Combustion Relevant Reactions of ortho-Substituted Phenyl Radicals

Matthew B. Prendergast

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Combustion Relevant Reactions of ortho-Substituted Phenyl Radicals

Matthew B. Prendergast

Supervisor:
Assoc. Prof. Adam J. Trevitt

This thesis is presented as part of the requirements for the conferral of the degree:

Doctor of Philosophy

The University of Wollongong
School of School of Chemistry
Faculty of Science, Medicine and Health

March 2018
Abstract

This thesis explores the gas-phase reactions of ortho-substituted phenyl radicals with neutral species including O₂, allene, and propyne using mass spectrometry. It is revealed that after formation of the reaction adduct, the presence of an ortho-substituent provides an unique intermediate to affect the final product distribution in a manner distinct from meta- and para-substituted phenyl radical reactions.

Experimental and theoretical investigations into the oxidation of o-methylphenyl radicals are detailed, including oxidation of trimethylammonium-substituted o-methylphenyl radical cations using linear quadrupole ion trap mass spectrometry. These results are compared to the oxidation of neutral ortho- and meta-methylphenyl radicals studied using synchrotron-based photoionisation mass spectrometry. G3SX(MP3) and M06-2X methodologies are deployed to examine key decomposition pathways of the 5-(N,N,N-trimethylammonium)-2-methylphenylperoxyl radical and rationalise the observed product ions with the G3X-K composite method is used for oxidation of neutral ortho- and meta-methylphenyl radicals. Experimental and theoretical evidence supports a mechanism for formation of o-quinone methide from o-methylphenyl + O₂ via O₂ addition, H-atom migration to form the QOOH intermediate (hydroperoxy-substituted carbon-centred radical), and subsequent OH elimination.

Synchrotron-based photoionisation mass spectrometry is also used to reveal that the o-hydroxyphenyl + O₂ reaction produces two major products detected at m/z 80 and 108, consistent with cyclpentadienone and o-benzoquinone. The G3X-K method is used to rationalise the o-benzoquinone as a primary product following O₂ addition, H-atom migration, and subsequent OH loss (reminiscent of the Waddington mechanism for β-hydroxyperoxyl radicals). It is concluded that cyclopentadienone forms from prompt decomposition of o-benzoquinone. Distonic ammonium-tagged o-hydroxyphenyl + O₂ reactions were studied and found to produce ions consistent with charged-tagged o-benzoquinone. CID of the charged-tagged o-benzoquinone cation lead to the formation of a cyclopentadienone analogue by CO loss.

Reaction efficiencies for oxidation of ammonium- and trimethylammonium-substituted o-methylphenyl and o-hydroxyphenyl radicals are reported at around 5%, not significantly affected by the identify of the ortho-substituent.
The thesis extends beyond the oxidation of ortho-substituted phenyl radicals to explore reactions of o-methylphenyl radical reactions with C₃H₄ isomers: allene (CH₂CCH₂) and propyne (CHCCH₃). Synchrotron-based photoionisation mass spectrometry reveals two product mass channels for both allene and propyne reactions with o-methylphenyl radicals, consistent with CH₃ and H-atom loss. The CH₃ loss co-product is conclusively assigned indene (C₉H₈). But, H-atom loss produced two different products for allene and propyne reactions: a mixture of 1,2- and 1,4-dihydronaphthalene from allene reactions and exclusively 1,2-dihydronaphthalene from propyne reactions.

The reactions described in this thesis could serve as unique sources of both OH radicals and CO from oxidation reactions and fused-ring structures from C₃H₄ reactions in reactive environments (e.g. lignin combustion and carbon-rich atmospheres). The underlying premise is: the addition of a neutral closed shell species to an ortho-substituted radical forms a reaction intermediate with an ortho-substituent that will undergo intramolecular 1,5-H atom migration and subsequent elimination reactions to produce new products. Such pathways are deemed unlikely for the corresponding meta- and para-cases.
Acknowledgments

To my Mum and Dad,

I never felt I was favoured over my siblings and never felt I had to meet some bizarre set of unrealistic expectations. For that, I am grateful.

To the friends that I have kept, rediscovered, and made over years,

I hope that our friendship has brought and continues to bring you as much joy as it has to me.

To Dr. Gabriel da Silva, and Prof. Stephen J. Blanksby, and Assoc. Prof. Adam J. Trevitt (supervisor),

I thank you for your efforts to instruct me in Computational Chemistry, Mass Spectrometry, Physical Chemistry, and the improved use of the English language. I hope the products of our research lead to interesting discoveries in the coming years.

Dr. John D. Savee, Dr. Craig A. Taatjes, and Dr. David L. Osborn,

Through this collaboration we have studied many systems and I hope the continued collaboration will foster great research in the years to come.

Current and past members of the Laser Chemistry Group:

Thank you Dr. Benjamin B. Kirk, Dr. Christopher S. Hanson, Dr. Bartholomew S. Vaughn, Dr. Phillip J. Tracy, Mr. James P. Bezzina, Mr. Cameron B. Bright. And, also, thank you Steve Cooper, Thomas Griffith, and Dr. Alan T. Maccarone.

I would also like to acknowledge the people we have lost during my PhD studies:

Nan, you were an example of what it meant to be smart and tough. I will remember the things you did for us.

Dr. Phillip J. Tracy, I will never entirely understand what happened but I know you worked hard.
Publications

Chapter 3 resulted in the following publication:

URL: http://dx.doi.org/10.1039/C3CP53690D

Chapter 5 resulted in the following publication:

URL: http://dx.doi.org/10.1039/C5CP02953H

The candidate also co-authored the following papers:

URL: http://dx.doi.org/10.1021/jp404965k

URL: http://dx.doi.org/10.1016/j.ijms.2015.07.006

• Cameron C. Bright, Matthew B. Prendergast, Patrick D. Kelly, James P. Bezzina, Stephen J. Blanksby, Gabriel da Silva and Adam J. Trevitt, “Highly
URL: http://dx.doi.org/10.1039/C7CP06644A

URL: http://dx.doi.org/10.1021/acs.jpca.7b09411
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<th>Full Form</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AIE</td>
<td>Adiabatic ionisation energy</td>
</tr>
<tr>
<td>ALS</td>
<td>Advanced Light Source</td>
</tr>
<tr>
<td>CID</td>
<td>Collision induced dissociation</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>IRC</td>
<td>Intrinsic reaction coordinate</td>
</tr>
<tr>
<td>IE</td>
<td>Ionisation energy</td>
</tr>
<tr>
<td>LBNL</td>
<td>Lawrence Berkeley National Laboratory (commonly known as Berkeley Lab)</td>
</tr>
<tr>
<td>MPIMS</td>
<td>Multiplexed photoionisation mass spectrometry</td>
</tr>
<tr>
<td>Nd-YAG</td>
<td>Neodymium-doped yttrium aluminium garnet</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>PD</td>
<td>Photodissociation</td>
</tr>
<tr>
<td>PE</td>
<td>Photoelectron</td>
</tr>
<tr>
<td>PEPICO</td>
<td>Photoelectron photoion coincidence spectroscopy</td>
</tr>
<tr>
<td>PI</td>
<td>Photoionisation</td>
</tr>
<tr>
<td>PI-MS</td>
<td>Photoionisation mass spectrometry</td>
</tr>
<tr>
<td>RMG</td>
<td>Reaction Mechanism Generator</td>
</tr>
<tr>
<td>RRKM</td>
<td>Rice-Ramsperger-Kassel-Marcus theory</td>
</tr>
<tr>
<td>TE</td>
<td>Threshold electron detection</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of flight</td>
</tr>
<tr>
<td>VIE</td>
<td>Vertical ionisation energy</td>
</tr>
<tr>
<td>VRI</td>
<td>Valley-ridge inflection</td>
</tr>
<tr>
<td>VUV</td>
<td>Vacuum ultraviolet</td>
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Chapter 1

Introduction

The Paris Agreement aims to reduce global greenhouse gas emissions (including CO$_2$) to limit the average global temperature rise by 2°C above pre-industrial temperatures.$^{1-3}$ Currently, fossil fuel combustion represents a significant contribution toward the total global CO$_2$ budget$^4$ and projected to account for 78% of energy use in 2040.$^5$

A strategy for mitigating CO$_2$ emissions in fossil fuel combustion is the improved efficiency and performance of combustion technology.$^6$ Historically, this requires empirical study of engine performance, fuel consumption, and fuel blend properties (e.g. the research octane number).$^7$ However, the combustion characteristics of new low-emission alternatives to conventional spark and diesel engines, e.g. homogeneous charge compression ignition (HCCI), are determined by fuel chemistry.$^8$ Tuning new fuels for these technologies requires a fundamental understanding of combustion chemistry.$^9$ A recent review advocated the construction of predictive chemical models, that include fundamental chemical processes, to inform development of more efficient fuels: “There is not enough time to innovate by empirical approaches... Some of the most promising new engine strategies hinge upon control by chemistry, rather than control by physics (e.g., spark plug timing).”$^{10}$

Predictive models of complex reaction systems require empirical data to construct plausible reaction mechanisms for fuel ignition and pyrolysis, but also to assess outputs of the model. Substituted aromatics represent a significant proportion of transport fuels and biofuel stocks.$^{11}$ Methylbenzenes, for example, are used for their high research octane number and energy density,$^{12,13}$ while phenolic species enhance the oxidative stability of diesel fuels.$^{14-17}$

Following H-atom abstraction in reactive environments, substituted aromatic radicals do not always follow the conventional phenyl oxidation mechanisms outlined in Scheme 1.$^{19-28}$ The two key pathways for phenyl + O$_2$, after O$_2$ addition are: (i) O$(3P)$ loss from the peroxyl radical adduct at temperatures >900 K, and (ii) formation of the reactive oxeinoxyl radical followed by prompt decomposition at
<900 K. In the case of ortho-substituted phenyl radicals, e.g. after O₂ addition to form the methylphenylperoxyl radical, the peroxy radical can abstract a H atom from the proximal methyl substituent to react along new pathways. The primary aim of this thesis is to identify dominant products and pathways for oxidation of o-methylphenyl radicals (Chapters 3 and 4) and o-hydroxyphenyl radicals (Chapter 5), and reactions of o-methylphenyl radicals with C₃H₄ isomers (Chapter 6).

The reactions of ortho-substituted methylphenyl and hydroxyphenyl radicals are implicated in mechanisms for oxidation of o-xylene at 1155 K, benzyl decomposition, and lignin pyrolysis. H-atom abstraction from toluene and phenol will predominantly result in resonantly stabilised benzyl and phenoxy radicals, respectively. This is rationalised by the relatively large difference between bond dissociation energies for benzyl C-H and phenolic O-H (89.8 ± 0.6 and 90 ± 3
kcal mol\(^{-1}\)) and the benzene C-H (112.9 ± 0.5 kcal mol\(^{-1}\)).\(^{37}\) In the case of toluene, at 1000 K the product branching ratio for methylphenyl and benzyl radicals by \(^{\bullet}\)OH abstraction reactions is close to 1:3, increasing to 1:2 at 2000 K.\(^{34}\) Furthermore, the lifetime of the methylphenyl species near low-temperature autoignition conditions (1100 K) is sufficient for bimolecular reactions.\(^{38,39}\) In the case of phenol, H-abstraction from the phenyl ring is expected at temperatures >390 K.\(^{40}\)

Theoretical work on the isomerisation of methylphenyl radicals to resonantly stabilised benzyl radicals suggests that the lifetime of ortho-substituted phenyl radicals at <1100 K (in the low-temperature combustion regime\(^{10,18}\)) is sufficient for bimolecular reactions.\(^{38}\) However, the ortho-, meta-, and para-methylphenyl isomers are treated similarly when considered for both low-temperature\(^{41-43}\) and high-temperature combustion models (i.e. >1100 K).\(^{44-46}\) These models presume the abundance of methylphenyl radicals is near zero, or treat the substituent as a spectator to the phenyl-like oxidation reactions illustrated in Scheme 1.1.\(^{27,28}\) The latter is also said for o-hydroxyphenyl radicals.\(^{47}\)

The oxidation of para-methylphenyl radicals, for example, is rationalised by phenyl-like oxidation mechanisms.\(^{48}\) However, for o-methylphenyl radicals, a computational study has revealed a new mechanism after O\(_2\) addition.\(^{29}\) After O\(_2\) addition, the proximity of the peroxy and methyl groups in the o-methylphenylperoxy radical allows a 1,5-H atom shift and subsequent OH elimination to produce quinone methide. It is plausible that such a mechanism occurs for o-methylphenyl radicals in low-temperature combustion but not at higher temperatures (>1100 K) where the radical lifetime is far shorter. Chapters 3 and 4 provide experimental evidence for the low-temperature oxidation of o-methylphenyl radicals, producing o-quinone methide + OH. An analogous pathway for o-hydroxyphenyl radicals is also supported by data presented in Chapter 5. This mechanism also has similarities to the Waddington mechanism for \(\beta\)-hydroxyperoxy radicals.\(^{49-51}\)

The reactions of phenyl radicals with both allene and propyne (C\(_3\)H\(_4\)), similar to phenyl radical oxidation, have been studied\(^{52-58}\) and are of interest to PAH formation. The addition of phenyl radical radicals to both C\(_3\)H\(_4\) isomers leads to a common intermediate and H-atom loss to form indene.\(^{55,56}\) Transition state theory and RRKM-master equation analyses\(^{57,58}\) also predict indene + H at low temperatures and pressures while styrene + CH\(_3\) is the main CH\(_3\) loss channel. Unlike with hydrogen abstraction, acetylene addition (HACA) mechanism for PAH growth,\(^{59}\) the C\(_3\)H\(_4\) reaction products are not highly symmetrical.

An investigation by para-methylphenyl radicals with both C\(_3\)H\(_4\) isomers produced 5- and 6-methylindene + H\(_2\),\(^{60}\) consistent with the findings of previous phenyl radical + C\(_3\)H\(_4\) studies. As with para-methylphenyl oxidation\(^{48}\) and meta-methylphenyl oxidation in 4, the methyl substituent was a spectator to the reaction. Chapter 6
reveals two fused-ring structures formed by the reaction of o-methylphenyl radicals with allene and propyne that are rationalised by participation of the o-methyl substituent (as was done with o-methylphenyl oxidation).

The reactions of radicals are difficult to study in isolation due to the high reactivity and difficulty in producing high quantities. Identification and characterisation of reaction intermediates and the subsequent products remain a challenge. Consequently, computational chemistry has dominated the literature especially in elucidation of reaction mechanisms and reaction enthalpies. However, a number of experimental strategies have been implemented to understand fundamental phenyl radical reactions. They include, but not limited to: single-collision crossed molecule beam studies that provide important dynamical information, heated micro-reactor studies, and shock tube experiments.

The two methods used in this thesis are synchrotron-based time-resolved photoionisation mass spectrometry and distonic ion mass spectrometry. The former utilises a multiplexed photoionisation mass spectrometer at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) synchrotron, which is described in Chapter 2. The high-flux and tunability of the VUV radiation from the ALS synchrotron is effectively unobtainable with conventional bench-top laser based methods. Coupled with time-of-flight mass spectrometry, this endstation has the ability to distinguish isomers by photoionisation onsets using known and calculated adiabatic ionisation energies, and quantify product branching ratio by examination of photoionisation spectra.

Distonic ion mass spectrometry, as described in Chapters 3 and 5, exploits charge-tagged derivatives of neutral radical species to study radical kinetics and reaction products by ion-trap mass spectrometry. These distonic ion oxidation experiments build on a framework provided by previous studies of distonic phenyl radical oxidation, which established that phenyl oxidation typically occurs with around 5% reaction efficiency, (i.e. measured second-order rate coefficient divided by the collision limit). This approach can allow the isolation and characterisation of intermediates and products. This ability, coupled with photo- and collision-induced dissociation, can provide information on dissociation pathways e.g. the CO loss described in Chapter 3. This capacity is essential to the development of reaction mechanisms that accurately describe the generation of isomeric products.

A challenge in the study of radical reactions is the isolation of reactive intermediates and products. One approach is the use of ion-trap mass spectrometry and distonic radical ions as analogues to neutral radicals. Distonic radical cations are characterised by the spatial and electronic separation of the radical and charge site. Examples of distonic pyridine and aniline radical cations are juxtaposed with their conventional radical ions in Scheme 1.2. It is not necessary that the
distonic radical cation be less stable, for example, \(N\)-protonated pyridinyl radical cations are more stable than the conventional radical cation in Scheme 1.2.\textsuperscript{73} The separate charge and radical sites of distonic ion allows the use of ion-trap mass spectrometry to isolate and hold reactants and probe reaction products. Barriers to distonic radical and molecule reaction can be treated as an avoided curve crossing\textsuperscript{74} under the ionic curve-crossing model.\textsuperscript{61,75} Gryn’ova \textit{et al.} have also demonstrated for negative ions that the effect of the charged-tag substituent is a through-space Coulombic affect, \textit{i.e.} reducing at 1/r where \(r\) is the separation between charge and radical sites.\textsuperscript{76} Distonic radical cations were used to probe the reactions of peroxyl radicals, such as the 4-(\(N,N,N\)-trimethylammonium)phenylperoxyl radical cation.\textsuperscript{70,77,78}

The utility of distonic cations is illustrated in Chapter 3 and 5 where the oxidation of \textit{ortho}-substituted radicals produced a quinone-type product from OH elimination. These results are complemented by the studies of neutral radicals in 4 and 5. Though the intrinsic reactivity of the radical may be perturbed by the presence of a near-by charge,\textsuperscript{61,76,79} studies on distonic radical ions provide useful information on the reactions of their neutral counterparts.\textsuperscript{77,79–81}

This thesis explores the reactions of select \textit{ortho}-substituted phenyl radicals (distonic and neutral) with a neutral species (\(O_2\), allene, and propyne). Chapter 2 describes the instrumentation and methodology used to investigate the reactions described in subsequent chapters. Chapters 3 and 4 describe oxidation of distonic and neutral \(o\)-methylphenyl radicals, respectively. Chapter 5 is also a complementary study of distonic and neutral \(o\)-hydroxyphenyl radical reactions with \(O_2\). The \(O_2\) reactant is changed for allene and propyne in Chapter 6 for \(o\)-methylphenyl radical reactions. Conclusions and future directions are summarised in the final Chapter 7.
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Chapter 1. Introduction


Chapter 1. Introduction


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Chapter 1. Introduction


Chapter 2

Instrumentation and Methodology

Reactions of distonic radical cations were investigated using ion trap mass spectrometry at the University of Wollongong, as described in Chapters 3 and 5 with further details in Section 2.2. The reactions of neutral substituted-phenyl radicals were investigated using multiplexed time-resolved photoionisation mass spectrometry (MPIMS) with synchrotron-generated VUV radiation as described in Chapters 4-6 with additional details provided in Section 2.1. Quantum chemical calculations for both neutral and distonic systems were conducted as described in Chapters 3–6 and summarised in Section 2.3 using programs such as Gaussian 09.¹

Segments of Chapter 2 are reiterated in subsequent Chapters 4, 5, and 6. These chapters were originally produced for publication in peer-reviewed journals and therefore include descriptions important to understanding the instrumentation and methodology.

2.1 Synchrotron-Based Photoionisation Mass Spectrometry

Experiments that utilise the multiplexed photoionisation mass spectrometer (MPIMS) with synchrotron-generated VUV ionising radiation are conducted on the Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source, Lawrence Berkeley National Labs (ALS, LBNL) in collaboration with scientists from LBNL and the Combustion Research Facility at Sandia National Laboratory in Livermore. An overview and important considerations for the Chemical Dynamics Beamline 9.0.2 and MPIMS experiment are outlined in Section 2.1.1 and 2.1.2.
### 2.1.1 Chemical Dynamics Beamline (Beamline 9.0.2)

The VUV radiation utilised at the Chemical Dynamics Beamline (Beamline 9.0.2) is generated using a synchrotron, these are instruments that accelerate electrons travelling close to the speed of light. Synchrotron radiation is emitted from these electrons as they are accelerated by bending magnets or undulators. On Beamline 9.0.2, the VUV radiation is generated by an undulator.

At the ALS, free electrons are generated by heating a barium aluminate cathode and separated into electron packages with radiation from two klystron microwave amplifiers. The electron packages are then accelerated by a linear accelerator before entering the smaller of two synchrotrons. In the smaller synchrotron, microwave cavities resonant at 500 Hz accelerate the electron packages close to the speed of light. When the electron packages have reached a target speed they are injected into the larger of two synchrotrons where microwave cavities maintain the speed of electron packages. In the larger synchrotron, an undulator oscillates electrons travelling close to the speed of light to generate VUV synchrotron radiation. Figure 2.1 is a schematic representation of an undulator utilised on Beamline 9.0.2, which has $43 \times 10$ cm periods.

![Figure 2.1. Schematic representation of an undulator used to generate VUV radiation. Electrons within the synchrotron are directed along the z-axis of an alternating, periodic magnetic structure: an undulator. The alternating magnetic field accelerates the electrons normal to the direction of their velocity, causing the electrons to oscillate horizontally (x-axis). Arrows on the magnets indicate the peak magnetic field direction. In reference to Equations 2.2 and 2.3: the y-axis distance between the two array of magnets ($d_y$) is adjusted to control the peak magnetic field strength ($B_0$) experienced by electrons and therefore, control the fundamental wavelength of radiated light ($\lambda_1$). Interference of radiation from many electrons result in a coherent light source when $K \leq 1$.](image)

In reference to Figure 2.1, y-axis distance between the two array of magnets ($d_y$) can be adjusted to control the peak magnetic field strength ($B_0$) and, in turn,
the deflection parameter ($K$) parameter. This $K$ parameter describes the electron motion within the undulator. Small $K$ values infer a small amplitude of oscillation within the $x$-axis of Figure 2.1 while a large $K$ parameter should infer a large amplitude. Typical operation of an undulator requires $K \leq 1$ and it is calculated from Equation 2.2.

$$K = \frac{eB_0\lambda_u}{2\pi mc} \quad (2.1)$$

$$= 0.934B_0\lambda_u \quad (2.2)$$

Where $e$ is electron charge (Coulomb), $B_0$ is the peak magnetic field strength (Teslas), $\lambda_u$ is the spatial period of the alternating periodic structure (cm), $m$ is the electron mass, and $c$ is the electron speed.

The fundamental wavelength of radiated light ($\lambda_1$) is calculated from Equation 2.3 and is a function of the $K$ parameter, which is dependent on $d_y$ as defined in Figure 2.1.

$$\lambda_1 = \frac{1 + \frac{K^2}{2}}{2m^2c^4}\lambda_u \quad (2.3)$$

Synchrotron radiation produced at the undulator is directed along the Chemical Dynamics Beamline. Figure 2.2 shows a schematic of the Chemical Dynamics Beamline reproduced from Ref. 2. The MPIMS is coupled to Terminal 3 of the Chemical Dynamics Beamline.

The VUV radiation from the undulator is directed by a spherical mirror (M1) and toroidal mirror (M2) though a windowless harmonic gas filter, transmitted through a 3 m path length monochromator (10$^{14}$ s$^{-1}$ flux, 0.1% bandwidth), and the monochromatised light is reflected toward Terminal 3 (T3). Typically, argon gas is used in the windowless harmonic gas filter to transmit primary undulator harmonics <15.8 eV. Secondary harmonics <7.8 eV are also transmitted. To limit the effect of secondary harmonics when exploring photon energies near 7.8 eV a low-pass MgF$_2$ filter is inserted before T3 to transmit photons with energies <11.4 eV and secondary harmonics <5.7 eV–less than the photon energies normally achieved at T3 (7.4 eV).
Figure 2.2. Schematic diagram of the Chemical Dynamics Beamline 9.0.2 at the ALS, LBNL. VUV undulator radiation (5–30 eV) is directed by a spherical mirror (M1) and toroidal mirror (M2) through a windowless harmonic gas filter, transmitted through a 3 m path length monochromator ($10^{14}$ s$^{-1}$ flux, 0.1% bandwidth), and then reflected toward Terminal 3 (T3). The monochromatised output at T3: photon energies between 7.4–15.8 eV with $10^{12}$–$10^{14}$ s$^{-1}$ flux and a resolution between 10–50 meV. T1, T2, T4, and T5 are other terminals on beamline 9.0.2. Beamline 9.0.1 shares an undulator with 9.0.2.


2.1.2 Multiplexed Time-Resolved Photoionisation Mass Spectrometry (MPIMS)

The MPIMS instrument was constructed and reported by Osborn et al.\textsuperscript{5} then subsequently refitted with an orthogonal-extraction time-of-flight (TOF) mass detector.\textsuperscript{6} The MPIMS instrument coupled to the Chemical Dynamics Beamline via Terminal 3 shown in Figure 2.2. Figure 2.3 is a schematic representation of the MPIMS instrument coupled with Beamline 9.0.2.

Information on the MPIMS instrument and its application to the study of radical-neutral reaction is provided in Chapters 4, 5, and 6. A brief description is provided here. The apparatus includes: a slow-flow reactor tube with a pinhole to allow the escape of reacted gases, a skimmer to produce a near- effusive molecular beam from gases escaping the reactor, a vacuum region where gas-phase species experience VUV synchrotron radiation and undergo photoionisation, and an orthogonal acceleration time-of-flight (TOF) mass spectrometer. Additional information helpful to understanding the measurement of photoionisation signal intensity is provided in Section 2.1.2.1.

Radicals are generated within the reactor by photolysis of gas-phase halogenated radical precursors at 248 nm from a pulsed KrF excimer laser operating at 4 Hz. The radical precursors and co-reactants, such as O\textsubscript{2} and C\textsubscript{3}H\textsubscript{4}, are supplied to the reactor via separate mass flow controllers. A detailed description of the reactor gas flow can be derived from Section 2.1.2.2, which includes an example calculation.

2.1.2.1 Instrumental Parameters

The arrival times for each detectable ion are recorded with respect to the KrF excimer laser pulse in a duty cycle (250 ms).

Mass measurement with the orthogonal acceleration time-of-flight (TOF) mass spectrometer is achieved by applying Equation 2.4.\textsuperscript{7} Where \( m \) is the ion mass, \( q \) is the ionic charge, \( \alpha \) and \( \beta \) are the instrument-dependent calibration constants.

\[
m = q (\alpha \tau + \beta)^2
\]  

(2.4)

The \( \alpha \) and \( \beta \) constants are derived experimentally. First, a standard mixture containing ethene (C\textsubscript{2}H\textsubscript{4}), propene (C\textsubscript{3}H\textsubscript{6}), and butene (C\textsubscript{4}H\textsubscript{8}) is supplied to the MPIMS. Second, uncalibrated mass spectra are acquired with \( \tau \) along the x-axis. Finally, Equation 2.5 is to a plot of \( \sqrt{\frac{m}{q}} \) against \( \tau \) where \( \alpha \) is the slope and \( \beta \) is the y-axis intercept.
Figure 2.3. Schematic illustration of the MPIMS instrument interfaced with Terminal 3 on the Chemical Dynamics Beamline at the ALS. The MPIMS instrument comprises a slow-flow quartz reactor tube, a vacuum chamber where interaction VUV synchrotron radiation generates ions, and orthogonal acceleration time-of-flight (TOF) mass spectrometer.

\[
\sqrt{\frac{m}{q}} = \alpha \tau + \beta
\]  

(2.5)

The energy-dependent ion signal intensity from photoionisation of a neutral species \(S_{PI}^i(E)\) is described by Equation 2.6 (Ref. 6) where \(\Lambda\) is a combination of instrumental constants, \(\sigma_{PI}^i(E)\) is the energy-dependent photoionisation cross section of the neutral, \(N_i\) is the ion concentration, and \(\alpha_i\) is the mass-discrimination factor.

\[
S_{PI}^i(E) = \Lambda \sigma_{PI}^i(E) N_i \alpha_i
\]  

(2.6)

If multiple ionic species are detected with the same mass-to-charge ratio, the total \(S_{PI}^i(E)\) is described by Equation 2.7. In Equation 2.8 the \(\Lambda, N_i, \text{and } \alpha_i\) terms are combined in the \(\omega_i\) weighting term.

Absolute PI spectra can be fitted to experimental PI spectra using Equation 2.8. The ratio of \(\omega_i\) terms will provide relative branching ratios for a mass-to-charge ratio. However, if a relative PI spectrum is substituted for \(\sigma_{PI}^i(E)\), the product branching ratio cannot be quantified though still providing a product assignment.
\[ S_{\text{total}}^{PI}(E) = \sum_{i=1}^{n} S_{i}^{PI}(E) \]  
\[ = \omega_1 \sigma_1^{PI}(E) + \omega_2 \sigma_2^{PI}(E) + ... + \omega_n \sigma_n^{PI}(E) \]

### 2.1.2.2 Gas Flow Calculations

Assuming the gas flow within the quartz reactor tube is ideal, the number density of a gas supplied to the reactor by a mass flow controller \((N_A)\) is derived from Equation 2.11

\[ \frac{N_A}{N_{\text{total}}} = \frac{Q_A}{Q_{\text{total}}} \]  
\[ \Rightarrow N_A = \frac{Q_A}{Q_{\text{total}}} \times N_{\text{total}} \]  
\[ N_A = \frac{Q_A}{Q_{\text{total}}} \times \frac{P_{\text{total}}}{kT_{\text{total}}} \]

where \(N_{\text{total}}\) is the total number density of the reactor flow (including all reactants and additional He). \(Q_A\) is the mass flow rate of a gas controlled by a mass flow controller and \(Q_{\text{total}}\) is the total mass flow rate through the reactor in sccm units (standard cm\(^3\) min\(^{-1}\)). \(P_{\text{total}}\) and \(T_{\text{total}}\) are the pressure and temperature of the gas flow within the reactor (typically \(P_{\text{total}} = 4\) Torr).

The number density of a radical precursor \((R)\) supplied to the reactor as a radical precursor + He gas mixture is derived from Equation 2.12 or 2.13 when \(N_A\) is known

\[ N_R = \frac{P_R}{P_A} \times N_A \]  
\[ N_R = \frac{\rho_R}{1\ \text{atm}} \times N_A \]

where \(P_R\) is the partial pressure of the halogenated precursor in the gas mixture, and \(\rho_R\) is the vapour pressure of the halogenated precursor.

The reactor gas flow velocity \((v)\) through the reactor’s cross-sectional area \((a)\) is calculated using Equation 2.14 where the total volumetric flow rate at non-standard conditions \(Q_{\text{total}}^*\) is provided by Equation 2.15

\[ v = \frac{Q_{\text{total}}^*}{a} \]
\[ Q^*_{\text{total}} = Q_{\text{total}} \times \frac{P_{\text{ref}}}{P_{\text{total}}} \times \frac{T_{\text{total}}}{T_{\text{ref}}} \]  \hspace{1cm} (2.15)

where \( T_{\text{ref}} \) and \( P_{\text{ref}} \) are the reference temperature and pressure for the sccm unit (standard \( \text{cm}^3 \text{ min}^{-1} \)).\(^a\)

An example calculation is provided below at 25 °C (298.15 K) and 4 Torr with a mass flow rate of 100 sccm and reactor diameter of 1.05 cm.

\[ Q^*_{\text{total}} = 100 \text{sccm} \times \frac{760 \text{Torr}}{4.00 \text{Torr}} \times \frac{298.15 \text{K}}{273.15 \text{K}} \]
\[ = 20700 \text{ cm}^3 \text{ min}^{-1} \]
\[ = 346 \text{ cm}^3 \text{ s}^{-1} \]

The reactor is cylindrical with a diameter of 1.05 cm therefore, \( a = 0.866 \text{ cm}^2 \)

\[ a = \pi r^2 \]  \hspace{1cm} (2.16)
\[ = \pi \times \left( \frac{1.05 \text{ cm}}{2} \right)^2 \]
\[ = 0.866 \text{ cm}^2 \]

Substituting \( Q^*_{\text{total}} = 346 \text{ cm}^3 \text{ s}^{-1} \) and \( a = 0.866 \text{ cm}^2 \) into Equation 2.14 returns \( v = 3.99 \text{ m s}^{-1} \).

\[ v = \frac{Q^*_{\text{total}}}{a} \]  \hspace{1cm} (2.14)
\[ = \frac{346 \text{ cm}^3 \text{ s}^{-1}}{0.866 \text{ cm}^2} \]
\[ = 399 \text{ cm s}^{-1} \]
\[ = 3.99 \text{ m s}^{-1} \]

### 2.2 Ion Trap Mass Spectrometry

Distonic radical cation experiments conducted using ion-trap mass spectrometry at the University of Wollongong are described in Chapters 3 and 5. A schematic of the Thermo Fisher Scientific LTQ linear quadrupole ion trap mass spectrometer

\(^a\) MKS Instruments define “standard” to be referenced to 0°C and 760 Torr.
utilised in these experiments is included in Figure 2.4. The following section provides a detailed description of the methodology for kinetic data analysis.

![Figure 2.4. Schematic illustration of the modified Thermo Fisher Scientific LTQ linear quadrupole ion trap mass spectrometer coupled with a Minilite Nd:YAG pulsed laser operating in the 4th harmonic ($\lambda = 266$ nm). The pressure within the linear ion trap region is approximately 2 mTorr at 318 ± 23 K.](image)

### 2.2.1 Overview of Kinetic Data Analysis

#### 2.2.1.1 Measuring Change in Radical Cation Quantities with Time

Reactive radical ions isolated and held within the ion trap are allowed to react with neutral reactants fed into the ion-trap region. The reaction time is controlled by adjusting the activation period parameter with the control software, which corresponds to a period of ion storage, while maintaining a normalised collision energy of 0% (zero percent). At least 10 individual mass spectral acquisitions were collected for each reaction time. Unlike conventional kinetic measurements, a new sample of reactive radical cations is required to measure the effect of each reaction time. Automatic gain control (via ion optics and algorithms) is utilised to minimise signal saturation and space charge effects that would otherwise affect signal quality between MS acquisitions.

The radical cation number density is not measured directly. Instead, changes in radical cation number density with reaction time is determined from product mass spectra with the presumption that ion signal intensity at each $m/z$ is linearly proportional to the ion number density.

The typical product mass spectrum at a set reaction time is the average of at least 10 individual mass spectral acquisitions. For each mass spectral acquisition that composes a product mass spectrum:

---

$^b$Normalised collision energy, within the linear ion trap, the RF voltage is adjusted so the collisional energy is linearly proportional to mass-to-charge. Zero (0%), on this scale, means that no additional resonant excitation is applied.
1. The integrated ion signal is calculated by summation of heights for data points that compose the \( m/z \) peak profile, typically a \( m/z \) range of 1 centred around the nominal \( m/z \).

2. The peak integral is normalised to the summation of heights for all data points that compose the mass spectral acquisition.

3. And, the normalised peak integral is averaged for all mass spectral acquisition that compose a product mass spectrum to obtain the average normalised integrated signal intensity \( (S) \).

However, for Figure 3.2 in Section 3, the product mass spectra were averaged of at least 50 mass spectral acquisitions and the integral of the peak within the product mass spectrum was normalised to the integral over all data points that compose the product mass spectrum.

### 2.2.1.2 Pseudo-First Order and Second-Order Rate Coefficients

For a bimolecular second-order reaction between a radical cation (A) and neutral reactant (B), the decay rate for A is represented by Equation 2.17. If \([B] \gg [A]\) and \(\frac{d[B]}{dt}\) is small compared to \([B]\) (i.e. \(\frac{d[B]}{dt} \approx 0\)), then \(k_{2nd}[B]\) is approximately constant and equated with \(k'\) to provide Equation 2.18.

\[
\begin{align*}
-\frac{d[A]}{dt} &= k_{2nd}[A][B] \\
-\frac{d[A]}{dt} &= k'[A]
\end{align*}
\]  

(2.17)  

(2.18)

The average normalised integrated signal intensity for a \( m/z \) \((S)\), described in Section 2.2.1.1, is substituted into Equation 2.18 to obtain Equation 2.19 presuming \(S\) is linearly proportional to radical cation number density. Subsequent rearrangement of Equation 2.19 and the integration of Equation 2.20 yields Equation 2.23, which is simplified further to Equation 2.25.
\[ -\frac{dS}{dt} = k'S \quad (2.19) \]
\[ \frac{dS}{S} = -k' \, dt \quad (2.20) \]
\[ \int_0^t \frac{1}{S} \, dS = \int_0^t -k' \, dt \quad (2.21) \]
\[ \ln S_t - \ln S_{t=0} = -k't + k' \times 0 \quad (2.22) \]
\[ \ln S_t = -k't + \ln S_{t=0} \quad (2.23) \]
\[ \exp(\ln S_t) = \exp(-k't + \ln S_{t=0}) \quad (2.24) \]
\[ S_t = S_{t=0} \exp(-k't) \quad (2.25) \]

If the average normalised integrated signal intensity exhibits exponential decay and approaches a constant non-zero value \( C \) attributed to an unreactive portion of the ion population then the total average normalised integrated signal intensity \( (S_{\text{total}}) \) is described by Equation 2.26 and 2.27, where \( 0 \leq C \leq 1 \) and \( S_{t=0} = 1 - C \).

\[ S_{\text{total}} = S_t + C \quad (2.26) \]
\[ S_{\text{total}} = S_{t=0} \exp(-k't) + C \quad (2.27) \]

The pseudo-first order rate coefficient \( (k') \) is derived by fitting Equation 2.27 to experimental data. If the concentration of the neutral reactant \( ([B]) \) is known the second-order rate coefficient \( (k_{2\text{nd}}) \) is calculated with Equation 2.29.

\[ k' \times S = k_{2\text{nd}}[B] \times S \quad (2.28) \]
\[ \implies k_{2\text{nd}} = \frac{k'}{[B]} \quad (2.29) \]

The importance of fitting Equation 2.27 instead of utilising a semi-log plot and fitting Equation 2.23 is demonstrated by Figure 2.5, which shows seven hypothetical exponential decay curves presented in two fashions. The data in Figure 2.5(a) is described by Equation 2.27 while Figure 2.5(b) shows that semi-log plots cannot be utilised to derive pseudo-first order rate coefficients \( (k') \) when \( S_{\text{total}} \) is affected by non-zero values of \( C \).

### 2.2.1.3 Reaction Efficiencies

The ion-molecule reaction efficiency \( (\Phi) \) from Equation 2.30 compares the experimental second-order rate coefficient \( (k_{2\text{nd}}) \) from Equation 2.29 to the bimolecular
collisional rate coefficient \( k_{\text{collision}} \) for the ion-molecule collision pair. If every collision between the ion-molecule collision pair resulted in a reaction then the reaction efficiency \( \Phi \) will equal 100%.

\[
\Phi = \frac{k_{2nd}}{k_{\text{collision}}} \times 100\%
\]  

(2.30)

The Langevin collisional rate coefficient, \( k_L \), from Equation 2.31 provides an estimate for \( k_{\text{collision}} \) in Equation 2.30.\(^{11,12}\) The reduced mass term \( \mu \) is a common factor to \( k_{2nd} \) and \( k_{\text{collision}} \), and therefore cancels out. This allows \( \Phi \) for charge-tagged phenyl + \( \text{O}_2 \) to be compared between similar reactions, e.g. ammonium-substituted \( o \)-methylphenyl + \( \text{O}_2 \), to identify possible substituent effects. Interestingly, the phenyl oxidation reactions communicated in this thesis are typically around 5% efficient.

\[
k_L = 2\pi e \left( \frac{\alpha_n}{\mu} \right)
\]  

(2.31)

### 2.3 Computational Chemistry

Quantum chemical calculations were conducted using Gaussian 09\(^1\) to determine reaction enthalpies at 0 K, frequency of molecular vibrational modes, and adiabatic
ionisation energies (AIE). The methods utilised for each investigation are identified within the relevant chapters and include: G3SX(MP3)\textsuperscript{13} and G3X-K\textsuperscript{14} composite methods, M06-2X DFT\textsuperscript{15} with 6-311++G(d,p) basis set, and the CBS-QB3 complete basis set method.\textsuperscript{16,17} Each can reproduce DBH24/08 barrier heights\textsuperscript{18} to within 1 kcal mol\textsuperscript{-1} except for CBS-QB3 (mean absolute error of 1.62 kcal mol\textsuperscript{-1}). For CBS-QB3, errors in AIEs are excepted to within 0.1 eV and 1.1 kcal mol\textsuperscript{-1} for enthalpies of formation (\(\Delta H_0\)).\textsuperscript{17}

Stationary points located an potential energy surfaces were classified as minima with no imaginary frequencies, or as transition states with a single imaginary frequency whose normal mode projection approximates motion along the reaction coordinate. Intrinsic reaction coordinate (IRC) analyses\textsuperscript{19} were conducted to assign transition states between two minima.

Reaction enthalpies were calculated as the difference in zero-point corrected energies between a stationary point and some reference point on the potential energy surface, e.g. the energy of the reactants at infinite separation. The adiabatic ionisation energies (AIEs) for plausible reaction products were calculated as the energy difference between the product (P) and the cation produced from photoionisation (P\(^{•+}\)), both in their ground vibrational state.

In Chapter 5, utilising the MultiWell suite of programs,\textsuperscript{20–22} a preliminary RRKM analysis is conducted to compare pathways for the \(\text{o-hydroxyphenyl} + \text{O}_2\) reaction. DenSum, from the MultiWell suite, uses the Stein-Rabinovitch extension\textsuperscript{23} of the Beyer-Swinehart algorithm\textsuperscript{24} to compute both the sum and density of states necessary for this analysis. This requires computed geometries and normal mode frequencies.
References


Chapter 2. Instrumentation and Methodology


Chapter 3

Distonic

\[ o\text{-Methylphenyl Radical } + \text{O}_2 \]

This chapter examines the oxidation processes and products of ammonium-substituted \textit{o}-methylphenyl radicals. It was published as a peer-reviewed publication (reproduced as Appendix A). The presented form excludes the long table of cartesian coordinates for stationary points along the potential energy surface. It includes updated citation numbers, updated formatting for consistency within the thesis (\textit{e.g.} italicisation of “m/z”), and corrections to the publication (listed in Section 3.8). The reference to the peer-reviewed publication is provided below:

URL: http://dx.doi.org/10.1039/C3CP53690D

Author contributions

Matthew B. Prendergast interpreted mass spectra and completed all theoretical work. Matthew B. Prendergast prepared the manuscript with input from all authors.

Certification

I, Assoc. Prof. Adam J. Trevitt, as the primary supervisor for Matthew B. Prendergast and the principal investigator on this project, agree with and certify the author contributions described above.

Assoc. Prof. Adam J. Trevitt  Date

19/11/2018
3.1 Abstract

The reactions of distonic 4-((N,N,N-trimethylammonium)-2-methylphenyl and 5-
(N,N,N-trimethylammonium)-2-methylphenyl radical cations (m/z 149) with O₂ are
studied in the gas phase using ion-trap mass spectrometry. Photodissociation (PD)
of halogenated precursors gives rise to the target distonic charge-tagged methyl-
phenyl radical whereas collision-induced dissociation (CID) is found to produce un-
reactive radical ions. The PD generated distonic radicals, however, react rapidly
with O₂ to form [M + O₂]⁺⁺ and [M + O₂ - OH]⁺⁺ ions, detected at m/z 181 and
m/z 164, respectively. Quantum chemical calculations using G3SX(MP3) and M06-
2X theories are deployed to examine key decomposition pathways of the 5-(N,N,N-
trimethylammonium)-2-methylphenylperoxyl radical and rationalise the observed
product ions. The prevailing product mechanism involves a 1,5-H shift in the per-
oxyl radical forming a QOOH-type intermediate that subsequently eliminates *OH
to yield charge-tagged 2-quinone methide. Our study suggests that the analogous
process should occur for the neutral methylphenyl + O₂ reaction, thus serving as a
plausible source of *OH radicals in combustion environments.

3.2 Introduction

The study of aryl-radical + O₂ reactions is fundamental to understanding combus-
tion chemistry due to the prevalence of aromatic hydrocarbons in liquid transporta-
tion fuels. Considerable work has been performed on the phenyl radical (C₆H₅.) and
its reactions with O₂.¹⁻¹⁰ Notably, phenyl oxidation does not follow the ROO →
QOOH isomerisation route often encountered when rationalising hydrocarbon radical
oxidation;¹¹ instead, more elaborate peroxyl radical isomerisation channels are
accessed. For substituted phenyl radicals there remains significant uncertainty
around the key mechanisms and dominant reaction products in their oxidation.

Toluene (C₆H₅CH₃) is utilised in transportation fuels at high levels because of
its high energy density and research octane number¹²,¹³ and is also an intermediate
in schemes of polycyclic aromatic hydrocarbon (PAH) and soot formation.¹⁴ The
primary combustion intermediate associated with toluene is generally considered
to be the benzyl radical (C₆H₅CH₂•), rather than methylphenyl radical isomers
(C₆H₄CH₃•), due to the relatively large difference in C-H bond dissociation energies
for methyl (ca. 90 kcal mol⁻¹) and ring (ca. 113 kcal mol⁻¹) hydrogens.¹⁵ Despite the
difference in bond dissociation energies, abstraction reactions by reactive free radic-
als are expected to provide significant yields of methylphenyl radicals; for instance
at 1000 K the product branching ratio for methylphenyl and benzyl radicals by
*OH abstraction reactions is close to 1:3, increasing to 1:2 at 2000 K.¹⁶ The toluene
C-CH\textsubscript{3} bond scission, yielding the phenyl radical, is also significant during thermal decomposition: 20% at 1200 K, and 40% at 1500 K.\textsuperscript{17} Likewise, decomposition of poly-methyl substituted benzenes, such as ortho-xylene, can produce methylphenyl radicals.\textsuperscript{18,19} Isomerisation of the methylphenyl radical to benzyl radical is generally competitive under high-temperature combustion conditions, however lifetimes of methylphenyl species near autoignition temperatures (∼1000 K) are such as to permit bimolecular reactions with O\textsubscript{2}.\textsuperscript{19,20} Despite their plausible contribution in combustion environments, the methylphenyl + O\textsubscript{2} reaction has received relatively little attention. One computational study has suggested that the 2-methylphenyl + O\textsubscript{2} reaction is substantially different from that of the unsubstituted phenyl radicals, in which formation of 2-quinone methide + \textbullet OH is thought to compete (via a process shown in Scheme 3.1) with phenylperoxyl-type isomerisation.\textsuperscript{18} Experimental investigation of the methylphenyl + O\textsubscript{2} system can further the current understanding of toluene oxidation. However, identification and characterisation of reaction intermediates and products remain a challenge. Charge-tagged derivatives of the methylphenyl radicals, \textit{i.e.} the addition of a substituent with a formal charge, can be employed via mass spectrometry to qualitatively assess dominant reaction processes. Here, we provide the first experimental evaluation of 2-methylphenyl + O\textsubscript{2} reaction using the distonic radical ion approach.

\begin{equation}
\begin{align*}
\text{CH}_3	ext{C-CH}_3 & + O_2 \\
\text{2-methylphenyl} & \rightarrow \rightarrow \rightarrow \rightarrow \\
\text{CH}_3\text{CH}_2\text{OO} & \rightarrow \rightarrow \rightarrow \rightarrow \\
\text{2-quinone methide} & + \text{OH}
\end{align*}
\end{equation}

\textbf{Scheme 3.1}

Distonic ions are radical ions characterised by the spatial and electronic separation of the radical and charge site.\textsuperscript{21–23} Though the intrinsic reactivity of the radical may be perturbed to some degree by the presence of a near-by charge,\textsuperscript{24} studies on distonic radical ions undertaken using mass spectrometry nonetheless provide useful information on the reactions of their neutral counterparts.\textsuperscript{24–27} A distonic radical ion approach has previously been employed to probe the fate of peroxyl radical intermediates; including, pyridinium-2-ethylperoxyl radical cation,\textsuperscript{28,29} N-methylpyridinium-4-peroxyl\textsuperscript{27,30} and 4-(N,N,N-trimethylammonium)phenylperoxyl radical cation,\textsuperscript{27,31,32} in addition to 4-(N,N,N-trimethylammoniummethyl)phenylperoxyl, 3-(N,N,N-trimethylammonium)phenylperoxyl, and 4-ammoniumphenylperoxyl radical cations.\textsuperscript{32} In each case, these distonic studies provided insight into the reactivity of the neutral radical analogue.

In this report we investigate the gas-phase synthesis and oxidation of distonic 2-methylphenyl radical cations. Radicals generated in a linear ion-trap mass spec-
trometer by both photodissociation (PD) and collision-induced dissociation (CID) of suitable halogenated precursors are compared and the dehalogenated radical cations are characterised by reactions with O$_2$. CID generated radical cations are found to exhibit low reactivity with O$_2$ on the timescale of the experiment (up to 10 s) suggesting that CID results in concomitant isomerisation, forming an unreactive radical ion isomer. In contrast, the PD generated radical cations readily react with O$_2$ to form the peroxyl radical that is followed by a H-atom shift and *OH elimination, consistent with the formation of charge-tagged 2-quinone methide product. This reaction scheme is supported by quantum chemical calculations.

3.3 Experimental

3.3.1 Materials

4-Bromo-3-methylaniline (97%), 3-bromo-4-methylaniline (98%), and methyl iodide (99.5%) were purchased from Sigma Aldrich (Milwaukee, USA). 3-Iodo-4-methylaniline (98%) was purchased from Alfa Aesar (Ward Hill, USA). 4-(Dimethylamino)benzyl alcohol was purchased from TCI Chemicals (Tokyo, Japan). Acetonitrile, ethyl acetate, methanol (HPLC grade), petroleum ether and potassium carbonate (anhydrous) were purchased from Ajax (Sydney, Australia). Industrial grade O$_2$ was obtained from BOC gases (Sydney, Australia). All commercial compounds were used without additional purification.

4-Bromo-$N,N,N,3$-tetramethylbenzenaminium ($4\text{Br}3\text{Me}$), 3-bromo-$N,N,N,4$-tetramethylbenzenaminium ($3\text{Br}4\text{Me}$) and 3-iodo-$N,N,N,4$-tetramethylbenzenaminium ($3\text{I}4\text{Me}$) iodide salts were synthesised by $N$-methylation of the corresponding primary amines listed above using a method previously described$^{31}$ with modifications detailed in Section 3.7.1 of the Supporting Information. 4-Iodomethyl-$N,N,N$-trimethylbenzenaminium ($4\text{I}\text{Me}$) iodide was synthesised from 4-(dimethylamino)benzyl alcohol by $N$-methylation$^{31}$ followed by iodo-dehydroxylation.$^{33}$ Synthesised compounds were characterised by $^1$H NMR, data provided in Section 3.7.2.

3.3.2 Mass Spectrometry

Experiments were performed on a modified Thermo Fisher Scientific LTQ linear quadrupole ion-trap mass spectrometer (San Jose, USA)$^{34}$ fitted with an IonMax electrospray ionisation source operated in positive ion mode (+ESI) and controlled by Xcalibur 2.0 software. Ions were generated by infusing 5-15 µM methanolic solutions of 4-bromo-$N,N,3$-tetramethylbenzenaminium ($4\text{Br}3\text{Me}$), 3-bromo-$N,N,N,4$-tetramethylbenzenaminium ($3\text{Br}4\text{Me}$), 3-iodo-$N,N,N,4$-tetramethylbenzenaminium ($3\text{I}4\text{Me}$), and 4-iodomethyl-$N,N,N$-trimethylbenzenaminium ($4\text{I}\text{Me}$) iodide salts.
into the electrospray ion source at 5 µL min⁻¹. Typical instrumental settings were: spray voltage (4.5 kV), capillary temperature (200°C), sheath gas flow at 5 (arbitrary units), sweep and auxiliary gas flow at 10 (arbitrary units). Ions were mass-selected using an isolation window of 5–6 Th for 4Br3Me and 3Br4Me, and 1–2 Th for 3I4Me and 4IMe with a q-parameter of 0.250. Mass spectra presented herein are the average of at least 50 scans. In CID experiments, the normalised collision energy applied was typically 20–30 (arbitrary units) with an activation time of 30 ms set within the control software.

3.3.2.1 Photodissociation (PD)

The modifications to the ion-trap mass spectrometer allowing optical access to trapped ions are similar to those previously reported and are described in detail elsewhere. Briefly, a 10 mm aperture was milled into the removable backplate of the vacuum chamber. A 2.75 inch quartz viewport was mounted over the aperture with a CF flange. At the beginning of a MSn ion activation step, the mass spectrometer transmits a TTL-signal to a digital delay generator that subsequently triggers a Nd:YAG laser (operating on the 4th harmonic, λ = 266 nm) such that only a single laser pulse is generated per duty cycle. The λ = 266 nm laser pulse (ca. 30 mJ cm⁻²) is transmitted through the quartz window and 2 mm orifice centred on the back lens of the ion-trap assembly allowing for PD of isolated ionic species.

3.3.2.2 Ion-Molecule Reactions

O₂ is present in background concentrations due to the use of an atmospheric pressure ionisation source. Typically, N₂ is used as the nebulising gas within the ionisation source, however, to increase the background O₂ concentration, O₂ can be used instead. The O₂ concentration (molecule cm⁻³) within the ion trap region was derived by following the 4-(N,N,N-trimethylammonium)phenyl radical + O₂ reaction kinetics, which has a known second-order rate coefficient (k₂nd) of 2.8 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The O₂ concentration within the ion trap was measured at 2.2 × 10⁹ molecule cm⁻³ for background O₂ with the standard nitrogen nebuliser gas, and 8.6 × 10⁹ molecule cm⁻³ with O₂ used as the nebuliser gas.

The stoichiometric excess of O₂, by many orders of magnitude, established pseudo-first order kinetic behaviour with reactive ions. The temperature within the ion trap was previously measured at 307 ± 1 K and is used as the effective temperature for ion-molecule reactions herein. This is consistent with recent measurements by Donald et al. of 318 ± 23 K. Reaction times of 0.030–10 s were achieved by setting the activation time parameter with the control software while the normalised collision energy was maintained at 0 (arbitrary units).
pseudo-first order ($k$) and second-order ($k_{2nd}$) rate coefficients were extracted from the slope of a semi-logarithmic plot of normalised abundance against reaction time.

Statistical errors in rate measurements were typically $2\sigma < 5\%$, where $\sigma$ is the standard deviation obtained from the least-squares fit to the pseudo-first order decay. Systematic uncertainty in the ion-trap pressure and $O_2$ concentration, and the formation of neutrals or ions with a $m/z$ less than the low mass cut-off (ca. 50 Th) result in a upper limit of 50% uncertainty in second-order rate coefficients ($k_{2nd}$). Reported reaction efficiencies are calculated from the second-order rate coefficient as a percentage of the reactants’ collision frequency derived from average dipole orientation (ADO) theory.\textsuperscript{43}

### 3.3.3 Quantum Chemical Calculations

Electronic structure calculations were performed using both the M06-2X/6-311+G(d,p) density functional theory\textsuperscript{44} and G3SX(MP3) composite method,\textsuperscript{45} in the Gaussian 09 program.\textsuperscript{46} All stationary points were characterised as either minima (no imaginary frequencies) or transition states (one imaginary frequency). All reported energies are at 0 K and include zero-point energy corrections. The selected theoretical methods are capable of reproducing well-defined test set barrier heights to within 1.5 kcal mol\textsuperscript{-1}, on average.\textsuperscript{45,47}

### 3.4 Results and Discussion

#### 3.4.1 Synthesis of Distonic 2-Methylphenyl Radical Cations

Two synthetic routes for the production of radical cations within the linear ion-trap mass spectrometer were compared: laser photodissociation (PD) and collision-induced dissociation (CID). Methanolic solutions of the precursor iodide salts were infused \textit{via} positive electrospray ionisation (+ESI) to yield the $M^+$ ions at $m/z$ 228 and 230 for the brominated (4Br3Me and 3Br4Me), and $m/z$ 276 for the iodinated (3I4Me and 4IMe) precursor ions, as listed in Table 3.1.

Isolation and subsequent PD of the $M^+$ ions listed in Table 3.1 resulted in $m/z$ 149 product ions consistent with the loss of the halogen atom (Section 3.7, Figure 3.4). PD of the brominated precursors 4Br3Me and 3Br4Me resulted also in $[M - Br - 15]^+$ signal at $m/z$ 134 and $[M - CH_3]^+$ signal at $m/z$ 213 and 215. In the case of PD of the iodinated precursors 3I4Me and 4IMe, $m/z$ 134 is also apparent and likely corresponds to $[M - I - CH_3]^+$.

The dominant product observed after CID of 4Br3Me, 3Br4Me, and 3I4Me was the $[M - 15]^+$ ion at $m/z$ 213 and 215 for the brominated species (both Br isotopes), and $m/z$ 261 for 3I4Me. These odd-electron processes are consistent
Table 3.1. Distonic radical precursor ions [M]+ introduced by +ESI of methanolic solutions of the corresponding salt.

<table>
<thead>
<tr>
<th>Precursor ions [M]^+</th>
<th>Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-bromo-N,N,N,3-tetramethylbenzenamminium cation (m/z 228 and 230)</td>
<td><img src="image1" alt="Structure" /></td>
<td>4Br3Me</td>
</tr>
<tr>
<td>3-bromo-N,N,4-tetramethylbenzenamminium cation (m/z 228 and 230)</td>
<td><img src="image2" alt="Structure" /></td>
<td>3Br4Me</td>
</tr>
<tr>
<td>3-iodo-N,N,4-tetramethylbenzenaminium cation (m/z 276)</td>
<td><img src="image3" alt="Structure" /></td>
<td>3I4Me</td>
</tr>
<tr>
<td>4-(iodomethyl)-N,N,N-trimethylbenzenaminium cation (m/z 276)</td>
<td><img src="image4" alt="Structure" /></td>
<td>4Ime</td>
</tr>
</tbody>
</table>

with •CH₃ loss from the trimethylammonium charge tag of the respective M⁺ ions. A minor ion signal at m/z 149 is assigned to ejection of the halogen. In contrast, CID of 4Ime resulted predominately in the m/z 149 and 134 ions, assigned as loss of I⁺ followed by elimination of a methyl radical from the charge tag, respectively.

Activation of 4Br3Me, 3Br4Me, 3I4Me, and 4Ime ions by both PD and CID resulted in formation of m/z 149 ions with varying efficiencies. PD of the 4Br3Me, 3Br4Me, and 3I4Me halogenated precursors resulted in significantly higher abundances of the putative distonic radical ion (ca. 25–45%) than CID (ca. <2%). In contrast, CID of the 4Ime ion resulted in a notably higher abundance of the m/z 149 ion (ca. 90%) than that observed for the PD route (ca. 10%). In each case, the m/z 149 ion population was isolable and probed by reactions with O₂.
Figure 3.1. PD (left panel) and CID (right panel) mass spectra of 4Br3Me (a and b), 3Br4Me (c and d), 3I4Me (e and f) and 4IMe (g and h) isolated for a period of 2 s in the presence of background O$_2$. Trace ions at $m/z$ 164 and 181 observed in (g) are likely the result of contamination by isomeric distonic radical cations.

3.4.2 Charge-Tagged 2-Methylphenyl + O$_2$

The $m/z$ 149 ions generated by PD and CID of 4Br3Me, 3Br4Me, 3I4Me and 4IMe were isolated and allowed to react with background O$_2$ over time periods of 0.030–10 s. Mass spectra measured with a reaction time of 2 s are provided in Figure
3.1. Second-order rate coefficients \( k_{\text{2nd}} \) were derived and are discussed below in Section 3.4.2.1. Isolation of \( m/z \) 149 ions, generated by PD of 4Br3Me, 3Br4Me, and 3I4Me, in the presence of background \( \text{O}_2 \) resulted in a small \([M + 32]^{\ddagger}\) product ion signal at \( m/z \) 181, consistent with the formation of a peroxyl radical. The dominant product observed was the \([M + 15]^{\ddagger}\) ion at \( m/z \) 164 rationalised by \( \text{O}_2 \) addition and subsequent \( {}^\ddagger\text{OH} \) elimination, as depicted in Scheme 3.2. This is consistent with the \( ^\ddagger\text{OH} \) elimination mechanism proposed in the theoretical study of the analogous neutral 2-methylphenyl radical + \( \text{O}_2 \) reaction by da Silva et al.\(^{18}\) (Scheme 3.1). CID of \( m/z \) 164 ions (Supporting Information, Figure 3.5) gives rise to \( m/z \) 149, presumably the results of \( \text{CH}_3 \) (15 Da) loss from the trimethylammonium charge tag. There is also a product ion consistent with CO (28 Da) loss at \( m/z \) 136, and another at \( m/z \) 121 consistent with both loss of \( \text{CH}_3 \) and CO. The primary fragmentation pathway for the neutral 2-quinone methide is loss of CO.\(^{48,49}\) A more detailed mechanism and energy schematic, including the formation of \( m/z \) 164, will be outlined below. The reactions of \( m/z \) 149 ions with \( \text{O}_2 \), after PD of 4IMe, yielded only traces of oxidation products likely the result of contamination by isomeric distonic radical cations as the majority of the \( m/z \) 149 species is likely to be the resonance stabilised benzyl radical.

![Scheme 3.2](image)

Prolonged isolation (up to 10 s) of \( m/z \) 149 ions generated by CID of 4Br3Me, 3Br4Me, and 4IMe under the same experimental conditions [Figure 3.1 (b), (d), and (h)] did not result in observable \([M + \text{O}_2]^{2\ddagger}\) or \([M + \text{O}_2 - \text{OH}]^{2\ddagger}\) product ions, while isolation of \( m/z \) 149 ions from CID of 3I4Me resulted in only low intensity signals at corresponding \( m/z \) ratios [Figure 3.1 (e) with \( \times 5 \) magnification compared to (f) with \( \times 50 \)]. The low abundance, or even absence, of the respective \([M + \text{O}_2]^{2\ddagger}\) and \([M + \text{O}_2 - \text{OH}]^{2\ddagger}\) ions, when compared with analogous PD experiments, suggests that the \( m/z \) 149 ions resulting from CID of 4Br3Me and 3Br4Me are less reactive isomeric species born from CID-induced rearrangement. The isomerisation of phenyl-type radical cations upon CID of halogenated precursors has been previously noted.\(^{50}\) Herein, PD was used for all subsequent experiments.
Table 3.2. Second-order rate coefficients ($k_{2nd}$, cm$^3$ molecule$^{-1}$ s$^{-1}$) and reaction efficiencies ($\Phi$) for reactions of PD generated distonic radicals with O$_2$ (molecule cm$^{-3}$). Estimated upper limit of 50% uncertainty in second-order rate coefficients. O$_2$ collision frequency from average dipole orientation (ADO) theory$^{43}$ is $5.7 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for all species of m/z 149.

<table>
<thead>
<tr>
<th>Precursor ions</th>
<th>Distonic radicals</th>
<th>[O$_2$] (molecule cm$^{-3}$)</th>
<th>$k_{2nd}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$\Phi$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4Br3Me</td>
<td>4-(N,N,N-trimethylammonium)-2-methylphenyl</td>
<td>$2.23 \times 10^9$</td>
<td>$2.4 \times 10^{-11}$</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$8.53 \times 10^9$</td>
<td>$2.1 \times 10^{-11}$</td>
<td>3.7</td>
</tr>
<tr>
<td>3Br4Me</td>
<td>5-(N,N,N-trimethylammonium)-2-methylphenyl</td>
<td>$2.23 \times 10^9$</td>
<td>$2.9 \times 10^{-11}$</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$8.53 \times 10^9$</td>
<td>$2.6 \times 10^{-11}$</td>
<td>4.5</td>
</tr>
<tr>
<td>3I4Me</td>
<td>5-(N,N,N-trimethylammonium)-2-methylphenyl</td>
<td>$2.23 \times 10^9$</td>
<td>$2.8 \times 10^{-11}$</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$8.53 \times 10^9$</td>
<td>$2.6 \times 10^{-11}$</td>
<td>4.6</td>
</tr>
<tr>
<td>4IMe</td>
<td>4-(N,N,N-trimethylammonium)-benzyl</td>
<td>$2.23 \times 10^9$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$8.53 \times 10^9$</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Figure 3.2. Semi-logarithmic plot for depletion of m/z 149 ions generated by PD of 4Br3Me (closed circles), 3Br4Me (diamonds), 3I4Me (squares) and 4I4Me (open circles) precursors ions, in reactions with O2 ([O2] = 8.53 × 10^9 molecule cm⁻³). Second-order rate coefficients provided in Table 3.2.

3.4.2.1 Reaction Kinetics

The reactions of PD generated m/z 149 ions with O2 were further characterised by second-order rate coefficients (k₂nd, cm³ molecule⁻¹ s⁻¹) and reaction efficiencies (Φ), reported in Table 3.2, derived from measured pseudo-first order rate coefficients at background O2 ([O2] = 2.23 × 10⁹ molecule cm⁻³) and increased O2 concentrations ([O2] = 8.53 × 10⁹ molecule cm⁻³). The O₂ collision frequency calculated with average dipole orientation (ADO) theory is 5.7 ×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for all species of m/z 149. Pseudo-first order kinetic behaviour, as shown by a linear semi-logarithmic plot (Figure 3.2), is observed for m/z 149 ions generated by PD of 4Br3Me, 3Br4Me and 3I4Me, implying that each of these radical ion populations consist of only a single species. The general agreement between k₂nd values for radical ions generated by PD of 3Br4Me and 3I4Me suggests the identity of the radical formed by λ = 266 nm photolysis is unaffected by the halogen substituent on the radical precursor. Rate coefficients for m/z 149 from PD of 3Br4Me and 4Br3Me reveal a slight, but reproducible, difference in reaction rate where the radical is at the 3- over the 4-position relative to the charge-tag, i.e., k₃Br4Me > k₄Br3Me. This effect could be due to small differences in the electrophilicity of the two positive distonic radical ions but overall the reaction efficiencies are very similar to each other and to previous measurements for phenyl-type radicals. For example, the measured reaction efficiencies in Table 3.2 are similar to those reported by Kirk et al. for positively charge-tagged distonic phenyl radicals (about 5%).
suggesting, intriguingly, that the methyl substituent, although presenting a new reaction pathway, does not drastically alter the overall reaction efficiency. More discussion on the reaction pathway is provided below.

The m/z 149 species generated by PD of 4IMe, expected to provide a benzylic radical ion for comparison, was unreactive on the timescale of these experiments (0.030–10 s). The addition of O2 to the neutral benzyl radical is reported to produce a benzylperoxyl radical with a reaction exothermicity of 22 kcal mol\(^{-1}\); however, reformation of benzyl + O2 reactants dominates at low temperatures.\(^{53}\) In the analogous charge-tagged benzyl radical + O2 reaction, it is expected that upon O2 addition the vibrationally excited charge-tagged benzylperoxyl radical will dissociate to regenerate the charge-tagged benzyl + O2 before being collisionally deactivated in the ion trap or undergoing further unimolecular reaction.

3.4.2.2 Reaction Mechanism

Figure 3.3 depicts a potential energy diagram for the addition of O2 to the 5-(N,N,N-trimethylammonium)-2-methylphenyl radical cation (generated by PD of 3Br4Me or 3I4Me). This scheme essentially reproduces the reaction mechanism identified in the analogous neutral system.\(^{18}\) Energies were calculated using the M06-2X/6-311++G(d,p) (black) and G3SX(MP3) (blue) methods, reported in kcal mol\(^{-1}\) relative to the peroxyl radical intermediate. The ensuing discussion will refer to the G3SX(MP3) energies.

The addition of O2 to the charge-tagged 2-methylphenyl radical (I) proceeds without a barrier and results in a charge-tagged methylphenylperoxyl species (II) with 46.4 kcal mol\(^{-1}\) activation. Figure 3.3 depicts four low-energy unimolecular reaction pathways available to the charge-tagged 2-methylphenylperoxyl radical. First, the reverse reaction reforms the distonic 2-methylphenyl radical + O2 (I); second, formation of a phenoxy radical + O(3P) (III); third, isomerisation to methyloxepinoxyl species (V and VI); and fourth, the generation of charge-tagged 2-quinone methide + •OH (VIII). In the context of forming new product species, the latter three pathways will be discussed further below.

Formation of 5-(N,N,N-trimethylammonium)-2-methylphenoxy + O(3P) (III) occurs via cleavage of the peroxyl RO-O\(^{\bullet}\) bond. Delocalisation of the unpaired electron is evidenced by a predicted contraction of the C-O bond from 1.392 Å in the peroxyl to 1.235 Å in the phenoxy, closer to that expected for a CO double bond. The barrier for this process is calculated at 38.8 kcal mol\(^{-1}\) compared with 46.4 kcal mol\(^{-1}\) for the reactants. The O(3P) loss mechanism would result in a m/z 165 ion corresponding to the 16 Da mass loss. Subsequent CO loss from this phenoxy radical\(^{10}\) would result in an [M + O2 - O - CO]•\(^{+}\) ion at m/z 137. Neither O atom nor CO loss product ions were observed within the detection limits of the
Chapter 3. Distonic o-Methylphenyl Radical + O₂

Figure 3.3. Potential energy diagram depicting key intermediates for N,N,N-trimethylammonium charged-tagged 2-methylphenyl radical cation + O₂. Energies were calculated at the M06-2X/6-311++G(d,p) (black) and G3SX(MP3) (blue) levels, reported in kcal mol⁻¹ relative to the initial intermediate.
experiment pointing to a lack of competitiveness for this pathway. Other accessible pathways outcompete the O(3P) loss channel as shown by the dominance of alternate product channels in Figure 3.1.

The third pathway from II proceeds by ipso addition of the peroxyl radical oxygen to the aromatic ring (TS II → IV, 25.4 kcal mol⁻¹) resulting in the dioxiranyl intermediate (IV). The sequential transition states, TS1 (37.5 kcal mol⁻¹) and TS2 (30.7 kcal mol⁻¹), succeeding the dioxiranyl intermediate, represent a bifurcation of the potential energy surface. Following the intrinsic reaction coordinate (IRC) from TS1, reactive species encounter a valley-ridge inflection (VRI) near which the single reaction pathway becomes two. Past the VRI, along the developing ridge, the second transition state (TS2) is located, which connects the charge-tagged 3-methylloxepinoxyl (V) and 7-methylloxepinoxyl (VI) species (confirmed by calculation of the IRC for TS2). Ring-opening of the dioxiranyl moiety (TS1), i.e., cleavage of the dioxiranyl O-O bond, has a barrier that is 8.9 kcal mol⁻¹ less than the chemical activation of the system. At these temperatures (ca. 307 K), we do not expect any significant reaction flux through TS1 due to its high energy (37.5 kcal mol⁻¹), thus these pathways were not extended beyond the methylloxepinoxyl radicals (V and VI). Guided by Kirk et al., it is likely the end-product species could comprise five-membered ring products, such as a charge-tagged methyl-substituted cyclopentadienone species but no such channels were detected in our charge-tagged experiments. This implicates the presence of lower-energy reaction pathways not available to the charge-tagged phenylperoxyl radical systems investigated by Kirk et al.

The final pathway considered here leads to charge-tagged 2-quinone methide via H-migration followed by •OH elimination. The 1,5-H shift via TS II → VII proceeds with a 27.2 kcal mol⁻¹ barrier (19.1 kcal mol⁻¹ below the reactants’ energy) and results in a hydroperoxybenzyl radical species (VII), reminiscent of a QOOH combustion intermediate. The formation of this radical is facilitated by close proximity of the labile benzylic methyl hydrogen to the peroxyl group. The forward reaction barrier of 9.4 kcal mol⁻¹ for TS VII → VIII is considerably less than that for the reverse reaction (22.7 kcal mol⁻¹). Thus, H atom migration and •OH elimination is energetically competitive and results in the formation of charge-tagged 2-quinone methide (VIII), consistent with the [M + O₂ - OH]⁺ ion detected at m/z 164, shown in Figure 3.1 (left panel).

The G3SX(MP3) and M06-2X methods both predict, based purely on reaction barriers, the dominance of the charge-tagged 2-quinone methide + •OH product channel and the numbers are generally in good agreement. The greatest deviations were observed for TS1 and TS2, with a difference of 6.5 and 7.1 kcal mol⁻¹ (Table S2). These are perhaps more peculiar stationary points and could warrant future
investigation. Nevertheless, both methods are in agreement that the TS1 barrier is likely to be prohibitively high. The scheme depicted in Figure 3.3 supports the notion that H-atom migration followed by *OH elimination is the dominant product channel. This is in agreement with experimental data that shows charge-tagged 2-methylphenyl radicals react with O₂ to eliminate *OH, forming the [M + 15]*⁺ ion detected at m/z 164 consistent with the charge-tagged 2-quinone methide.

### 3.5 Conclusions

The reaction of two distonic radical ions [4-(N,N,N-trimethylammonium)-2-methylphenyl and 5-(N,N,N-trimethylammonium)-2-methylphenyl radicals] with O₂ were successfully used to explore the 2-methylphenyl + O₂ reaction. Subjecting the halogenated precursors 4Br₃Me, 3Br₄Me and 3I₄Me to PD resulted in exclusive formation of the distonic radical ion targets, while CID of the same precursors led to complications due to isomerisation to an unreactive isomeric species. The distonic 2-methylphenyl radical + O₂ reaction gave rise to [M + O₂]*⁺ and [M + O₂ - OH]*⁺ ions from O₂ addition followed by *OH elimination as the dominant oxidation product. Second-order rate coefficients for these reactions were measured between 2.1–2.9 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ representing reaction efficiencies of ca. 5%. Quantum chemical calculations are in accord with our experimental observations, where H migration and *OH elimination, via the QOOH intermediate, is the minimum energy pathway and should thus dominate product formation. The proposed generation of the charge-tagged 2-quinone methide suggests similar processes may occur in the neutral system and therefore serve as a *OH radical source for further radical chemistry in reactive environments.

### 3.6 Acknowledgements

The authors are grateful for the financial support of the Australian Research Council through the Discovery program (SJB: DP0986738; AJT and GdS: DP 130100862; GdS: DP110103889) and Centre of Excellence For Free Radical Chemistry and Biotechnology (CE0561607). The authors also acknowledge the generous allocation of computing resources by the NCI National Facility (Canberra, Australia) under Merit Allocation Scheme.
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3.7 Supporting Information

3.7.1 Methylation of Halogen-Substituted Methylaniline

The 4-iodomethyl-$N,N,N$-trimethylbenzenaminium, 3-iodo-$N,N,N,4$-tetramethylbenzenaminium, 3-bromo-$N,N,N,4$-tetramethylbenzenaminium and 4-bromo-$N,N,N,3$-tetramethylbenzenaminium iodide salts were synthesised using a modified procedure previously reported by Kirk et al. for the synthesis of 4-iodo-$N,N,N$-trimethylbenzenaminium iodide.\textsuperscript{31} In brief, to a reaction vial was added halogenated aniline species (ca. 1 mmol), 10 mL of dry CH$_3$OH, and CH$_3$I (0.7 mL, 10 mol equiv) that was then heated at reflux for two hours. K$_2$CO$_3$ (0.2 g, 1.3 mmol) was added to the reaction vial and the solution heated at reflux for a further two hours. The solvent was removed in vacuo and the crude product recrystallised from CH$_3$CN. The recrystallised solid was washed with diethyl ether and dried.

3.7.2 Structural Characterisation

\textbf{4-bromo-3-methyl-$N,N,N$-trimethylbenzenaminium iodide}. $^1$H NMR (300 MHz, D$_2$O): $\delta$ 2.49 (s, 3H), $\delta$ 3.64 (s, 9H), $\delta$ 7.55 (dd, 1H, $J = 8.79, 3.21$ Hz), $\delta$ 7.80 (d, 1H, $J = 9.07$ Hz).

\textbf{3-bromo-4-methyl-$N,N,N$-trimethylbenzenaminium iodide}. $^1$H NMR (300 MHz, D$_2$O): $\delta$ 2.45 (s, 3H), $\delta$ 3.64 (s, 9H), $\delta$ 7.55 (d, 1H, $J = 8.79$ Hz), $\delta$ 7.72 (dd,
1H, J = 8.5, 2.64 Hz), \( \delta \) 8.10 (d, 1H, J = 2.93 Hz).

3-iodo-4-methyl-\( N,N,N \)-trimethylbenzenaminium iodide. \(^1\)H NMR (500 MHz, DMSO-\( d_6 \)): \( \delta \) 8.35 (s, 1H), \( \delta \) 7.90 (d, H, J = 7.3 Hz), \( \delta \) 7.56 (d, 1H, J = 8.8 Hz), \( \delta \) 3.57 (s, 9H), \( \delta \) 2.43 (s, 3H).

3-iodo-4-methyl-\( N,N,N \)-trimethylbenzenaminium iodide. \(^1\)H NMR (500 MHz, DMSO-\( d_6 \)): \( \delta \) 7.90 (d, 2H, J = 8.6 Hz), \( \delta \) 7.67 (d, 2H, J = 8.8 Hz), \( \delta \) 4.67 (s, 2H), \( \delta \) 3.59 (s, 9H).

3.7.3 Supplementary Mass Spectra
Figure 3.4. Gas-phase ions produced by ESI of 4Br3Me (a and b), 3Br4Me (c and d), 3I4Me (e and f) and 4I Me (g and h) were isolated and activated by PD (left panel) and CID (right panel) to generate the \( m/z \) 149 ions via loss of the halogen.
Figure 3.5. CID of $m/z$ 164 ions generated via PD of 3-bromo-4,N,N,N-tetramethylbenzenaminium (3Br4Me) and subsequent isolation of the resultant $m/z$ 149 ions for 10 s in the presence of background O$_2$. Peaks at $m/z$ 149 (15 Da loss), 136 (28 Da loss), and 121 (43 Da loss) are consistent with loss of CH$_3$, CO, and both CH$_3$ and CO, respectively.$^{48,49}$
Table 3.3. Comparison of M06-2X/6-311++G(d,p) and G3SX(MP3) energies presented in kcal mol\(^{-1}\) relative to the initial intermediate (II) for the charge-tagged 2-methylphenyl + O\(_2\) reaction.

<table>
<thead>
<tr>
<th>Structure</th>
<th>M06-2X/6-311++G(d,p) (kcal mol(^{-1}))</th>
<th>G3SX(MP3) (kcal mol(^{-1}))</th>
<th>Difference (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>42.96</td>
<td>46.37</td>
<td>3.41</td>
</tr>
<tr>
<td>II</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>III</td>
<td>37.52</td>
<td>38.83</td>
<td>1.31</td>
</tr>
<tr>
<td>TS II→IV</td>
<td>28.86</td>
<td>25.38</td>
<td>3.48</td>
</tr>
<tr>
<td>IV</td>
<td>19.50</td>
<td>16.02</td>
<td>3.48</td>
</tr>
<tr>
<td>TS1</td>
<td>44.00</td>
<td>37.51</td>
<td>6.49</td>
</tr>
<tr>
<td>TS2</td>
<td>37.77</td>
<td>30.65</td>
<td>7.12</td>
</tr>
<tr>
<td>V</td>
<td>-41.66</td>
<td>-42.40</td>
<td>0.74</td>
</tr>
<tr>
<td>VI</td>
<td>-46.50</td>
<td>-47.02</td>
<td>0.52</td>
</tr>
<tr>
<td>TS II→VII</td>
<td>28.65</td>
<td>27.23</td>
<td>1.42</td>
</tr>
<tr>
<td>VII</td>
<td>4.72</td>
<td>4.51</td>
<td>0.21</td>
</tr>
<tr>
<td>TS VII→VIII</td>
<td>14.88</td>
<td>13.91</td>
<td>0.97</td>
</tr>
<tr>
<td>VIII</td>
<td>1.46</td>
<td>-3.96</td>
<td>5.42</td>
</tr>
</tbody>
</table>

Average difference 2.7

3.8 Corrections


Page, paragraph, line and figure numbers reference the publication reproduced as Appendix A. Corrections are implemented in this Chapter 3.

Erratum in page 20582, paragraph 4 of Section 3.2.2, line 11:

- “methyloxepinoxy” should read “methyloxepinoxyl”
Chapter 3. Distonic o-Methylphenyl Radical + O$_2$

References


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(42) *Normalized Collision Energy is a term used by the instrument vendor as Explained here: https://static.thermoscientific.com/images/D13507~.pdf. Zero, on this scale, means that no additional resonant excitation is applied.*


Chapter 4

Neutral

\( o\)-Methylphenyl Radical + \( \text{O}_2 \)

4.1 Introduction

Toluene and multiply-methylated benzene additives improve fuel octane numbers, \(^1\) \textit{i.e.} inhibit unintended autoignition in spark-ignition engines.

In combustion environments these methylated benzenes may undergo H-atom abstraction by OH radicals to produce methylphenyl and benzyl radicals. \(^2\) The \( o\)-methylphenyl radical is also implicated in the oxidation of \( o\)-xylene at 1155 K, \(^3\) and benzyl decomposition. \(^4,5\)

The isomerisation of \( o\)-methylphenyl radical to benzyl radical is reported at 43.1 kcal mol\(^{-1}\) (180 kJ mol\(^{-1}\)) with a reverse barrier of 64.6 kcal mol\(^{-1}\) (270 kJ mol\(^{-1}\)). \(^6\) Theoretical work on this isomerisation suggests that lifetimes for the \( o\)-methylphenyl radical at temperatures <1000 K is sufficient for bimolecular reactions. \(^7\) Available \( \text{O}_2 \) could intercept the \( o\)-methylphenyl radical at temperatures relevant to low temperature combustion to form \( o\)-methylphenylperoxyl and subsequently decompose.

The activated reactions of \( m\)- and \( p\)-methylphenyl + \( \text{O}_2 \) result in formation of \( m\)- and \( p\)-methylphenoxy + \( \text{O}(\text{P}) \), \(^8-10\) which is understood by applying phenyl-like oxidation mechanisms \(^11,12\) to substituted phenyl radicals. Similarly, the formation of methyloxepinoxy radicals is anticipated at lower temperatures (<900 K) or with less activation. These two pathways are shown as pathways (i) and (ii) in Scheme 4.1 for the \textit{ortho}-radical case after \( \text{O}_2 \) addition. However, pathway (iii) is proposed as the major pathway for \( o\)-methylphenylperoxyl decomposition due to the proximity of peroxy and methyl substituents. \(^13\)

An experimental study of trimethylammonium-methylphenyl radical oxidation, \(^14\) an analogue for \( o\)-methylphenyl radical oxidation, revealed evidence supporting the appearance of \( o\)-quinone methide \textit{via} a QOOH radical intermediate as proposed by
da Silva et al.,\textsuperscript{13} i.e. pathway (iii) in Scheme 4.1. The mechanism is similar to that for \(o\)-hydroxyphenyl + \(O_2\) forming \(o\)-benzoquinone + OH via a QOOH-like phenoxyl radical,\textsuperscript{15} which is likened to the Waddington mechanism for \(\beta\)-hydroxyperoxyl radicals.\textsuperscript{16–18}

We report the gas-phase oxidation of \(o\)- and \(m\)-methylphenyl radicals using synchrotron-based multiplexed photoionisation mass spectrometry (MPIMS). This work builds on framework provided by a previous computational study\textsuperscript{13} and experimental investigation of distonic analogues for \(o\)-methylphenyl + \(O_2\).\textsuperscript{14} The reactions of both \(o\)- and \(m\)-methylphenyl radicals result in various products with two differences: the detection of \(m/z\) 80 and 106 ions from \(o\)-methylphenyl + \(O_2\). Computational chemistry calculations show competition between pathways (ii) and (iii) for \(o\)-methylphenyl + \(O_2\) while an analogous pathway (iii) for \(m\)-methylphenyl + \(O_2\) is deemed inaccessible.

## 4.2 Experimental

### 4.2.1 Multiplexed Photoionisation Mass Spectrometry

The \(o\)-methylphenyl + \(O_2\) reaction was investigated using multiplexed photoionisation mass spectrometry\textsuperscript{19,20} with synchrotron radiation from the Chemical Dynamics Beamline\textsuperscript{21–23} at the Advanced Light Source (ALS) synchrotron, Lawrence Berkeley National Laboratory (USA). The apparatus comprised a quartz slow-flow tube reactor, differentially pumped vacuum chamber, and an orthogonal time-of-flight mass spectrometer.

Photolysis of \(o\)-iodotoluene and \(m\)-iodotoluene with a pulsed KrF excimer laser (248 nm) operating at 4 Hz and a fluence of \(~50\) mJ cm\(^{-2}\) was used to generate
methylphenyl radicals within the reactor via C-I bond homolysis. The quartz reactor is 62 cm long with an internal diameter of 1.05 cm maintained at 4 Torr (533.3 Pa) and ambient temperatures.

Gas continuously effused from the reactor through a 650 µm diameter pinhole situated 37 cm along the flow tube into a differentially pumped vacuum chamber. The effused gas was sampled by a skimmer to create a near-efusive molecular beam that is intersected by quasi-continuous undulator vacuum-ultraviolet (VUV) synchrotron radiation. Photo-ionisable species within the molecular beam were sampled using a 50 kHz pulsed orthogonal-extraction time-of-flight mass spectrometer.

Background subtraction of ion signal is achieved by recording signal 20 ms prior to the 248 nm photolysis pulse and subtracting the average of that signal from the dataset. The synchrotron photoionisation energy was typically scanned from 8.00 to 10.20 eV with 0.025 eV steps. Mass spectra were compiled into threedimensional arrays of mass-to-change, reaction time, and photoionisation energy.

All data presented herein are normalised for variations in the ALS photocurrent using a NIST-calibrated photodiode (SXUV-100, International Radiation Detectors Inc.). Signal acquired before photolysis is background subtracted from normalised data so that only positive signal intensities are the result of laser photolysis.

Photoionisation (PI) onsets and the PI spectra are acquired by integrating a \( m/z \) signal over a period and plotting that integrated signal as a function of PI energy. The resulting PI spectra were normalised to an integral of one, averaged, and presented herein. Error bars at a given photoionisation energy represent two standard deviations (2σ) for an average of at least three measurements. The absolute photoionisation cross sections for many species assigned in this investigation are unknown. Consequently, a quantitative comparison of product yields is not conducted.

Iodotoluene entrained in He, O\(_2\) gas, and additional He buffer gas are supplied to the reactor through separate mass-flow controllers at an overall rate of 102 sccm. Iodotoluene vapour was entrained in He by passing He through a fritted bubbler that contained liquid \( o \)-iodotoluene kept at 20°C (293 K) and 470 Torr (62.7 kPa) or \( m \)-iodotoluene at 20°C (293 K) and 364 Torr (48.5 kPa). \( o \)-Iodotoluene (98%) and \( m \)-iodotoluene (99%) were purchased from Sigma Aldrich. Vapour pressures were approximated using Antoine parameters for \( o \)-iodotoluene.\(^{24}\) In experiments with \( o \)-iodotoluene at 298 K and 4 Torr, number densities within the reactor were approximately \( 1.1 \times 10^{13} \) molecule cm\(^{-3} \) \( o \)-iodotoluene, \( 2.5 \times 10^{16} \) molecule cm\(^{-3} \) O\(_2\) gas, and a total of \( 1.0 \times 10^{17} \) molecule cm\(^{-3} \) He gas. In the case of \( m \)-iodotoluene, at 298 K and 4 Torr the number densities were approximately \( 1.1 \times 10^{13} \) molecule cm\(^{-3} \) \( m \)-iodotoluene, \( 1.3 \times 10^{16} \) molecule cm\(^{-3} \) O\(_2\) gas, and a total of \( 1.2 \times 10^{17} \) molecule cm\(^{-3} \) He gas. Gas flow velocities and total gas flow densities at 298 K,
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4 Torr, and a flowrate of 102 sccm are calculated to be 4.1 m s$^{-1}$ and 1.3 x 10$^{17}$ molecule cm$^{-3}$. The collision rate for o- and m-iodotoluene with the wall of the reactor at 298 K was estimated to be 5.49 x 10$^{18}$ s$^{-1}$ using an expression for the impingement rate as detailed in the Supporting Information.

### 4.2.2 Quantum Chemical Calculations

Adiabatic ionisation energies (AIEs) reported in electron volts (eV) were calculated with the CBS-QB3 composite method$^{25,26}$ using Gaussian09.$^{27}$ Reported enthalpies and AIEs incorporate the zero-point energy correction.

To rationalise mechanisms for generation of detected products, enthalpies of key reaction intermediates and transition states were calculated for o-methylphenyl + O$_2$ and m-methylphenyl + O$_2$ using the G3X-K method.$^{28}$ The relative reaction enthalpies are reported in kcal mol$^{-1}$ relative to the o-methylphenyl + O$_2$ (as done in Figure 4.4, Figure 4.6, and Figure 4.7) and m-methylphenyl + O$_2$ (as done in Figure 4.5, Figure 4.8, and Figure 4.9).

### 4.3 Results and Discussion

#### 4.3.1 Photolysis Products of

**o-Iodotoluene and m-Iodotoluene**

As background measurements, product mass spectra from photolysis of o-iodotoluene and m-iodotoluene without O$_2$ added to the flow reactor are provided in Figure 4.10 in the Supporting Information. The major product peaks at m/z 90 and 92 are assigned fulvenallene$^{29}$ and toluene$^{30}$ by comparing experimental photoionisation (PI) spectra to reference data. The production of fulvenallene is attributed to HI loss from photodissociation of iodotoluene, by analogy to HBr loss from o-bromophenol.$^{31}$ Toluene is attributed to H-atom abstraction by methylphenyl radicals from abundant iodotoluene.

#### 4.3.2 Oxidation of

**o-Methylphenyl and m-Methylphenyl Radicals**

Figure 4.1a and Figure 4.1b are product mass spectra resulting from 248 nm photolysis of o-iodotoluene and m-iodotoluene, respectively, in the presence of O$_2$ added to the reactor. These spectra are integrated over 0–80 ms after photolysis and acquired with a photoionisation energy of 10.2 eV at ambient temperature. Isomerisation of thermalised methylphenyl radicals to the benzyl radical at temperatures <1000 K
is calculated to be sufficiently slow to allow the methylphenyl + O\textsubscript{2} reaction.\textsuperscript{7} Compared with the background measurements in Figure 4.10, all new product ion signals in Figure 4.1 were attributed to methylphenyl + O\textsubscript{2} reactions. From both Figure 4.1a and Figure 4.1b, the major oxidation product ion signals are present at m/z 66, 67, 70, 80, 94, 106, 108, and 122. The most notable difference between Figure 4.1a and Figure 4.1b is the m/z 80 and 106 ion signals in Figure 4.1a for o-methylphenyl + O\textsubscript{2} are absent in Figure 4.1b for m-methylphenyl + O\textsubscript{2}. Also, the m/z 67 ion intensity is significantly diminished for Figure 4.1b compared to Figure 4.1a while the inverse is true for m/z 108 signal. These signals are consistent with C\textsubscript{5}H\textsubscript{7}O (67 Da), C\textsubscript{5}H\textsubscript{4}O (80 Da), and C\textsubscript{7}H\textsubscript{6}O (106 Da).

The combination of MPIMS with tuneable synchrotron radiation\textsuperscript{19,20} provides a means to measure PI spectra by acquiring photo-ion signal intensity as a function of photon energy. The onset of photoionisation can be used to identify isomers with known adiabatic ionisation energies (AIE) and PI spectra can be compared with reference PI spectra (when available) to assign reaction products. Quantifying product branching fractions requires absolute PI cross sections. Unfortunately, the absolute PI cross sections for many products relevant to o- and m-methylphenyl + O\textsubscript{2} reactions are unknown and this prohibits any quantitative comparison of absolute product yields.
4.3.2.1 \( m/z \) 106 via the \( o \)-Methylphenylperoxyl Radical

Figure 4.2. The PI spectrum for \( m/z \) 106 from \( o \)-methylphenyl + O\(_2\) at ambient temperatures (empty red circles) integrated 0–80 ms after photolysis. Vertical error bars represent 2\( \sigma \) deviation for an average of three PI spectra. An integrated He(I) photoelectron spectrum for \( o \)-quinone methide (Eck et al.)\(^{32}\) is shown.

Figure 4.2 shows the PI spectrum for \( m/z \) 106 with an onset at 8.75 eV that agrees with the calculated adiabatic ionisation energy (AIE) at 8.7 eV for \( o \)-quinone methide (\( o \)-QM, C\(_7\)H\(_6\)O). The \( o \)-QM species is reactive\(^{33,34}\) and not suitably stable to obtain a reference PI spectrum. For some comparison, an integrated He(I) PE spectrum for \( o \)-QM\(^{32}\) that was generated in situ, is shown in Figure 4.2. The \( m/z \) 106 PI spectrum in Figure 4.2 is well matched to the integrated PE spectrum between 8.75–9.2 eV and deviates near 9.3 eV. Although PI spectra and integrated PE spectra do not necessarily agree, this point of deviation could signify the presence of another isomer on this \( m/z \) channel, such as \( p \)-quinone methide (\( p \)-QM, C\(_7\)H\(_6\)O). The reference PI spectrum for benzaldehyde\(^{35}\) (C\(_7\)H\(_6\)O, AIE = 9.5 eV\(^{36}\)) was also considered but the co-added spectra provided a poor fit to the experimental data between 9.3–9.7 eV and mechanistically, this product requires significant rearrangement. Cyclisation of \( o \)-quinone methide to form the bicyclic 7-oxabicyclo[4.2.0]octa-1(6),2,4-triene (C\(_7\)H\(_6\)O, AIE = 8.4 eV) was not considered because its AIE is less than the \( m/z \) 106 PI onset.

To ascertain if the \( m/z \) 106 ion signal between 8.75–10.2 eV is the result of multiple 106 Da isomers, the \( m/z \) 106 product kinetics were examined at PI energies before and after the deviation at 9.3 eV in Figure 4.2. Figure 4.11 in the Supporting Information shows a comparison of kinetic traces for \( m/z \) 106 integrated between
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8.8–9.2, 9.4–9.8, and 9.8–10.2 eV. These kinetic traces are all very similar and consistent with the dominant ion signal arising from the PI of one 106 Da isomer before and after 9.3 eV in Figure 4.2 because it is reasonable to expect different kinetics in Figure 4.11 for a new isomer appearing with an AIE $\geq$9.3 eV. Therefore, our tentative explanation of this spectrum is the $o$-QM is the dominant isomer and that the deviation from the integrated PE spectrum is due to a spectroscopic photoionisation process (e.g. a shape resonance) affecting photo-ion detection but does not manifest in the fixed-energy PE spectrum. However, without reference PI spectra, the possibility of $o$-QM and $p$-QM (or other 106 Da isomers) exhibiting similar kinetic behaviour cannot be excluded. A $p$-QM product could result from isomerisation of the 2-methylphenoxy radical and subsequent H-atom elimination like the isomerisation between 2-methylbenzyl and 4-methylbenzyl radicals, or isomerisation of $o$-QM to $p$-QM. Therefore, a definitive assignment remains elusive. A viable strategy to producing $o$-QM for acquisition of reference PI spectra is pyrolysis of 2-(methoxymethyl)-phenol or methylanisole using a heated silicon carbide reactor coupled to a MPIMS instrument.

A mechanism proposed for the formation of $o$-QM from $o$-methylphenyl + O$_2$ is reported and described later in Section 4.3.3. After O$_2$ addition to $o$-methylphenyl radical, the proximity of the methyl and peroxy groups facilitates a 1,5-H atom shift between the groups and subsequently, OH is eliminated from the QOOH intermediate. Experimental investigations into the oxidation of distonic $o$-methylphenyl radical ions support the proposed mechanism. This pathway is unlikely for $m$-methylphenyl + O$_2$ as the H-atom shift would require substantial deformation of the phenyl ring.

4.3.2.2 $m/z$ 80 via an Oxepinoxyl Radical

Figure 4.3 shows the $m/z$ 80 PI spectrum and a PI spectrum for cyclopentadienone (C$_5$H$_4$O, AIE = 9.41 eV) from the phenyl + O$_2$ reaction. The PI onsets and spectra are well matched and therefore, the $m/z$ 80 ion signal is assigned to cyclopentadienone. As shown later in Figure 4.6, the formation of cyclopentadienone is rationalised via 7-methyl-oxepinoxyl radical decomposition and loss of CH$_3$CO. There are weak ion signals ($\leq$4%) at $m/z$ 43, 42, and 58 consistent with acetyl radicals (CH$_3$CO, AIE = 8.05 ± 0.17 eV), and CH$_3$CO oxidation products: ketene (CH$_2$CO, 42 Da) and C$^*$$\text{H}_2$(C=O)O$^*$ (58 Da). Extracting PI spectra is difficult given the low signal intensity, however.
4.3.2.3 \( m/z \) 94 via an Oxepinoxyl Radical

A \( m/z \) 94 signal is present in both Figure 4.1a and Figure 4.1b, with a PI onset for both o- and m-methylphenyl + O\(_2\) reactions at 8.85 eV. This immediately excludes phenol as a contributor to ion signal because its ionisation onset is 8.508 ± 0.001 eV.\(^{36,46}\) The \( m/z \) 94 PI spectra from o- and m-methylphenyl + O\(_2\) included in Figure 4.12 are matched near the onsets at 8.85 eV but deviate near 9.00 eV. The 8.85 eV onset is consistent with the calculated AIE for 2-methylcyclopentadienone (AIE = 8.9 eV). The deviation near 9.00 eV is consistent with the later PI onset of 3-methylcyclopentadienone (AIE = 9.1 eV) or cyclohexa-2,4-dienone (AIE = 9.1 eV) formed as an additional product in the m-methylphenyl + O\(_2\) case.

4.3.2.4 \( m/z \) 108 via the Phenoxyl Radical

The \( m/z \) 108 PI spectra from the o-methylphenyl + O\(_2\) and m-methylphenyl + O\(_2\) reactions are well matched. The PI spectra feature an onset at 8.2 eV and a sharp onset near 9.9 eV that are consistent with the integrated PE spectra for cresols\(^{47}\) and the sharp PI onset for \( p \)-benzoquinone (AIE = 9.96 ± 0.01 eV).\(^{36,48,49}\) The presence of \( o \)-benzoquinone (AIE = 9.2 eV) needs to also be considered.

Figure 4.13 shows the \( m/z \) 108 PI spectrum from \( m \)-methylphenyl + O\(_2\) is well matched to the integrated PE spectrum for \( m \)-cresol\(^{47}\) between 8.2–9.2 eV. The 7–12
eV PE spectra reported for o-, m-, and p-cresol isomers have similar PI onsets and spectral features, particularly between 8–10.2 eV,\(^{47}\) which frustrates the assignment of the individual cresol isomers.

Cresol formation is rationalised by O\(_2\) addition to the methylphenyl radical, O(\(^{3}\)P) loss from the peroxyl adduct, and intermolecular H-atom abstraction by the methylphenoxyl radical. The first-order rate coefficient appearance of \(m/z\) 108 from o- and m-methylphenyl + O\(_2\) is 500 ± 70 (1\(\sigma\)) s\(^{-1}\) and 400 ± 20 (1\(\sigma\)) s\(^{-1}\) between 0–10 ms after photolysis. As a reference rate coefficient for primary reactions, the rate coefficient for appearance of \(m/z\) 80 ion signal is 1100 ± 200 s\(^{-1}\). The relatively small rate coefficient for appearance of \(m/z\) 108 is consistent with a secondary reaction and cresol dominating the \(m/z\) 108 ion signal between 8.0–10.0 eV.

The appearance of o-benzoquinone (o-QM, AIE = 9.2 eV) also needs to be considered. It is noted that o-BQ undergoes dissociative ionisation at photoionisation energies greater than 9.8 eV, which enhances ion signal at \(m/z\) 80 via loss of CO.\(^{15}\) The \(m/z\) 80 PI spectrum from o-methylphenyl + O\(_2\) is compared to such affected \(m/z\) 80 PI spectra from o-hydroxyphenyl + O\(_2\) (Ref. 15) in Figure 4.15. The apparent absence of an enhanced \(m/z\) 80 ion signal at PI energies >9.8 eV and the agreement with cyclopentadienone PI spectra included in Figure 4.3 from Ref. 41 suggest that any o-benzoquinone is produced in low yields, if at all.

### 4.3.2.5 \(m/z\) 122 via Secondary Reactions

The \(m/z\) 122 PI spectrum from o-methylphenyl + O\(_2\) features a PI onset near 8.6 eV and a sharp onset near 9.6 eV. The weak signal between 8.6–9.6 eV from both o- and m-methylphenyl + O\(_2\) is difficult to distinguish from noise, however. The species contributing to the \(m/z\) 122 PI spectra in Figure 4.16 are likely secondary products of the o- and m-methylphenyl + O\(_2\) reactions. The appearance of \(m/z\) 122 ion signal at 10.2 eV is approximately 200 s\(^{-1}\) between 0–10 ms. This is even slower than the appearance rate of \(m/z\) 108 signal (Section 4.3.2.4) so it is concluded that \(m/z\) 122 is not a primary reaction product. The AIEs for a range of C\(_7\)H\(_6\)O\(_2\) isomers were calculated and listed in Table 4.2. The hydroxy-1,2-quinone methide and methide oxepinone isomers are unlikely to be present because their AIEs are <8.6 eV. Other species in Table 4.2 have calculated AIEs between 8.6–10.2 eV and 2-hydroxy-benzaldehyde is the most stable by approximately 20–30 kcal mol\(^{-1}\). The weak \(m/z\) 122 signal, and absence of a reference PI spectra for plausible assignments, leave the \(m/z\) 122 ion signal unassigned.
4.3.2.6 \( m/z \) 66, 67 and 70

In Figure 4.1a and Figure 4.1b, there are peaks at \( m/z \) 66, 67, and 70 in Figure 4.1 that are consistent with \( C_5H_6, C_5H_7, \) and \( C_5H_{10} \) (or \( C_4H_6O \)), respectively. For \( o \)-methylphenyl + \( O_2 \), the ions appear at a kinetic rate of \( 1500 \pm 300 \) s\(^{-1}\) for \( m/z \) 66, \( 510 \pm 40 \) s\(^{-1}\) for \( m/z \) 67, and \( 1000 \pm 100 \) s\(^{-1}\) for \( m/z \) 70. When compared to the appearance of \( m/z \) 80 (\( 1100 \pm 200 \) s\(^{-1}\)), a reference for primary reactions, these rate coefficients suggest that \( m/z \) 66 and 70 are primary reaction products and \( m/z \) 67 is not.

The appearance of \( m/z \) 66, 67, and 70 is attributed to decomposition of a highly activated methyloxepinoxyl radical. Pathways to these smaller fragment products were not investigated in detail here. The \( m/z \) 66 PI spectra are included in Figure 4.17. The PI spectrum from \( o \)-methylphenyl + \( O_2 \) is well matched to a PI spectrum for cyclopentadiene\(^{50} \) (\( C_5H_6, \) AIE = 8.57 \pm 0.01 \) eV).\(^{51} \) However, the \( m/z \) 66 PI spectrum from \( m \)-methylphenyl + \( O_2 \) shows systematic deviation from the cyclopentadiene PI spectrum around 9.4 eV. Cyclopentadiene could result from decomposition of methyloxepinoxyl radicals into cyclopentadiene + HCOCO with a relative reaction enthalpy of -57.4 kcal mol\(^{-1}\). The \( m/z \) 67 PI spectrum from both \( o \)- and \( m \)-methylphenyl + \( O_2 \) reactions are well matched with each other in Figure 4.18, with an initial onset near 8.6 eV. H-atom addition to cyclopentadiene is an unlikely pathway to \( C_5H_7 \) (67 Da) because the calculated AIEs for 2-, and 3-cyclopentenyl radicals are <8.6 eV, as listed in Table 4.1, and \( m/z \) 66 kinetic curves did not show signal decay. For \( m/z \) 70, in Figure 4.19, the PI onset is consistent with the calculated AIE for methyl-vinyl-ketone (AIE = 9.7 eV). The 70 Da ion precursor may result from decomposition of methyloxepinoxyl radicals with CCCHO or HCCCCO fragments.

4.3.3 Computational Investigation of Methylphenyl + \( O_2 \)

Potential energy schemes were calculated using the G3X-K method\(^{28} \) to assist the rationalization of experimental results and comparisons between the \( o \)- and \( m \)-methylphenyl + \( O_2 \) reaction systems. All reaction enthalpies are reported in kcal mol\(^{-1}\) relative to the respective entrance channel (\( o1 \) for \( o \)-methylphenyl + \( O_2 \) and \( m1 \) for \( m \)-methylphenyl + \( O_2 \)). Dashed lines are used in the following schemes to represent reaction coordinates where a TS is not located using the G3X-K method, which may indicate a small or non-resistant reverse energy barrier for reaction.

A potential energy scheme for \( o \)-methylphenyl + \( O_2 \) (\( o1 \)) is shown in Figure 4.4 that follows the salient pathways identified in Ref. 13. The \( o \)-methylphenylperoxyl radical, at -47.3 kcal mol\(^{-1}\), can undergo: (i) separation back to \( o \)-methylphenyl + \( O_2 \), (ii) O\(^{(3P)} \) loss to produce the \( o \)-methylphenoxy radical, (iii) isomerisation to 3-
or 7-methyl-oepinoxyl radicals via a bifurcated region of the reaction surface\textsuperscript{11,52} followed by numerous decomposition channels, and (iv) an intramolecular 1,5-H-atom shift between the methyl and peroxy substituents and subsequent OH loss to form o-QM.

In Figure 4.5, the potential energy schematic for decomposition of \textit{m}-methyl-phenylperoxyl (\textit{m}2) is shown. The H-atom shift and OH loss pathway accessible in the \textit{ortho}-case is not included for the \textit{meta}-case because the analogous H-atom shift is 51.7 kcal mol\textsuperscript{-1} above \textit{m}1, compared to a reaction enthalpy of -19.9 kcal mol\textsuperscript{-1} in the \textit{ortho}-case.

Experimental study of analogous distonic \textit{o}-methylphenyl + O\textsubscript{2} reaction have indicated that \textit{o}-quinone methide (106 Da, C\textsubscript{7}H\textsubscript{6}O) is the dominant product for neutral \textit{o}-methylphenyl + O\textsubscript{2}. The computational investigation suggested the 1,5-H-atom shift and OH loss was the minimum energy pathway. The \textit{m}/\textit{z} 106 signal in Figure 4.1 is consistent with \textit{o}-quinone methide formation and is likely produced by this 1,5-H-atom shift and OH loss mechanism (\textit{o}2 to \textit{o}8). The absence of the \textit{m}/\textit{z} 106 product signal for \textit{m}-methylphenyl + O\textsubscript{2} reaction clearly shows that this pathway is unique to the \textit{ortho}-radical case. Energetically, in the meta-radical case, the transition state for the 1,5-H-atom shift is 51.7 kcal mol\textsuperscript{-1} above \textit{m}1.

In Figure 4.4, the rate limiting TS \textit{o}2–\textit{o}4 toward 3- and 7-methyloxepinoxy radicals (\textit{o}5 and \textit{o}6) is 4.1 kcal mol\textsuperscript{-1} below TS \textit{o}2–\textit{o}7 toward \textit{o}-QM + OH (\textit{o}8). This methyloxepinoxyl pathway will compete. In the case of \textit{m}-methylphenyl + O\textsubscript{2}, the formation of 4- and 6-methyloxepinoxy radicals (\textit{m}5 and \textit{m}6) dominates at low temperatures as is the case with the phenyl + O\textsubscript{2} reaction.\textsuperscript{53}

Decomposition pathways for \textit{o}5 and \textit{o}6 from \textit{o}-methylphenyl + O\textsubscript{2} are shown in Figure 4.6 and Figure 4.7, respectively. Similarly, decomposition of \textit{m}5 and \textit{m}6 from \textit{m}-methylphenyl + O\textsubscript{2} are shown in Figure 4.8 and Figure 4.9. These schemes are not exhaustive. The four methyl-oepinoxyl isomers are highly activated (95–99 kcal mol\textsuperscript{-1} below \textit{o}1 and \textit{m}1) and therefore undergo decomposition to many products.\textsuperscript{54}

Decomposition of \textit{o}6 in Figure 4.6 can lead to \textit{o}-benzoquinone + CH\textsubscript{3} (\textit{o}6.4, not detected) and cyclopentadienone + CH\textsubscript{3}CO (\textit{o}6.6, detected) while \textit{o}5 decomposition in Figure 4.7 results in 3-methyl-1,2-benzoquinone + H (\textit{o}5.4) and 2-methyl-cyclopentadienone + CHO (\textit{o}5.6, detected), all with limiting stationary points more than 50 kcal mol\textsuperscript{-1} below \textit{o}1. Pathways from \textit{o}5 and \textit{o}6 are analogous, with CH\textsubscript{3} essentially being a spectator. These schematics are in accord with the \textit{o}-methylphenyl + O\textsubscript{2} products detected with \textit{m}/\textit{z} 80, 94, 108, 122, as shown in Figure 4.1a. But, the possibility of \textit{o}-BQ contributing to the \textit{m}/\textit{z} 108 signal is excluded in Section 4.3.2 and attributed in part to cresol. By comparison, \textit{m}5 and \textit{m}6 decomposition in Figure 4.8 and Figure 4.9 results in 3- and 4-methyl-1,2-benzoquinone + H (\textit{m}6.4
and $m5.4$), and 2- and 3-methyl-cyclopentadienone + CHO ($m6.6$ and $m5.6$). In Figure 4.1b, the meta-radical case, these products are in accord with signals with $m/z$ 94 and 108. These four schemes rationalise the appearance of $m/z$ 80 from $o$-methylphenyl + O$_2$ as cyclopentadienone but does not explain $m/z$ 108, partly assigned cresol, for both ortho- and meta-radical cases.

Figure 4.4 and Figure 4.5 show formation of $o$- and $m$-methylphenoxy + O($^3$P) at -10.8 and -9.0 kcal mol$^{-1}$, respectively, and without a reverse energetic barrier. The absence of a locatable stationary point between the respective methylphenylperoxyl and methylphenoxy + O($^3$P) suggests the intrinsic TS structure is close to products along the reaction coordinate.$^{55,56}$ The $m/z$ 108 PI spectra for $o$- and $m$-methylphenyl + O$_2$ are assigned in part to cresol species but, as mentioned earlier, the isomers cannot be easily disentangled here. It is rationalised that, after formation, the phenoxy radical in Figure 4.4 and Figure 4.5 abstracts a H atom to produce what is likely $o$-cresol from $o3$ and $m$-cresol from $m3$.

As shown in Figure 4.1, the $o$-methylphenyl + O$_2$ reaction results in many products. Experiments with $m$-methylphenyl + O$_2$ revealed that two peaks are unique to the ortho-case: $m/z$ 80 and 108. Previous study of the $o$-hydroxyphenyl + O$_2$ reaction found that only $o$-BQ is produced as a primary product.$^{15}$ Both $o$-methylphenyl and $o$-hydroxyphenyl oxidation reactions were explored computationally in Gaussian 09 using the G3X-K method. For the $o$-hydroxyphenyl + O$_2$ reaction, the 1,5-H atom shift and OH loss occurs with a 9.6 kcal mol$^{-1}$ barrier. This small barrier pushes the product distribution toward $o$-BQ + OH. As shown in Figure 4.4, the overall barrier to the corresponding $o$-QM + OH is 27.5 kcal mol$^{-1}$, which allows reactions toward the methyloxepinoxy radicals to compete. Looking at the TS for the 1,5-H atom shift, the barrier for TS $o2$$\rightarrow$$o7$ is 27.4 kcal mol$^{-1}$ compared to 1.7 kcal mol$^{-1}$ for the corresponding TS for the $o$-hydroxyphenyl + O$_2$ reaction. For $o$-methylphenyl + O$_2$, similar reaction enthalpies for corresponding stationary points previously reported.$^{13}$
Figure 4.4. Potential energy schematic showing four pathways for decomposition of \( o_2 \). The barriers toward the methyloxepinoxyl radicals (\( o_5 \) and \( o_6 \)) and \( o \)-quinone methide (\( o_8 \)) differ by 4.1 kcal mol\(^{-1}\). G3S-K 0 K enthalpies are reported in kcal mol\(^{-1}\) relative to \( o_1 \).
Figure 4.5. Potential energy scheme showing three major pathways for decomposition of $m_2$. The intramolecular H-atom shift from the methyl to the peroxy group in $m_2$ is not shown because the TS is 51.7 kcal mol$^{-1}$ above $m_1$. G3S-K 0 K enthalpies are reported in kcal mol$^{-1}$ relative to $m_1$. 

$\text{CH}_3 + \text{O}_2 \rightarrow m_1, 0.0$

$\text{CH}_3 + \text{O(3P)} \rightarrow m_3, -9.0$

$m_2, -47.2$

$m_3$ does not lead to the formation of $m_4, -10.3$

$m_4, -31.1$

$m_5, -95.9$

$m_6, -95.2$

$\text{TS2, 9.2}$
Figure 4.6. Potential energy schematic for decomposition of the 7-methyl-oxepinoxyl radical (o6) from isomerisation of o2. G3X-K 0 K enthalpies are reported in kcal mol\(^{-1}\) relative to o1.
Figure 4.7. Potential energy schematic for decomposition of the 3-methyl-oxepinoxyl radical (o5) from isomerisation of o2. G3X-K 0 K enthalpies are reported in kcal mol$^{-1}$ relative to o1.
Figure 4.8. Potential energy scheme showing the decomposition of 4-methyloxepinoxy (m5) from isomerisation of m2. G3X-K 0 K enthalpies are reported in kcal mol\(^{-1}\) relative to m1.
Figure 4.9. Potential energy scheme showing the decomposition of 6-methyloxepinoxyl radical (m6) from isomerisation of m2. G3X-K 0 K enthalpies are reported in kcal mol$^{-1}$ relative to m1.
4.4 Conclusion

MPIMS experiments revealed two stark differences in the numerous products from \( o- \) and \( m- \)-methylphenyl + \( \mathrm{O}_2 \) reactions: the \( m/z \) 80 and 106 signals unique to \( o- \)-methylphenyl + \( \mathrm{O}_2 \). The \( m/z \) 106 signal assigned \( o \)-quinone methide is analogues to formation of \( o \)-benzoquinone from \( o \)-hydroxyphenyl + \( \mathrm{O}_2 \),\(^{15}\) where the ortho-substituent participates in a 1,5-H shift and subsequent OH elimination.

Other reaction products are rationalised by applying conventional understanding of phenyl + \( \mathrm{O}_2 \) reaction mechanisms.\(^{11,12}\) Such pathways include formation of methyl-substituted phenoxy and oxepinoxyl radicals. Cyclopentadienone, assigned to \( m/z \) 80, is attributed to decomposition of the 7-methyloxepinoxyl radical from \( o \)-methylphenyl + \( \mathrm{O}_2 \). Decomposition of 3-methyloxepinoxyl radicals likely result in 2-methyl-cyclopentadienone (94 Da). In the \textit{meta}-radical case, decomposition of 4- and 6-methyloxepinoxyl radicals should produce 2- and 3-methycyclopentadienone. In accord with MPIMS experiments.

Product assignments are supported by calculated AIE and potential energy schemes derived from quantum chemical calculations. However, \( m/z \) 122 assignment remains inconclusive. The \( m/z \) 66, 67, 70 signals attributed to decomposition of highly activated methyloxepinoxyl radicals.
4.5 Supporting Information

4.5.1 Collisions with the Reactor Wall

The collision rate per a unit of area per time was estimated using the impingement rate from Equation 4.1; where NB is the number density of a species (molecule m$^{-3}$), $\langle v \rangle$ is the average velocity of the species (m s$^{-1}$), $P$ is its pressure, $k_B$ is the Boltzmann constant, $T$ is temperature (K), and $m$ is the mass of the species.

\[
Z_{\text{wall}} = \frac{1}{4} N_B \langle v \rangle \tag{4.1}
\]

\[
= \frac{1}{4} \frac{P}{k_B T} \sqrt{\frac{8k_B T}{\pi m}} \tag{4.2}
\]

\[
= P \sqrt{\frac{1}{2k_B T \pi m}} \tag{4.3}
\]

The collision rate, per unit of time, expressed in Equation 4.4 is derived by multiplying $Z_{\text{wall}}$ from Equation 4.1 by the internal wall area ($A_{\text{wall}}$) of the reactor tube 37 cm above the 650 m pin hole, from where gas enters the differentially pumped vacuum chamber.

\[
k_{\text{wall}} = Z_{\text{wall}} \times A_{\text{wall}} \tag{4.4}
\]

\[
= Z_{\text{wall}} \times (0.37 \text{ m} \times 0.0105 \text{ m} \times \pi) \tag{4.5}
\]

An example calculation for a He partial pressure of 429 Pa (3.22 Torr) at 298 K at a total pressure of 4 Torr:

\[
k_{\text{He, wall}} = \frac{P}{\sqrt{2k_B T \pi m}} \times A_{\text{wall}} \tag{4.6}
\]

\[
= \frac{429 \text{ Pa} \times 0.0122 \text{ m}^2}{\sqrt{2} \times 1.3807 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} \times \pi \times 6.64 \times 10^{-27} \text{ kg}} \tag{4.7}
\]

\[
= 3.99 \times 10^{23} \text{ s}^{-1} \tag{4.8}
\]

4.5.2 Background Measurements (without Added O$_2$)
Figure 4.10. Photoionisation mass spectra at 10.2 eV integrated 0–80 ms after 248 nm photolysis of (a) $o$-iodotoluene and (b) $m$-iodotoluene without O$_2$ added to the reactor and at ambient temperatures (approximately 303 K).
4.5.3 Oxidation of \( o \)- and \( m \)-Methylphenyl Radicals

4.5.3.1 Series of Photoionisation Spectra and Kinetic Traces Comparing \( O_2 \) Reaction Products Between the \( o \)- and \( m \)-Methylphenyl + \( O_2 \) Reactions

**Figure 4.11.** Co-added \( m/z \) 106 kinetic traces integrated between 8.8–9.2 eV (red), 9.4–9.8 eV (black) and 9.8–10.2 eV (blue) from \( o \)-methylphenyl + \( O_2 \) at ambient temperatures. The domain of the graph is time relative to the photolysis laser pulse. The \( m/z \) 106 ion signal is shown to be a laser dependent signal and the kinetic traces are well match over the three photoionisation energy ranges.
Figure 4.12. Photoionisation spectra integrated 0–80 ms after photolysis for m/z 94 from o-methylphenyl + O$_2$ (red empty circles) and m-methylphenyl + O$_2$ (black empty squares), representing an average of three PI spectra with error bars representing 2 standard deviations. The PI spectrum from o-methylphenyl + O$_2$ is assigned 2-methylcyclopentadiene. The PI spectrum from m-methylphenyl + O$_2$ is assigned as a mixture of 2- and 3-methylcyclopentadienone.
Figure 4.13. Photoionisation spectrum integrated 0–80 ms after photolysis for m/z 108 from m-methylphenyl + O₂ (black empty squares). In Figure 4.1 (main document) the relative ion intensity of m/z 108 for o-methylphenyl + O₂ is near 50%, compared to 100% for m-methylphenyl + O₂. This results in a lower signal-to-noise ratio and increased deviation around the mean. The m/z 108 PI spectrum from o-methylphenyl + O₂ is not shown though it is well matched to the PI spectrum from m-methylphenyl + O₂. An integrated PE spectrum for m-cresol (Kobayashi et al., Ref. 47) is scaled and well matched to the PI spectrum from o-methylphenyl + O₂ between 8.2–9.2 eV.
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Figure 4.14. Co-added m/z 108 kinetic traces at 10.2 eV and ambient temperatures. The traces, timed relative to the photolysis laser pulse, show laser dependent signal that increases intensity gradually until 20 ms after the laser pulse. The rate coefficient for m/z 108 appearance from o- and m-methylphenyl + O₂ is 500 ± 70 s⁻¹ and 400 ± 20 s⁻¹ between 0–10 ms after photolysis, with the uncertainty representing 1 standard deviation.

Figure 4.15. Photoionisation spectrum integrated 0–80 ms after photolysis for m/z 80 from o-methylphenyl + O₂ (red empty circles) with error bars representing 2 standard deviations is compared to m/z 80 PI spectra for cyclopentadienone from o-hydroxyphenyl + O₂, which is affected by dissociative ionisation of o-benzoquinone at 9.8 eV. The absence of an enhanced signal between 9.8–10 eV indicates o-benzoquinone has insufficient quantities to affect the m/z 80 PI spectrum from o-methylphenyl + O₂.
Figure 4.16. Photoionisation spectra integrated 0–80 ms after photolysis for m/z 122 from o-methylphenyl + O\textsubscript{2} (red empty circles) and m-methylphenyl + O\textsubscript{2} (black empty squares).

Figure 4.17. Photoionisation spectra integrated 0–80 ms after photolysis for m/z 66 from o-methylphenyl + O\textsubscript{2} (red empty circles) and m-methylphenyl + O\textsubscript{2} (black empty squares), representing an average of three PI spectra with error bars representing 2 standard deviations. The absolute PI spectrum reported by Taatjes et al. for cyclopentadiene is scaled and well matched to the PI spectrum from o-methylphenyl + O\textsubscript{2} (solid purple line, Ref. 50).
Figure 4.18. Photoionisation spectra integrated 0–80 ms after photolysis for m/z 67 from o-methylphenyl + O$_2$ (red empty circles) and m-methylphenyl + O$_2$ (black empty squares), representing an average of three PI spectra with error bars representing 2 standard deviations. The m/z 67 PI spectra from o- and m-methylphenyl + O$_2$ are well matched.

Figure 4.19. Photoionisation spectra integrated 0–80 ms after photolysis for m/z 70 from o-methylphenyl + O$_2$ (red empty circles) and m-methylphenyl + O$_2$ (black empty squares), representing an average of three PI spectra with error bars representing 2 standard deviations. The m/z 70 PI spectra from o- and m-methylphenyl + O$_2$ are well matched.
4.5.3.2 Tables of Calculated CBS-QB3 Adiabatic Ionisation Energies for Product Isomers with Reference Data

Table 4.1. Calculated CBS-QB3 adiabatic ionisation energies for C$_5$H$_7$ isomers (67 Da). The CBS-QB3 relative heats of formation ($\Delta H_f$) are provided in kcal mol$^{-1}$ with zero-point energy.

<table>
<thead>
<tr>
<th>C$_5$H$_7$ isomers</th>
<th>Calculated adiabatic IE (eV)</th>
<th>Literature IE (eV)</th>
<th>Relative $\Delta H_f$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-cyclopentenyl radical</td>
<td>7.0</td>
<td>7.0 (vertical)$^{51}$</td>
<td>0.0</td>
</tr>
<tr>
<td>3-cyclopentenyl radical</td>
<td>7.4</td>
<td>7.54 (vertical)$^{36}$</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 4.2. Calculated CBS-QB3 adiabatic ionisation energies for C$_7$H$_6$O$_2$ isomers (122 Da). The CBS-QB3 enthalpies ($\Delta H_f$) are provided in kcal mol$^{-1}$ with zero-point energy.

<table>
<thead>
<tr>
<th>C$_5$H$_7$ isomers</th>
<th>Calculated adiabatic IE (eV)</th>
<th>Literature IE (eV)</th>
<th>Relative $\Delta H_f$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methyl-1,2-benzoquinone</td>
<td>9.1</td>
<td>27.5</td>
<td></td>
</tr>
<tr>
<td>4-methyl-1,2-benzoquinone</td>
<td>9.0</td>
<td>27.7</td>
<td></td>
</tr>
<tr>
<td>2-methyl-1,4-benzoquinone</td>
<td>10.0</td>
<td>19.1</td>
<td></td>
</tr>
<tr>
<td>3-hydroxy-1,2-quinone methide</td>
<td>8.3</td>
<td>28.0</td>
<td></td>
</tr>
<tr>
<td>4-hydroxy-1,2-quinone methide</td>
<td>8.2</td>
<td>28.4</td>
<td></td>
</tr>
<tr>
<td>5-hydroxy-1,2-quinone methide</td>
<td>8.5</td>
<td>25.1</td>
<td></td>
</tr>
<tr>
<td>6-hydroxy-1,2-quinone methide</td>
<td>8.2</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td>2-hydroxy-1,4-quinone methide</td>
<td>8.7</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>3-hydroxy-1,4-quinone methide</td>
<td>9.1</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td>2-hydroxy-benzaldehyde</td>
<td>8.7</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>3-hydroxy-benzaldehyde</td>
<td>8.9</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>4-hydroxy-benzaldehyde</td>
<td>8.8</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>3-methide-oxepinone</td>
<td>8.3</td>
<td>38.9</td>
<td></td>
</tr>
<tr>
<td>7-methide-oxepinone</td>
<td>8.5</td>
<td>38.5</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4. Neutral o-Methylphenyl Radical + O₂

References


Chapter 4. Neutral $\sigma$-Methylphenyl Radical + $\text{O}_2$


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Chapter 4. Neutral o-Methylphenyl Radical + O$_2$


Chapter 5

Distonic and Neutral
\( o \)-Hydroxylphenyl Radical + \( O_2 \)

This chapter examines the oxidation processes and products of distonic ammonium-substituted and neutral \( o \)-hydroxyphenyl radicals. It was published as a peer-reviewed publication (reproduced as Appendix B). The presented form includes updated citation numbers, updated formatting for consistency within the thesis (e.g. italicisation of “\( m/z \)”), and corrections to the publication (listed in Section 5.8). The reference to the peer-reviewed publication is provided below:


URL: http://dx.doi.org/10.1039/C5CP02953H

Author contributions
Matthew B. Prendergast performed all of the experimental and theoretical work, excluding synthesis of 4-(\( N,N,N \)-trimethylammonium)-2-iodophenol. Matthew B. Prendergast prepared the manuscript with input from all authors.

Certification
I, Assoc. Prof. Adam J. Trevitt, as the primary supervisor for Matthew B. Prendergast and the principal investigator on this project, agree with and certify the author contributions described above.

Assoc. Prof. Adam J. Trevitt

Date 19/11/2018
5.1 Abstract

Gas-phase product detection studies of \( o \)-hydroxyphenyl radical and \( O_2 \) are reported at 373, 500, and 600 K, at 4 Torr (533.3 Pa), using VUV time-resolved synchrotron photoionisation mass spectrometry. The dominant products are assigned as \( o \)-benzoquinone (\( C_6H_4O_2, \) \( m/z \) 108) and cyclopentadienone (\( C_5H_4O, \) \( m/z \) 80). It is concluded that cyclopentadienone forms as a secondary product from prompt decomposition of \( o \)-benzoquinone (and dissociative ionization of \( o \)-benzoquinone may contribute to the \( m/z \) 80 signal at photon energies \( \geq 9.8 \) eV). Ion-trap reactions of the distonic \( o \)-hydroxyphenyl analogue, the 5-ammonium-2-hydroxyphenyl radical cation, with \( O_2 \) are also reported and concur with the assignment of \( o \)-benzoquinone as the dominant product. The ion-trap study also provides support for a mechanism where cyclopentadienone is produced by decarbonylation of \( o \)-benzoquinone. Kinetic studies compare oxidation of the ammonium-tagged \( o \)-hydroxyphenyl and \( o \)-methylphenyl radical cations along with trimethylammonium-tagged analogues. Reaction efficiencies are found to be \( ca. \) 5\% for both charge-tagged \( o \)-hydroxyphenyl and \( o \)-methylphenyl radicals irrespective of the charged substituent. G3X-K quantum chemical calculations are deployed to rationalise experimental results for \( o \)-hydroxyphenyl + \( O_2 \) and its charge-tagged counterpart. The prevailing reaction mechanism, after \( O_2 \) addition, involves a facile 1,5-H shift in the peroxyl radical and subsequent elimination of \( OH \) to yield \( o \)-benzoquinone that is reminiscent of the Waddington mechanism for \( \beta \)-hydroxyperoxyl radicals. These results suggest \( o \)-hydroxyphenyl + \( O_2 \) and decarbonylation of \( o \)-benzoquinone serve as plausible \( OH \) and \( CO \) sources in combustion.

5.2 Introduction

Phenolic compounds, including alkylphenols, represent a substantial portion of lignin-derived biofuel stocks\(^1\) and the lighter fractions from lignite pyrolysis.\(^2\) They are also used as additives to enhance the oxidative stability of biodiesel and diesel.\(^3\)–\(^6\) Phenol is a product of catechol thermal decomposition,\(^7\) benzene and hydroxyl radical reactions\(^8\) as well as phenyl\(^9\) and benzyl radical oxidation.\(^10\)

The pyrolysis of phenol proceeds with H-migration and CO elimination to produce cyclopentadiene or, at higher temperatures, H-loss to produce the phenoxy radical.\(^11\) Investigations into the phenol + \( OH \) reaction report the H-abstraction product as the phenoxy radical.\(^12,13\) However, at \( >390 \) K, H-abstraction from the phenyl ring and \( OH \) addition reactions are also expected with the former process resulting in hydroxyphenyl radicals.\(^14\) The \( o \)-hydroxyphenyl radical is an intermediate in the pyrolysis reaction reported for dimethoxybenzene (a model compound
for the $\beta$-04 aryl ether unit within G-type lignin).\textsuperscript{15} The addition of O$_2$ to the $o$-hydroxyphenyl radical site will produce the $o$-hydroxyphenylperoxyl radical, with its hydroxy H-atom within close proximity to the peroxyl radical substituent. As is the case for the $o$-methylphenylperoxyl radical,\textsuperscript{16,17} $o$-hydroxyphenylperoxyl is expected to isomerise and eliminate OH via a phenoxy QOOH intermediate to produce $o$-benzoquinone ($o$-BQ), a known precursor to cyclopentadienone (CPO) + CO.\textsuperscript{18–21} This mechanism was reported for the oxidation of protonated tyrosinyl radicals\textsuperscript{22} and has some similarities to the Waddington mechanism for $\beta$-hydroxyperoxyl radicals.\textsuperscript{23–25} Yet, to date, no direct experimental results have validated this mechanism for the $o$-hydroxyphenyl + O$_2$ reaction system.

In this work, we report reactions of gas-phase $o$-hydroxyphenyl with O$_2$ using two approaches: synchrotron-based time-resolved photoionisation mass spectrometry and distonic-ion mass spectrometry. The synchrotron-based method couples a slow-flow kinetic reactor to a time-of-flight mass spectrometer and VUV photoionisation that allows detection of reaction products with kinetic and isomeric details. The distonic ion approach exploits charge-tagged derivatives of neutral radical species to study radical kinetics by ion-trap mass spectrometry.\textsuperscript{26} These distonic ion oxidation experiments build on a framework provided by previous studies of distonic phenyl\textsuperscript{27} and $o$-methylphenyl radical oxidation.\textsuperscript{17} In combination, we show that OH elimination follows the reaction of $o$-hydroxyphenyl radicals with O$_2$ to form $o$-BQ. The stability of this nascent $o$-BQ is also investigated.

## 5.3 Experimental

### 5.3.1 Synchrotron Photoionisation Mass Spectrometry

The $o$-hydroxyphenyl + O$_2$ reaction was investigated using time-resolved photoionisation mass spectrometry\textsuperscript{28} at the Chemical Dynamics Beamline\textsuperscript{29,30} at the Advanced Light Source (ALS at Lawrence Berkeley National Laboratories, USA). The apparatus comprises a slow-flow tube reactor, quasi-continuous vacuum-ultraviolet (VUV) synchrotron light source and an orthogonal acceleration time-of-flight mass spectrometer. $o$-Hydroxyphenyl radicals were generated within the flow tube by photolysis of $o$-bromophenol using a pulsed KrF excimer laser (248 nm) operating at 4 Hz with a fluence of ca. 50 mJ cm$^{-2}$.

The heatable quartz reactor flow tube is 62 cm long with a 1.05 cm inner diameter maintained at 4 Torr (533.3 Pa). Gas continuously escapes the reactor into a differentially pumped vacuum chamber through a 650 $\mu$m pinhole situated 37 cm along the flow tube. In the experiments reported here, $o$-bromophenol, O$_2$ gas, and He gas are supplied to the reactor through separate mass-flow controllers at the
overall rate of 202 sccm. The \( o \)-bromophenol was entrained in He gas using a fritted bubbler with the liquid sample maintained at 291 K (18 °C) and ~573 Torr (76.4 kPa). The vapour pressure of \( o \)-bromophenol is roughly approximated at 291 K to be 0.17 Torr using Antoine parameters known for phenol.\(^{31}\) At 373 K and 4 Torr, number densities within the reactor are ca. \( 1.7 \times 10^{12} \) molecule cm\(^{-3} \) for \( o \)-bromophenol, \( 7.7 \times 10^{15} \) molecule cm\(^{-3} \) for \( O_2 \) gas, and a total of \( 9.6 \times 10^{16} \) molecule cm\(^{-3} \) for He gas. Reactions were conducted with the reactor temperature maintained at 373 K, 500 K and 600 K. The temperature profile of the reactor is such that the length ca. 20 cm above the pinhole is maintained at the set temperature. Gas flow velocities are as follows: 10.1 m s\(^{-1} \) at 373 K, 13.5 m s\(^{-1} \) at 500 K, and 16.2 m s\(^{-1} \) at 600 K. Total gas flow densities were: \( 1.0 \times 10^{17} \) molecule cm\(^{-3} \) at 373 K, \( 7.7 \times 10^{16} \) molecule cm\(^{-3} \) at 500 K, and \( 6.4 \times 10^{16} \) molecule cm\(^{-3} \) at 600 K.

The gas that escapes through the 650 \( \mu \)m pinhole is sampled by a skimmer to create a near-effusive molecular beam that is intersected by quasi-continuous vacuum-ultraviolet (VUV) synchrotron light. Ions produced by photoionisation are detected using a 50 kHz pulsed orthogonal-acceleration time-of-flight mass spectrometer. The photoionisation energy was typically scanned from 9 to 10 eV with 0.025 eV steps. Mass spectra are compiled into three-dimensional arrays of mass-to-change \((m/z)\), reaction time, and photoionisation energy. All data are normalised for variations in the ALS photocurrent using a NIST-calibrated photodiode (SXUV-100, International Radiation Detectors Inc.). Background subtraction is achieved by subtracting the average signal during the 20 ms prior to the photolysis pulse from the dataset. The resulting photoionisation spectra and kinetic traces are normalised by the area under the curve and averaged together for each temperature. The error bars provided at a given photoionisation energy represent two standard deviations \((2\sigma)\) for a mean of at least three measurements at 373 and 500 K, and two measurements at 600 K.

### 5.3.2 Ion-Trap Mass Spectrometry

Distonic radical cation experiments were conducted on a modified Thermo Fisher Scientific LTQ ion-trap mass spectrometer (Thermo Fisher Scientific Inc., San Jose, USA) situated at the University of Wollongong. Radical precursor ions were generated by infusing methanolic solutions of 10 \( \mu \)M 2-bromo-4-aminophenol ([M + H]\(^+ \) at \( m/z \) 188 and 190), 3-bromo-4-methylaniline ([M + H]\(^+ \) at \( m/z \) 186 and 188), or 3-iodo-4-hydroxy-\( N,N,N \)-trimethylbenzenaminium iodide ([M – I]\(^+ \) at \( m/z \) 278) into the electrospray ion source at 5 \( \mu \)L min\(^{-1} \) and were mass-selected using an isolation window of 5–6 Th (mass-to-charge) for brominated, and 1–2 Th for the iodinated cations with a \( q \)-parameter of 0.250. Mass spectra acquired with the ion-trap mass
spectrometer and presented herein are an average of 50 scans unless otherwise stated. Typical instrumental settings: electrospray voltage (4–5 kV), capillary temperature (250 °C), and sheath gas flow at 10–15, auxiliary gas flow at 0–5 and sweep gas flow at 0 (arbitrary units). The normalised collision energy was typically 20–30% (Ref. 32) for CID experiments with an activation time of 30 ms as defined within the control software.

5.3.2.1 Photodissociation (PD).

Modifications to the ion-trap mass spectrometer required for PD of trapped ions are similar to those previously reported\textsuperscript{33,34} and are detailed elsewhere.\textsuperscript{35,36} At the beginning of a specified MS\textsuperscript{n} ion activation step, where laser PD is desired, the mass spectrometer transmits a signal to a digital delay generator that subsequently triggers the flashlamp of the Nd:YAG laser (4th harmonic, $\lambda = 266$ nm) such that only a single laser pulse is delivered per MS\textsuperscript{n} cycle. The unfocussed laser pulse (ca. 30 mJ cm$^{-2}$) is directed through a 2 mm orifice in the back lens of the ion-trap assembly to overlap with the ion cloud within the ion trap.

5.3.2.2 Ion-Molecule Reactions.

Distonic radical cations generated within the ion trap were mass selected and then allowed to react with O\textsubscript{2} for 0.030–10000 ms (set by the control software). Background O\textsubscript{2} resides in the trap due to air entrained by the atmospheric pressure ESI source. Reactions were also conducted with an increased O\textsubscript{2} concentration by using a He bath gas doped with O\textsubscript{2} (770 ± 45 ppm; BOC, Australia). Similarly, a He bath gas doped with oxygen-18 was used for isotopic labelling experiments. The O\textsubscript{2} concentration (molecule cm$^{-3}$) within the ion-trap region was determined using the measured pseudo-first order rate coefficient for 3-carboxylatoadamantyl + O\textsubscript{2} and its known second-order rate coefficient of $8.5 \pm 0.4 \times 10^{-11}$ cm$^{3}$ molecule$^{-1}$ s$^{-1}$ with the O\textsubscript{2} concentration determined for each experiment.\textsuperscript{37} The background O\textsubscript{2} concentration within the ion trap is typically $6.4 \times 10^{-9}$ molecule cm$^{-3}$ and the increased O\textsubscript{2} concentrations ranged from $1.6$–$2.2 \times 10^{11}$ molecule cm$^{-3}$ with an O\textsubscript{2}-doped bath gas. The effective temperature of ions stored within a linear quadrupole ion trap has been estimated at 318 ± 23 K,\textsuperscript{38} consistent with an earlier estimate of 307 K.\textsuperscript{37} The kinetic plots that show ion signal decay with increasing reaction time were produced by integrating the ion signal intensity over a selected mass-to-charge range and normalising it to the integrated total ion signal intensity. The normalised integrated ion signal intensity is then averaged for at least 10 scans and plotted against reaction time (0.030–10000 ms) to track changes in ion signal intensity due to reactions with O\textsubscript{2}. Measured pseudo-first order rate coefficients ($k_{1st}$) were obtained
by fitting Equation 5.1 to the average normalised integrated peak intensity against reaction time, for a select mass-to-charge range, using the Levenberg–Marquardt algorithm. Satisfactory fits with Equation 5.1 are consistent with pseudo-first order kinetic behaviour. Thus, allowing the second-order rate coefficient \((k_{2nd})\) to be calculated using Equation 5.2 with a measured \([O_2]\). The residual plots accompanying kinetic curves in Figure 5.5, Figure 5.15, and Figure 5.16 (Section 5.7) show the difference between the average normalised integrated ion signal intensity and the expected value from Equation 5.1, i.e. the residuals, plotted as a function of reaction time.

\[
y = A_0 \exp(-k_{1st}t) + \text{constant} \tag{5.1}
\]

\[
k_{2nd} = \frac{k_{1st}[O_2]}{[O_2]} \tag{5.2}
\]

At least five kinetic decay curves were acquired in succession to ensure consistent conditions, with one decay curve taking 20–30 min to acquire. For the ion-molecule reactions below, pseudo-first order kinetic character was observed. The second-order rate coefficient for 5-ammonium-2-hydroxyphenyl + O\(_2\) is an average from 17 decay curves over three experiments at low \([O_2]\) and 20 decay curves over two experiments at increased \([O_2]\). The 5-ammonium-2-methylphenyl + O\(_2\) second order rate coefficient is calculated as the average of 19 decay curves at low \([O_2]\) and 30 decay curves at increased \([O_2]\) over three experiments at each concentration. The second-order rate coefficient for 5-(N,N,N-trimethylammonium)-2-hydroxyphenyl radical + O\(_2\) is an average of 5 decay curves at low \([O_2]\). Reported reaction efficiencies were calculated from the second-order rate coefficients as a percentage of the reactants collision frequency estimated using the Langevin collision model for ion-molecule collision pairs.\(^{39}\)

Statistical uncertainty from fitting pseudo-first order rate coefficients \((k_{1st})\) to experimental decay curves was typically \(2\sigma \leq 10\%\). Systematic uncertainty in the ion-trap pressure and O\(_2\) concentration, including the generation of neutrals and charged species with mass-to-charge less than the low mass cut-off (50 Th) result in an upper limit of 50% uncertainty in the O\(_2\) concentration that is accumulated in reported second-order rate coefficients and reaction efficiencies.

### 5.3.3 Quantum Chemical Calculations

Reaction enthalpies were calculated from electronic energies computed with the G3X-K composite method\(^{40}\) in Gaussian 09.\(^{41}\) G3X-K is a modified G3SX composite method that uses M06-2X density functional theory in place of B3LYP and
is parameterised for thermochemical kinetics. It is capable of reproducing barrier heights in the DBH24/08 test set\textsuperscript{42} to within 1 kcal mol\textsuperscript{-1}, on average.\textsuperscript{40} The CBS-QB3 method was used for the calculation of adiabatic ionisation energies (AIE) and cation dissociation barriers, with an estimated error of 1 kcal mol\textsuperscript{-1} (0.05 eV) for AIEs\textsuperscript{43,44} and 2 kcal mol\textsuperscript{-1} for barriers from the DBH24/08 database.\textsuperscript{42} All stationary points were characterised as either minima (no imaginary frequencies) or transition states (one imaginary frequency whose normal mode projection approximates motion along a reaction coordinate). The assignment of a transition state between minima was verified by IRC calculations. The M06-2X geometries and frequencies and G3X-K energies were used to calculate preliminary product ratios within the MultiWell 2013 suite of programs.\textsuperscript{45–47} All reported energies include the zero-point energy correction for 0 K enthalpies and AIEs.

### 5.3.4 Materials

3-Bromo-4-methylaniline, 4-amino-2-bromophenol, oxygen-18 (97%), and \textit{o}-bromo-phenol (98%) were purchased from Sigma Aldrich. Gases and reagents obtained from commercial sources were used without further purification. The synthesis of 3-iodo-4-hydroxy-\textit{N,N,N}-trimethylbenzenaminium iodide is described in Section 5.7.1 of the Supporting Information.

### 5.4 Results and Discussion

#### 5.4.1 Synchrotron Photoionisation Mass Spectrometry: \textit{o}-Hydroxyphenyl + O\textsubscript{2}

Figure 5.1a is a product mass spectrum after photolysis of \textit{o}-bromophenol with no O\textsubscript{2} added to the reactor, serving as a background measurement. The spectrum is integrated from 0 to 20 ms after photolysis at a photoionisation energy of 10 eV with a reactor temperature of 373 K. Major photolysis product peaks are present at \textit{m/z} 92 and 94. The photoionisation (PI) spectra for \textit{m/z} 92 and 94 (not shown) are well matched to the integrated photoelectron spectrum for cyclopenta-2,4-dien-1-yldidenemethanone (C\textsubscript{5}H\textsubscript{4}CO, AIE = 8.09 eV)\textsuperscript{48–50} and the known photoionisation spectrum for phenol (C\textsubscript{6}H\textsubscript{5}OH, AIE = 8.49 eV),\textsuperscript{51–53} respectively. However, since the characteristic AIEs are below the photoionisation energy range scanned, these are tentative assignments for these background species. As an aside, cyclopenta-2,4-dien-1-yldidenemethanone (C\textsubscript{5}H\textsubscript{4}CO, \textit{m/z} 92) may arise from \textit{o}-bromophenol photolysis via HBr loss\textsuperscript{54} and phenol (C\textsubscript{6}H\textsubscript{5}OH, \textit{m/z} 94) is probably formed via H-abstraction by the \textit{m/z} 93 radical from the abundant \textit{o}-bromophenol precursor.
Figure 5.1. Product photoionisation mass spectra at 373 K and 10 eV integrated 0–20 ms after 248 nm photolysis of (a) o-bromophenol and (b) o-bromophenol in the presence of additional O$_2$ ($7.7 \times 10^{15}$ molecule cm$^{-3}$). In product spectrum (b) m/z 108 and 80 are reaction product peaks but, as discussed in the text, a portion of the m/z 80 signal may arise from dissociative ionisation of o-BQ (assigned to m/z 108).
Figure 5.1b is a product mass spectrum from photolysis of o-bromophenol in the presence of 7.7 \( \times 10^{15} \) molecule cm\(^{-3} \) O\(_2\). The new product peaks at \( m/z \) 80, 108 and the minor peak at \( m/z \) 110 are consistent with C\(_5\)H\(_4\)O, C\(_6\)H\(_4\)O\(_2\), and C\(_6\)H\(_6\)O\(_2\) and are attributed to the o-hydroxyphenyl + O\(_2\) reaction. The PI spectra for \( m/z \) 80 and 108, integrated 0 to 20 ms after photolysis at 373 K, are provided in Figure 5.2a and 5.2b. PI spectra at 500 K and 600 K are provided in the Section 5.7 (Figure 5.9 and Figure 5.10, respectively). The PI onsets for \( m/z \) 80 at 9.4 eV and \( m/z \) 108 at 9.2 eV are in agreement with reference spectra for cyclopentadienone (CPO, \( m/z \) 80) and o-benzoquinone (o-BQ, \( m/z \) 108),\(^{55-57}\) and consistent with AIEs provided in Table 5.1. Ionization onsets for CPO and o-BQ were recently reported by Ormond \textit{et al.}\(^{55}\) and compared within the inset of Figure 5.2. The \( p\)-benzoquinone isomer can be excluded as a \( m/z \) 108 product contributor as its AIE is 9.96 eV with a sharp photoionisation onset,\(^{57,58}\) and there is no such feature in the PI spectrum up to 10 eV. The \( m/z \) 109 signal present in mass spectra obtained at 373, 500 and 600 K (Section 5.7 Figure 5.11) could result, in part, from decomposition of o-hydroxyphenylperoxyl to o-hydroxyphenoxyl + O\(^{3}\)P. The hydroxyphenoxyl cation is expected at \( m/z \) 109, however unequivocal assignment of the \( m/z \) 109 species is confounded by the \(^{13}\)C isotope peak of the dominant \( m/z \) 108 product. In unpublished studies, we have observed phenoxyl radical decay that is kinetically matched to the growth of a +1 Da ion signal intensity. A \( m/z \) 110 product ion is present in Figure 5.11 (Section 5.7) and kinetic traces in Figure 5.13 (Section 5.7) show that the appearance of \( m/z \) 110 ions is delayed relative to \( m/z \) 108 ions (a primary product kinetic reference). Therefore, the delayed appearance of \( m/z \) 110 ions could be explained via H-abstraction by the o-hydroxyphenoxyl radical to produce o-catechol (C\(_6\)H\(_4\)OHOH, \( m/z \) 110).

<table>
<thead>
<tr>
<th>Species</th>
<th>Measured (eV)</th>
<th>Calculated AIE (eV)</th>
<th>Literature values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentadienone (CPO, ( m/z ) 80)</td>
<td>9.4</td>
<td>9.41</td>
<td>9.41 ± 0.01</td>
</tr>
<tr>
<td>o-Benzoquinone (o-BQ, ( m/z ) 108)</td>
<td>9.2</td>
<td>9.18</td>
<td>9.3 ± 0.1</td>
</tr>
<tr>
<td>o-Hydroxyphenoxyl radical (( m/z ) 109)</td>
<td>8.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Hydroxyphenol (catechol, ( m/z ) 110)</td>
<td>8.22</td>
<td>8.56</td>
<td></td>
</tr>
<tr>
<td>p-Benzoquinone (( p)-BQ)</td>
<td>9.89</td>
<td>9.96 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>

The detection of o-BQ (\( m/z \) 108) is rationalised by O\(_2\) addition to the o-
Chapter 5. Distonic and Neutral \( o \)-Hydroxylphenyl Radical + \( O_2 \)

Figure 5.2. Photoionisation spectra integrated 0–20 ms after photolysis for (a) \( m/z \) 80 and (b) \( m/z \) 108 from \( o \)-hydroxyphenyl + \( O_2 \) at 373 K. Each spectrum is an average of three PI spectra and the 2\( \sigma \) statistical uncertainty is represented by vertical error bars. Figures inset within (a) and (b) compare the experimental PI spectra near the onset to reference spectra for CPO and \( o \)-BQ from Ref. 55 (1000 K). Reference PI spectra are also provided in (a) for CPO from Ref. 56 and 57 (873 K).
hydroxyphenyl radical, followed by isomerisation of the hydroxyphenylperoxyl intermediate to hydroperoxyphenoxyl and subsequent OH loss to form o-BQ (Scheme 5.1). This pathway is analogous to the O\textsubscript{2} addition and subsequent OH loss mechanism that operates in the o-methylphenyl + O\textsubscript{2} reaction\textsuperscript{16,17} and OH loss in the Waddington mechanism for β-hydroxyperoxyl radicals.\textsuperscript{23,24} Scheme 5.1 also includes pathways from o-BQ that lead to CPO and the CPO radical cation that will now be discussed.

Scheme 5.1

Included in Figure 5.2a are reference PI spectra for CPO from Yang et al.\textsuperscript{56} and Parker et al.\textsuperscript{57} The close agreement between the m/z 80 and reference PI spectra shown in Figure 5.2a from 9 to 9.8 eV support our assignments of m/z 80 as CPO. It is evident that at PI energies \( \geq 9.8 \) eV all m/z 80 PI spectra diverge with the reference spectra under-predicting the current experimental data. Additional PI spectra acquired at 500 and 600 K (Figure 5.9 and Figure 5.10, Section 5.7) also diverge from the reference spectra at PI energies \( \geq 9.8 \) eV.

The possibility of other C\textsubscript{5}H\textsubscript{4}O isomers contributing to the m/z 80 ion signal was ruled out by calculating AIEs for closed-shell linear C\textsubscript{5}H\textsubscript{4}O isomers listed in Table 5.3 (Section 5.7). Isomers were excluded on the basis of having: an AIE <9.2 eV, or an AIE >10.0 eV and a relatively high formation enthalpy. As it stands, CPO is the only plausible isomer contributing to the m/z 80 PI spectra, however, the source of neutral CPO and the cause of the disparity around 9.8 eV in the m/z 80 PI spectra (Figure 5.2a) require further examination.

The systematic differences between the m/z 80 signal and CPO reference spectra in Figure 5.2a at photoionisation energies \( \geq 9.8 \) eV could arise from dissociative ionisation of higher mass species, where o-BQ is a likely candidate. It is known that dissociative ionisation of 1,2-naphthoquinone and 9,10-phenanthrenequinone result in CO loss (both contain the o-BQ substructure).\textsuperscript{60} Figure 5.11 (Section 5.7) shows product mass spectra at 373, 500 and 600 K integrated over two energy ranges; 9.40–9.75 eV (Figure 5.11a–c, Section 5.7) and 9.85–10.00 eV (Figure 5.11d–f, Section 5.7). These mass spectra reveal some variation in the product ratios but no additional product signals. Comparing the kinetic traces for m/z 80 and 108 at 500
K integrated over 9.40–9.75 eV (Figure 5.12a, Section 5.7) shows that the kinetic traces are clearly different and consistent with the dominant fraction of each ion population arising from photoionisation of different neutrals. However, at higher energies (9.85–10.00 eV, Figure 5.12b, Section 5.7), the m/z 80 and 108 kinetic traces appear more similar—this is consistent with a portion of C₆H₄O₂ (108 Da) undergoing dissociative ionisation to yield product ions with m/z 80. Furthermore, the potential energy scheme for CO loss from the o-BQ radical cation (m/z 108) provided in Figure 5.3 shows the cation dissociation barrier to be 9.7 eV relative to neutral o-BQ. These results support the proposition that at photoionisation energies ≥9.8 eV some of the m/z 80 signal arises from the dissociative ionisation of o-BQ. This contribution is in addition to the ionisation of CPO produced within the reactive flow.

Analogous to product pathways of the phenylperoxyl radical in phenyl + O₂ reactions, CPO could be produced after decomposition of hydroxyl-substituted oxepinoxyl radicals. Unimolecular reaction pathways leading directly to CPO are discounted on the basis of experiments in Section 5.4.2 and prohibitively high energy pathways reported in Section 5.4.3.3. Ultimately, we propose that the m/z 80 and 108 products are generated according to processes summarised in Scheme 5.1: the o-hydroxyphenyl radical undergoes O₂ addition to form the hydroxyphenylperoxyl radical and subsequent OH loss to produce o-BQ. And, a portion of the nascent vibrationally-excited o-BQ population then decomposes via decarbonylation to produce CPO. In addition, dissociative ionisation of o-BQ possibly contributes to the measured m/z 80 signal at energies ≥9.8 eV.

To further establish connections between the reaction products of o-hydroxyphenyl + O₂ (cf. Scheme 5.1), charge-tagged derivatives of o-hydroxyphenyl radicals
were prepared within an ion-trap mass spectrometer (at the University of Wollongong). The study of distonic radical ions can provide useful insight into the reactions of their neutral radical counterparts. The presence of a relatively unreactive charged substituent enables isolation and manipulation of reactive intermediates using ion-trap mass spectrometry, while products arise from reactions with the spatially separated radical moiety.\textsuperscript{17,65,66} Quantum chemical calculations were also conducted, and discussed later in Section 5.4.3, to rationalise experimental results for both the neutral and charge-tagged systems.

### 5.4.2 Ion-Trap Mass Spectrometry: Distonic o-Hydroxyphenyl + \( \text{O}_2 \)

Photodissociation (PD, \( \lambda = 266 \text{ nm} \)) of isolated \( m/z \) 188 and 190 ions ([M + H]\(^+\), assigned 3-bromo-4-hydroxybenzenaminium cation) resulted in the \( m/z \) 109 signal in Figure 5.4a. The \( m/z \) 109 ion, consistent with Br loss, was assigned to the 5-ammonium-2-hydroxyphenyl radical cation shown in Scheme 5.2. Isolation of this radical cation in the presence of background \( \text{O}_2 \) (6.4 \( \times \) 10\(^9\) molecules cm\(^{-3}\)) resulted in a major product ion at \( m/z \) 124 and a minor product ion at \( m/z \) 96 (<1%) that both grew in with increasing reaction times (0.030–10000 ms). A mass spectrum acquired with 2000 ms reaction time is shown in Figure 5.4b. The \( m/z \) 124 product ion is rationalised by \( \text{O}_2 \) addition to the charge-tagged 2-hydroxyphenyl radical followed by prompt OH elimination to yield 4-ammonium-2-benzoquinone.

![Scheme 5.2](image)

The mass spectrum in Figure 5.4c, from isolation and subsequent collision-induced dissociation (CID) of \( m/z \) 124 product ions, shows major signals at \( m/z \) 96 and 107 and minor signals at \( m/z \) 79 and 81. The product ion at \( m/z \) 96 (–28 Da) is consistent with decarbonylation of ammonium-tagged o-BQ to yield ammonium-tagged CPO + CO. Fragment ions at \( m/z \) 107, 79, and 81 are assigned to loss of \( \text{NH}_3 \) (–17 Da), \( \text{NH}_3 + \text{CO} \) (–45 Da) and \( \text{NC}_2\text{H}_5 \) or \( \text{C}_2\text{H}_3\text{O} \) (–43 Da) from \( m/z \) 124, respectively. To verify these assignments, \( ^{18}\text{O}_2 \) was introduced into the ion trap and reacted with \( m/z \) 109 radical cations. The \( m/z \) 126 ions produced are consistent with \( ^{18}\text{O}_2 \) addition and \( ^{18}\text{OH} \) loss (–19 Da, Figure 5.4d) and exclude any contribution of \( \text{NH}_3 \) loss (–17 Da). Isolation and subsequent CID of the \( m/z \) 126 ions resulted in
Figure 5.4. Mass spectra resulting from (a) PD of 3-bromo-4-hydroxybenzen-aminium ($m/z$ 188 and 190), (b) isolation of $m/z$ 109 ions resulting from 266 nm PD of 3-bromo-4-hydroxybenzenaminium and storage for 2 seconds in the presence of background $O_2$ ($10^9$ molecules cm$^{-3}$), and (c) CID of the product ion at $m/z$ 124. Experiments were repeated with $^{18}O_2$ and (d) the product ion at $m/z$ 126 was subjected to CID.
fragments at \(m/z\) 96 and 98 consistent with loss of \(^{18}\text{C}^{18}\text{O}\) and \(^{16}\text{C}^{16}\text{O}\) from \(^{18}\text{O}\)-labelled \(o\)-BQ to yield CPO. Taken together, these data demonstrate a connection between the \(o\)-BQ intermediate \((m/z \ 124)\) and the CPO structure \((m/z \ 96)\) via processes summarised in Scheme 5.2. These data do not provide evidence for a phenyl-like oxidation mechanism for the direct formation of CPO \(via\) phenoxy and oxepinoxyl radicals.\(^{61-64}\) Other fragment ions at \(m/z\) 79, 81, 83, and 109 are assigned to loss of \(\text{NH}_3 + \text{C}^{18}\text{O} \ (-47 \text{ Da})\), \(\text{NH}_3 + \text{C}^{16}\text{O}\) or \(\text{C}_2\text{H}_3^{18}\text{O} \ (-45 \text{ Da})\), \(\text{NC}_2\text{H}_5\) or \(\text{C}_2\text{H}_3^{16}\text{O} \ (-43 \text{ Da})\), and \(\text{NH}_3 \ (-17 \text{ Da})\) from \(m/z\) 126, respectively.

Potential energy schemes for formation of \(o\)-BQ and CPO are compared and discussed for both neutral and distonic cases in Section 5.4.3. Reactions of the PD generated 5-ammonium-2-hydroxyphenyl radical cation \((m/z \ 109)\) with \(\text{O}_2\) were characterised further by kinetic measurements.

### 5.4.2.1 Distonic Ion + \(\text{O}_2\) Reaction Kinetics

Product mass spectra for the reactions of \(m/z\) 109 ions with background \(\text{O}_2\) \(([\text{O}_2] = 6.4 \pm 0.4 \times 10^9 \text{ molecules cm}^{-3}\)) and increased \(\text{O}_2\) concentrations \(([\text{O}_2] = 1.6 - 2.2 \times 10^{11} \text{ molecules cm}^{-3}\)) were recorded as a function of reaction time. The normalised integrated intensity for a selected mass-to-charge range \((1 - 2 \text{ Th})\) was plotted against reaction time \((0.030 \text{ to } 10000 \text{ ms})\) to produce kinetic curves that describe decay of
Chapter 5. Distonic and Neutral \(o\)-Hydroxyphenyl Radical + \(O_2\)

\(m/z\) 109 ion signal intensity due to reactions with \(O_2\).

A single exponential decay (Equation 5.1) was satisfactorily fitted to the experimental data, in accord with pseudo-first order kinetic behaviour. Representative kinetic curves for \(m/z\) 109 and 124 ions are provided in Figure 5.5 with fitted data and residuals from Equation 5.1 for \(m/z\) 109 signal decay. The \(k_{1st}\) values for \(m/z\) 109 signal decay and \(m/z\) 124 signal growth are in agreement (e.g., in Figure 5.5a, 0.19 ± 0.02 s\(^{-1}\) compared to 0.18 ± 0.01 s\(^{-1}\) within 2\(\sigma\)) and the \(m/z\) 124 intensity is well matched to the \(m/z\) 109 signal decay. This indicates that \(m/z\) 124 ions are the main reaction product from depletion of \(m/z\) 109 ions. As shown in Figure 5.5b, at increased \(O_2\) concentrations the \(m/z\) 109 ion signal intensity ultimately approaches a constant value of ca. 10% at 1000 ms and remains constant up to a reaction time limit of 10000 ms. This indicates the presence of an unreactive isomer (or isomers) and is accounted for by the constant offset included in Equation 5.1.

Additional experiments that compare the oxidation kinetics of the ammonium-tagged \(o\)-hydroxyphenyl and \(o\)-methylphenyl radical cations along with trimethylammonium-tagged analogues are now described. Sample kinetic plots are provided in Figure 5.15 (Section 5.7) for oxidation of 5-ammonium-2-methylphenyl radical cations (\(m/z\) 107) and in Figure 5.16 (Section 5.7) for 5-(\(N,N,N\)-trimethylammonium)-2-hydroxyphenyl radical cations (\(m/z\) 151). For reactions of 5-ammonium-2-methylphenyl radical cations (\(m/z\) 107) the non-zero horizontal offset (shown in Figure 5.15b, Section 5.7) is ca. 40% of the isolated \(m/z\) 107 ion population. Interestingly, \(k_{1st}\) values for 5-ammonium-2-methylphenyl radical (\(m/z\) 107) and 5-ammonium-2-hydroxyphenyl radical (\(m/z\) 109) signal decay are separable with 2\(\sigma\) uncertainty, where the \(k_{1st}\) for the 5-ammonium-2-hydroxyphenyl radical cations is reproducibly greater by ca. 15%. In the case of trimethylammonium-tagged \(o\)-hydroxyphenyl radical + \(O_2\) reactions, the \(m/z\) 151 ion population can be completely depleted by \(O_2\) reaction, suggesting that a pure population of trimethylammonium-tagged \(o\)-hydroxyphenyl radicals are formed from PD of the precursor. This observation is consistent with our previous investigation of trimethylammonium-tagged \(o\)-methylphenyl + \(O_2\) reaction kinetics\(^{17}\) and may be attributed to the greater number of internal degrees of freedom from the trimethylammonium substituent thus reducing the propensity for isomerisation.

Second-order rate coefficients (\(k_{2nd}\), cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) and reaction efficiencies (\(\Phi\%\)) derived from fitted pseudo-first order rate coefficients (\(k_{1st}\)) are reported in Table 5.2. Collision frequencies were calculated using the Langevin collision model.\(^{39}\) Kinetic measurements were conducted at background \(O_2\) ([\(O_2\]) = 6.4 ± 0.4 \(\times\) 10\(^9\) molecule cm\(^{-3}\)) and increased \(O_2\) concentrations ([\(O_2\]) = 1.6–2.2 \(\times\) 10\(^{11}\) molecule cm\(^{-3}\)). Repeated kinetic measurements provided consistent results and statistical uncertainties from fitting \(k_{1st}\) were typically 2\(\sigma\) ≤ 10\%. These results indicate stable
Chapter 5. Distonic and Neutral o-Hydroxylphenyl Radical + O₂

absolute O₂ concentrations within the ion trap as indicated by the linear relationship between \( k_{1at} \) and \([O₂]\) (Figure 5.17, Section 5.7). However, the uncertainty in the ion-trap pressure ultimately results in an upper limit of 50% uncertainty in the trap \([O₂]\), and consequently, a 50% uncertainty for the reported second-order rate coefficients and reaction efficiencies in Table 5.2.

Reaction efficiencies for all species reported in Table 5.2 are all approximately equal to 5%, similar to reported reaction efficiencies for neutral phenyl radicals and a range of positively charged distonic phenyl radical ions, including trimethyl-ammonium and pyridinium-tagged phenyl radicals, and distonic o-methylphenyl radicals. For the 5-ammonium-2-hydroxyphenyl + O₂ reaction mechanism discussed further below, proximity of the ortho-OH-substituent to the peroxy radical site in the o-hydroxyphenylperoxyl radical provides a notably low-energy reaction pathway (refer to Figure 5.6) that competes with dissociation of the peroxy radical intermediate toward separated reactants, however, it does not appear to significantly affect measured reaction efficiencies compared to the other values reported in Table 5.2 and for the phenyl-type radical + O₂ reactions cited above. This moderate reaction efficiency of \(~5\%\), consistent for a range of phenyl-type radicals, indicates that the rate of reaction is not controlled by the microcanonical rate for forward dissociation pathways. Instead, it may result from an entropic bottleneck after formation of the non-covalent complex between the phenyl radical and O₂ (Ref. 67–69 that reflects reaction flux back to the free reactants. More experiments and insights are required to address this question.

5.4.3 Reaction Mechanism

5.4.3.1 o-Hydroxyphenyl + O₂ → o-BQ + OH

To assist in rationalising the experimental data, enthalpies of key reaction intermediates and transition states were calculated for the neutral and ammonium-tagged o-hydroxyphenyl + O₂ systems using the G3X-K method. The potential energy schematic in Figure 5.6 shows O₂ addition, 1,5-H-transfer and subsequent OH elimination to produce the neutral (scheme shown in black) and charge-tagged o-BQ (shown in blue). Potential energy schemes for other possible reaction processes, including those involving the hydroxyl-substituted oxepinoyl radical intermediate, are also discussed below and provided in the Section 5.7 (Figure 5.8 and Figure 5.20–5.23).

Addition of O₂ to the neutral o-hydroxyphenyl radical produces the o-hydroxyphenylperoxyl radical species (N2) that is 49.0 kcal mol⁻¹ below the energy of separated reactants (N1), as shown in Figure 5.6. Close proximity of the OH substituent to the peroxy radical site in the o-hydroxyphenylperoxyl radical (N2) al-
Table 5.2. Second-order rate coefficients \(k_{2nd} \text{, cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and reaction efficiencies \(\Phi\%\) for reactions of PD generated distonic radical cations with \(O_2\) (molecule cm\(^{-3}\)). Uncertainties are an estimated upper limit of 50% in second-order rate coefficients and reaction efficiencies. \(O_2\) collision frequencies calculated using the Langevin collision model.\(^{39}\)

<table>
<thead>
<tr>
<th>Distonic radical</th>
<th>([O_2]) (molecule cm(^{-3}))</th>
<th>(k_{2nd}) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>Collision frequency (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>(\Phi%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-Ammonium-2-hydroxyphenyl</td>
<td>Low [10(^9)]</td>
<td>2.9 \times 10(^{-11})</td>
<td>5.9 \times 10(^{-10})</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>High [10(^{11})]</td>
<td>3.2 \times 10(^{-11})</td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td>5-Ammonium-2-methylphenyl</td>
<td>Low [10(^9)]</td>
<td>2.6 \times 10(^{-11})</td>
<td>5.9 \times 10(^{-10})</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>High [10(^{11})]</td>
<td>2.6 \times 10(^{-11})</td>
<td></td>
<td>4.4</td>
</tr>
<tr>
<td>5-((N,N,N)-Trimethylammonium)-2-hydroxyphenyl</td>
<td>6.6 \times 10(^9)</td>
<td>2.5 \times 10(^{-11})</td>
<td>5.7 \times 10(^{-10})</td>
<td>4.4</td>
</tr>
<tr>
<td>5-((N,N,N)-Trimethylammonium)-2-methylphenyl(^a)</td>
<td>8.5 \times 10(^9)</td>
<td>2.6 \times 10(^{-11})</td>
<td></td>
<td>4.5</td>
</tr>
</tbody>
</table>

\(^a\)Rate coefficients reported in Ref. 17. Ions of \(m/z\) 149 were generated by PD of the 3-bromo-\(N,N,N\)-trimethylbenzenaminium cation.
Figure 5.6. Potential energy schematic depicting the peroxy → hydroperoxy radical isomerisation and subsequent OH elimination for both neutral (black) and ammonium-tagged (blue) \( o \)-hydroxyphenyl + \( O_2 \). G3X-K 0 K enthalpies are provided in kcal mol\(^{-1}\) relative to the respective \( o \)-hydroxyphenyl + \( O_2 \) reactants.
allows for a 1,5-H shift \textit{via} TS N2 $\rightarrow$ N3 with a small 1.7 kcal mol$^{-1}$ barrier to the \textit{o}-hydroperoxyphenoxyl radical (N3). Elimination of OH from the hydroperoxyl group in N3 \textit{via} TS N3 $\rightarrow$ N4 (11.5 kcal mol$^{-1}$ barrier) results in \textit{o}-BQ + OH with a reaction exothermicity of 51.9 kcal mol$^{-1}$. Comparing this to the charge-tagged case, the \textit{o}-hydroxyphenylperoxyl radical analogue (C2) is 44.8 kcal mol$^{-1}$ below the energy of the separated reactants (C1). The barrier to the 1,5-H shift in C2 and subsequent OH loss from C3 is 27.4 kcal mol$^{-1}$ below reactants and the resulting 4-ammonium-2-benzoquinone + OH (C4) products are formed with an exothermicity of 38.9 kcal mol$^{-1}$ (13.0 kcal mol$^{-1}$ less than in the neutral case). As shown by Figure 5.18 in the Section 5.7, the reaction enthalpy for charge-tagged \textit{o}-BQ + OH is reduced by separation of the charge tag and ring structure \textit{via} inclusion of methylene linkages, indicating that differences shown in Figure 5.6 are (in part) due to a through-space charge effect. Still, intermediates and transition states for both cases shown in Figure 5.6 are well below the energy of the reactants and, therefore, OH-elimination is expected to be facile. This mechanism is consistent with the appearance of \textit{o}-BQ (m/z 108) in neutral flow-tube experiments and ammonium-tagged \textit{o}-BQ (m/z 124) in the distonic radical cation experiments.

### 5.4.3.2 \textit{o}-BQ $\rightarrow$ CPO + CO

The appearance of signal at m/z 80 in the ALS neutral experiments is rationalised by prompt CO elimination from \textit{o}-BQ (m/z 108)$^{21}$ and is supported by distonic radical cation experiments (Figure 5.4c and d). The potential energy schematic for CO elimination from \textit{o}-BQ is provided in Figure 5.7 and Figure 5.19 (Section 5.7) for the charge-tagged case, with reaction enthalpies reported relative to the \textit{o}-BQ species. Shown in Figure 5.7, the pathway \textit{via} N7 has the lower barrier of 41.9 kcal mol$^{-1}$ (-10.0 kcal mol$^{-1}$ relative to \textit{o}-hydroxyphenyl + O$_2$). An alternate mechanism \textit{via} TS N6 $\rightarrow$ N8 (Ref. 70) has a higher 43.5 kcal mol$^{-1}$ barrier. A transition state for concerted CO loss was located with a 62.6 kcal mol$^{-1}$ barrier, 10.7 kcal mol$^{-1}$ in excess of the \textit{o}-hydroxyphenyl + O$_2$ entrance channel (not shown). The CPO + CO + OH product is 45.5 kcal mol$^{-1}$ below the energy of the \textit{o}-hydroxyphenyl + O$_2$ reactants.

Figure 5.19 (Section 5.7) shows the potential energy scheme for CO elimination from ammonium-tagged \textit{o}-BQ. The mechanisms shown in Figure 5.19a (Section 5.7) feature barriers that exceed the entrance channel (5-ammonium-2-hydroxyphenyl + O$_2$) by 2.8 kcal mol$^{-1}$ \textit{via} TS C6a $\rightarrow$ C8 and 6.7 kcal mol$^{-1}$ \textit{via} TS C6b $\rightarrow$ C8. In Figure 5.19b (Section 5.7), however, the highest barrier is 35.0 kcal mol$^{-1}$ \textit{via} TS C4 $\rightarrow$ C5 (3.8 kcal mol$^{-1}$ below 5-ammonium-2-hydroxyphenyl + O$_2$). The decomposition reactions shown in Figure 5.19 (Section 5.7) are less likely to proceed due to the reduced exothermicity of the charge-tagged \textit{o}-BQ + OH and barriers to
Figure 5.7. Potential energy schematic for CO loss from o-BQ (N4) along the singlet C₆H₄O₂ surface. G3X-K 0 K enthalpies are provided in kcal mol⁻¹ relative to o-BQ.
decarbonylation approaching the entrance channel limit. Collisional activation of the charge-tagged \( o \)-BQ intermediate should provide the activation energy required to generate charge-tagged CPO + CO, consistent with a loss of 28 Da from CID of \( m/z \) 124 ions shown in Figure 5.4c. The appearance of a small \( m/z \) 96 ion peak in Figure 5.4b (<1%), prior to isolation of the \( m/z \) 124 ion, may result from decomposition of the high-energy portion of the nascent \( m/z \) 124 ion ensemble. It is likely that further exploration of \( o \)-BQ decomposition is required to reveal additional competitive pathways resulting in CPO + CO.

### 5.4.3.3 OH-Substituted Phenoxy and Oxepinoxyl Mechanisms

In the case of unsubstituted phenyl radical oxidation, the direct phenoxy + O(\(^3\)P) channel and the indirect oxepinoxyl radical decomposition pathways can lead to CHO, CO, O, and H losses to produce CPO and \( o \)-BQ.\(^{61,62,64,71-73}\) To explore the possible role of phenoxy and oxepinoxyl pathways here, analogous hydroxy-substituted intermediates and transition states were located along the neutral \( o \)-hydroxyphenyl and 4-ammonium-2-hydroxyphenyl radical oxidation schemes. Potential energy schematics are provided in the Section 5.7 (Figure 5.8 and Figure 5.20–5.23). The O(\(^3\)P) loss from hydroxyphenylperoxyl has a 30.6 kcal mol\(^{-1}\) barrier and subsequent decomposition of the \( o \)-hydroxyphenoxyl radical (\( N_{40} \), Figure 5.20, Section 5.7) to produce CPO occurs via stationary points that exceed \( o \)-hydroxyphenyl + O\(_2\) by as much as 61.1 kcal mol\(^{-1}\) (\( TS_{N43} \rightarrow N_{44} \)). In the charge-tagged case, O(\(^3\)P) loss occurs with a 32.0 kcal mol\(^{-1}\) barrier (inset Figure 5.20, Section 5.7) and the overall barrier to 3-ammonium-cyclopentadienone + H + CO + O(\(^3\)P) is 69.9 kcal mol\(^{-1}\) above the reactants. These high reaction barriers are unlikely to compete with lower energy pathways. As previously mentioned in Section 5.4.1 above, small quantities of \( o \)-hydroxyphenoxyl radicals are likely generated and later react by H-atom addition to produce \( o \)-catechol (\( C_6H_4OHOH, m/z \) 110). These data together indicate that generation of CPO from \( o \)-hydroxyphenoxyl radicals is unlikely.

Rearrangement of \( o \)-hydroxyphenylperoxyl (\( N_2 \)) toward 7-hydroxyoxepinoxyl (\( N_{23} \)) and 6-carboxy-1-oxo-hex-2,4-dienyl radicals (\( N_{21} \)) via dioxirane-hydroxy-cyclohexadienyl intermediates are described in Figure 5.8. The reactions of these intermediates represent plausible unimolecular pathways to both \( m/z \) 80 and 108 ions in the ALS experiments. Reactions toward the 7-hydroxyoxepinoxyl radical proceeds through \( TS_{N2} \rightarrow N_{22} \) 18.1 kcal mol\(^{-1}\) above the barrier to \( o \)-BQ (\( TS_{N3} \rightarrow N_4 \) in Figure 5.6) with an exothermicity of 102.3 kcal mol\(^{-1}\). Formation of the 6-carboxy-1-oxo-hex-2,4-dienyl radical (\( N_{21} \)) occurs via \( TS_{N2} \rightarrow N_{20} \) at 11.6 kcal mol\(^{-1}\) above \( TS_{N3} \rightarrow N_4 \). Reactions of charged-tagged \( o \)-hydroxyphenylperoxyl toward hydroxyoxepinoxyl and 6-carboxyoxohexadienyl, shown in Figure 5.21 (Section 5.7), generally parallel those described by Figure 5.8. The rate limiting
Figure 5.8. Potential energy schematic comparing the OH-\textit{cis} and OH-\textit{trans} reaction pathways to the hydroxyoxepinoxyl and 6-carboxy-1-oxo-hex-2,4-dienyl intermediates along the neutral \textit{o}-hydroxyphenyl + O$_2$ reaction surface. The barrier to TS N3 $\rightarrow$ N4 (leading to \textit{o}-BQ) and reaction enthalpy for the \textit{o}-hydroxyphenoxy radical (N40) are included for comparison. G3X-K energies are reported in kcal mol$^{-1}$ relative to \textit{o}-hydroxyphenyl + O$_2$. 
steps toward the two hydroxyoxepinoxyl (TS3c) and carboxyoxohexadienyl radicals (TS1c) are 22.2 and 5.1 kcal mol\(^{-1}\), respectively, above the barrier to charge-tagged \(o\)-BQ (TS C3 \(\rightarrow\) C4, Figure 5.6).

In the case where either hydroxyoxepinoxyl or carboxyoxohexadienyl radicals are produced, their decomposition could possibly follow pathways described by Figure 5.22 and 5.23 (Section 5.7). Likely products, by analogy to phenyl radical oxidation,\(^{16,63}\) include \(o\)-BQ + OH, CPO + HOCO, 3-hydroxy-2-benzoquinone + H, and 2-hydroxy-cyclopentadienone + HCO with barriers far below the reactants. The absence of peaks at \(m/z\) 96 and 124 within ALS experimental results (Figure 5.1) and the high barriers to hydroxyoxepinoxyl and carboxyoxohexadienyl intermediates indicate that at most only a small fraction of the reaction flux follows these channels. Furthermore, preliminary RRKM modelling of the \(o\)-hydroxyphenylperoxyl radical (N2) decomposition, utilizing MultiWell,\(^{45–47}\) indicates H-migration and OH-loss to form \(o\)-BQ (N4, shown in Figure 5.6) comprehensively outcompetes the pathways toward hydroxyoxepinoxyl and carboxyoxohexadienyl radicals (shown in Figure 5.8, N2 toward TS1n and TS4n). The sums of states for salient transition states and corresponding rate coefficients are provided in Table 5.4 (Section 5.7). The oxepinoxyl pathways (via TS1n and TS4n) experience comparatively tight transition states with state counts several orders of magnitude lower than any other along the \(o\)-BQ pathway. This is in accord with our previous statement that the prevailing mechanism is formation of \(o\)-BQ via an \(o\)-hydroxyperoxylphenoxyl radical intermediate (N3). The appearance of \(m/z\) 80 in ALS experiments is explained by \(o\)-BQ decomposition, supported by distonic experiments that show connectivity between the analogous charge-tagged species.

5.5 Conclusions

Product detection experiments conducted at the ALS synchrotron reveal that the \(o\)-hydroxyphenyl + O\(_2\) reaction produces two major products detected at \(m/z\) 80 and 108 that are consistent with CPO and \(o\)-BQ. We conclude that CPO forms as a secondary product from prompt decomposition of \(o\)-BQ and dissociative ionisation of \(o\)-BQ leads to some enhancement of the \(m/z\) 80 signal at photoionisation energies \(\geq 9.8\) eV. There are indications of a minor \(o\)-hydroxyphenoxyl + O(\(^{3}\)P) pathway in the ALS experiments. To establish connections between the major reaction products, distonic radical analogue ammonium-tagged \(o\)-hydroxyphenyl + O\(_2\) reactions were studied using ion-trap mass spectrometry. Reactions of the 5-ammonium-2-hydroxyphenyl radical cation (\(m/z\) 109) with O\(_2\) produced product ions consistent with ammonium-tagged \(o\)-BQ produced via O\(_2\) addition, H-atom migration and subsequent OH loss. CID of the \(m/z\) 124 ions yielded a species
assigned ammonium-tagged CPO produced by CO loss.

Second order rate coefficients ($k_{2nd}$) for 5-ammonium-2-hydroxyphenyl (m/z 109) + O$_2$ were measured to have a 5% reaction efficiency. Additional kinetic measurements for O$_2$ reactions with PD generated 5-ammonium-2-methylphenyl and 5-(N,N,N-trimethylammonium)-2-hydroxyphenyl radical cations and a previous investigation of trimethylammonium-tagged $o$-methylphenyl + O$_2$ reaction kinetics$^{17}$ demonstrate for this small set that the identity of the charged-tag and ortho-substituent does not significantly affect the reaction efficiency (ca. 5%).

Quantum chemical calculations are in accord with our experimental observations, where a 1,5-H shift in the $o$-hydroxyphenylperoxyl adduct and subsequent OH elimination is the minimum energy pathway for both $o$-hydroxyphenyl + O$_2$ and the ammonium-tagged counterpart. Decomposition of the $o$-BQ toward CPO does encounter large barriers. However, the indication from preliminary kinetic modelling is that production of $o$-BQ is the dominant unimolecular pathway.

The prevailing mechanism for decomposition of the $o$-hydroxyphenylperoxyl radical produced by O$_2$ addition is via 1,5-H migration and OH loss from the hydroperoxynaphenoxyl radical intermediate to produce $o$-BQ. Its decomposition via ring opening, cyclisation, and CO elimination is the likely pathway to CPO. These proposed pathways to $o$-BQ and CPO serve as source of OH and CO species in reactive environments. OH radicals could contribute to chain propagation reactions and affect the hydrocarbon radical pool in low-temperature combustion ($<1100$ K).$^{74-76}$ Harmful CO emissions from decarboxylation and other sources (e.g. fuel lean low-temperature combustion)$^{77-79}$ are implicated in photochemical cycle producing toxic tropospheric ozone.$^{80}$

5.6 Acknowledgements

The authors are grateful for the financial support of the Australian Research Council through the Discovery programs (SJB: DP140101237; AJT and GdS: DP 130100862; GdS: FT130101304) and Centre of Excellence For Free Radical Chemistry and Biotechnology (CE0561607). The authors also acknowledge the generous allocation of computing resources by the NCI National Facility (Canberra, Australia) under Merit Allocation Scheme. BBK is supported by the National Aeronautics and Space Administration (NNH13AV43I). JDS, DLO, and CAT are supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U.S. Department of Energy. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facil-
ity at the Lawrence Berkeley National Laboratory. MBP would like to acknowledge Dr. Phillip J. Tracey for discussions on distonic radical cation experiments.

5.7 Supporting Information

5.7.1 Synthesis of 4-Hydroxy-3-iodo-N,N,N-trimethylbenzenaminium Iodide

![Chemical Reaction Diagram]

Scheme 5.3

1) 2,6-Diiodo-4-nitropheno1. (Method from Ref. 81)
To a stirred solution of sodiumchlorite trihydrate (11.6 g, 80 mmol) and NaI (23.9 g, 160 mmol) in water (500 mL) was added 4-nitropheno1 (5.56 g, 40 mmol) in methanol (500 mL) followed by HCl (11.7 M, 100 mL). After 4 hours the reaction mixture was poured into water (1000 mL) and then extracted with ethyl acetate until the yellow colouration was mostly gone (3–4 × 200 mL). The organics were washed with a saturated aqueous sodium chloride (100 mL) containing sodium thiosulfate (1.0 g), then dried over sodium sulfate. The volatiles were removed on the rotary evaporator (to 30 mBar) to give a yellow-brown solid, 14.1 g, 90% yield. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 8.65\) (s, 2H); The spectral characteristics were in accordance with those reported in the literature.

2) 4-Amino-2-Iodopheno1. (Method from Ref. 82)
To a vigorously-stirred suspension of 2,6-diiodo-4-nitropheno1 (13.0 g, 33.3 mmol) in NaOH\(_{aq}\) (25%, 250 mL), was added sodium dithionite (187 g, 1.07 mol) and the reaction mixture stirred and heated to 75 °C, at which temperature the yellow colouration quickly dissipated. The suspension was then cooled to ambient temperature and quenched with water (500 mL). Repeated extraction of the aqueous phase with ethyl acetate (5 × 250 mL) gave an organic phase that was washed with water (3 × 200 mL) then saturated aqueous sodium chloride (100 mL) and dried over sodium sulfate. The volatiles were removed on the rotary evaporator (to 30 mBar) to give a viscous brown oil. The viscous brown oil was purified by column chromatography on SiO\(_2\) (Grace), with hexanes/ethyl acetate (4:1; careful elution was required to ensure separation from 2,6-diiodo-4-aminopheno1, which was a significant by-product), yielding the title compound as a beige solid (4.31 g). \(^1\)H-NMR
(400 MHz, d$_6$-DMSO): $\delta$ 9.08 (s, 1H), 6.91 (d, $J = 2.4$ Hz, 1H), 6.57 (d, $J = 8.3$ Hz, 1H), 6.42 (dd, $J = 8.3$, 2.4 Hz, 1H), 4.59 (broad s, 2H). The spectral characteristics were in accordance with those reported in the literature.

3) 4-Hydroxy-3-iodo-$N,N,N$-trimethylbenzenaminium iodide (Adapted from the Ref. 27)

To a reaction vial was added 4-amino-2-iodophenol (141 mg, 0.60 mmol), anhydrous K$_2$CO$_3$ (85 mg, 0.62 mmol) and dry MeOH (5.0 mL). Methyl iodide (370 $\mu$L, 6.0 mmol) was added and the vial capped and stirred at 50°C for 12 hours. The solvent was then removed on the rotary evaporator (to 30 mBar) to yield a dark brown sticky solid. The crude material was dissolved in hot acetonitrile, filtered, and then precipitated by addition of a greater volume of diethyl ether. The precipitate was filtered, washed with a minimal amount of diethyl ether and air dried to yield a dark-grey powder. This material contained a small amount of the anisole derivative, which could be removed by chromatography of this crude material (silica gel, MeOH) to give a beige powder; 141 mg (0.35 mmol, 58% yield). $^1$H-NMR (400 MHz, D$_2$O): $\delta$ 8.15 (d, $J = 1.2$ Hz, 1H), 7.54 (d, $J = 9.2$ Hz, 1H), 6.88 (dd, $J = 9.2$, 1.2 Hz, 1H), 3.45 (s, 1H), 3.43 (s, 9H); $^{13}$C-NMR (400 MHz, D$_2$O): $\delta$ 157.0 (C), 139.3 (C), 130.7 (CH), 121.3 (CH), 115.1 (CH), 83.9 (C), 57.1 (CH$_3$); LRMS (ESI$^+$) $m/z =$ 278 [$M$ - I]$^+$; HRMS (ESI$^+$) $m/z$ for C$_9$H$_{13}$INO$^+$ [$M$ - I]$^+$ Calculated: 278.0036; Observed: 278.0032.

5.7.2 Supporting Information for Synchrotron Photoionisation Mass Spectrometry: $o$-Hydroxyphenyl + O$_2$

The multiplexed photoionisation mass spectrometer is comprised of a reactor flow tube, quasi-continuous vacuum-ultraviolet (VUV) synchrotron light source and an orthogonal time-of-flight mass spectrometer. The $o$-hydroxyphenyl + O$_2$ radical reaction was initiated within the flow tube by photolysis of $o$-bromophenol in the presence of O$_2$ using a pulsed KrF excimer laser (248 nm) operating at 4 Hz with a fluence of $\sim$50 mJ/cm$^2$. Gas flow velocities within the reactor were as follows: 10.1 m s$^{-1}$ at 373 K, 13.5 m s$^{-1}$ at 500 K, and 16.2 m s$^{-1}$ at 600 K. And, the total gas flow densities were: $1.0 \times 10^{17}$ molecule cm$^{-3}$ at 373 K, $7.7 \times 10^{16}$ molecule cm$^{-3}$ at 500 K, and $6.4 \times 10^{16}$ molecule cm$^{-3}$ at 600 K.

The kinetic traces in Figure 5.12 show the ion signal rapidly rise following the photolysis laser pulse at ca. 20 ms and thus, demonstrates the laser dependency of radical generation. As the temperature of the reactor is raised, because the pressure and gas delivery parameters are held constant, the volumetric flow rate increases while the number density decreases. This manifests in faster reactor pump-out times as indicated by ion signals rapidly dropping at about 50 ms at 500 K (Figure 5.12).
Figure 5.9. Photoionisation spectra integrated 0–15 ms after 248 nm photolysis for (a) m/z 80 and (b) m/z 108 from the o-hydroxyphenyl + O$_2$ reaction at 500 K. Each spectrum is an average of three PI spectra and the 2σ statistical uncertainty is represented by vertical error bars. Reference PI spectra are provided in (a) for CPO from Ref. 56 and Ref. 57 (873 K).

Figure 5.10. Photoionisation spectra integrated 0–13 ms after 248 nm photolysis for (a) m/z 80 and (b) m/z 108 from the o-hydroxyphenyl + O$_2$ reaction at 600 K. Each spectrum is an average of two PI spectra and the 2σ statistical uncertainty is represented by vertical error bars. Reference PI spectra are provided in (a) for CPO from Ref. 56 and Ref. 57 (873 K).
Table 5.3. Calculated CBS-QB3 adiabatic ionisation energies for linear C$_5$H$_4$O isomers ($m/z$ 80). None of the C$_5$H$_4$O isomers listed have a calculated adiabatic ionisation energy of 9.8 eV. G3XK enthalpies ($\Delta H_f$) provided in kcal mol$^{-1}$ with zero-point energy.

<table>
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<tr>
<th>C$_5$H$_4$O isomer</th>
<th>Adiabatic Ionisation Energies CBS-QB3 (eV)</th>
<th>Literature Ionisation Energies (eV)</th>
<th>Relative $\Delta H_f$ (kcal mol$^{-1}$)</th>
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</thead>
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<td>Cyclopentadienone (CPO)</td>
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<td></td>
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<tr>
<td>penta-1,4-diyn-3-ol</td>
<td>10.4</td>
<td>60.2</td>
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<tr>
<td>penta-1,2-dien-4-yn-3-ol</td>
<td>8.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pentatetraen-1-ol</td>
<td>8.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pent-2-en-4-ynal</td>
<td>10.0</td>
<td>27.7</td>
<td></td>
</tr>
<tr>
<td>pent-1-en-4-yn-3-one</td>
<td>10.1</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td>penta-1,2,4-trien-1-one</td>
<td>8.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>penta-1,3,4-trien-1-one (allenylketene)</td>
<td>8.2</td>
<td>8.12$^{83}$</td>
<td></td>
</tr>
<tr>
<td>pent-1-en-3-yn-1-one (propynylketene)</td>
<td>8.4</td>
<td>8.25$^{83}$</td>
<td></td>
</tr>
<tr>
<td>pent-1-en-4-yn-1-one</td>
<td>9.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[\begin{align*}
\text{penta-1,4-diyn-3-ol} & \quad \text{penta-1,2-dien-4-yn-3-ol} & \quad \text{pentatetraen-1-ol} \\
\text{pent-2-en-4-ynal} & \quad \text{pent-1-en-4-yn-3-one} & \quad \text{penta-1,2,4-trien-1-one} \\
\text{penta-1,3,4-trien-1-one (allenylketene)} & \quad \text{pent-1-en-3-yn-1-one (propynylketene)} & \quad \text{pent-1-en-4-yn-1-one}
\end{align*}\]
Figure 5.11. Product mass spectra for $o$-hydroxyphenyl radical + $O_2$ reaction integrated from 9.4 to 9.75 eV (left panel: a, b, and c) and 9.85 to 10 eV (right: d, e, and f) at 373 K (a and d) 0–20 ms, 500 K (b and e) 0–15 ms, and 600 K (c and f) 0–13 ms after photolysis.
Figure 5.12. Kinetic traces of the ion signal at $m/z$ 80 (red with empty circles) and $m/z$ 108 (black) for the $o$-hydroxyphenyl + O$_2$ reaction integrated (a) from 9.4 to 9.75 eV and (b) from 9.85 to 10 eV 500 K. Gas flow velocity was 13.5 m s$^{-1}$ and the total gas flow density was $7.7 \times 10^{16}$ molecule cm$^{-3}$ at 500 K.

Figure 5.13. Kinetic traces of the ion signal at $m/z$ 108 (red) and $m/z$ 110 (black) from the $o$-hydroxyphenyl + O$_2$ reaction integrated 9.0 to 10.0 eV at 600 K. The gas flow velocity was 16.2 m s$^{-1}$ and the total gas flow density was $6.4 \times 10^{16}$ molecule cm$^{-3}$ at 600 K.
5.7.3 Supporting Information for Ion-Trap Mass Spectrometry: Distonic o-Hydroxyphenyl + O₂

Radical precursor ions were generated by infusing methanolic solutions of ca. 10 μM of 3-bromo-4-methylaniline ([M + H]⁺ at m/z 186 and 188) or 3-iodo-4-hydroxy-N,N,N-trimethylbenzenaminium iodide ([M + H]⁺ at m/z 278) into the electrospray ion source at 5 μL min⁻¹. The resulting cations were mass-selected using an isolation window of 5–6 Th for brominated, and 1–2 Th for the iodinated cations with a q-factor of 0.250.

![Figure 5.14](image)

**Figure 5.14.** Mass spectrum (a) is produced by PD of 3-bromo-4-methylanilinium (m/z 186 and 188) and isolation of the resulting m/z 107 ion in the presence of background O₂ ([O₂] = 6.4 ± 0.4 × 10⁹ molecules cm⁻³) for 2000 ms and (b) by PD of 3-iodo-4-hydroxy-N,N,N-trimethylbenzenaminium cations (m/z 278) and isolation of the resulting m/z 151 ion in background O₂ ([O₂] = 6.6 ± 0.3 × 10⁹ molecules cm⁻³) for 2000 ms.

Equation 5.1 was fitted to experimental data (e.g. Figure 5.15 and 5.16) for decay of m/z 107 and 151 radical cations by reactions with O₂. Experimental data was found to be consistent with pseudo-first order kinetic behaviour. Residuals from the fitting of Equation 5.1 also are provided in Figure 5.13 and 5.14 above the respective kinetic plots. The second-order rate coefficient (k₂nd) for m/z 151 and 107 radical cation decay are provided in Table 5.2 in the main document.
Equation 5.1 is repeated here for the reader

\[ y = A_0 \exp(-k_{1st}t) + \text{constant} \]  

(5.1)

where \( A_0 \) is the pre-exponential factor, \( k_{1st} \) is the exponential decay coefficient, and the constant term presents the vertical-offset.

**Figure 5.15.** Example kinetic curves for \( m/z \) 107 (solid green circles), from PD of 3-bromo-4-methylbenzenamination cation, from reactions with (a) background \( \text{O}_2 \) \( (6.4 \times 10^9 \text{ molecules cm}^{-3}) \) and (b) increased \( \text{O}_2 \) \( (1.9 \times 10^{11} \text{ molecules cm}^{-3}) \). Residual plots from the fitting of Equation 5.1 is provided above.
Chapter 5. Distonic and Neutral o-Hydroxylphenyl Radical + O₂

Figure 5.16. An example kinetic curves for m/z 151 (solid purple circles), from PD of 3-iodo-4-hydroxy-\(N,N,N\)-trimethylbenzenaminium cations, reactions with background O₂ \(6.6 \times 10^9\) cm\(^{-3}\). A residual plot from the fitting of Equation 5.1 is provided above.

Figure 5.17. A plot of the measured pseudo-first order rate coefficients \(k_{1st}\) versus measured [O₂] for m/z 109 ions (solid blue diamonds), from PD of 3-bromo-4-hydroxybenzenaminium cations, and m/z 107 (green circles), from PD of 3-bromo-4-methylbenzenaminium cations. The error bars in \(k_{1st}\) are 2σ and the linear regression uses 50% uncertainty for [O₂]. The slope of the fitted lines for m/z 109 (solid) and m/z 107 (dashed) are in accord with reported \(k_{2nd}\) in Table 5.2 in the main document.
5.7.4 Supporting Information for Computational Chemistry and Reaction Mechanism

To determine whether a through-space effect from the positively charged ammonium could account for the 13.0 kcal mol\(^{-1}\) difference in reaction enthalpy shown in Figure 5.6 (main document) we employed an approach undertaken by Grob et al.\(^{84}\) and used again more recently\(^{85,86}\) for understanding the effect of a change tag on a property of interest. In this investigation the reaction enthalpies for a series of \(\text{H}_3\text{N}^+-(\text{CH}_2)_n\)-tagged \(\text{o-hydroxyperoxyl} \rightarrow \text{o-BQ} + \text{OH}\) reactions were calculated using the M06-2X/6-311++G(d,p) method, where the number methylene links \((n = 0 \text{ to } 7)\) was increased in a zig-zag configuration to progressively separate the ammonium tags from the ring structures. The dihedral angle between the \(\text{H}_3\text{N}^+-(\text{CH}_2)_n\) substituent and the \(\text{o-hydroxyphenylperoxyl}\), and \(\text{o-BQ}\) ring structures was maintain at \(\sim 90^\circ\). Charge separation \((r)\) was measured between the ammonium-nitrogen and hydroxy-oxygen of the respective \(\text{H}_3\text{N}^+-(\text{CH}_2)_n\)-tagged \(\text{o-hydroxyphenylperoxyl}\) radical. The reaction enthalpies plotted in Figure 5.18 decrease linearly with \(1/r\) and approach the reaction enthalpy for neutral \(\text{o-hydroxyperoxyl} \rightarrow \text{o-BQ}\) (-0.9 kcal mol\(^{-1}\)), as can be expected for though-space charge effects. The reported 0 K enthalpies in Figure 5.18 were calculated using the M06-2X/6-311++G(d,p) method and include the zero-point energy correction.

The \(\text{N}4 \rightarrow \text{N}5 \rightarrow \text{N}6 \rightarrow \text{N}8\) CO elimination mechanism in Figure 5.7 (main document) was applied to the ammonium-tagged \(\text{o-BQ}\) decomposition as \(\text{C}4 \rightarrow \text{C}5\) \(\rightarrow \text{C}6\text{a} \rightarrow \text{C}8\) and \(\text{C}4 \rightarrow \text{C}5 \rightarrow \text{C}6\text{b} \rightarrow \text{C}8\) as shown Figure 5.19. These mechanisms feature barriers that exceed the energy of 5-ammonium-2-hydroxyphenyl + \(\text{O}_2\) by 2.8 kcal mol\(^{-1}\) \(\text{via TS C}6\text{a} \rightarrow \text{C}8\) and 6.7 kcal mol\(^{-1}\) \(\text{via TS C}6\text{b} \rightarrow \text{C}8\). When the alternate mechanism in Figure 5.7 \((i.e. \text{via N}7)\) is applied to the distonic system, greater differences between the neutral and distonic systems emerge. A mechanism was found that connects \(\text{via TS C}5 \rightarrow \text{C}7\) without transmitting through the \(\text{C}6\text{a}\) or \(\text{C}6\text{b}\) intermediates. Also, CO may eliminate from the \(\text{C}5\) to produce the ammonium-tagged CPO \((m/z \ 96)\). The reaction barrier for the last two mechanisms is 35.0 kcal mol\(^{-1}\) (3.8 kcal mol\(^{-1}\) below \(5\text{-ammonium-2-hydroxyphenyl} + \text{O}_2\)).

Figure 5.20 shows the formation of the \(\text{o-hydroxyphenoxyl}\) radical \(\text{via O}^{(3}\text{P})\) elimination and subsequent CO loss to generate CPO. Elimination of \(\text{O}^{(3}\text{P})\) from \(\text{o-hydroxyphenylperoxyl}\) requires 30.6 kcal mol\(^{-1}\) to produce OH-\text{cis} \(\text{o-hydroxyphenoxyl}\) and 39.3 kcal mol\(^{-1}\) for OH-\text{trans} \(\text{o-hydroxyphenoxyl}\) radicals \(\text{(a difference of 8.7 kcal mol}^{-1})\). The loss of CO from \(\text{o-hydroxyphenoxyl}\) results in a OH-substituted cyclopentadienyl radical\(^{87}\) that eliminates the hydroxy-H atom to produce CPO.\(^{88}\) The reaction barrier to CPO + H + CO + O\(^{(3}\text{P})\), \text{via o-hydroxyphenoxyl}, exceeds
Chapter 5. Distonic and Neutral \( o \)-Hydroxylphenyl Radical + O\(_2\)

**Figure 5.18.** Reaction enthalpies (0 K) for H\(_3\)N\(^+\)-(CH\(_2\))\(_n\) tagged \( o \)-hydroxyphenylperoxyl (C2) \( \rightarrow \) \( o \)-BQ + OH reduced linearly as a function of 1/r and converged toward that for the corresponding neutral reaction (-0.9 kcal mol\(^{-1}\)). When n = 7, the difference is \( \sim 0.2 \) kcal mol\(^{-1}\). Structures were calculated using the M06-2X/6-311++G(d,p) method and are reported in kcal mol\(^{-1}\) relative to the H\(_3\)N\(^+\)-(CH\(_2\))\(_n\)-C\(_6\)H\(_3\)(OH)OO\(^•\) homologue series.
Figure 5.19. Potential energy schematics for (a) CO elimination mechanism proposed by Skokov et al. (Ref. 70) as applied to the ammonium-tagged o-BQ and (b) additional pathways that also result in tagged CPO + CO. Coloured pathways indicate which of the two carbonyl groups in o-BQ is eliminated: Red for the para-carbonyl and blue for the meta-carbonyl group. G3X-K energies are reported in kcal mol$^{-1}$ relative to 4-ammonium-2-benzoquinone.
the energy of $o$-hydroxophenyl + $O_2$ by 61.1 kcal mol$^{-1}$. Within the corresponding distonic radical ion scheme, reactions leading to OH-$cis$ ammonium-tagged $o$-hydroxophenoxyl proceed with a 32.0 kcal mol$^{-1}$ barrier (7.5 kcal mol$^{-1}$ below the corresponding OH-$trans$ barrier) and with an overall reaction barrier 69.9 kcal mol$^{-1}$ above the distonic $o$-hydroxophenyl + $O_2$ reactants. These high barriers may be surmounted at high temperatures, e.g. in combustion, however, may be prohibitive under the experimental conditions reported here without additional activation.

Figure 5.8 (main document) shows the potential energy schematic for reactions of $o$-hydroxyphenylperoxyl ($N_2$) toward 7-hydroxyoxepinoxy ($N_22$) and 6-carboxy-1-oxo-hex-2,4-dienyl radicals ($N_21$) via dioxirane-hydroxycyclohexadienyl intermediates. Formation of the 6-carboxy-1-oxo-hex-2,4-dienyl radical ($N_21$) is initiated via $TS_{N2} \rightarrow N20$ with a barrier 11.6 kcal mol$^{-1}$ above $TS_{N3} \rightarrow N4$ (Figure 5.6 in the main document). Projection of imaginary frequency normal modes for succeeding $TS_{3n}$ and $TS_{4n}$ reveal another possible first-order saddle point on the reaction surface. The $TS_{2n}$ IRC was calculated and was found to proceed through a 1,4-H atom shift and C-C bond cleavage to produce 6-carboxy-1-oxo-hex-2,4-dienyl with 97.1 kcal mol$^{-1}$ activation.

Reactions toward 7-hydroxyoxepinoxy proceed through the rate limiting $TS_{N2} \rightarrow N22$ with a 27.7 kcal mol$^{-1}$ barrier. This transition state exceeds the rate limiting step toward $o$-BQ by 18.1 kcal mol$^{-1}$ at 0 K. Cleavage of the O-O bond in $N22$ through $TS_{3n}$ is accompanied by O-atom ring insertion ($TS_{4n}$) to produce 7-hydroxyoxepinyl with 102.3 kcal mol$^{-1}$ activation. By analogy to $o$-methyphenyl + $O_2$, both 3-hydroxyoxepinoxy and 7-hydroxyoxepinoxy radicals are expected after bifurcation$^{89}$ of the reaction surface after $TS_{3n}$. However, projection of the imaginary frequency normal mode in $TS_{3n}$ and the subsequent $TS_{4n}$ suggest the presence of a first-order saddle point at $TS_{4n}$ that exceeds $TS_{3n}$ in energy with ZPE correction and not a point for bifurcation.

Reaction processes of the charged-tagged $o$-hydroxyphenylperoxyl toward hydroxyoxepinoxy and 6-carboxyoxohexadienyl radicals in Figure 5.21 generally parallel those described by Figure 5.8 for the neutral reaction scheme. The sequential $TS_{3c}$ (-5.2 kcal mol$^{-1}$) and $TS_{4c}$ (30.7 kcal mol$^{-1}$), succeeding the OH-$trans$ dioxiranyl intermediate ($C_{22}$), represent a bifurcation of the potential energy surface toward the 4-ammonium-7-hydroxyoxepinoxy radical ($C_{23}$) and new 6-ammonium-3-hydroxyoxepinoxy radical ($C_{24}$). In addition, the rate limiting $TS_{3c}$ is 22.2 kcal mol$^{-1}$ above $TS_{C3} \rightarrow C4$ (Figure 5.6). Production of the ammonium-tagged carboxyoxohexadienyl radical is more competitive than the hydroxyoxepinoxy intermediate with the rate limiting $TS_{1c}$ just 5.1 kcal mol$^{-1}$ greater than $TS_{C3} \rightarrow C4$.

Informed by Kirk et al.$^{27}$ the 7-hydroxyoxepinoxy and 3-hydroxyoxepinoxy radicals can possibly decompose to generate $o$-BQ and CPO, including hydroxy-
Figure 5.20. Potential energy schematic for O(3P) and subsequent CO loss from o-hydroxyphenoxy, followed by H-atom elimination to generate the CPO + H + CO + O(3P) product (N44). The corresponding O(3P) loss on the charge-tagged reaction surface is provided as an inset. Energies were calculated using the G3X-K composite method and reported in kcal mol$^{-1}$ relative to the respective o-hydroxyphenyl + O$_2$. 
Figure 5.21. Potential energy schematic comparing the OH-\textit{cis} and OH-\textit{trans} reaction pathways to the ammonium-tagged hydroxyoxepinoxyl and 6-carboxy-1-oxo-hex-2,4-dienyl intermediates along the charge-tagged \textit{o}-hydroxyphenyl + O\textsubscript{2} reaction surface. The reaction enthalpy for the tagged \textit{o}-hydroxyphenoxyl radical (C40) is also included for comparison. G3X-K energies are reported in kcal mol\textsuperscript{-1} relative to 5-ammonium-2-hydroxyphenyl + O\textsubscript{2}. 
substituted equivalents \textit{via} the pathways described in Figure 5.22 and Figure 5.23.

In Equation 5.3, $k(E)$ is the rate coefficient for a unimolecular process with the total energy of $E$, which is taken as the energy of the $o$-hydroxyphenyl + $O_2$ reactants. The $N^+(E - E_0)$ term is the sum of states for a transition state with the critical energy of $E_0$ up to the total energy and $\rho(E)$ is the density of states for the reactant intermediate for the total energy.

$$k(E) = \frac{N^+(E - E_0)}{\hbar \rho(E)}$$

(5.3)
Figure 5.22. Potential energy schematic showing decomposition pathways for 7-hydroxyoxepinoxyl and 6-carboxy-1-oxo-hex-2,4-dienyl toward o-BQ + OH and CPO + HOCO. G3X-K energies are reported in kcal mol⁻¹ relative to o-hydroxyphenyl + O₂.
Figure 5.23. Potential energy schematic showing decomposition pathways for the 3-hydroxyoxepinoxy radical toward 3-hydroxy-2-benzoquinone + H and 2-hydroxy-cyclopentadienone + HCO. G3X-K energies are reported in kcal mol$^{-1}$ relative to o-hydroxyphenyl + O$_2$. 
Table 5.4. The sum of states for the transition structures (i.e., $N^\dagger(E - E_0)$) and the energy dependent rate coefficient from Equation 5.3 are provided for salient unimolecular processes from 2-hydroxyphenylperoxyl radical toward o-BQ, hydroxy-oxepinoxyl and carboxyoxohexdienyl radicals.

<table>
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<th>Reaction Process</th>
<th>$N^\dagger(E - E_0)$</th>
<th>$k(E) (s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-hydroxpropylperoxyl radical (N2)</td>
<td>$5.06 \times 10^{16}$</td>
<td>$2.73 \times 10^{12}$</td>
</tr>
<tr>
<td>OH-cis dioxiranyl radical (N20)</td>
<td>$5.06 \times 10^{16}$</td>
<td>$2.73 \times 10^{11}$</td>
</tr>
<tr>
<td>2-hydroxyphenylperoxyl radical (N2)</td>
<td>$2.47 \times 10^{16}$</td>
<td>$6.00 \times 10^{10}$</td>
</tr>
<tr>
<td>OH-trans dioxiranyl radical (N22)</td>
<td>$5.06 \times 10^{16}$</td>
<td>$2.73 \times 10^{11}$</td>
</tr>
<tr>
<td>2-hydroxpropylperoxyl radical (N2)</td>
<td>$1.83 \times 10^{14}$</td>
<td>$9.88 \times 10^{8}$</td>
</tr>
<tr>
<td>6-carboxyoxohexdienyl radical (N21)</td>
<td>$2.47 \times 10^{16}$</td>
<td>$6.00 \times 10^{10}$</td>
</tr>
<tr>
<td>OH-cis dioxiranyl radical (N20)</td>
<td>$1.83 \times 10^{13}$</td>
<td>$9.88 \times 10^{8}$</td>
</tr>
<tr>
<td>2-hydroxyoxepinoxyl radical (N23)</td>
<td>$3.79 \times 10^{12}$</td>
<td>$3.77 \times 10^{11}$</td>
</tr>
<tr>
<td>OH-trans dioxiranyl radical (N22)</td>
<td>$3.79 \times 10^{12}$</td>
<td>$3.77 \times 10^{11}$</td>
</tr>
<tr>
<td>2-hydroxyphenylperoxyl radical (N2)</td>
<td>$3.79 \times 10^{12}$</td>
<td>$3.77 \times 10^{11}$</td>
</tr>
</tbody>
</table>
5.8 Corrections


Page, paragraph, line and figure numbers reference the publication reproduced as Appendix B. Corrections are implemented in this Chapter 5.

Erratum in page 4324, Table 1:

- The calculated adiabatic ionisation energy for catechol was incorrectly transcribed as “8.14 [eV]” and should be read as “8.22 [eV]”.

A photoionisation onset for the m/z 110 ion signal was not measured between 9.0–10.2 eV. The assignment of catechol to m/z 110 is rationalised via H-abstraction by the ortho-hydroxyphenoxy radical (m/z 109) to produce ortho-catechol (C₆H₄OHOH, m/z 110).

Erratum in page 4325, paragraph 1 of Section 3.2, line 2:

- “3-bromo-4-hydroxybenzaminium” should read “3-bromo-4-hydroxybenzenaminium”

Erratum in page 4326, figure caption to Figure 5, line 1:

- “3-bromo-4-hydroxybenzaminium” should read “3-bromo-4-hydroxybenzenaminium”

Erratum in page 4326, paragraph 2 of Section 3.2.1, line 5–7:

- The text “...The k₁ values for m/z 109 signal decay and m/z 124 signal growth are in agreement (e.g., in Fig. 5a, 1.9 ± 0.2 s⁻¹ compared to 1.8 ± 0.1 s⁻¹ within 2σ) ...” should read “...The k₁ values for m/z 109 signal decay and m/z 124 signal growth are in agreement (e.g., in Fig. 5a, 0.19 ± 0.02 s⁻¹ compared to 0.18 ± 0.01 s⁻¹ within 2σ) ...”

The pseudo-first order rate coefficient for appearance of m/z 124 from charge-tagged ortho-hydroxyphenyl + O₂ is still in agreement with the m/z 109 ion signal decay. This is consistent with m/z 124 being the dominant reaction product.

Erratum in page 4329, Figure 8:

- The 0 K G3X-K enthalpy for TS4n was incorrectly transcribed as “-26.0 [kcal mol⁻¹]” and should read “-23.0 [kcal mol⁻¹]”.

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Chapter 5. Distonic and Neutral ortho-Hydroxylphenyl Radical + O₂

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Chapter 5. Distonic and Neutral o-Hydroxylphenyl Radical + O₂

The overall barrier to 7-hydroxy-oxepinoxyl radical (N23) along the potential energy scheme in Figure 8 is still -21.3 kcal mol⁻¹ at TS N2 → N22 with respect to reactants. The relative positioning of the TS4n marker is correct. In addition, the sum of states for transition structures and the energy dependent rate coefficients in Table S2 (above: Table 5.4) were calculated with the correct barriers.

Erratum in page 10 of the Supporting Information, figure caption to Figure S7, line 1:

- “3-bromo-4-methylbenzaminium” should read “3-bromo-4-methylbenzenaminium”

Erratum in page 10 of the Supporting Information, figure caption to Figure S7, line 2:

- The unit “cm⁻³” was incorrectly transcribed as “cm⁻³” in both figure captions for the publication.

Erratum in page 11 of the Supporting Information, figure caption to Figure S8, line 2:

- The unit “cm⁻³” was incorrectly transcribed as “cm⁻³” in both figure captions for the publication.

Erratum in page 11 of the Supporting Information, figure caption to Figure S9, line 2:

- “3-bromo-4-hydroxybenzaminium” should read “3-bromo-4-hydroxybenzenaminium”

Erratum in page 11 of the Supporting Information, figure caption to Figure S9, lines 2–3:

- “3-bromo-4-methylbenzaminium” should read “3-bromo-4-methylbenzenaminium”

Erratum in page 14 of the Supporting Information, figure caption to Figure S11, line 1:

- The text “Shokov et al” should read “Skokov et al.”

Erratum in page 17 of the Supporting Information, paragraph 3, line 1:

- “o-hydroxophenylperoxyl” should read “o-hydroxyphenylperoxyl”
Chapter 5. Distonic and Neutral \( \sigma \)-Hydroxyphenyl Radical + \( \text{O}_2 \)

References


(32) *Normalized Collision Energy is a term used by the instrument vendor as Explained here: https://static.thermoscientific.com/images/D13507~.pdf. Zero, on this scale, means that no additional resonant excitation is applied.*


Chapter 5. Distonic and Neutral o-Hydroxyphenyl Radical + O₂


Chapter 5. Distonic and Neutral \( o \)-Hydroxylphenyl Radical + \( O_2 \)


Chapter 5. Distonic and Neutral o-Hydroxylphenyl Radical + O₂


(70) S. Skokov, A. Kazakov and F. L. Dryer, Presented at the Fourth Joint Meeting of the U.S. Sections of the Combustion Institute, 2005.


Chapter 5. Distonic and Neutral \( o \)-Hydroxylphenyl Radical + \( O_2 \)


Chapter 6

Neutral

\( o \)-Methylphenyl Radical + C\( _3 \)H\( _4 \)

6.1 Introduction

Elucidating the key formation pathways of fused-ring structures and polycyclic aromatic hydrocarbons (PAHs), from radical-molecule reactions, is essential to understanding soot formation\(^1\) and molecular weight growth in the interstellar medium.\(^2\) Reactions of phenyl radicals (C\( _6 \)H\( _5 \)) with small hydrocarbons (e.g. C\( _2 \)H\( _2 \) and C\( _4 \)H\( _4 \)) are plausible contributors to ring-growth processes forming PAHs.\(^3\)–\(^8\)

Studies of phenyl radical reactions with allene and propyne have identified H-atom and CH\( _3 \)-loss channels from the phenyl–C\( _3 \)H\( _4 \) adduct.\(^9\)–\(^13\) In single-collision crossed beam and photoionisation studies, indene + H is identified as the dominant product channel.\(^9\)–\(^11\) Transition state theory and RRKM-master equation analyses\(^12,13\) predict that indene + H should dominate under conditions of the interstellar medium (i.e. <500 K and below \( 10^\text{-}4 \) Pa). However, at conditions relevant to flames (>1000 K), products include allenyl-benzene + H and ethynyl-benzene + CH\( _3 \).

Chapters 3 and 4 demonstrated that an ortho-methyl substituent can directly influence phenyl radical reactions with molecular oxygen. The ortho-methyl substituent provides a labile H-atom to the proximal peroxyl group that is inaccessible for meta- and para-methylphenyl radicals after O\( _2 \) addition. In this chapter, we extend on this study to investigate C\( _3 \)H\( _4 \) as the co-reactant.

To date, there are no reported studies on the reactions of \( o \)-substituted phenyl radicals with small unsaturated hydrocarbons, such as allene and propyne (C\( _3 \)H\( _4 \)). Studies of \( m \)- and \( p \)-methylphenyl radical reactions with C\( _3 \)H\( _4 \) (Ref. 14) and C\( _4 \)H\( _4 \) (Ref. 7 and 8), for example, show the \( m \)- and \( p \)-methyl substituents are essentially spectators of the unimolecular reactions after adduct formation. Here, we report the
reactions of \( o \)-methylphenyl with allene and propyne using multiplexed photoionisation mass spectrometry. This synchrotron-based technique combines a flow reactor, time-of-flight mass spectrometry, and VUV photoionisation to allow detection of reaction products with kinetic and isomeric resolution. We show that addition reactions of \( o \)-methylphenyl radicals with allene and propyne result in H atom and CH\(_3\) loss. But, unlike with phenyl radical reactions, the products include two bicyclic products as indene + CH\(_3\) and dihydronaphthalene + H, which demonstrate that an \( o \)-methyl substituent can directly influence the radical reaction. Results suggest indene + CH\(_3\) is the predominant product set for \( o \)-methylphenyl + propyne, and not for allene reactions. Plausible reaction pathways are examined with quantum chemical calculations.

6.2 Experimental

6.2.1 Multiplexed Photoionisation Mass Spectrometry

Reactions were investigated using multiplexed photoionisation mass spectrometry\(^{15,16}\) with VUV synchrotron radiation at the Chemical Dynamics Beamline,\(^{17–19}\) Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, USA.

The multiplexed photoionisation mass spectrometer comprises a quartz flow tube reactor, differentially pumped vacuum chamber, photoionisation source (i.e. synchrotron radiation), and an orthogonal time-of-flight mass spectrometer. Photolysis of \( o \)-iodotoluene with 248 nm radiation from a pulsed KrF excimer laser, operating at 4 Hz and a fluence of approximately 50 mJ cm\(^{-2}\), was used to generate \( o \)-methylphenyl radicals within the reactor from C-I bond homolysis. A 650 \( \mu \)m diameter hole allowed gas to continuously effuse from the quartz slow-flow reactor into a differentially pumped vacuum chamber. This gas was sampled by a skimmer to create a near-effusive molecular beam that is intersected orthogonally by quasi-continuous vacuum-ultraviolet (VUV) synchrotron radiation. Photo-ionisable species within the molecular beam were then detected using a 50 kHz pulsed orthogonal-extraction time-of-flight mass spectrometer.

Reactions were conducted with the reactor maintained at 600 K and 4 Torr (533 Pa). The temperature profile of the reactor is such that the 20 cm length above the pinhole is maintained at the set temperature, which corresponds to a reaction time of 0–50 ms for a gas flow velocity of 4 m s\(^{-1}\). \( o \)-Iodotoluene, C\(_3\)H\(_4\) gas (either allene or propyne), and He gas are supplied to the reactor through separate mass-flow controllers at a total rate of 50 sccm. The \( o \)-iodotoluene sample was entrained in He gas using a fritted bubbler with the liquid sample maintained at 19°C (292.15 K) and about 400 Torr (53.3 kPa). The vapour pressure of \( o \)-iodotoluene is calculated to be
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295 mTorr (39.3 Pa) at 292.15 K using Antoine parameters derived from Stull. The number densities within the reactor at 600 K and 4 Torr were $6.2 \times 10^{12}$ molecule cm$^{-3}$ for $o$-iodotoluene, $2.1 \times 10^{16}$ molecule cm$^{-3}$ of either allene or propyne, and $4.3 \times 10^{16}$ molecule cm$^{-3}$ for He buffer gas. The total number density was $6.4 \times 10^{16}$ molecule cm$^{-3}$ at 600 K and 4 Torr.

Commercial samples of indene, 1,2-dihydronaphthene, and 2-methylindene were used to obtain reference PI spectra (Sigma Aldrich). The samples were entrained in He gas using a fritted bubbler and supplied to the reactor with additional He gas at an overall rate of 50 sccm at 600 K to acquire relative PI spectra.

All photoionisation data are normalised to the ALS photocurrent measured with a NIST-calibrated photodiode (SXUV-100, International Radiation Detectors Inc.). Ion signal acquired 20 ms before laser photolysis is background subtracted from the normalised data set so the resulting data is the result of photolysis and subsequent reactions. The PI spectra presented herein are the average of three individual acquisitions normalised to the integral over the spectrum, with vertical error bars representing $2\sigma$ statistical uncertainty. Mass spectra and kinetic traces present the co-addition of at least three separate acquisitions of at least 900 laser pulses.

6.2.2 Computational Chemistry

Reaction enthalpies and adiabatic ionisation energies are calculated from electronic and zero-point energies computed in Gaussian 09. The M06-2X density functional theory with 6-311++G(d,p) basis was used for calculating reaction enthalpies and barriers at 0 K.

The CBS-QB3 method was used to calculate adiabatic ionisation energies (AIEs) and relative enthalpies for sets of 78 Da ($C_6H_6$), 116 Da ($C_9H_8$), and 130 Da ($C_{10}H_{10}$) isomers. Enthalpies are reported in kcal mol$^{-1}$ and AIE are reported in electron volts (eV). Both are 0 K electronic energies and include the zero-point energy correction. Stationary points were classified as either minima (no imaginary frequencies) or transition states (one imaginary frequency). The assignment of a transition state between minima was verified by IRC calculations.

6.3 Results and Discussion

6.3.1 $o$-Methylphenyl + $C_3H_4$

Figure 6.1 (a) and (b) are product mass spectra from 248 nm photolysis of $o$-iodotoluene in the presence of either (a) allene or (b) propyne gas within the flow reactor. These mass spectra are integrated 0–50 ms after photolysis at 600 K, acquired at a PI energy of 9.325 eV. Background $m/z$ 90 and 92 signals result from photolysis
Figure 6.1. Product mass spectra at 9.325 eV integrated 0–50 ms after 248 nm photolysis of \( o \)-iodotoluene in the presence of (a) allene and (b) propyne at 600 K and 4 Torr. These mass spectra are background subtracted with the average of 20 ms pre-laser signal. Both mass spectra are normalised so the intensity of the \( m/z \) 92 signal is 100 arbitrary units.
of o-iodotoluene. These were assigned to fulvenallene and toluene by comparing PI spectra with an integrated mass-selected threshold photoelectron spectrum for fulvenallene (C₇H₆, 90 Da)²⁶ and reference PI spectrum for toluene (C₇H₈, 92 Da).²⁷ Laser-dependent ion signal at m/z 39, 40 and 78 were not the result of o-methylphenyl radical reactions with either allene or propyne. The assignments of m/z 39, 40 and 78 are discussed in Section 6.5 and are propargyl radical (CHCCH₂, 39 Da), allyl radical (CH₂CHCH₂, 41 Da), and a mixture of C₆H₆ including fulvene and benzene.

In both Figure 6.1 (a) and (b), reaction products appeared at m/z 116 and 130 and attributed to reactions of the o-methylphenyl radical with either (a) allene or (b) propyne.

It is worth noting that the relative ion intensity of m/z 130 from o-methylphenyl + allene in Figure 6.1(a) is significantly greater than the corresponding signals in Figure 6.1(b). Also, the relative intensity of m/z 116 from propyne reactions in Figure 6.1(b) is greater than in Figure 6.1(a). As discussed later, the relative difference in ion signal intensities may infer different product branching ratios between o-methylphenyl + allene and o-methylphenyl + propyne reactions.

Table 6.1. Measured PI thresholds for detected ion signals compared to CBS-QB3 adiabatic ionisation energies (AIEs) for the assigned species. Literature ionisation energies are provided and marked according to the technique of measurement. PE values were obtained from photoelectron spectroscopy and EI values from electron impact techniques.

<table>
<thead>
<tr>
<th>Species</th>
<th>m/z</th>
<th>Measured AIE (eV)</th>
<th>Calculated AIE (eV)</th>
<th>Literature values (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>propargyl radical (CHCCH₂)</td>
<td>39</td>
<td>8.65</td>
<td>8.7</td>
<td>8.67 ± 0.02 (PE)²⁸</td>
</tr>
<tr>
<td>allyl radical (CH₂CHCH₂)</td>
<td>41</td>
<td>8.10</td>
<td>8.2</td>
<td>8.13 ± 0.02 (PE)²⁹</td>
</tr>
<tr>
<td>fulvene</td>
<td>78</td>
<td>8.40</td>
<td>8.4</td>
<td>8.36 ± 0.02 (PE)²⁹</td>
</tr>
<tr>
<td>indene</td>
<td>116</td>
<td>8.15</td>
<td>8.2</td>
<td>8.15 ± 0.015 (VIE, PE)²⁹</td>
</tr>
<tr>
<td>1,2-dihydromaphthalene</td>
<td>130</td>
<td>7.95</td>
<td>8.0</td>
<td>8.14 (EI)³⁰</td>
</tr>
<tr>
<td>1,4-dihydromaphthalene</td>
<td>130</td>
<td>8.65</td>
<td>8.6</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.2 shows PI spectra for m/z 116 ion signal from reactions with allene and propyne. Both PI spectra are well matched to the relative PI spectrum for indene (C₉H₈, 116 Da), which was acquired on the same instrument and included in Figure 6.2. The PI signal onset at 8.1 eV also agrees with the calculated and literature IE for indene in Table 6.2. This leads us to conclude that indene is the sole 116 Da isomer detected between 7.800–9.325 eV. Using the m/z 92 ion signal in Figure 6.1 as a relative standard between allene and propyne reactions we can
conclude that the relatively large $m/z$ 116 ion signal intensity for $o$-methylphenyl + propyne reactions correspond to a greater indene + H yield than reactions with allene.

The $m/z$ 130 PI spectra from reactions with allene and propyne are included in Figure 6.3 with a reference PI spectrum for 1,2-dihydronaphthalene ($C_{10}H_{10}$, AIE = 8.0 eV) acquired on the same instrument. In the propyne case, the match is compelling across the PI energy range in Figure 6.3 and the $m/z$ 130 signal is assigned exclusively to 1,2-dihydronaphthalene. However, in the allene case, there appears to be a detectable amount of 1,4-dihydronaphthalene since the $m/z$ 130 PI spectrum from allene reactions is well matched between 8.000–8.600 eV but systematically deviates at photon energies $>8.6$ eV. This deviation at 8.6 eV corresponds to the AIE of 1,4-dihydronaphthalene (AIE = 8.6 eV) in Table 6.1. Unfortunately, it is difficult to acquire high purity samples of 1,4-dihydronaphthalene from commercial sources so there is no reference PI spectrum.

A reference PI spectrum for 2-methylindene (130 Da, AIE = 7.9 eV) acquired on the same instrument is included in Figure 6.12, Section 6.5. The PI onset at 7.8 eV appears earlier than the $m/z$ 130 PI spectra in Figure 6.3. The poor match between the PI spectrum for 2-methylindene and the $m/z$ 130 PI spectra from reactions with propyne and allene suggest that 2-methylindene is not produced in significant quantities to affect the $m/z$ 130 ion signal.
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6.3 Reaction Mechanisms

To assist rationalisation of these experimental results, the relative enthalpies for key intermediates and transition states were calculated for both o-methylphenyl + allene and o-methylphenyl + propyne using M06-2X/6-311++G(d,p). As demonstrated by previous studies on ortho-substituted phenyl radical oxidation, the ortho-substituent is expected to participate in the reaction and affect the final product distribution. In the schemes below, A denotes stationary points from o-methylphenyl + allene, P for reactions with propyne, and C for stationary points common to both C₃H₄ cases, accessible from C1 as shown later in Figure 6.10 and Figure 6.11.
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Figure 6.4. Potential energy schematic for adduct formation and isomerisation between P\textsubscript{1} and P\textsubscript{2} propyne adducts from o-methylphenyl + propyne (P\textsubscript{0}). M06-2X 0 K enthalpies reported in kcal mol\textsuperscript{-1} relative to o-methylphenyl + allene (A\textsubscript{0}).

Figure 6.4 shows two possible intermediates from o-methylphenyl + propyne (P\textsubscript{0}) at -41.0 kcal mol\textsuperscript{-1} for P\textsubscript{1} and -35.5 kcal mol\textsuperscript{-1} for P\textsubscript{2} relative to the separated o-methylphenyl radical and allene reactant (A\textsubscript{0}). Isomerisation between P\textsubscript{1} and P\textsubscript{2} is mediated by TS P\textsubscript{2}→P\textsubscript{3} at -12.3 kcal mol\textsuperscript{-1}. The barriers toward propyne addition and formation of P\textsubscript{1} and P\textsubscript{2} from P\textsubscript{0} in Figure 6.4 are within 0.5 kcal mol\textsuperscript{-1} of the corresponding barriers toward A\textsubscript{1} and A\textsubscript{2} from A\textsubscript{0} in Figure 6.7.

Figure 6.5. Potential energy schematic for reactions of the P\textsubscript{1} to indene + CH\textsubscript{3} (C\textsubscript{4}). This mechanism is in accord with propyne-\textit{d}\textsubscript{4} experimental data (mass spectrum in Figure 6.17). M06-2X 0 K enthalpies reported in kcal mol\textsuperscript{-1} relative to o-methylphenyl + allene (A\textsubscript{0}).

If the P\textsubscript{1} intermediate is produced directly by propyne addition, it can rearrange and decompose to indene + CH\textsubscript{3} \textit{via} a 1,5-H atom shift, cyclisation \textit{via} the limiting TS P\textsubscript{4}→P\textsubscript{5} at -27.6 kcal mol\textsuperscript{-1}, and subsequent CH\textsubscript{3} loss as shown in Figure 6.5. This mechanism is consistent with o-methylphenyl + propyne reactions repeated
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with propyne-d₄ (44 Da). The resulting mass spectrum in Figure 6.17 shows an ion at m/z 117, a 1 Da shift (C₉H₇D) from m/z 116 (C₉H₈) that is consistent with CD₃ loss.

Figure 6.6 shows an alternate pathway from P₄ toward 1,2-dihydronaphthalene + H via P₆ and P₇. The limiting TS P₆→P₇ at -2.9 kcal mol⁻¹ approaches the energy of P₀ at -0.2 kcal mol⁻¹ and therefore unlikely to compete with formation of indene + CH₃ (shown in Figure 6.5). This scheme is in accord with the relative m/z 116 ion signal intensity dominant over that for m/z 130 signal intensity, as shown in Figure 6.1(b).

Figure 6.7 shows the formation of two adducts from o-methylphenyl + allene (A₀) with reaction enthalpies at -36.8 kcal mol⁻¹ for A₁ and -57.2 kcal mol⁻¹ for the resonance-stabilised A₂, with respect to A₀. Isomerisation between A₁ and A₂ is also included in Figure 6.7 with a rate limiting transition state at -15.5 kcal mol⁻¹ (TS A₁→A₃).

The m/z 130 PI signal from o-methylphenyl + allene is assigned 1,2- and 1,4-dihydronaphthalene, where Figure 6.3 shows 1,2-dihydronaphthalene likely dominates the m/z 130 PI signal. Pathways toward 1,2-dihydronaphthalene + H (C₇) at -33.5 kcal mol⁻¹ and 1,4-dihydronaphthalene + H (C₈) at -30.8 kcal mol⁻¹ from A₀ are rationalised via 1-5 H-atom shift from the methyl group through TS A₁→A₄ at -22.3 kcal mol⁻¹, cyclisation of A₄ to form the 1,2,4-trihydronaphthalen-3-yl radical (C₆) at -52.3 kcal mol⁻¹ and then subsequent H-atom loss toward C₇ or C₈ (1,2-dihydronaphthalene or 1,4-dihydronaphthalene, respectively).

On route to C₇ and C₈, the reaction barriers for TS C₆→C₇ and TS C₆→C₈ differ by <1 kcal mol⁻¹. The M06-2X frequencies for TS C₆→C₇ and TS C₆→C₈ does not reveal an apparent kinetic preference for TS C₆→C₇ and TS C₆→C₈ that could explain the experimental result. Based on presented schemes, the m/z 130 product branching ratio should be approximately 1:1 (C₇:C₈) for reactions with allene and propyne. However, the experimental m/z 130 PI spectra shown in Figure 6.3 indicate that the m/z 130 ion signal from propyne reactions is entirely 1,2-dihydronaphthalene and, for the allene case, dominated by PI of 1,2-dihydronaphthalene with a minor contribution from 1,4-dihydronaphthalene.

In the case of the allene reaction, the assignment of 1,2-dihydronaphthalene as the dominant product is based on several assumptions: (1) the reference PI spectrum for 1,2-dihydronaphthalene is reliable and not contaminated by 1,4-dihydronaphthalene and, (2) the two dihydronaphthalene isomers have similar PI cross sections. A PI spectrum acquired with a second, separately-purchased 1,2-dihydronaphthalene sample is included in Figure 6.13 and agrees with the original PI spectrum included in Figure 6.3. In addressing assumption (2), the PI cross section for 1,2-dihydronaphthalene would need to be ~10 times greater than that for 1,4-dihydronaphthalene in
Figure 6.6. Potential energy schematic for reactions of the P4 to 1,2-dihydronaphthalene + H (C7). The limiting TS P6→P7 at -2.9 kcal mol⁻¹ approaches the energy of P0 at -0.2 kcal mol⁻¹. M06-2X 0 K enthalpies reported in kcal mol⁻¹ relative to o-methylphenyl + allene (A0).
Figure 6.7. Potential energy schematic for adduct formation and isomerisation between A1 and A2 allene adducts from o-methylphenyl + allene (A0). M06-2X 0 K enthalpies reported in kcal mol$^{-1}$ relative to A0.

Figure 6.8. Potential energy schematic for reactions of A1 toward 1,2- and 1,4-dihydronaphthalene + H (C7 and C8). M06-2X 0 K enthalpies reported in kcal mol$^{-1}$ relative to o-methylphenyl + allene (A0).
order for Figure 6.3 to represent a product branching ratio of 1:1. However, without absolute PI spectra for both 1,2- and 1,4-dihydronaphthalene, the m/z 130 product branching ratio cannot be quantified.

![Figure 6.9](image)

**Figure 6.9.** Potential energy schematic for isomerisation between the A2 and P2 (the carbon-2 adducts for allene and propyne, respectively). Decomposition of the 2-(propen-2-yl)benzyl radical (C1) is shown in Figure 6.10. M06-2X 0 K enthalpies reported in kcal mol\(^{-1}\) relative to o-methylphenyl + allene (A0).

Figure 6.9 shows that the propyne and allene reaction schemes are interconnected. The P2 adduct can isomerise to the resonantly stabilised A2 (both carbon-2 adducts) through sequential 1,5-H atom shifts with the methyl substituent and limiting TS P2→C1 at -27.0 kcal mol\(^{-1}\). As shown in Figure 6.10, the C1 radical connecting A2 and P2 can undergo unimolecular decomposition to form C4, C7, and C8. As C1 is common in both allene and propyne reaction schemes, Figure 6.10 details plausible pathways toward indene + CH\(_3\) and dihydronaphthalene + H from reactions with both C\(_3\)H\(_4\) isomers. The low indene yield from allene reactions, for example, is rationalised by an overall slower multi-step reaction pathway via C1 because a direct competitive indene + H pathway from allene reactions is not easily conceived.

Figure 6.10, however, is inconsistent with results from o-methylphenyl + propyne because the m/z 130 signal appears to be entirely from 1,2-dihydronaphthalene. The pathway presented in Figure 6.6 is an unlikely contributor to m/z 130 signal intensity due to the limiting TS P6→P7 at -2.9 kcal mol\(^{-1}\), which approaches the energy of reactants (P0). As stated before, on these calculated pathways, we expect 1:1 product branching ratio between 1,2- and 1,4-dihydronaphthalene from C6 and 1,4-dihydronaphthalene does not significantly contribute to m/z 130 signal from propyne reactions.

Alternative pathways were explored to determine if the dominance of 1,2-dihydronaphthalene can be explained. In Figure 6.11 the limiting TS C10→C7 toward 1,2-dihydronaphthalene + H is marginally lower than TS C10→C6 and 2.8 kcal mol\(^{-1}\) below the limiting TS C6→C7 in Figure 6.10. However, with m/z 130 from the propyne reaction being entirely 1,2-dihydronaphthalene, and no compet-
Figure 6.10. Potential energy schematic for unimolecular decomposition of C1 to either indene + CH₃, 1,2- or 1,4-dihydronaphthalene + H. The scheme is accessible via isomerisation of A2 and P2 to C1, as shown in Figure 6.9. The limiting transition structures to each product have enthalpies within 2 kcal mol⁻¹. M06-2X 0 K enthalpies reported in kcal mol⁻¹ relative to o-methylphenyl + allene (A0).
Figure 6.11. Potential energy schematic for reactions of C5 toward 1,2-dihydronaphthalene + H (C7). The 1,2-atom shift from C10 to C6 and an alternative pathway via TS C5−C10 are included. The limiting TS C10−C7 toward 1,2-dihydronaphthalene + H is 2.8 kcal mol$^{-1}$ below the limiting TS C6−C7 in Figure 6.10. M06-2X 0 K enthalpies reported in kcal mol$^{-1}$ relative to o-methylphenyl + allene (A0).
itive pathways described toward C8, the potential energy schematics are possibly incomplete and warrant further investigation. Secondary H-assisted isomerisation\(^{33}\) of any 1,4-dihydronaphthalene product could also explain the dominance of 1,2-dihydronaphthalene; 1,4-dihydronaphthalene + H by the (C6) intermediate should form the thermodynamically preferred 1,2-dihydronaphthalene + H.

### 6.4 Conclusions

VUV photoionisation mass spectrometry conducted at the ALS revealed two major product mass channels, \(m/z\) 116 and 130 from o-methylphenyl radical reactions with allene and propyne, consistent with CH\(_3\) and H-atom loss. The \(m/z\) 116 product from reactions with allene and propyne is conclusively assigned indene (C\(_9\)H\(_8\)) by comparing experimental PI spectra to reference PI spectra for indene. Experiments with propyne-\(d_4\) indicate the CH\(_3\) fragment originates from the propyne reactant. The \(m/z\) 130 product product branching ratio for allene and propyne differs, however. In the case of propyne reactions, \(m/z\) 130 is assigned entirely to 1,2-dihydronaphthalene + H. On the other hand, the \(m/z\) 130 signal from allene reactions is attributed to photoionisation of 1,2- and 1,4-dihydronaphthalene where 1,2-dihydronaphthalene represents the dominant fraction.

Quantum chemical calculations reveal pathways to indene + CH\(_3\), 1,2- and dihydronaphthalene + H. The pathways identified in Section 6.3.2 toward 1,2- and 1,4-dihydronaphthalene + H suggest a \(m/z\) 130 product branching ratio of approximately 1:1. However, the \(m/z\) 130 ion signal from propyne reactions is assigned 1,2-dihydronaphthalene with because of its close match with a reference PI spectrum. Further investigation is warranted to identify alternate pathways to 1,2- and 1,4-dihydronaphthalene, and determine the kinetically preferred mechanism or isomerisation processes.

### 6.5 Supporting Information

#### 6.5.1 Supplementary Photoionisation Spectra and AIE Values

The laser-dependent ion signals detected at \(m/z\) 39, 40 and 78 in Figure 6.1(a) result from photolysis of allene at 600 K while \(m/z\) 39 in Figure 6.1(b) results from propyne photolysis under similar conditions. The \(m/z\) 39 signals from both allene and propyne photolysis were assigned propargyl radical (CHC\(_2\)H\(_2\), 39 Da) by comparison with a reference PI spectrum in Figure 6.14.\(^{16}\) Similarly, \(m/z\) 41 signal is assigned to the allyl radical (CH\(_2\)CHCH\(_2\), 41 Da) by comparison to a reference
Table 6.2. Calculated CBS-QB3 adiabatic ionisation energies (AIEs) for C$_9$H$_8$ isomers (116 Da). Relative CBS-QB3 enthalpies ($\Delta$H$_f$) are provided. The techniques used to obtain literature values are indicated within brackets with EI meaning electron impact techniques, and PI meaning photoionisation mass spectrometry.

<table>
<thead>
<tr>
<th>C$_9$H$_8$ isomer</th>
<th>Calculated AIE (eV)</th>
<th>Literature IE (eV)</th>
<th>Relative $\Delta$H$_f$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>indene</td>
<td>8.2</td>
<td>8.15 ± 0.015 (PE)$^{34}$</td>
<td>0.0</td>
</tr>
<tr>
<td>2-methylphenylacetylene</td>
<td>8.7</td>
<td>8.61 ± 0.02 (PE)$^{35}$</td>
<td>28.6</td>
</tr>
<tr>
<td>propadienyl-benzene</td>
<td>8.3</td>
<td>8.29$^{36}$</td>
<td>29.6</td>
</tr>
<tr>
<td>propynyl-benzene</td>
<td>8.4</td>
<td>8.42 ± 0.08 (PE)$^{29}$</td>
<td>27.0</td>
</tr>
<tr>
<td>3-phenyl-propyne</td>
<td>9.0</td>
<td></td>
<td>34.5</td>
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</table>

Figure 6.12. Average PI spectra of m/z 130 from o-methylphenyl + allene (open red circles) and o-methylphenyl + propyne (open black triangles). A reference PI spectrum for a 2-methylindene sample is shown (solid purple line).
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Figure 6.13. Average PI spectra of m/z 130 from original 1,2-dihydronaphthalene sample (solid purple line, included in Figure 6.3) and PI spectrum from a new sample of 1,2-dihydronaphthalene acquired on the same instrument (solid red line).

Table 6.3. Calculated CBS-QB3 AIEs for C₁₀H₁₀ isomers (130 Da). Relative CBS-QB3 enthalpies (ΔH_f) are provided. The techniques used to obtain literature values are indicated within brackets with EI meaning electron impact techniques, and PI meaning photoionisation mass spectrometry.

<table>
<thead>
<tr>
<th>C₁₀H₁₀ isomer</th>
<th>Calculated AIE (eV)</th>
<th>Literature IE (eV)</th>
<th>Relative ΔH_f (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydronaphthalene</td>
<td>8.0</td>
<td>8.14 (EI)³⁰</td>
<td>1.8</td>
</tr>
<tr>
<td>1,4-dihydronaphthalene</td>
<td>8.6</td>
<td></td>
<td>4.8</td>
</tr>
<tr>
<td>2-methylindene</td>
<td>7.9</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>3-methylindene</td>
<td>8.0</td>
<td>7.97 (PI)³⁰</td>
<td>0.0</td>
</tr>
<tr>
<td>4-methylindene</td>
<td>8.0</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>2-propynyl-toluene</td>
<td>8.3</td>
<td></td>
<td>28.0</td>
</tr>
<tr>
<td>2-propadienyl-toluene</td>
<td>8.1</td>
<td></td>
<td>32.1</td>
</tr>
</tbody>
</table>
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PI spectrum in Figure 6.15. Propargyl radicals likely result from photolysis of allene and propyne while allyl radicals presumably result from H-atom addition to allene.⁴⁷,⁴⁸

Figure 6.16 shows the PI spectrum for m/z 78 from allene photolysis. Its onset at 8.4 eV is consistent with the CBS-QB3 AIE and literature IE for fulvene (C₆H₆, 78 Da) in Table 6.4. However, as shown in Figure 6.16, the PI spectrum systematically deviates from the reference spectrum for fulvene at photon energy >8.6 eV. Without reference spectra for many C₆H₆ isomers the assignment of m/z 78 signal >8.6 eV remains incomplete. Calculated and reference IE for a number of C₆H₆ isomers are listed in Table 6.4 with relative enthalpies. Benzene (IE = 9.24 eV, Ref. 40) is more stable than fulvene and likely contributes to signal between 9.24–9.30 eV. Both fulvene and benzene could result from propargyl radical + allene reactions.⁴⁷,⁴⁸

![Figure 6.14. Average PI spectra of m/z 39 from o-methylphenyl + allene (open red circles) and o-methylphenyl + propyne (open black triangles). A vertically scaled PI spectrum for the propargyl radical (CHCCH₂) is included from Ref. 16 (Savee et al., solid purple line).](image)
Figure 6.15. Average PI spectra for m/z 41 from o-methylphenyl + allene (open red circles). A vertically scaled PI spectrum for the allyl radical (CH$_2$CHCH$_2$) is included as a solid purple line from Ref. 37 (Hansen et al., solid purple line).

Figure 6.16. Average PI spectra of m/z 78 from o-methylphenyl + allene (open red circles). A vertically scaled PI spectrum for fulvene is included (solid purple line).
Table 6.4. Calculated CBS-QB3 AIEs for $C_6H_6$ isomers (78 Da). Relative CBS-QB3 enthalpies ($\Delta H_f$) are provided. The techniques used to obtain literature values are mentioned in brackets where PE means photoelectron spectroscopy, TE means threshold electron detection.

<table>
<thead>
<tr>
<th>$C_6H_6$ isomer</th>
<th>Calculated AIE (eV)</th>
<th>Literature IE (eV)</th>
<th>Relative $\Delta H_f$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fulvene</td>
<td>8.4</td>
<td>8.36 ± 0.02 (PE)$^{29}$</td>
<td>0.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>9.3</td>
<td>9.24384 ± 0.00006 (TE)$^{28}$</td>
<td>-32.3</td>
</tr>
<tr>
<td>1,3-hexen-5-yne</td>
<td>8.6</td>
<td>9.20 (PE)$^{30}$</td>
<td>30.3</td>
</tr>
<tr>
<td>3,4-dimethylene-cyclobutene</td>
<td>8.8</td>
<td>8.80 ± 0.02 (PE)$^{29}$</td>
<td>29.4</td>
</tr>
<tr>
<td>hex-1,5-dien-3-yne</td>
<td>8.6</td>
<td>8.50 ± 0.02 (PE)$^{29}$</td>
<td>30.8</td>
</tr>
<tr>
<td>hex-2,4-yne</td>
<td>8.9</td>
<td>8.90 ± 0.05 (PI)$^{29}$</td>
<td>35.2</td>
</tr>
</tbody>
</table>
6.5.2 Supplementary Product Mass Spectra

![Mass spectrum](image)

**Figure 6.17.** Product PI mass spectrum at 9.325 eV integrated 0-50 ms after 248 nm photolysis of o-iodotoluene in the presence of propyne-d$_4$ (44 Da) at 600 K. The ions at m/z 42 and 117 were assigned isotopologues of the propargyl radical (C$_3$D$_3$) and indene (C$_9$H$_7$D).

To assist with elucidation of plausible mechanisms for indene + CH$_3$ from o-methylphenyl + propyne the reaction was repeated with propyne-d$_4$ (44 Da). Figure 6.17 shows ions detected at m/z 42 and 117 that are assigned to isotopologues of propargyl radical (C$_3$D$_3$) and indene (C$_9$H$_7$D), respectively. The detection of m/z 117 represents a 1 Da shift (C$_9$H$_7$D) from the m/z 116 signal (C$_9$H$_8$) and is consistent with CD$_3$ loss. This isotope study is in accord with the pathway shown in Figure 6.5 for o-methylphenyl + propyne reaction toward indene + CH$_3$. 
Chapter 6. Neutral o-Methylphenyl Radical + C\textsubscript{3}H\textsubscript{4}

References


(7) D. S. N. Parker, B. B. Dangi, R. I. Kaiser, A. Jamal, M. N. Ryazantsev, K. Morokuma, A. Korte and W. Sander, “An Experimental and Theoretical Study on the Formation of 2-Methylnaphthalene (C\textsubscript{11}H\textsubscript{10}/C\textsubscript{11}H\textsubscript{3}D\textsubscript{7}) in the Reactions of the \textit{para}-Tolyl (C\textsubscript{7}H\textsubscript{7}) and \textit{para}-Tolyl-d\textsubscript{7} (C\textsubscript{7}D\textsubscript{7}) with Vinylacetylene (C\textsubscript{4}H\textsubscript{4})”, J. Phys. Chem. A, 2014, 118, 2709–2718.


Chapter 6. Neutral o-Methylphenyl Radical + C₃H₄


Chapter 6. Neutral $o$-Methylphenyl Radical + C$_3$H$_4$


Chapter 7

Conclusions and Future Directions

7.1 Conclusions

Chapters 3, 4, 5, and 6 of this thesis explore the reactions of ortho-substituted phenyl radicals with neutral closed shell species. In all cases, the ortho-substituent of the phenyl radical participated in intramolecular H-atom transfer after the formation of an adduct and affected the final product distribution in a manner distinct from meta- and para-substituted phenyl radical reactions i.e. resulted in new reaction products.

Chapters 3 and 4 described experimental and theoretical investigations into the oxidation of o-methylphenyl radicals. Specifically, Chapter 3 explored distonic radical cation reactions in comparison with neutral o-methylphenyl + O₂ reactions, and Chapter 4 described the distinguishing features for the oxidation of neutral ortho- and meta-methylphenyl radicals. The key finding is new experimental evidence for formation of o-quinone methide from o-methylphenyl + O₂ from O₂ addition, H-atom migration to the QOOH intermediate, and subsequent OH elimination.

In Chapter 3 the photodissociation of the trimethylammonium-substituted halogenated precursors produced radical cations that reacted with excess O₂ and exhibited pseudo-first order rate behaviour. The distonic o-methylphenyl radicals reacted with O₂ to give rise to an O₂ adduct and an ion signal (after O₂ addition) that is consistent with H-atom migration and OH elimination to produce o-quinone methide.

The synchrotron-based photoionisation mass spectrometry experiments (PIMS) described in Chapter 4 for both o- and m-methylphenyl radical + O₂ revealed two stark differences: the m/z 80 and 106 ion signals are unique to o-methylphenyl + O₂. The m/z 106 signal was assigned o-quinone methide, analogues to charged-tagged o-quinone methide in Chapter 3 and o-benzoquinone from o-hydroxyphenyl radical + O₂ in Chapter 5. The other reaction products were rationalised by conventional phenyl + O₂ reaction mechanisms. The m/z 80 ion signal was assigned
cyclopentadienone, which is attributed to decomposition of the 7-methyloxepinoxyl radical from \( o \)-methylphenyl + \( O_2 \), which was not theorised for \( m \)-methylphenyl + \( O_2 \).

In Chapter 5, synchrotron-based PIMS revealed that the \( o \)-hydroxyphenyl + \( O_2 \) reaction produces two major products detected at \( m/z \) 80 and 108, consistent with cyclopentadienone and \( o \)-benzoquinone. The \( o \)-benzoquinone is likely a primary product following \( O_2 \) addition, H-atom migration, and subsequent OH loss. We conclude that cyclopentadienone forms from prompt decomposition of \( o \)-benzoquinone. Distonic ammonium-tagged \( o \)-hydroxyphenyl + \( O_2 \) reactions were studied and found to produce ions consistent with charged-tagged \( o \)-benzoquinone. CID of the charged-tagged \( o \)-benzoquinone cation lead to the formation of a cyclopentadienone analogue by CO loss.

Second order rate coefficients for oxidation of distonic \( o \)-methylphenyl and \( o \)-hydroxyphenyl radicals in Chapters 3 and 5 were measured and found to have a 5% reaction efficiency. By comparing trimethylammonium and ammonium charged tags, and the identity of the \( ortho \)-substituent, the results reported in this thesis demonstrate that the identity of the \( ortho \)-substituent does not significantly affect the reaction efficiency (approximately 5%).

Chapter 6 reported \( o \)-methylphenyl radical reactions with \( C_3H_4 \) isomers: allene (\( CH_2CCH_2 \)) and propyne (\( CHCCH_3 \)). Synchrotron-based PIMS revealed two product mass channels for both allene and propyne reactions with \( o \)-methylphenyl radicals. The peaks at \( m/z \) 116 and 130 are consistent with \( CH_3 \) and H-atom loss, respectively. The \( CH_3 \) loss co-product is conclusively assigned indene (\( C_9H_8 \)). But, H-atom loss produced two different products for allene and propyne reactions: mostly 1,2- but traces of 1,4- dihydronaphthalene from allene reactions and exclusively 1,2-dihydronaphthalene from propyne reactions.

### 7.2 Future Directions

To extend the study of \( o \)-methylphenyl radical reactions with allene and propyne, an investigation of the reaction with \( ortho \)-hydroxylphenyl radicals is underway. Initial results indicate that products are benzofuran (\( C_8H_6O \)) and hydroxy-indene (\( C_9H_8O \)). Compared with \( ortho \)-methylphenyl radical reactions, this study will reveal the effect of the \( ortho \)-substituted in the context of reactions with small hydrocarbons.

Future experiments to test the conclusions presented in this thesis include: OH laser-induced fluorescence\(^3\) and threshold photoelectron photoion coincidence spectroscopy (TPEPICO).\(^4-6\) The laser-induced fluorescence of OH radicals can be used to record kinetic rates for OH formation from oxidation of neutral \( o \)-methyl- and
o-hydroxy-phenyl radicals. This information would facilitate a comparison between the neutral and distonic reaction kinetics, which ultimately can explain the impact of the charge-tag on the phenyl radical reactivity. Currently, for the distonic case, the appearance rate for a signal consistent with OH loss can be used to measure the appearance of OH radicals but there are no data for the neutral system. The second experiment, threshold photoelectron photoion coincidence spectroscopy (TPEPICO) has at times a key benefit over photoionisation spectra: vibronic structure. The photoionisation spectra of many isomers can be difficult to discriminate, e.g. o-, m-, and p-cresol. The photoelectron spectra from TPEPICO can exhibit defining features that distinguish isomers. Additionally, vibrationally-resolved photoelectron spectra can be simulated from quantum chemical outputs using programs like ezSpectrum\textsuperscript{7} and compared to reveal striking resemblances.\textsuperscript{8,9}

There are many reaction pathways after the addition of O\textsubscript{2} or C\textsubscript{3}H\textsubscript{4} to o-substituted phenyl radicals. While the salient pathways required to explain key reaction products are presented for this thesis, they are not exhaustive. To achieve a “complete” potential energy scheme that is able to predict accurate product distributions, with application of computational kinetics, it is necessary to identity all essential pathways. Ideally, we should utilise programs with chemical knowledge to complete our reaction mechanisms. Two approaches in automated chemical mechanism discovery are KinBot\textsuperscript{10,11} and Reaction Mechanism Generator (RMG).\textsuperscript{12} KinBot was developed by Zádor at the Combustion Research Facility, Sandia National Laboratories. This program expands potential energy schemes from quantum chemical calculations by applying knowledge of different reaction types (e.g. β-scission) to computed molecular structures. The optimised molecular geometries, calculated frequencies, rotational constants, and enthalpies can then be used in RRKM modelling. Reaction Mechanism Generator was developed by Green at Massachusetts Institute of Technology and West at Northeastern University. This program uses Benson’s group method\textsuperscript{13} to estimate thermal chemical data and expands an initial skeletal mechanism to include the most significant reaction pathways according to rates and reaction flux. A simple but distinguishing feature between the two programs is KinBot should locate all plausible mechanisms while RMG should locate the most significant mechanisms. If these approaches could be applied to understand the CO loss from o-benzoquinone, for example, we (i.e. a computer and myself) could elucidate new and salient mechanisms not predicted by a human alone.
Chapter 7. Conclusions and Future Directions

References


(7) V. A. Mozhaskiy and A. I. Krylov, ezSpectrum 3.0, iopenshell.usc.edu/downloads.


Appendix A

Appendix for Chapter 3:
Original Publication

Chapter 3 was published in a peer-reviewed publication and included here. The reference is provided below:

URL: http://dx.doi.org/10.1039/C3CP53690D
Hydroxyl radical formation in the gas phase oxidation of distonic 2-methylphenyl radical cations†

Matthew B. Prendergast,a Phillip A. Cooper,a Benjamin B. Kirk,a,b Gabriel da Silva,c Stephen J. Blanksbyab and Adam J. Trevitt*a,b

The reactions of distonic 4-(N,N,N-trimethylammonium)-2-methylphenyl and 5-(N,N,N-trimethylammonium)-2-methylphenyl radical cations (m/z 149) with O₂ are studied in the gas phase using ion-trap mass spectrometry. Photodissociation (PD) of halogenated precursor gives rise to the target distonic charge-tagged methylphenyl radical whereas collision-induced dissociation (CID) is found to produce unreactive radical ions. The PD generated distonic radicals, however, react rapidly with O₂ to form [M + O₂]+ and [M + O₂ – OH]+ ions, detected at m/z 181 and m/z 164, respectively. Quantum chemical calculations using G3SX(MP3) and M06-2X theories are deployed to examine key decomposition pathways of the 5-(N,N,N-trimethylammonium)-2-methylperoxyl radical and rationalise the observed product ions. The prevailing product mechanism involves a 1,5-H shift in the peroxy radical forming a QOOH-type intermediate that subsequently eliminates *OH to yield charge-tagged 2-quinone methide. Our study suggests that the analogous process should occur for the neutral methylphenyl + O₂ reaction, thus serving as a plausible source of *OH radicals in combustion environments.

1. Introduction

The study of aryl-radical + O₂ reactions is fundamental to understanding combustion chemistry due to the prevalence of aromatic hydrocarbons in liquid transportation fuels. Considerable work has been performed on the phenyl radical (C₆H₅•) and its reactions with O₂.1–10 Notably, phenyl oxidation does not follow the ROO → QOOH isomerisation route often encountered when rationalising hydrocarbon radical oxidation;11 instead, more elaborate peroxy radical isomerisation channels are accessed. For substituted phenyl radicals there remains significant uncertainty around the key mechanisms and dominant reaction products in their oxidation.

Toluene (C₆H₅CH₃) is utilised in transportation fuels at high levels because of its high energy density and research octane number12,13 and is also an intermediate in schemes of polycyclic aromatic hydrocarbon (PAH) and soot formation.14 The primary combustion intermediate associated with toluene is generally considered to be the benzyl radical (C₆H₅CH₂•), rather than methylphenyl radical isomers (C₆H₈CH₃•), due to the relatively large difference in C–H bond dissociation energies for methyl (ca. 90 kcal mol⁻¹) and ring (ca. 113 kcal mol⁻¹) hydrogens.15 Despite the difference in bond dissociation energies, abstraction reactions by reactive free radicals are expected to provide significant yields of methylphenyl radicals; for instance at 1000 K the product branching ratio for methylphenyl and benzyl radicals by *OH abstraction reactions is close to 1:3, increasing to 1:2 at 2000 K.16 The toluene C–CH₃ bond scission, yielding the phenyl radical, is also significant during thermal decomposition: 20% at 1200 K, and 40% at 1500 K.17 Likewise, decomposition of poly-methyl substituted benzenes, such as ortho-xylene, can produce methylphenyl radicals.18,19 Isomerisation of the methylphenyl radical to benzyl radical is generally competitive under high-temperature combustion conditions, however lifetimes of methylphenyl species near autoignition temperatures (∼1000 K) are such as to permit bimolecular reactions with O₂.19,20 Despite their plausible contribution in combustion environments, the methylphenyl + O₂ reaction has received relatively little attention. One computational study has suggested that the 2-methylphenyl + O₂ reaction is substantially different from that of the unsubstituted phenyl radicals, in which formation of 2-quinone methide + *OH is thought to compete (via a process shown in Scheme 1) with phenylperoxyl-type isomerisation.18 Experimental investigation of the methylphenyl + O₂ system can further the current understanding of toluene oxidation. However, identification and characterisation of

Received 1st September 2013,
Accepted 21st October 2013
DOI: 10.1039/c3cp53690d
www.rsc.org/pccp

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cp53690d
reaction intermediates and products remain a challenge. Charge-tagged derivatives of the methylphenyl radicals, i.e. the addition of a substituent with a formal charge, can be employed via mass spectrometry to qualitatively assess dominant reaction processes. Here, we provide the first experimental evaluation of 2-methylphenyl + O₂ reaction using the distonic radical ion approach.

Distonic ions are radical ions characterised by the spatial and electronic separation of the radical and charge site.

In this report we investigate the gas-phase synthesis and oxidation of distonic 2-methylphenyl radical cations. Radicals generated in a linear ion-trap mass spectrometer by both photodissociation (PD) and collision-induced dissociation (CID) of radicals generated in a linear ion-trap mass spectrometer by both photodissociation (PD) and collision-induced dissociation (CID) of mass-selected using an isolation window of 5–6 Th for at least 50 scans. In CID experiments, the normalised collision energy applied was typically 20–30 (arbitrary units) with an activation time of 30 ms set within the control software. Mass spectra presented herein are the average of at least 50 scans. In CID experiments, the normalised collision energy applied was typically 20–30 (arbitrary units) with an activation time of 30 ms set within the control software. 2.2 Mass spectrometry

Experiments were performed on a modified Thermo Fisher Scientific LTQ linear quadrupole ion-trap mass spectrometer (San Jose, USA) fitted with an IonMax electrospray ionisation source operated in positive ion mode (+ESI) and controlled by Xcalibur 2.0 software. Ions were generated by infusing 5–15 μM methanolic solutions of 4-bromo-N,N,N,N3-tetramethylbenzenaminium (4Br3Me), 3-bromo-N,N,N,N4-tetramethylbenzenaminium (3Br4Me), 3-iodo-N,N,N,N4-tetramethylbenzenaminium (3I4Me), and 4-iodomethyl-N,N,N,N-trimethylbenzenaminium (4IMe) iodide salts into the electrospray ion source at 5 μL min⁻¹. Typical instrumental settings were: spray voltage (4.5 kV), capillary temperature (200 °C), sheath gas flow at 5 (arbitrary units), sweep and auxiliary gas flow at 10 (arbitrary units). Ions were mass-selected using an isolation window of 5–6 Th for 4Br3Me and 3Br4Me, and 1–2 Th for 3I4Me and 4IMe with a q-parameter of 0.250. Mass spectra presented herein are the average of at least 50 scans. In CID experiments, the normalised collision energy applied was typically 20–30 (arbitrary units) with an activation time of 30 ms set within the control software.

2.1 Materials

4-Bromo-3-methylaniline (97%), 3-bromo-4-methylaniline (98%), and methyl iodide (99.5%) were purchased from Sigma Aldrich (Milwaukee, USA). 3-Iodo-4-methylaniline (98%) was purchased from Alfa Aesar (Ward Hill, USA). 4-(Dimethylamino)benzyl alcohol was purchased from TCI Chemicals (Tokyo, Japan). Acetonitrile, ethyl acetate, methanol (HPLC grade), petroleum ether and potassium carbonate (anhydrous) were purchased from Ajax (Sydney, Australia). Industrial grade O₂ was obtained from BOC gases (Sydney, Australia). All commercial compounds were used without additional purification.

4-Bromo-N,N,N3-tetramethylbenzenaminium (4Br3Me), 3-bromo-N,N,N4-tetramethylbenzenaminium (3Br4Me) and 3-iodo-N,N,N4-tetramethylbenzenaminium (3I4Me) iodide salts were synthesised by N-methylation of the corresponding primary amines listed above using a method previously described with modifications detailed in Section S1 of the ESI. 4-Iodomethyl-N,N,N-trimethylbenzenaminium (4IMe) iodide was synthesised from 4-(dimethylamino)benzyl alcohol by N-methylation followed by iodo-dehydroxylation. Synthesised compounds were characterised by ¹H NMR, data provided in Section S2 (ESI).

2.2.1 Photodissociation (PD). The modifications to the ion-trap mass spectrometer allowing optical access to trapped ions are similar to those previously reported and are described in detail elsewhere. Briefly, a 10 mm aperture was milled into the removable backplate of the vacuum chamber. A 2.75 inch quartz viewport was mounted over the aperture with a CF flange. At the beginning of a MS sweep and auxiliary gas flow at 10 (arbitrary units). Ions were mass-selected using an isolation window of 5–6 Th for 4Br3Me and 3Br4Me, and 1–2 Th for 3I4Me and 4IMe with a q-parameter of 0.250. Mass spectra presented herein are the average of at least 50 scans. In CID experiments, the normalised collision energy applied was typically 20–30 (arbitrary units) with an activation time of 30 ms set within the control software.

2.2.2 Ion–molecule reactions. O₂ is present in background concentrations due to the use of an atmospheric pressure ionisation source. Typically, N₂ is used as the nebulising gas within the ionisation source, however, to increase the background O₂ concentration, O₂ can be used instead. The O₂ concentration (molecule cm⁻³) within the ion trap region was derived by following the 4-[N,N,N-trimethylammonium]phenyl radical + O₂ reaction kinetics, which has a known second-order rate coefficient (k₂) of 2.8 × 10⁻¹¹ cm³ molecule⁻² s⁻¹.
The O₂ concentration within the ion trap was measured at 2.2 × 10⁻⁹ molecule cm⁻³ for background O₂ with the standard nitrogen nebuliser gas, and 8.6 × 10⁻⁹ molecule cm⁻³ with O₂ used as the nebuliser gas.

The stoichiometric excess of O₂, by many orders of magnitude, established pseudo-first order kinetic behaviour with reactive ions. Reaction times of 0.030–10 s were achieved by setting the reaction time parameter with the control software while the normalised collision energy was maintained at 0 (arbitrary units). Measured pseudo-first order (k₁) and second-order (k₂num) rate coefficients were extracted from the slope of a semi-logarithmic plot of normalised abundance against reaction time.

Statistical errors in rate measurements were typically 2σ < 5%, where σ is the standard deviation obtained from the least-squares fit to the pseudo-first order decay. Systematic uncertainty in the ion-trap pressure and O₂ concentration, and the formation of neutrals or ions with a m/z less than the low mass cut-off (ca. 50 Th) result in a upper limit of 50% uncertainty in second-order rate coefficients (k₂num). Reported reaction efficiencies are calculated from the second-order rate coefficient as a percentage of the reactants’ collision frequency derived from average dipole orientation (ADO) theory.

2.3 Quantum chemical calculations

Electronic structure calculations were performed using both the M06-2X®/6-311+G(d,p) density functional theory and G3/SQ(MP3) composite method in the Gaussian 09 program. All stationary points were characterised as either minima (no imaginary frequencies) or transition states (one imaginary frequency). All reported energies are at 0 K and include zero-point energy corrections. The selected theoretical methods are capable of reproducing well-defined test set barrier heights to within 1.5 kcal mol⁻¹, on average.

3. Results and discussion

3.1 Synthesis of distonic 2-methylphenyl radical cations

Two synthetic routes for the production of radical cations within the linear ion-trap mass spectrometer were compared: laser photodissociation (PD) and collision-induced dissociation (CID). Methanolic solutions of the precursor iodide salts were infused via positive electrospray ionisation (þESI) to yield the M⁺ ions at m/z 228 and 230 for the brominated (4Br3Me and 3Br4Me), and m/z 276 for the iodinated (3I4Me and 4I4Me) precursor ions, as listed in Table 1.

Isolation and subsequent PD of the M⁺ ions listed in Table 1 resulted in m/z 149 product ions consistent with the loss of the halogen atom (ESI,† Fig. S1). PD of the brominated precursors 4Br3Me and 3Br4Me resulted also in [M – Br – 15]⁺ signal at m/z 134 and [M – CH₃]⁺ signal at m/z 213 and 215. In the case of PD of the iodinated precursors 3I4Me and 4I4Me, m/z 134 is also apparent and likely corresponds to [M – I – CH₃]⁺.

The dominant product observed after CID of 4Br3Me, 3Br4Me, and 3I4Me was the [M – 15ℶ]⁺ ion at m/z 213 and 215 for the brominated species (both Br isotopes), and m/z 261 for 3I4Me. These odd-electron processes are consistent with CH₃ loss from the trimethylammonium charge tag of the respective M⁺ ions. Minor ion signal at m/z 149 is assigned to ejection of the halogen. In contrast, CID of 4I4Me resulted predominately in the m/z 149 and 134 ions, assigned as loss of ℶ following elimination of a methyl radical from the charge tag, respectively.

Activation of 4Br3Me, 3Br4Me, 3I4Me, and 4I4Me ions by both PD and CID resulted in formation of m/z 149 ions with varying efficiencies. PD of the 4Br3Me, 3Br4Me, and 3I4Me halogenated precursors resulted in significantly higher abundances of the putative distonic radical ion (ca. 25–45%) than CID (ca. <2%). In contrast, CID of the 4I4Me ion resulted in a notably higher abundance of the m/z 149 ion (ca. 90%) than that observed for the PD route (ca. 10%). In each case, the m/z 149 ion population was isolable and probed by reactions with O₂.

3.2 Charge-tagged 2-methylphenyl + O₂

The m/z 149 ions generated by PD and CID of 4Br3Me, 3Br4Me, 3I4Me, and 4I4Me were isolated and allowed to react with background O₂ over time periods of 0.030–10 s. Mass spectra measured with a reaction time of 2 s are provided in Fig. 1. Second-order rate coefficients (k₂num) were derived and are discussed below in Section 3.2.1. Isolation of m/z 149 ions, generated by PD of 4Br3Me, 3Br4Me, and 3I4Me, in the presence of background O₂ resulted in a small [M + 32ℶ]⁺ product ion signal at m/z 181, consistent with the formation of a peroxy radical.

Table 1 Distonic radical ions [M⁺] introduced by þESI of methanolic solutions of the corresponding salt

<table>
<thead>
<tr>
<th>Precursor ions [M⁺]</th>
<th>Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Bromo-N,N,N,3-tetramethylbenzenaminium cation (m/z 228 and 230)</td>
<td><img src="Image" alt="Structure Image" /></td>
<td>4Br3Me</td>
</tr>
<tr>
<td>3-Bromo-N,N,4-tetramethylbenzenaminium cation (m/z 228 and 230)</td>
<td><img src="Image" alt="Structure Image" /></td>
<td>3Br4Me</td>
</tr>
<tr>
<td>3-Iodo-N,N,4-tetramethylbenzenaminium cation (m/z 276)</td>
<td><img src="Image" alt="Structure Image" /></td>
<td>3I4Me</td>
</tr>
<tr>
<td>4-(Iodomethyl)-N,N,N-trimethylbenzenaminium cation (m/z 276)</td>
<td><img src="Image" alt="Structure Image" /></td>
<td>4I4Me</td>
</tr>
</tbody>
</table>
The dominant product observed was the [M + 15]⁺ ion at m/z 164 rationalised by O₂ addition and subsequent *OH elimination, as depicted in Scheme 2. This is consistent with the *OH elimination mechanism proposed in the theoretical study of the analogous neutral 2-methylphenyl radical + O₂ reaction by da Silva et al.¹⁸ (Scheme 1). CID of m/z 164 ions (ESI† Fig. S2) gives rise to m/z 149, presumably the result of CH₃ (15 Da) loss from the trimethylammonium charge tag. There is also a product ion consistent with CO (28 Da) loss at m/z 136, and another at m/z 121 consistent with both loss of CH₃ and CO. The primary fragmentation pathway for the neutral 2-quinone methide is loss of CO.⁴⁶,⁴⁹ A more detailed mechanism and energy schematic, including the formation of m/z 164, will be outlined below. The reactions of m/z 149 ions with O₂, after PD of 4IMe, yielded only traces of oxidation products likely the result of contamination by isomeric distonic radical cations as the majority of the m/z 149 species is likely to be the resonance stabilised benzyl radical.

Prolonged isolation (up to 10 s) of m/z 149 ions generated by CID of 4Br3Me, 3Br4Me, and 4IMe under the same experimental conditions [Fig. 1(b), (d) and (h)] did not result in observable [M + O₂]⁺ or [M + O₂ – OH]⁺ product ions, while isolation of m/z 149 ions from CID of 3I4Me resulted in only low intensity signals at corresponding m/z ratios [Fig. 1(e) with ×5 magnification compared to Fig. 1(f) with ×50]. The low abundance, or even absence, of the respective [M + O₂]⁺ and [M + O₂ – OH]⁺ ions, when compared with analogous PD experiments, suggests that the m/z 149 ions resulting from CID of 4Br3Me and 3Br4Me are less reactive isomeric species born from CID-induced rearrangement. The isomerisation of phenyl-type radical cations upon CID of halogenated precursors has been previously noted.⁵⁰ Herein, PD was used for all subsequent experiments.

3.2.1 Reaction kinetics. The reactions of PD generated m/z 149 ions with O₂ were further characterised by second-order rate coefficients (k₂nd cm² molecule⁻¹ s⁻¹) and reaction efficiencies (Φ), reported in Table 2, derived from measured pseudo-first order rate coefficients at background O₂ ([O₂] = 2.23 × 10⁹ molecule cm⁻³) and increased O₂ concentrations ([O₂] = 8.53 × 10²⁰ molecule cm⁻³). The O₂ collision frequency calculated with average dipole orientation (ADO) theory⁴³ is 5.7 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for all species of m/z 149. Pseudo-first order kinetic behaviour, as shown by a linear semi-logarithmic plot (Fig. 2), is observed for m/z 149 ions generated by PD of 4Br3Me, 3Br4Me and 3I4Me, implying that each of these radical ion populations consist of only a single species.⁵⁰,⁵¹ The general agreement between k₂nd values for radical ions generated by PD

![Table 2](attachment:table2.png)

Table 2: Second-order rate coefficients (k₂nd cm² molecule⁻¹ s⁻¹) and reaction efficiencies (Φ) for reactions of PD generated distonic radicals with O₂ (molecule cm⁻³). Estimated upper limit of 50% uncertainty in second-order rate coefficients. O₂ collision frequency from average dipole orientation (ADO) theory⁴³ is 5.7 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for all species of m/z 149

**Precursor ions** | **Distonic radicals** | **[O₂] (molecule cm⁻³)** | **k₂nd (cm² molecule⁻¹ s⁻¹)** | **Φ (%)**
---|---|---|---|---
4Br3Me | 4-(N,N,N-Trimethylammonium)-2-methylphenyl | 2.23 × 10⁹ | 2.4 × 10⁻¹¹ | 4.1
 | 8.53 × 10⁹ | 2.1 × 10⁻¹¹ | 3.7
3Br4Me | 5-(N,N,N-Trimethylammonium)-2-methylphenyl | 2.23 × 10⁹ | 2.9 × 10⁻¹¹ | 5.1
 | 8.53 × 10⁹ | 2.6 × 10⁻¹¹ | 4.5
3I4Me | 5-(N,N,N-Trimethylammonium)-2-methylphenyl | 2.23 × 10⁹ | 2.8 × 10⁻¹¹ | 5.0
 | 8.53 × 10⁹ | 2.6 × 10⁻¹¹ | 4.6
4I Me | 4-(N,N,N-Trimethylammonium)-benzyl | 2.23 × 10⁹ | — | —
 | 8.53 × 10⁹ | — | —

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PCCP  
Published on 29 October 2013. Downloaded by University of Wollongong on 25/10/2016 01:05:39.
The \( m/z \) 149 species generated by PD of \( 4\text{Ime} \) expected to provide a benzylic radical ion for comparison, was unreactive on the timescale of these experiments (0.030–10 s). The addition of \( \text{O}_2 \) to the neutral benzy1 radical is reported to produce a benzylperoxyl radical with a reaction exothermicity of 22 kcal mol\(^{-1}\); however, reformation of benzyl + \( \text{O}_2 \) reactants dominates at low temperatures.\(^{33} \) In the analogous charge-tagged benzy1 radical + \( \text{O}_2 \) reaction, it is expected that upon \( \text{O}_2 \) addition the vibrationally excited charge-tagged benzylperoxyl radical will dissociate to regenerate the charge-tagged benzy1 + \( \text{O}_2 \) before being collisionally deactivated in the ion trap or undergoing further unimolecular reaction.

### 3.2.2 Reaction mechanism.

Fig. 3 depicts a potential energy diagram for the addition of \( \text{O}_2 \) to the \( \text{S}(\text{N},\text{N},\text{N}-\text{trimethylammonium})-2\text{-methylphenyl radical cation} \) (generated by PD of \( 3\text{Br}4\text{Me} \) or \( 3\text{I}4\text{Me} \)). This scheme essentially reproduces the reaction mechanism identified in the analogous neutral system.\(^{18} \) Energies were calculated using the M06-2X/6-311++G(d,p) (black) and G3SX(MP3) (blue) methods, reported in kcal mol\(^{-1}\) relative to the peroxyl radical intermediate. The ensuing discussion will refer to the G3SX(MP3) energies.

The addition of \( \text{O}_2 \) to the charge-tagged 2-methylphenyl radical (I) proceeds without a barrier and results in a charge-tagged methylphenylperoxyl species (II) with 46.4 kcal mol\(^{-1}\) activation. Fig. 3 depicts four low-energy unimolecular reaction pathways available to the charge-tagged 2-methylphenylperoxyl radical. First, the reverse reaction reforms the distonic 2-methylphenyl radical + \( \text{O}_2 \) (I); second, formation of a phenoxy radical + \( \text{O}(^3\text{P}) \) (III); third, isomerisation to methyl-oxepinoxyl species (V and VI); and fourth, the generation of charge-tagged 2-quinone methide + \( \text{OH} \) (VIII). In the context of...
forming new product species, the latter three pathways will be discussed further below.

Formation of 5-[N,N,N-trimethylammonium]-2-methylphenoxyl + O(3P) ([II]) occurs via cleavage of the peroxyl RO-O bond. Delocalisation of the unpaired electron is evidenced by a predicted contraction of the C-O bond from 1.392 Å in the peroxyl to 1.235 Å in the phenoxy, closer to that expected for a CO double bond. The barrier for this process is calculated at 38.8 kcal mol⁻¹ compared with 46.4 kcal mol⁻¹ for the reactants. The O(3P) loss mechanism would result in a m/z 165 ion corresponding to the 16 Da mass loss. Subsequent CO loss from this phenoxy radical[10] would result in an [M + O₂ – O – CO]⁺ ion at m/z 137. Neither O atom nor CO loss product ions were observed within the detection limits of the experiment pointing to a lack of competitiveness for this pathway. Other accessible pathways outcompete the O(3P) loss channel as shown by the dominance of alternate product channels in Fig. 1.

The third pathway from II proceeds by ipso addition of the peroxyl radical oxygen to the aromatic ring (TS II → IV, 25.4 kcal mol⁻¹) resulting in the dioxiranyl intermediate (IV). The sequential transition states, TS1 (37.5 kcal mol⁻¹) and TS2 (30.7 kcal mol⁻¹), succeeding the dioxiranyl intermediate, represent a bifurcation[10] of the potential energy surface. Following the intrinsic reaction coordinate (IRC) from TS1, reactive species encounter a valley-ridge inflection (VRI) near which the single reaction pathway becomes two. Past the VRI, along the developing ridge, the second transition state (TS2) is located, which connects the charge-tagged 3-methyloxepinoyl (V) and 7-methyl-oxepinoyl (VI) species (confirmed by calculation of the IRC for TS2). Ring-opening of the dioxiranyl moiety (TS1), i.e., cleavage of the dioxiranyl O-O bond, has a barrier that is 8.9 kcal mol⁻¹ less than the chemical activation of the system. At these temperatures (ca. 307 K), we do not expect any significant reaction flux through TS1 due to its high energy (37.5 kcal mol⁻¹), thus these pathways were not extended beyond the methylxepinoy radicals [V and VI]. Guided by Kirk et al.,[11] it is likely the end-product species could comprise five-membered ring products, such as a charge-tagged methyl-substituted cyclopentadienone species but no such channels were detected in our charge-tagged experiments. This implicates the presence of lower-energy reaction pathways not available to the charge-tagged phenylperoxyl radical systems investigated by Kirk et al.

The final pathway considered here leads to charge-tagged 2-quinone methide via H-migration followed by *OH elimination. The 1.5-H shift (via TS VII → VII) proceeds with a 27.2 kcal mol⁻¹ barrier (19.1 kcal mol⁻¹ below the reactants' energy) and results in a hydroperoxybenzyl radical species (VII), reminiscent of a QOOH combustion intermediate. The formation of this radical is facilitated by close proximity of the labile benzylc methyl hydrogen to the peroxy group.[18] The forward reaction barrier of 9.4 kcal mol⁻¹ for TS VII → VIII is considerably less than that for the reverse reaction (22.7 kcal mol⁻¹). Thus, H atom migration and *OH elimination is energetically competitive and results in the formation of charge-tagged 2-quinone methide (VIII), consistent with the [M + O₂ – OH]⁺ ion detected at m/z 164, shown in Fig. 1 (left panel).

References


Hydroxyl Radical Formation in the Gas Phase Oxidation of Distonic 2-Methylphenyl Radical Cations

Matthew B. Prendergast,¹ Phillip A. Cooper,¹ Benjamin B. Kirk,¹,² Gabriel da Silva,³
Stephen J. Blanksby,¹,² and Adam J. Trevitt.¹,²,*

SUPPORTING INFORMATION

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2. ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, University of Wollongong, NSW 2522, Australia.
3. Department of Chemical and Biomolecular Engineering, The University of Melbourne, VIC 3010, Australia
1. Methylation of halogen-substituted methylaniline

Scheme S1 Overview of synthesis for \(N,N,N\)-trimethylammonium charge tagged aniline derivatives

The 4-iodomethyl-\(N,N,N\)-trimethylbenzenaminium, 3-iodo-\(N,N,N\),4-tetramethylbenzenaminium, 3-bromo-\(N,N,N\),4-tetramethylbenzenaminium and 4-bromo-\(N,N,N\),3-tetramethylbenzenaminium iodide salts were synthesised using a modified procedure previously reported by Kirk et. al. for the synthesis of 4-iodo-\(N,N,N\)-trimethylbenzenaminium iodide.\(^1\) In brief, to a reaction vial was added halogenated aniline species (ca. 1 mmol), 10 mL of dry CH\(_3\)OH, and CH\(_3\)I (0.7 mL, 10 mol equiv) that was then heated at reflux for two hours. K\(_2\)CO\(_3\) (0.2 g, 1.3 mmol) was added to the reaction vial and the solution heated at reflux for a further two hours. The solvent was removed \textit{in vacuo} and the crude product recrystallised from CH\(_3\)CN. The recrystallised solid was washed with diethyl ether and dried.
2. Structural characterisation

4-bromo-3-methyl-N,N,N-trimethylbenzenaminium iodide. $^1$H NMR (300 MHz, D$_2$O): $\delta$ 2.49 (s, 3H), $\delta$ 3.64 (s, 9H), $\delta$ 7.55 (dd, 1H, $J = 8.79$, 3.21 Hz), $\delta$ 7.80 (d, 1H, $J = 2.05$ Hz), $\delta$ 7.21 (d, 1H, $J = 9.07$ Hz).

3-bromo-4-methyl-N,N,N-trimethylbenzenaminium iodide. $^1$H NMR (300 MHz, D$_2$O): $\delta$ 2.45 (s, 3H), $\delta$ 3.64 (s, 9H), $\delta$ 7.55 (d, 1H, $J = 8.79$ Hz), $\delta$ 7.72 (dd, 1H, $J = 8.5$, 2.64 Hz), $\delta$ 8.10 (d, 1H, $J = 2.93$ Hz).

3-iodo-4-methyl-N,N,N-trimethylbenzenaminium iodide. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.35 (s, 1H), $\delta$ 7.90 (d, H, $J = 7.3$ Hz), $\delta$ 7.56 (d, 1H, $J = 8.8$ Hz), $\delta$ 3.57 (s, 9H), $\delta$ 2.43 (s, 3H).

3-iodo-4-methyl-N,N,N-trimethylbenzenaminium iodide. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.90 (d, 2H, $J = 8.6$ Hz), $\delta$ 7.67 (d, 2H, $J = 8.8$ Hz), $\delta$ 4.67 (s, 2H), $\delta$ 3.59 (s, 9H).
3. Supplementary Mass Spectra

**Figure S1** Gas-phase ions produced by ESI of 4Br3Me (a and b), 3Br4Me (c and d), 3I4Me (e and f) and 4IMe (g and h) were isolated and activated by PD (left panel) and CID (right panel) to generate the m/z 149 ions via loss of the halogen.
Figure S2 CID of m/z 164 ions generated via PD of 3-bromo-4,N,N,N-tetramethylbenzenaminium (3Br4Me) and subsequent isolation of the resultant m/z 149 ions for 10 s in the presence of background O₂. Peaks at m/z 149 (15 Da loss), 136 (28 Da loss), and 121 (43 Da loss) are consistent with loss of CH₃, CO, and both CH₃ and CO, respectively.²,³
4. Computational results

Table S1 Comparison of M06-2X/6-311++G(d,p) and G3SX(MP3) energies presented in kcal mol$^{-1}$ relative to the initial intermediate (II) for the charge-tagged 2-methylphenyl + O$_2$ reaction.

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Average difference 2.7

Table S2 Geometries optimised by M06-2X/6-311++G(d,p) method provided in Cartesian coordinates for intermediates and transition states identified in Figure 3 of the main document

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Appendix B

Appendix for Chapter 5:
Original Publication

‘Article below removed for copyright reasons, please refer to the citation: citation’

Chapter 5 was published in a peer-reviewed publication and included here. The reference is provided below:

URL: http://dx.doi.org/10.1039/C5CP02953H