Supporting Information

Evaluation of the role of superoxide as chain carrier of ozone decomposition to hydroxyl radicals during ozonation

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S1. Composition of synthetic solutions

Table S1. Composition of synthetic solutions used in this study (buffered with 10 mM phosphate at pH = 8) with the concentrations and the first-order scavenging rate constants. The second-order rate constants for the reaction of methanol, acetate, and tert-butanol with \textsuperscript{•}OH are 9.7 × 10\textsuperscript{8} M\textsuperscript{−1} s\textsuperscript{−1}, 7.9 × 10\textsuperscript{7} M\textsuperscript{−1} s\textsuperscript{−1}, and 5 × 10\textsuperscript{8} M\textsuperscript{−1} s\textsuperscript{−1}, respectively. (Buxton et al., 1988; Wolfenden and Willson, 1982)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Methanol [C] (M)</th>
<th>\textsuperscript{•}OH[C] (s\textsuperscript{−1})</th>
<th>Acetate [C] (M)</th>
<th>\textsuperscript{•}OH[C] (s\textsuperscript{−1})</th>
<th>tert-Butanol [C] (M)</th>
<th>\textsuperscript{•}OH[C] (s\textsuperscript{−1})</th>
<th>Overall \textsuperscript{•}OH scavenging rate (s\textsuperscript{−1})</th>
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<td>1.2 × 10\textsuperscript{5}</td>
<td>1.2 × 10\textsuperscript{5}</td>
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S2. Determination of the second-order rate constant for the reaction of $O_2^-$ with acetate

The second-order rate constant for the reaction of $O_2^-$ with acetate ($k_{O_2^-,ACT}$) was measured by competition kinetics in a xanthine-xanthine oxidase (XOD) system (Guo et al., 2021b; Pasternack and Halliwell, 1979). The system (3 mL) contained xanthine (400 μM), XOD (0.2 U) and DETAPAC (1 mM). The reference compound was nitrotetrazolium blue chloride (NBT), which reacts with $O_2^-$ with a second-order rate constant of $6 \times 10^4$ M$^{-1}$ s$^{-1}$.

The reaction of $O_2^-$ with NBT$^{2+}$ yields the stable and colored formazan, for which the concentrations was measured by spectrophotometry (Hach DR6000, USA) at $\lambda=560$ nm ($\varepsilon = 13800$ M$^{-1}$cm$^{-1}$).

In the experiments where the test compound (M) was added together with the NBT$^{2+}$ to the xanthine and XOD system, the generated $O_2^-$ were mainly consumed in the parallel reactions with NBT$^{2+}$ and M

\[ \text{NBT}^{2+} + O_2^- \xrightarrow{k_{O_2^-,NBT}^{2+}} \text{Formazan} + O_2 \]  \hspace{3em} \text{(S1)}

\[ M + O_2^- \xrightarrow{k_{O_2^-,M}} M' + O_2 \]  \hspace{3em} \text{(S2)}

where $M$ and $M'$ are the test compound and the product from the reaction of $O_2^-$ with M, respectively; $k_{O_2^-,M}$ is the second-order rate constant for the reaction of $O_2^-$ with M.

Assuming a steady-state approximation to $O_2^-$, we can obtain

\[ \frac{d[O_2^-]}{dt} = 0 = r - k_{O_2^-,NBT}^{2+} [\text{NBT}^{2+}][O_2^-] - k_{O_2^-,M} [M][O_2^-] \]  \hspace{3em} \text{(S3)}

where $r$ is the rate of $O_2^-$ production from the enzymatically catalyzed reaction of xanthine with XOD. By rearranging Eq. S3, the concentration of $O_2^-$ is given as

\[ [O_2^-] = \frac{r}{k_{O_2^-,NBT}^{2+} [\text{NBT}^{2+}] + k_{O_2^-,M} [M]} \]  \hspace{3em} \text{(S4)}

Meanwhile, the rate of formazan production ($v$) from Eq. S1 can be expressed as

\[ v = \frac{d[\text{formazan}]}{dt} = k_{O_2^-,NBT}^{2+} [\text{NBT}^{2+}][O_2^-] \]  \hspace{3em} \text{(S5)}
By substituting Eq. S4 into Eq. S5, we obtain

\[ v = \frac{d[\text{formazan}]}{dt} = r \cdot \frac{k_{O_2^{-}, NBT^{2+}} \cdot [\text{NBT}^{2+}]}{k_{O_2^{-}, NBT^{2+}} \cdot [\text{NBT}^{2+}] + k_{O_2^{-}, M} \cdot [M]} \]  

(S6)

In the experiment where only the reference compound (NBT^{2+}) was added in the system (no test compound was added), Eq. S3 changes to

\[ \frac{d[O_2^{-}]}{dt} = 0 = r - k_{O_2^{-}, NBT^{2+}} \cdot [\text{NBT}^{2+}] \cdot [O_2^{-}] \]  

(S7)

and the rate of formazan production (V) in the absence of M is given as

\[ V = \frac{d[\text{formazan}]}{dt} = k_{O_2^{-}, NBT^{2+}} \cdot [\text{NBT}^{2+}] \cdot [O_2^{-}] \]  

(S8)

Combining Eq. S7 and S8, we obtain

\[ r = V \]  

(S9)

Finally, by substituting Eq. S9 into Eq. S6 and rearranging the obtained equation, we can get

\[ \frac{V}{v} = \frac{k_{O_2^{-}, M} \cdot [M]}{k_{O_2^{-}, NBT^{2+}} \cdot [\text{NBT}^{2+}]} + 1 \]  

(S10)

Therefore, by following the production rate of formazan in the absence and presence of M (V and v), the second-order rate constant for the reaction of O₂⁻ with the test compound can be estimated from the slope of linear regression of Eq. S10. (Guo et al., 2021b; Pasternack and Halliwell, 1979). As shown in Fig. S1, the slope of the regression line represents the \( k_{O_2^{-}, \text{NBT}^{2+}} \) ratio between target compound and NBT^{2+} (Eq. (S10)). Based on the \( k_{O_2^{-}, \text{NBT}^{2+}} \), the second-order rate constant for the reaction of O₂⁻ with acetate was determined as 3.2 \( \times \) 10⁴ M⁻¹ s⁻¹.
**Fig. S1.** Determination of the second-order rate constant for the reaction of acetate with $O_2^-$. Ratio of production rate of the reference compound (NBT$^{2+}$) as a function of molar ratios of acetate and NBT$^{2+}$. Reaction conditions: $[\text{NBT}^{2+}] = 1 \text{ mM}, [\text{Acetate}] = 0.5, 1.0, 1.5, \text{ and } 2 \text{ mM.}$

**S3. Reaction of CCl$_4$ with O$_2$**

The second-order rate constant for the reaction of CCl$_4$ with O$_2^{-}$ has been determined to be $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in a previous study using the same method as described in Text S1 (Guo et al., 2021a). In the present study, the second-order rate constant for the reaction of O$_2^{-}$ with CCl$_4$ was further verified using the competition kinetic method with 2,5-dichloro-p-benzoquinone ($k_{O_2^-} = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Bielski et al., 1985)) as the reference compound. As shown in Fig. S2a, the concentration of CCl$_4$ decreased only slightly slower than that of 2,5-dichloro-p-benzoquinone in the xanthine-xanthine oxidase system. After 20 min, the concentration of CCl$_4$ was abated by $\sim$20% in the system. Although the decreases of CCl$_4$ concentrations are relatively small under the tested reaction conditions, they can still provide a valid estimation of the second-order rate constant. Based on the linear regression between the natural logarithm of the relative residual concentrations of CCl$_4$ and chlorobenzoquinone (Fig. S2a inset), the second-order rate constant for the reaction of O$_2^{-}$ with CCl$_4$ was determined as
8.4 \times 10^8 \text{ M}^{-1} \text{s}^{-1}, \text{ which is very close to the previously reported value (within the experimental}
81 \text{ errors). This result confirms that CCl}_4 \text{ can react rapidly with O}_2^{•−}, \text{ and the previously reported}
82 \text{ rate constant is reliable. Note that loss of CCl}_4 \text{ through evaporation was evaluated in pure water}
83 \text{ and found to be negligible under the tested conditions (Fig. S2b).}

**Fig. S2.** Determination of the kinetics of the reaction between O$_2^{•−}$ and CCl4. (a) Decrease of
87 CCl4 and 2,5-dichloro-p-benzoquinone concentrations in the xanthine-xanthine oxidase system;
88 (b) blank experiment to test the stability of CCl4 concentrations in water; (c) degraded CCl4
89 and released Cl$^−$ during the xanthine-xanthine oxidase process; (d) chlorine concentration
90 balance before and after the xanthine-xanthine oxidase process. Experimental conditions: (a)
91 [CCl4] = [2,5-dichloro-p-benzoquinone]$_0$ = 200 μg/L, [xanthine] = 400 μM, [XOD] = 0.3 U,
To examine dechlorination of CCl₄ by O₂⁻⁻, 20 μM CCl₄ was added in the xanthine-xanthine oxidase system. After the reaction was completed, approximately 4.1 μM CCl₄ was degraded, while 15.1 μM Cl⁻ was detected in the system. These data suggest that on average, 3.68 moles of Cl⁻ are released per mole of CCl₄ degraded during the reaction. Meanwhile, dechlorination transformation products of CCl₄ (CHCl₃, CH₂Cl₂, and CH₃Cl) were detected in the water, yielding a good overall molar Cl balance (Fig. S2c). The results observed herein are in agreement with the previous findings that O₂⁻⁻ is a strong nucleophile and can degrade chlorinated organics through a nucleophilic substitution mechanism (Hayyan et al., 2016; Mitchell et al., 2014; Smith et al., 2004).

**S4. Ozone decomposition in the presence of CCl₄**

Fig. S3 shows that with increasing CCl₄ concentrations, the rate of O₃ depletion decreased considerably during ozonation. This change can be mainly attributed to an enhanced suppression of the O₂⁻⁻-promoted O₃ decomposition at higher CCl₄ concentrations. For the highest concentration of CCl₄ (6.3 mM), the observed pseudo-first order rate of O₃ depletion was 1.9 × 10⁻³ s⁻¹, which is about three times the rate of O₃ depletion caused by the reaction with OH⁻ at pH 9 (k = 7 × 10⁻⁴ s⁻¹). This difference suggests that the O₂⁻⁻-promoted O₃ decomposition is not fully suppressed at the applied CCl₄ concentration, or there are some impurities in the synthetic solutions that may initiate the O₃ decomposition (e.g., chemicals and buffers added in the synthetic solutions may contain some impurities that can react with O₃).
Fig. S3. Ozone decomposition kinetics in synthetic solutions containing varying concentrations of CCl₄. Reaction condition: O₃ dose = 1.0 mg/L (0.021 mM), [CCl₄] = 0.0021–6.3 mM, pH = 9 (buffered with 10 mM borate). The line of O₃ depletion by the reaction with OH⁻ is simulated using a second-order rate constant of 70 M⁻¹ s⁻¹ (Merényi et al., 2010).

S5. Methanol and acetate as a chain promoter and inhibitor, respectively

Fig. S4 shows the evolution of O₃, •OH, and O₂⁻ concentrations during ozonation of synthetic solutions with constant total scavenging rate and various scavenging ratios of promotor (methanol)/inhibitor (acetate) (see Table 1).
Fig. S4. Evolution of \( \text{O}_3 \), \( \cdot \text{OH} \), and \( \text{O}_2^{\cdot-} \) concentrations for various promoter (P):inhibitor (I) scavenging ratios (P/I). (a) P = 100%, (b) P/I = 3:1, (c) P/I = 1:3 and (d) I = 100% during ozonation. Reaction conditions: \( \text{O}_3 \) dose = 0.021 mM, pH ~8.0 (phosphate buffer, 10 mM), total scavenging rate = \( 1.2 \times 10^5 \) s\(^{-1} \), P =100%: [MeOH] = 0.124 mM; P/I = 3: [MeOH] = 0.093 mM, [Acetate] = 0.38 mM; P/I = 1/3: [MeOH] = 0.031 mM, [Acetate] = 1.14 mM; I=100%: [Acetate] = 1.52 mM.
Fig. S5. Effects of the P/I ratios on the evolution of (a) O₃, (b) •OH, and (c) O₂⁻ concentrations during ozonation of MeOH- and/or acetate-containing solutions. Reaction condition: O₃ dose = 0.021 mM, [MeOH] = 0–0.124 mM, [acetate] = 0–1.14 mM, pH ~8.0 (phosphate buffer, 10 mM), total scavenging rate = 1.2 × 10⁵ s⁻¹, P = 100%: [MeOH] = 0.124 mM; P/I = 3: [MeOH] = 0.093 mM, [acetate] = 0.38 mM; P/I = 1: [MeOH] = 0.062 mM, [acetate] = 0.76 mM; P/I = 1/3: [acetate] = 0.031 mM, [acetate] = 1.14 mM; I = 100%: [acetate] = 1.52 mM.

Fig. S6. Modelling of ozone decomposition in MeOH- and/or acetate-containing solutions by Eq. 15 (k_{\text{•OH, O₃}} = 1.1 × 10⁸ M⁻¹ s⁻¹). The symbols are experimental and the dashed lines modelling results. Reaction condition: O₃ dose = 0.021 mM, pH ~8.0 (phosphate buffer, 10 mM).
mM), total scavenging rate = $1.2 \times 10^5$ s$^{-1}$, P =100%: [MeOH] = 0.124 mM, P/I = 3: [MeOH] = 0.093 mM, [acetate] = 0.38 mM; P/I = 1: [MeOH] = 0.062 mM, [acetate] = 0.76 mM; P/I = 1/3: [MeOH] = 0.031 mM, [acetate] = 1.14 mM; I =100%: [acetate] = 1.52 mM.

S6. Methanol and tert-butanol as a chain promoter and inhibitor, respectively

The results obtained with tert-butanol as an inhibitor (Fig. S6) were generally very similar to those obtained with acetate (Fig. 1).
**Fig. S7.** Ozonation of synthetic solutions with constant total scavenging rate and various promotor (methanol):inhibitor (tert-butanol) scavenging ratios (P/I): Effect of the P/I ratios on (a) ozone decrease, (b) \( p \)-CBA abatement and (c) CCl\(_4\) abatement during ozonation of MeOH- and/or TBA-containing solutions. The insets in Fig. S6a, b and c show the O\(_3\) exposures, ‘OH
exposures, and $O_2^-$ exposures, respectively. Reaction conditions: $O_3$ dose = 0.021 mM, pH 
~8.0 (phosphate buffer, 10 mM), total scavenging rate = $1.2 \times 10^5 \text{s}^{-1}$, P = 100%: [MeOH] =
0.124 mM; P/I = 3: [MeOH] = 0.093 mM, [TBA] = 0.06 mM; P/I = 1: [MeOH] = 0.062 mM,
[TBA] = 0.12 mM; P/I = 1/3: [MeOH] = 0.031 mM, [TBA] = 0.18 mM; I = 100%: [TBA] =
0.24 mM.

**Fig. S8.** Ozonation of synthetic solutions with constant total scavenging rate and various
promotor (methanol):inhibitor (tert-butanol) scavenging ratios (P/I): (a) $R_{ct}$, (b) $R_{SO}$, and (c)
$R_{SH}$ as a function of the P/I ratios. Reaction conditions: $O_3$ dose = 0.021 mM, pH ~8.0
(phosphate buffer, 10 mM), total scavenging rate = $1.2 \times 10^5 \text{s}^{-1}$. P = 100%: [MeOH] = 0.124
mM; P/I = 3: [MeOH] = 0.093 mM, [TBA] = 0.06 mM; P/I = 1: [MeOH] = 0.062 mM, [TBA]
= 0.12 mM; P/I = 1/3: [MeOH] = 0.031 mM, [TBA] = 0.18 mM; I = 100%: [TBA] = 0.24 mM.
Fig. S9. Ozonation of synthetic solutions with constant total scavenging rate and various promotor (methanol):inhibitor (tert-butanol) scavenging ratios (P/I): Effects of the P/I ratios on the evolution of (a) O$_3$, (b) •OH, and (c) O$_2^-$ concentrations. Reaction conditions: O$_3$ dose = 0.021 mM, pH ~8.0 (phosphate buffer, 10 mM), total scavenging rate = 1.2 $\times$ 10$^5$ s$^{-1}$. P =100%: [MeOH] = 0.124 mM; P/I = 3: [MeOH] = 0.093 mM, [TBA] = 0.06 mM; P/I = 1: [MeOH] = 0.062 mM, [TBA] = 0.12 mM; P/I = 1/3: [MeOH] = 0.031 mM, [TBA] = 0.18 mM; I =100%: [TBA] = 0.24 mM.
**Fig. S10.** Modelling of ozone decomposition in MeOH/TBA-containing solutions using Eq. 15 \(k_{\text{OH,O}_3} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}\). The filled circles are experimental results, the open triangles are modelling results calculated using Eq. 15, and the dash lines are drawn based on the relative contribution of \(\text{OH}^\cdot\), \(\cdot\text{OH}\), and \(\text{O}_2^\cdot\), respectively, to the \(\text{O}_3\) decay calculated by Eqs. 16-18. Reaction conditions: \(\text{O}_3\) dose = 0.021 mM, pH ~8.0 (phosphate buffer, 10 mM), total scavenging rate = 1.2 \times 10^5 \text{ s}^{-1}. P = 100\%: [\text{MeOH}] = 0.124 \text{ mM}; P/I = 3: [\text{MeOH}] = 0.093 \text{ mM}, [\text{TBA}] = 0.06 \text{ mM}; P/I = 1: [\text{MeOH}] = 0.062 \text{ mM}, [\text{TBA}] = 0.12 \text{ mM}; P/I = 1/3: [\text{MeOH}] = 0.031 \text{ mM}, [\text{TBA}] = 0.18 \text{ mM}; I = 100\%: [\text{TBA}] = 0.24 \text{ mM}.

**S7. Ozonation of natural waters**

**Fig. S11.** Ozonation of a selected groundwater (GW) and two surface waters (SW-1, SW-2): (a) \(R_{ct}\), (b) \(R_{SO}\), and (c) \(R_{SH}\). Reaction conditions: Specific \(\text{O}_3\) dose = 1.0 mg \(\text{O}_3/\text{mg DOC}\). For water quality data of the three real waters see Table 2.
Fig. S12. Relative contribution of OH\(^-\), 'OH, O\(_2\)\(^{2-}\), and DOM to the relative ozone depletion (C/C\(_0\)) in the selected (a) groundwater (GW) and (b, c) surface waters (SW-1, SW-2). The solid circles are experimental data and the dash lines are drawn based on the relative contributions of OH\(^-\), 'OH, O\(_2\)\(^{2-}\), and DOM to O\(_3\) decay calculated using Eqs. 21-24. Reaction conditions: Specific O\(_3\) dose = 1.0 mg O\(_3\)/mg DOC. Refer to Table 2 for water quality data of the three real waters.

References


