

Supporting Information

Mononuclear nonheme ferric-peroxo complex in aldehyde deformylation

Jamespandi Annaraj, Yumi Suh, Mi Sook Seo, Sun Ok Kim and Wonwoo Nam*

Department of Chemistry, Division of Nano Sciences, and Center for Biomimetic Systems,
Ewha Womans University, Seoul 120-750, Korea

Contact Information

Professor Wonwoo Nam

Department of Chemistry, Division of Nano Sciences, and Center for Biomimetic Systems
Ewha Womans University, Seoul 120-750, Korea

Tel: (+82) 2-3277-2392

Fax: (+82) 2-3277-4441

E-mail: wwnam@ewha.ac.kr

Experimental Conditions

Materials and Instrumentation. All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures [1] and distilled under Ar prior to use. H₂¹⁸O₂ (90% ¹⁸O-enriched, 2% H₂¹⁸O₂ in water), H₂¹⁸O (95% ¹⁸O-enriched), and ¹⁸O₂ (90% ¹⁸O-enriched) were purchased from ICON Services Inc. (Summit, NJ, USA). 2-Methyl-2-phenylpropionaldehyde was prepared by a literature method [2]. Iron(II) complexes such as Fe(TMC)(CF₃SO₃)₂, Fe(TPA)(ClO₄)₂, Fe(N4Py)(ClO₄)₂, and Fe(BPMEN)(ClO₄)₂ were synthesized in a glovebox by literature methods [3-6].

Caution: Perchlorate salts are potentially explosive and should be handled with great care.

UV-vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with a circulating water bath or with *Optostat*^{DN} variable-temperature liquid-nitrogen cryostat (Oxford Instruments). Electrospray ionization mass spectra (ESI MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20 μL/min using a syringe pump. The spray voltage was set at 4 kV and the capillary temperature at 70 °C. Product analysis for the deformylation of 2-phenylpropionaldehyde was performed with DIONEX Pump Series P580 equipped with a variable wavelength UV-200 detector (HPLC), Thermo Finnigan Surveyor Integrated HPLC Systems interfaced with Thermo Finnigan LCQTM Advantage MAX quadrupole ion trap instrument (LC-MS), Agilent Technologies 6890N gas chromatograph (GC), and a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with Hewlett-Packard model 5989B mass spectrometer (GC-MS).

Generation and Reactivity Studies of [(TMC)Fe^{III}-O₂]⁺ and [(N4Py)Fe^{III}-O₂]⁺.
The intermediates, [(TMC)Fe^{III}-O₂]⁺ and [(N4Py)Fe^{III}-O₂]⁺ were prepared by treating Fe(TMC)(CF₃SO₃)₂ (2 mM) at 0 °C and Fe(N4Py)(ClO₄)₂ (2 mM) at -30 °C, respectively,

with 10 equiv H₂O₂ in the presence of 5 equiv triethylamine in CF₃CH₂OH (2 mL). Then, appropriate amounts of 2-phenylpropionaldehyde (2-PPA) were added to the reaction solutions at the given temperatures. Product analysis was performed with HPLC, LS-MS, GC, and GC-MS, and products were identified by comparing retention times and mass patterns of the products to those of authentic samples. Product yields were determined by comparison against standard curves prepared with authentic samples. The yield of acetophenone was ~30% based on H₂O₂ used. All reactions were followed by monitoring UV-vis spectral changes of the reaction solutions, and rate constants were determined by fitting the changes in absorbance at 750 nm.

Isotope Labeling Studies. All reactions were followed by monitoring UV-vis spectral changes of the reaction solutions. [(TMC)Fe^{III}-¹⁸O₂]⁺ was prepared by adding 10 equiv H₂¹⁸O₂ (16 μL, 90% ¹⁸O-enriched, 2% H₂¹⁸O₂ in water) to a solution of Fe(TMC)(CF₃SO₃)₂ (2 mM) in CF₃CH₂OH (0.5 mL) at 0 °C under ¹⁶O₂ atmosphere. Then, 60 equiv 2-PPA (0.12 M, diluted in 20 μL CF₃CH₂OH) was added to the reaction solution. After 30 min stirring, product analysis was performed with LC-MS, and the ¹⁶O and ¹⁸O compositions in acetophenone product were analyzed by the relative abundances of *m/z* = 120 for acetophenone-¹⁶O and *m/z* = 122 for acetophenone-¹⁸O.

A control reaction for the oxygen exchange of acetophenone with H₂¹⁸O was performed by reacting acetophenone (5 mM) with H₂¹⁸O (16 μL) in CF₃CH₂OH (0.5 mL) at 0 °C. After 30 min stirring, the reaction mixture was directly analyzed by LS-MS. The ¹⁶O and ¹⁸O compositions in acetophenone were analyzed by the relative abundances of *m/z* = 120 for acetophenone-¹⁶O and *m/z* = 122 for acetophenone-¹⁸O.

Catalytic Aerobic Oxidation of 2-Phenylpropionaldehyde. Reactions were run at least in triplicate, and the data represent average of these reactions. A reaction solution containing Fe(TMC)(CF₃SO₃)₂ (2 mM), triethylamine (5 equiv, 10 mM), and 2-

phenylpropionaldehyde (100 equiv, 200 mM) in CF₃CH₂OH (2 mL) was exposed to O₂ atmosphere at 25 °C. After 2 h incubation under O₂ atmosphere, the reaction mixture was analyzed with HPLC, LC-MS, GC, and GC-MS. Product yields were determined by comparison against standard curves prepared with authentic samples.

References

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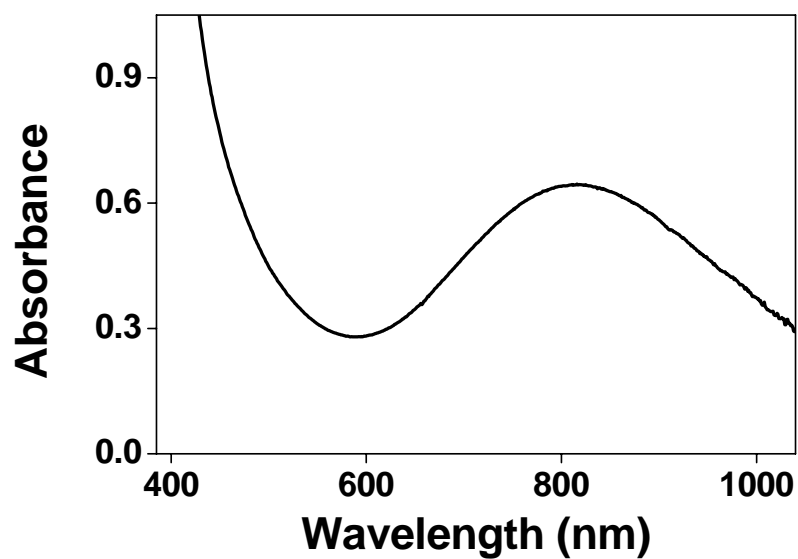


Figure S1. UV-vis spectrum of $[(\text{TMC})\text{Fe}^{\text{III}}-\text{O}_2]^+$ (**1**) formed in the reaction of $\text{Fe}(\text{TMC})(\text{CF}_3\text{SO}_3)_2$ (2 mM) and O_2 in the presence of 5 equiv of triethylamine (10 mM) in $(\text{CH}_3)_2\text{CHOH}$ (2 mL) at 25 °C. The maximum absorption wavelength of **1** in $(\text{CH}_3)_2\text{CHOH}$ is at 806 nm, and the difference from 750 nm in $\text{CF}_3\text{CH}_2\text{OH}$ is owing to the solvent effect.