Electrochemical Activation of a Metal Oxo Bond; Oxidation of *cis*-Dioxomolybdenum(VI) Tetraphenylporphyrin

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The one electron oxidation and coupled oxygen atom transfer of *cis*-dioxomolybdenum(VI) tetraphenylporphyrin, $O_2Mo(TPP)$, was investigated by the use of cyclic voltammetry and thin-layer spectroelectrochemistry.

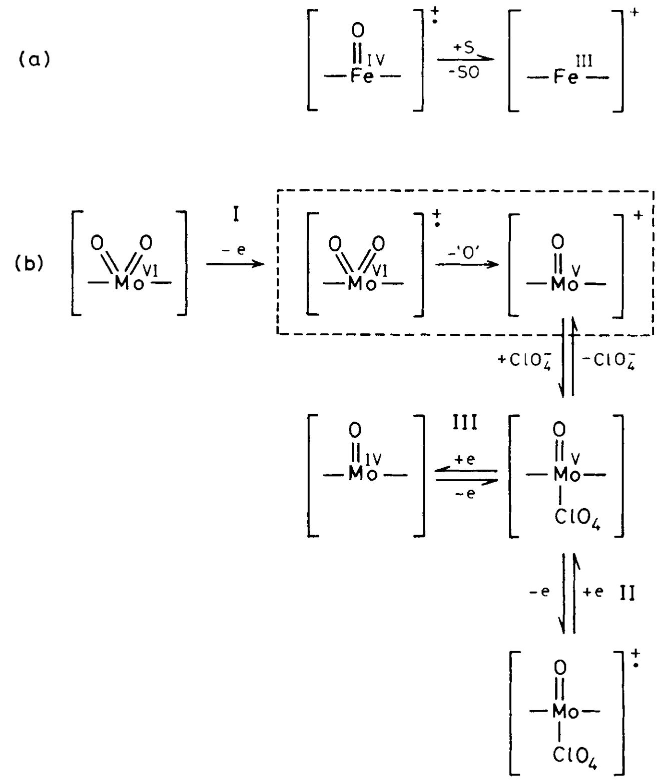
Ferryl ($Fe^{IV}O$) radical cations of porphyrins have been proposed as the active species in the dioxygen activation of cytochrome P_{450}[1] as shown schematically in Scheme 1a. Because of this, attempts to design simple biomimetic models for these high valent iron complexes has led to much interest in oxometalloporphyrin chemistry in the last few years.[2–5] In an attempt to model this enzyme we have investigated the reductive chemistry and electrochemistry of *cis*-dioxomolybdenum(VI) tetraphenylporphyrin, $O_2Mo(TPP)$.[4,6] This compound was synthesized by photolysis of bisperoxomolybdenum(VI) tetraphenylporphyrin, $(O_2)_2Mo(TPP)$, as described in the literature.[3] We now present data for the electrochemical oxidation of $O_2Mo(TPP)$ and illustrate an electro-oxidation mechanism which involves oxygen atom transfer similar to that of the modelled enzyme, and yields as a final product $[OMo(TPP)]^+$.

The electrochemical oxidation of $O_2Mo(TPP)$ was carried out at a Pt electrode in 1,2-dichloroethane and 0.1 M tetrabutylammonium perchlorate by cyclic voltammetry and thin layer spectroelectrochemistry at an optically transparent gold electrode. As shown in Figure 1 the electrochemical oxidation of $O_2Mo(TPP)$ proceeds in two steps. The first step (reaction I) has an anodic peak potential at $E_p = 1.25$ V *vs.* saturated calomel electrode and does not have a coupled reverse reduction process. Both the shape of the peak and the current dependence on scan rate suggest a diffusion controlled one electron oxidation followed by a fast irreversible chemical reaction (EC mechanism).

A reversible diffusion controlled one electron oxidation also occurs at $E_{1/2} = 1.49$ V (reaction II). This latter reaction is at a potential characteristic of $(ClO_4)OMo(TPP)$ oxidation to yield a cation radical. Finally, reversal of the potential scan at either 1.4 or 1.7 V yields a new reduction peak (peak III) at $E_{p,c} = 0.00$ V. This peak is not observed upon initial reductive scans of $O_2Mo(TPP)$ solutions and is at a potential identical to that for the Mo^V/Mo^{IV} reaction of $OMo(TPP)$ or $[OMo(TPP)]^+$.[7]

Stepwise coulometric measurements at potentials more anodic than peaks I and II show the abstraction of one electron in each of the two oxidation processes. The spectra of the first electrogenerated species (Figure 2a) is characterized by a Soret peak at 489 nm. This peak, and peaks at 607 and 655 nm, are identical to those obtained for $(ClO_4)OMo(TPP)$.[6] Spectra containing Soret peaks at wavelengths greater than 450 nm have been reported for $(X)OMo(TPP)$ where $X = OH^-$ (464 nm),[5] OAc^- (485 nm),[8] and Cl^- (498 nm).[5] The spectrum recorded after the second oxidation (Figure 2b) has peaks at 490, 609, 655, and 902 nm and is characteristic of a Mo^V cation radical. Again, as in the case of $(X)OMo(TPP)$, the Soret peak is shifted to longer wavelengths than that characteristic of non-molybdenum containing porphyrin cation radicals.

A representation of the activated species in cytochrome P_{450} is presented in Scheme 1a. The spectrophotometric data, as well as the voltammetric and coulometric results in this study, suggest that the initial oxidation of $O_2Mo(TPP)$ can be



Scheme 1. Oxidation mechanisms of (a) cytochrome P_{450} and (b) $O_2Mo(TPP)$ in $(ClCH_2)_2$ (0.1 M Bu_4NClO_4). The roman numerals I—III refer to the reactions given in Figure 1.

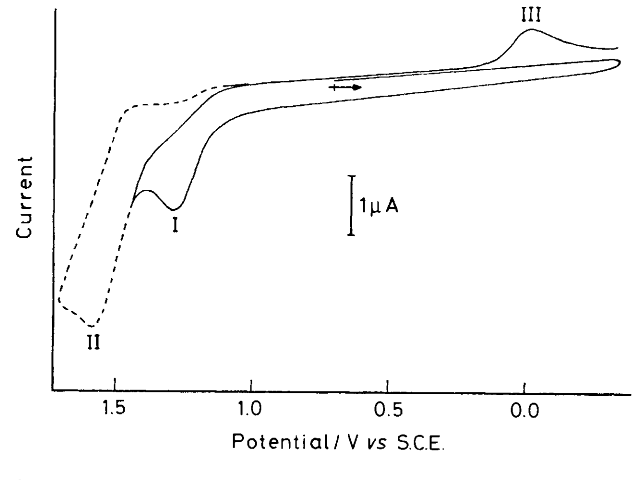


Figure 1. Cyclic voltammogram of $O_2Mo(TPP)$ in $(ClCH_2)_2$ (0.1 M Bu_4NClO_4). Scan rate 0.1 V s^{-1}. S.C.E. = saturated calomel electrode.

described by a similar mechanism, as shown in Scheme 1b. In this mechanism the ultimate product of the initial one electron oxidation is the well characterized $(ClO_4)OMo(TPP)$ complex.

For the case of metalloporphyrin oxidation, electron abstraction may be from the central metal, from the conjugated porphyrin ring, or occasionally from a bound axial ligand. For the $O_2Mo(TPP)$ complex under investigation,

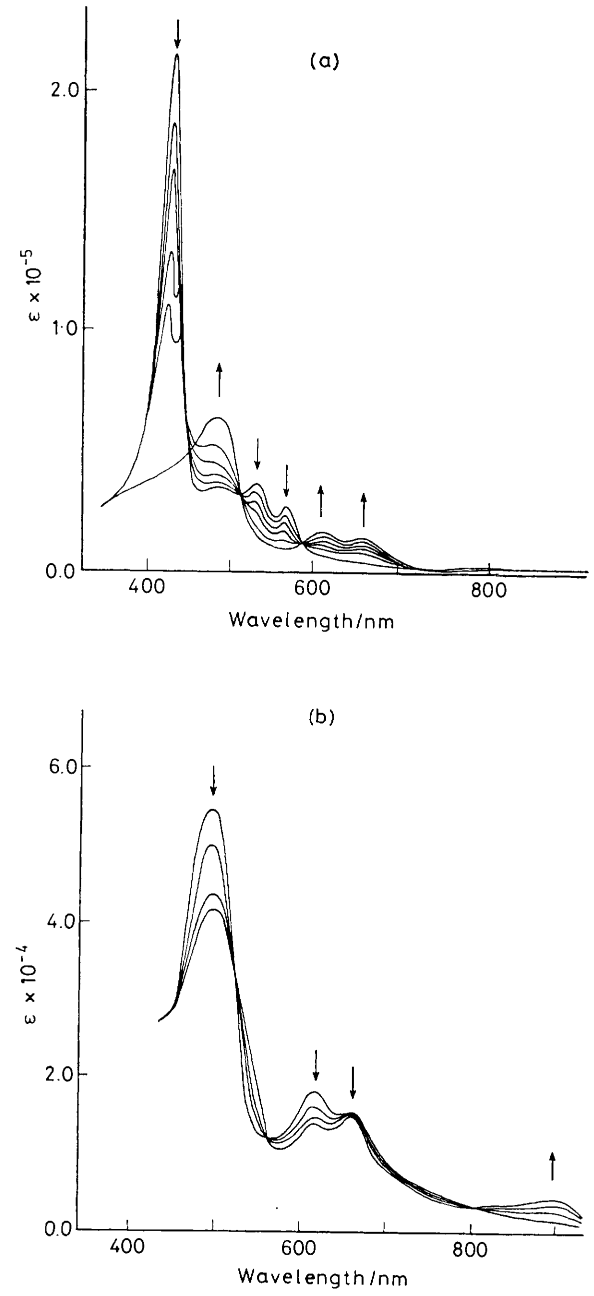


Figure 2. Time-resolved electronic absorption spectra of $O_2Mo(TPP)$ obtained (a) during the first oxidation step at $E_p = 1.25$ V and (b) during second oxidation step at $E_{1/2} = 1.49$ V.

abstraction of an electron from Mo^{VI} or from the oxo ligand is not possible and the only reasonable site of oxidation is from the π ring system producing the cation radical $[O_2Mo(TPP)]^{\cdot +}$.

However, the spectrum for this radical was not observed within the lower time scale of thin-layer spectroelectrochemistry (0.1 s) and the only observed spectrum was that of $(ClO_4)OMo(TPP)$ which is produced by loss of an oxo ligand from $[O_2Mo(TPP)]^{\cdot +}$. Since isosbestic points are observed at $\lambda = 445$, 518, and 590 nm, one can only assume that very low concentrations of radical are present in solution and that the chemical reaction (oxygen atom transfer) is faster than the time scale of our measurements. This would imply that this radical is highly reactive, unlike $O_2Mo(TPP)$ which is only a mild oxidizing agent.

In summary we have shown that $O_2Mo(TPP)$ may be oxidized by a one electron transfer pathway followed by oxygen atom transfer similar to the commonly accepted mechanism for oxidation of cytochrome P_{450}. This is the first electrochemical investigation of a simple high valent metalloporphyrin exhibiting these characteristics.

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