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) porphyrins³ and oxoiron(IV) porphyrin radical cations are generated by reaction with peracids⁴ 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 atoms⁸ 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 ([H₂tsmp]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 H₂O,⁶ was observed. The stability of the oxidized [Zn(tsmp)] was confirmed by spectroelectrochemistry (Fig. 1) from which stable $[Zn(tsmp^{+.})]^{3-}-[Zn(tsmp)]^{4-}$ equilibria can be obtained at various potentials. The redox reaction

involves a one-electron transfer and the formal potential is at $+0.63 \text{ V}.^{10}$ 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)(H₂O)]³⁻ with pK_a for bound H₂O 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.

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(spectroelectrochemical results¹⁰). Bulk electrolysis at E_{appl} = +0.720 V for a solution containing 1.0 × 10⁻⁴ mol dm⁻³ [Fe(tsmp)(H₂O)]⁻ and 0.05 mol dm⁻³ cyclopent-2-en-1-acetic



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^{+.})].



 $[Fe^{III}(H_2O)(tsmp)]^{3-} \xrightarrow{E^{0'} = + 0.885 V \text{ vs. Ag-AgCI}}_{PH = 5.0} [Fe^{IV}(O)(tsmp^{+*})]^{3-} + 2H^{+} + 2e^{-4}$



Scheme 2

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.

In a pH 5.0 buffer solution, $[Fe^{III}(tsmp)(H_2O)]$ undergoes a two-electron oxidation to $[Fe^{IV}(O)(tsmp^{+})]$ (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 $[Fe^{IV}(O)(tmp^{+})]$ is only stable at $-71 \text{ }^{\circ}\text{C}$ in dry CH₂Cl₂.¹³ 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 $[Fe^{III}(tsmp)-(H_2O)]^{3-}$.

Bulk electrolysis of 1.0×10^{-4} mol dm⁻³ [Fe^{III}(tsmp)-(H₂O)]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 $[Fe^{IV}(O)(tsmp^+)]^{3-}$ 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⁺·)]³⁻ reacts with $[Fe^{III}(tsmp)(H_2O)]^{3-}$ 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^{+.})]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.

This work was supported by the National Science Council of the Republic of China.

References

- 1 Metalloporphyrins in Catalytic Oxidations, ed. R. A. Sheldon, Marcel Dekker, New York, 1994.
- 2 B. Meunier, Chem. Rev., 1992, 92, 1411.
- 3 P. N. Balasubramanian, R. W. Lee and T. C. Bruice, J. Am. Chem. Soc., 1989, 111, 8714.
- 4 W. A. Lee, L.-C. Yuan and T. C. Bruice, J. Am. Chem. Soc., 1988, 110, 4277.
- 5 J. T. Groves and Y. Watanabe, J. Am. Chem. Soc., 1988, 110, 8443.
- 6 Y. O. Su, D. Kim and T. G. Spiro, J. Electroanal. Chem., 1988, 246, 363.
- 7 A. S. Hinman, B. J. Pavelich, A. E. Kondo and S. Pons, J. Electroanal. Chem., 1987, 234, 145.
- 8 M. H. Liu and Y. O. Su, J. Chem. Soc., Chem. Commun., 1994, 971.
- 9 T. G. Traylor, K. W. Hill, W. P. Fann, S. Tsuchiya and B. E. Dunlap, J. Am. Chem. Soc., 1992, **114**, 1308.
- 10 S.-M. Chen and Y. O. Su, J. Chem. Soc., Chem. Commun., 1990, 491.
- 11 M. F. Zipplies, W. A. Lee and T. C. Bruice, J. Am. Chem. Soc., 1986, 108, 4433.
- 12 S. H. Cheng, Y. S. Chen and Y. O. Su, J. Chin. Chem. Soc., 1991, 38, 15.
- 13 T. S. Calderwood and T. C. Bruice, Inorg. Chem., 1986, 25, 3722.

Received, 13th February 1996; Com. 6/01040G