SUPPLEMENTARY INFORMATION (SI)

Removal of 3,4-dichlorophenol from water utilizing ferrate(VI): Kinetic and mechanistic investigations, and effect of coexisting anions

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This file includes: 5 texts, 2 tables and 2 figures are available for further information addressing experimental procedures and additional data.

Supporting Texts (5 Texts)

SI-Text-1. Materials

3,4-dichlorophenol (3,4-DCP, > 99%), HPLC-grade 2,2'-azino-bis (3-ethylbenzthiazoline-6-sulphonate) (ABTS), and HPLC-grade methanol were supplied by Sigma-Aldrich (Missouri, USA). Sodium bicarbonate, sodium chloride, sodium nitrate, sodium sulfate, sodium phosphate, sodium borate, disodium hydrogen phosphate, sodium dihydrogen phosphate, and acetic acid were procured from Kelong Chemical Co., Ltd. (Chengdu, China). All reagents were at least analytical grade if not specially stated and utilized without further purification. All the solutions were prepared in doubly distilled water obtained from an 18.2 MΩ·cm Millipore water-purification system.

Fe(VI) solutions were made by addition of solid K_2FeO_4 samples to a 5 mM $Na_2HPO_4 \cdot 12H_2O$/1 mM $Na_2B_4O_7 \cdot 10H_2O$ buffer (pH ≈ 9.2) and used immediately after preparation to ensure that the self-decomposition of Fe(VI) can be neglected. 3,4-DCP solutions were prepared by dissolving solid 3,4-DCP in a 10 mM phosphate buffer under continuous mechanical stirring until it was completely dissolved. A buffer solution of pH 4.10 containing 0.6 M acetate and 0.2 M phosphate was prepared by dissolving 34.40 mL of CH_3COOH, 53.72 g of $Na_2HPO_4 \cdot 12H_2O$, and 7.80 g of $NaH_2PO_4 \cdot 2H_2O$ in 1 L of doubly distilled water. 1g/L of ABTS solutions (1.82 mM) were prepared by adding 1 g of its solid powder to 1 L doubly distilled water, and then stored at 4 °C before use. Inorganic salt solutions were made by adding the corresponding solid compounds to a 10mM phosphate buffer.

SI-Text-2. Procedures for collection of real water samples

Jialing River water (JRW) samples were taken from Jialing River of Chongqing, China. Yangtze River water (YRW) samples were withdrawn from Yangtze River in Chongqing Section, China. Tap water (TW) samples and deionized water (DW) samples were collected from our lab in Chongqing University, China. Deionized water with a buffer function (DWB) (10 mM phosphate) was prepared by adding $Na_2HPO_4 \cdot 12H_2O$ into deionized water to buffer solution pH. All water samples were filtered through a glass-fiber membrane of 0.45 μm pore size, and then were directly used without further treatment. Before use, all water samples should be stored under refrigeration at 4 °C, and used within 3 days after collection. The real water samples did not contain 3,4-DCP by HPLC analysis of 3,4-DCP.

SI-Text-3. Analytical methods

The concentration of Fe(VI) was measured on a 752 UV/Vis spectrophotometer (Jinghua instruments, China). Fe(VI) concentration ($\geq$ 10 μM) was determined by direct spectrophotometry. The absorbance at the maximum absorption wavelength of 510 nm was monitored, and a molar absorptivity ($\varepsilon_{510\ nm} = 1150\ M^{-1} \cdot cm^{-1}$) was used for calculating Fe(VI) concentrations according to the Lambert-Beer Law. Fe(VI) concentration (< 10 μM) was measured using indirect spectrophotometry, i.e. the ABTS method, which is based on the fact that one mole of Fe(VI) yields one mole of ABTS•+ (a green radical cation) from its reaction with excess ABTS [1]. The absorption maximum for ABTS•+ was found to occur at 415 nm ($\varepsilon_{415\ nm} = 33600\ M^-$

$^1 \cdot cm^{-1}$), which was previously reported by our group [2]. Fe(VI) concentration was obtained by measuring the absorbance at 415 nm of the reaction mixture of the Fe(VI) sample and the ABTS solution in the 0.6 M acetate/0.2 M phosphate buffer.

3,4-DCP was analyzed with an 1200 high performance liquid chromatography (HPLC, Agilent Instruments, USA) connected in-line to an UV-visible detector at a wavelength of 291 nm. The chromatographic separation was achieved on a Symmetry C18 column (2.1×150 mm, 3.5 μm particle size; WAT106005, Waters Instruments, USA), and the column temperature was set at 25.0 °C. A binary mobile phase for the measurement was composed of 30% ultra-pure water and 70% methanol at a flow rate of 1 mL·min^{-1}. A 10-μL sample was injected by an autosampler in an isocratic elution mode.

The concentration of chlorine ion was monitored by a 2010 ion chromatography (IC, Tosoh Instruments, Japan) coupled with a TSKgel SuperIC-Anion HS analytical column (4.6 × 100 mm), a TSKgel SuperIC-A HS guard column (4.6 × 10 mm), and a conductivity detector. The column temperature was set at 25.0 °C. The eluent consisting of a mixture of $3.8×10^{-3}$ M NaHCO$_3$ solution and $3.0×10^{-3}$ M Na$_2$CO$_3$ solution was pumped at a flow rate of 1 mL·min^{-1}. A 30-μL injection of each sample was conducted by an autosampler.

All the pH measurements were conducted via a pHS-3C pH meter (Inesa Instrument, China) equipped with a combined glass-calomel electrode using standard buffer solutions at pH 4.00, 6.86 and 9.18 for calibration.

Identification of organic degradation products were performed on a high

performance liquid chromatography-mass spectrometry (HPLC-MS, Shimadzu Instruments, Japan). The HPLC-MS system contained a LC-30AD pump, a SIL-30AC autosampler LC system, and an 8060 MS system. A symmetry C_{18} 2 μm column (150 × 2.1 mm) was set at 25.0 °C and used for separation. The capillary temperature was set at 250 °C, and the vaporizer temperature was kept at 400 °C. The mobile phase consisted of methanol and water (55:45, v/v) at a flow rate of 1.0 mL·min^{-1}. For ionizing analyte molecules, the electrospray ionization (ESI) source operated in the negative mode with the spray voltage of 3 kV. The mass spectra analysis was performed with a mass scan scope of 50-300 *m/z*.

SI-Text-4. Principle of kinetic investigation

Chemical kinetics is the study of how fast a chemical reaction occurs, focusing on the reaction rate which is the change in the amount of a reactant (or a product) with time during the reaction. Consider a typical chemical reaction of reactants A and B to yield products C and D,

$$aA + bB \rightarrow cC + dD \qquad (1)$$

where a, b, c and d stand for the stoichiometric coefficients of the given substances, respectively.

According to the principle for chemical kinetics [3], the rate law for reaction (1) is often given by a power equation such as

$$\text{rate} = k[A]^x[B]^y \qquad (2)$$

where [A] and [B] are concentrations of reactants A and B, the exponents x and y are

the reaction orders with respect to A and B, and k is the reaction rate coefficient.

The reaction order not only specifies a clear correlation between the reactant concentration and the reaction rate, but also helps to identify the rate-determining step, even deduce the reaction mechanism. Therefore, it is very important to acquire the reaction order for kinetic investigation. However, the reaction order with respect to a given substance is generally not equal to its stoichiometric coefficient, which must be determined only by experiment. Three methods, such as integral method, initial rate method, and method of isolation are usually utilized for determination of the reaction order. Method of isolation is widely used by researchers in the kinetic studies [2,4,5], which is based on the fact that the change in the concentration of one reactant over time is monitored with all other reactants in large excess so that their concentrations are kept essentially constant during the reaction. That is, the reaction followed pseudo-order kinetics. Under pseudo-order conditions with A in excess, Eq.(2) can be rewritten as:

$$\text{rate} = -d[B]/dt = k_{obs}[B]^y \tag{3}$$

where
$$k_{obs} = k[A]^x \tag{4}$$

Eq.(4) can be expressed with a linear equation by taking the natural logarithm of its both sides:
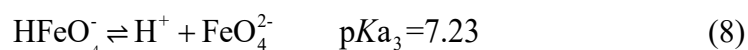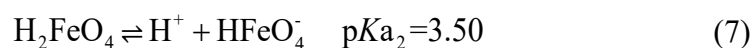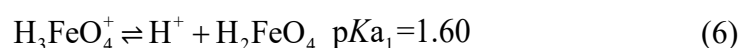
$$\ln k_{obs} = \ln k + x \ln[A] \tag{5}$$

The reaction order y and the pseudo-order rate constant k_{obs} can be acquired from Eq.(3) by the integral method, in which the variation of the concentration of B was monitored as a function of time and then the experimental data was fitted to the

corresponding linear equation. Furthermore, the reaction order x and the reaction rate constant k can be gained from Eq.(5) by determining the values for k_{obs} at different initial concentrations of A.

SI-Text-5. The protonation equilibrium of Fe(VI) and 3,4-DCP and their mutual reactions

The protonation equilibrium of Fe(VI) can be described as follows:

$$H_3FeO_4^+ \rightleftharpoons H^+ + H_2FeO_4 \quad pKa_1=1.60 \tag{6}$$

$$H_2FeO_4 \rightleftharpoons H^+ + HFeO_4^- \quad pKa_2=3.50 \tag{7}$$

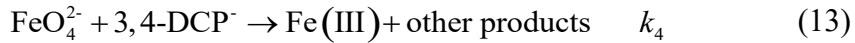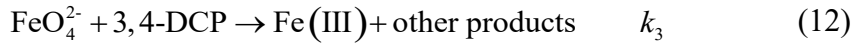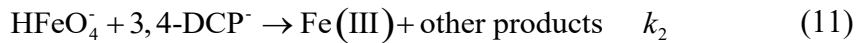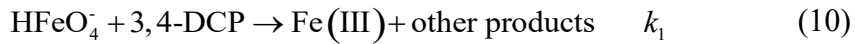$$HFeO_4^- \rightleftharpoons H^+ + FeO_4^{2-} \quad pKa_3=7.23 \tag{8}$$

On the basis of the dissociation constants of Fe(VI) mentioned above, four species, i.e., triprotonated ($H_3FeO_4^+$), diprotonated (H_2FeO_4), monoprotonated ($HFeO_4^-$), and deprotonated (FeO_4^{2-}) species are present over the entire pH scale tested. A fraction of species plot was generally utilized to see how the relative amounts of the compounds change with pH. Therefore, according to the value of pKa for dissociation of Fe(VI), the fraction of Fe(VI) species as a function of pH is plotted in Fig. 4(a). From this figure, only two species of Fe(VI), i.e. $HFeO_4^-$ and FeO_4^{2-} were predominant at neutral and alkaline pH. Furthermore, as can be seen from the speciation of Fe(VI) (Fig. 4(a)), the fraction of $HFeO_4^-$ decreased with increasing pH whereas that of FeO_4^{2-} increased with pH, contributing to a decrease in the k value with an increase in solution pH (see Fig. 3(b)).

3,4-DCP also goes through a protonation equilibrium:

$$3,4\text{-DCP} \rightleftharpoons H^+ + 3,4\text{-DCP}^- \quad pK_{a,\,3,4\text{-DCP}} = 8.62 \quad [2] \quad (9)$$
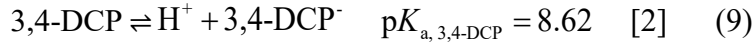
Its pKa value could be used to calculate the speciation of 3,4-DCP, and a fraction

of species plot for 3,4-DCP is presented in Fig. 4(a). From this figure, it was observed

that 3,4-DCP had two equilibrium species, i.e. 3,4-DCP and 3,4-DCP$^-$. Therefore,

individual species of Fe(VI) and 3,4-DCP had to be explicitly taken into account for

the reaction between Fe(VI) and 3,4-DCP. That is, in the studied pH range two Fe(VI)

species (HFeO$_4^-$ and FeO$_4^{2-}$) and two 3,4-DCP species (3,4-DCP and 3,4-DCP$^-$)

reacted with each other, leading to the fact that four parallel reactions take place in the

solution as follows.

$$HFeO_4^- + 3,4\text{-DCP} \rightarrow Fe(III) + \text{other products} \quad k_1 \quad (10)$$

$$HFeO_4^- + 3,4\text{-DCP}^- \rightarrow Fe(III) + \text{other products} \quad k_2 \quad (11)$$

$$FeO_4^{2-} + 3,4\text{-DCP} \rightarrow Fe(III) + \text{other products} \quad k_3 \quad (12)$$

$$FeO_4^{2-} + 3,4\text{-DCP}^- \rightarrow Fe(III) + \text{other products} \quad k_4 \quad (13)$$

where k_1, k_2, k_3, and k_4 are the species-specific rate constants for reactions (10)-(13),

respectively.

Supporting Tables (2 Tables)

Table S1. The values of $\ln(k/T)$ and $1/T$ at various temperatures.

T (K)	k (M^{-1}S^{-1})	1/T	$\ln(k/T)$
283.15	18.65	0.003532	-2.72
288.15	21.75	0.003470	-2.58
293.15	30.00	0.003411	-2.28
298.15	41.75	0.003354	-1.97
303.15	54.75	0.003299	-1.71
308.15	63.25	0.003245	-1.58

Table S2. Second-order rate constants for hydroxyl radical reaction with various anions.
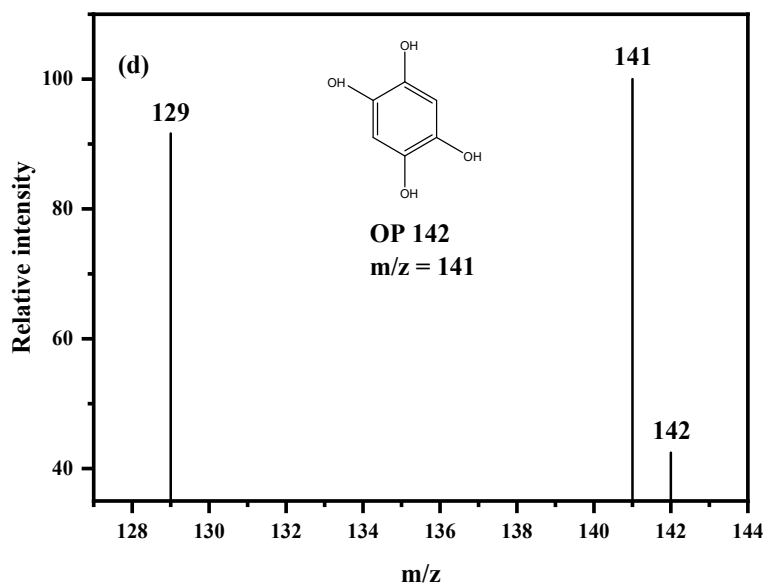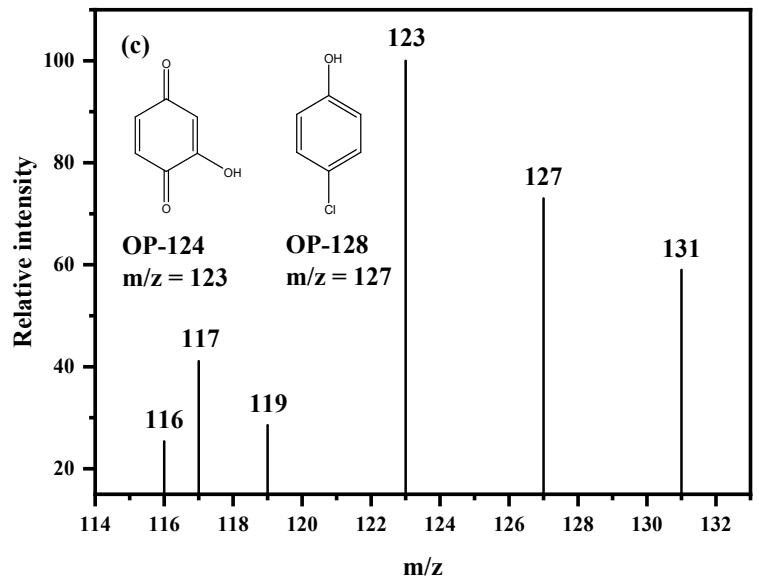
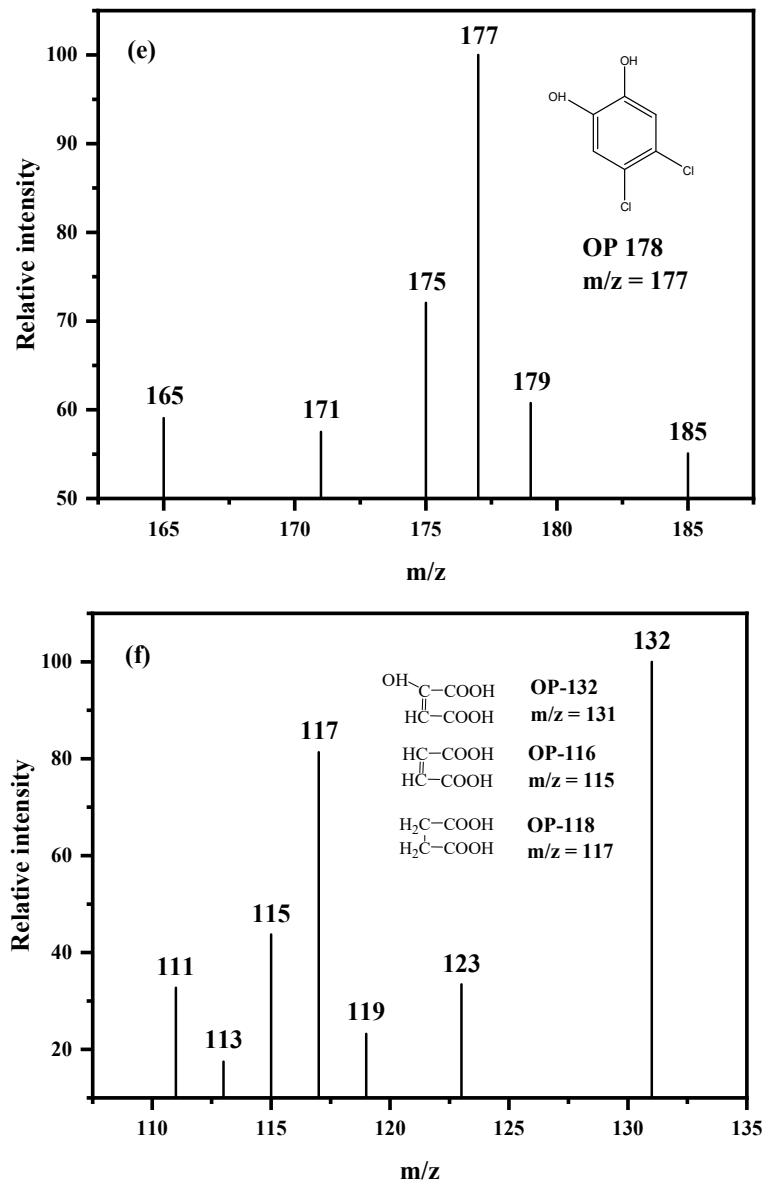| Reaction	Symbol	Rate constant (M^{-1}s^{-1})	Reference
$\cdot OH + PO_4^{3-} \rightarrow PO_4^{2-} + OH^-$	R1	1.0×10^7	[6]
$\cdot OH + NO_2^- \rightarrow NO_2^{\cdot} + OH^-$	R2	8.0×10^9	[7]
$\cdot OH + SO_4^{2-} \rightarrow SO_4^{\cdot-} + OH^-$	R3	3.5×10^5	[8]
$\cdot OH + Cl^- \rightarrow ClOH^{\cdot-}$	R4	4.3×10^9	[9]

Supporting Figures (2 Figures)
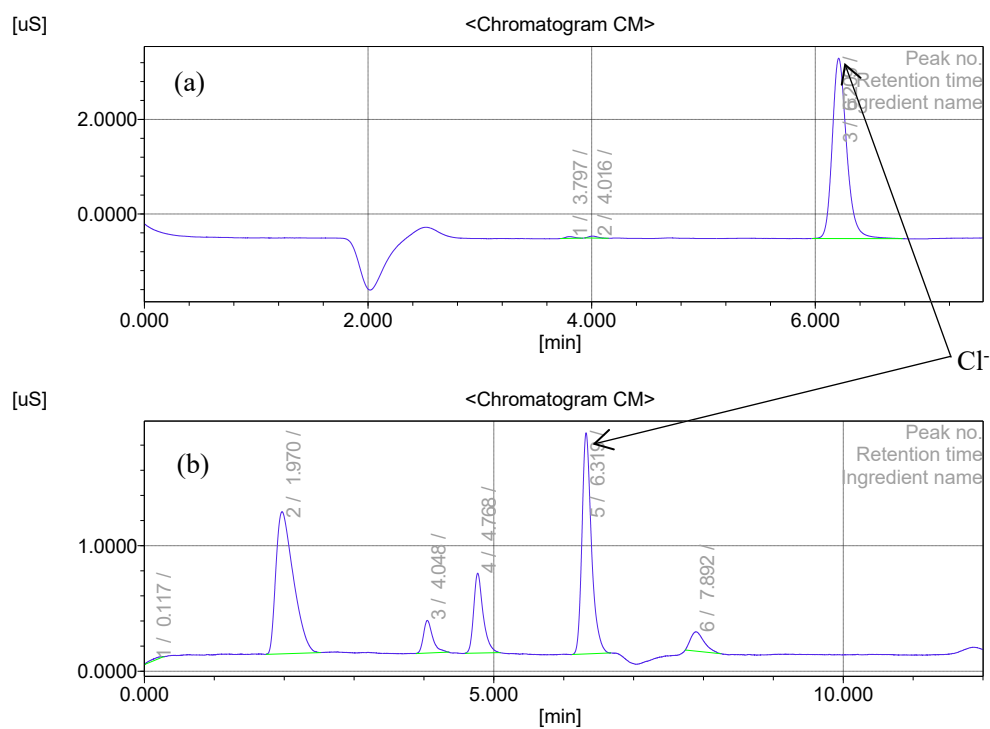
Fig. S1. The ion chromatograms of chloride ion standard solution (a) and the reaction mixture of Fe(VI) and 3,4-DCP (b).
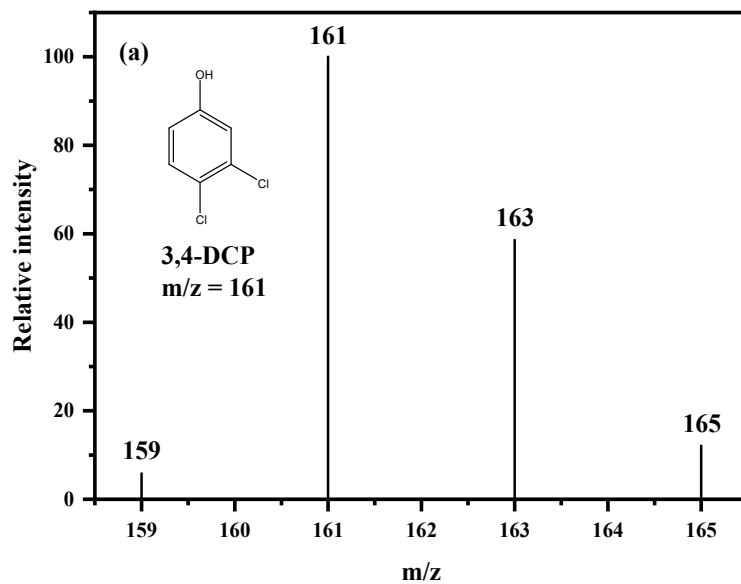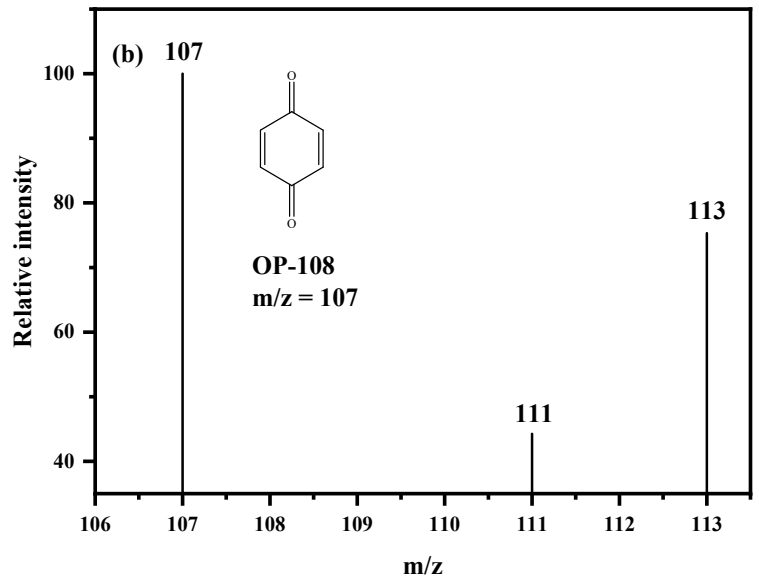
Fig. S2. Mass spectrum of Ops.

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