Oxidation of Substituted Catechols at the Air-Water Interface: Production of Carboxylic Acids, Quinones, and Polyphenols

Elizabeth A. Pillar  
*University of Kentucky*, epillar86@gmail.com

Marcelo I. Guzman  
*University of Kentucky*, marcelo.guzman@uky.edu

Click here to let us know how access to this document benefits you.

Follow this and additional works at: [https://uknowledge.uky.edu/chemistry_facpub](https://uknowledge.uky.edu/chemistry_facpub)

Part of the Agricultural Science Commons, Analytical Chemistry Commons, Atmospheric Sciences Commons, Biochemistry Commons, Environmental Chemistry Commons, Environmental Engineering Commons, Fresh Water Studies Commons, Laboratory and Basic Science Research Commons, Molecular and Cellular Neuroscience Commons, Organic Chemistry Commons, Physical Chemistry Commons, and the Wood Science and Pulp, Paper Technology Commons

Repository Citation

https://uknowledge.uky.edu/chemistry_facpub/77

This Article is brought to you for free and open access by the Chemistry at UKnowledge. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of UKnowledge. For more information, please contact UKnowledge@lsv.uky.edu.
Oxidation of Substituted Catechols at the Air–Water Interface: Production of Carboxylic Acids, Quinones, and Polyphenols

Elizabeth A. Pillar and Marcelo I. Guzman*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, United States

ABSTRACT: Anthropogenic activities contribute benzene, toluene, and anisole to the environment, which in the atmosphere are converted into the respective phenols, cresols, and methoxyphenols by fast gas-phase reaction with hydroxyl radicals (HO•). Further processing of the latter species by HO• decreases their vapor pressure as a second hydroxyl group is incorporated to accelerate their oxidative aging at interfaces and in aqueous particles. This work shows how catechol, pyrogallol, 3-methylcatechol, 4-methylcatechol, and 3-methoxycatechol (all proxies for oxygenated aromatics derived from benzene, toluene, and anisole) react at the air–water interface with increasing O3(g) during contact time (τ) and contrasts their potential for electron transfer and in situ reactivity. A unifying mechanism is provided to explain the oxidation of the five proxies, which includes the generation of semiquinone radicals. Functionalization in the presence of HO• results in the formation of polyphenols and hydroxylated quinones. Instead, fragmentation produces polyfunctional low molecular weight carboxylic acids after oxidative cleavage of the aromatic bond with two vicinal hydroxy groups to yield substituted cis,cis-muconic acids. The generation of maleic, maleic, pyruvic, glyoxylic, and oxalic acids confirms the potential of oxygenated aromatics to produce light-absorbing aqueous secondary organic aerosols in the troposphere.

INTRODUCTION

Chemical and physical processes resulting in the generation of secondary organic aerosol (SOA) particles that scatter and absorb sunlight and serve as ice and cloud condensation nuclei play an important role in the earth’s radiation fluxes. Aromatic species emitted to the atmosphere during fossil fuel combustion and biomass burning (e.g., wildfires) processes provide phenol precursors for SOA formation through competing fragmentation and functionalization oxidation reactions.2,3 Previous work has explored the catalytic effect played by interfaces and the role of variable relative humidity (RH) during the atmospheric oxidation of phenols, e.g., by O3(g) and hydroxyl radicals (HO•). A combination of analytical methods (infrared spectroscopy, mass spectrometry (MS), and chromatography) employed in our laboratory revealed the importance of competitive oxidation mechanisms.2,3 The production of several reactive oxygen species (ROS), including the formation of semiquinone radicals, has been demonstrated,2,3 suggesting that aromatics provide a significant missing mechanism for the production of low-volatility species found in aerosols.2,3 Furthermore, the common products identified during offline analysis of reactions lasting a few hours and in situ studies under a few microseconds of contact time (τ) validated a flow-through ultrafast interfacial oxidation MS setup for inspecting reactions at the air–water interface.2,3

Combustion and biomass burning emissions provide the two main aromatic species to the atmosphere, benzene and toluene, that total 5.6 and 6.9 Tg of C yr−1, respectively.4 We have previously explained that the oxidative processing of benzene by hydroxyl radicals (HO•) consecutively yields phenol (reaction R1 Scheme 1) and dihydroxybenzenes such as catechol (reaction R2) with gas-phase rate constants kR1;benzene+HO• = 1.2 × 10−12 cm3 molecule−1 s−1 and kR2;phenol+HO• = 2.7 × 10−11 cm3 molecule−1 s−1,5 respectively. The aromatic structures and names, the ring functionalization reactions (e.g., numbered as reactions R1, R2, etc.,) and the products formed and their m/z values are introduced in Scheme 1 and Tables S1 and S2 (Supporting Information). By analogy to the reactivity observed for benzene, reactions R1 and R2 also show that toluene (kR1;toluene+HO• = 5.6 × 10−12 cm3 molecule−1 s−1)5 can generate methlyphenols (p-, m-, and o-cresols) and dihydroxylouene (e.g., kR2;2-methoxyphenol+HO• = 4.3 × 10−11 cm3 molecule−1 s−1)6 such as 3- or 4-methylcatechol, respectively. In addition, by consecutive hydrogen abstractions from the –CH3 group of toluene, reactions R3a and R3b show...
that benzaldehyde and benzoic acid can be produced. In general, phenols and dihydroxybenzenes with methoxy (−OCH₃), methyl (−CH₃), carbonyl (C=O), and carboxylic acid (−COOH) substituent groups (−R) are ubiquitous aromatic species in the atmosphere, as proved from the analysis of cloudwater that has scavenged combustion and biomass burning emissions. The surfactant properties of these polyfunctional phenols make them especially susceptible to undergo oxidations as they accumulate at the air–water interface or partition into aqueous particles (reaction R4). In this work, the interfacial oxidations of a series of substituted catechols found in the environment are contrasted to understand their reactivity and potential for electron transfer during ultrafast contact (τₑ ≈ 1 μs) and detection (τ_d ≈ 1 ms) times. Electron-density-donating substituents of the aromatic ring alter the reactivity of each molecule relative to catechol. Mass spectral data confirm the interfacial production of short-lived species can proceed through two pathways: (1) functionalization of the aromatic ring by hydroxylation and (2) fragmentation of the aromatic ring and intermediates by ozone (O₃(g))-driven oxidative cleavage. The first pathway implies that semiquinone radicals are formed en route to more hydroxylated aromatic and quinone products. In the alternate pathway, the fragmentation of unsaturated C=C bonds provides polyfunctional low molecular weight carboxylic acids widely found in tropospheric aerosols.

**EXPERIMENTAL SECTION**

**Sample Preparation.** Solutions of catechol (Sigma-Aldrich, 99.9%), pyrogallol (Acros, 99.7%), 3-methylcatechol (TCI,
The experimental conditions employed were dilute 61-fold with the N2(g) nebulizing gas (12.0 L min

spectrophotometry (Evolution Array UV

in a 10 cm path length cuvette (Starna cell) by UV absorption

catechols encounters a 0.2 L min

The interface of the microdroplets containing substituted

°

quanti

aerosols can be neutral or slightly basic, which indicates the

water interface has been described in depth.15,16 The 100

through reactor to investigate ultrafast oxidations at the air

produce, they are observed as anions by the mass

The conversion of terephthalic acid (Acros, 99.0%) to 2-

hydroxycatechol (TCI, 98.3%) with a rate constant

The interfacial oxidation of 100 μM substituted
catechols was examined in the absence of O3(g) or in its

RESULTS AND DISCUSSION

Reactions of Substituted Catechols at the Air–Water Interface. The interfacial oxidation of 100 μM substituted
catechols at pH 7.8 provides an example case that demonstrates the

Oxidation of Substituted Catechols. The ESI-MS flow-through reactor to investigate ultrafast oxidations at the air–

water interface has been described in depth.3,5,16 The 100 μM aqueous solution of the selected substituted catechol undergoes

pneumatically assisted aerosolization to form a fine mist of micrometer size droplets at ambient pressure. A spark discharge
generator (Ozone Solutions) acting over a 0.5 L min

flow of O2(g) (Scott-Gross, UHP) produces O3(g), which is quantified

in a 10 cm path length cuvette (Starna cell) by UV absorption

spectrophotometry (Evolution Array UV–visible spectrophotometer, Thermo Scientific) after dilution with 0.0–5.0 L min

of N2(g) (Scott Gross, UHP) in a flow-through borosilicate

chamber (3.785 L capacity).24 In the final stage, O3(g) is
diluted 61-fold with the N2(g) nebulizing gas (12.0 L min

The interface of the microdroplets containing substituted
catechols encounters a 0.2 L min

flow of 0 ppbv ≤ [O3(g)] ≤ 3 ppmv during a few microseconds.3,5,16 If oxidized species are produced, they are observed as anions by the mass

spectrometer at specific m/z values (reported in the text, figures, and schemes) in less than 1 ms after their formation.13,16

The experimental conditions employed were the same used during the previous study with catechol and

trihydroxybenzenes: nebulizer pressure, 70 psi; nebulizer

voltage, −1.9 kV; cone voltage, −50 V; drying gas temperature,

250 °C. Reported m/z values correspond to solvent background

subtracted raw data acquired at fixed time intervals (e.g., time

≥30 s).

The reaction of terephthalic acid (Acros, 99.0%) to 2-

hydroxycatechol (TCI, 98.3%) with a rate constant

ktereophthalic acid+HO

2 × 10

M

s

was used for in situ quantification of HO*

at the air–water interface.9 The reaction of 100 μM (1) pyrogallol, (2) 4-methylcatechol, (3) 3-

methylcatechol, and (4) 3-methoxycatechol with 2.7 ppmv

O3(g) was studied at pH 7.8 in the presence of 5 μM
terephthalic acid. The characteristic product peak at m/z 181 for 2-hydroxyterephthalic acid was used to quantify the

production of HO* by standard addition after subtraction of

the background produced during the controls under 1 atm of N2(g).

aerosolized aqueous solutions of (top) pyrogallol and (bottom) 3-methoxycatechol at pH 7.8 impinged by a flow of 0.2 L min

of 0 ppbv, 223 ppb, and 2.42 ppm O3(g). Both traces in the absence of O3(g) display the anions of pyrogallol (m/z 125) and

methoxycatechol (m/z 139). For comparison, experiments with
catechol (m/z 109) have been studied in detail.2 The
direct oxidation of catechol by O3(g) has been shown to produce glyoxylic acid (m/z 73), oxalic acid (m/z 89),

maleinaldehydic acid (m/z 99), 5-oxo-3-pentenoic acid (m/z

113), maleic acid (m/z 115), 3-hydroxy-α-quinone or 4-

hydroxy-α-quinone (m/z 123), 1,2,3- and 1,2,4-trihydroxybenzenes (m/z 125), glutaric acid (m/z 129), 3,4-dihydroxy-α-

quinone or 3,6-dihydroxy-α-quinone (m/z 139), cis,cis-muconic

acid, 1,2,3,4- and 1,2,4,5-tetrahydroxybenzenes (m/z 141),

Figure 1. ESI-MS spectra of 100 μM solutions of (top) pyrogallol and (bottom) 3-methoxycatechol at pH 7.8 exposed to a 0.200 L min

flow of (purple trace) 1 atm of N2(g), (blue trace) 223 ppb O3(g), and (yellow trace) 2.42 ppm O3(g). Ion count values are normalized

percentages relative to the most intense peak in each mass spectrum, I125 for pyrogallol and I139 for 3-methoxycatechol.
3,4,5-tridihydroxy-o-quinone and 3,4,6-tridihydroxy-o-quinone (m/z 155), pentahydroxybenzene (m/z 157), and benzenepheno-
( m/z 173).2

Following the oxidation channels exhibited by catechol, it is possible to assign the products for pyrogallol in Figure 1 to also
be oxalic acid (m/z 89), malealdehyde acid (m/z 99), 5-oxo-3-pentenoic acid (m/z 113), 3- and 4-hydroxy-o-quinones (m/z 123), 3,4-dihydroxy-o-quinone (m/z 139), 1,2,3,4-trihydroxy-
benzene and 2-hydroxy-cis,cis-muconic acid (both m/z 141), 3,4,5-tridihydroxy-o-quinone (m/z 153), and pentahydroxyben-
ze ( m/z 157). Similarly, Figure 1 shows that 3-
methoxyacetophenone (m/z 139) is oxidized to give the hydroxy-
ated products 4-methoxypyrogallol or 3-methoxy-4,5-dihy-
drocatechol (m/z 155) and their corresponding quinone pairs,
e.g., 3-methoxy-6-hydroxy-o-quinone and 3-methoxy-4-hy-
droxy-o-quinone (m/z 135), 4-methoxy-5-hydroxypyr-
gallol or 3-methoxy-4,5-dihydroxyacetophenone (m/z 171) and their
 corresponding quinones pairs, e.g., 3-methoxy-4,6-dihydroxy-
o-quinone and 3-methoxy-4,5-dihydroxy-o-quinone (m/z 169),
and 4-methoxy-5,6-dihydroxy-pyraddock (m/z 187) and its
corresponding 3-methoxy-4,5,6-trihydroxy-o-quinone (m/z 185). When comparing the pairs at m/z 155 and 153, m/z 171 and 169, and m/z 187 and 185, for oxidized 3-
methoxyacetophenone (Figure 1), it is obvious that the peak for
the dihydroxylated product of 3-methoxyacetophenone at m/z 171
largely exceeds the expected value from correlation to the peak
at m/z 169. For these quinone/hydroquinone pairs (signals
separated by 2 amu), it is obvious that the peak at m/z 171
displays a large contribution of another species, which is 2-
 methoxymuconic acid, the major product from aromatic ring
 cleavage.

Figure 2 displays the ESI mass spectra for aerosolized
solutions of (top) 3-methylcatechol and (bottom) 4-methyl-
catechol under the same conditions listed for Figure 1. Both
traces in the absence of O3(g) display the anion for
methylcatechol (m/z 123) and a small peak for its dihydrate
(m/z 159), a feature also exhibited by catechol. Some of the
products observed during the oxidation of both catechates-
ols are oxalic acid (m/z 89), malealdehyde acid (m/z 99),
4-methyl-o-quinone (m/z 121) (no 3-methyl-o-quinone is
registered probably due to steric impediments), 3-methyl-4-
 hydroxy-, 3-hydroxy-4-methyl- and 4-methyl-5-hydroxy-o-
quinones (m/z 137), 3-methyl-4-hydroxyacetophenone, 4-methyl-
pyrogallol, and 4-methyl-hydroxyacetophenon (m/z 139), 3-
methyl-4,5-dihydroxy- and 3,5-dihydroxy-4-methyl-o-quinones
(m/z 153), 2-methyl-cis,cis-muconic acid (m/z 155), 3-methyl-
4,5-dihydroxy- and 3,5-dihydroxy-4-methyl-catechols (m/z
155), 4-methyl-3,5,6-trihydroxy-o-quinone (m/z 171), and 3-
methyl-4,5,6-trihydroxy- and 3,5,6-trihydroxy-4-methyl-catech-
ols (m/z 173).

Figure 3 gathers information from experiments with
increasing [O3(g)] displaying the exponential drop of I0/2
for pyrogallol, 3-methycatechol, 4-methylcatechol, and 3-meth-
catechol. In agreement with our previous work with catechol,2
the information in Figure 3 suggests the first-order reaction on
[O3] for all the substituted catechols studied takes place within
τc = 0.1 μs. Indeed, the reaction with O3(g) molecules occurs at
the outermost layers of the interfaces of a few nanometers
thickness without diffusion limitations while replenishment of
the organic molecule from the core is facilitated.2,16

Electron and Proton Transfers. The speciation of the
substituted catechols in Figures 1 and 2 can be calculated using

Figure 2. ESI-MS spectra of 100 μM solutions of (top) 3-
methoxyacetophenone and (bottom) 4-methylcatechol at pH 7.8 exposed
to a 0.200 L min\(^{-1}\) flow of (purple trace) 1 atm of N\(_2\)O(g), (blue trace)
223 ppb O3(g), and (yellow trace) 2.42 ppm O3(g). Ion count values
are normalized percentages relative to I\(_{113}\), the most intense peak in
each mass spectrum.

both pK\(_{a1}\) and pK\(_{a2}\) for these weak diprotic species (H\(_3\)Q) and
their intermediate form (H\(_2\)Q):  

\[
\begin{align*}
H_3Q & \rightleftharpoons H_2Q^- + H^+ \quad pK_{a1} \\
H_2Q^- & \rightleftharpoons HQ^2^- + H^+ \quad pK_{a2}
\end{align*}
\]  

While this information is available for catechol and pyrogallol,22
the instability of this class of compounds precludes access to
experimental values of the other acid dissociation constants.
However, theoretical methods capable of accurately predicting
pK\(_{a1}\) and pK\(_{a2}\) values have been developed.26-28 Thus, Table 1
combines the experimental and theoretical values for pK\(_{a1}\) and
pK\(_{a2}\), which can be used to solve the speciation of the H\(_3\)Q
species vs pH. For example, at working pH 7.8, the fractions
of fully associated catechols, α\(_{H_3Q}\) ≥ 0.95, and their intermediate
monoprotic acid, α\(_{H_2Q^-}\) ≤ 0.05, are reported in Table 1. Clearly,
the diprotic catechols are the dominant species available for
the oxidations displayed in Figures 1 and 2.

Under the oxidizing experimental conditions, the substituted
catechols and/or their products can act as two-electron
reductants, getting converted into the corresponding quinones by
two coexisting pathways. The first pathway proceeds through
initial electron transfer from the more abundant
undissociated catechols to O\(_3\) (reaction R5a). This electron
transfer pathway is supported by the dominant fractions in
equilibrium at pH 7.8, $\alpha_{\text{HQ}} \geq 0.95$ (Table 1), which continues by a fast proton transfer (reaction R5b). Reactions R5a and R5b are equivalent to the net loss of a hydrogen atom. However, direct hydrogen atom transfer should be unfavorable in these molecular ensembles as exemplified by the ~10-fold larger hydrogen bond dissociation energies, calculated from data in dimethyl sulfoxide, than the thermal energy available for the system. The second mechanism involves initial dissociation of the diprotic catechols followed by electron transfer (reactions R6a and R6b), which is less likely to be the dominant process given $\alpha_{\text{HQ}} \leq 0.05$ (Table 1). The equilibrium constant for reaction R6a corresponds to the first acid dissociation constant, $K_{a1}$. The self-reaction of two semiquinone radicals (HQ$^\cdot$) via reaction R7 finally produces a quinone (Q) while regenerating a substituted catechol: 2HQ$^\cdot$ → Q + H$_2$Q. Analogously, the cross-reaction between two different semiquinone radicals also generates a quinone: HQ$^\cdot$ + HQ$^\cdot$ → Q + H$_2$Q (reaction R8).

The electron-donating capacity of the substituents and their position relative to the $-$OH groups should be considered together with molecular specific properties (e.g., redox potentials and first and second proton dissociation constants) to understand why reactions RS and R5b are favored herein. Table 1 also lists the one-electron redox potentials of the semiquione radical cation (HQ$^\cdot$+) and undissociated substituted catechol pairs, $E_{\text{HQ}^\cdot+/\text{H}_2\text{Q}}$ which except for catechol reported at pH 7.30 are predicted using structure–activity relationships derived from computational methods.29 The linear dependence of the redox potentials vs the normal hydrogen electrode (NHE) on the sum of the Hammett substituent parameters ($\sigma$) available in the literature is given by the following equation:29

$$E_{\text{HQ}^\cdot+/\text{H}_2\text{Q}} = 1.85 \sum \sigma_i + 0.46$$

(3)

Table 1 reports the positive $\Delta E = E_{\text{O}_3/\text{O}_3^+} - E_{\text{HQ}^\cdot+/\text{H}_2\text{Q}}$ for electron transfer (reaction R5a) between the substituted catechols and dissolved O$_3$ ($E_{\text{O}_3/\text{O}_3^+} = 1.01$ V). The $\Delta E$ values correspond to thermodynamically favorable processes as indicated in Table 1 by the calculated $\Delta G^o = nF\Delta E$, where $n = 1$ and $F = 96.485$ kJ mol$^{-1}$ V$^{-1}$ is the Faraday constant. From the increasing $\Delta E$ values in Table 1, it is observed that electron transfer occurs more easily following the trend catechol < pyrogallol < 4-methylcatechol = 3-methylcatechol < 3-methoxycatechol. In other words, the decreasing $E_{\text{HQ}^\cdot+/\text{H}_2\text{Q}}$, observed with these electron-donating groups favors electron transfer from H$_2$Q to O$_3$ (reaction R5a). The directly generated semiquinone radicals H$_2$Q$^\cdot$+ (p$K_{a1}$ ≈ −1)31 promptly release a proton (reaction R5b), while the ozonide radical anion O$_3^\cdot$− from reaction R5a coexists in equilibrium R9a with very basic O$_3$− (p$K_c = 11.8$).32 Therefore, for environmentally relevant atmospheric waters and other aqueous systems (pH < 10) and in the present experiments, O$_3$− is quickly converted into HO$^\cdot$ (equilibrium R9b). As a consequence, this work also provides an opportunity to understand how HO$^\cdot$ continues the oxidation of substituted catechols at the air–water interface, in aqueous aerosols, and in other relevant water media.

Reactions of the Substituted Catechols with HO$^\cdot$. In addition to reactions R7 and R8, the semiquinone radicals can also be produced by the attack of HO$^\cdot$ on the catechols (reaction R10), which generates resonance-stabilized cyclohexadienyl radicals capable of undergoing fast acid- or base-catalyzed elimination of water (reaction R11). For instance, reaction R10 for unsubstituted catechol proceeds at pH 9 with

<table>
<thead>
<tr>
<th>name</th>
<th>MW (amu)</th>
<th>$pK_{a1}$</th>
<th>$pK_{a2}$</th>
<th>$\alpha_{\text{HQ}}$</th>
<th>$\alpha_{\text{HQ}}$</th>
<th>$E_{\text{HQ}^\cdot+/\text{H}_2\text{Q}}$ (V)</th>
<th>$\Delta E^\circ$ (V)</th>
<th>$\Delta G^o$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>catechol</td>
<td>110.11</td>
<td>9.34$^d$</td>
<td>12.60$^d$</td>
<td>0.972</td>
<td>0.028</td>
<td>0.53$^f$</td>
<td>0.48</td>
<td>−46.31</td>
</tr>
<tr>
<td>pyrogallol</td>
<td>126.11</td>
<td>9.12$^d$</td>
<td>11.19$^d$</td>
<td>0.954</td>
<td>0.046</td>
<td>0.47$^g$</td>
<td>0.54</td>
<td>−52.10</td>
</tr>
<tr>
<td>4-methylcatechol</td>
<td>124.14</td>
<td>9.59$^b$</td>
<td>12.69$^b$</td>
<td>0.983</td>
<td>0.017</td>
<td>0.42$^c$</td>
<td>0.59</td>
<td>−56.93</td>
</tr>
<tr>
<td>3-methylcatechol</td>
<td>124.14</td>
<td>9.59$^b$</td>
<td>12.66$^b$</td>
<td>0.984</td>
<td>0.016</td>
<td>0.42$^c$</td>
<td>0.59</td>
<td>−56.93</td>
</tr>
<tr>
<td>3-methoxycatechol</td>
<td>140.14</td>
<td>9.59$^b$</td>
<td>12.69$^b$</td>
<td>0.984</td>
<td>0.016</td>
<td>0.33$^c$</td>
<td>0.68</td>
<td>−65.61</td>
</tr>
</tbody>
</table>

$^a$Experimental values. 26,45 $^b$Predicted using ChemAxon. 27,28 $^c$Calculated using linear free energy relationships. 26,29,30 $^d$At working pH 7.8. *For the diprotic form H$_2$Q$^\cdot$. At pH 7.0. $^f$Accounting for the equivalent $-$OH groups in carbons 1 and 3. $^g$$\Delta E = E_{\text{O}_3/\text{O}_3^+} - E_{\text{HQ}^\cdot+/\text{H}_2\text{Q}}$ and $E_{\text{O}_3/\text{O}_3^+} = 1.01$ V. 46

$\Delta G^o = −nF\Delta E$. 

Figure 3. Ion count, $I_{m/z}$, of pyrogallol (m/z 125), 3-methylcatechol (m/z 123), 4-methylcatechol (m/z 123), 3-methoxycatechol (m/z 139), and the respective oxidation products from exposing aerosolized solutions of each compound to increasing mixing ratios of O$_3$(g).
a large rate constant $k_{\text{HO\textsubscript{-}catechol}} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.\textsuperscript{33} The rate constants for the aqueous reactions of pyrogallol, 3-methoxycatechol, and 3- and 4-methylcatechols with HO\textsuperscript{*} should be larger than that for catechol due to the presence of electron-donating groups.\textsuperscript{34} For example, the reaction rate constants for 3-methylcatechol and 4-methylcatechol with HO\textsuperscript{*} (available in the gas phase) are 1.9 and 1.5 times larger than for catechol.\textsuperscript{35} Comparable oxidation conditions are supported by experiments under a fixed 100 $\mu$M concentration for each substituted catechol at pH 7.8 reacting with 2.7 ppmv O\textsubscript{3}(g), which constrain the produced [HO\textsuperscript{+}]\textsubscript{interface} = (1.1 ± 0.3) $\times$ 10\textsuperscript{13} radicals cm\textsuperscript{-3}. Thus, the attack of HO\textsuperscript{*} on the activated rings should also be expected to be $\geq 2 \times 10^4$ times larger than for the corresponding reaction with O\textsubscript{3} ($k_{\text{O\textsubscript{3\textsubscript{-}catechol}} = 5.2 \times 10^6$ M$^{-1}$ s$^{-1}$ at pH 7).\textsuperscript{36} Once HO\textsuperscript{*} is produced, it can also directly abstract a hydrogen atom from H\textsubscript{2}Q to form H\textsubscript{2}Q\textsuperscript{+}. Under typical atmospheric conditions, the competitive fate of the cyclohexadienyl radicals is fast O\textsubscript{2} addition,\textsuperscript{37} forming a peroxy radical that decomposes into a hydroxylated product releasing hydroperoxyl radical (HO\textsubscript{2})\textsuperscript{*} by reaction R12.\textsuperscript{38} Thus, reaction R12 represents the formation of pyrogallol (m/z 125) from catechol, 3-methyl-4-hydroxycatechol, 4-methylpyrogallol, and 4-methyl-5-hydroxycatechol (all m/z 139) from 3- and 4-methylcatechols, and 4-methoxy- and 3-methoxy-4-hydroxycatechol (both with m/z 155) from anisole. It is particularly interesting to compare the relative ion counts for the first hydroxylated products (m/z 139) of both methyl catechols studied. The fact that $I_{m}$ for 4-methylcatechol is about 2 times larger than for 3-methylcatechol in experiments with 2.42 ppm O\textsubscript{3} (Figure 2), and that their $\alpha_{\text{H\textsubscript{2}Q\textsubscript{-}O\textsubscript{3}}}$ and $E_{\text{H\textsubscript{2}Q\textsubscript{-}O\textsubscript{3}}}$ values (Table 1) are practically identical (Table 1) for both species, suggests that the efficiency for electron transfer must not be the cause for this discrepancy. Indeed, the presence of a vicinal –CH\textsubscript{3} causes steric hindrance that could decrease the reactivity of 3-methylcatechol relative to 4-methylcatechol for this electron transfer initiated process.

The quick production of HQ\textsuperscript{*} and HO\textsuperscript{*} is also reflected in Figure 3 showing the profiles of each species for increasing [O\textsubscript{3}(g)]. For example, the top panel of Figure 3 shows how pyrogallol (m/z 125) generates a large production of (1) 3- and 4-hydrox-y-o-quinones (m/z 123) likely from self-reaction R7 and (2) tetrahydroxynzenes (m/z 141) via the sequence represented by reaction R13. Reaction R7 can also be invoked for the considerable production of 4-methyl-o-quinone (m/z 121) from 4-methylcatechol in Figures 3. Interestingly, reaction R7 is not observed in the cases of 3-methylcatechol and 3-methoxycatechol, showing the steric hindrance introduced by –CH\textsubscript{3} and –OCH\textsubscript{3} groups in position 3 (next to the bond with both –OH groups). In addition, reaction R13 also explains the large production of (1) 3-methyl-4,5-dihydroxycatechol and 4-methyl-3,5-dihydroxycatechol (both m/z 155) from 3-methyl-4-hydroxycatechol, 4-methylpyrogallol, and 4-methyl-5-hydroxycatechol and (2) 4-methoxy-5-hydroxypropiroglallol and 3-methoxy-4,5-dihydroxypropiroglallol (both m/z 171) from 4-methoxypropiroglallol and 3-methoxy-4-hydroxycatechol (both m/z 155). Alternatively, another very likely mechanism for incorporation of –OH to the catechols (not displayed in Scheme 1) is the direct reaction with O\textsubscript{3} at positions 3 and 6 that eliminates O\textsubscript{3}($\Delta$)\textsubscript{2}.\textsuperscript{39,40}

In general, the maximum $I_{m}$ values for the products from the first electrophilic addition of HO\textsuperscript{*} to the substituted catechols via reaction R13 dominate the composition of products (see blue squares in Figure 3). However, pyrogallol is an exception due to its extraordinary ability to form 3- and 4-hydroxy-o-quinones (m/z 123). For increasing [O\textsubscript{3}(g)], $I_{m}$ of the monohydroxylated products starts to decay, indicating further oxidation occurs. Interestingly, $I_{m}$ for 3-methoxy catechol (see teal stars in Figure 3) keeps growing instead of decaying for higher [O\textsubscript{3}(g)]. This anomaly clearly indicates that 2-methoxymuconic acid originating from oxidative cleavage of the aromatic ring contributes further to the peak intensity than the isomeric second hydroxylation product of 3-methoxy catechol. Otherwise, less intense growing patterns are observed from reactions R13 and R14 for $I_{m}$ of the respective second and third hydroxylation products (see teal stars in Figure 3). Reaction R14 represents a third-generation product with a new –OH group added to (1) tetrahydroxynzenes (m/z 141) to form penta hydroxynzenes (m/z 157), (2) 3-methyl-4,5-dihydroxycatechol and 4-methyl-3,5-dihydroxycatechol (both m/z 155) to form 3-methyl-4,5,6-trihydroxycatechol and 4-methyl-3,5,6-trihydroxycatechol (both m/z 171), and (3) 4-methoxy-5-hydroxypropiroglallol and 4-methoxy-4,5-dihydroxypropiroglallol (both m/z 171) to form 4-methoxy-5,6-dihydroxypropiroglallol (m/z 187). The conversion of penta hydroxynzenes into benzenehexol (reaction R15) represents a fourth-generation aqueous product from catechol (Table S1, Supporting Information).\textsuperscript{2}

The reactions for the production of all the quinones experimentally observed in Figures 1 and 2 can be explained to proceed analogously to self-reaction R7 and/or cross-reaction R8. An alternate pathway for their production is the elimination of H\textsubscript{2}O\textsubscript{2} after O\textsubscript{3} attack to vacant positions 3 and 4 of the substituted catechols.\textsuperscript{3} These complex reactions likely proceed through a cyclic ozonide intermediate.\textsuperscript{16} The structures for the quinones named above for m/z 121, 123, 137, 139, 153, 155, 169, and 171 are provided in Table S2 (Supporting Information) together with the corresponding precursors. Figure 3 shows the profiles of these quinones are slightly less intense than the corresponding H\textsubscript{2}Q species 2 amu heavier but generally resemble each other’s behavior with increasing [O\textsubscript{3}(g)].

**Oxidative Cleavage of Substituted Catechols.** While the substituted catechols react at the air–water interface, generating a distribution of products dominated by the functionalized aromatic rings described in Scheme 1, fragmentation of the bond between C1 and C2 by electrophilic O\textsubscript{3} generates polyfunctional carboxylic acids. The small ion count for the representative fragmentation products with m/z 89 and 99 included in Figure 3 is expected because these secondary oxidation products cannot accumulate during the short $r_{f}$ in the setup.\textsuperscript{16} The detailed analysis explaining the mechanism of reaction for catechol\textsuperscript{2} should also be applicable to its substituted counterparts. Catechol, pyrogallol, both methyl catechols, and 3-methoxycatechol undergo a series of oxidative fragmentations summarized in Scheme 2 to yield muconic acid (m/z 141), 2-hydroxymuconic acid (m/z 157), 2- and 3-methy lmuconic acids (m/z 155), and 2-methoxymuconic acid (m/z 171), respectively.

The produced substituted muconic acids result from an ozonide that is sequentially converted into a Criegee intermediate and a hydroperoxide that also releases H\textsubscript{2}O\textsubscript{2} which further oxidizes the ozonide.
Scheme 2. Products and Observed m/z Values from Substituted Catechol Oxidation by O₃ and H₂O₂ Following the Mechanisms from Ref 2⁴

<table>
<thead>
<tr>
<th>Catechol</th>
<th>m/z</th>
<th>Pyruvate</th>
<th>m/z</th>
<th>Glutamic Acid</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>catechol</td>
<td>109</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pyrogallol</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-methylcatechol</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-methylcatechol</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-methoxy catechol</td>
<td>139</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>muconic acid</td>
<td>141</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-hydroxy muconic acid</td>
<td>157</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methyl/muconic acid</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-methyl/muconic acid</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methoxy muconic acid</td>
<td>173</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glyoxylic acid</td>
<td>73</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pyruvic acid</td>
<td>87</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>crotonic acid</td>
<td>85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-oxopropanoic acid</td>
<td>89</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-hydroxy2-butenoic acid</td>
<td>101</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-oxo-2-pentenoic acid</td>
<td>113</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>maleic acid</td>
<td>115</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glutaric acid</td>
<td>129</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

“Names in bold colored fonts match the precursors and products.

101, S-oxo-3-pentenoic (m/z 113), maleic (m/z 115), and glutaric (m/z 129) acids. While the majority of the compounds (e.g., glyoxylic and oxalic acids) could originate from all the catechols, the color coding in Scheme 2 clearly indicates that pyruvic acid only arises from the oxidation of the methylcatechols. Thus, together with the pathways from isoprene photooxidation, the oxidative channel for the oxidation of methylated aromatics such as tolune, producing cresols (reactions R1 and R2), is responsible for the production of this important tropospheric compound.

The common oxidative fate of the low molecular weight carboxylic acids is to continue getting oxidized en route to form CO, CO₂, oxalic acid, and formic acid. Interestingly, glyoxylic acid was the most abundant product during the oxidation of catechol at the air–water interface, lasting τ ≈ 1 μs.²² Glyoxylic acid can be oxidized to form oxalic acid (m/z 89),²³ but photooxidation in water yields CO, CO₂, formic acid, glyoxylic, and a small amount of tartaric acid.²⁵ Both pyruvic and glyoxylic acid also yield these common products by Baeyer–Villiger (BV) oxidation in the presence of in situ generated H₂O₂.²⁶ In addition, a comparison of the reactivity of both methylcatechols shows that the –CH₃ group in position 3 creates a more electron rich vicinal carbon–carbon bond with –OH groups and enhances fragmentation by electrophilic O₃. The previous fact can be visualized in Figure 2 as well as by the brown times signs for m/z 99 in the center panel of Figure 3. Consequently, a slight increase in the number of low molecular weight carboxylic acids is observed for 3-methylcatechol relative to 4-methylcatechol. Finally, it is possible to consider the attack of HO* on the substituted catechols followed by the addition of O₂ to form an endoperoxide that will add a second O₂. The peroxide formed can decompose, contributing quinones and mainly low molecular weight carbonyls and carboxylic acids. For example, the production of glyoxal, glyoxylic acid, oxalic acid, and pyruvic acid from both methylcatechols can proceed through this channel.

Implications. This laboratory study contributes to characterizing the evolution of combustion and biomass burning emissions, an important subject to understand how the surface of carbonaceous materials is affected during interfacial oxidations that can potentially alter the morphology of particles that play a role in the direct radiative effect.³² The most important process governing the initial oxidation of aromatic species in the atmosphere is controlled by the presence of HO*. The results from ultrafast experiments analyzed by mass spectrometry reveal the identity of low-volatility reaction products. Quinone (Table S2, Supporting Information) and polyphenol reactive intermediates coexist at the air–water interface, where low molecular weight carboxylic acids found in brown clouds are produced. The quick oxidation of all substituted catechols proceeds by competing functionalization and fragmentation reactions. Although for acidic hygroscopic particles containing sulfate a lower amount of hydroxyl radical should be generated in situ by the electron transfer mechanism presented, the reactions of phenols with this radical will proceed as reported here regardless of the source of HO*. Thus, the studied phenols, available on the surface of tropospheric particles, should react with impinging HO* produced in the gas phase through the same pathways presented.

The proposed pathways agree with observations previously made for catechol at the air–water and air–solid interfaces under variable relative humidity,²⁷ which generate more hydrophilic products that partition into the aqueous phase. In addition, photochemical oxidation should also contribute to the degradation of aromatics in the aqueous phase.⁴³ However, the substituted catechols display an enhancement in their reactivity due to the ring-activating functional groups. Similarly, the functionalized rings with more –OH groups are also highly activated toward fragmentation and should be relevant intermediates in the degradation of aromatics emitted during combustion and biomass burning. In addition, this information can also be applied to support the same chemical processing of particulate matter with a diameter of <1 μm (PM₁) from the greater London area in winter 2012.⁴⁴ This PM₁ contains nonvolatile organics associated with refractory black carbon that could originate from either combustion or biomass burning emissions. Finally, this work also explains typical degradation pathways for aromatic pollutants derived from benzene, toluene, and anisole in water media and at the air–water interface.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00232.
Environmental Science & Technology

Additional environmental justification and tables giving the parent species and produced hydroyx aromatics expected from Scheme 1 and names, structures, observed m/z values, and precursors of the produced quinones (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*Phone: 859-323-2892; fax: 859-323-9985; e-mail: marcelo.guzman@uky.edu.

ORCID
Marcelo I. Guzman: 0000-0002-6730-7766

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation for funding under NSF CAREER Award CHE-1255290.

■ REFERENCES


