Formation and stability of gas-phase o-benzoquinone from oxidation of ortho-hydroxyphenyl: a combined neutral and distonic radical study
Formation and stability of gas-phase \(\text{o-benzoquinone from oxidation of ortho-hydroxyphenyl: a combined neutral and distonic radical study}^{+}\)

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Gas-phase product detection studies of \(\text{o-hydroxyphenyl radical and } \text{O}_2\) 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 \(\text{o-benzoquinone (C}_6\text{H}_4\text{O}_2, \text{m/z} \ 108\) and cyclopentadienone \((\text{C}_5\text{H}_4\text{O}, \text{m/z} \ 80)\). It is concluded that cyclopentadienone forms as a secondary product from prompt decomposition of \(\text{o-benzoquinone (and dissociative ionization of } \text{o-benzoquinone may contribute to the m/z 80 signal at photon energies } \geq 9.8 \text{ eV). Ion-trap reactions of the distonic } \text{o-hydroxyphenyl analogue, the 5-ammonium-2-hydroxyphenyl radical cation, with } \text{O}_2\) are also reported and concur with the assignment of \(\text{o-benzoquinone as the dominant product. The ion-trap study also provides support for a mechanism where cyclopentadienone is produced by decarbonylation of } \text{o-benzoquinone. Kinetic studies compare oxidation of the ammonium-tagged } \text{o-hydroxyphenyl and } \text{o-methylphenyl radical cations along with trimethylammonium-tagged analogues. Reaction efficiencies are found to be ca. 5% for both charge-tagged } \text{o-hydroxyphenyl and } \text{o-methylphenyl radicals irrespective of the charged substituent. G3X-K quantum chemical calculations are deployed to rationalise experimental results for } \text{o-hydroxyphenyl + } \text{O}_2\) and its charge-tagged counterpart. The prevailing reaction mechanism, after \(\text{O}_2\) addition, involves a facile 1,5-H shift in the peroxyl radical and subsequent elimination of OH to yield \(\text{o-benzoquinone that is reminiscent of the Waddington mechanism for } \beta\text{-hydroxyperoxyl radicals. These results suggest } \text{o-hydroxyphenyl + } \text{O}_2\) and decarbonylation of \(\text{o-benzoquinone serve as plausible OH and CO sources in combustion.}

Phenol is a product of catechol thermal decomposition,⁷ benzene and hydroxyl radical reactions⁸ as well as phenyl⁹ 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 \(\beta\text{-hydroxyphenyl radical is an intermediate in the pyrolysis reaction reported for dimethoxybenzene (a model compound for the } \beta\text{-04 aryl ether unit within G-type lignin).¹⁵ The addition of } \text{O}_2\) to the \(\beta\text{-hydroxyphenyl radical site will produce the } \beta\text{-hydroxyphenylperoxyl radical, with its hydroxy H-atom within close proximity to the peroxyl radical substituent. As is the case for the } \beta\text{-methylphenylperoxyl radical,¹⁶,¹⁷ } \beta\text{-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. This mechanism was reported for the oxidation of protonated tyrosinyl radicals and has some similarities to the Waddington mechanism for β-hydroxypersulphyl radicals. Yet, to date, no direct experimental results have validated this mechanism for the o-hydroxyphenyl + O₂ reaction system.

In this work, we report reactions of gas-phase o-hydroxyphenyl with O₂ 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. These distonic ion oxidation experiments build on a framework provided by previous studies of distonic phenyl and o-methylphenyl radical oxidation. In combination, we show that OH elimination follows the reaction of o-hydroxyphenyl radicals with O₂ to form o-BQ. The stability of this nascent o-BQ is also investigated.

2. Experimental

2.1 Synchrotron photoionisation mass spectrometry

The o-hydroxyphenyl + O₂ reaction was investigated using time-resolved photoionisation mass spectrometry at the Chemical Dynamics Beamline at the Advanced Light Source (ALS at Lawrence Berkeley National Laboratories, USA). The apparatus comprises a slow-flow tube reactor, a 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 flow velocities are as follows: 10.1 m s⁻¹ at 4 Torr (533.3 Pa). The vapour pressure of o-bromophenol was entrained in He gas using a fritted bubbler with the liquid sample maintained at 291 K (18 °C) and 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 × 10¹⁷ molecule cm⁻³ at 373 K, 7.7 × 10¹⁶ molecule cm⁻³ at 500 K, and 6.4 × 10¹⁶ molecule cm⁻³ at 600 K.

The gas that escapes through the 650 μm 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 (2σ) for a mean of at least three measurements at 373 and 500 K, and two measurements at 600 K.

2.2 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 μM 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 μL 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.

2.2.1 Photodissociation (PD). Modifications to the ion-trap mass spectrometer required for PD of trapped ions are similar to those previously reported and are detailed elsewhere. At the beginning of a specified MS² 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, λ = 266 nm) such that only a single laser pulse is delivered per MS² 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.

2.2.2 Ion-molecule reactions. Distonic radical cations generated within the ion trap were mass selected and then allowed to
react with O₂ for 0.030–10 000 ms (set by the control software). Background O₂ resides in the trap due to air entrained by the atmospheric pressure ESI source. Reactions were also conducted with an increased O₂ concentration by using a He bath gas doped with O₂ (770 ± 45 ppm; BOC, Australia). Similarly, a He bath gas doped with oxygen-18 was used for isotopic labelling experiments.

The O₂ concentration (molecule cm⁻³) within the ion-trap region was determined using the measured pseudo-first order rate coefficient for 3-carboxylatoadamantyl + O₂ and its known second-order rate coefficient of 8.5 ± 0.4 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ with the O₂ concentration determined for each experiment. The background O₂ concentration within the ion trap is typically 6.4 × 10⁹ molecule cm⁻³ and the increased O₂ concentrations ranged from 1.6–2.2 × 10¹¹ molecule cm⁻³ with an O₂-doped bath gas. The effective temperature of ions stored within a linear quadrupole ion trap has been estimated at 318 ± 23 K, consistent with an earlier estimate of 307 K.⁵⁷

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 (0.030–10 000 ms) to track changes in ion signal intensity due to reactions with O₂. Measured pseudo-first order rate coefficients (k₁₈) were obtained by fitting eqn (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 eqn (1) are consistent with pseudo-first order kinetic behaviour. Thus, allowing the second-order rate coefficient (k₂₉₂) to be calculated using eqn (2) with a measured [O₂]. The residual plots accompanying kinetic curves in Fig. 5, Fig. S7, and S8 (ESI†) show the difference between the average normalised integrated ion signal intensity and the expected value from eqn (1), i.e. the residuals, plotted as a function of reaction time.

\[ y = A_0 \exp(-k_{18}t) + \text{constant} \]  
\[ k_{292} = \frac{k_{18}}{[O_2]} \]

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 + O₂ is an average from 17 decay curves over three experiments at low [O₂] and 20 decay curves over two experiments at increased [O₂]. The 5-ammonium-2-methylphenyl + O₂ second order rate coefficient is calculated as the average of 19 decay curves at low [O₂] and 30 decay curves at increased [O₂] over three experiments at each concentration. The second-order rate coefficient for 5-(N,N,N-trimethylammonium)-2-hydroxyphenyl radical + O₂ is an average of 5 decay curves at low [O₂]. 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.⁴⁹

Statistical uncertainty from fitting pseudo-first order rate coefficients (k₁₈) to experimental decay curves was typically 2σ ≤ 10%. Systematic uncertainty in the ion-trap pressure and O₂ 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 O₂ concentration that is accumulated in reported second-order rate coefficients and reaction efficiencies.

### 2.3 Quantum chemical calculations

Reaction enthalpies were calculated from electronic energies computed with the G3X-K composite method⁴⁰ 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 set⁴² to within 1 kcal mol⁻¹, on average.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⁻¹ (0.05 eV) for AIEs⁴³,⁴⁴ and 2 kcal mol⁻¹ for barriers from the DBH24/08 database.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.⁴⁵ All reported energies include the zero-point energy correction for 0 K enthalpies and AIEs.

### 2.4 Materials

3-Bromo-4-methylaniline, 4-amino-2-bromophenol, oxygen-18 (97%), and o-bromophenol (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-N,N,N-trimethylbenzenaminium iodide is described in Section 1 of the ESI†.

### 3. Results and discussion

#### 3.1 Synchrotron photoionisation mass spectrometry: o-hydroxyphenyl + O₂

Fig. 1a is a product mass spectrum after photolysis of o-bromophenol with no O₂ 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 /m/z 92 and 94. The photoionisation (PI) spectra for /m/z 92 and 94 (not shown) are well matched to the integrated photoelectron spectrum for cyclopenta-2,4-dien-1-ylidene-methanone (C₅H₄CO, AIE = 8.09 eV)⁴⁶–⁴⁸ and the known photoionisation spectrum for phenol (C₆H₅OH, AIE = 8.49 eV),⁴⁹–⁵¹ 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-ylidenemethanone (C$_5$H$_4$CO, $m/z$ 92) may arise from o-bromophenol photolysis via HBr loss$^{52}$ and phenol (C$_6$H$_5$OH, $m/z$ 94) is probably formed via H-abstraction by the $m/z$ 93 radical from the abundant o-bromophenol precursor.

Fig. 1b is a product mass spectrum from photolysis of o-bromophenol in the presence of 7.7 x 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 Fig. 2a and b. PI spectra at 500 K and 600 K are provided in the ESI† (Fig. S1 and S2, 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)$^{53-55}$ and consistent with AIEs provided in Table 1. Ionization onsets for CPO and o-BQ were recently reported by Ormond et al.$^{53}$ and compared within the inset of Fig. 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$^{55,56}$ 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 (ESI† Fig. S3) could result, in part, from decomposition of o-hydroxyphenyl peroxy to o-hydroxyphenoxyl + O(3P). 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 Fig. S3 (ESI†) and kinetic traces in Fig. S5 (ESI†) 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$_4$OH$^+$, $m/z$ 110).

The detection of o-BQ ($m/z$ 108) is rationalised by O$_2$ addition to the o-hydroxyphenoxyl radical, followed by isomerisation...
of the hydroxyphenylperoxyl intermediate to hydroperoxyphenoxyl and subsequent OH loss to form o-BQ (Scheme 1). This pathway is analogous to the O₂ addition and subsequent OH loss mechanism that operates in the o-methylphenyl + O₂ reaction and OH loss in the Waddington mechanism for β-hydroxyperoxyl radicals.

Scheme 1 also includes pathways from o-BQ that lead to CPO and the CPO radical cation that will now be discussed.

Included in Fig. 2a are reference PI spectra for CPO from Yang et al. and Parker et al. The close agreement between the m/z 80 and reference PI spectra shown in Fig. 2a from 9 to 9.8 eV support our assignments of o-BQ, m/z 80 as CPO. It is evident that at PI energies ≥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 (Fig. S1–S3) require further examination.

The systematic differences between the m/z 80 signal and CPO reference spectra in Fig. 2a at photoionisation energies ≥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). Fig. S3 (ESI†) shows product mass spectra at 373, 500 and 600 K integrated over two energy ranges; 9.40–9.75 eV (Fig. S3a–c, ESI†) and 9.85–10.00 eV (Fig. S3d–f, ESI†). 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 (Fig. S4a, ESI†) 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, Fig. S4b, ESI†), 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 Fig. 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 \( \geq 9.8 \) 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 + \( \text{O}_2 \) reactions,\(^{59-62}\) 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 3.2 and prohibitively high energy pathways reported in Section 3.3.3. Ultimately, we propose that the \( m/z \) 80 and 108 products are generated according to processes summarised in Scheme 1: the o-hydroxyphenyl radical undergoes \( \text{O}_2 \) 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.\(^{19-26}\) In addition, dissociative ionisation of o-BQ possibly contributes to the measured \( m/z \) 80 signal at energies \( \geq 9.8 \) eV.

To further establish connections between the reaction products of o-hydroxyphenyl + \( \text{O}_2 \) (cf. Scheme 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.\(^{17,63,64}\) Quantum chemical calculations were also conducted, and discussed later in Section 3.3, to rationalise experimental results for both the neutral and charge-tagged systems.

### 3.2 Ion-trap mass spectrometry: distonic o-hydroxyphenyl + \( \text{O}_2 \)

Photodissociation (PD, \( \lambda = 266 \) 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 Fig. 4a. The \( m/z \) 109 ion, consistent with Br loss, was assigned to the 5-ammonium-2-hydroxyphenyl radical cation shown in Scheme 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 (0.030–10 000 ms). A mass spectrum acquired with 2000 ms reaction time is shown in Fig. 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.

The mass spectrum in Fig. 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 + \( \text{CO} \). 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, Fig. 4d) and exclude any contribution of \( \text{NH}_3 \) loss (\(-17 \) Da).

Isolation and subsequent CID of the \( m/z \) 126 ions resulted in fragments at \( m/z \) 96 and 98 consistent with loss of \( \text{C}_2\text{H}_3\text{O} \) and \( \text{C}_2\text{H}_4\text{O} \) 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 2. These data do not provide evidence for a “phenyl-like” oxidation mechanism for the direct formation of CPO via phenoxyl and oxepinoxyl radicals.\(^{59-62}\) Other fragment ions at \( m/z \) 79, 81, 83, and 109 are assigned to loss of \( \text{NH}_3 + \text{C}_2\text{H}_3\text{O} \) (\(-47 \) Da), \( \text{NH}_3 + \text{C}_2\text{H}_3\text{O} \) or \( \text{C}_2\text{H}_4\text{O} \) (\(-45 \) Da), \( \text{NC}_2\text{H}_5 \) or \( \text{C}_2\text{H}_3\text{O} \) (\(-43 \) Da), and \( \text{NH}_3 \) (\(-17 \) 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 3.3. Reactions of the PD generated 5-ammonium-2-hydroxyphenyl radical cation (\( m/z \) 109) with \( \text{O}_2 \) were characterised further by kinetic measurements.

#### 3.2.1 Distonic \( \text{ion} + \text{O}_2 \) reaction kinetics

Product mass spectra for the reactions of \( m/z \) 109 ions with background \( \text{O}_2 \) ([O\(_2\)] = 6.4 \( \pm \) 0.4 \( \times \) \( 10^9 \) molecules cm\(^{-3}\)) and increased \( \text{O}_2 \) concentrations ([O\(_2\)] = 1.6–2.2 \( \times \) \( 10^{11} \) molecules cm\(^{-3}\)) were
recorded as a function of reaction time. The normalised integrated intensity for a selected mass-to-charge range (1–2 Th) was plotted against reaction time (0.030 to 10 000 ms) to produce kinetic curves that describe decay of m/z 109 ion signal intensity due to reactions with O₂.

A single exponential decay (eqn (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 Fig. 5 with fitted data and residuals from eqn (1) for m/z 109 signal decay. The k₁st 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) 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 Fig. 5b, at increased O₂ 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 10 000 ms. This indicates the presence of an unreactive isomer (or isomers) and is accounted for by the constant offset included in eqn (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 Fig. S7 (ESI†) for oxidation of 5-ammonium-2-methylphenyl radical cations (m/z 107) and in Fig. S8 (ESI†) for 5-(N,N,N-trimethylammonium)-2-hydroxymethylphenyl radical cations (m/z 151). For reactions of 5-ammonium-2-methylphenyl radical cations (m/z 107) the non-zero horizontal offset (shown in Fig. S7b, ESI†) is ca. 40% of the isolated m/z 107 ion population. Interestingly, k₁st values for 5-ammonium-2-methylphenyl radical (m/z 107) and 5-ammonium-2-hydroxyphenyl radical (m/z 109) signal decay are separable with 2σ uncertainty, where the k₁st for the 5-ammonium-2-hydroxyphenyl radical cations is reproducibly greater by ca. 15%. In the case of trimethylammonium-tagged o-hydroxyphenyl radical + O₂ reactions, the m/z 151 ion population can be completely depleted by O₂ 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 + O₂ reaction kinetics 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 (k₂nd, cm³ molecule⁻¹ s⁻¹) and reaction efficiencies (Φ%) derived from fitted pseudo-first order rate coefficients (k₁st) are reported in Table 2. Collision frequencies were calculated using the Langevin collision model. Kinetic measurements were conducted at background O₂ ([O₂] = 6.4 ± 0.4 × 10⁸ molecule cm⁻³) and increased O₂ concentrations ([O₂] = 1.6–2.2 × 10¹ⁱ molecule cm⁻³). Repeated kinetic measurements provided consistent results and statistical uncertainties from fitting k₁st were typically 2σ ≤ 10%. These results indicate stable absolute O₂ concentrations within the ion trap as indicated by the linear relationship between k₁st and [O₂] (Fig. S9, ESI†). However, the uncertainty in the ion-trap pressure ultimately
Table 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 \(\text{ cm}^{-3}\)). 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.\(^{19}\)

<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 (\text{ 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>5-Ammonium-2-methylphenyl</td>
<td>High ([10^{10}])</td>
<td>(2.6 \times 10^{-11})</td>
<td>(5.9 \times 10^{-10})</td>
<td>4.4</td>
</tr>
<tr>
<td>5-(N,N,N-Trimethylammonium)-2-hydroxyphenyl</td>
<td>Low ([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</td>
<td>High ([10^{10}])</td>
<td>(2.9 \times 10^{-11})</td>
<td>(5.7 \times 10^{-10})</td>
<td>5.1</td>
</tr>
<tr>
<td>6.6 \times 10^4</td>
<td>(2.2 \times 10^4)</td>
<td>(8.5 \times 10^3)</td>
<td>(2.6 \times 10^2)</td>
<td>4.3</td>
</tr>
</tbody>
</table>

\(^{a}\) Rate coefficients reported in ref. 17. Ions of \text{m/z} \ 149 were generated by PD of the \(3\)-bromo-\(N,N,N,4\)-trimethylbenzenonium cation.

results in an upper limit of 50% uncertainty in the trap \([O_2]\), and consequently, a 50% uncertainty for the reported second-order rate coefficients and reaction efficiencies in Table 2.

Reaction efficiencies for all species reported in Table 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 trimethylammonium and pyridinium-tagged phenyl radicals,\(^{27}\) and distonic charged distonic phenyl radical ions, including trimethylall approximately equal to 5%, similar to reported reaction order rate coefficients and reaction efficiencies in Table 2. and consequently, a 50% uncertainty for the reported second-order rate coefficients and reaction efficiencies in Table 2.

3.3 Reaction mechanism

3.3.1 \(o\)-Hydroxyphenyl + \(O_2\) \(\rightarrow\) \(o\)-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 + \(O_2\) systems using the G3X-K method.\(^{40}\) The potential energy schematic in Fig. 6 shows \(O_2\) 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 oxepinoxyl radical intermediate, are also discussed below and provided in the ESI† (Fig. 8 and Fig. S12–S15).

Addition of \(O_2\) 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 Fig. 6. Close proximity of the \(OH\) substituent to the peroxyl radical site in the \(o\)-hydroxyphenylperoxyl radical (N2) allows for a 1,5-H shift to the \(o\)-hydroperoxyphenoxyl radical (N3). Elimination of \(OH\) from the hydroperoxyl group in N3 via \(TS\) N3 \(\rightarrow\) N4 (11.5 kcal mol\(^{-1}\)) barrier results in \(o\)-BQ + \(OH\) with a reaction exothermcity of 51.9 kcal mol\(^{-1}\). Comparing this to the charge-tagged case, the \(o\)-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 exothermcity of 38.9 kcal mol\(^{-1}\) (13.0 kcal mol\(^{-1}\) less than in the neutral case). As shown by Fig. S10 in the ESI† the reaction enthalpy for charge-tagged \(o\)-BQ + \(OH\) is reduced by separation of the charge tag and ring structure via inclusion of methylene linkages, indicating that differences shown in Fig. 6 are (in part) due to a through-space charge effect. Still, intermediates and transition states for both cases shown in Fig. 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 o-BQ (m/z 108) in neutral flow-tube experiments and ammonium-tagged o-BQ (m/z 124) in the distonic radical cation experiments.

### 3.3.2 o-BQ → CPO + CO

The appearance of signal at m/z 80 in the ALS neutral experiments is rationalised by prompt CO elimination from o-BQ (m/z 108)\(^{21}\) and is supported by distonic radical cation experiments (Fig. 4c and d). The potential energy schematic for CO elimination from o-BQ is provided in Fig. 7 and Fig. S11 (ESI\(^{†}\)) for the charge-tagged case, with reaction enthalpies reported relative to the o-hydroxyphenyl + O\(_2\) reactants. Shown in Fig. 7, the pathway via \(N7\) has the lower barrier of 41.9 kcal mol\(^{-1}\) (−10.0 kcal mol\(^{-1}\) relative to o-hydroxyphenyl + O\(_2\)). An alternate mechanism via \(TS\ N6\ →\ N8\) (ref. 68) has a higher 43.5 kcal mol\(^{-1}\) barrier. A transition state for concerted CO loss was located along the neutral \(N4\) → \(N8\) pathway (Fig. 6) with an 11.6 kcal mol\(^{-1}\) barrier. The decomposition reactions shown in Fig. S11 (ESI\(^{†}\)) are less likely to proceed due to the reduced exothermicity of the charge-tagged o-BQ + OH and barriers to decarboxylation approaching the entrance channel limit. Collisonal 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 Fig. 4c. The appearance of a small m/z 96 ion peak in Fig. 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.

### 3.3.3 OH-substituted phenoxyl and oxepinoxyl mechanisms

In the case of unsubstituted phenyl radical oxidation, the direct phenoxyl + O(\(^{13}\)P) channel and the indirect oxepinoxyl radical decomposition pathways can lead to CHO, CO, O, and H losses to produce CPO and o-BQ.\(^{29,60,61,69-71}\) To explore the possible role of phenoxyl and oxepinoxyl pathways here, analogous hydroxyl-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 ESI\(^{†}\) (Fig. 8 and Fig. S12–S15). The O(\(^{13}\)P) loss from hydroxyphenylperoxyl has a 30.6 kcal mol\(^{-1}\) barrier and subsequent decomposition of the o-hydroxyphenyl radical (\(N4\), Fig. S12, ESI\(^{†}\)) to produce CPO occurs via stationary points that exceed o-hydroxyphenyl + O\(_2\) by as much as 61.1 kcal mol\(^{-1}\) (TS \(N43\) → \(N44\)). In the charge-tagged case, O(\(^{13}\)P) loss occurs with a 32.0 kcal mol\(^{-1}\) barrier (inset Fig. S12, ESI\(^{†}\)) and the overall barrier to 3-ammonium-cyclopentadienone + H + CO + O(\(^{13}\)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 3.1 above, small quantities of o-hydroxyphenoxyl radicals are likely generated and later react by H-atom addition to produce o-catechol (\(C_9H_4HOH\), m/z 110). These data together indicate that generation of CPO from o-hydroxyphenoxyl radicals is unlikely.

Rearrangement of o-hydroxyphenylperoxyl (\(N2\)) toward 7-hydroxyoxepinoyl (\(N23\)) and 6-carboxy-1-oxo-2,4-dienyl radicals (\(N21\)) via dioxirane-hydroxycyclohexadienyl intermediates are described in Fig. 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-hydroxyoxepinoyl radical proceeds through TS \(N2\) → \(N22\) 18.1 kcal mol\(^{-1}\) above the barrier to o-BQ (TS \(N3\) → \(N4\) in Fig. 6) with an exothermicity of 102.3 kcal mol\(^{-1}\). Formation of the 6-carboxy-1-oxo-hexa-2,4-dienyl radical (\(N21\)) occurs via TS \(N2\) → \(N20\) at 11.6 kcal mol\(^{-1}\) above TS \(N3\) → \(N4\). Reactions of charged-tagged o-hydroxyphenylperoxyl toward hydroxyoxepinoyl and 6-carboxyoxohexadienyl, shown in Fig. S13 (ESI\(^{†}\)), generally parallel those described by Fig. 8. The rate limiting steps toward the two hydroxyoxepinoyl (\(TS3c\)) and carboxyoxohexadienyl radicals (\(TS1e\)) are 22.2 and 5.1 kcal mol\(^{-1}\), respectively, above the barrier to charge-tagged o-BQ (TS \(C3\) → \(C4\), Fig. 6).

In the case where either hydroxyoxepinoyl or carboxyoxohexadienyl radicals are produced, their decomposition could possibly follow pathways described by Fig. S14 and S15 (ESI\(^{†}\)). Likely products, by analogy to phenyl radical oxidation,\(^{16,61}\)

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**Fig. 7** Potential energy schematic for CO loss from o-BQ (N4) along the singlet \(C_6H_4O_2\) surface. G3X-K 0 K enthalpies are provided in kcal mol\(^{-1}\) relative to o-BQ.

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include o-BQ + OH, CPO + HOOC, 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 (Fig. 1) and the high barriers to hydroxyepinoxyl 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, indicates H-migration and OH-loss to form o-BQ (N4, shown in Fig. 6) comprehensively outcompetes the pathways toward hydroxyepinoxyl and carboxyoxohexadienyl radicals (shown in Fig. 8, N2 toward TS1n and TS4n). The sums of states for salient transition states and corresponding rate coefficients are provided in Table S2 (ESI†). The oepinoxyl 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-hydroxyperoxynaphthalene 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.

### 4. Conclusions

Product detection experiments conducted at the ALS synchrotron reveal that the o-hydroxyphenyl + O2 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 \( \geq 9.8 \text{ eV} \). There are indications of a minor o-hydroxyphenoxyl + O(3P) pathway in the ALS experiments. To establish connections between the major reaction products, distonic radical analogue ammonium-tagged o-hydroxyphenyl + O2 reactions were studied using ion-trap mass spectrometry. Reactions of the 5-ammonium-2-hydroxyphenyl radical cation (m/z 109) with O2 produced product ions consistent with ammonium-tagged o-BQ produced via O2 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 \( k_{\text{2nd}} \) for 5-ammonium-2-hydroxyphenyl (m/z 109) + O2 were measured to have a 5% reaction efficiency. Additional kinetic measurements for O2 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 + O2 reaction kinetics demonstrate for this small set that the identity of the charged-tag and \textit{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 + O2 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 O2 addition is via 1,5-H migration and OH loss from the hydroperoxyphenoxyl 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.
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References


32 Normalised 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.


