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Electrochemical Studies of Oxo(*meso*-tetraphenylporphinato)chromium(IV). Direct Evidence for Epoxidation of Olefins by an Electrochemically Generated Formal Chromium(V) State

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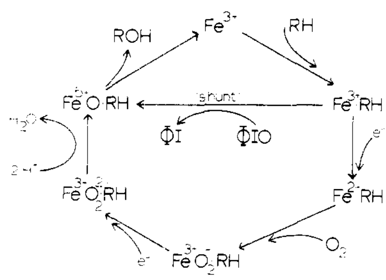
We have shown that it is possible to generate a stable formal metal(V) oxo-porphyrin species by electrochemical oxidation of the corresponding metal(IV) oxo-porphyrin. The product of the one-electron oxidation of [(CrTPP)O] is, by electrochemical and spectroelectrochemical criteria, reactive toward olefins, notably norbornene, and the exo epoxide of norbornene has been chromatographically identified and quantified as a reaction product. The yield of epoxide has been shown to follow a 1:1 stoichiometry of oxo-porphyrin to substrate olefin. A 2:1 mixture of [(CrTPP)Cl] and iodosobenzene produces a product solution with distinctive voltammetry exhibiting no spectral residue for [(CrTPP)Cl]. These and the [(CrTPP)O] results lead to a scheme for the 2:1 mixture's reactivity with olefins involving an oxo-bridged Cr(IV)-Cr(IV) dimer, which can disproportionate into a Cr(III) species and a reactive Cr(V) species. Relevance to natural systems is discussed.

There is considerable interest in understanding and imitating the oxidizing state involved in the enzymatic oxidation of substrates by cytochrome P-450. The proposed[1] representation of the catalytic cycle of the enzyme (Scheme I) postulates that the active oxidizing species is an oxo-Fe(IV)-porphyrin radical cation, a formal Fe(V) species. Understanding this chemistry is important because, among other things, cytochrome P-450 is one of the few enzymes capable of activating carbon-hydrogen bonds. Cytochrome P-450 is important to both biosynthetic and xenobiotic systems because of its ability to hydroxylate hydrocarbons.[2]

A number of workers have contributed to the problem of imitating cytochrome P-450 oxidation chemistry, by studies with model metalloporphyrin systems. A common strategy utilizes the so-called "shunt mechanism", where by analogy with Scheme I the active oxidizing metalloporphyrin state is generated directly from its rest state by reaction with oxygen atom donor species like iodosobenzene, alkyl hydroperoxides, and hypochlorite. Groves[3] demonstrated the catalytic epoxidation of olefins with all these oxidants using iron, manganese, and chromium tetraphenylporphyrins as catalysts in methylene chloride. Hill[4] has shown that, in the MnTPP/iodosobenzene system, an oxo-bridged metalloporphyrin-iodosobenzene adduct can be isolated and characterized by X-ray crystallography. In solution, this adduct will also epoxidize olefins. Collman[5] has shown that olefin epoxidation can be supported in a two-phase system with substrate and metalloporphyrin catalyst in methylene chloride and hypochlorite in aqueous solution. A phase-transfer catalyst transported oxidant into the methylene chloride phase. In these studies, the general approach has been to add oxidant to a solution containing the substrate and the metal(III) state of the catalyst with periodic analysis of the reaction pot for products.

We present here a new strategy, for electrochemical generation of a metal(V) formal state like that in Scheme I. The strategy is based on oxidizing a metal(IV) oxo-porphyrin and is demonstrated with use of solutions of oxo(*meso*-tetraphenylporphinato)chromium(IV), a known, characterized species.[6a,7]

Scheme I



Starting with [(CrTPP)O], prepared from [(CrTPP)Cl] and iodosobenzene, we electrochemically abstract an electron, resulting in a $[(CrTPP)O]^+$ species formally analogous to the active state of cytochrome P-450 (eq 1). We have observed that this species

$$[(CrTPP)O] - e^- \rightarrow [(CrTPP)O]^+ \qquad (1)$$

$$[(CrTPP)O]^+ + \text{olefin} \rightarrow [CrTPP]^+ + \text{epoxide} \qquad (2)$$

(eq 2) can quantitatively transfer an oxygen atom to an olefinic substrate, norbornene, to generate its epoxide and regenerate a $[Cr^{III}TPP]^+$ state. The chromium porphyrin system was chosen both because [(CrTPP)O] is stable enough to be isolated and because [(CrTPP)Cl] has been shown to catalyze the epoxidation of olefins by iodosobenzene in methylene chloride. We will refer to the latter chemistry as the "[(CrTPP)Cl]/iodosobenzene/olefin system"; it has been studied extensively by Groves et al.[6] and others.[7] Norbornene was chosen as substrate since it has been shown[6] to yield 99% epoxide. Though stoichiometric rather than catalytic, Reactions 1 and 2 represent one turnover of a cytochrome P-450 like oxidation.

Our electrochemical approach uses cyclic voltammetry, optically transparent thin-layer electrochemistry (OTTLE), and bulk electrolysis to generate the active $[(CrTPP)O]^+$ species in a controlled manner and study its subsequent decay. These methods were also applied to study the oxo species generated by reaction of a 2:1 mixture of [(CrTPP)Cl] and iodosobenzene. The electrochemical data, when combined with other data collected on the [(CrTPP)Cl]/iodosobenzene/olefin system, leads to a clearer picture of the chemistry of that system.

Experimental Section

All electrochemical experiments were performed in methylene chloride distilled over phosphorous pentoxide, passed through anhydrous potas-

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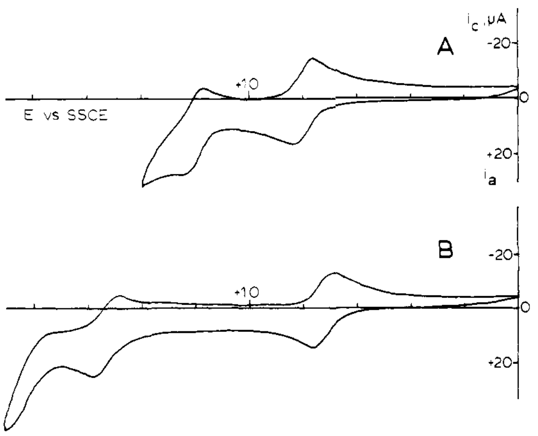

Figure 1. Cyclic voltammetry (50 mV/s) of 1.0 mM solutions of (A) [(CrTPP)Cl] in 0.2 M Bu_4NClO_4/methylene chloride and (B) [(CrTPP)O] in 0.2 M Bu_4NClO_4/methylene chloride (potentials vs. SSCE).

sium carbonate, and stored in brown bottles over 4-Å molecular sieves. Supporting electrolyte was tetrabutylammonium perchlorate (Bu_4NClO_4) (G. Frederick Smith) recrystallized twice from ethyl acetate and dried in a vacuum oven at 50 °C. All potentials are reported vs. the NaCl-saturated calomel electrode (SSCE). Working electrodes for cyclic voltammetry were Teflon-shrouded platinum disks, polished with 1-μm diamond paste (Buehler), washed with water, and dried briefly in a vacuum oven prior to use. Cyclic voltammetry was done with a three-electrode potentiostat and triangle waveform generator of local construction.

Optically transparent thin-layer electrochemistry was performed with a 500 lines/in. gold minigrid working electrode sandwiched between two glass plates, as described previously.[10] Cells were calibrated individually; typical dimensions were 80 μm thin solution layer thickness and 2×10^{-3} cm^3 electroactive volume. UV-vis spectra of the thin-layer solution were taken with either a Tracor Northern 6051 system or a Hewlett-Packard 8450A spectrometer. Both spectrometers utilize diode array detection, permitting rapid acquisition of spectra without interrupting the sweep of the thin-layer electrode potential.

Bulk electrolysis of [(CrTPP)O]/olefin solutions was done in a two-compartment glass cell with a Pt auxiliary electrode isolated from the magnetically stirred working electrode cavity. The working electrode was a Pt gauze poised at +0.775 V. Data were taken with a PAR Model 173 potentiostat coupled with a microcomputer of local construction. Typical solutions were 5 mL of 1 mM porphyrin and 100 mM olefin with 0.5 M supporting electrolyte. Electrolysis time was ca. 45 min.

For experiments involving norbornene epoxidation, product formation was monitored by GLC with a Hewlett-Packard 5750 chromatograph fitted with an SE-30 column. The column temperature was 100 °C, helium was the carrier gas, and detection was by flame ionization. Authentic samples of norbornene and *exo*-norbornene epoxide (Aldrich) gave retention times of 2.1 and 6.0 min, respectively. Samples were injected directly from reaction mixtures or electrochemical cells.

The following syntheses were performed:

Chloro(*meso*-tetraphenylporphinato)chromium(III), [(CrTPP)Cl]. Free base H_2TPP (Strem Chemicals) was metalated with anhydrous $CrCl_2$ in refluxing DMF and purified by treatment with concentrated HCl in chloroform, passage through an alumina column, and recrystallization from chloroform/hexane, as described by Basolo et al.[8] Purity was judged by comparison of UV-vis spectra with the published spectrum.[8]

Oxo(*meso*-tetraphenylporphinato)chromium(IV), [(CrTPP)O]. Preparation followed the method of Groves,[6a] as follows. [(CrTPP)Cl] (132 mg, 0.19 mmol) was added to 10 mL of degassed methylene chloride, followed by iodosobenzene (132 mg, 0.60 mmol), and the mixture was stirred for 5 min. Iodosobenzene was prepared from the diacetate by literature methods.[9] After addition of 500 mg of powdered KOH and 5 min more of stirring, the reaction mixture was applied to a dry alumina column. The orange fraction was collected and twice recrystallized from methylene chloride/pentane; final yield 50%. Elemental analysis was consistent with one water of hydration. Anal. Found: C, 75.70; H, 4.27; N, 7.90. Calcd for [(CrTPP)O]: C, 77.64; H, 4.14; N, 8.23. Calcd for [(CrTPP)O]·H_2O: C, 75.64; H, 4.32; N, 8.02. Repeated attempts at recrystallization from a variety of solvents did not produce an analysis consistent with the anhydrous material. While we are unable to rule out the possibility of a six-coordinate dihydroxy structure, $(CrTPP)(OH)_2$, the UV-vis spectroscopic data (λ_{max} = 430, 544 nm) match exactly that of the previously characterized[6a,7b] [(CrTPP)O] species.

Table I. Electrochemical and Spectral Data on [(CrTPP)Cl] and [(CrTPP)O]

(A) Cyclic Voltammetry[a]

	[(CrTPP)Cl]		[(CrTPP)O]	
	$E_{1/2}$, V	ΔE_p, mV	$E_{1/2}$, V	ΔE_p, mV
$Cr^{2+/+}$	−1.26	63		
$Cr^{3+/2+}$	−1.10[b]		−1.51	
$Cr^{4+/3+}$	+0.80	64	−1.12[b]	
$Cr^{5+/4+}$	+1.19[c]		+0.71	70
$Cr^{6+/5+}$			+1.53[d]	

(B) UV-Vis Spectroscopy

	λ_{max}, nm		λ_{max}, nm
[(CrTPP)Cl]	447 (Soret)	[(CrTPP)O]	429 (Soret)
	396		543
	562	$[(CrTPP)O]^+$[e]	408 (Soret)
	601		

[a] Metal oxidation states are listed for electron-counting purposes only and do not imply metal-centered redox processes. [b] Irreversible. [c] Wave obscured by solvent limits. [d] Supporting electrolyte 0.2 M Bu_4NPF_6. [e] Generated electrochemically.

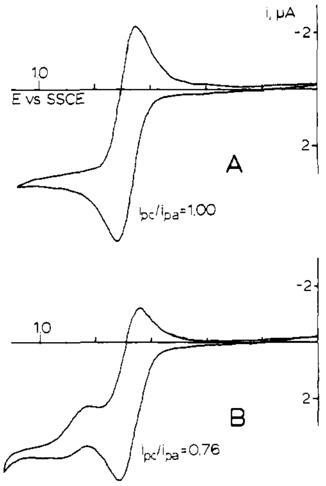

Figure 2. Cyclic voltammetry (5 mV/s) of 1.0 mM [(CrTPP)O] in the absence (A) and presence (B) of 100 mM norbornene, in 0.2 M Bu_4NClO_4/methylene chloride.

Results and Discussion

Electrochemical Experiments. Cyclic voltammograms of the oxidation of [(CrTPP)Cl] and of [(CrTPP)O] in methylene chloride are given in Figure 1 with a summary of cyclic voltammetric and UV-vis spectroscopic data for both compounds in Table I. [(CrTPP)Cl] is oxidized in two sequential one-electron waves at +0.80 and +1.18 V vs. SSCE to formal Cr(IV) and Cr(V) states, respectively, which judging from ΔE_p values are generated reversibly. [(CrTPP)O] is oxidized quasi-reversibly at +0.71 V vs. SSCE to the formal Cr(V) state (reaction 1), and at much more positive potential (+1.53 V) to a formal Cr(VI) state whose chemistry we have not yet investigated. (Neither will we attempt here an assignment of ligand- or metal-centered character to the waves.) It is relevant that the observed spectrum of [(CrTPP)Cl] is almost identical with that published[11] for [(CrTPP)ClO$_4$], and the first oxidation wave for [(CrTPP)ClO$_4$] is reported[11] at +1.03 V vs. SCE.

The voltammetry shows that the Cr(IV) state is remarkably stabilized by the electron-rich oxo ligand, relative to chloride. The $[(CrTPP)O]^+$ species is thermodynamically less potent, by 0.47 V, as an oxidizing agent compared to $[(CrTPP)Cl]^{2+}$, due in part

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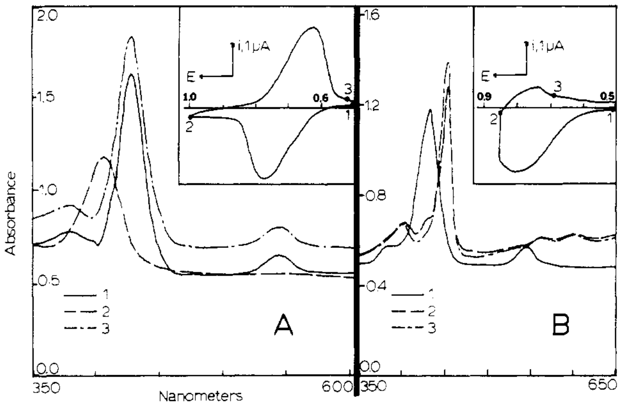

Figure 3. Optically transparent thin-layer electrochemistry (2 mV/s, insets) and spectra for [(CrTPP)O] in the absence (A) and presence (B) of 100 mM norbornene. The number on the spectrum means that it was taken at the indicated position during the thin-layer cyclic voltammogram. In the presence of norbornene, which starts to react on Au electrodes at ca. +0.9 V, the Au minigrid was potentiostated at +0.88 V for 10 min until the current died down, before the spectral acquisition. The offset of curve A-3 and sloping base line of curves B-2 and B-3 are artifacts due to dried electrolyte on the external thin-cell wall.

to this stabilization. However, $[(CrTPP)O]^+$ is a much more interesting oxidant chemically, due to its inner-sphere reactivity as an oxygen donor.

Addition of the olefinic substrate norbornene to the [(CrTPP)O] solution produces significant changes in its electrochemistry (Figure 2). Figure 2 shows the $[(CrTPP)O]^{+/0}$ cyclic voltammetry before (curve A) and after (curve B) norbornene addition. (Norbornene and the other olefins studied here are not electroactive at Pt electrodes in the potential region shown.) The major differences between curves A and B are that (i) the wave for re-reduction of $[(CrTPP)O]^+$ is attenuated in the presence of olefin (i.e., $i_{p,c}/i_{p,a} < 1$) and (ii) a new wave appears at $E^{\circ\prime} = +0.87$ V. The first difference is readily interpreted as a chemical step following electron transfer (called an EC reaction), where the chemical reaction occurs on roughly the same time scale as the voltammetric potential sweep.[12] Review of eq 1 and 2 shows that, if the EC chemical step involves oxygen transfer, a [(CrTPP)X] species should be generated, the Cr(III/IV) electrochemistry of which would be expected by reference to the [(CrTPP)Cl] and $[(CrTPP)ClO_4]$ potentials[11] to show up at a more positive potential than the $[(CrTPP)O]^{+/0}$ reaction.

Investigation of other olefinic substrates showed that *cis*-stilbene displays similar electrochemistry, giving an $i_{p,c}/i_{p,a}$ ratio of 0.77 and exhibiting a new, more positive wave like that in Figure 2B. However, styrene gave a ratio of only 0.93, and *trans*-stilbene gave a ratio of 1.00, showing no reactivity at all. It would seem that cis olefins are more reactive than trans olefins and that sterically strained olefins like norbornene are reactive. Cyclohexene gave an $i_{p,c}/i_{p,a}$ ratio of 0.34, but this is misleading because cyclohexene reacts directly with [(CrTPP)O] as revealed by spectral degradation.

To support the hypothesis of oxygen atom transfer to norbornene by reactions 1 and 2, a spectroelectrochemical experiment was done in which the $[(CrTPP)O]^+$ species was generated in an optically transparent thin-layer cell both in the presence and absence of olefin. In the thin layer cell experiment, the working electrode is an optically transparent gold minigrid, sandwiched in a thin layer of solution between two transparent walls, and in a spectrometer light beam. In a thin-layer cell, all the solution next to the minigrid working electrode can be exhaustively oxidized (or reduced) on the time scale of a slow voltammetric scan, and the composition of oxidized (or reduced) solution in the thin-layer cell can be monitored spectroscopically. The potential scan usually takes 1–2 min but can take longer.

The results of the optically transparent thin-layer experiment are summarized in Figure 3. The figure insets represent the current–potential patterns for the thin cell; the ΔE_p value (ideally zero) in the absence of olefin (Figure 3A, insert) is larger than that in Figure 2A due to the ohmic potential losses typical of thin-layer electrochemistry. The charge under the voltammetric peak represents the coulometric oxidation and reduction of all the material in the cell. Spectra 1–3 are taken during the voltammetric scans as indicated in the insets. Figure 3A clearly shows that, in the absence of olefin, the oxidized metalloporphyrin $[(CrTPP)O]^+$ generated by the electrochemical reaction is stable on the time scale of the experiment. Both the charge due to oxidation of [(CrTPP)O] and its original spectrum are quantitatively recovered upon re-reduction of the oxidized species. Neither the [(CrTPP)O] charge or spectrum is recovered in a cyclic potential scan conducted in the presence of olefin, however, as shown in Figure 3B. The spectral product seen upon oxidation in Figure 3B (---) is that of a (CrTPP)X species. The oxo ligand has been transferred irreversibly, from $[(CrTPP)O]^+$ to the substrate. The transformation is the same as but is more complete than that in Figure 2B, due to the slower time scale of the thin-layer experiment and its capacity to effect complete coulometric oxidation.

Confirmation of our assertion of oxygen atom transfer as in reactions 1 and 2 is supported by detection of the epoxide product. This was done by electrolyses of a larger volume solution of [(CrTPP)O] first in the absence and then in the presence of olefin. The course of the electrolysis was followed by UV–vis spectroscopy and cyclic voltammetry, and the resulting solution was analyzed directly by gas chromatography for product formation. For a system in which the electrogenerated species ($[(CrTPP)O]^+$) is stable, this experiment can supply a great deal of information. The charge passed in both the (CrTPP)O and (CrTPP)O/norbornene electrolyses gave $n = 0.80 \pm 0.05$. The spectroscopic data paralleled that shown in Figure 3. At the end of an electrolysis of a mixture of [(CrTPP)O] and norbornene (norbornene in 100× excess), a new chromatographic peak was detected at precisely the same retention time as observed for authentic *exo*-norbornene epoxide, confirming oxygen transfer from metalloporphyrin to olefin. Quantitative chromatographic determination of epoxide product reveals a 1:1 stoichiometry between the charge passed to form $[(CrTPP)O]^+$ and epoxide detected; the yield of epoxide is 98% based on charge passed.

The above experiments provide strong evidence that oxygen atom transfer occurs from electrochemically generated Cr(V) and that reaction in the presence of substrate is irreversible, consumes all the Cr(V), and produces epoxide in close to 100% yield. With these observations in mind, we next considered the [(CrTPP)Cl]/iodosobenzene/olefin system.

(CrTPP)Cl/Iodosobenzene/Olefin System. Our goal with respect to this chemistry is to define initially formed and intermediate species and to make some statement about how the system is able to epoxidize olefins. Our first experiment along these lines aimed at determination of the *stoichiometry* of the iodosobenzene/[(CrTPP)Cl] reaction. We mixed stoichiometric amounts of solid [(CrTPP)Cl] and iodosobenzene in glass vials, added methylene chloride solvent, incubated the mixture 90 min, and took UV–vis spectra. As seen in Figure 4, in the product solution spectrum, with increasing proportions of iodosobenzene there is a smooth conversion (three isosbestic points) from the initial spectrum (-●-), and at a 2:1 [(CrTPP)Cl]:iodosobenzene mixture, the product spectrum furthermore shows *no* residual spectral features of the initial [(CrTPP)Cl] spectrum. This is inconsistent with a simple oxygen atom transfer to give a six-coordinate oxochlorochromium porphyrin as suggested[6b] in experiments where larger amounts of iodosobenzene were added. We speculate from this result that in the 2:1 mixture an oxo-bridged dimer may be present. The final spectrum of Figure 4 is in fact remarkably similar to that of [(CrTPP)O] but must be different from that species, since [(CrTPP)O] cannot epoxidize olefins by itself but the solutions of Figure 4 can, as shown by chromatographic detection of norbornene epoxide after addition of norbornene. Addition of

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(12) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; pp 451–455.

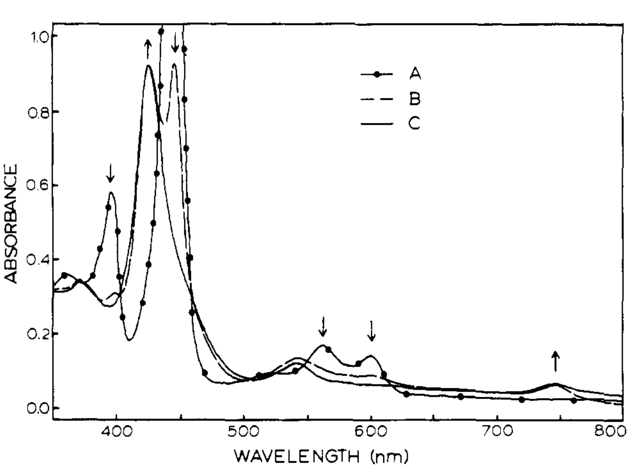


Figure 4. Spectrophotometric titration of 1 × 10^{-5} M [(CrTPP)Cl] with iodosobenzene. Curves A–C contain 0, 0.2 × 10^{-5}, and 0.5 × 10^{-5} M iodosobenzene, respectively; each solution is incubated 90 min prior to measurement.

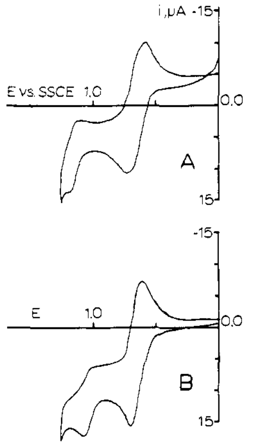


Figure 5. Cyclic voltammetry (50 mV/s) of 1.0 mM [(CrTPP)Cl]/0.5 mM iodosobenzene mixture in 0.2 M Bu_4NClO_4/methylene chloride, untreated (A) and treated (B) with solid KOH. The solutions contain no olefin.

chloride ion or iodobenzene to solutions of [(CrTPP)O] does not impart an ability to epoxidize olefins.

There must, however, be some connection between authentic [(CrTPP)O] and the product of a 2:1 [(CrTPP)Cl]:isodosobenzene mixture, since [(CrTPP)O] is synthesized by treatment of [(CrTPP)Cl] with excess iodosobenzene. Review of the synthesis of [(CrTPP)O] shows that, after iodosobenzene is reacted with [(CrTPP)Cl], the reaction mixture is treated with solid KOH and passed through an alumina column to yield [(CrTPP)O]. We have found that, when a 2:1 mixture of [(CrTPP)Cl] and iodosobenzene is treated with solid KOH, the spectrum of [(CrTPP)O] is obtained, and, when norbornene is added, no norbornene epoxide is chromatographically detected. In a complementary experiment, a solution that was 2:1 [(CrTPP)Cl]:iodosobenzene and contained no olefin was examined by cyclic voltammetry both before (Figure 5A) and after (Figure 5B) treatment with KOH. Note the irreversible wave at +1.07 V apparent after treatment with KOH. The electrochemistry of free chloride ion (as the tetraethylammonium salt) exhibits an irreversible wave in methylene chloride at almost exactly this potential. The wave in Figure 5B is almost certainly due to free chloride ion, and its presence after treatment with KOH leads one to conclude that, prior to treatment with KOH, the chloride was somehow bound so as to be electroinactive. Treatment with KOH both frees the bound chloride and takes away the system's ability to epoxidize olefins. (Experiments were also done in which an excess (>10×) of iodosobenzene was added to a dilute solution of [(CrTPP)Cl] and the solution was monitored spectroscopically. The results (Figure 6) show two things. First, at early times, the spectrum is that of a Cr(IV) species, implying that the Cr(V) species of Groves' work[6] is not formed by direct means but through a Cr(IV) intermediate. Second, this reaction mixture shows no isosbestic points and in fact is found to undergo complete spectral decay (no Soret band) when left overnight. The excess iodosobenzene brings about a slow blue shift in the Soret band, probably indicating formation of Cr(V) as seen by Groves.[6] We have not studied this spectroscopically unstable situation further.)

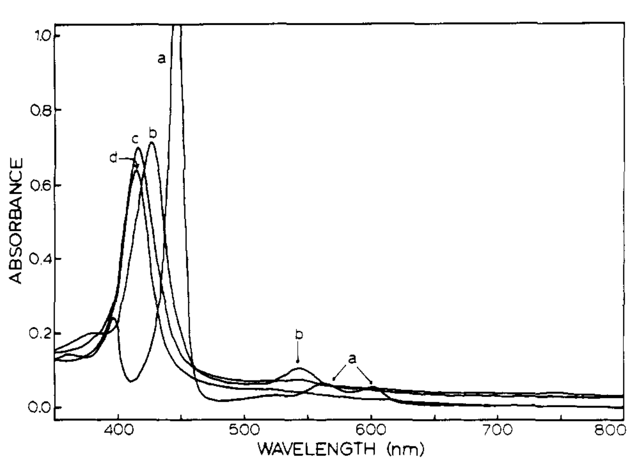
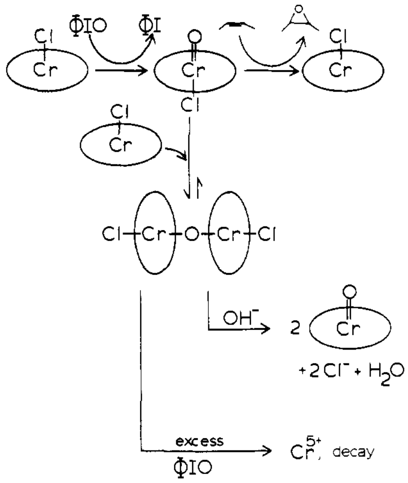


Figure 6. Reactivity of 1 × 10^{-5} M [(CrTPP)Cl] with excess iodosobenzene: (a) initial; (b) 3 min; (c) 10 min; (d) 40 min.

Scheme II



On the basis of the above results, the chemistry in Scheme II is proposed for iodosobenzene/[(CrTPP)Cl] mixtures. It seems logical that the first step would be a biomolecular oxygen atom transfer. The net Cr:O ratio of 2:1 for complete [(CrTPP)Cl] consumption and the electrochemically inferred requirement of bound chloride suggests the oxo-bridged dimer with bound chloride shown. While the involvement of metalloporphyrin–iodosobenzene adducts is not easily ruled out, it is difficult to imagine how such adducts would fit in with the 2:1 stoichiometry of the reaction. Treatment of the dimer with hydroxide gives [(CrTPP)O] and free chloride. Electrochemical data suggests that olefin epoxidation occurs only from the Cr(V) state, so we suggest a monomer/dimer equilibrium favoring the dimer. Disproportionation of the dimer into Cr(V) and Cr(III) would permit olefin epoxidation via Cr(V) even though much of the metalloporphyrin is present as dimer. This is consistent with Groves' observation[6c] of a Cr(V) ESR signal in solutions that we propose contain mainly Cr(IV). The importance of the chloride ligand in this scheme is unclear, but both the 2:1 [(CrTPP)Cl]:iodosobenzene system, which contains chloride, and the [(CrTPP)O] system, studied electrochemically in the absence of chloride, produce epoxide.

In summary, then, it is possible to generate a Cr(V) oxoporphyrin species by two distinct pathways. Both the chemical (iodosobenzene) and electrochemical pathways produce an active species whose chemical reactivity with olefins is distinctive. Since the electrochemically generated species must be Cr(V), we conclude that the active species in both Scheme II and eq 1 and 2 is a Cr(V) oxo–porphyrin.

Relevance to Natural Systems

As given in Scheme I, the active species in the cytochrome P-450 mechanism is supposed to be an Fe(IV)–oxo porphyrin radical cation, a formal Fe(V) species. Our electrochemically generated $[(CrTPP)O]^+$ state is reactive in a formally similar fashion. There are, of course, considerable differences between cytochrome P-450 and the present work, notably that cytochrome P-450 is able to activate dioxygen to form its active state and is kinetically faster. It was mainly because of the slow $[(CrTPP)O]^+$ reaction kinetics that we were able to study it effectively. The dimer chemistry proposed in Scheme II has no analogue in cytochrome P-450 chemistry, but free heme also shows a rich oxo-bridged dimer chemistry. It seems likely that immobilization of the metalloporphyrin in the polypeptide is important in preventing dimer formation, as has been shown for hemoglobin and myoglobin.[13]

In principle, it should be possible to extend the $[(CrTPP)O]^{+/0}$ strategy to different metal ions, specifically iron and manganese. Also, the methods described here should be useful in extending oxo-porphyrin reactivity to other substrates besides olefins.

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Equilibria and Mechanism of the Interaction of Indium(III) with the Indicator 1-(2-Pyridylazo)-2-naphthol (PAN)

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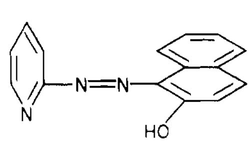
The interaction between In(III) and the indicator PAN (HL) has been investigated at 25 °C, ionic strength 0.2 M ($NaClO_4$), and $[H^+] = 0.003–0.2$ M in methanol–water mixtures of different composition. One complex, InL^{2+}, has been observed, with $K = [InL^{2+}][H^+]/[In^{3+}][HL] \simeq 1.2$ in pure water. The formation of this complex proceeds mainly via three parallel paths, one involving $InOH^{2+}$ and HL, and two proton-ambiguous paths, involving In^{3+} and HL, and $InOH^{2+}$ and H_2L^+, respectively. Rate constants for these processes (upper limits only for the proton-ambiguous paths) are reported. The unusually low values of the forward rate constants are interpreted in terms of an internal hydrogen-bond mechanism.

Introduction

Whereas the mechanism of complex formation of divalent metal ions is quite well established,[1] the position with respect to tervalent cations is much less clear. This is mainly due to the extensive hydrolysis and polymerization,[2] which seriously limit the range of concentrations and acidity that can be investigated. In addition, the presence of differently protonated forms of both metal ions and ligands introduces proton ambiguity,[3] which often makes it impossible to assign the observed rate constants uniquely to a given reaction path.

Furthermore, as far as tervalent metal ions of the group 13[21] atoms such as Al(III), Ga(III), and In(III) are concerned, there is the additional difficulty of finding ligands suitable for spectrophotometric monitoring of their complexation.

This difficulty can be overcome by using metallochromic indicators, and we have done so[4,5] in the course of our program of studying substitution reactions at tervalent cations. In the present paper, we present the results of an investigation of the reaction of In(III) with PAN (1-(2-pyridylazo)-2-naphthol)



a diprotic acid that, in its monoprotonated, neutral form, we shall designate by HL. Unfortunately, this indicator does not dissolve in pure water; the experiments therefore had to be carried out in the presence of methanol.

Experimental Section

Chemicals. All reagents were analytical grade. PAN was Carlo Erba RP and was used without further purification. Indium perchlorate solutions were prepared by dissolving the pure metal in perchloric acid. The resulting solution was titrated as described previously.[5] Triply distilled water was used to prepare the solutions. The temperature was 25.0 ± 0.1 °C. The ionic strength was 0.2 M obtained with sodium perchlorate. Stock solutions of PAN were 10^{-3} M in 60% aqueous methanol.

Methods. (a) Equilibria. Spectrophotometric titrations were carried out by using a Perkin-Elmer E 200 double-beam spectrophotometer. Increasing amounts of $In(ClO_4)_3$ were added with a microsyringe to a solution of the ligand already thermostated in the spectrophotometric cell.

The acid concentration and solvent composition were kept constant at the desired values during each titration. A wavelength of 545 nm was chosen since in this region the spectrum of the complex shows a broad shoulder whereas the absorptivity of the ligand is low and the relative difference of absorptivities is most favorable.

(b) Kinetics. Kinetic runs were carried out in a Durrum-Gibson stopped-flow apparatus. All experiments were performed under pseudo-first-order conditions ($c_M \gg c_L$, where c_M and c_L are the stoichiometric concentrations of metal and ligand, respectively), either by mixing two solutions containing metal ion and ligand, respectively, or by mixing a solution containing both constituents with a solution of perchloric acid. In the latter case the decrease of absorbance owing to the decomposition of the complex was recorded. The agreement between the two procedures was within the limit of experimental error. The data were evaluated with the aid of a microcomputer (Radio Shack TRS 80). The signal from the stopped-flow apparatus was fed into a Biomation 802 transient recorder and from there, through an appropriate interface, was transferred in digital form to the computer and processed as described elsewhere.[6] The maximum spread between repeated runs (four to seven) never exceeded 10%.

Measurements were again carried out at a wavelength of 545 nm.

Results

Equilibrium Constants. The equilibria of the In(III)–PAN system have been identified, and the relevant equilibrium pa-

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