

Supporting Information For:  
Heterogeneous Oxidation of Catechol

[DOI: 10.1021/acs.jpca.5b07914](https://doi.org/10.1021/acs.jpca.5b07914)

*Publication Date (Web): September 25, 2015*

---

*Elizabeth A. Pillar, Ruixin Zhou, and Marcelo I. Guzman\**

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

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

---

The Journal of Physical Chemistry A

---

<b>Content</b>	<b>Pages</b>
<b>Tables</b>	
Table S1	S2
Table S2	S3
Table S3	S4
Table S4	S5
Table S5	S6
Table S6	S7
Table S7	S8
Table S8	S9
Table S9	S10
<b>References</b>	S11

**Table S1.** Vibrational assignment for catechol film

Wavenumber (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment <sup>b</sup>
3450	s	v(O-H)
3323	s	v(O-H)
3051	m	v(C-H)
1618, 1595	m, m	v(C=C)
1512	s	v(C=C)
1471	s	v(C=C)
1363	s	v(C=C)
1255	s	δ(C-H)
1190	s	δ(O-H)
1095	s	δ(C-H)
1041	s	δ(C-H)
918	w	ρ(C-H)
849	m	ρ(C-H)
769	s	v(C=C)
741	s	ρ(C-H)

<sup>a</sup> w = weak; m = medium; s = strong.

<sup>b</sup> v = stretching; δ = in plane bending; ρ = out of plane bending.

All assignments are based on theoretical and experimental studies.<sup>1</sup>

**Table S2.** Vibrational assignments for oxidized film

Wavenumber (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment <sup>b</sup>
3393	m	v(O-H)
3100 - 2500	w,b	v(O-H)
1737	sh	v(C=O)
1694	sh	v(C=O)
1679	s	v(C=O)
1632	w	v(C=C)
1594	s	v(C=C)
1520	w	v(C=C)
1408	m	δ(C=C)
1355,1315	m, m	δ(C=C-H)
1262, 1197	s, s	v(C-O)
1216	w	δ(C=C-H)
1118	w	v(C-O)
835	m	ρ(C=C-H)

<sup>a</sup> w = weak; m = medium; s = strong; sh = shoulder; b = broad.

<sup>b</sup> v = stretching; δ = in plane bending; ρ = out of plane bending.

**Table S3.** Vibrational assignment of *cis,cis*-muconic acid

Wavenumber (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment <sup>b</sup>
3300 - 2200	m, br	v(O-H)
1680	s	v(C=O)
1635	sh	v(C=C)
1591	s	v(C=C)
1408	m	δ(C=C)
1355,1316	m, m	δ(C=C-H)
1258, 1197	s, s	v(C-O)
914	w	ρ(O-H)

<sup>a</sup> w = weak; m = medium; s = strong; sh = shoulder; br = broad.

<sup>b</sup> v = stretching; δ = in plane bending; ρ = out of plane bending.

Assignments based on experimental results.<sup>2</sup>

**Table S4.** Vibrational assignment of maleic acid

Wavenumber (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment <sup>b</sup>
3059	m	$\nu(\text{C-H})$
3200 - 2100	m, b	$\nu(\text{O-H})$
1708	s	$\nu(\text{C=O})$
1637	w	$\nu(\text{C=C})$
1579	s	$\nu(\text{C=C})$
1461	m	$\delta(\text{C-O-H})$
1436	m	$\delta(\text{C=C-H})$
1264	s	$\nu(\text{C-O})$
1221	m	$\delta(\text{C=C-H})$
950	w	$\nu(\text{C=C})$
871	m	$\rho(\text{C-H})$

<sup>a</sup> w = weak; m = medium; s = strong; b = broad.

<sup>b</sup>  $\nu$  = stretching;  $\delta$  = in plane bending;  $\rho$  = out of plane bending.

Assignments based on experimental and theoretical results.<sup>3</sup>

**Table S5.** Vibrational assignment of glyoxylic acid.

<b>Wavenumber (cm<sup>-1</sup>)</b>	<b>Intensity<sup>a</sup></b>	<b>Assignment<sup>b</sup></b>
3700-2250	vs, br	v(O-H)
1727	vs	v(C=O)
1630	m	v <sub>as</sub> (O-C-O)
1231	s	v(C-O) + δ(O-H)
1087, 1043	s, vs	δ(C-C-H)

<sup>a</sup> w = weak; m = medium; s = strong; br = broad.

<sup>b</sup> v = stretching; δ = in plane bending; ρ = out of plane bending.

Assignments based on experimental results.<sup>4</sup>

**Table S6.** Vibrational assignment of oxalic acid

Wavenumber (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment <sup>b</sup>
3458	vs	$\nu(\text{O-H})$
1684	vs	$\nu_{\text{as}}(\text{O-C-O})$
1251	vs	$\nu_{\text{s}}(\text{C-O})$ + $\delta(\text{O-C-O})$
1133	m	$\nu(\text{C-OH})$
725	s	$\delta(\text{O-C-O})$

<sup>a</sup> w = weak; m = medium; s = strong.

<sup>b</sup>  $\nu$  = stretching;  $\delta$  = in plane bending;  $\rho$  = out of plane bending.

Assignments based on experimental results.<sup>4</sup>

**Table S7.** Vibrational assignment of 1,2,3-trihydroxybenzene

Wavenumber (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment <sup>b</sup>
3375	s	v(O-H)
3245	s	v(O-H)
3056	w	v(C-H)
1633	sh	v(C=C)
1622	s	v(C=C)
1525	s	v(C=C)
1488	s	δ(C-O-H)
1363	s	δ(O-H)
1290	s	δ(C-O-H)
1243	s	δ(C-H)
1190	s	δ(C=C-H)
1061	m	v(C=C)
1004	s	ρ(C=C-H)
847	w	ρ(C=C-H)
830	w	ρ(C=C-O)
764	m	v(C=C)
805	s	ρ(=C-O-H)

<sup>a</sup> w = weak; m = medium; s = strong; sh = shoulder.

<sup>b</sup> v = stretching; δ = in plane bending; ρ = out of plane bending.

Assignments based on experimental and theoretical results.<sup>5</sup>



**Table S8.** Vibrational assignment of 1,2,4-trihydroxybenzene

Wavenumber (cm <sup>-1</sup> )	Intensity <sup>a</sup>	Assignment <sup>b</sup>
3256	s	$\nu(\text{O-H})$
1622	m	$\nu(\text{C=C})$
1577	sh	$\nu(\text{C=C})$
1514	sh	$\nu(\text{C=C})$
1386	s	$\delta(\text{O-H})$
1300	s	$\delta(\text{C-O-H})$
839	m	$\delta(\text{C-O-H})$
790	s	$\rho(\text{C-H})$

<sup>a</sup> w = weak; m = medium; s = strong; sh = shoulder.

<sup>b</sup>  $\nu$  = stretching;  $\delta$  = in plane bending;  $\rho$  = out of plane bending.

Assignments based on experimental and theoretical results.<sup>6</sup>

**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  $[\text{cis,cis-muconic acid}] / [\text{cis,cis-muconic acid}]_{\text{inf}} = (1 - e^{-k_{\text{cis,cis-muconic acid}} t})$ .

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

## References

- (1) Ramirez, F. J.; Navarrete, J. T. L. Normal Coordinate and Rotational Barrier Calculations on 1,2-dihydroxybenzene. *Vibrational Spectroscopy* **1993**, *4*, 321-334.
- (2) Söhár, P.; Varsányi, G. Y. An IR spectroscopic study of muconate isomers. *J. Mol. Struct.* **1968**, *1*, 437-448.
- (3) Maçôas, E. M. S.; Fausto, R.; Lundell, J.; Pettersson, M.; Khriachtchev, L.; Räsänen, M. A Matrix Isolation Spectroscopic and Quantum Chemical Study of Fumaric and Maleic Acid. *J. Phys. Chem. A* **2001**, *105*, 3922-3933.
- (4) Niculescu, M.; Ledeti, I.; Bîrzescu, M. New methods to obtain carboxylic acids by oxidation reactions of 1,2-ethanediol with metallic nitrates. *J. Organomet. Chem.* **2014**, *767*, 108-111.
- (5) Mustafa, C. Vibrational Spectroscopy of Pyrogallol with a glance on the problems of formation of a Dimer. *Research Journal of Chemistry and Environment* **2013**, *17*, 117-128.
- (6) Etaiw, S. E. H.; Werida, A. H. Three-dimensional organotin–hexacyanoferrate polymers as effective oxidizing reagents towards phenols. *Appl. Organomet. Chem.* **2010**, *24*, 805-808.