the 1A_2 and 3A_2 are somewhat close in energy, but it would be expected that the triplet would be lower by a larger amount due to the favorable exchange energy of parallel spins. Both the 1A_2 and 3A_2 states utilize the promotion of an electron from the nitrogen lone pair to the oxygen π orbital.

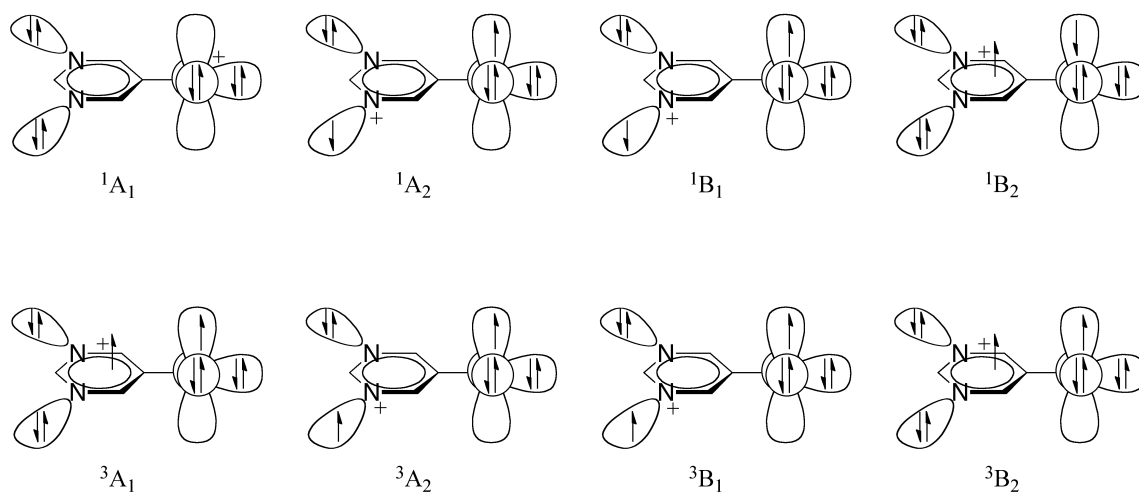


Figure 8: Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of the pyrimidinylloxonium ion **5**.

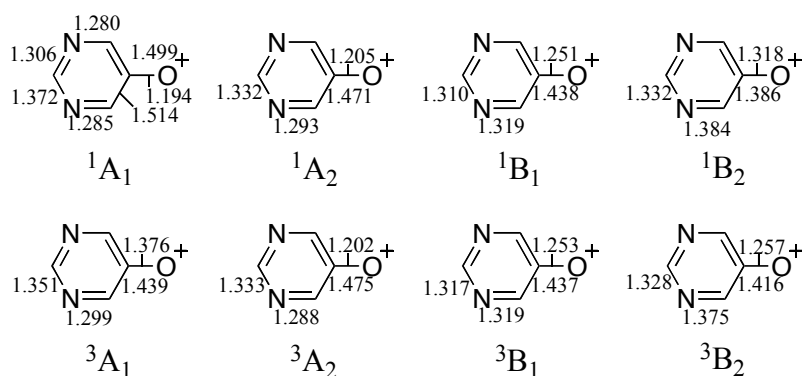


Figure 9: Heavy atom-heavy atom bond lengths (Å) for irreducible representations of **5** (C_{2v} , CASSCF(12,10)/pVTZ).

Table 5. Energies of the lowest irreducible representations of the pyridinyloxenium ion.

Irreducible Representation (C_s)	Relative energy adiabatic (vertical)
$1^1A'$	0
$1^1A''$	3.88† (3.87)
$1^3A'$	9.51
$1^3A''$	1.34

Electronic State Orderings of the pyridinyloxenium ion. As shown in Table 5, the ΔE_{ST} of the pyridinyloxenium ion **6** is computed to be 1.3 kcal/mol. Thus, as with the pyrimidinyloxenium ion, there can be little certainty as to whether the $1^1A'$ or $3^1A''$ state is the ground state of the pyridinyloxenium ion. In fact, with the $1^1A''$ state only 3.88 kcal/mol higher in energy than the $1^1A'$ it is uncertain if the closed shell is actually the lowest energy singlet state. As with the 4-pyridinyloxenium ion, the closed shell singlet is likely destabilized since it has a quinoidal character, which places the positive charge on the more electronegative nitrogen. It should be noted that since the nitrogens' non-bonding orbitals overlap, it was not possible to differentiate one nitrogen from the other, so even though Figure 10 shows the promotion of the electron from the meta nitrogen, it is most likely a mixing interaction between the two nitrogens.

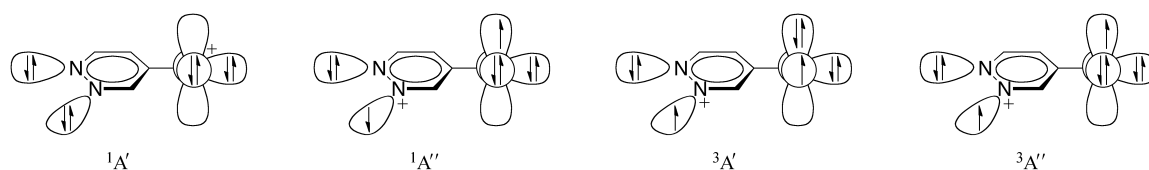


Figure 10: Approximate schematic configurations of the singlet and triplet irreducible representations (C_{2v}) of pyridineoxenium ion **6**.

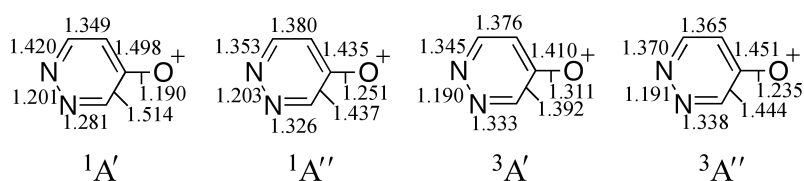


Figure 11: Heavy atom-heavy atom bond lengths (\AA) for irreducible representations of **6** (C_s , CASSCF(12,10)/pVTZ).

CONCLUSIONS

Compared to the phenyloxenium ion **1**, nitrogen based aryloxenium ions have lower ΔE_{ST} in favor of the triplet states. It was shown that the 2- and 3-pyridyloxenium ions only slightly favored the triplet over the phenyloxenium ion, and had very similar orbital energies. The 4-pyridyl, pyridinyl, and pyrimidyl oxenium ions all have a ΔE_{ST} of less than -4 kcal/mol. Stabilization of the triplet state by ca. 20 kcal/mol opens the possibility of ground state triplets as well as rarely seen open shell singlets as ground states.

Supplemental information provides all coordinates and energies for data shown.

Special thanks to Ohio State Supercomputing and Dr. Arthur H. Winter

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Chapter 5

Conclusions

This thesis was designed to show the work that has been done to investigate oxenium ions. The first chapter showed that originally the photoelectron spectroscopy of the phenyloxenium ion was miss assigned and the ΔE_{ST} of the phenyloxenium ion is ca. -20 kcal/mol, which represents the 1A_1 to the 3A_2 (n to π^*) state. Further it was discovered that electron-donating groups in the para position of the ring lead to an increase in the ΔE_{ST} in favor of the triplet where electron-withdrawing groups lead to a smaller ΔE_{ST} in favor of the singlet. It was also discovered that electron-donating groups at the meta position lead to near degenerate $^1A'$ and $^3A'$ (π to π^*) states. The results show that there is a potential to form phenyloxenium ions that would have both ground state singlets as well as triplets.

Chapter 2 was the experimental studies on the phenyloxenium ions that were studied in chapter 1. Precursors to the phenyloxneium ion were formed, and studies showed that the phenyloxenium ion is most likely the intermediate to form the final products. The Laser Flash Photolysis studies were not able to identify any transient species, which is most likely a product of the time frame of the intermediate not being long enough.

Chapter 3 was a computational study on heteroaryl oxenium ions. Specifically these were pyridinyl type oxenium ions with one or two nitrogens placed in the aromatic ring. The reason for this study was to investigate the effect that these nitrogens would have on the energetics. The major conclusion was that the 2- and 3-pyridinyl oxenium

ions have electronic structures and energies that were relatively close to the phenyloxenium ion. However, the 4-pyridyl, pyrimidinyl, and pyrizidinyl oxenium ions all had drastically different energies and electronic states compared to the phenyloxenium ion.

There is still a lot of work to be done in order to further understand these intermediates. Computational chemistry needs to be used at the beginning of these studies in order to give an idea as to what may be observed experimentally. In order to have better experimental studies, precursors to oxenium ions need to take into account problems that have become relevant in past studies.