

## Supporting Information

*for*

### **Coagulation of Iodide-containing Resorcinol Solution or Natural Water with Ferric Chloride can Produce Iodinated Coagulation Byproducts**

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**Text S1.** Quantification of iodide, iodate, iodine and DBPs.

Iodide and iodate were analyzed using a Dionex ICS 1000 ion chromatography (Sunnyvale, USA).<sup>1</sup> Separation was achieved by a Dionex AS19-HC anion-exchange analytical column (250 × 4 mm, I.D.) coupled with a Dionex AG9-HC guard column (50 × 4.0 mm, I.D.). The detection limits for both iodide and iodate were 0.1 μM and 0.3 μM, respectively.

Analysis of HOI is available in detail elsewhere.<sup>2</sup> The samples containing HOI were quenched with phenol (200 μM) and analyzed as a summation of 2-iodo- and 4-iodophenol by Shimadzu LC-20A HPLC (Kyoto, Japan) with UV detection at 231 nm. Separation was achieved with the Waters C18 column (150 × 4 mm, 5 μm particle size, Milford, USA) using a mobile phase consisting of 70% of 10 mM phosphoric acid (pH 2.2) and 30% of methanol at a flow rate of 1.0 mL/min. The detection limit for both 2-iodophenol and 4-iodophenol was 0.05 μM for a 100 μL sample injection volume.

At pre-determined time interval, 10 mL aliquot of sample containing iodinated halomethanes (I-HMs) was quenched with ascorbic acid at the same initial iodide molar concentration and extracted with 2 mL of MTBE, and then the mixed solution was shaken for 5 min with a multi-tube vortex mixer (DMT-2500, Shanghai, China) at 2300 rpm before a 5-min settling. Lastly, 1 mL supernatant was withdrawn and analyzed by Shimadzu QP2010plus gas chromatography equipped with electron capture detection (GC/ECD, Kyoto, Japan). The column used was a RTX-5MS silica capillary column (30 m × 0.25 mm, I.D. with 0.25 μm film thickness, Restek). The GC temperature program consisted of an initial temperature of 40 °C for 10 min, ramping to 200 °C at 20 °C/min and holding for 5 min. The carrier gas was nitrogen and the flow rate was 1 mL/min. The injection port was controlled at 165 °C and the ECD detector temperature at 300 °C. The detection limits for DIM and TIM were 0.4 nM (0.1 μg/L) and 0.05 nM (0.02 μg/L), respectively.

At pre-determined time, 20 mL aliquot of sample was quenched with ascorbic acid at the same molar concentration as the initial iodide concentration and the pH of I-HAA sample was adjusted to < 0.5 with 1 mL of sulfuric acid (95%-98%), followed by the addition of 3 g of sodium sulfate and 4 mL of MTBE. The mixed solution was shaken for 5 min with a multi-tube vortex mixer at 2300 rpm before a 5-min sedimentation. Then 2 mL extracted I-HAA sample was taken and derivatized to their corresponding esters with 1 mL 10% acidic methanol (sulfuric acid/methanol (v/v) = 10%)

at 50 °C for 2 h. Cooled mixtures were neutralized with 4 mL saturated sodium bicarbonate solution, and then were shaken for 5 min and settled for 5 min. Lastly, 1 mL supernatant was withdrawn and analyzed using a Shimadzu QP2010plus GC-ECD (Kyoto, Japan). The column used was a RTX-5MS silica capillary column (30 m × 0.25 mm, I.D. with 0.25 µm film thickness, Restek). The GC temperature program consisted of an initial temperature of 34 °C for 8 min, ramping to 74 °C at 20 °C/min and holding for 1 min, and then increased to 200 °C at 50 °C/min and held for 2 min. The carrier gas was nitrogen and the flow rate was 1 mL/min. The injection port was controlled at 165 °C and the ECD temperature at 300 °C. The limits of detection for MIAA and DIAA were 2.7 nM (0.5 µg/L) and 1.0 nM (0.3 µg/L), respectively.

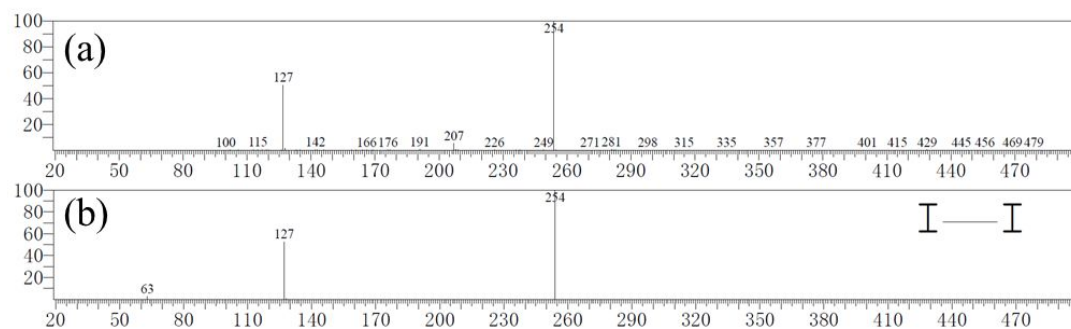
**Table S1.** Water quality characteristics of three natural waters.

Parameters	QCS	HP	HA
DOC (mg/L)	5.84	7.48	5
UV <sub>254</sub> (cm <sup>-1</sup> )	0.113	0.172	0.338
SUVA (L×mg <sup>-1</sup> ×m <sup>-1</sup> )	1.93	2.23	6.76
Iodide (µg/L)	ND	ND	ND
TOX (µg/L as I)	6.4	13.2	ND

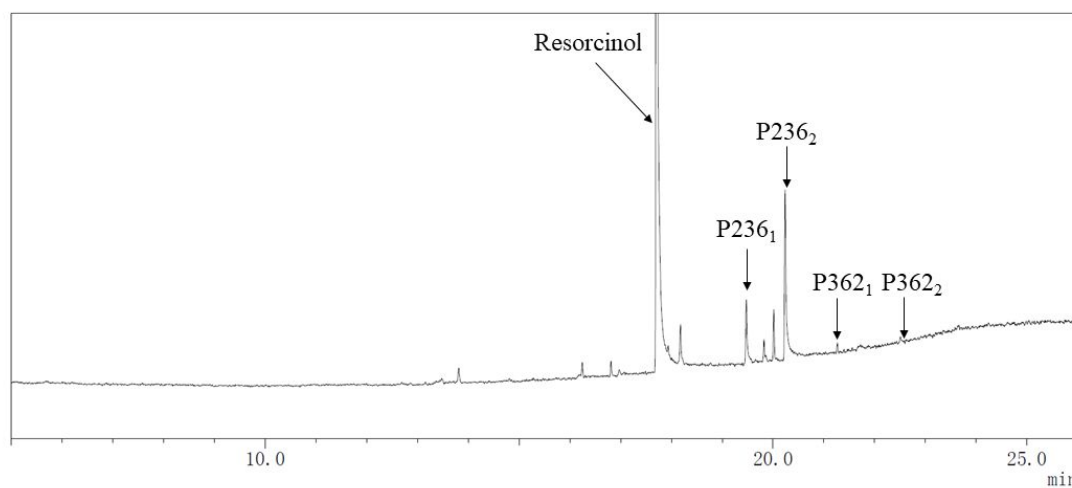
ND = Not detected.

**Table S2.** Characteristics of DBP standards.

DBP species	CAS No.	Chemical formula	Molecular weight	Source and purity
DIM	75-11-6	CH <sub>2</sub> I <sub>2</sub>	267.84	Aladdin Industrial Inc., 98%
TIM	75-47-8	CHI <sub>3</sub>	393.73	Aladdin Industrial Inc., 99%
MIAA	64-69-7	CH <sub>2</sub> ICOOH	185.95	Aladdin Industrial Inc., 98%
DIAA	598-89-0	CHI <sub>2</sub> COOH	311.84	CanSyn Chem. Corp., 99%

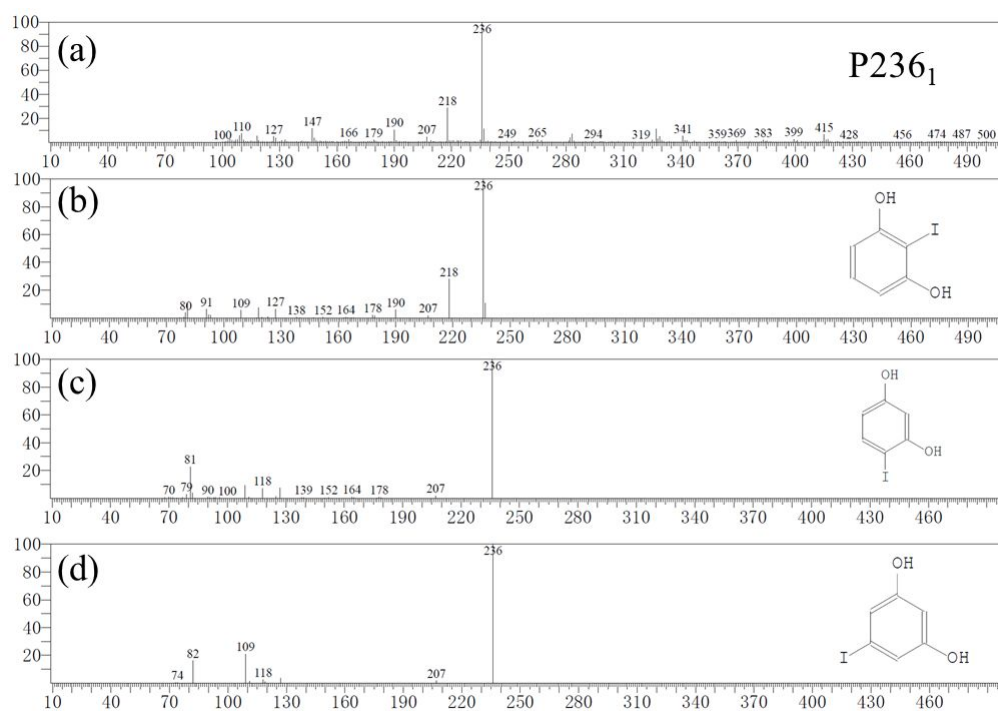


**Figure S1.** Mass spectrum of  $P_{254}$  (a) obtained from GC-MS and iodine (b) obtained from NIST database.

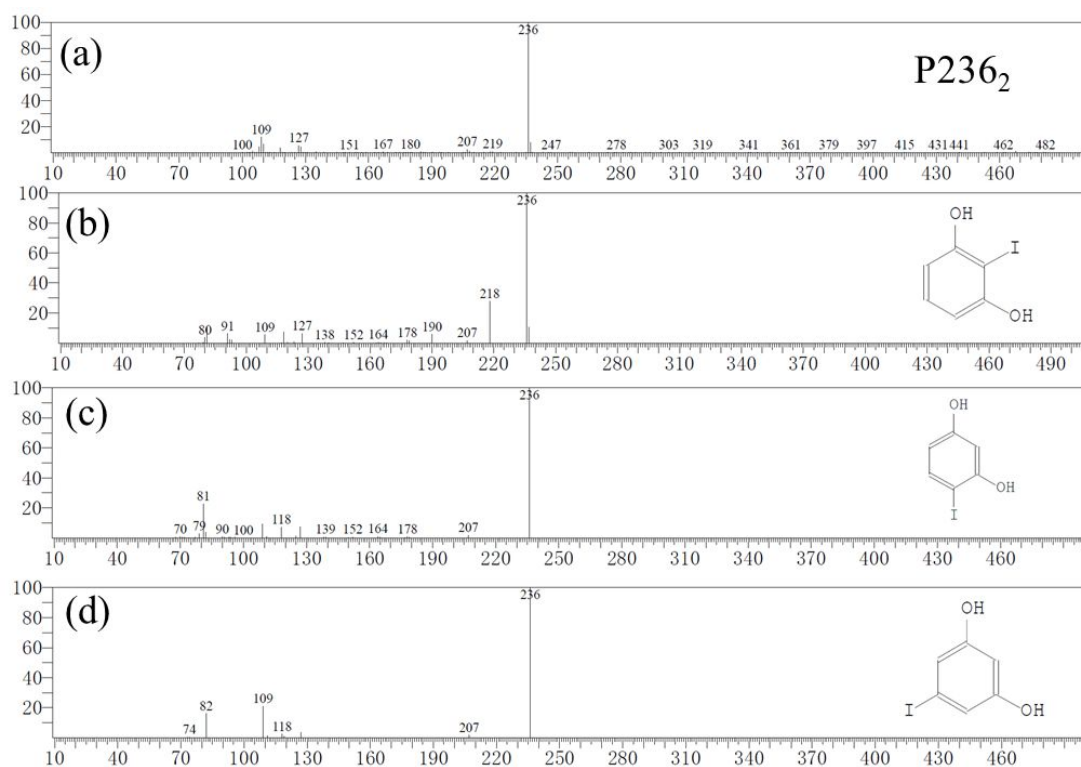


**Figure S2.** Total ion chromatogram (GC-MS) of resorcinol after the reaction with ferric chloride in the presence of iodide (Reaction condition: resorcinol = 50  $\mu\text{M}$ ;  $\text{FeCl}_3$  = 200  $\mu\text{M}$  and iodide = 200  $\mu\text{M}$ ).

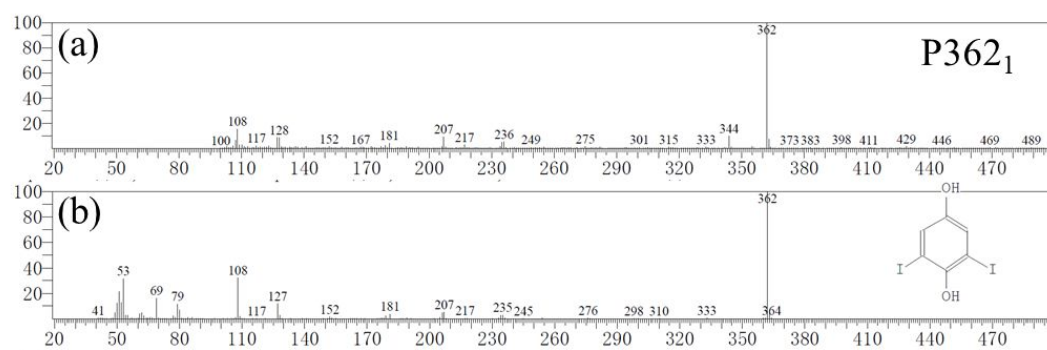




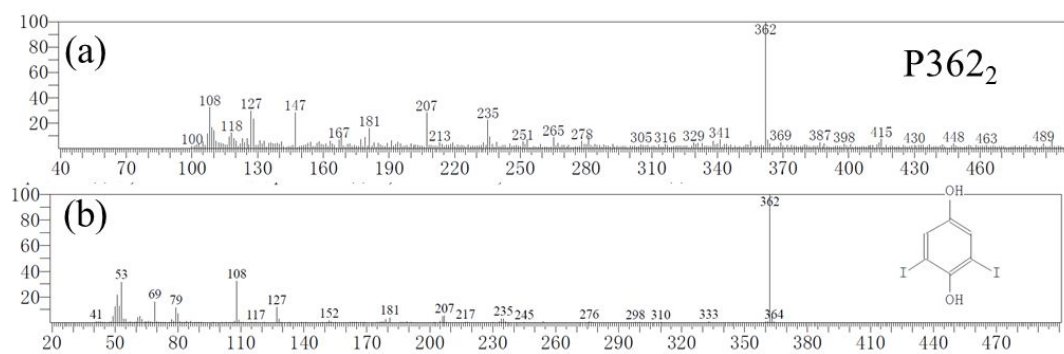
**Figure S3.** Mass spectrum of P236<sub>1</sub> (a) obtained from GC-EI and 2-iodoresorcinol (b), 4-iodoresorcinol (c), 5-iodoresorcinol (d) obtained from NIST database.



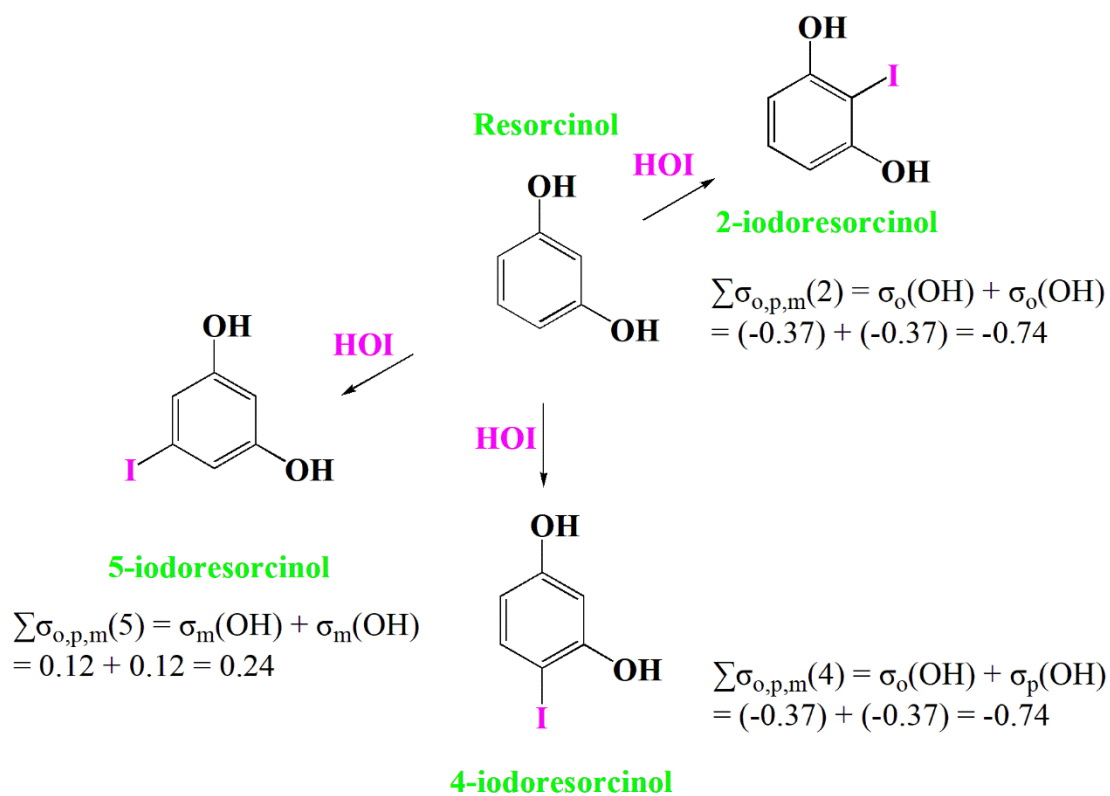
**Figure S4.** Mass spectrum of P236<sub>2</sub> (a) obtained from GC-EI and 2-iodoresorcinol (b), 4-iodoresorcinol (c), 5-iodoresorcinol (d) obtained from NIST database.



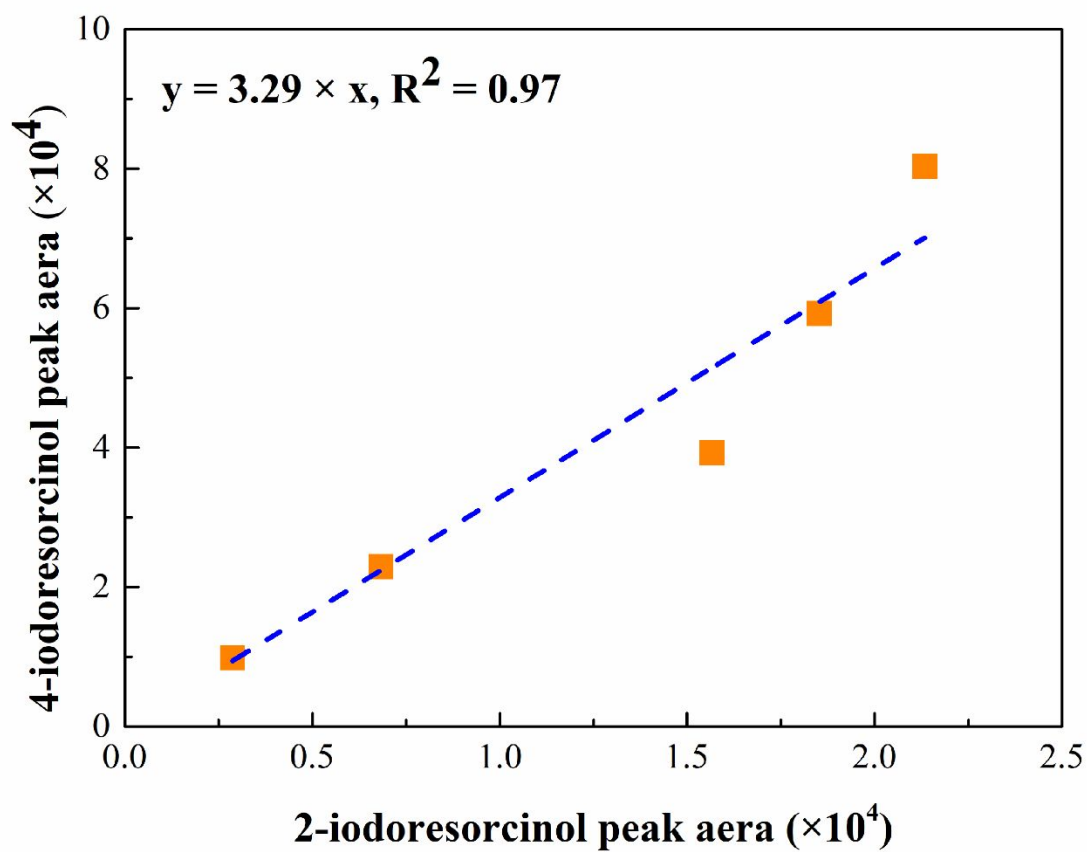
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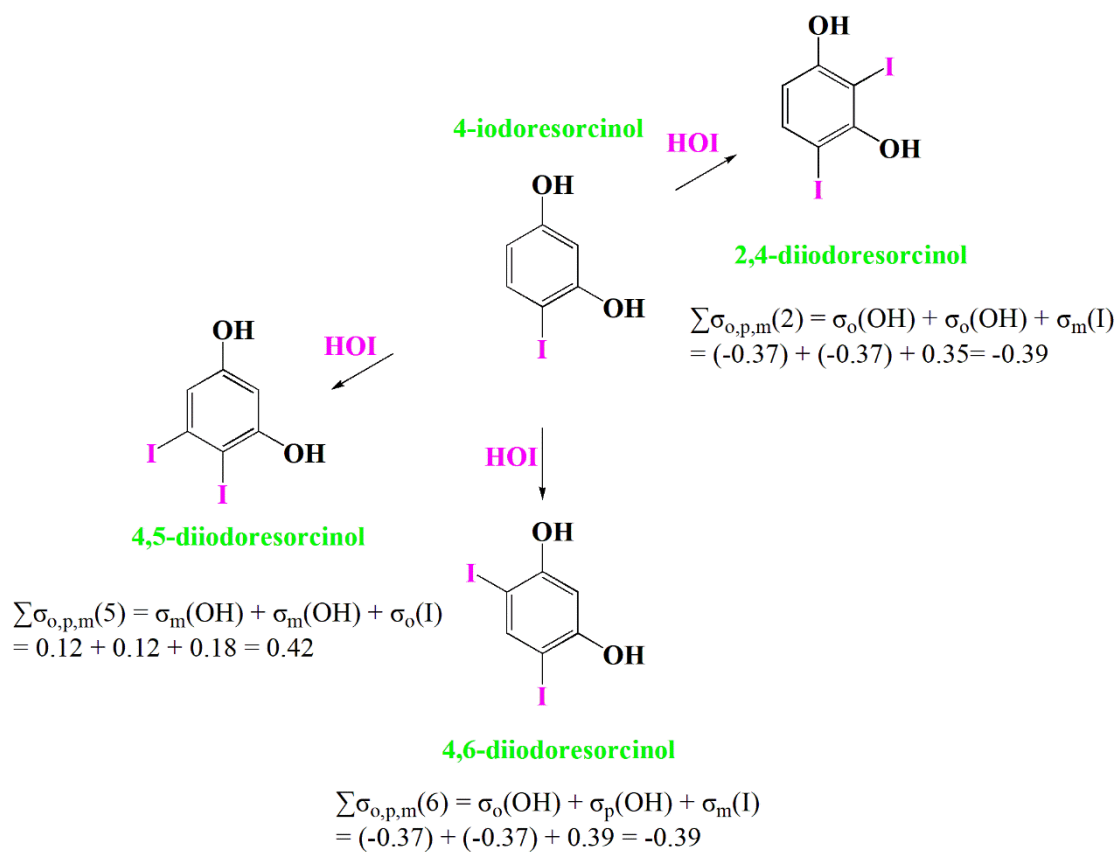
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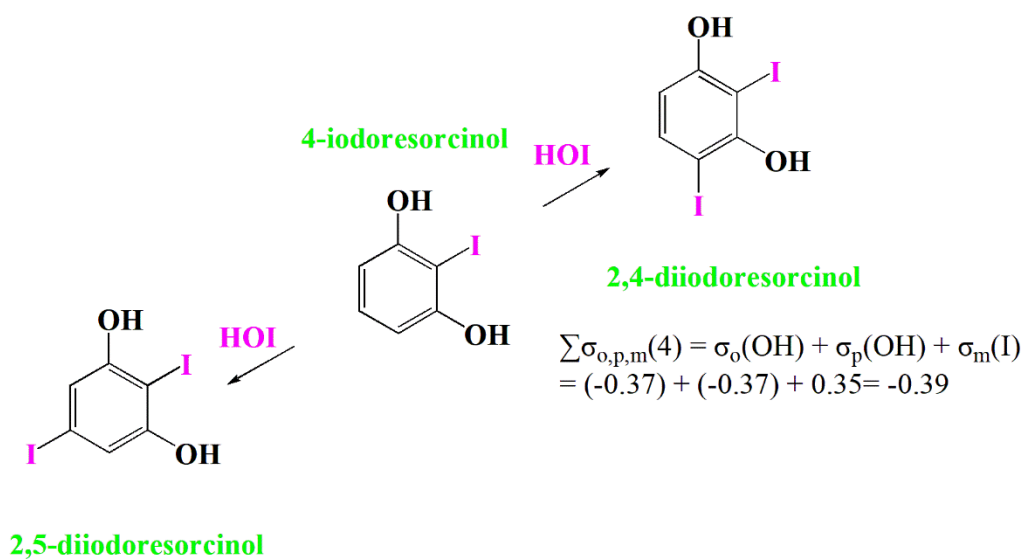
**Figure S7.**  $\Sigma\sigma_{o,p,m}$  calculation for determining the most probable HOI reactive sites on aromatic ring of resorcinol.



**Figure S8.** Linear relationship between P236<sub>1</sub> and P236<sub>2</sub> during coagulation of resorcinol with ferric chloride.



**Figure S9.**  $\sum \sigma_{o,p,m}$  calculation for determining the most probable HOI reactive sites on aromatic ring of 4-iodoresorcinol.



$$\sum \sigma_{o,p,m}(5) = \sigma_m(\text{OH}) + \sigma_m(\text{OH}) + \sigma_p(\text{I})$$

$$= 0.12 + 0.12 + 0.18 = 0.42$$

**Figure S10.**  $\sum \sigma_{o,p,m}$  calculation for determining the most probable HOI reactive sites on aromatic ring of 2-iodoresorcinol.



## References

- (1) Ding, S. K.; Chu, W. H.; Bond, T.; Cao, Z. Q.; Xu, B.; Gao, N. Y., Contribution of amide-based coagulant polyacrylamide as precursors of haloacetamides and other disinfection by-products. *Chem. Eng. J.* **2018**, *350*, 356-363.
- (2) Bichsel, Y.; Gunten, U. V., Formation of iodo-trihalomethanes during disinfection and oxidation of iodide-containing waters. *Environ. Sci. Technol.* **2000**, *34*, (13), 2784-2791.