Table S1. Vibrational assignment for catechol film

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Intensity$^a$</th>
<th>Assignment$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3450</td>
<td>s</td>
<td>v(O-H)</td>
</tr>
<tr>
<td>3323</td>
<td>s</td>
<td>v(O-H)</td>
</tr>
<tr>
<td>3051</td>
<td>m</td>
<td>v(C-H)</td>
</tr>
<tr>
<td>1618, 1595</td>
<td>m, m</td>
<td>v(C=С)</td>
</tr>
<tr>
<td>1512</td>
<td>s</td>
<td>v(C=С)</td>
</tr>
<tr>
<td>1471</td>
<td>s</td>
<td>v(C=С)</td>
</tr>
<tr>
<td>1363</td>
<td>s</td>
<td>v(C=С)</td>
</tr>
<tr>
<td>1255</td>
<td>s</td>
<td>δ(C-H)</td>
</tr>
<tr>
<td>1190</td>
<td>s</td>
<td>δ(O-H)</td>
</tr>
<tr>
<td>1095</td>
<td>s</td>
<td>δ(C-H)</td>
</tr>
<tr>
<td>1041</td>
<td>s</td>
<td>δ(C-H)</td>
</tr>
<tr>
<td>918</td>
<td>w</td>
<td>ρ(C-H)</td>
</tr>
<tr>
<td>849</td>
<td>m</td>
<td>ρ(C-H)</td>
</tr>
<tr>
<td>769</td>
<td>s</td>
<td>v(C=С)</td>
</tr>
<tr>
<td>741</td>
<td>s</td>
<td>ρ(C-H)</td>
</tr>
</tbody>
</table>

$^a$ w = weak; m = medium; s = strong.

$^b$ v = stretching; δ = in plane bending; ρ = out of plane bending.

All assignments are based on theoretical and experimental studies.$^1$
## Table S2. Vibrational assignments for oxidized film

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity(^a)</th>
<th>Assignment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3393</td>
<td>m</td>
<td>ν(O-H)</td>
</tr>
<tr>
<td>3100 - 2500</td>
<td>w,b</td>
<td>ν(O-H)</td>
</tr>
<tr>
<td>1737</td>
<td>sh</td>
<td>ν(C=O)</td>
</tr>
<tr>
<td>1694</td>
<td>sh</td>
<td>ν(C=O)</td>
</tr>
<tr>
<td>1679</td>
<td>s</td>
<td>ν(C=O)</td>
</tr>
<tr>
<td>1632</td>
<td>w</td>
<td>ν(C=C)</td>
</tr>
<tr>
<td>1594</td>
<td>s</td>
<td>ν(C=C)</td>
</tr>
<tr>
<td>1520</td>
<td>w</td>
<td>ν(C=C)</td>
</tr>
<tr>
<td>1408</td>
<td>m</td>
<td>δ(C=C)</td>
</tr>
<tr>
<td>1355,1315</td>
<td>m, m</td>
<td>δ(C=C-H)</td>
</tr>
<tr>
<td>1262, 1197</td>
<td>s, s</td>
<td>ν(C-O)</td>
</tr>
<tr>
<td>1216</td>
<td>w</td>
<td>δ(C=C-H)</td>
</tr>
<tr>
<td>1118</td>
<td>w</td>
<td>ν(C-O)</td>
</tr>
<tr>
<td>835</td>
<td>m</td>
<td>ρ(C=C-H)</td>
</tr>
</tbody>
</table>

\(^a\) w = weak; m = medium; s = strong; sh = shoulder; b = broad.

\(^b\) ν = stretching; δ = in plane bending; ρ = out of plane bending.
**Table S3. Vibrational assignment of cis,cis-muconic acid**

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Intensityᵃ</th>
<th>Assignmentᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300 - 2200</td>
<td>m, br</td>
<td>v(O-H)</td>
</tr>
<tr>
<td>1680</td>
<td>s</td>
<td>v(C=O)</td>
</tr>
<tr>
<td>1635</td>
<td>sh</td>
<td>v(C=C)</td>
</tr>
<tr>
<td>1591</td>
<td>s</td>
<td>v(C=C)</td>
</tr>
<tr>
<td>1408</td>
<td>m</td>
<td>δ(C=C)</td>
</tr>
<tr>
<td>1355, 1316</td>
<td>m, m</td>
<td>δ(C=C-H)</td>
</tr>
<tr>
<td>1258, 1197</td>
<td>s, s</td>
<td>v(C-O)</td>
</tr>
<tr>
<td>914</td>
<td>w</td>
<td>ρ(O-H)</td>
</tr>
</tbody>
</table>

ᵃ w = weak; m = medium; s = strong; sh = shoulder; br = broad.
ᵇ v = stretching; δ = in plane bending; ρ = out of plane bending.
Assignments based on experimental results.²
Table S4. Vibrational assignment of maleic acid

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity(^a)</th>
<th>Assignment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3059</td>
<td>m</td>
<td>ν(C-H)</td>
</tr>
<tr>
<td>3200 - 2100</td>
<td>m, b</td>
<td>ν(O-H)</td>
</tr>
<tr>
<td>1708</td>
<td>s</td>
<td>ν(C=O)</td>
</tr>
<tr>
<td>1637</td>
<td>w</td>
<td>ν(C=C)</td>
</tr>
<tr>
<td>1579</td>
<td>s</td>
<td>ν(C=C)</td>
</tr>
<tr>
<td>1461</td>
<td>m</td>
<td>δ(C-O-H)</td>
</tr>
<tr>
<td>1436</td>
<td>m</td>
<td>δ(C=C-H)</td>
</tr>
<tr>
<td>1264</td>
<td>s</td>
<td>ν(C=O)</td>
</tr>
<tr>
<td>1221</td>
<td>m</td>
<td>δ(C=C-H)</td>
</tr>
<tr>
<td>950</td>
<td>w</td>
<td>ν(C=C)</td>
</tr>
<tr>
<td>871</td>
<td>m</td>
<td>ρ(C-H)</td>
</tr>
</tbody>
</table>

\(^a\) w = weak; m = medium; s = strong; b = broad.

\(^b\) ν = stretching; δ = in plane bending; ρ = out of plane bending.

Assignments based on experimental and theoretical results.\(^3\)
Table S5. Vibrational assignment of glyoxylic acid.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Intensityᵃ</th>
<th>Assignmentᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>3700-2250</td>
<td>vs, br</td>
<td>v(O-H)</td>
</tr>
<tr>
<td>1727</td>
<td>vs</td>
<td>v(C=O)</td>
</tr>
<tr>
<td>1630</td>
<td>m</td>
<td>v_{as}(O-C-O)</td>
</tr>
<tr>
<td>1231</td>
<td>s</td>
<td>v(C-O) +</td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ(O-H)</td>
</tr>
<tr>
<td>1087, 1043</td>
<td>s, vs</td>
<td>δ(C-C-H)</td>
</tr>
</tbody>
</table>

ᵃ w = weak; m = medium; s = strong; br = broad.
ᵇ v = stretching; δ = in plane bending; ρ = out of plane bending.
Assignments based on experimental results.⁴
Table S6. Vibrational assignment of oxalic acid

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity(^a)</th>
<th>Assignment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3458</td>
<td>vs</td>
<td>v(O-H)</td>
</tr>
<tr>
<td>1684</td>
<td>vs</td>
<td>v(_{\text{as}})(O-C-O)</td>
</tr>
<tr>
<td>1251</td>
<td>vs</td>
<td>v(_{\text{s}})(C-O)  + \δ(O-C-O)</td>
</tr>
<tr>
<td>1133</td>
<td>m</td>
<td>v(C-OH)</td>
</tr>
<tr>
<td>725</td>
<td>s</td>
<td>δ(O-C-O)</td>
</tr>
</tbody>
</table>

\(^a\) w = weak; m = medium; s = strong.

\(^b\) ν = stretching; δ = in plane bending; ρ = out of plane bending.

Assignments based on experimental results.\(^d\)
Table S7. Vibrational assignment of 1,2,3-trihydroxybenzene

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity(^a)</th>
<th>Assignment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3375</td>
<td>s</td>
<td>(v(O-H))</td>
</tr>
<tr>
<td>3245</td>
<td>s</td>
<td>(v(O-H))</td>
</tr>
<tr>
<td>3056</td>
<td>w</td>
<td>(v(C-H))</td>
</tr>
<tr>
<td>1633</td>
<td>sh</td>
<td>(v(C=C))</td>
</tr>
<tr>
<td>1622</td>
<td>s</td>
<td>(v(C=C))</td>
</tr>
<tr>
<td>1525</td>
<td>s</td>
<td>(v(C=C))</td>
</tr>
<tr>
<td>1488</td>
<td>s</td>
<td>(\delta(C-O-H))</td>
</tr>
<tr>
<td>1363</td>
<td>s</td>
<td>(\delta(O-H))</td>
</tr>
<tr>
<td>1290</td>
<td>s</td>
<td>(\delta(C-O-H))</td>
</tr>
<tr>
<td>1243</td>
<td>s</td>
<td>(\delta(C-H))</td>
</tr>
<tr>
<td>1190</td>
<td>s</td>
<td>(\delta(C=\text{C-H}))</td>
</tr>
<tr>
<td>1061</td>
<td>m</td>
<td>(v(C=\text{C}))</td>
</tr>
<tr>
<td>1004</td>
<td>s</td>
<td>(\rho (C=\text{C-H}))</td>
</tr>
<tr>
<td>847</td>
<td>w</td>
<td>(\rho (C=\text{C-H}))</td>
</tr>
<tr>
<td>830</td>
<td>w</td>
<td>(\rho(C=\text{C-O}))</td>
</tr>
<tr>
<td>764</td>
<td>m</td>
<td>(v(C=\text{C}))</td>
</tr>
<tr>
<td>805</td>
<td>s</td>
<td>(\rho (=\text{C-O-H}))</td>
</tr>
</tbody>
</table>

\(^a\) w = weak; m = medium; s = strong; sh = shoulder.

\(^b\) \(v\) = stretching; \(\delta\) = in plane bending; \(\rho\) = out of plane bending.

Assignments based on experimental and theoretical results.\(^5\)
Table S8. Vibrational assignment of 1,2,4-trihydroxybenzene

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity(^a)</th>
<th>Assignment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3256</td>
<td>s</td>
<td>(\nu\text{(O-H)})</td>
</tr>
<tr>
<td>1622</td>
<td>m</td>
<td>(\nu\text{(C=C)})</td>
</tr>
<tr>
<td>1577</td>
<td>sh</td>
<td>(\nu\text{(C=C)})</td>
</tr>
<tr>
<td>1514</td>
<td>sh</td>
<td>(\nu\text{(C=C)})</td>
</tr>
<tr>
<td>1386</td>
<td>s</td>
<td>(\delta\text{(O-H)})</td>
</tr>
<tr>
<td>1300</td>
<td>s</td>
<td>(\delta\text{(C-O-H)})</td>
</tr>
<tr>
<td>839</td>
<td>m</td>
<td>(\delta\text{(C-O-H)})</td>
</tr>
<tr>
<td>790</td>
<td>s</td>
<td>(\rho\text{(C-H)})</td>
</tr>
</tbody>
</table>

\(^a\) w = weak; m = medium; s = strong; sh = shoulder.
\(^b\) \(\nu\) = stretching; \(\delta\) = in plane bending; \(\rho\) = out of plane bending.
Assignments based on experimental and theoretical results.\(^6\)
Table S9. Pseudo-first order rate constants ($k$) and associated standard deviations ($s$) for the decay of catechol and production of cis,cis-muconic acid at variable RH extracted from the equations $[\text{catechol}] = [\text{catechol}]_0 + e^{-k_{\text{catechol}+\text{O}_3} t}$ and $[\text{cis,cis-muconic acid}]^\text{inf} = (1 - e^{-k_{\text{cis,cis-muconic acid}} t})$.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>$k_{\text{catechol+O}_3}$ (s$^{-1}$)</th>
<th>$k_{\text{cis,cis-muconic acid}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$2.156 \times 10^{-8}$</td>
<td>$1.958 \times 10^{-10}$</td>
</tr>
<tr>
<td>29</td>
<td>$3.260 \times 10^{-8}$</td>
<td>$3.057 \times 10^{-9}$</td>
</tr>
<tr>
<td>48</td>
<td>$5.471 \times 10^{-5}$</td>
<td>$1.105 \times 10^{-4}$</td>
</tr>
<tr>
<td>71</td>
<td>$4.863 \times 10^{-4}$</td>
<td>$3.867 \times 10^{-4}$</td>
</tr>
<tr>
<td>90</td>
<td>$8.183 \times 10^{-4}$</td>
<td>$4.133 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
References


