Electronic Supplementary Information (ESI)

for

High-valent iron (FeVI, FeV, and FeIV) species in water: Characterization and oxidative transformation of estrogenic hormones

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Number of pages: 10
Number of figures: 9
Number of tables: 1
Fig. S1. $^{57}$Fe Mössbauer spectra and X-ray diffraction pattern of initial ferrate(IV), ferrate(V), and ferrate(VI) samples used for degradation of estrogens: (a) Room-temperature $^{57}$Fe Mössbauer spectrum and (b) X-ray powder diffraction pattern of ferrate(IV) compound (i.e., Na$_4$FeO$_4$). The values of hyperfine Mössbauer parameters, derived upon fitting the $^{57}$Fe Mössbauer spectrum in panel (a), are listed in Table S1 with assignment of individual spectral components. The bars in panel (b) indicate the diffraction peaks of individual compounds found upon the analysis of the X-ray powder diffractogram. (c) Room-temperature $^{57}$Fe Mössbauer spectrum and (d) X-ray powder diffraction pattern of ferrate(V) compound (i.e., K$_3$FeO$_4$). The values of hyperfine Mössbauer
parameters, derived upon fitting the $^{57}$Fe Mössbauer spectrum in panel (c), are listed in Table S1 with assignment of individual spectral components. The bars in panel (d) indicate the diffraction peaks of individual compounds found upon the analysis of the X-ray powder diffractogram. (e) Room-temperature $^{57}$Fe Mössbauer spectrum and (f) X-ray powder diffraction pattern of ferrate(VI) compound (i.e., K$_2$FeO$_4$). The values of hyperfine Mössbauer parameters, derived upon fitting the $^{57}$Fe Mössbauer spectrum in panel (e), are listed in Table S1 with assignment of individual spectral components. The bars in panel (f) indicate the diffraction peaks of individual compounds found upon the analysis of the X-ray powder diffractogram.

Table S1. Values of the Mössbauer hyperfine parameters, derived from the fitting of the room-temperature $^{57}$Fe Mössbauer spectrum of ferrate(IV), ferrate(V), and ferrate(VI), where $\delta$ is the isomer shift, $\Delta E_Q$ is the quadrupole splitting, and RA is the relative spectral area of individual spectral components identified during spectrum fitting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>$\delta \pm 0.01$ (mm/s)</th>
<th>$\Delta E_Q \pm 0.01$ (mm/s)</th>
<th>RA ± 1 (%)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrate(IV)</td>
<td>Doublet</td>
<td>– 0.23</td>
<td>0.41</td>
<td>94</td>
<td>Fe$^{IV}$</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
<td>0.35</td>
<td>0.73</td>
<td>6</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td>Ferrate(V)</td>
<td>Doublet</td>
<td>– 0.51</td>
<td>0.89</td>
<td>93</td>
<td>Fe$^{V}$</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
<td>0.35</td>
<td>0.72</td>
<td>7</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td>Ferrate(VI)</td>
<td>Singlet</td>
<td>– 0.90</td>
<td>-----</td>
<td>96</td>
<td>Fe$^{VI}$</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
<td>0.34</td>
<td>0.72</td>
<td>4</td>
<td>Fe$^{III}$</td>
</tr>
</tbody>
</table>
Fig. S2. Comparison of the Raman spectra of degradation products of E1, E2, E3, EE2, and DES estrogens after the treatment with ferrate(IV). The spectra are normalized with respect to the most intensive peak (located at 934 cm$^{-1}$).

Fig. S3. Comparison of the Raman spectra of degradation products of E1, E2, E3, EE2, and DES estrogens after treatment with ferrate(V). The spectra are normalized with respect to the peak located at 2953 cm$^{-1}$ for the sake of the visualization of less intensive peaks.
Fig. S4. Comparison of the Raman spectra of degradation products of E1, E2, E3, EE2, and DES estrogens after treatment with ferrate(VI). Raman spectrum of K\textsubscript{2}FeO\textsubscript{4} dissolved in water is shown for the sake of a direct comparison. The spectra are normalized with respect to the most intensive peak (located at 1048 cm\textsuperscript{-1}).
Fig. S5. Comparison of full ESI mass spectra of degradation products of (a) E1, (b) E2, (c) E3, (d) EE2, and (e) DES estrogens after treatment with ferrate(IV).
Fig. S6. Comparison of full ESI mass spectra of degradation products of (a) E1, (b) E2, (c) E3, (d) EE2, and (e) DES estrogens after treatment with ferrate(V).
Fig. S7. Comparison of full ESI mass spectra of degradation products of (a) E1, (b) E2, (c) E3, (d) EE2, and (e) DES estrogens after treatment with ferrate(VI) together with (f) ESI mass spectrum of pure $K_2FeO_4$ decomposed in water/MeOH.
**Fig. S8.** Data from HPLC-MS analysis of E1 degradation by ferrate(VI) (UV-VIS detector (230 nm) – in red color, positive MS mode (total ion current) in black color) together with the table summarizing the proposed structures of the observed intermediates with the corresponding masses, retention times, and assignment (positions) in chromatogram. The intermediates are numbered according to the oxidation pathway.
Fig. S9. Structural formulas and ESI mass spectra of intermediates of E1 degradation by ferrate(VI).