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Electronic supplementary information

Degradation of roxarsone in sulfate radical mediated oxidation process and formation of polynitrated by-products

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Text S1. *Detailed experimental procedures for separation and enrichment of intermediate products.*

An aqueous solution (100 mL) contained 50 μM ROX or nitrophenols and 2 mM persulfate was allowed to react for 420 min at 60°C and then chilled in an ice bath for 10 min to stop the reaction. Prior to SPE, the reaction mixture was acidified to pH 3.0 by 50 mM H_2SO_4. The reaction solution was then concentrated by SPE workstation using Oasis HLB cartridges (WAT106202, Waters). Prior to extraction, the cartridge was activated by 5 mL methanol, 5 mL Milli-Q water followed by 5 mL acidified Milli-Q water (pH adjusted to 3.0 with 50 mM H_2SO_4). The quenched reaction solution was percolated through the cartridge at a flow rate of 5 mL min^{-1}. After sample passage, the cartridge was rinsed with 2 mL Milli-Q water and 2 mL 5% aqueous methanol, sequentially. The extracts were finally eluted with 2 mL methanol twice. The eluents were combined and purged by gentle stream of N_2 to approximately 1 mL.

Text S2. *Intermediate products identification by LC-ESI-MS/MS*

Reaction products were identified using liquid chromatography with tandem mass spectrometry (HPLC-MS/MS), consisting of an Agilent 1200 series HPLC coupled to a G6410B triple quadrupole mass spectrometer (Agilent Technologies, USA). Separation was accomplished using an Agilent ZORBAX Eclipse Plus C18 column (3.5 μm, 2.1 mm × 150 mm). Elution was performed at a flow rate of 0.2 mL min^{-1} with H_2O containing 0.1% (v/v) formic acid as eluent A and MeOH containing 0.1% (v/v) formic acid as eluent B, employing a linear gradient as follows. 50% B, 0 – 20 min; 50% to 100% B, 20 -20.1 min; 100% B, 20.1 – 25 min. Mass spectral analysis was conducted in positive mode using an electrospray ionization (ESI) source. Instrument parameters were as follows: capillary voltage 3.8 kV, fragmentor 135 V, desolvation gas (nitrogen, ≥ 99.995%) flow 8 L min^{-1}, temperature 350 °C, nebulizer pressure 30 psi, and nitrogen (≥ 99.999%) was used as collision gas. Mass analyzer was operated in full scan mode (*m/z* range 50 - 600) in order to identify the products. Products ion scan MS/MS was performed for both sample and authentic standard (collision energy 10 to 30 eV, precursor ion *m/z*: 183 and 228) for structural assignment of 2,4-dinitrophenol and 2,4,6-trinitrophenol, respectively. Instrument control, data acquisition and processing were performed using the associated Agilent Mass Hunter Qualitative analysis software (version B.04.00).

Table S1. Parameters for quantification of ROX and structurally related nitrophenols by HPLC analysis.

Compound	Analytical column[a]	Eluent composition[b]	Detection wavelength (nm)[c]
Roxarsone (ROX)	Agilent Zorbax Eclipse Plus C18	70% H_2O + 30% MeOH	280
2-Nitrophenol (2-NP)	Agilent Zorbax Eclipse Plus C18	50% H_2O + 50% MeOH	275
3-Nitro-4-hydroxybenzoic acid (3N4HBA)	Agilent Zorbax Eclipse Plus C18	50% H_2O + 50% MeOH	235
4-Chloro-2-nitrophenol (4Cl2NP)	Agilent Zorbax Eclipse Plus C18	50% H_2O + 50% MeOH	272

[a] Agilent Zorbax Eclipse Plus C18 column (5 μm, 250 mm × 4.6 mm I.D.). [b] Both mobile phases contained 0.1% formic acid, and the flow rate of eluent was 1.0 mL min^{-1}. [c] The detection wavelength was chosen according to the maximum absorbance in UV-vis spectrum of each compound.

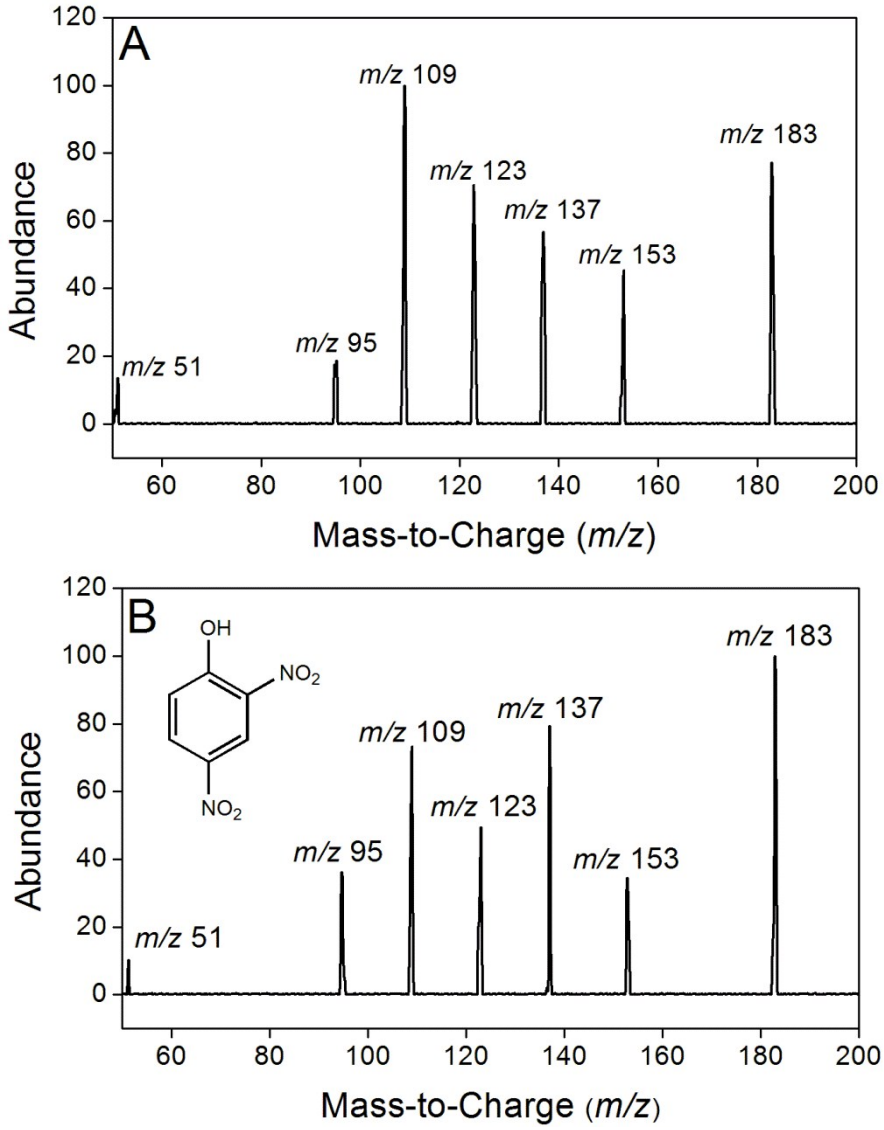

Fig. S1. Product ion scan mass spectrum of (A) *m/z* 183 in concentrated ROX degradation sample, and (B) 10 μM 2,4-trinitrophenol (2,4-DNP) standard. A comparison of the two spectra confirms the formation of 2,4-DNP in heat activated PS oxidation of ROX. Chromatographic separation conditions were provided in Text S2. MS analysis condition: ESI(+), fragmentor voltage, 135 V; collision voltage, 20 eV; precursor ion, *m/z* 183.

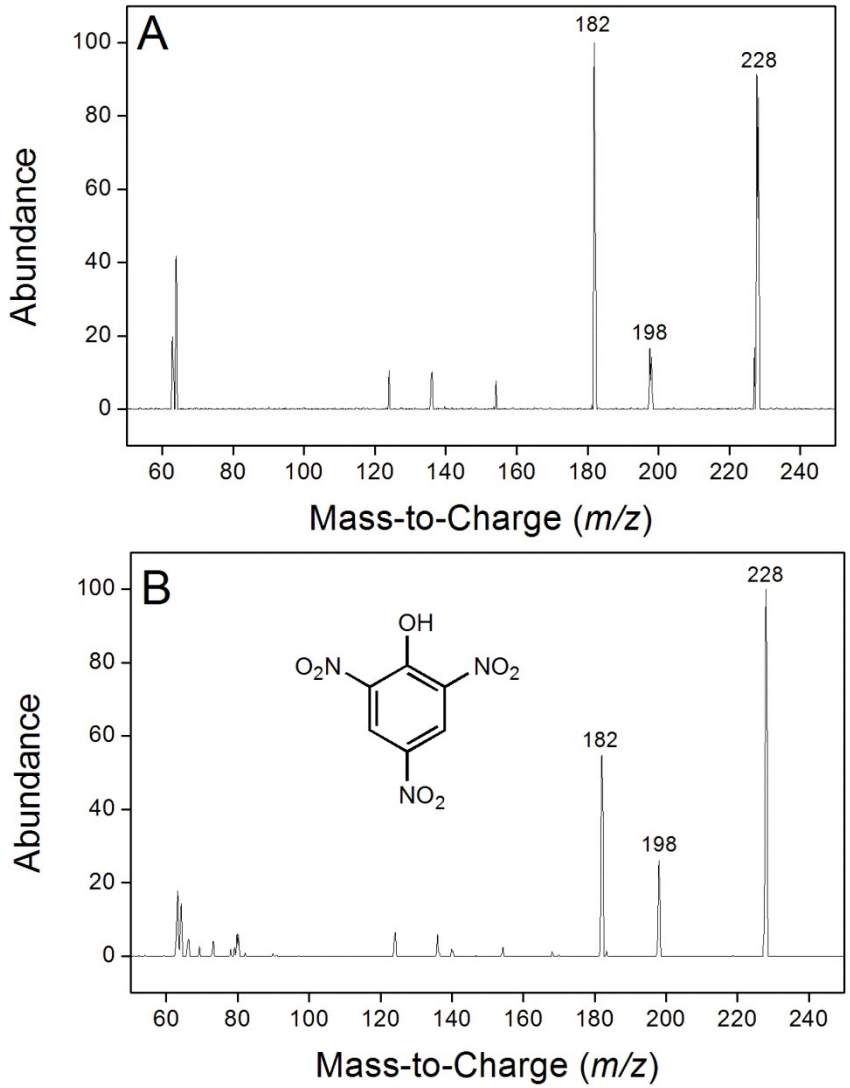

Fig. S2. Product ion scan mass spectrum of (A) *m/z* 228 in concentrated ROX degradation sample, and (B) 10 μM 2,4,6-trinitrophenol (2,4,6-TNP) standard. A comparison of the two spectra confirms the formation of 2,4,6-TNP in heat activated PS oxidation of ROX. Chromatographic separation conditions were provided in Text S2. MS analysis condition: ESI(+), fragmentor voltage, 135 V; collision voltage, 20 eV; precursor ion, *m/z* 228.

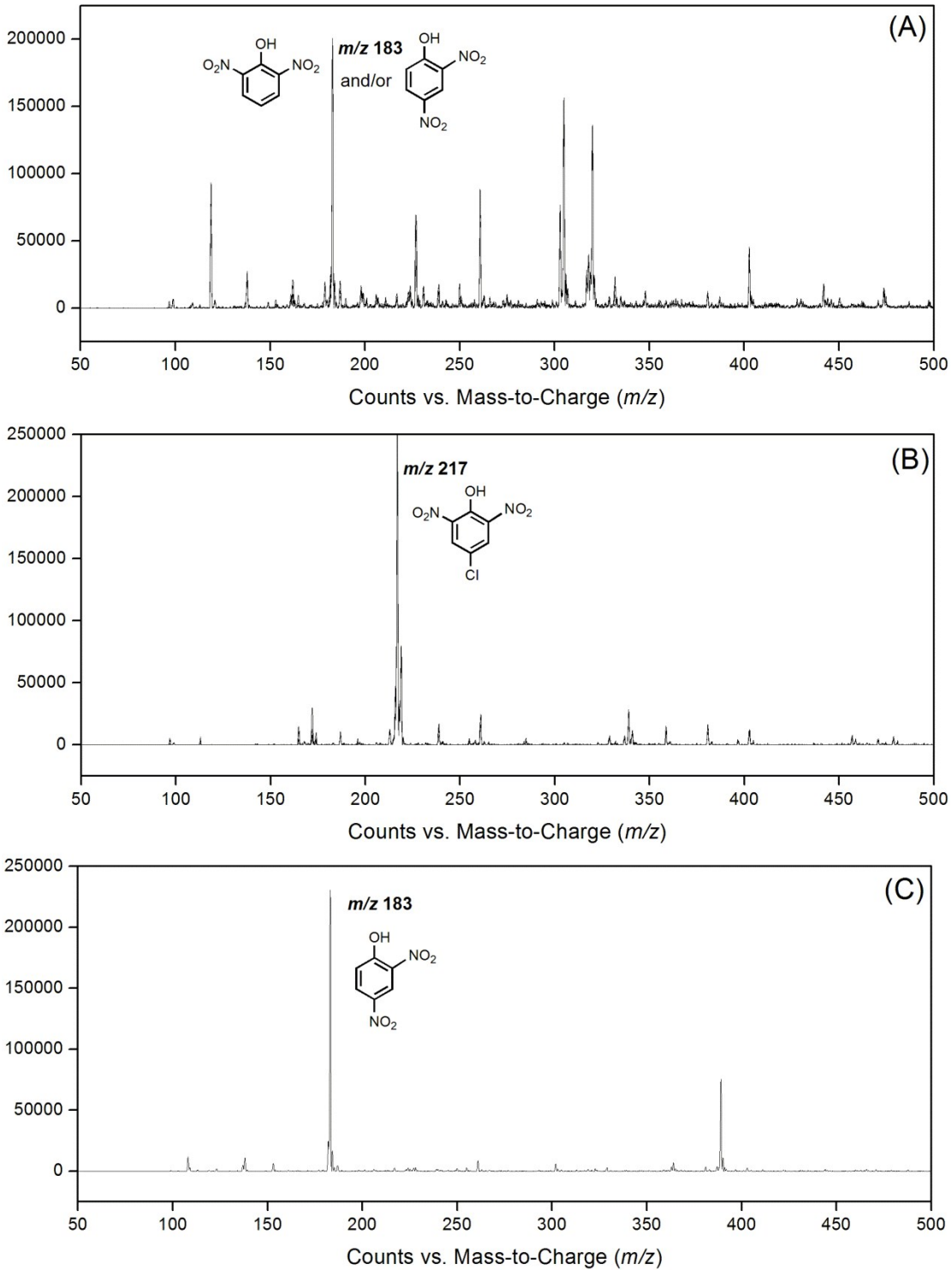

Fig. S3. Negative full scan mass spectra of the degradation products generated by heat activated persulfate oxidation of: (A) 2-nitrophenol (2-NP); (B) 4-chloro-2-nitrophenol (4Cl2NP); and (C) 3-nitro-4-hydroxybenzoic acid (3N4HBA). Results showed that 2,4-DNP and 2,6-DNP, 4-chloro-2,6-dinitrophenol, and 2,4-DNP were generated in heat activated persulfate oxidation of 2-NP, 4Cl2NP, and 3N4HBA, respectively. Note that, characteristic isotope ratio of 3:1 was observed for *m/z* 217 in (B), implying that the Cl atom was maintained in the product.