

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

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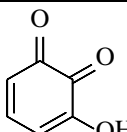
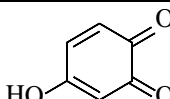
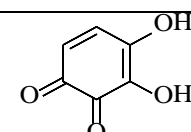
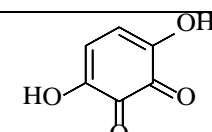
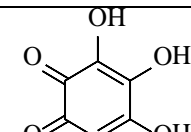
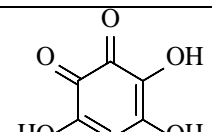
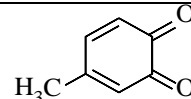
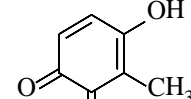
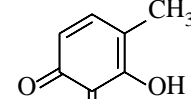
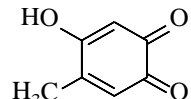
Justification of the pH Conditions Examined.

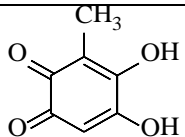
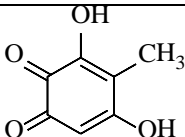
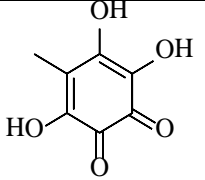
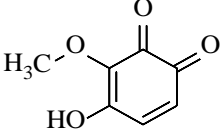
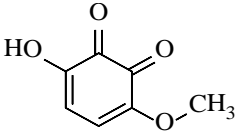
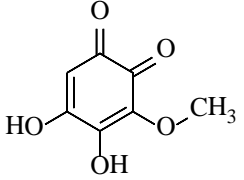
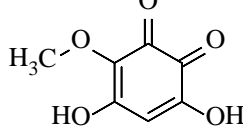
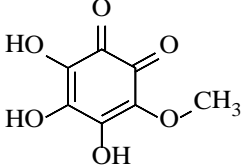
While the oxidations were explored in the atmospheric relevant pH range 5-10, reporting the results at pH 7.8 provides an example case that demonstrates the complexity of all the chemistry observed. Although many atmospheric studies are commonly aimed to reproduce highly acidic aerosol conditions, there is considerable evidence demonstrating that basic particles exist in the atmosphere. For example, particulate matter with a diameter less than 2.5 μm ($\text{PM}_{2.5}$) collected in and around agricultural regions is predominately alkaline.^{1, 2} Importantly, anthropogenic biomass burning emissions from agricultural practices (slash and burn, controlled burns, etc.) often coincide with increased ammonia (NH_3) emissions from livestock and fertilizers.^{3, 4} Once these species are emitted to the atmosphere, they can effectively neutralize available nitric and sulfuric acids from industrial emissions.^{5, 6} Recent work has shown that in most of the Midwest Region and the Pacific coast of the United States, where agriculture is a primary economic activity, NH_3 emissions are estimated to be sufficient to neutralize all acidic components.² Therefore, the experiments outlined are representative of true atmospheric conditions because even fine aerosols can be neutral or slightly basic. Indeed, for atmospheric particles occurring under the basic conditions described, a high ionic strength is expected due to presence of ammonium salts. Importantly, our work has demonstrated that for increasing ionic strength (e.g., for a series sodium halides) the solubility of gaseous ozone at the air-water interface is enhanced.⁷ Therefore, for a higher dissolved ozone level, the probability for electron transfer induced HO^\bullet production should also growth. In summary, the oxidation of the substituted catechols in aerosols with higher ionic strength is expected to also be enhanced.

Table S1. Complete List of Products Resulting from the Mechanism in Scheme 1 with Species Observed Indicated by their m/z Values

Parent	1 st Generation	2 nd Generation	m/z	3 rd Generation	m/z	4 th Generation	m/z	5 th Generation	m/z
Benzene	Phenol	Catechol	109	Pyrogallol	125	Tetrahydroxybenzenes	141	Pentahydroxybenzene	157
Toluene	o-Cresol	3-Methylcatechol	123	3-Methyl-4-hydroxycatechol	139	3-Methyl-4,5-dihydroxycatechol	155	Pentahydroxytoluene	171
Toluene	p-Cresol	4-Methylcatechol	123	4-Methylpyrogallol	139	5-Methyl-1,2,3,4-tetrahydroxybenzene	155		
				4-Methyl-5-hydroxycatechol	139	4-Methyl-3,5-dihydroxycatechol			
Anisole	Guaicol	3-Methoxycatechol	139	3-Methoxy-4-hydroxycatechol	155	3-Methoxy-4,5-dihydroxycatechol	171	Pentahydroxyanisole	187
			139	4-Methoxypyrogallol	155	4-Methoxy-5-hydroxypyrogallol	171		

Table S2. Produced Quinones and their Initial Precursors from Scheme 1.

<i>m/z</i>	Product 1	Product 2	Product 3	Precursor(s)
123	 3 ⁻ Hydroxy ⁻ <i>o</i> ⁻ quinone	 4 ⁻ Hydroxy ⁻ <i>o</i> ⁻ quinone		Catechol and Pyrogallol
139	 3 ⁻ 4 ⁻ Dihydroxy ⁻ <i>o</i> ⁻ quinone	 3 ⁻ 6 ⁻ Dihydroxy ⁻ <i>o</i> ⁻ quinone		Catechol and Pyrogallol
155	 3 ⁻ 4 ⁻ 5 ⁻ Trihydroxy ⁻ <i>o</i> ⁻ quinone	 3 ⁻ 4 ⁻ 6 ⁻ Trihydroxy ⁻ <i>o</i> ⁻ quinone		Catechol and Pyrogallol
121	 4 ⁻ methyl ⁻ <i>o</i> ⁻ quinone			4-Methylcatechol
137	 3 ⁻ methyl ⁻ 4 ⁻ hydroxy ⁻ <i>o</i> ⁻ quinone	 4 ⁻ methyl ⁻ 3 ⁻ hydroxy ⁻ <i>o</i> ⁻ quinone	 4 ⁻ methyl ⁻ 5 ⁻ hydroxy ⁻ <i>o</i> ⁻ quinone	3-Methylcatechol and 4-Methylcatechol

153	 <p>3⁻methyl⁻4⁻5⁻dihydroxy⁻o⁻quinone</p>	 <p>4⁻methyl⁻3⁻5⁻dihydroxy⁻o⁻quinone</p>	<p>3-Methylcatechol and 4-Methylcatechol</p>
171	 <p>4⁻methyl⁻3⁻5⁻6⁻trihydroxy⁻o⁻quinone</p>		<p>3-Methylcatechol and 4-Methylcatechol</p>
153	 <p>3⁻methoxy⁻4⁻hydroxy⁻o⁻quinone</p>	 <p>3⁻methoxy⁻6⁻hydroxy⁻o⁻quinone</p>	3-Methoxycatechol
169	 <p>3⁻methoxy⁻4⁻5⁻dihydroxy⁻o⁻quinone</p>	 <p>3⁻methoxy⁻4⁻6⁻dihydroxy⁻o⁻quinone</p>	3-Methoxycatechol
185	 <p>3⁻methoxy⁻4⁻5⁻6⁻trihydroxy⁻o⁻quinone</p>		3-Methoxycatechol

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