Selective electrocatalysis of alkenes in aqueous media. A comparison of reactivities for oxoferryl porphyrin and oxoferryl porphyrin radical cation at room temperature

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A stable high-valent oxoferryl porphyrin radical cation is electrochemically generated in aqueous media at room temperature which rapidly catalyses the oxidation of alkenes to give eneones and diols; by contrast the oxoferryl porphyrin only slowly catalyses oxidation and gives only the eneone.

Metalloporphyrins have been used as catalysts and can be regarded to mimic cytochrome P-450 in oxygen-transfer reactions.[1,2] Formation of a high-valent oxo–metal complex is essential for such catalytic reactions. Iron(III) porphyrins react with alkyl hydroperoxides to form oxoiron(IV) porphyrins[3] and oxoiron(IV) porphyrin radical cations are generated by reaction with peracids[4] and iodosylbenzene.[5]

It is believed that the additional positive or negative charge of porphyrins is mainly localized at the *meso*-carbons, which are thus susceptible to chemical reaction. Oxidation of zinc tetrakis(sulfonatophenyl)porphyrin $[Zn(tspp)]^{4-}$ readily leads to zinc isoporphyrins in the presence of nucleophiles prior to decomposition.[6,7] When electrocatalytic oxidation of alkenes proceeds in aqueous solution, water is a good source of oxygen atoms[8] but hydroxide acts as a nucleophile. Use of sterically hindered porphyrins is known to provide better protection for the *meso*-carbons in redox reactions.[9]

We synthesized water-soluble tetrakis(sulfonatomesityl)porphyrin ($[H_2tsmp]^{4-}$) and found that the *ortho*-methyl groups in the porphyrin provide very good steric protection towards the *meso*-carbons against nucleophilic attack. Spectroelectrochemistry of $[Zn(tsmp)]^{4-}$ clearly shows the stability of the porphine radical cation. We judiciously chose various potentials to generate different oxidized forms of [Fe(tsmp)], which exhibit different activities for catalysis, by adjusting the pH of the solution.

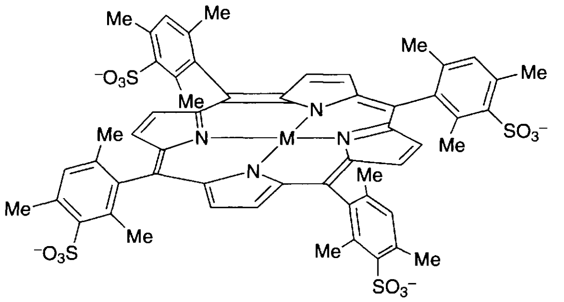


Fig. 1 shows the cyclic voltammograms of $[Zn(tsmp)]^{4-}$ in an aqueous medium. It was found that the CV exhibits two reversible oxidation reactions even at scan rates as low as 1 mV s^{-1}. For $[Zn(tspp)]^{4-}$, significant irreversibility, due to the formation of isoporphyrin from the reaction of oxidized $[Zn(tspp)]^{4-}$ with H_2O,[6] was observed. The stability of the oxidized [Zn(tsmp)] was confirmed by spectroelectrochemistry (Fig. 1) from which stable $[Zn(tsmp^{+\cdot})]^{3-}$–$[Zn(tsmp)]^{4-}$ equilibria can be obtained at various potentials. The redox reaction involves a one-electron transfer and the formal potential is at +0.63 V.[10] To our knowledge, this is the first reported stable porphyrin radical cation in aqueous solution at room temperature. The protection of *meso*-positions by the *ortho*-methyl groups on the phenyl rings is thus shown to be effective.

Tetrakis(sulfonatomesityl)porphyrinate]iron(III) $[Fe^{III}(tsmp)(H_2O)]^{3-}$ with pK_a for bound H_2O of 6.6, exclusively forms monomers even under basic conditions.[12,13]

In pH 2.0 buffer solution $[Fe^{III}(tsmp)(H_2O)]^{3-}$ undergoes a one-electron oxidation to generate $[Fe^{III}(tsmp^{+\cdot})(H_2O)]^{2-}$ at a formal potential $E^{\circ\prime}$ of +0.930 V. The wavelength of the Soret band shifts from 394 to 388 nm. A typical radical cation mode of broad absorption in the Q band region is observed (Fig. 2). However, the oxidized iron porphyrin does not exhibit activity for alkene oxidation.

In a pH 8.0 buffer solution $[Fe^{III}(tsmp)(OH)]^{4-}$ is initially oxidized to $[Fe^{IV}(O)(tsmp)]^{4-}$ at a formal potential of +0.720 V

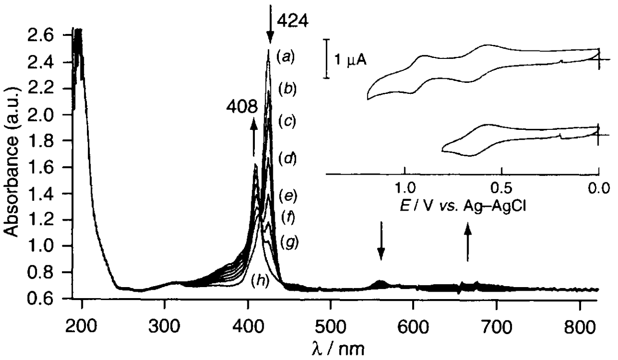


Fig. 1 Thin-layer spectra of 5.0×10^{-5} mol dm^{-3} [Zn(tsmp)] at different oxidation potentials in pH 4.0 buffer solution. E_{appl} = (*a*) 0.20, (*b*) 0.59, (*c*) 0.61, (*d*) 0.63, (*e*) 0.65, (*f*) 0.67, (*g*) 0.69, (*h*) 0.80 V. Inset: Cyclic voltammogram of 5.0×10^{-4} mol dm^{-3} [Zn(tsmp)] in pH 4.0 buffer solution. Scan rate = 5 mV s^{-1}.

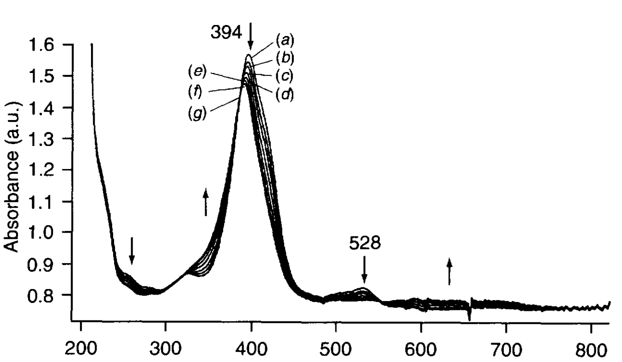


Fig. 2 Thin-layer spectra of 1.0×10^{-4} mol dm^{-3} [Fe(tsmp)] at different oxidation potentials in pH 2.0 buffer solution. E_{appl} = (*a*) 0.40, (*b*) 0.89, (*c*) 0.91, (*d*) 0.93, (*e*) 0.95 (*f*) 0.97, (*g*) 1.05 V.

(spectroelectrochemical results[10]). Bulk electrolysis at E_{appl} = +0.720 V for a solution containing 1.0×10^{-4} mol dm^{-3} [Fe(tsmp)(H$_2$O)]$^-$ and 0.05 mol dm^{-3} cyclopent-2-en-1-acetic acid leads to an increase in absorption at 240 nm. Ion chromatography and product analysis shows that the only product is cyclopent-2-ene-4-one-1-acetic acid.[8] Only about 1 turnover is observed for each iron porphyrin.

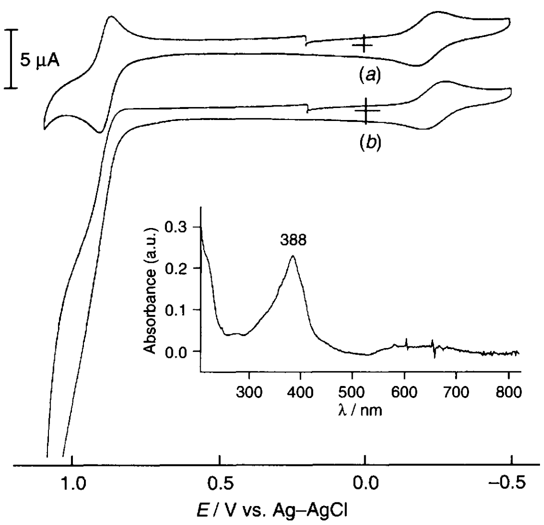
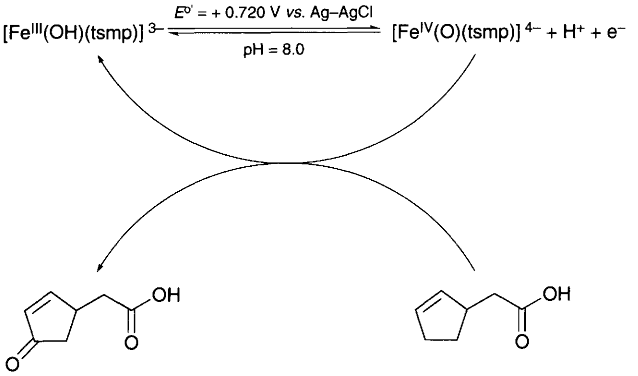
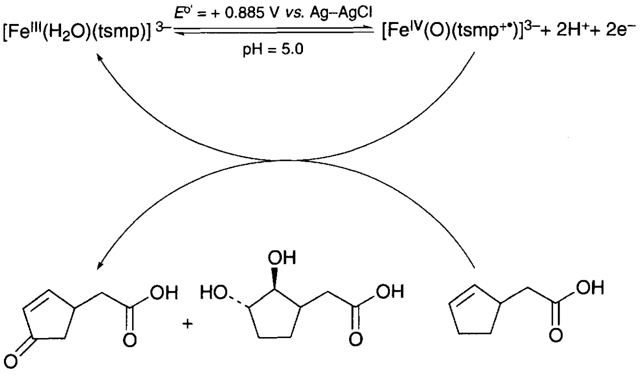


Fig. 3 Cyclic voltammograms of 5.0×10^{-4} mol dm^{-3} [Fe(tsmp)] containing (*a*) 0.0, (*b*) 50 mmol dm^{-3} cyclopent-2-ene-1-acetic acid in pH 5.0 buffer solution. Scan rate = 20 mV s^{-1}. Inset: the absorption spectrum of 5.0×10^{-5} mol dm^{-3} [Fe^{IV}(O)(tsmp$^{+\cdot}$)].



Scheme 1



Scheme 2

In a pH 5.0 buffer solution, [Fe^{III}(tsmp)(H$_2$O)] undergoes a two-electron oxidation to [Fe^{IV}(O)(tsmp$^{+\cdot}$)] (Fig. 3). The formal potential is +0.885 V and i_{pa}/i_{pc} is *ca.* 1.0 even at a scan rate of 0.02 V s^{-1}. The absorption spectrum of the oxoferryl porphyrin radical cation exhibits a Soret band at 388 nm and a broad band in the region 530–730 nm. Another reported oxoferryl porphyrin radical cation [Fe^{IV}(O)(tmp$^{+\cdot}$)] is only stable at −71 °C in dry CH$_2$Cl$_2$.[13] In the presence of 0.05 mol dm^{-3} cyclopent-2-en-1-acetic acid, the oxidation current increases hugely while the reduction current disappears in the reverse scan. The CV exhibits a typical pattern for the fast electrocatalytic oxidation of the alkene by [Fe^{III}(tsmp)-(H$_2$O)]$^{3-}$.

Bulk electrolysis of 1.0×10^{-4} mol dm^{-3} [Fe^{III}(tsmp)-(H$_2$O)]$^{3-}$ and 0.05 mol dm^{-3} cyclopent-2-en-1-acetic acid was conducted at E_{appl} = 1.00 V in a pH 5.0 buffer solution and ion chromatography showed two peaks corresponding to cyclopent-2,3-diol-1-acetic acid and cyclopent-2-en-4-one-1-acetic acid.[8] Thus [Fe^{IV}(O)(tsmp$^{+\cdot}$)]$^{3-}$ can undergo both epoxidation and allylic oxidation[1,2] towards alkenes in aqueous media. There are *ca.* 120 turnovers for each catalyst and the ratio for diol/eneone is *ca.* 120. It is noteworthy that this yield of eneone is very similar to that at pH 8.0. The results suggest that in pH 5.0 solution, the electrogenerated [Fe^{IV}(O)(tsmp$^{+\cdot}$)]$^{3-}$ reacts with [Fe^{III}(tsmp)(H$_2$O)]$^{3-}$ conproportionally to form [Fe^{IV}(O)-(tsmp)]$^{4-}$, which then reacts with cyclopent-2-en-1-acetic acid to form the eneone product. The fast formation of the diol is due to the catalytic reaction *via* [Fe^{IV}(O)(tsmp$^{+\cdot}$)]$^{3-}$, as evidenced by the CV in Fig. 3. The electrocatalytic oxidations of cyclopent-2-en-1-acetic acid by two states of high-valent iron porphyrins are summarized in Schemes 1 and 2.

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