

Supporting Information For:

Oxidation of Phenolic Aldehydes by Ozone and Hydroxyl Radical at the Air-Water Interface

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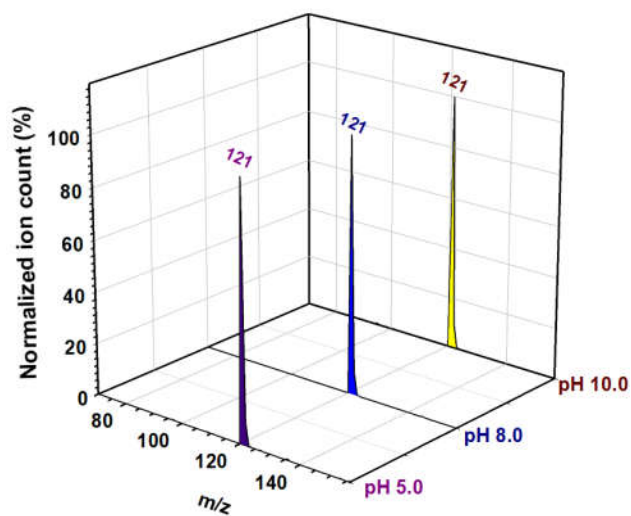


Figure S1. OESI-MS Spectra of 4-hydroxybenzaldehyde exposed to 0.2 L min^{-1} flow of gas without $\text{O}_3(\text{g})$ under variable pH. Ion count values (I) are normalized percentages relative to the most intense peak in each mass spectrum at m/z 121, I_{121} .

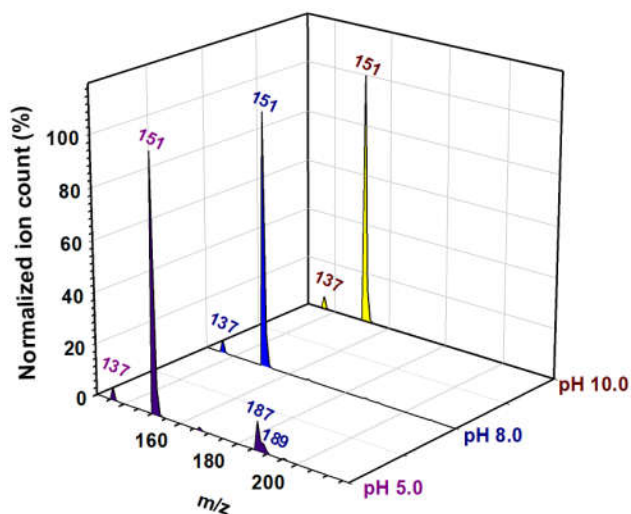


Figure S2. OESI-MS Spectra of vanillin exposed to 0.2 L min^{-1} flow of gas without $\text{O}_3(\text{g})$ under variable pH. Ion count values are normalized percentages relative to the most intense peak in each mass spectrum, I_{151} . The anion peak of vanillin at m/z 151 is stable, and the observed minor fragment ion at m/z 137 corresponds to the loss of 14 amu typical from methoxyphenols breakup by collision-induced dissociation (CID). The integration of the areas under the peaks with m/z 187 and m/z 189 of the mass spectrum at pH 5.0 show relative abundances of 76% and 24%, respectively, verifying they correspond to an aerosolization adduct of chloride (m/z 34.97 and 36.97), from 0.001 M HCl used for pH adjustment, to a neutral molecule of vanillin (151.15 amu).

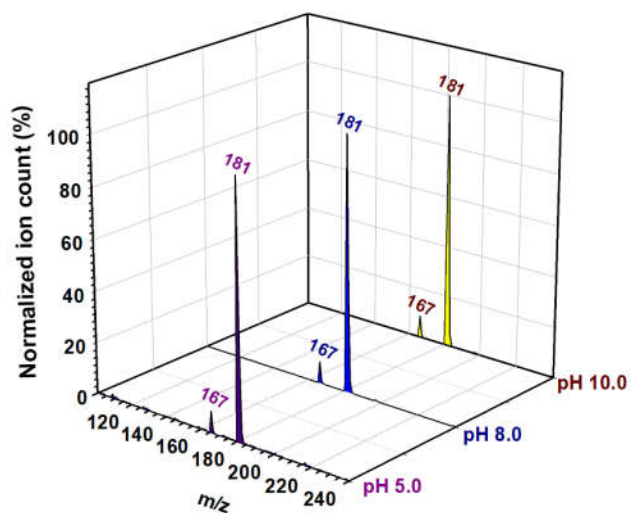


Figure S3. OESI-MS Spectra of syringaldehyde exposed to 0.2 L min^{-1} flow of gas without $\text{O}_3(\text{g})$ under variable pH. Ion count values are normalized percentages relative to the most intense peak in each mass spectrum, I_{181} . The anion peak of syringaldehyde at m/z 181 is stable, and the observed minor fragment ion at m/z 167 corresponds to the loss of 14 amu typical from methoxyphenols breakup by collision-induced dissociation (CID).

Cyclic Voltammetry.

Figure S4 shows the cyclic voltammograms of the three phenolic aldehydes for the range $4.98 \leq \text{pH} \leq 10.04$. While the oxidation of 4-hydroxybenzaldehyde (panel A) and vanillin (panel B) showed an irreversible behavior in Figure S4, syringaldehyde (panel C) experienced a quasi-reversible process.^{1,2} The labels within Figure S4 indicate the first and second anodic oxidation potentials, $E_{p,1}$ and $E_{p,2}$ for peaks 1 and 2, respectively. The three phenolic aldehydes display a first anodic oxidation peak for the whole pH range, while second anodic oxidation peak is only registered for $\text{pH} \geq 7.0$. The values of $E_{p,1}$ and $E_{p,2}$ were obtained from the respective voltammogram using CHI Software version 18.03. The oxidation of the fully protonated phenol corresponds to peak 1 ($E_{p,1}$), which participates in reaction S1 (reaction R2 in Scheme 1 of the main text):^{3,4}



The oxidation of the conjugated phenoxide anion is assigned to peak 2 ($E_{p,2}$), which participates in reaction S2 (reaction R1 in Scheme 1 of the main text):^{3,4}



Cyclic voltammetry provides additional support for the irreversible oxidation of the three phenolic aldehydes, proving the instability of the phenoxy radicals generated in the system.

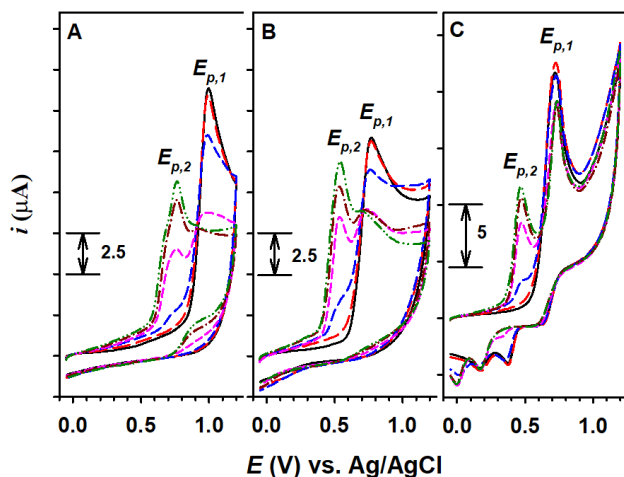


Figure S4. Cyclic voltammograms at 50 mV s^{-1} scan rate for 1.00 mM (A) 4-hydroxybenzaldehyde, (B) vanillin, and (C) syringaldehyde for pH 4.98 (solid black trace), pH 6.01 (long dash red trace), pH 7.04 (medium dash blue trace), pH 8.03 (short dash pink trace), pH 9.04 (dash-dot brown trace), and pH 10.04 (dash-dot-dot green trace).

Inflection Potential Determination.

Peak potentials have been widely used as equivalent to redox potentials for irreversible electrochemical systems. However, peak potentials are susceptible to changes in the concentration of the analyte, pH, scan rate, and the kinetics of interfacial electron transfer.⁵ A more representative redox potential is obtained for irreversible systems from the inflection potential (E_i).⁵ Figure S5, Figure S6, and Figure S7 show examples of the procedure used to determine inflection potential from the cyclic voltammogram of 4-hydroxybenzaldehyde, vanillin, and syringaldehyde at pH 8.03, respectively. The first and second derivatives of the cyclic voltammograms were obtained with the software using 49 least square points. Peak labels $E_{p,1}$ and $E_{p,2}$ in Figures S5-S7 correspond to anodic peak potentials in the original cyclic voltammogram. The maximum of the first derivative ($\frac{di}{dE} = 0$) and inflection point of the second derivative ($\frac{d^2i}{dE^2} = 0$) representing the potentials of the voltammograms are labeled $E_{i,1}$ and $E_{i,2}$ in Figures S5-S7.⁵ The data treatment exemplified for Figures S5-S7 for the determination of the inflection points is used to report the correct redox potentials (E_{red}) of the phenolic aldehydes at the corresponding pH. The pK_a values of the three compounds^{6,7,8} (Table 1 of the main text) point out that at $pH \leq 7.00$ mostly undissociated phenols are present, while at $pH \geq 8.00$ the dissociated form (phenoxide) is the major form present in equilibrium.⁴ Thus, the inflection points $E_{i,1}$ and $E_{i,2}$ are the best representation of the redox potential for the fully undissociated phenols ($E_{red,1}$) and their dissociated bases ($E_{red,2}$), respectively. The experimentally determined redox potentials (E_{red}) for phenolic aldehydes are provided in Table S1 versus the Ag/AgCl reference electrode used, and in Table 1 versus the standard hydrogen electrode (SHE) after conversion of the previous values with the relationship $E_{red}(\text{SHE}) = E_{red}(\text{Ag/AgCl sat. KCl}) + 0.197$.⁹

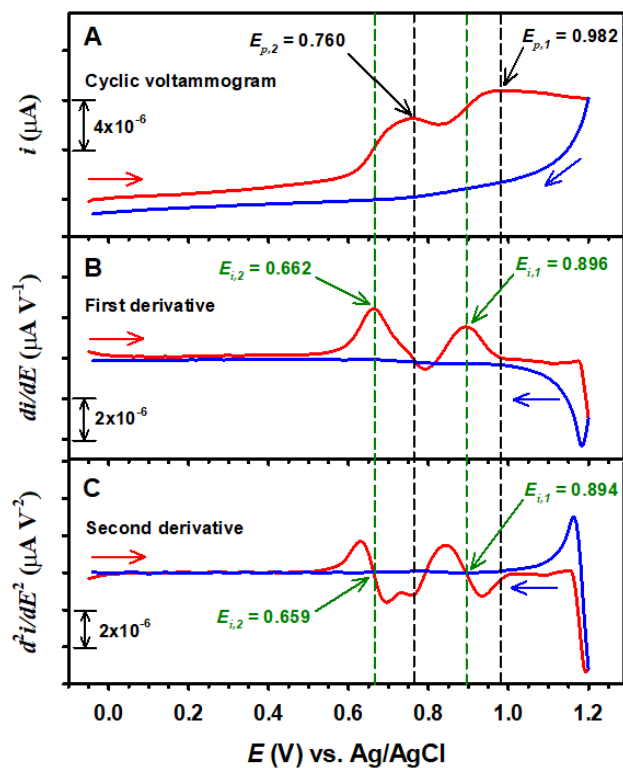


Figure S5. (A) Cyclic voltammogram of 1.00 mM 4-hydroxybenzaldehyde at pH 8.03 (scan rate of 50 mV s^{-1}), (B) first derivative of cyclic voltammogram, and (C) second derivative of the cyclic voltammogram. Red and blue arrows indicate the forward and backward scan directions, respectively. Black dash lines show the position of peak potentials (E_p) and green dash lines show the position of maximum of first derivative and inflection potentials (E_i) of the second derivative, respectively.

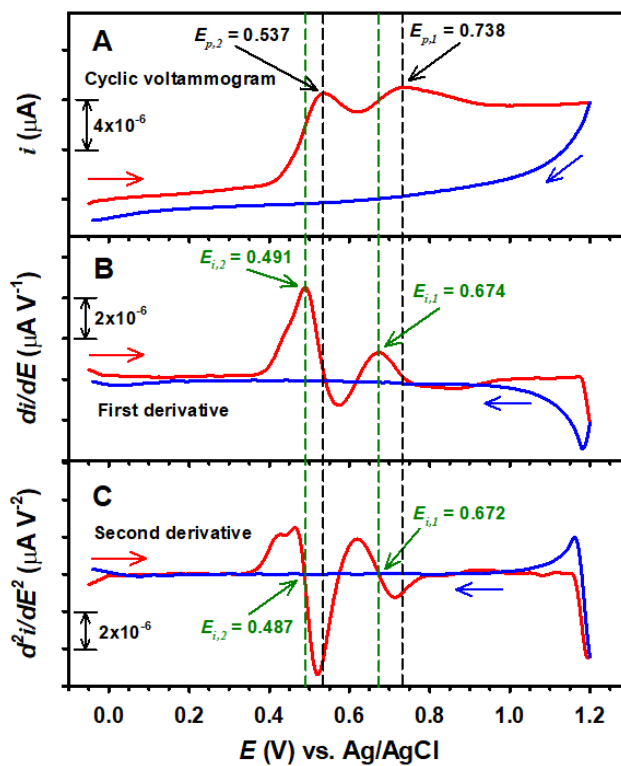


Figure S6. (A) Cyclic voltammogram of 1.00 mM vanillin at pH 8.03 (scan rate of 50 mV s^{-1}), (B) first derivative of cyclic voltammogram, and (C) second derivative of the cyclic voltammogram. Red and blue arrows indicate the forward and backward scan directions, respectively. Black dash lines show the position of peak potentials (E_p) and green dash lines show the position of maximum of first derivative and inflection potentials (E_i) of the second derivative, respectively.

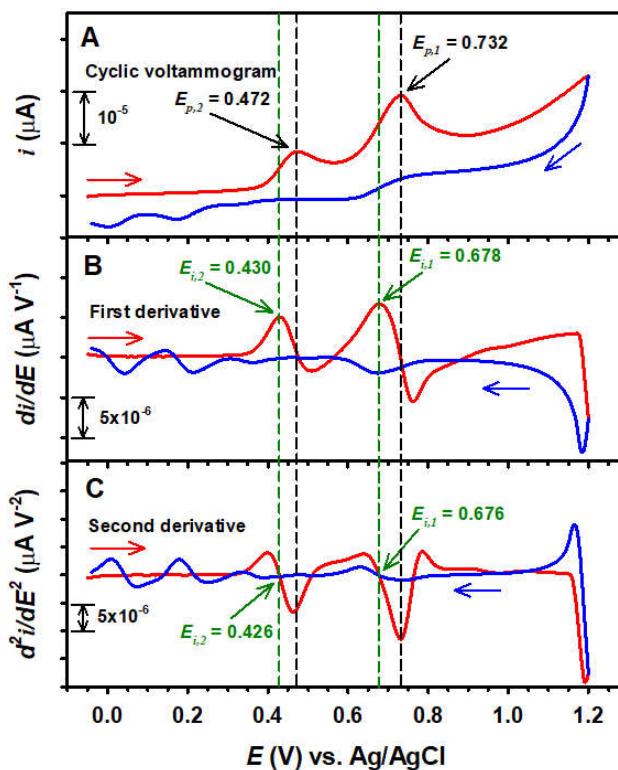


Figure S7. (A) Cyclic voltammogram of 1.00 mM syringaldehyde at pH 8.03 (scan rate of 50 mV s^{-1}) (B) first derivative of cyclic voltammogram, and (C) second derivative of the cyclic voltammogram. Red and blue arrows indicate the forward and backward scan directions, respectively. Black dash lines show the position of peak potentials (E_p) and green dash lines show the position of maximum of first derivative and inflection potentials (E_i) of the second derivative, respectively.

Table S1. Experimental Redox Potentials (E_{red}) at Variable pH using Ag/AgCl as Reference Electrode.

pH	4-Hydroxybenzaldehyde		Vanillin		Syringaldehyde	
	$E_{red,1}$ (V)	$E_{red,2}$ (V)	$E_{red,1}$ (V)	$E_{red,2}$ (V)	$E_{red,1}$ (V)	$E_{red,2}$ (V)
4.98	0.939±0.002	-	0.705±0.000	-	0.651±0.001	-
6.01	0.936±0.001	-	0.702±0.000	-	0.651±0.001	-
7.04	0.922±0.000	0.687±0.004	0.686±0.001	0.472±0.002	0.650±0.000	0.436±0.001
8.03	0.894±0.002	0.659±0.002	0.672±0.000	0.487±0.002	0.675±0.001	0.426±0.000
9.04	0.889±0.001	0.646±0.005	0.674±0.000	0.475±0.001	0.689±0.000	0.424±0.000
10.06	0.900±0.000	0.626±0.002	0.678±0.000	0.455±0.001	0.693±0.001	0.421±0.000

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