Characterization and Alkane Oxidation Activity of a Diastereopure Seven-coordinate Iron(III) Alkylperoxo Complex

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Experimental.

Materials. Decane (5-6 M) and water (70%) solutions of *t*BuOOH were purchased from Aldrich and Acros, respectively, and the concentration was determined via iodometric titration.[1] Cyclohexane, 1,2-dimethylcyclohexane and ethylbenzene were distilled prior to use and adamantane was used without further purification. Complex **2**, [Fe(OTf)$_2$(**1**)], was synthesized according to a previously published procedure.[2] Solvents were dried and freshly distilled prior to use.

Physical methods. UV-Vis spectra were recorded on a Varian Cary 50 Varian spectrometer using a Helma immersion probe. Electrospray mass spectrometry was performed on an API3000 triple quadrupole mass spectrometer (MDS-Sciex, Concord, Canada), with special adjustments to allow direct electrospray from a cooled sample. The syringe pump (KD Scientific, Boston, USA) was cooled with a bag of crushed dry ice during the entire analysis, and the syringe was precooled with crushed dry ice before taking the solution of the intermediate. A syringe with a removable, beveled tipped needle (point style 2, Hamilton, Reno, USA) was used, and a potential of +3.5 kV from a PM5 power supply (Wallis, Worthing, UK) was applied directly to the needle. The syringe needle was placed perpendicular to the curtain plate at a distance of approximately 10 mm and about 5 mm off-axis, until a stable spray was observed at a sample flow rate of 10 μl/min. No ion source was used; the ion source sensor was overridden by a home-made switch-box that mimics the presence of a TurboIonSpray source. (Warning: high voltage is present on an exposed syringe needle; take proper safety precautions). Mass spectra were recorded in positive ion mode, with a declustering potential of 3.0 V, a focussing potential of 20.0 V, and an entrance potential of 4.0 V. Solution IR spectra were recorded with a Mettler Toledo ReactIR^{TM} 1000 spectrometer with a SiComp^{TM} probe which was fitted in a reaction vessel at –40 °C under N_2 atmosphere. Solvent spectra were subtracted as a background. EPR spectra were measured in frozen acetonitrile solution at 77K with a modified Bruker ESP 300 spectrometer equipped with an ER 4103 TM cavity (TM_{110} mode with unloaded Q = 10000). The microwave frequency was near 9.52 GHz and the spectrometer settings involved 4 Gauss field modulation. The Raman spectra were recorded with a Kaiser immersion optic probe for reaction monitor with a laser of 532 nm (60 mW) fitted in a reaction vessel at –40 °C under N_2 atmosphere.

Preparation of intermediate (4). For the generation of **4** a solution of [Fe(OTf)$_2$(**1**)] (**2**) in MeCN with known concentration (0.1 mM) was prepared and precooled to –40 °C followed by the addition of oxidant (3 eq unless stated otherwise), prepared as a stock solution in MeCN. Reaction of **2** with oxidants for the UV-Vis, Raman, IR and EPR measurements were carried out using standard Schlenk techniques.

Catalytic procedure. All experiments were carried out under ambient conditions, unless noted otherwise. To a solution of **2** (3.5 μmol) dissolved in acetonitrile (2.8 mL) was added alkane (1.75 mmol, 500 eq) followed by slow, dropwise addition of 0.5 mL of 70 mM *t*BuOOH solution in acetonitrile (diluted from 5-6 M decane solution or 70% H_2O solution, 35 μmol, 10 eq) over 30 min. The reaction mixture was stirred at ambient temperature for another 30 min, followed by addition of a known amount of internal standard (PhBr). To an aliquot (1 mL) taken from the reaction mixture was added Et_2O and it was analyzed by GC. Products were identified by comparison of the retention times with those of authentic compounds in GC and of GC/MS spectra.

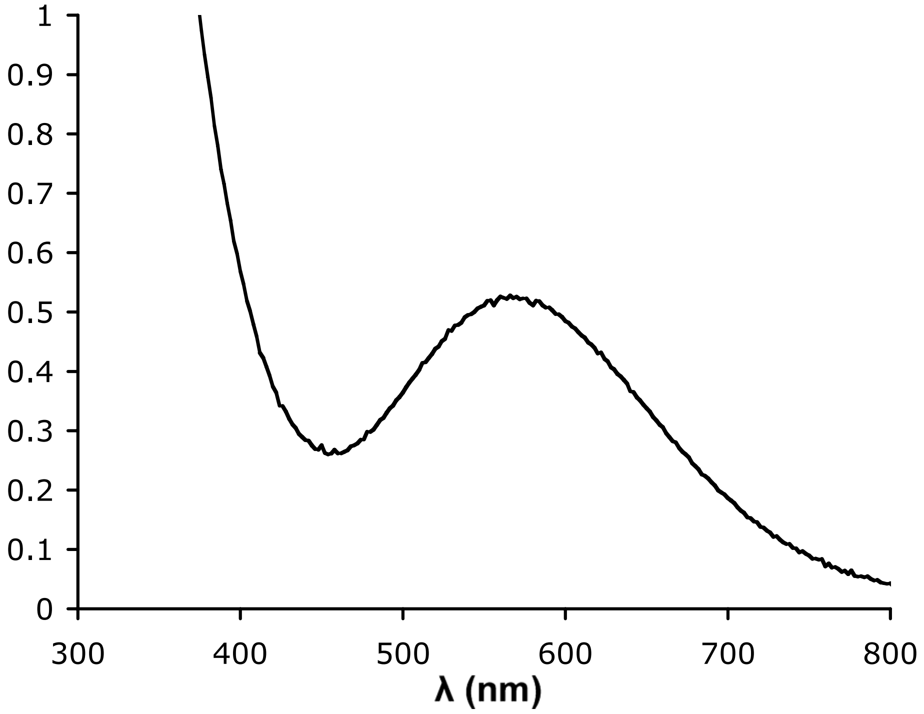

Fig. S1. UV-Vis spectra of intermediate **4** generated with 3 equivalents of TBHP/water.

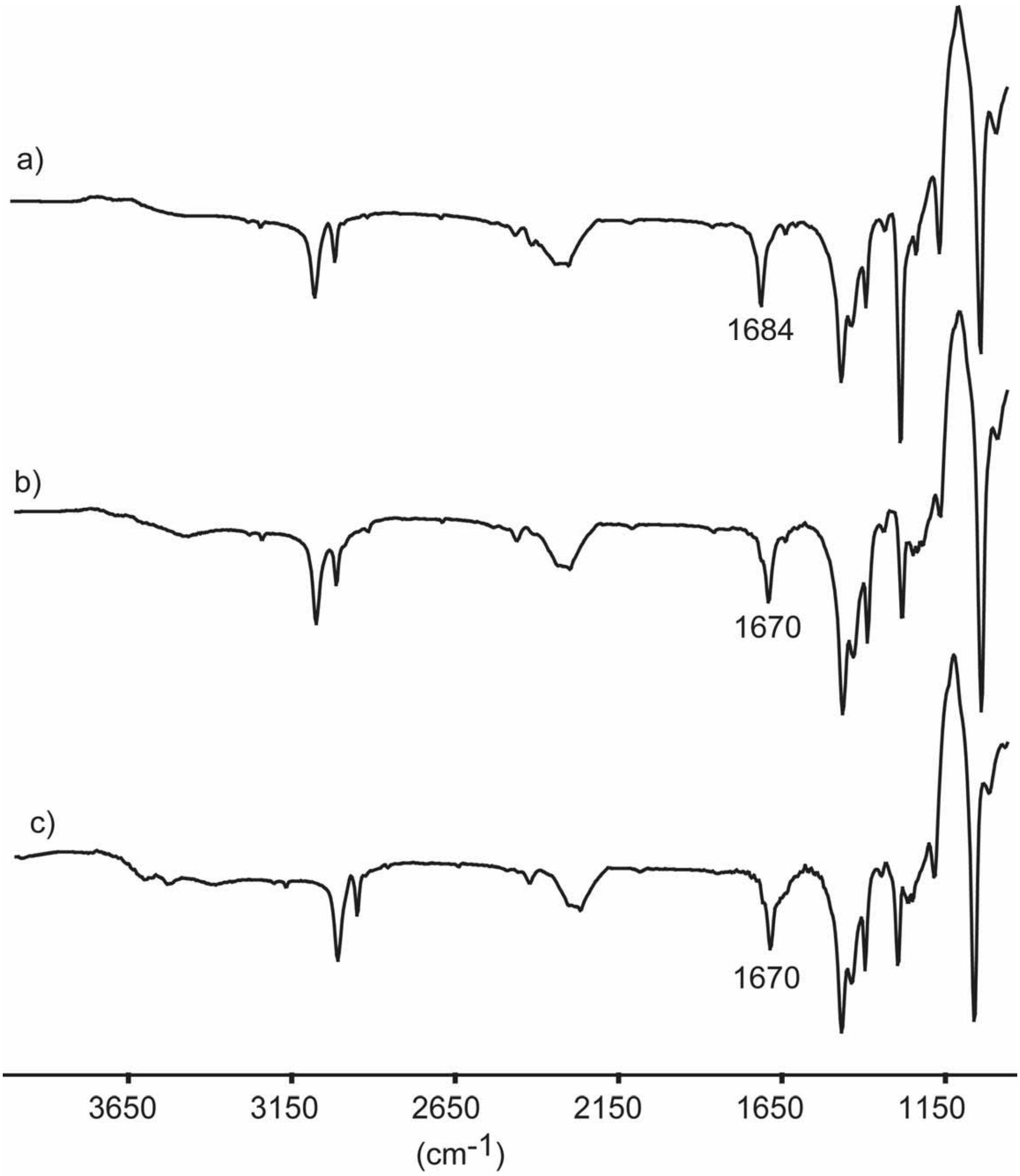

Fig. S2. Solution IR spectra of a) complex **3**, b) intermediate **4** generated with 3 equivalents of TBHP/decane and c) intermediate **4** generated with 3 equivalents of TBHP/water.

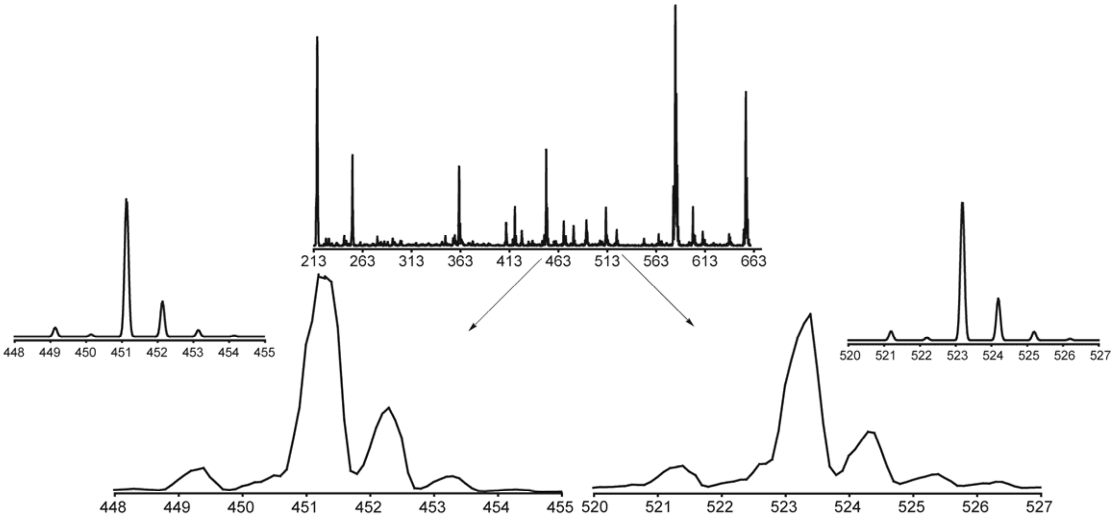

Fig. S3. The ESI-MS spectrum of **4** generated from 3 eq. of TBHP/decane, with ions at m/z = 451 and 523 and their calculated isotope patterns corresponding to $\{[Fe^{III}(OH)_2(\mathbf{1})]\}^+$ and $\{[Fe^{III}(OOtBu)(OH)(\mathbf{1})]\}^+$ ions.

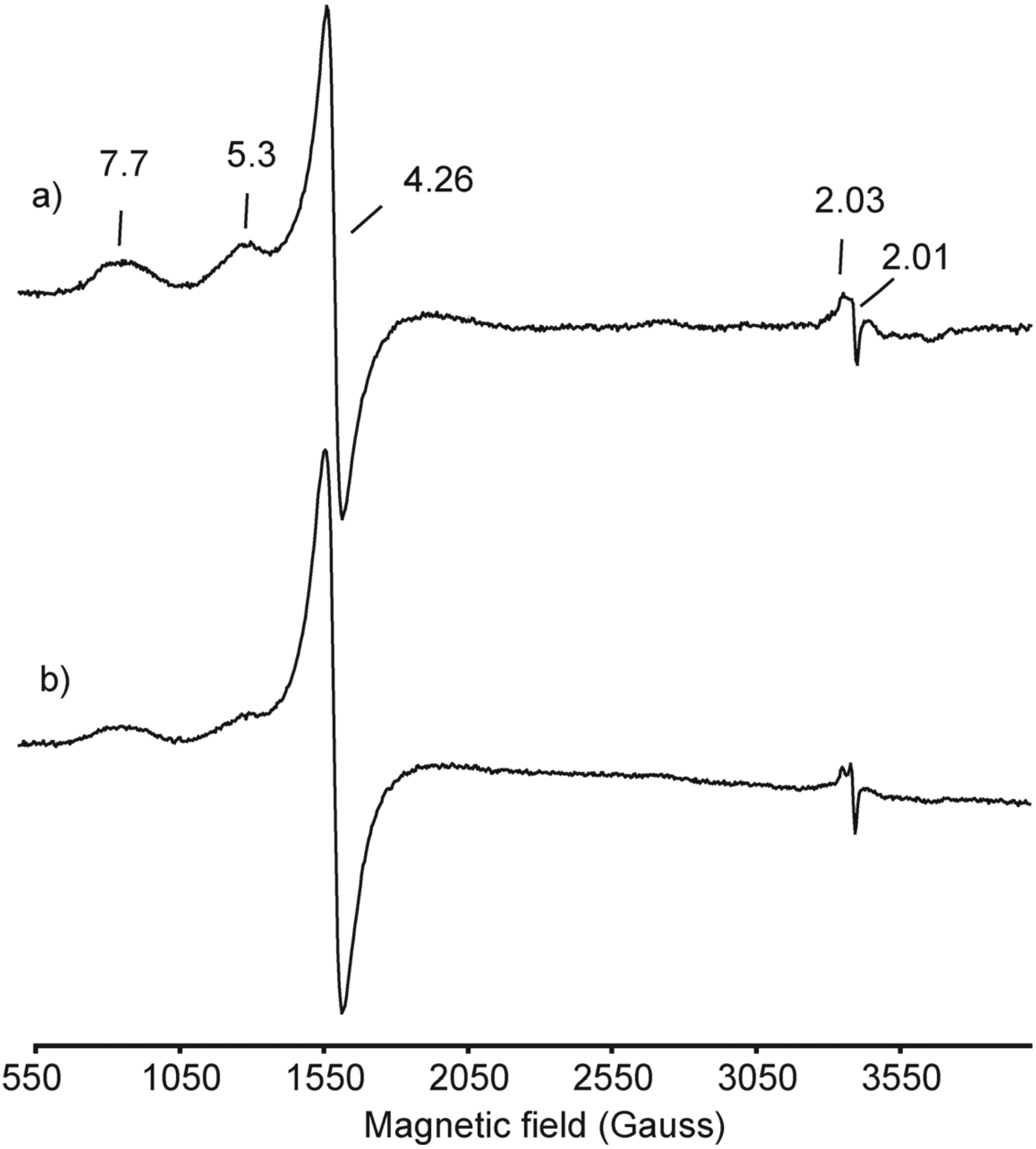

Fig. S4. EPR spectra of **4** generated with a) 3equivalents of TBHP/decane solution and b) 3 equivalents of TBHP/water solution.

Table S5 Oxidation of alkanes catalyzed by [Fe(**1**)(OTf)$_2$] (**2**) with TBHP/decane[a]

Entry	Substrate	Product	TON[b]	Conversion of oxidant	Remarks
1	cyclohexane	cyclohexanol	0.26	6.7%	in acetone
		cyclohexanone	0.41		A/K 0.63
2[c]	cyclohexane	cyclohexanol	1.21	31.2%	CCl$_4$ (c =15 mM)
		cyclohexanone	1.91		A/K 0.63
3	cyclohexane	cyclohexanol	0.4	10.2%	BHT[d] (c =15 mM)
		cyclohexanone	0.52		A/K 0.8
4[e]	cyclohexane	cyclohexanol	1.5	40%	A/K 0.6
		cyclohexanone	2.5		
5	adamantane	adamant-1-ol[f]	2.5	25%	in acetone
6[g]	adamantane	adamant-1-ol[f]	1.1	11%	CCl$_4$ (c = 15 mM)
7	adamantane	adamant-1-ol[f]	1.34	13%	BHT[d] (c = 15 mM)

[a] For conditions see Table 1. [b] Moles of product/moles of catalyst. [c] No cyclohexylchloride or cyclohexyl *tert*-butylperoxide observed. [d] BHT = 2,6-di-*tert*-butyl-4-methylphenol. [e] The reaction performed with 70 mM acetonitrile solution of *t*BuOOH (70% water solution). [f] The adamant-2-ol and adamant-2-one products were not observed (n.o.) in the GC spectra. [g] A small amount of 1-chloro-adamantane detected in GC-MS.

References.

1. (a) J. G. Hanna, *Quantitative Organic Analysis via Functional groups*, 4th Ed., Wiley, 1976, p. 328; (b) I. M. Kolthof, R. Beleher, G. Matsuyama, V. A. Stenger, *Volumetric Analysis*, Volume III: Titration Methods, New York, Interscience Publishers, 1957, p. 399.

2. S. Gosiewska, J. L. M. Cornelissen, M. Lutz, A. L. Spek, G. van Koten, R. J. M. Klein Gebbink, *Inorg. Chem.*, 2006, **45**, 4214.