

Unusual redox properties of a sterically hindered water-soluble chromium porphyrin. Electrochemical and spectral speciation

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***meso*-Tetrakis(3-sulfonatomesityl)porphyrinato]chromium(III) [Cr^{III}(tsmp)] in aqueous solution can undergo electrochemical reduction to form a stable radical anion and oxidation to generate very stable radical cations Cr^{III}(tsmp^{•+}) and O=Cr^{IV}(tsmp^{•+}), which reacts with alkenes to produce enones at room temperature.**

Cytochrome P-450 is a monooxygenase which acts as a mediator for oxygen transfer reactions in biological systems. Metalloporphyrins have been intensively used as catalysts in mimicking cytochrome P-450.^{1–3} Formation of a high-valent oxo-metal complex is essential for such catalytic reactions, and can be generated by reacting metalloporphyrins with chemical oxidants such as ClO⁻,⁴ H₂O₂,⁵ alkyl peroxides,⁶ percarboxylic acid,⁷ iodosylbenzene,⁸ KHSO₅,⁹ or nitrogen oxides.¹⁰ Also, electrochemical methods have been developed in aqueous¹¹ and non-aqueous¹² solutions.

We have synthesized water-soluble [*meso*-tetrakis(3-sulfonatomesityl)porphyrinato]chromium(III) [Cr^{III}(tsmp)] and found that the *ortho*-methyl groups in the tetramesitylporphyrin provided good steric protection for the *meso*-carbons upon radical cation or anion formation. The steric hindrance also prevents the formation of the μ -oxo dimer¹³ in aqueous solutions. Cr^{III}(tsmp) exhibits two pK_a values at 8.5 and 11.6, respectively, according to spectrophotometric titration and can be compared with the pK_{a1} and pK_{a2} values for [*meso*-tetrakis(4-sulfonatophenyl)porphyrinato]chromium(III) [Cr^{III}(tspp)] of 7.63 and 11.45, respectively.¹⁴

In pH 0.0–3.0 buffer solutions, Cr^{III}(tsmp)(H₂O)₂ undergoes a one-electron oxidation at a formal potential of 0.875 V (vs. Ag/AgCl), which is invariant in this pH range. λ_{\max} of the Soret band shifts from 448 to 424 nm and the molar absorption decreases dramatically. A broad band in the region 600–800 nm indicates cation radical formation in the porphine ring. An isosbestic point is observed clearly at 434 nm which shows only two components are present in equilibrium. The number of electrons transferred (*n*) and formal potential were determined from the literature procedure¹⁵ to be 1.0 and +0.875 V, respectively. On the other hand, oxidation of Cr^{III}(tspp) leads to decomposition and the absorption spectrum becomes featureless. The instability of Cr^{III}(tspp) to oxidation is consistent with ring oxidation.¹⁶

In pH 3.2 buffer solution, two distinct one-electron transfer steps could be observed spectroelectrochemically and both oxidation products are very stable. The first oxidation follows the same pattern as that at pH 0.0–pH 3.0 and thus is ring-centred [Fig. 1(a)]. In the second step, λ_{\max} of the Soret band shifts from 424 to 406 nm with similar absorbance [Fig. 1(b)].

In pH 3.5–5.5 buffer solutions, the first oxidation potential is invariant while the second one shifts cathodically with increase in pH. The two oxidation potentials become closer and finally merge. In pH 6.0–8.0 buffer solutions, the two one-electron oxidations merge into a two-electron step (Fig. 2). The final absorption spectra are identical for both pH ranges. The number of electrons transferred (*n*) and the slope of formal potential were determined to be 2.0 and –56 mV/pH, respectively.

Hence, according to the Nernst equation,¹⁷ the oxidation step involves transfer of two protons upon two-electron oxidation.

Spectroelectrochemical studies show that O=Cr(H₂O)(tsmp^{•+}) is also very stable and can be reversibly reduced in 6.0 ≤ pH ≤ 8.0 buffer solution. This oxochromium(IV) porphyrin radical cation is apparently more stable than its iron counterpart.^{11b}

Fig. 3 shows thin-layer spectra of 5 × 10⁻⁵ M Cr^{III}-(H₂O)₂(tsmp) and 0.05 M cyclopent-2-en-1-acetic acid in pH 7.0 buffer solution at E_{appl} = 0.73 V, which should correspond to a

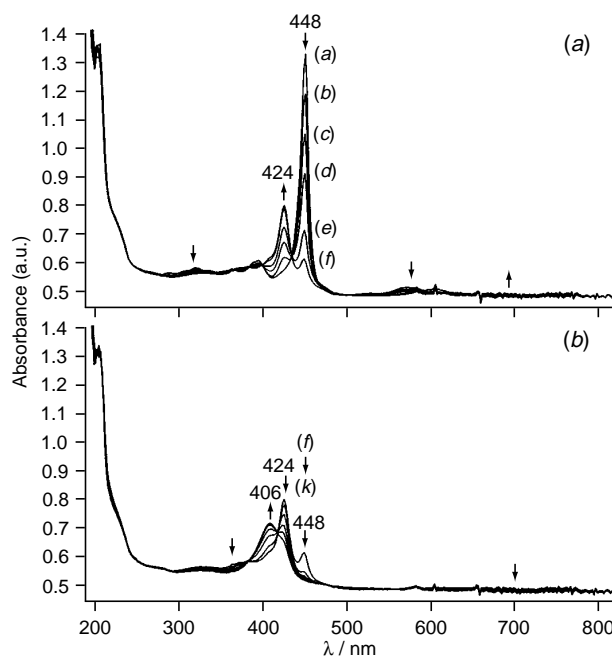


Fig. 1 Thin-layer spectra of 5 × 10⁻⁵ M Cr(tsmp) at different oxidation potentials in pH 3.2 buffer solution. E_{appl} = (a) 0.50 (b) 0.83 (c) 0.85 (d) 0.87 (e) 0.91 (f) 0.95 (g) 1.01 (h) 1.07 (i) 1.09 (j) 1.11 (k) 1.15 V.

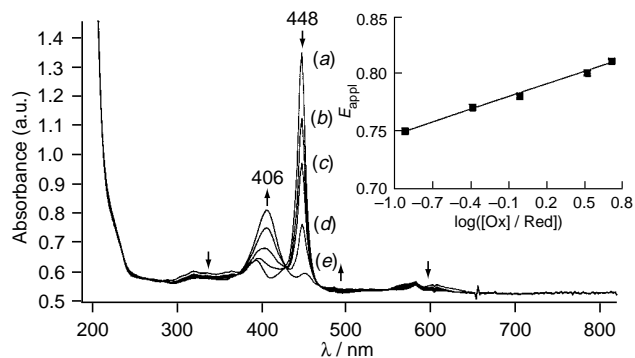


Fig. 2 Thin-layer spectra of 5 × 10⁻⁵ M Cr(tsmp) at different oxidation potentials in pH 6.0 buffer solution. E_{appl} = (a) 0.50 (b) 0.77 (c) 0.78 (d) 0.80 (e) 0.89 V. Inset: plot of E_{appl} vs. log ([Ox]/[Red]) for Cr(tsmp).

1 : 1 mixture of $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{tsmp})$ and $\text{O}=\text{Cr}^{\text{IV}}(\text{tsmp}^+)$. However, the absorption band of the latter at 406 nm is not seen. Rather, the absorption band of $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{tsmp})$ decreases slightly. In the 240 nm region, an absorbance corresponding to enone formation¹¹ increases gradually. Bulk electrolysis of 5×10^{-5} M $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{tsmp})$ and 0.05 M cyclopent-2-en-1-acetic acid was conducted at $E_{\text{appl}} = 0.73$ V in pH 7.0 buffer solution. Ion chromatography of the reaction mixture showed that the peak of cyclopent-2-en-1-acetic acid was reduced and a peak corresponding to cyclopent-2-en-4-one-1-acetic acid was observed (Fig. 3). The turnover rate is ca. 0.5 turnovers min^{-1} based on the spectroelectrochemical results. Purging the solution with N_2 during electrolysis led to significantly less enone.

Electrocatalysis at $E_{\text{appl}} = 0.99$ V in pH 3.6 buffer solution can also produce cyclopent-2-en-4-one-1-acetic acid but the turnover rate is slower, ca. 1/4 that at pH 7.0. To the best of our knowledge, this is the first reported oxochromium(IV) porphyrin radical cation reaction with alkenes in aqueous solutions at room temp.† The 424 nm band of $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{tsmp}^+)$ is still observed in the pH 3.6 solution while at pH 7.0 $\text{O}=\text{Cr}^{\text{IV}}(\text{H}_2\text{O})(\text{tsmp}^+)$ is reduced to $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{tsmp})$. Reaction pathways are thus proposed in Scheme 1.¹¹

We also observed spectroelectrochemically¹⁵ that $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{tsmp})$ can undergo stable and reversible one-electron reduction in pH 9.0 buffer solution. The Soret band shifts from

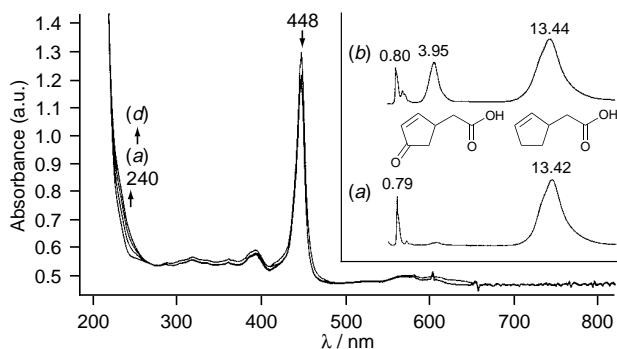
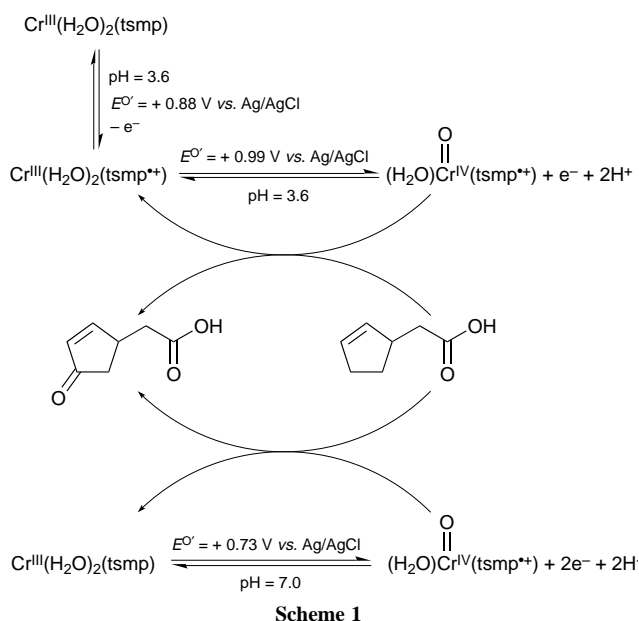


Fig. 3 Thin-layer spectra of 5×10^{-5} M $\text{Cr}(\text{tsmp})$ at different oxidation potentials in pH 7.0 buffer solution containing 0.05 M cyclopent-2-en-1-acetic acid. $E_{\text{appl}} =$ (a) 0.19 V (b) 0.73 V for 20 min. (c) 0.73 V for 30 min. (d) 0.73 V for 40 min. Inset: ion chromatograph of the mixture. (a) before electrolysis (b) after electrolysis at $E_{\text{appl}} = 0.73$ V for 80 min.



440 to 420 nm and the intensity drops to about 1/3. A broad band is observed in 600–800 nm region. The absorption spectrum indicates the formation of a radical anion, which is consistent with reported results by radiolysis.²⁰ It suggests that Cr^{III} , which has the surplus of an extra positive charge by subtracting the dianion of the porphyrin coordination, stabilizes the extra electron on the porphine ring. The stabilization effect does not occur with $\text{Zn}^{\text{II}}(\text{tsmp})$.^{11b}

This work was supported by the National Science Council of the Republic of China under Grant No. NSC 85-2113-M-002-021.

Footnotes

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† The reported catalytic oxidations of alkenes by chromium porphyrins have relied on the activity of the oxochromium(V) porphyrin. See refs. 18 and 19.

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Received in Cambridge, UK, 5th December 1996; Com. 6/08211D