Oxoiron(V) Mediated Selective Electrochemical Oxygenation of Unactivated C-H and C=C Bonds using Water as Oxygen Source

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Experimental Details

General procedure.

All reagents were obtained commercially and used without further purification unless otherwise noted. [Et₄N]₂[(bTAML)Fe-Cl] (**1a**), [Ph₄P][(bTAML)Fe-OH₂] (**1b**) (bTAML = biuret-modified tetraamidomacrocyclic ligand) were synthesized by our previously reported method.¹ All the solvents used were purchased and used after distillation over drying agents.² Glassy Carbon, Pt, Ag/AgNO₃ (Non-aqueous), and Ag/AgCl (Sat. KCl) electrodes were purchased from CH Instruments. All the cyclic voltammetry studies were carried out in CHI-660 potentiostat. All the catalytic reactions were performed in an IKA ElectraSyn 2.0 instrument brought from IKA. The electrasyn setup consisting of a simple undivided cell (5 ml/ 10 ml), reticulated vitreous carbon (RVC foam) (0.5 cm x 0.5 cm x 3.5 cm) as working electrode, nickel (Ni foam) (0.8 cm x 0.1 cm x 5 cm) as counter electrode and Ag/AgCl (3 M) or Ag/AgNO₃ (10 mM AgNO₃) as the reference electrode. UV–vis spectral studies were carried out using an Agilent diode array cary-8454 spectrophotometer with an attached electrically controlled thermostat. GC-MS was performed on a Thermo Scientific ISQ QD Mass Spectrometer attached with Thermo Scientific TRACE 1300 gas chromatograph using an HP-5 ms capillary column (30 m × 0.25 mm × 0.25 µm, J&W Scientific) with helium as the carrier gas.

Electrochemical Measurements.

Cyclic voltammetry and differential pulse voltammetry experiment were carried out in CHI-660 potentiostat instrument. Solutions of **1a/1b** were placed in simple undivided three electrode cells. Glassy Carbon (GC) (3 mm of diameter) was used as working electrode, Silver/Silver nitrate (10 mM) as reference electrode (unless explicitly mentioned) and Pt wire as counter electrode. Before each measurement, working electrode was polished with 0.05 μ m alumina paste and rinsing with water/acetone and finally blow-drying. All redox potentials in the present work are reported versus Ag/AgNO₃ (10 mM). DPVs were obtained with the following parameters: amplitude = 50 mV, step height = 4 mV, pulse width = 0.05 s, pulse period = 0.5 s and sampling width = 0.0167 s. All the CVs were collected under IR compensation mode. A mixture of acetonitrile (90%) and water (10%) was used as solvent where tetrabutylammonium hexafluorophosphate (NBu₄PF₆) (0.1 M) acting as a supporting electrolyte.

Constant Potential Electrolysis for catalytic reactions (in IKA ElectraSyn Instrument)

The constant potential electrolysis experiment were performed in an IKA ElectraSyn 2.0 instrument which consisting of a three electrode undivided electrochemical cell with a RVC working electrode (0.5 cm x 0.5 cm x 3.5 cm), a Ni foam (0.8 cm x 0.1 cm x 5 cm) counter electrode and a $Ag/AgNO_3$ (10 mM $AgNO_3$ in acetonitrile) or Ag/AgCl (3 M KCl) reference electrode. The potential was set at 0.80 V vs $Ag/AgNO_3$ (10 mM) throughout the reaction.

Reaction Conditions:

- **Catalyst:** Fe^{III}-bTAML (**1a/1b**) (0.75 mM)
- Substrate: Alkanes/Alkenes (15 mM)
- **Solvent:** CH₃CN + Phosphate buffer

(4:1 v/v, 5 mM, pH 8)

- **Electrolyte:** $TBAPF_6$ (0.1 M)
- 3-eletrode simple undivided cell
- WE: RVC Foam
- **CE:** Nickel Foam
- **RE:** $Ag/AgNO_3$ (10 mM) or, Ag/AgCl (3 M KCl)
- **Time:** 4-10h
- Open Flask, room temperature

Product identification and quantification (in GC-MS)

All the products formed by electrochemical alkane and alkene oxidation reactions were analyzed by gas chromatography–mass spectrometry (GC-MS). After each electrolysis, 50 μ l of electrolyte solution was taken out from the electrochemical cell and diluted it with 950 μ l of acetonitrile. The 20-fold diluted solution was analyzed by GC-MS. An internal standard (bromobenzene) was used for all the reactions. The yield and conversion were estimated using the response factor of authentic substrates and products.



Crystal structure of 1b synthesized from 1a



Figure S1: Crystal structure of **1b** (with Ph_4P counter cation) with axially H_2O ligand obtained from CH_3CN-H_2O solution of **1a** (with Et_4N/Li counter cation) with axially chloro ligand and Ph_4PCl salt.³

Spectroelectrochemical generation of oxoiron(V) and μ -O-Fe₂^{IV} (dimer) species

For spectroelectrochemical studies, a three electrodes electrochemical cell was used consisting of a high surface area Pt mesh cylinder electrode as the working electrode, a Pt wire as a counter electrode, and an Ag/AgNO₃ (10 mM AgNO₃) nonaqueous electrode as a reference electrode. For the spectroelectrochemical study, controlled potential electrolysis experiments of **1a/1b** were performed in (9:1) CH₃CN-H₂O solvent mixtures having 0.1 M Bu₄NPF₆ electrolyte at 0.80 V vs Ag/AgNO₃ (10 mM). A small volume of electrolyte solution (300μ L) was removed each time for simultaneous UV-vis spectroscopy experiments using Agilent diode array Cary 8454 spectrophotometer. Alternatively, a home-made set up consisting of a Pt mesh (6.5 mm x 10 mm x 0.55 mm) as working, a Pt wire as counter and Ag/AgNO₃ reference electrode in a 3 mL cuvette used as electrochemical cell was used. The cell was placed in the spectrophotometer chamber in manner so that light passed through the cell of 1 cm path length.



Figure S2: UV-VIS spectral changes of **1a/1b** during spectroelectrochemical formation of oxoiron(V) from **1a/1b** (60 μ M) in (9:1) CH₃CN-H₂O using a Pt mesh working and Pt wire as counter electrode during CPE at 0.80 V vs Ag/AgNO₃. Orange spectra is for **1b** and green is for oxoiron(V) species (**3**).

Note: UV-Vis and HRMS spectra for the spectroelectrochemical formation of oxoiron(V) from 1a/1b (5 μ M) in (9:1) CH₃CN-H₂O has been recently shown by our group.³



Figure S3: UV-VIS spectral changes of **1a/1b** during spectroelectrochemical formation of μ -oxodiiron(IV) species, [{(bTAML)Fe^{IV}}₂O] (Dimer) (at a catalyst, **1a/1b** concentration > 0.2 mM) in (9:1) CH₃CN-H₂O. [Due to the comproportionation reaction of Fe^V(O) with Fe^{III} (**1a/1b**)]

The similar formation of μ -oxodiiron(IV) species (Dimer) observed during the catalytic reaction of **1a/1b** (0.75 mM) with adamantane (15 mM) in (4:1) CH₃CN-Phosphate buffer (5 mM, pH ~8) using ElectraSyn instrument having RVC as working and Ni foam as counter electrode during CPE at 0.80 V vs Ag/AgNO₃.

UV-Vis was performed in a diluted solution of reaction mixture taken out from the electrochemical cell time to time.

Determination of Diffusion Coefficient:

The relationship between current and scan rate for a diffusion-based redox event has been described by the Randles-Sevcik equation

$$i_p = 0.446 n_p FA[Fe] \sqrt{\frac{n_p FvD}{RT}}$$

Or,
$$i_p = 18810.5$$
 [Fe]D^{1/2} v^{1/2}

Where, n is the number of electrons transferred, v the scan rate (V/s), [Fe] is the concentration of catalyst (mol cm⁻³), *F*, *R*, and *T* are Faraday's constant (C mol⁻¹), the ideal gas constant (J K⁻¹ mol⁻¹), and temperature (K) respectively.

For Complex 1a:

Using the slope of the best fit line of i_{pa} and i_{pc} versus $v^{1/2}$ affords diffusion coefficients 6.0×10^{-6} cm² s⁻¹ and 9.3×10^{-6} cm² s⁻¹ for the oxidized and reduced form of Fe^{IV}/Fe^{III} couple, respectively (Figure S1). Similarly, diffusion coefficients of 1.46×10^{-5} cm² s⁻¹ and 4.8×10^{-6} cm² s⁻¹ have been derived for the oxidized and reduced form of Fe^V/Fe^{IV} couple.





Figure S4: (A) Cyclic voltammograms of **1a** in CH₃CN with variation of scan rates (0.01 - 2 Vs⁻¹). (B) Plot of anodic peak current ($i_{p,a}$) vs square root of scan rates (v^{0.5}) for Fe^{IV}/Fe^{III} anodic peak. (C) Plot of anodic peak current ($i_{p,a}$) vs square root of scan rates (v^{0.5}) for Fe^V/Fe^{IV} anodic peak. (D) Plot of cathodic peak current ($i_{p,c}$) vs

peak. (**D**) Plot of cathodic peak current $(i_{p,c})$ vs square root of scan rates $(v^{0.5})$ for Fe^{IV}/Fe^{III} cathodic peak. (E) Plot of cathodic peak current $(i_{p,c})$ vs square root of scan rates $(v^{0.5})$ for Fe^V/Fe^{IV} cathodic peak.

For Complex 1b:

Using the slope of the best fit line of i_{pa} and i_{pc} versus $v^{1/2}$ affords diffusion coefficients 6.66×10^{-6} cm² s⁻¹ and 4.6×10^{-6} cm² s⁻¹ for the oxidized and reduced form of Fe^{IV}/Fe^{III} couple respectively. Similarly, diffusion coefficients of 6.37×10^{-6} cm² s⁻¹ and 4.8×10^{-6} cm² s⁻¹ have been derived for the oxidized and reduced form of Fe^V/Fe^{IV} couple.



Note: A slight change in CV shape was observed in the second redox process in CH₃CN-H₂O (9:1) could be the result of axial ligation of water molecule to the oxoiron(V) formed. Since chemically synthesized oxoiron(V) undergoes ¹⁶O to ¹⁸O scrambling upon addition of H₂O¹⁸, such change in coordination environment after formation of oxoiron(V) is possible.



Figure S5: (A) Cyclic voltammograms of **1b** in CH₃CN-H₂O(5%) with variation of scan rates $(0.01-2 \text{ Vs}^{-1})$. (B) Plot of anodic peak current $(i_{p,a})$ vs square root of scan rates $(v^{0.5})$ for Fe^{IV}/Fe^{III} anodic peak. (C) Plot of anodic peak current $(i_{p,a})$ vs square root of scan rates $(v^{0.5})$ for Fe^V/Fe^{IV} anodic peak. (D) Plot of cathodic peak current $(i_{p,c})$ vs square root of scan rates $(v^{0.5})$ for Fe^V/Fe^{IV} anodic peak. (E) Plot of cathodic peak current $(i_{p,c})$ vs square root of scan rates $(v^{0.5})$ for Fe^V/Fe^{IV} cathodic peak. (E) Plot of cathodic peak current $(i_{p,c})$ vs square root of scan rates $(v^{0.5})$ for Fe^V/Fe^{IV} cathodic peak.



Figure S6: (A) Cyclic voltammograms of **1b** (0.2 mM) and adamantane (30 mM) in (9:1) CH₃CN-H₂O with variation of scan rates (0.01-1 Vs⁻¹). (B) Plot of anodic peak current ($i_{p,a}$) vs square root of scan rates (v^{0.5}) for Fe^{IV}/Fe^{III} anodic peak. No linearity is observed.



Figure S7: Differential pulse voltammograms (DPV) of complex **1a** (0.3 mM) in CH₃CN (Black) and (9:1) CH₃CN-H₂O (Red).



Figure S8: (A) Cyclic voltammogram of complex **1b** (0.3 mM) in (9:1) CH₃CN-H₂O, scan rate = 300 mVs^{-1} .

(**B**) Cyclic voltammogram of complex **1b** (0.3 mM) in (4:1) CH₃CN-Phosphate buffer (5 mM, pH 8), scan rate = 50 mVs^{-1} .

1 and 3 peaks indicate the $\text{Fe}^{\text{IV/III}}$ and $\text{Fe}^{\text{V/IV}}$ couples respectively whereas 2 peak indicates phosphate ligated Fe-bTAML. The binding of phosphate to Fe-TAML system observable in CV experiments has been reported recently by Stahl *et al.*⁴



Figure S9: (A) Cyclic voltammograms and differential pulse voltammograms of **1b** (0.3 mM) in (4:1) CH₃CN/phosphate buffer (5 mM) with variation of pH (6 to 9) at GC (0.07 cm²) working electrode at a scan rate of 50 mVs⁻¹ at RT.

(**B**) Differential pulse voltammograms of **1b** (0.3 mM) in (4:1) CH₃CN/phosphate buffer (5 mM) with variation of pH (6 to 9).

1 and 3 indicate the $\text{Fe}^{\text{IV/III}}$ and $\text{Fe}^{\text{V/IV}}$ couples respectively whereas 2 indicate phosphate ligated Fe-bTAML. The $\text{Fe}^{\text{IV/III}}$ couple (peak 1) only changes with variation of pH whereas $\text{Fe}^{\text{V/IV}}$ (peak 3) and peak 2 is unchanged with pH variation.



Figure S10: (A) Cyclic voltammograms of **1b** (0.3 mM) with styrene in (4:1) CH₃CN/phosphate buffer (5 mM, pH 8) at GC (0.07 cm²) working electrode at a scan rate of 50 mVs⁻¹ at RT. (B) Cyclic voltammograms of **1b** (0.3 mM) with adamantane in (4:1) CH₃CN/phosphate buffer (5 mM, pH 8) at GC (0.07 cm²) working electrode at a scan rate of 50 mVs⁻¹ at RT.



Figure S11: Cyclic voltammogram responses of **1b** (0.2 mM) (**A**) and **1b** (0.08 mM) (**B**) with different concentration of adamantane (0 - 30 mM) in (9:1) CH₃CN-H₂O (0.1 M TBAPF₆) at GC (0.07 cm²) at a scan rate of 0.05 Vs⁻¹ at RT.

(C) Plot of background corrected i_{cat} vs [Adamantane]^{0.5}, k₂ value was calculated from the slope of the best fit line, where, $n_{cat} = 2$, F = 96485 Cmol⁻¹, D = 6.37×10^{-6} cm² s⁻¹, [Fe] = 8×10^{-8} mol/cm³

$$i_{cat} = n_{cat} FA[Fe] \sqrt{Dk_{cat}} = n_{cat} FA[Fe] \sqrt{Dk_2[Adamantane]}$$



Figure S12: Cyclic voltammogram responses of **1b** (0.2 mM) with adamantane (10 mM) and adamantane- d_{12} (10 mM) in (9:1) CH₃CN-H₂O (0.1 M TBAPF₆) at GC (0.07 cm²) at a scan rate of 0.05 Vs⁻¹ at RT. This clearly shows that the higher catalytic current in presence of adamantane than adamantane- d_{16} .

The kinetic isotope effect (KIE) of 4 was obtained from k_2 values of adamantane and adamantane- d_{16} , which was calculated from the background corrected i_{cat} using the following equation

$$i_{cat} = n_{cat}FA[Fe]\sqrt{Dk_{cat}} = n_{cat}FA[Fe]\sqrt{Dk_2[Adamantane]}$$



Figure S13: Cyclic voltammogram responses of **1b** (0.05 mM) with xanthene (7.2 mM) in (9:1) CH₃CN-H₂O (0.1 M Bu₄NPF₆) at GC (0.07 cm²) at varied scan rate of 50 - 100 mVs⁻¹ at RT.

<u>Reaction order with respect to substrate (Xanthene):</u>

$$i_{cat} = n_{cat}FA[Fe]\sqrt{Dk_{cat}} = n_{cat}FA[Fe]\sqrt{Dk_2[xanthene]}$$



Figure S14: Cyclic voltammogram responses of **1b** (0.05 mM) with varied xanthene concentration in (9:1) CH₃CN-H₂O (0.1 M Bu₄NPF₆) at GC (0.07 cm²) at a scan rate of 0.1 Vs⁻¹ at RT. A plot of i_{cat} vs [xanthene]^{0.5} with current measurement at 0.95 V (Inset).

Reaction order with respect to catalyst (Fe-bTAML):

With variation of concentration of catalyst, catalytic current (i_{cat}) varies linearly. This shows the first order dependence w.r.t catalyst, [Fe-bTAML]



Figure S15: Cyclic voltammogram responses of with varying catalyst (Fe-bTAML) concentration in (9:1) CH₃CN-H₂O (0.1 M Bu₄NPF₆) (left). A plot of i_{cat} vs [Fe-bTAML] (right).

The rate of xanthene oxidation can be expressed as rate = $k_2 \times [Fe-bTAML] \times [Xanthene]$. Similar second-order rate equation has been found for the electrochemical oxidation of adamantane.

Determination of rate constant for xanthene oxidation:



Figure S16: Cyclic voltammogram responses of with varying scan rate (0.1 to 1 Vs⁻¹) in (9:1) CH₃CN-H₂O (0.1 M Bu₄NPF₆) (left). A plot of i_{cat}/i_p vs v^{-1/2} (right).

$$i_{cat} = n_{cat} FA[Fe] \sqrt{Dk_{cat}} = n_{cat} FA[Fe] \sqrt{Dk_2[substrate]} \qquad (1)$$

$$i_p = 0.446n_p FA[Fe] \sqrt{\frac{n_p FvD}{RT}} \qquad (2)$$

$$\frac{i_{cat}}{i_p} = \frac{n_{cat} FA[Fe] \sqrt{Dk_{cat}}}{0.446n_p FA[Fe] \sqrt{\frac{n_p FvD}{RT}}} = \frac{n_{cat}}{0.446n_p} \sqrt{\frac{RT}{n_p Fv} k_2[xanthene]} \qquad (3)$$

Slope of
$$i_{cat}/i_p$$
 vs v^{-1/2} plot = 0.97
 $k_{cat} = 1.82 \pm 0.4 \text{ s}^{-1}$
As, $k_{cat} = k_2$ [xanthene]; where, [xanthene] = 10 mM
Therefore, $k_2 = 182 \pm 40 \text{ M}^{-1} \text{ s}^{-1}$

Table S1: Optimization Table:



'-' denotes no conv. / no yield found after the reaction.

Table S2: Calculation of faradaic efficiency:

Charge (after 12 h) = 4 F/mol

Adamantane substrate = 0.06 mmol

Total charge (Q) passed for 0.06 mmol adamantane = $4 \times 0.06 \times 10^{-3} \times 96485 \text{ C} = 27.20 \text{ C}$

Hence, number of moles of product (n) = Q/zF = 27.02/ 2*96485 = 0.00012 mol = 0.12 mmol (According to electrochemistry)

Where, the number of electron transferred during the reaction, z = 2 and F = 96485 C/mol

Whereas, number of moles of product from reaction (bulk electrolysis) = $0.84 \times 0.06 \text{ mmol} = 0.0504 \text{ mmol}$

(According to 84% yield after 10 h of adamantane oxidation)

Faradaic efficiency = 0.0504 (*100)/0.12 = 42%



GC-MS traces of the electrochemical oxygenation reactions for alkane and alkene substrates:

Figure S17: GC-MS traces for electrochemical oxidation of adamantane.







Figure S19: GC-MS traces for electrochemical oxidation of *trans*-1,2-dimethylcyclohexane.



Figure S20: GC-MS traces for electrochemical oxidation of *cis*-decalin.



Figure S21: GC-MS traces for electrochemical oxidation of cedryl acetate.



Figure S22: GC-MS traces for electrochemical oxidation of ambroxide.



Figure S23: GC-MS traces for electrochemical oxidation of ethylbenzene.



Figure S24: GC-MS traces for electrochemical oxidation of diphenylmethane.



Figure S25: GC-MS traces for electrochemical oxidation of styrene.



Figure S26: GC-MS traces for electrochemical oxidation of 4-chloro styrene.



Figure S27: GC-MS traces for electrochemical oxidation of 4-methoxy styrene.



Figure S28: GC-MS traces for electrochemical oxidation of *cis*-stilbene.



Figure S29: GC-MS traces for electrochemical oxidation of *cis*-cyclooctene.

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