

Supporting Information For:

Catechol Oxidation by Ozone and Hydroxyl Radicals at the Air-Water Interface

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*Elizabeth A. Pillar, Robert C. Camm, and Marcelo I. Guzman**

Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA.

*Corresponding author's email: marcelo.guzman@uky.edu

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This material presents the Supporting Information explaining how catechol undergoes fast oxidation at the air-water interface by two competing pathways in the presence of O_3 . Hydroxylation and cleavage of the 1,2 position of the aromatic ring of catechol occurs at the air-water interface in agreement with observations made in bulk water for phenol.¹ The previously observed formation of HO^\bullet (~22% yield)² in the reaction of phenol ($pK_a = 9.99$)³ with ozone⁴ in the presence of *ter*-butanol and dimethyl sulfoxide (DMSO) scavengers^{4, 5} supports this work. The chain of oxidation reactions from direct O_3 action generates *cis,cis*-muconic acid and low molecular weight (LMW) oxocarboxylic acids and unsaturated dicarboxylic acids under tropospheric conditions. Under atmospheric conditions, the initial oxidation reaction of polyphenols is governed by HO^\bullet radicals formed at high yields. For polluted conditions of high $[O_3(g)]$, the production of mono- and poly-hydroxylated aromatic hydrocarbons (PHA), and mono- and poly-hydroxylated quinones (PHQ) from the hydroxylation channel should contribute to enhance the reactivity of biomass burning emissions toward atmospheric oxidants. The ozonolysis of catechol at variable pH described in the main text of the article is presented below in Figure S1.

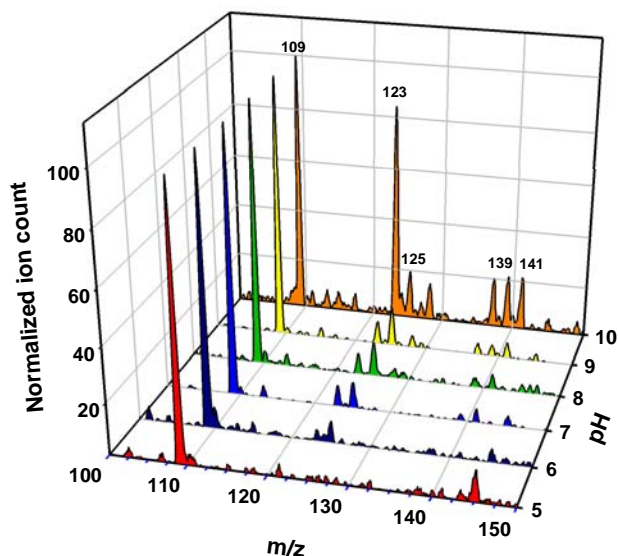


Figure S1. ESI-MS spectra of aerosolized solutions of 25 μ M catechol exposed to 3.18 ppmv $O_3(g)$ at variable pH.

Predominant products in the direct ozonolysis of catechol at the air-water interface

Under acidic conditions OH-initiated chemistry does not contribute considerable to the production of polyhydroxylated aromatic hydrocarbons such as tetrahydroxybenzenes. Therefore, experiments at pH 5 and 6 (Figure S1, Supporting Information) are useful to quantify the maximum contribution of *cis,cis*-muconic acid to the peak at m/z 141. The mean normalized ion count at m/z 141 at pH 5 and 6 is $I_{141,O_3} = 2.32 \pm 0.03 \text{ nM}^{-1}$ of *cis,cis*-muconic acid. In contrast, experiments at pH 8 and 9 display contributions from both $O_3(g)$ and OH competing reactions, and the mean normalized ion count is $I_{141,O_3+HO} = 1.83 \times I_{141,O_3}$. Therefore, the ion count at high pH corresponding to the presence of tetrahydroxybenzene is given by the difference $\Delta I_{141} = 1.83 - 1.00 = 0.83$. In other words, a 55 % of the observed peak at pH 8 and 9 corresponds to *cis,cis*-muconic acid. Therefore, spiked addition of *cis,cis*-muconic acid standard during experiments under the same conditions indicate that only a 55 % of $I_{141} \equiv 55 \% \times 236 \text{ nM}$ (the total measured from spiked samples) = 129 nM *cis,cis*-muconic arises from the experiment at pH = 8 in Figure S1.

The pseudo-quantification of tetrahydroxybenzene is performed taking into account the response of the MS detector. A detector response factor linking the ratio of concentrations per normalized ion counts at pH = 8 in the presence of 25 μM catechol was established for *cis,cis*-muconic acid and 1,2,3-trihydroxybenzene (Acros, 99.7 %). In this case, 1,2,3-trihydroxybenzene was used as a representative analyte for the (commercially unavailable) tetrahydroxybenzenes produced *in situ* during the interfacial reaction. The previous assumption was based on measurements confirming that the MS detector gives a similar linear response for I_{109} and I_{125} with increasing catechol and 1,2,3-trihydroxybenzene concentration, respectively. The response factor β was:

$$\beta = \frac{I_{141,standard}}{I_{125,standard}} \simeq 0.25 \frac{nM \text{ cis,cis-muconic acid}}{nM \text{ tetrahydroxybenzenes}} \quad (1)$$

The equivalent concentration of *cis,cis*-muconic acid to tetrahydroxybenzenes can be retrieved from the experimental 45 % I_{141} signal remaining at pH = 8:

$$236 \text{ nM} \times 45 \% = 106 \text{ nM equivalent } cis,cis\text{-muconic acid to tetrahydroxybenzenes} \quad (2)$$

after converting the concentration of 106 nM equivalent *cis,cis*-muconic acid to the actual concentration of tetrahydroxybenzenes using the response factor β :

$$[\text{tetrahydroxybenzenes}] = \frac{106 \text{ nM } cis,cis\text{-muconic acid}}{0.25 \frac{\text{nM } cis,cis\text{-muconic acid}}{\text{nM tetrahydroxybenzenes}}} \quad (3)$$

to obtain $[\text{tetrahydroxybenzenes}] = 424 \text{ nM tetrahydroxybenzenes}$. Similarly, from the high total $[\text{trihydroxybenzenes}] = 2260 \text{ nM}$ is evident that OH radicals quickly favor a mechanism of production of polyhydroxylated aromatic compounds.

The quantification of the predominant products of direct ozonolysis was performed by spiked addition of standards during ozonolysis. Aerosolized solutions of 25 μM catechol at pH 8.0 were exposed to 3.18 ppmv $\text{O}_3(\text{g})$. The standards were prepared from oxalic acid dihydrate (Mallinckrodt, 99.1 %), maleic acid (Sigma-Aldrich, 99.9%), glyoxylic acid (Sigma-Aldrich, 50 wt. % in H_2O), pyruvic acid (Sigma-Aldrich, 99.1 %) as a pseudo-standard to quantify 3-oxopropanoic acid, and *cis,cis*-muconic acid (Aldrich, 98.7 %). All analyses corresponded to experiments in which the normalized ion count of products increased only by 1 to 3 times the intensity registered in the absence of the spiked.

Concentration of standards after spiked addition bracket the range from 50 nM to 2500 nM. The results indicate the presence of [glyoxylic acid] = 200 nM > [oxalic acid] = 174 nM > [*cis,cis*-muconic acid] = 129 nM > 3-oxopropanoic acid] = 109 nM. Because [maleic acid] < 10 nM, it can be assumed that this species is quickly converted in glyoxylic acid.

Conversion of 1,2,4-trihydroxybenzene (THB) to 2-hydroxy-1,4-benzoquinone at variable pH

100 μ M solutions of THB (Alfa Aesar, 99.2 %) were freshly prepared in degassed ultra-pure water (18.2 M Ω cm). An aliquot of 50 mL of the solution was adjusted to initial pH 5.06 (Thermo Scientific pH-meter) with 0.01 M HCl in an amber bottle. Solutions of 0.001-0.09 M NaOH were used to adjust the pH of the solution to the values reported in Figure S2. An aliquot of 3.5 mL of this pH-adjusted solution was transferred to a 10 mm path length fused silica cuvette (Starna Cells) to register the absorption spectra with an Evolution 220 UV-visible spectrophotometer equipped with a linear 8-cell changer (Thermo Scientific) cuvette holder.

Figure S2 shows that at pH 5.06 (black line) the UV-visible spectrum of the colorless solution of THB presents two peaks A and B with maximum wavelengths $\lambda_{\max,A} = 194$ nm and $\lambda_{\max,B} = 287$ nm, respectively. Small increments in pH were accompanied by a decrease in the intensity of peak B, representing the loss of THB. Simultaneously, as the pH increased and the solution turned pinkish orange (from the production of the quinone form in equilibrium), peaks C, D, and E appeared at $\lambda_{\max,C} = 211$ nm, $\lambda_{\max,D} = 261$ nm, and $\lambda_{\max,E} = 486$ nm, respectively. The inset in Figure S2 shows how the absorption maxima for peaks B and E can be used to monitor the inter-conversion of both species at variable pH, as it has been observed in similar studies with denitrifying bacteria.⁶

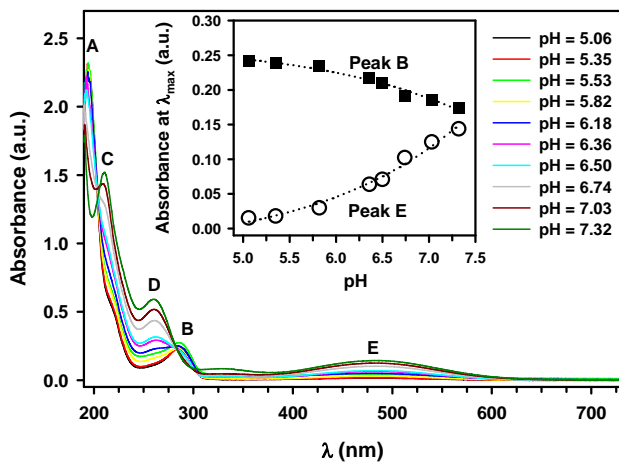


Figure S2. Conversion of 100 μM 1,2,4-trihydroxybenzene in 2-hydroxy-p-quinone at variable pH.

Ozonolysis of thin films of catechol studied by Fourier transform infrared (FTIR) spectroscopy

A Thermo Scientific FTIR spectrometer interfacing a Nicolet iZ10 module to an iN10 MX Infrared Imaging Microscope was used to study the heterogeneous ozonolysis of thin solid films of catechol. A fresh solution of catechol in acetone (British Drug Houses 99.97%) was freshly prepared before the experiment at a concentration of 2.0 mg mL^{-1} . A total of $500.0 \mu\text{L}$ of the solution was slowly deposited onto the circular ZnSe crystal (15 mm in diameter) of the 45° single-reflectance attenuated total reflectance (ATR) accessory (SpectraTech) by drop-wise addition, forming a stable film after two hours. A macro-loop program was used to collect spectra (64 scans, 4 cm^{-1} resolution) over time. The loss of catechol O-H bands during ozonolysis was monitored in the absorbance mode at 3458 cm^{-1} . Spectra of thin films of *cis,cis*-muconic acid (Sigma-Aldrich $\geq 97.0\%$) were also registered for comparison purposes.

Experiment at high relative humidity $\text{RH} \geq 80\%$ were conducted by mixing $0.8 \text{ L min}^{-1} \text{ N}_2(\text{g})$ bubbled through ultrapure water with $0.2 \text{ L min}^{-1} \text{ O}_3(\text{g})$ generated as described in the main text. Humidity measurements were registered in a mixing chamber with a relative humidity sensor (Fisher Scientific). A flow of 20 mL min^{-1} of this diluted $\text{O}_3(\text{g})$ was circulated through a homemade borosilicate glass cell covering the ATR crystal. A correction to the loss of catechol was applied by subtracting the

loss of absorbance at 3458 cm^{-1} when humid UHP $\text{N}_2(\text{g})$ serving as zero air (control with no $\text{O}_3(\text{g})$) was circulated under the same conditions.

The heterogeneous oxidation of catechol thin films proceeded promptly after addition of gaseous ozone at high relative humidity (RH). However, *cis,cis*-muconic acid, the previously unique identified product⁷ appears to be embed by other species and cannot explain the overall complexity of the spectrum after 2 h of reaction with 4 ppmv $\text{O}_3(\text{g})$ at 81% RH. Herein, we suggest that the broadening of the O-H vibration bands at high RH levels previously suggested to indicate hydrogen bonding between catechol and adsorbed water molecules,⁷ may actually correspond to the formation of the polyhydroxylated catechol products also observed by ESI-MS (see main text).

The spectra below for catechol and *cis,cis*-muconic acid thin films in Figure S3 agree with their crystalline structure features listed in Tables 1 and 2, respectively.

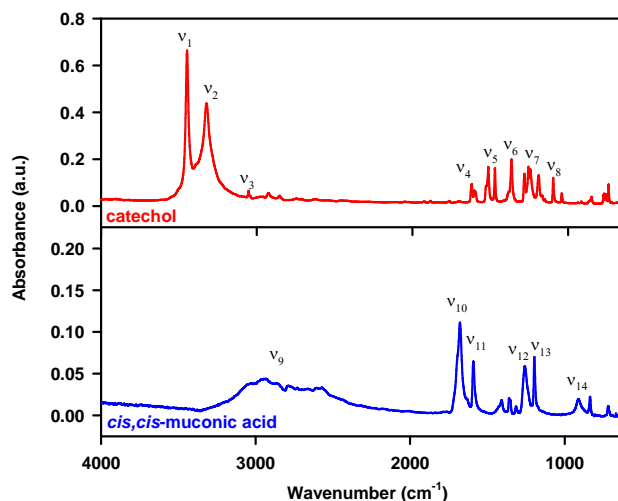


Figure S3. ATR-FTIR spectra of (red and top) catechol and (blue and bottom) *cis,cis*-muconic acid.

Table S1. Vibrational assignment of Catechol in the IR spectrum

Wavenumber (cm ⁻¹)	Strength	Assignment
3458 (ν ₁)	S	O-H
3322 (ν ₂)	S	O-H
3053 (ν ₃)	W	=C-H
1619 (ν ₄ ,) and 1513,1469 (ν ₅)	W	C=C
1365 (ν ₆)	M	C=C in aromatics
1256 (ν ₇)	S	C-H
1094 (ν ₈)	W	C-H

Key: S = Strong, M = Medium, and W = Weak

Table S2. Vibrational assignment of *cis,cis*-muconic acid in the IR spectrum

Wavenumber (cm ⁻¹)	Strength	Assignment
2936 (ν ₉)	W	O-H
1675 (ν ₁₀)	S	C=O
1590 (ν ₁₁)	M	C=C
1259 (ν ₁₂)	W	C-H
1198 (ν ₁₃)	W	C-O
909 (ν ₁₄)	W	C-H

Key: S = Strong, M = Medium, and W = Weak

The decrease of the characteristic O-H stretching (ν₁) peak at 3458 cm⁻¹ was used to monitor the loss of catechol in Figure S4. Several short lasting experiments at high [O₃(g)] were performed at RH ≥ 80 %. For example, Figure S4 displays the loss of catechol exposed to [O₃(g)] = 2.12 × 10¹⁵ molecules cm⁻³ at 80% RH, and Figure S5 shows the relative reaction rate measured by extracting the CD-line (corrected absorbance) at 3458 cm⁻¹ versus time. The corrected absorbance was measured using Omnic software (Thermo Scientific) from the A-B local baseline, to the left- and right-hand side of the peak, up to the maximum absorbance value or C-D line indicating the peak height depicted in Figure S4.

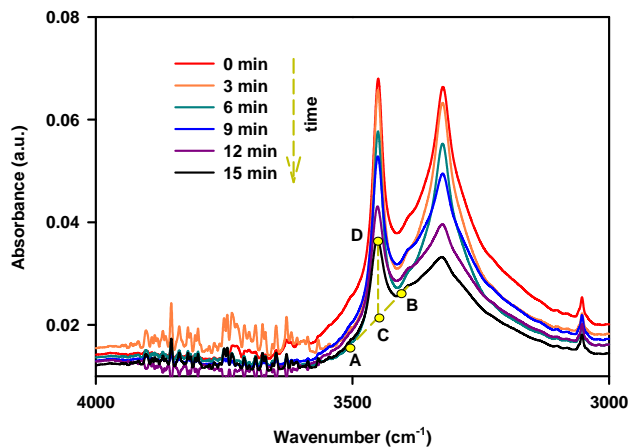


Figure S4. ATR-FTIR spectra of thin films of catechol exposed to $[O_3(g)] = 2.12 \times 10^{15}$ molecules cm^{-3} at 80 % RH.

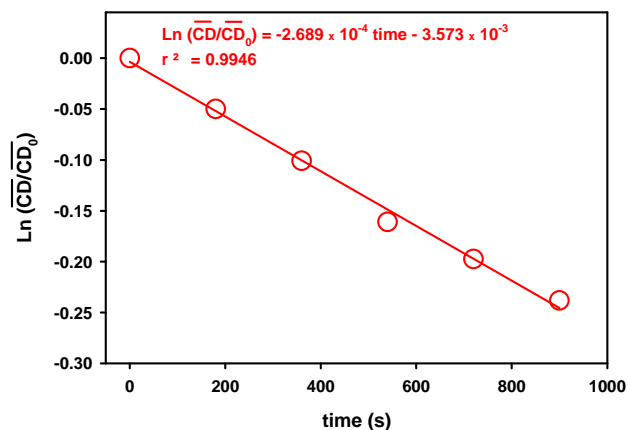


Figure S5. First-order decay of the CD-line of catechol at 3458 cm^{-1} relative to its initial value. Conditions: $[O_3(g)] = 2.12 \times 10^{15}$ molecules cm^{-3} and 80 % RH.

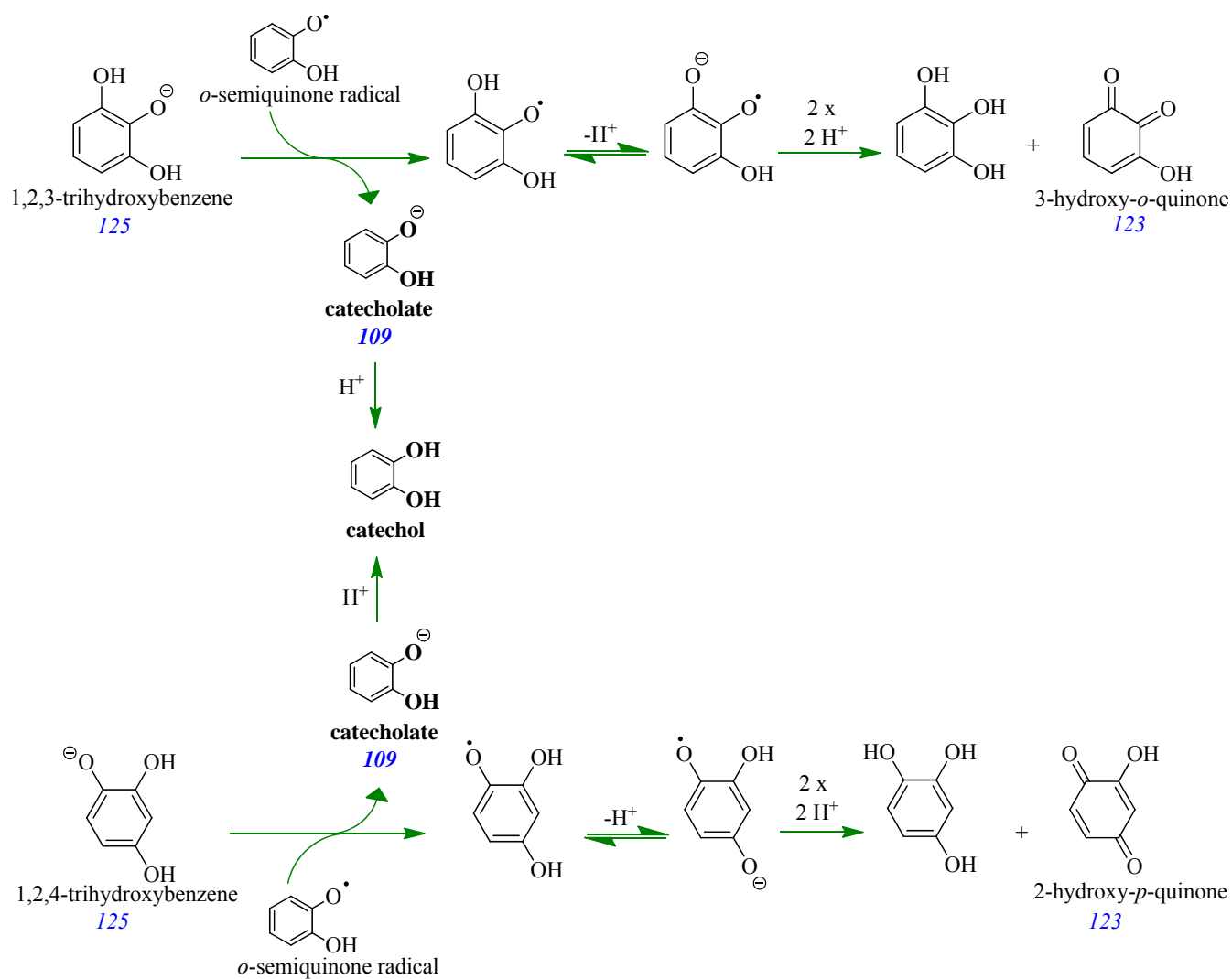
For high $[O_3(g)]$, the loss of catechol follows first order kinetics on the reactants⁷ with rate constant k :

$$-d[\text{catechol}]/dt = k [\text{catechol}] [O_3(g)] \quad (4)$$

Considering that for $[O_3(g)] = 2.12 \times 10^{15}$ molecules cm^{-3} , the level of this reactant remains constant in Figure S5, the equation simplifies to:

$$-d[\text{catechol}]/dt = k' [\text{catechol}] \quad (5)$$

where k' is the pseudo-first order rate constant resulting from $k \times [\text{O}_3(\text{g})]$. The film of catechol disappeared in Figure S5 with a pseudo-first order rate constant $k' = 2.689 \times 10^{-4} \text{ s}^{-1}$. Therefore, for this high $[\text{O}_3(\text{g})]$, it only takes 43 min for a half of the catechol film to quickly disappear in the ATR setup.



Scheme S1. Proposed recycling of *o*-semiquinone radical into catechol at the air-water interface showing observed *m/z* values in blue font.

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