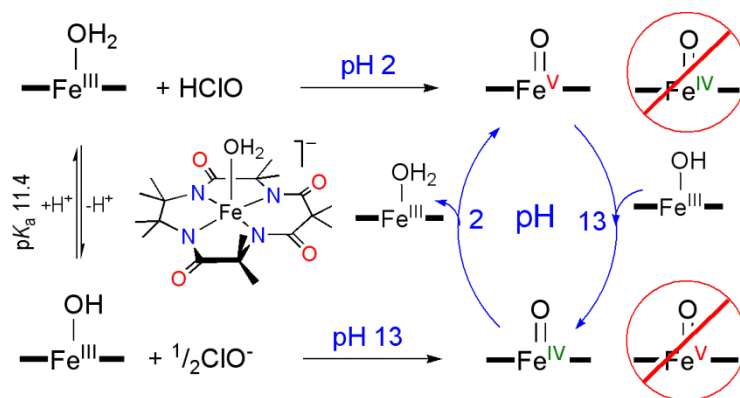


NaClO-Generated Iron(IV)oxo and Iron(V)oxo TAMLs in Pure Water

Matthew R. Mills, Andrew C. Weitz, Michael P. Hendrich,* Alexander D. Ryabov,* Terrence J. Collins*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States

Supporting Information



Experimental details

Chemicals. Unless otherwise stated, all chemicals were ACS reagent grade and used without further purification. TAML **3** was synthesized as previously described.¹ The ⁵⁷Fe-enriched **3** was prepared by metalation with ⁵⁷Fe-enriched FeCl₃. The latter was synthesized from ⁵⁷Fe-enriched iron powder suspended in ethanol by passing HCl gas through the reaction mixture for 3 h. The solvent was then removed by rotary evaporation and put under high vacuum for 12 h. Sodium hypochlorite solutions were obtained from Fisher Scientific and standardized daily by measuring the absorbance at 292 nm in basic solution ($\epsilon = 360 \text{ M}^{-1} \text{ cm}^{-1}$).²

Instrumentation. UV-Vis spectral studies were carried out using an HP 8453A diode array spectrophotometer. Low-temperature spectral studies were performed using a liquid nitrogen cooled cryostat set-up from UNISOKU Scientific Instruments, Japan. X-band EPR spectra were recorded on a Bruker spectrometer equipped with an Oxford ESR-910 liquid helium cryostat. The signal was quantified relative to a CuEDTA spin standard. The microwave frequency was calibrated with a frequency counter and the magnetic field with an NMR gaussmeter. A modulation frequency of 100 kHz was used for the EPR spectra. The EPR simulation software (Spin Count) was written by one of the authors.³ Mössbauer spectra were recorded with a spectrometer using a Janis Research Dewar. The isomer shifts were reported relative to Fe metal.

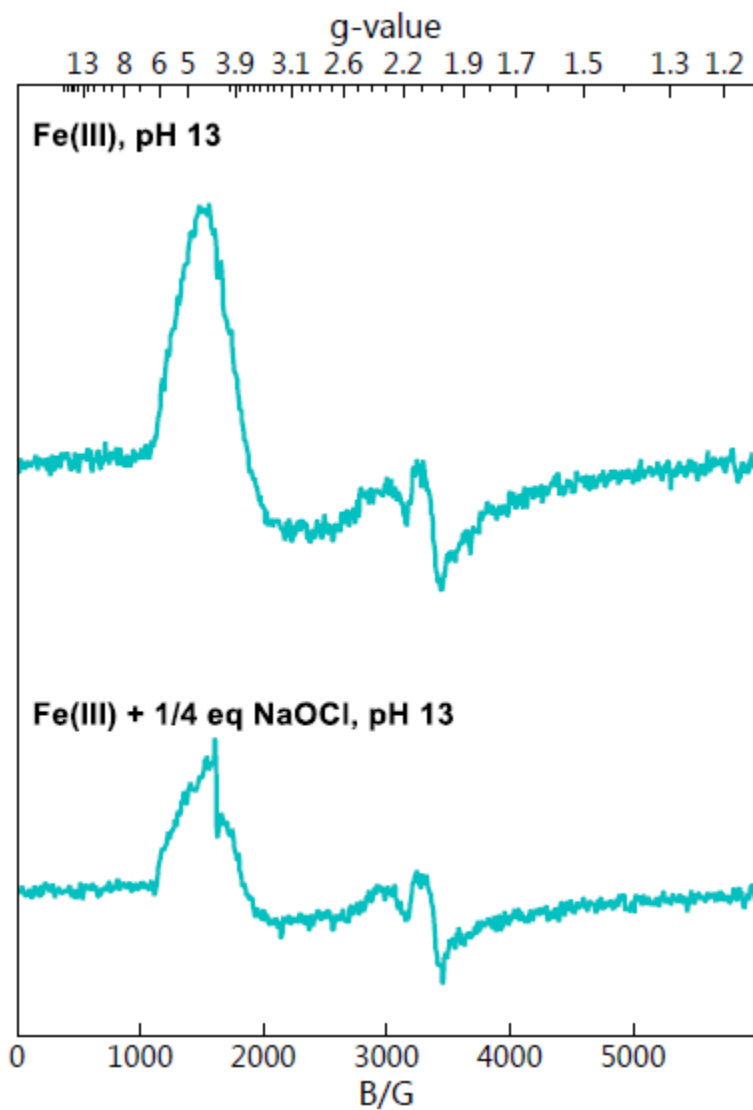


Figure S1. EPR spin quantification of the reaction of 0.25 eq NaClO with **3** (5×10^{-4} M) at pH 13. Upon completion of the reaction fifty percent of the iron(III) starting material remains, indicating that iron(V) comproportionates with iron(III) to form two iron(IV)oxo complexes.

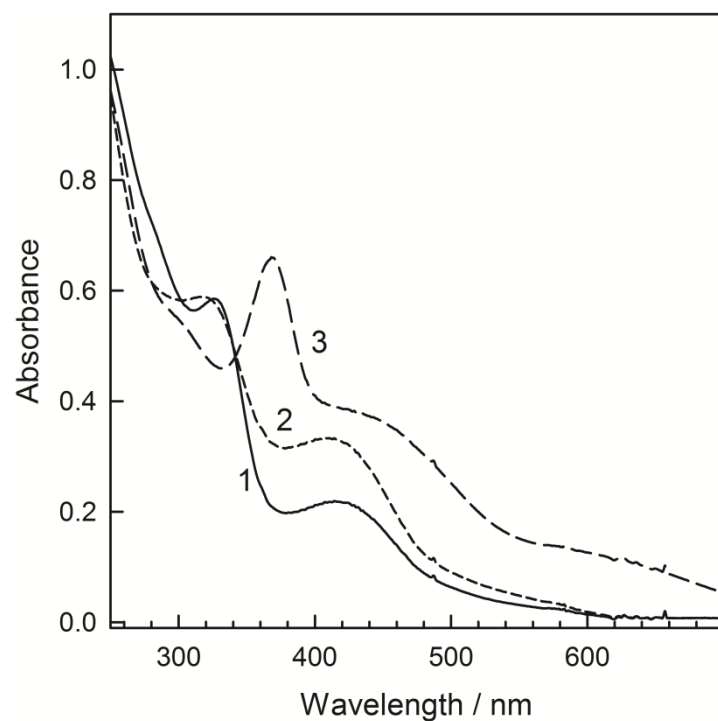


Figure S2. (1) Spectrum of **3** (1×10^{-4} M) at pH 13 and 13 °C. (2) Spectrum of the iron(IV)oxo product of oxidation of **3** with 0.5 equiv NaClO. (3) Spectrum generated by the addition of concentrated H₃PO₄ revealing disproportionation of iron(IV)oxo into iron(V)oxo and iron(III).

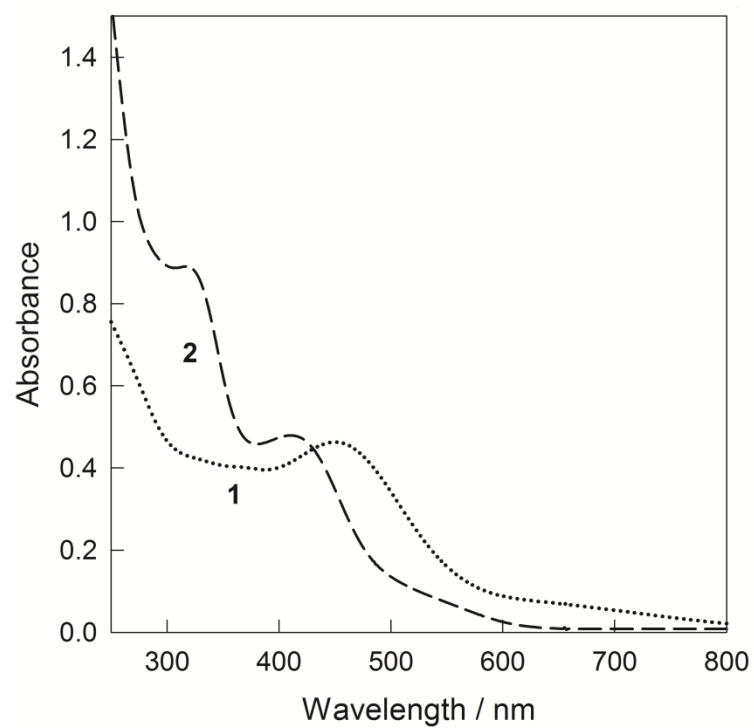


Figure S3. Base-induced conversion of iron(V)oxo into iron(IV)oxo: (1) spectrum of iron(V)oxo generated from **3** and one equivalent of NaClO at pH 10.6; (2) spectrum of obtained after addition of NaOH. Conditions: [**3**] = 1×10^{-4} M, 13 °C.

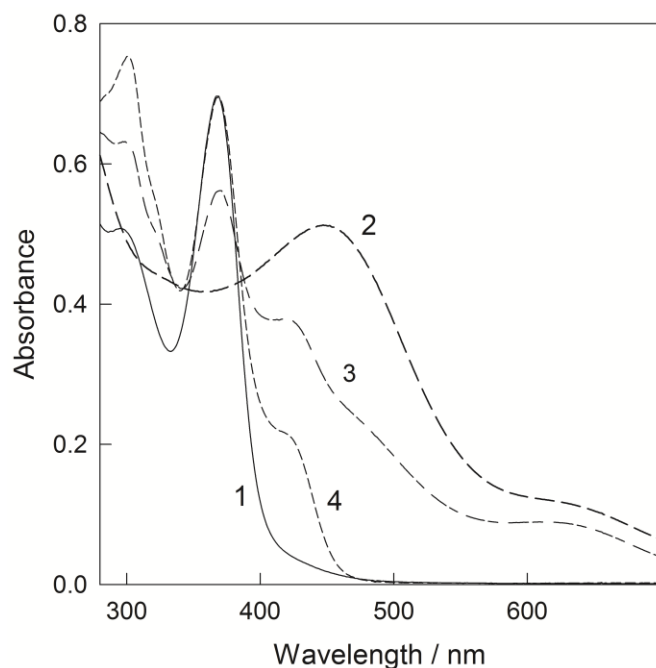


Figure S4. Evidence for unavailability of iron(IV)oxo at pH 10.6 and 13 °C: (1) spectrum of **3** (1×10^{-4} M); (2) spectrum of iron(V)oxo obtained after addition of 1 equiv NaClO; spectra (3) and (4) were recorded after consecutive addition of one equivalent of $\text{K}_4\text{Fe}(\text{CN})_6$, respectively. Note the identity of spectra 1 and 4 at 368 nm, which is the maximum of **3**. Divergence around 425 nm is due the generation of $[\text{Fe}(\text{CN})_6]^{3-}$, which has the maximal absorption at 420 nm.

References

- (1) DeNardo, M. A.; Mills, M. R.; Ryabov, A. D.; Collins, T. J. *J. Am. Chem. Soc.* **2016**, *138*, 2933-2936.
- (2) Hussain, A.; Trudell, P.; Repta, A. J. *J. Pharm. Sci.* **1970**, *59*, 1168-1170.
- (3) Petasis, D. T.; Hendrich, M. P. *Methods Enzymol.* **2015**, *563*, 171-208.