Supporting Information (SI)

Overlooked Role of Fe(IV) and Fe(V) During Organic Contaminants Oxidation by Fe(VI)

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Totally 40 pages including 9 texts, 4 tables, 25 figures, and 1 scheme.
Text S1. Reagents used in this study. (Page S5)

Text S2. The detailed experimental procedures. (Pages S5-S7)

Text S3. Analytical Methods. (Page S7)

Text S4. Quantification Method of Fe(VI). (Page S8-S9)

Text S5. Quantification Method of H$_2$O$_2$. (Pages S9-S11)

Text S6. The method of performing DFT calculations. (Pages S11-S12)

Text S7. The reaction of Fe(VI) with PMSO. (Page S12)

Text S8. Determination and sensitivity analysis for the rate constants in the kinetic model (Pages S13-S14)

Text S9. Theoretical investigation of the reaction kinetics by DFT calculations (Pages S15-S16)

Table S1. UPLC conditions for organic pollutants analysis. (Page S17)

Table S2. The calculated energy barriers of PMSO oxidation by ferrates. (Page S17)

Table S3. The calculated solvation energy (ΔE$_{solv}$) of different ferrate species. (Page S18)

Table S4. The apparent second-order rate constant for PMSO oxidation by Fe(VI) measured in the presence of excess PMSO. (Page S18)

Figure S1. Fit of PMSO, CAF, and CBZ oxidation by Fe(VI) with second-order reaction kinetics at different molar ratios of organics to Fe(VI) at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results with second-order rate law, respectively. Experimental conditions: [Fe(VI)]$_0$ = 50 μM. (Page S19)

Figure S2. Fit of PMSO, CAF, and CBZ oxidation by Fe(VI) with second-order reaction kinetics at different molar ratios of organics to Fe(VI) at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results with second-order rate law, respectively. Experimental conditions: [Fe(VI)]$_0$ = 75 μM. (Page S19)

Figure S3. Fit of CAF oxidation by Fe(VI) with second-order reaction kinetics at different molar ratios of CAF to Fe(VI) at pH (a) 7.7, (b) 8.0 and (c) 8.4; The variation of the reciprocal of Fe(VI) concentration with reaction time during the self-decay of Fe(VI) at pH (d) 7.7, (e) 8.0 and (f) 8.4. Symbols and solid lines stand for the experimental data and the model simulation results with second-order rate law, respectively. Experimental conditions: [Fe(VI)]$_0$ = 50 μM. (Page S20)

Figure S4. Influence of organics concentration on Fe(VI) decay during organics oxidation by Fe(VI) at pH 8.0. Experimental conditions: [Fe(VI)]$_0$ = 50 μM. (Page S21)

Figure S5. Oxidation of (a) NB and (b) PMSO$_2$ by Fe(VI) at pH 8.0. Experimental conditions: (a) [Fe(VI)]$_0$ = 50 μM, [NB]$_0$ = 5.0 μM; (b) [Fe(VI)]$_0$ = 50 μM, [PMSO$_2$]$_0$ = 5.0 μM. (Page S21)

Figure S6. Oxidation of (a) NB and (b) PMSO$_2$ by Fe(VI) at pH 8.0. Experimental conditions: (a) [Fe(VI)]$_0$ = 50 μM, [NB]$_0$ = 5.0 μM; (b) [Fe(VI)]$_0$ = 50 μM, [PMSO$_2$]$_0$ = 5.0 μM. (Page S21)
Figure S7. Influence of H$_2$O$_2$ on the oxidation of PMSO by Fe(VI) at pH 8.0. Experimental conditions: [Fe(VI)]$_0$ = 50 μM, [H$_2$O$_2$]$_0$ = 20 μM, [PMSO]$_0$ = 10 μM. (Page S22)

Figure S8. Comparison of color of the reaction mixture in different processes in the presence of BPY at pH 8.0. Experimental conditions: [Fe(VI)]$_0$ = 50 μM, [PMSO]$_0$ = [CBZ]$_0$ = [CAF]$_0$ = 20 μM, [BPY] = 2.0 mM. The reaction time was 2 h. (Page S23)

Figure S9. The kinetics of Fe(VI) decay and H$_2$O$_2$ evolution with or without added H$_2$O$_2$ at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results, respectively. (Page S24)

Figure S10. Influence of Fe$^{3+}$ on the self-decay of Fe(VI) at pH 8.0. Experimental conditions: [Fe(VI)]$_0$ = 50 μM. (Page S25)

Figure S11. Relative logarithmic concentration of Fe(VI) as a function of the reaction time during the reaction of Fe(VI) with an excess of (a) H$_2$O$_2$ and (b) PMSO at pH 8.0. The insets show the variations of the Fe(VI) decay rates as a function of initial concentrations of PMSO (a) and H$_2$O$_2$ (b), respectively. Symbols represent the experimental data and lines represent the best fits. Experimental conditions: (a) [Fe(VI)]$_0$ = 18 μM; (b) [Fe(VI)]$_0$ = 40 μM. (Page S25)

Figure S12. Relative logarithmic concentration of CBZ as a function of the Fe(VI) exposure during the CBZ oxidation by Fe(VI) with an excess of organics at pH 8.0. Symbols represent the experimental data and lines represent the best fits. Experimental conditions: [CBZ]$_0$ = (a, b) 5.0 μM; (c, d, e, f) 10.0 μM. (Page S26)

Figure S13. Model sensitivity analysis on the rate constant for R3 ($k_{Fe(IV)-H2O2}$). The model calculations from a range of $k_{Fe(IV)-H2O2}$ (1×10$^3$ – 1×10$^6$ M$^{-1}$s$^{-1}$) were compared to the experimental data for Fe(VI) degradation kinetics during the Fe(VI) self-decay. Experimental conditions: [Fe(VI)]$_0$ = (a) 70 μM; (b) 50 μM; (c) 30 μM. (Page S27)

Figure S14. Model sensitivity analysis on the rate constant for R4 ($k_{Fe(IV)-Fe(IV)}$). The model calculations from a range of $k_{Fe(IV)-Fe(IV)}$ (1×10$^3$ – 1×10$^7$ M$^{-1}$s$^{-1}$) were compared to the experimental data for Fe(VI) degradation kinetics during the Fe(VI) self-decay. Experimental conditions: [Fe(VI)]$_0$ = (a) 70 μM; (b) 50 μM; (c) 30 μM. (Page S27)

Figure S15. Model sensitivity analysis on the rate constant for R5 ($k_{Fe(IV)-Fe(II)}$). The model calculations from a range of $k_{Fe(IV)-Fe(II)}$ (1×10$^6$ – 1×10$^9$ M$^{-1}$s$^{-1}$) were compared to the experimental data for Fe(VI) degradation kinetics during the Fe(VI) self-decay. Experimental conditions: [Fe(VI)]$_0$ = (a) 70 μM; (b) 50 μM; (c) 30 μM. (Page S28)

Figure S16. Model sensitivity analysis for the rate constant for R1 ($k_{Fe(VI)-Fe(VI)}$). The model calculations with a range of $k_{Fe(VI)-Fe(VI)}$ (2.00 – 10.0 M$^{-1}$s$^{-1}$) were compared to the experimental data of Fe(VI) self-decay kinetics. Experimental conditions: [Fe(VI)]$_0$ = (a) 70 μM; (b) 50 μM;
Figure S17. Kinetics of PMSO degradation and Fe(VI) decay during PMSO oxidation by Fe(VI) at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results, respectively. (Page S29)

Figure S18. The kinetics of PMSO oxidation and Fe(VI) decay during PMSO oxidation by Fe(VI) under various initial conditions at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results, respectively. (Page S30)

Figure S19. Model sensitivity analysis for the rate constant for R9 ($k_{Fe(V)-PMSO}$). The model calculations with a range of $k_{Fe(V)-PMSO}$ ($1.00 \times 10^6 - 5.00 \times 10^7$ M$^{-1}$s$^{-1}$) were compared to the experimental data of PMSO degradation kinetics at pH 8.0. Experimental conditions: $[Fe(VI)]_0 = 50 \mu M$. (Page S31)

Figure S20. Model sensitivity analysis for the rate constant for R10 ($k_{Fe(IV)-PMSO}$). The model calculations with a range of $k_{Fe(IV)-PMSO}$ ($500 - 10000$ M$^{-1}$s$^{-1}$) were compared to the experimental data of PMSO degradation kinetics at pH 8.0. Experimental conditions: $[Fe(VI)]_0 = 50 \mu M$. (Page S31)

Figure S21. The contributions of Fe(VI), Fe(V), and Fe(IV) to the degradation of PMSO by Fe(VI) with the presence of H$_2$O$_2$ of different concentrations at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results, respectively. Kinetic simulation condition: $[Fe(VI)]_0 = 50 \mu M$, $[PMSO]_0 = 10 \mu M$. (Page S32)

Figure S22. Evolution of Fe(IV), Fe(V), and Fe(VI) in the reaction Fe(VI) with PMSO at different [PMSO]/[Fe(VI)] at pH 8.0. Kinetic simulation condition: $[Fe(VI)]_0 = 25 \mu M$ (a, b, c); $[Fe(VI)]_0 = 50 \mu M$ (d, e, f). (Page S33)

Figure S23. Influence of H$_2$O$_2$ concentration on the kinetics of CBZ and CAF oxidation and the amount of removed CBZ and CAF at equilibrium by Fe(VI) at pH 8.0. Experimental conditions: $[Fe(VI)]_0 = 25 \mu M$, $[CBZ]_0 = 10 \mu M$, $[CAF]_0 = 10 \mu M$. (Page S34)

Figure S24. The reaction profiles of PMSO oxidation by HFeO$_4^-$ and H$_2$FeO$_4$. The structure snapshots of the initial states (IS), transition states (TS), and final states (FS) were also indicated. To clearly display the structures, the solvation water molecules were not shown. Purple ball: Fe; red ball: O; grey ball: C; yellow ball: S; white ball: H. (Page S35)

Figure S25. The reaction profiles of PMSO oxidation by FeO$_4^{2-}$, HFeO$_4^{2-}$ and H$_2$FeO$_4$. The structure snapshots of the initial states (IS), transition states (TS), and final states (FS) were also indicated. To clearly display the structures, the solvation water molecules were not shown. Purple ball: Fe; red ball: O; grey ball: C; yellow ball: S; white ball: H. (Page S36)

Scheme 1. Proposed mechanisms for the PMSO oxidation by Fe(VI) at pH 8.0. The numbers in the brackets correspond to the reactions in Table 1. (Page S37)
**Text S1.** Reagents used in this study

Potassium ferrate (Fe(VI), purity > 95%) was prepared by wet chemical synthesis.\(^1\)

Fe(VI) solution was freshly prepared by dissolving solid potassium ferrate in a 1.0 mM \(\text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}\) buffer (pH ≈ 9.2) before the batch degradation experiments.

The Fe(VI) solution was filtered with a 0.45 μm hydrophilic polyethersulfone syringe filter and used within 10 min after preparation to minimize Fe(VI) self-decay. All solutions were prepared in Milli-Q water (>18.2 MΩ·cm resistivity; Millipore Milli-Q system).

Carbamazepine (CBZ), caffeine (CAF), methyl phenyl sulfoxide (PMSO), methyl phenyl sulfone (PMSO\(_2\)), 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS), 2,2′-bipyridine (BPY), horseradish peroxidase (HRP), and nitrobenzene (NB) were supplied by Aladdin Biological Technology Co., Ltd. (Shanghai, China). Dibasic sodium phosphate (\(\text{Na}_2\text{HPO}_4\)), sodium tetraborate (\(\text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}\)), and hydrogen peroxide (\(\text{H}_2\text{O}_2\)) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of reagent grade or higher and were used as received without further purification.

**Text S2.** The detailed experimental procedures

As the chemical property of Fe(VI) was strongly dependent on pH,\(^2,3\) buffers were usually used to maintain the solution pH in the experiments with Fe(VI). Since phosphate buffer was reported to suppress the oxidation ability of the intermediate iron species,\(^4\) borate, which has little influence on the kinetics of Fe(VI) self-decay...
and does not affect the oxidation pathways of PMSO by Fe(VI) (Figure SI-1), was selected as the buffer in this study.

**Figure SI-1.** The influence of borate on the η(PMSO₂) (the molar ratio of generated PMSO₂ produced to degraded PMSO) during PMSO oxidation by Fe(VI).

Experimental conditions: [Fe(VI)]₀ = 50 μM, [PMSO]₀ = 10 μM, initial pH = 8.0.

The second-order rate constants for the self-decay of Fe(VI) show a strong pH dependence and increase more than 3 orders of magnitude with a decrease of the pH from 9.0 to 7.0. Most of the experiments in this study were carried out at pH 8.0 since Fe(VI) has a moderate self-decay rate at this pH level and this is an environmentally relevant pH.

Generally, the experiments were initiated by dosing proper amount of filtered stock Fe(VI) solution to the working solution containing the organic contaminant. The initial molar ratios of organic contaminants to Fe(VI) were well controlled at 1:10, 1:5, and 2:5 in this study since most studies on organic contaminants degradation by Fe(VI) were carried out with Fe(VI) in excess. It should be noted that the experiments investigating the degradation of organic contaminants in Fe(VI)-H₂O₂ process were initiated by dosing filtered Fe(VI) stock solution immediately after the addition of
H₂O₂ into the working solution containing the target TrOCs. pH of the working solution was buffered with 10 mM borate and was adjusted to the desired value by dropwise addition of sodium hydroxide (5.0 M) or sulfuric acid (5.0 M), if necessary, and pH change of the reaction solutions was within ±0.05 during all of the tests in this study. At defined time intervals, 1.5 mL sample was collected and immediately mixed with 20 μL of 200 mM Na₂S₂O₃ to quench the reaction and then filtered (0.22 μm) before subject to analysis with Ultra High Performance Liquid Chromatography (UPLC). Along with the organic pollutants removal profiles, one aliquot of 2.0 mL was sampled and quenched with ABTS solution to measure the residual Fe(VI) concentration. Concomitantly, another aliquot of 2.0 mL was sampled, quenched with another ABTS solution, and catalyzed by horseradish peroxidase to measure the H₂O₂ concentration when necessary.

**Text S3. Analytical methods**

The concentrations of organic pollutants were quantified with UPLC (Waters Co.). These compounds were separated with a BEH C18 column (2.1 × 100 mm, 1.7 μm; Waters Co.) in an isocratic mode of elution at 35 ± 1 °C with a UV-visible detector. The mobile phases were methanol, acetonitrile, and 0.1% formic acid aqueous solution. Detailed analytical parameters are listed in Table S1.

**Text S4. Quantification method of Fe(VI)**

ABTS•⁺ has a well-defined absorbance at 645 nm ($ε_{645} = 11600 \text{ M}^{-1} \text{ cm}^{-1}$).⁶ At defined time intervals, 2.0 mL of the sample was collected and mixed with 4.0 mL of
ABTS solutions at excess concentration of 450 μM, prepared in 0.2 M phosphate/0.6 M acetate buffers at pH 4.0, to measure the absorbance at 645 nm ($\Delta A_{w/o}$) to calculated the concentration of residual Fe(VI) concentration.$^7$

Figure S1-2. The correlation of Fe(VI) concentration and the amount of ABTS$^{•}$ generated from the reaction of Fe(VI) with excess ABTS. Experimental conditions:

$[\text{ABTS}]_0 = 0.45$ mM, pH 4.0 buffered with 0.2 M phosphate and 0.6 M acetate.

According to the reaction stoichiometry of Fe(VI) with ABTS ($[\text{ABTS}^{•}] / [\text{Fe(VI)}] = 1.02$), the concentration of Fe(VI) in sample was calculated by followed equation:

$$[\text{Fe(VI)}] = [\text{ABTS}^{•}]_{w/o} \div 1.02 \times 3 = \Delta A_{w/o} \div \varepsilon_{645} \div 1.02 \times 3 \quad (S1)$$

Where $[\text{Fe(VI)}]$ represents the residual concentration of Fe(VI) in the samples collected at selected time intervals in batch degradation experiments; $[\text{ABTS}^{•}]_{w/o}$ represents the amount of ABTS$^{•}$ produced from the reaction of Fe(VI) in 2.0 mL of the sample with ABTS; $\Delta A_{w/o}$ represents the change of the absorbance at 645 nm after completion of the reaction between Fe(VI) and ABTS without the presence of HRP.

It should be noted that the amount of generated ABTS$^{•}$ was always equal to that of consumed ABTS during the reaction of Fe(VI) with ABTS, indicating that the
generated ABTS$^{+}$ cannot be further oxidized by ferrates.$^{4, 5}$

**Text S5. Quantification method of H$_2$O$_2$**

At the defined time intervals, another 2.0 mL of the sample was collected and mixed with 4.0 mL of ABTS solutions at excess concentration of 450 μM, prepared in 0.2 M phosphate/0.6 M acetate buffers at pH 4.0, to quench the reaction. Moreover, 50 μL of the horseradish peroxidase (HRP) stock solution (1 mg mL$^{-1}$) was added into glass bottles after the Fe(VI)-ABTS reaction was completed to catalyze the oxidation of ABTS by H$_2$O$_2$ so as to measure $\Delta$A$_w$. One mole of H$_2$O$_2$ could produce 2 moles of ABTS$^{+}$.$^{5}$

The reaction of Fe(VI) with ABTS would form H$_2$O$_2$ as a product.$^{4, 5}$ Thus, calculating the yield of H$_2$O$_2$ in the reaction of Fe(VI) with ABTS is necessary to measure the concentration of H$_2$O$_2$ in the samples in batch degradation experiments ($[H_2O_2]$).

**Figure SI-3.** The correlation of Fe(VI) concentration and the amount of H$_2$O$_2$ generated from the reaction of Fe(VI) with excess ABTS. Experimental conditions:
The yield of H$_2$O$_2$ was 0.84 in the reaction of Fe(VI) with excess ABTS at pH 4.0 ([H$_2$O$_2$]$_{Fe(VI)}/[Fe(VI)] = 0.84$). Thus, [H$_2$O$_2$] could be calculated by followed equations:

\[
[H_2O_2]_{\text{total}} = ([ABTS^+]^w - [ABTS^+]_{w/o}) ÷ 2 \times 3 = (\Delta A_w - \Delta A_{w/o}) ÷ \varepsilon_{645} ÷ 2 \times 3 \quad (S2)
\]

\[
[H_2O_2]_{Fe(VI)} = 0.84 \cdot [Fe(VI)] \quad (S3)
\]

\[
[H_2O_2] = [H_2O_2]_{\text{total}} - [H_2O_2]_{Fe(VI)} \quad (S4)
\]

Where [H$_2$O$_2$]$_{\text{total}}$ represents the concentration of H$_2$O$_2$ after the reaction of Fe(VI) with ABTS; [H$_2$O$_2$]$_{Fe(VI)}$ represents the formation of H$_2$O$_2$ in the reaction of Fe(VI) with ABTS; [Fe(VI)] and [H$_2$O$_2$] represent the concentrations of Fe(VI) and H$_2$O$_2$ in batch degradation experiments; [ABTS$^+$]$^w$ represents the ABTS$^+$ produced from the reaction of Fe(VI) in 2.0 mL of the sample with ABTS with the addition of HRP; $\Delta A_w$ represents the change of the absorbance at 645 nm after completion of the reaction between Fe(VI) and ABTS with the addition of HRP.

**Text S6.** The method of performing DFT calculations

All the DFT calculations were performed using the Vienna *ab initio* simulation package (VASP)\(^8\) with projected augmented wave (PAW) pseudo-potentials.\(^9\)\(^,\)\(^10\) The exchange–correlation energy was treated based on the generalized gradient approximation (GGA) by using Perdew–Burke–Ernzerhof (PBE) functional.\(^11\) The plane-wave cutoff energy was set to 500 eV. The vibrational frequency calculations were further performed via the finite-difference approach to correct the zero-point
energy for reaction barrier. Due to the predictable effect of the dispersion forces in the calculations, these were considered in this work by using the Grimme’s (GGA–PBE-D3).\textsuperscript{12, 13} The calculation of the transition state (TS) structures was performed with the Large-scale Atomistic Simulation with neural network Potential (LASP) program with constrained Broyden dimer (CBD) method\textsuperscript{14, 15} and double-ended surface walking (DESW) method.\textsuperscript{16}

During the PMSO oxidation by ferrates, the reacting O atoms of ferrate species would attack the S atom of PMSO with solvent water molecule. To obtain reliable reaction barriers, two explicit water molecules, which form hydrogen bond with the reacting O atom of ferrate species, were added to consider the solvation effect of the reacting species. The solvation energy ($\Delta E_{\text{solv}}$) calculated by Eq. S5 was shown in Table S3.

\[ \Delta E_{\text{solv}} = E_{\text{with H}_2\text{O}} - E_0 - E_{\text{Solv H}_2\text{O}} \]  
(S5)

where $E_{\text{with H}_2\text{O}}$ represents the total energy of the reaction intermediate containing two explicit H$_2$O molecules; $E_0$ represents the energy of the reaction intermediate without H$_2$O; $E_{\text{Solv H}_2\text{O}}$ represents the energy of solvated water molecules.

\textbf{Text S7.} The reaction of Fe(VI) with PMSO

The reaction kinetics of Fe(VI) with PMSO was investigated by measuring the drop
of Fe(VI) concentration in presence of excess PMSO ([Fe(VI)]₀ = 18 μM and
[PMSO]₀ = 582-873 μM) at pH 8.0. Under these conditions, the logarithmic Fe(VI)
concentration decreased linearly with time (Figure S11b), indicating that the reaction
is pseudo-first-order with respect to the Fe(VI) concentration (Eq. 3). Pseudo-first
order rate constants (k’_app[PMSO]₀) were calculated from the linear slopes in Figure
S11b, where k’_app represents the apparent second-order rate constant for Fe(VI) decay
in with excess PMSO.

With the presence of excess PMSO, two moles of Fe(VI) can be consumed per
every event of R8 as Fe(IV) produced from R8 will generate Fe(II) by R10, which in
turn will consume another Fe(VI) by R5 rapidly. Therefore, the second-order rate
constants for R8 should be one-half of the apparent second-order rate constant that
was measured in excess of PMSO (i.e., 2k₈ = k’_app) and a value of 3.75 M⁻¹ s⁻¹ was
obtained, as shown in Table S4.

**Text S8.** Determination and sensitivity analysis for the rate constants in the kinetic
model

R2: Lee et al. reported that the second-order rate constant for the reaction of Fe(VI)
with H₂O₂ was 16.50 M⁻¹ s⁻¹ at pH 8.0 in 10 mM phosphate/borate buffer,⁵ but we
found that this value was 21.18 M⁻¹ s⁻¹ at pH 8.0 in 10 mM borate buffer (Figure
S11a). The difference may be ascribed to the presence of phosphate in the buffer in
Lee et al.’s study.⁴
R3, R4, and R5: The second-order rate constants for the reaction between Fe(IV) and H$_2$O$_2$ ($k_{\text{Fe(IV)-H}_2\text{O}_2}$) were reported to be $1 \times 10^4$ M$^{-1}$s$^{-1}$ at pH 7.0$^5$ and $7.8 \times 10^5$ M$^{-1}$s$^{-1}$ at pH 10.0$^{18}$. The rate constants for Fe(IV) auto-decomposition ($k_{\text{Fe(IV)}-\text{Fe(IV)}}$) were reported to be $1 \times 10^6$ M$^{-1}$s$^{-1}$ at pH 7.5 and $1 \times 10^6$ M$^{-1}$s$^{-1}$ at pH 9.0, respectively.$^{18, 19}$ As for the reaction between Fe(VI) and Fe(II), rate constant ($k_{\text{Fe(VI)}-\text{Fe(II)}}$) was reported to be $\gg 10^7$ M$^{-1}$s$^{-1}$ at pH 7.0.$^5$ To initialize the model fitting, the values of $k_{\text{Fe(IV)-H}_2\text{O}_2}$, $k_{\text{Fe(IV)}-\text{Fe(IV)}}$, and $k_{\text{Fe(VI)}-\text{Fe(II)}}$ were set to be $1 \times 10^4$ M$^{-1}$s$^{-1}$, $1 \times 10^6$ M$^{-1}$s$^{-1}$, and $1 \times 10^7$ M$^{-1}$s$^{-1}$ in Model 1, respectively. The assumption for the values of $k_{\text{Fe(IV)-H}_2\text{O}_2}$, $k_{\text{Fe(IV)}-\text{Fe(IV)}}$, and $k_{\text{Fe(VI)}-\text{Fe(II)}}$ was then verified by performing model sensitivity analyses.

The model simulations using a range of $k_{\text{Fe(IV)-H}_2\text{O}_2}$ ($1 \times 10^3$–$1 \times 10^6$ M$^{-1}$s$^{-1}$), $k_{\text{Fe(IV)}-\text{Fe(IV)}}$ ($1 \times 10^5$–$1 \times 10^7$ M$^{-1}$s$^{-1}$), or $k_{\text{Fe(VI)}-\text{Fe(II)}}$ ($1 \times 10^6$–$1 \times 10^9$ M$^{-1}$s$^{-1}$) values were compared with the experimental data of Fe(VI) self-decay kinetics at three different initial Fe(VI) concentrations. The results suggested that the self-decay kinetics of Fe(VI) was not sensitive to the values of $k_{\text{Fe(IV)-H}_2\text{O}_2}$, $k_{\text{Fe(IV)}-\text{Fe(IV)}}$, or $k_{\text{Fe(VI)}-\text{Fe(II)}}$. It was thus concluded that the assumption was reasonable (Figures S13–S15).

R1: Taking the rate constants for R2-R7 as known parameters, the fitting-derived second-order rate constant for R1 was 4.05 M$^{-1}$s$^{-1}$ at pH 8.0 by simulating the decay kinetics of Fe(VI) demonstrated in Figure S9 with Model 1 (total amount of simulations performed = 102, final sum of error squares = 0.01). The obtained rate constant for R1 was verified by simulating the evolution behavior of H$_2$O$_2$ under
various reaction conditions, as shown in Figure S9. The validity of rate constant for R1 was also tested by performing a model sensitivity analysis (Figure S16). When the contributions of R2 and R5 to Fe(VI) decay were not taken into account, the rate constant for R1 would be over-estimated in previous study. Therefore, the value of $k$ for R1 reported in the literature (5.4 M$^{-1}$ s$^{-1}$ in 10 mM phosphate/borate buffer at pH 8.0)$^5$ was greater than that determined in our study (4.05 M$^{-1}$ s$^{-1}$ in 10 mM borate buffer at pH 8.0).

R9 and R10: The rate constants for R9 and R10 were determined to be 7.79×10$^6$ M$^{-1}$ s$^{-1}$ ($k_{\text{Fe(V)-PMSO}}$) and 2.58×10$^3$ M$^{-1}$ s$^{-1}$ ($k_{\text{Fe(IV)-PMSO}}$), respectively, by simulating the degradation kinetics of PMSO under various conditions with M2 (total amount of simulations performed = 455, final sum of error squares = 0.26), as shown in Figure S17. A sensitivity analysis for the fitting-derived rate constants for R9 and R10 is also performed, as shown in Figures S19-S20.
Text S9. Theoretical investigation of the reaction kinetics by DFT calculations

DFT method has emerged as a viable alternative for revealing the mechanisms in oxidation processes of pollutants and it was thus employed to offer extra evidences to test the robustness of rate constants for R9 and R10 obtained with Model 2. For ferrate in a specific valence state, multiple hydrolysis forms may co-exist in the solution at certain pH. Since the pK$_a$ values of Fe(IV) are not available in the literature, we only calculated the reaction barriers (ΔG$_a$) values of PMSO reacting with each possible hydrolysis form of Fe(VI) and Fe(V) (Table S2). Following Eqs. S6 and S7, the apparent reaction barriers (ΔG$_{app}$) of PMSO oxidation by Fe(VI) and Fe(V) were calculated to be 68.3 and 37.3 kJ/mol, respectively.$^{20}$

$$k_i = A \cdot \exp(-\Delta G_a/RT)$$  \hspace{1cm} (S6)  

$$\Delta G_{app} = -RT \cdot \ln(\sum_i k_i \alpha_i / A)$$  \hspace{1cm} (S7)  

where A stands for the pre-exponential factor ($A = 6.25 \times 10^{12}$ s$^{-1}$·mol$^{-1}$·L at 300 K from classic TS theory);$^{21}$ R (8.314 J·mol$^{-1}$·K$^{-1}$) and T represent molar gas constant and temperature, respectively; $k_i$ and $\alpha_i$ represent the rate constant and the respective fraction of ferrate species $i$ at pH 8.0, respectively.

As shown in Table S2, these values are well consistent with the experimentally-derived ΔG$_{app}$ (with difference less than 3.5 kJ/mol), which verified that kinetic modeling was solid and Fe(V) and Fe(IV) did contribute to the oxidation of PMSO. Moreover, the $k_i\alpha_i$ values of different ferrate species demonstrated that HFeO$_4^-$ and H$_2$FeO$_4^-$ were the major Fe(VI) and Fe(V) species contributing to PMSO oxidation.
at pH 8.0 (Table S2), respectively. The reaction profiles of PMSO reacting with HFeO$_4^-$ and H$_2$FeO$_4^-$, including the structure snapshots of initial states, transition states and final states are shown in Figure S24. The reaction profiles of PMSO oxidation by other Fe(VI) and Fe(V) species are illustrated in Figure S25.
Table S1. UPLC conditions for organic pollutants analysis.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Formic acid aqueous solution/methanol (v/v)</th>
<th>Formic acid aqueous solution/acetonitrile (v/v)</th>
<th>Wavelength (nm)</th>
<th>Flow rate (mL/min)</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBZ</td>
<td>50/50</td>
<td></td>
<td>286</td>
<td>0.22</td>
<td>1.75</td>
</tr>
<tr>
<td>CAF</td>
<td>65/35</td>
<td></td>
<td>273</td>
<td>0.18</td>
<td>2.38</td>
</tr>
<tr>
<td>PMSO</td>
<td>72/28</td>
<td></td>
<td>230</td>
<td>0.25</td>
<td>3.14</td>
</tr>
<tr>
<td>PMSO₂</td>
<td>72/28</td>
<td></td>
<td>264</td>
<td>0.25</td>
<td>2.10</td>
</tr>
</tbody>
</table>

Table S2. The calculated energy barriers of PMSO oxidation by ferrates.

<table>
<thead>
<tr>
<th>Ferrates</th>
<th>pK_a</th>
<th>Ferrate Species</th>
<th>Fraction of species</th>
<th>ΔG_a (kJ/mol)</th>
<th>a/k_i</th>
<th>ΔG_app (kJ/mol)</th>
<th>ΔG_app (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(VI)</td>
<td>(pK_1 = 1.5;)</td>
<td>(\text{FeO}_4^{2-})</td>
<td>86.32%</td>
<td>87.7</td>
<td>3.00×10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(VI)</td>
<td>(pK_2 = 3.5;)</td>
<td>(\text{HFeO}_4^-)</td>
<td>13.68%</td>
<td>63.3</td>
<td>8.13</td>
<td>68.3\textsuperscript{a}</td>
<td>70.2\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td>(pK_3 = 7.2;)</td>
<td>(\text{FeO}_4^2-)</td>
<td>75.40%</td>
<td>53.9</td>
<td>1.94×10^{3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(V)</td>
<td>(pK_1 \approx 6.5;)</td>
<td>(\text{HFeO}_4^-)</td>
<td>23.84%</td>
<td>35.0</td>
<td>1.20×10^{6}</td>
<td>37.3\textsuperscript{a}</td>
<td>33.9\textsuperscript{c}</td>
</tr>
<tr>
<td>Fe(V)</td>
<td>(pK_2 \approx 7.5;)</td>
<td>(\text{H}_2\text{FeO}_4^-)</td>
<td>0.76%</td>
<td>27.3</td>
<td>8.39×10^{5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(V)</td>
<td>(pK_3 = 10.1;)</td>
<td>(\text{H}_3\text{FeO}_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated by ΔG obtained in DFT calculations. \textsuperscript{b}Calculated by rate constants obtained in experiment. \textsuperscript{c}Calculated by rate constants obtained in kinetic modeling.
Table S3. The calculated solvation energy ($\Delta E_{\text{solv}}$) of different ferrate species.

<table>
<thead>
<tr>
<th>Ferrates</th>
<th>Ferrate species</th>
<th>$\Delta E_{\text{solv}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(VI)</td>
<td>FeO$_4^{2-}$</td>
<td>-0.82</td>
</tr>
<tr>
<td></td>
<td>HFeO$_4$</td>
<td>-0.26</td>
</tr>
<tr>
<td></td>
<td>HFeO$_4^{2-}$</td>
<td>-0.73</td>
</tr>
<tr>
<td>Fe(V)</td>
<td>H$_2$FeO$_4$</td>
<td>-0.34</td>
</tr>
<tr>
<td></td>
<td>H$_3$FeO$_4$</td>
<td>-0.07</td>
</tr>
</tbody>
</table>

Table S4. The apparent second-order rate constant for PMSO oxidation by Fe(VI) measured in the presence of excess PMSO.

<table>
<thead>
<tr>
<th>[PMSO]$_0$ (μM)</th>
<th>Pseudo-first order rate constants (s$^{-1}$)</th>
<th>$k'_{\text{app}}$ (M$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>582</td>
<td>0.0044</td>
<td>7.56</td>
</tr>
<tr>
<td>728</td>
<td>0.0053</td>
<td>7.28</td>
</tr>
<tr>
<td>873</td>
<td>0.0067</td>
<td>7.67</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>7.50 ± 0.16</td>
</tr>
</tbody>
</table>
Figure S1. Fit of PMSO, CAF, and CBZ oxidation by Fe(VI) with second-order reaction kinetics at different molar ratios of organics to Fe(VI) at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results with second-order rate law, respectively. Experimental conditions: [Fe(VI)]₀ = 50 μM.

Figure S2. Fit of PMSO, CAF, and CBZ oxidation by Fe(VI) with second-order reaction kinetics at different molar ratios of organics to Fe(VI) at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results with second-order rate law, respectively. Experimental conditions: [Fe(VI)]₀ = 75 μM.
Figure S3. Fit of CAF oxidation by Fe(VI) with second-order reaction kinetics at different molar ratios of CAF to Fe(VI) at pH (a) 7.7, (b) 8.0 and (c) 8.4; The variation of the reciprocal of Fe(VI) concentration with reaction time during the self-decay of Fe(VI) at pH (d) 7.7, (e) 8.0 and (f) 8.4. Symbols and solid lines stand for the experimental data and the model simulation results with second-order rate law, respectively. Experimental conditions: [Fe(VI)]₀ = 50 μM.
Figure S4. Influence of organics concentration on Fe(VI) decay during organics oxidation by Fe(VI) at pH 8.0. Experimental conditions: $[\text{Fe(VI)}]_0 = 50 \, \mu\text{M}$.

Figure S5. Oxidation of CAF by Fe(VI) in the presence of PMSO at pH 8.0. Experimental conditions: $[\text{Fe(VI)}]_0 = 75 \, \mu\text{M}$, $[\text{PMSO}]_0 = 10 \, \mu\text{M}$, $[\text{CAF}]_0 = 5.0 \, \mu\text{M}$. 

- [Image of graphs showing Fe(VI) decay and CAF oxidation]
Figure S6. Oxidation of (a) NB and (b) PMSO₂ by Fe(VI) at pH 8.0. Experimental conditions: (a) [Fe(VI)]₀ = 50 μM, [NB]₀ = 5.0 μM; (b) [Fe(VI)]₀ = 50 μM, [PMSO₂]₀ = 5.0 μM.

Figure S7. Influence of H₂O₂ on the oxidation of PMSO by Fe(VI) at pH 8.0. Experimental conditions: [Fe(VI)]₀ = 50 μM, [H₂O₂]₀ = 20 μM, [PMSO]₀ = 10 μM.
Figure S8. Comparison of color of the reaction mixture in different processes in the presence of BPY at pH 8.0. Experimental conditions: \([\text{Fe(VI)}]_0 = 50 \ \mu\text{M}, [\text{PMSO}]_0 = [\text{CBZ}]_0 = [\text{CAF}]_0 = 20 \ \mu\text{M}, [\text{BPY}] = 2.0 \ \text{mM}. \) The reaction time was 2 h.
Figure S9. The kinetics of Fe(VI) decay and H$_2$O$_2$ evolution with or without added H$_2$O$_2$ at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results, respectively.
**Figure S10.** Influence of Fe$^{3+}$ on the self-decay of Fe(VI) at pH 8.0. Experimental conditions: [Fe(VI)]$_0$ = 50 μM.

**Figure S11.** Relative logarithmic concentration of Fe(VI) as a function of the reaction time during the reaction of Fe(VI) with an excess of (a) H$_2$O$_2$ and (b) PMSO at pH 8.0. The insets show the variations of the Fe(VI) decay rates as a function of initial concentrations of PMSO (a) and H$_2$O$_2$ (b), respectively. Symbols represent the experimental data and lines represent the best fits. Experimental conditions: (a) [Fe(VI)]$_0$ = 18 μM; (b) [Fe(VI)]$_0$ = 40 μM.
Figure S12. Relative logarithmic concentration of CBZ as a function of the Fe(VI) exposure during the CBZ oxidation by Fe(VI) with an excess of organics at pH 8.0. Symbols represent the experimental data and lines represent the best fits. Experimental conditions: [CBZ]₀ = (a, b) 5.0 μM; (c, d, e, f) 10.0 μM.
Figure S13. Model sensitivity analysis for the rate constant for R3 ($k_{\text{Fe(IV)-H}_2\text{O}_2}$). The model calculations with a range of $k_{\text{Fe(IV)-H}_2\text{O}_2}$ ($1 \times 10^{3} - 1 \times 10^{6}$ M$^{-1}$s$^{-1}$) were compared to the experimental data of Fe(VI) self-decay kinetics. Experimental conditions: $[\text{Fe(VI)}]_0 = (a) 70 \mu$M; (b) 50 $\mu$M; (c) 30 $\mu$M.

Figure S14. Model sensitivity analysis for the rate constant for R4 ($k_{\text{Fe(IV)-Fe(IV)}}$). The model calculations with a range of $k_{\text{Fe(IV)-Fe(IV)}}$ ($1 \times 10^{5} - 1 \times 10^{7}$ M$^{-1}$s$^{-1}$) were compared to the experimental data of Fe(VI) self-decay kinetics. Experimental conditions: $[\text{Fe(VI)}]_0 = (a) 70 \mu$M; (b) 50 $\mu$M; (c) 30 $\mu$M.
Figure S15. Model sensitivity analysis for the rate constant for R5 ($k_{\text{Fe(VI)}-\text{Fe(II)}}$). The model calculations with a range of $k_{\text{Fe(VI)}-\text{Fe(II)}}$ (1×10⁶–1×10⁹ M⁻¹s⁻¹) were compared to the experimental data of Fe(VI) self-decay kinetics. Experimental conditions: [Fe(VI)]₀ = (a) 70 μM; (b) 50 μM; (c) 30 μM.

Figure S16. Model sensitivity analysis for the rate constant for R1 ($k_{\text{Fe(VI)}-\text{Fe(VI)}}$). The model calculations with a range of $k_{\text{Fe(VI)}-\text{Fe(VI)}}$ (2.00–10.0 M⁻¹s⁻¹) were compared to the experimental data of Fe(VI) self-decay kinetics. Experimental conditions: [Fe(VI)]₀ = (a) 70 μM; (b) 50 μM; (c) 30 μM.
**Figure S17.** Kinetics of PMSO degradation and Fe(VI) decay during PMSO oxidation by Fe(VI) at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results, respectively.
Figure S18. The kinetics of PMSO oxidation and Fe(VI) decay during PMSO oxidation by Fe(VI) under various initial conditions at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results, respectively.
Figure S19. Model sensitivity analysis for the rate constant for R9 \( (k_{\text{Fe(V)-PMSO}}) \). The model calculations with a range of \( k_{\text{Fe(V)-PMSO}} \) \( (1.00 \times 10^6 - 5.00 \times 10^7 \ \text{M}^{-1}\text{s}^{-1}) \) were compared to the experimental data of PMSO degradation kinetics at pH 8.0. Experimental conditions: \([\text{Fe(VI)}]_0 = 50 \ \mu\text{M}\).

Figure S20. Model sensitivity analysis for the rate constant for R10 \( (k_{\text{Fe(IV)-PMSO}}) \). The model calculations with a range of \( k_{\text{Fe(IV)-PMSO}} \) \( (500 - 10000 \ \text{M}^{-1}\text{s}^{-1}) \) were compared to the experimental data of PMSO degradation kinetics at pH 8.0. Experimental conditions: \([\text{Fe(VI)}]_0 = 50 \ \mu\text{M}\).
Figure S21. The contributions of Fe(VI), Fe(V), and Fe(IV) to the degradation of PMSO by Fe(VI) with the presence of H$_2$O$_2$ of different concentrations at pH 8.0. Symbols and solid lines stand for the experimental data and the model simulation results, respectively. Kinetic simulation condition: [Fe(VI)]$_0$ = 50 μM, [PMSO]$_0$ = 10 μM.
Figure S22. Evolutions of Fe(IV), Fe(V), and Fe(VI) in the reaction Fe(VI) with PMSO at different $[\text{PMSO}]_0/[\text{Fe(VI)}]_0$ at pH 8.0. Kinetic simulation condition:

$[\text{Fe(VI)}]_0 = 25 \mu\text{M (a, b, c); } [\text{Fe(VI)}]_0 = 50 \mu\text{M (d, e, f).}$
Figure S23. Influence of H$_2$O$_2$ concentration on the kinetics of CBZ and CAF oxidation and the amount of removed CBZ and CAF at equilibrium by Fe(VI) at pH 8.0.

Experimental conditions: [Fe(VI)]$_0$ = 25 μM, [CBZ]$_0$ = 10 μM, [CAF]$_0$ = 10 μM.
Figure S24. The reaction profiles of PMSO oxidation by HFeO$_4^-$ and H$_2$FeO$_4^-$. The structure snapshots of the initial states (IS), transition states (TS), and final states (FS) were also indicated. To clearly display the structures, the solvation water molecules were not shown. Purple ball: Fe; red ball: O; grey ball: C; yellow ball: S; white ball: H.
Figure S25. The reaction profiles of PMSO oxidation by FeO$_4^{2-}$, HFeO$_4^{2-}$ and H$_3$FeO$_4$.

The structure snapshots of the initial states (IS), transition states (TS), and final states (FS) were also indicated. To clearly display the structures, the solvation water molecules were not shown. Purple ball: Fe; red ball: O; grey ball: C; yellow ball: S; white ball: H.
Scheme 1. Proposed mechanisms for the PMSO oxidation by Fe(VI) at pH 8.0. The numbers in the brackets correspond to the reactions in Table 1.

Reference:


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