

Oxygen Atom Transfer Reactions of Chromium Porphyrins: An Electronic Rationale for Oxo Transfer versus μ -Oxo Product Formation

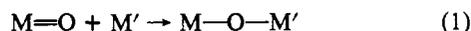
L. Keith Woo,^{*,1a,b} James G. Goll,^{1b} Lisa M. Berreau,^{1b} and Rob Weaving^{1c}

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.
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Abstract: Treatment of (*meso*-tetra-*p*-tolylporphyrinato)chromium(IV) oxide, (TTP)Cr=O, with (octaethylporphyrinato)chromium(III) chloride, (OEP)Cr—Cl, in benzene results in the reversible exchange of axial ligands to form (TTP)Cr—Cl and (OEP)Cr=O. The net result is a formal one-electron redox process. This occurs with a second-order rate constant of $0.14 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$ to form an equilibrium mixture with $K = 2.7 \pm 0.1$ at 30 °C ($\Delta H^\ddagger = 15.4 \pm 0.7 \text{ kcal/mol}$, $\Delta S^\ddagger = -12 \pm 2 \text{ cal/(mol}\cdot\text{K)}$, $\Delta H^\circ = -2.0 \pm 0.4 \text{ kcal/mol}$, and $\Delta S^\circ = -4.6 \pm 1.2 \text{ cal/(mol}\cdot\text{K)}$). Use of pivalate in place of chloride on the Cr(III) complex causes no significant change in the rate of this one-electron redox process. The sterically protected Baldwin's C_2 -capped (porphyrinato)chromium(III) complex, (CAP)Cr—Cl, also undergoes oxygen atom transfer with (OEP)Cr=O at a similar rate. In addition, excess chloride inhibits the rate of oxygen transfer with chlorochromium(III) complexes. These results support an inner-sphere mechanism involving a μ -oxo intermediate which is formed after an initial ligand (chloride or pivalate) dissociation from the chromium(III) reductant.

Introduction

Many oxygen-transfer reactions are important in synthetic and biological oxidations. Enzymes such as cytochrome P-450, peroxidases, catalases, xanthine oxidase, sulfite oxidase, and nitrate reductase operate via atom-transfer processes in the course of oxidizing an organic substrate.²⁻⁶ Holm⁷ and Jorgensen⁸ have recently reviewed the subject of oxygen atom transfer. Most examples of oxygen atom transfer occur between a metal oxo donor and non-metal oxo acceptors such as alkenes and phosphines. Examples of inter-metal oxygen atom transfer are much less common. Typically, reactions of a metal oxo complex with transition metal reducing agents yield μ -oxo-bridged products and involve a net one-electron transfer. This process has been termed by Holm as incomplete atom transfer (eq 1), where M=O is an



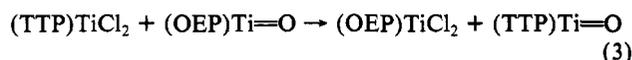
oxo donor and M' is an oxo acceptor (ancillary ligands on M and M' have been omitted).⁷ When the oxo ligand is cleaved completely from the donor species, the process is termed complete atom transfer (eq 2). Documented examples of complete inter-metal



oxo transfer thus far have been limited to molybdenum,⁷ tungsten,^{7,9} and vanadium¹⁰ complexes. Oxo transfer between two ruthenium centers has been implicated in the aerobic epoxidation of alkenes catalyzed by ruthenium porphyrins.¹¹ Complete oxygen atom transfer reactions as represented by eq 2 formally mediate a two-electron redox process.

The fundamental factors which dictate the occurrence of complete versus incomplete oxygen atom transfer are not well understood. However, it is clear that steric factors can promote

complete oxygen atom transfer by destabilizing the μ -oxo species.¹² Incomplete oxygen atom transfer (eq 1) typically involves a net one-electron change. However, complete oxygen atom transfer can mediate both one- and two-electron redox processes. Thus, an understanding of the factors that influence the number of redox equivalents exchanged during an oxygen atom transfer is also not well developed. For example, we have discovered an oxo-transfer reaction which involves no net electron transfer, as illustrated by eq 3.^{13,14}



In the work presented here, we focus on a more detailed account of oxygen atom transfer reactions of chromium porphyrin complexes. Much research has focused on the use of these complexes as catalysts for the transfer of an oxo group to organic molecules, presumably via a Cr=O species. A great deal of our knowledge of these oxo-transfer reactions derives from studies by Groves¹⁵ and Bruce.¹⁶ We recently reported that complete, inter-metal oxygen atom transfer can be observed directly between chromium porphyrins.¹³

Experimental Section

Instrumentation. UV-visible spectroscopic measurements were obtained on a Hewlett-Packard HP 8452A diode array spectrophotometer. IR spectra were recorded on either an IBM IR98 Fourier transform spectrometer or a Perkin-Elmer 680 IR spectrometer using mineral oil mulls. NMR spectra were recorded on a Varian VXR 300-MHz spectrometer. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY.

Chemicals. Benzene and tetrahydrofuran were distilled from purple solutions of sodium/benzophenone, and dichloromethane was dried with

(12) Holm, R. H.; Berg, J. M. *Pure Appl. Chem.* **1984**, *56*, 1645.

(13) Woo, L. K.; Hays, J. A.; Goll, J. G. *Inorg. Chem.* **1990**, *29*, 3916.

(14) Abbreviations: TTP = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; POR = general porphyrinato dianion.

(15) (a) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613. (b) Groves, J. T.; Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* **1981**, 1165. (c) Groves, J. T.; Kruper, W. J., Jr. *Isr. J. Chem.* **1985**, *25*, 148. (d) Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169.

(16) (a) Yuan, L.-C.; Bruce, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 512. (b) Yuan, L.-C.; Calderwood, T. S.; Bruce, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 8273. (c) Bruce, T. C. *Aldrichimica Acta* **1988**, *21*, 87. (d) Garrison, J. M.; Bruce, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 191. (e) Garrison, J. M.; Ostović, D.; Bruce, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 4960. (f) Garrison, J. M.; Lee, R. W.; Bruce, T. C. *Inorg. Chem.* **1990**, *29*, 2019.

(1) (a) 1990-1995 Presidential Young Investigator. (b) Iowa State University. (c) Undergraduate exchange student, Nottingham Polytechnic, England.

(2) *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986.

(3) Guengerich, F. P.; MacDonald, T. C. *Acc. Chem. Res.* **1984**, *17*, 9.

(4) Deisseroth, A.; Dounce, A. L. *Physiol. Rev.* **1970**, *60*, 319.

(5) Schonbaum, G. R.; Chance, B. *Enzymes (3rd Ed.)* **1976**, *13*, 363.

(6) Holm, R. H. *Coord. Chem. Rev.* **1990**, *100*, 183.

(7) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(8) Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.

(9) Templeton, J. E.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248.

(10) Zhang, Y.; Holm, R. H. *Inorg. Chem.* **1990**, *29*, 911.

(11) Groves, J. T.; Quinn, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5790.

Table I. T_1 Values of (Porphyrinato)chromium Oxo Complexes and Anthracene in Benzene- d_6

compd	signal	T_1 (s)	compd	signal	T_1 (s)
(OEP)Cr=O	meso-H	0.40 (6)	(TPP)-	methyl-H	1.12 (3)
(OEP)Cr=O	methyl-H	0.52 (5)		Cr=O	
(TTP)Cr=O	β -H	0.90 (3)	anthracene	9,10-H	1.16 (2)

Table II. Molar Absorptivities of Metalloporphyrins in Benzene at 572 nm Used for Kinetics

compd	molar absorptivity $\times 10^{-4}$ ($M^{-1} cm^{-1}$)	compd	molar absorptivity $\times 10^{-4}$ ($M^{-1} cm^{-1}$)
(TTP)Cr=O	0.307	(TTP)Cr-Cl	0.641
(OEP)Cr=O	2.69	(OEP)Cr-Cl	0.761

calcium hydride prior to distillation. Ethanol-free chloroform was prepared by washing with water and distilling from sodium carbonate. Pentane and *N,N*-dimethylformamide were stored over molecular sieves overnight. All other materials were used as received unless otherwise indicated. Tetraatolylporphyrin, H_2 (TTP), was prepared by the method of Adler¹⁷ and purified by the method of Dolphin.¹⁸ Baldwin's C_2 -capped porphyrin, H_2 (CAP), was made by literature procedures.¹⁹ (Tetraatolylporphyrinato)chromium chloride, (TTP)Cr-Cl, (octaethylporphyrinato)chromium chloride, (OEP)Cr-Cl, and (CAP)Cr-Cl were prepared by Adler's method²⁰ as modified by Hoffman and Basolo.²¹ (TTP)Cr=O was prepared by a method developed by Groves.^{22,23} (OEP)Cr=O was prepared by the method described by Büchler.^{24,25} (OEP)Cr(O₂CC(CH₃)₃) was prepared using a modification of a previously developed procedure.²⁶ (TTP)Cr=O, (OEP)Cr=O, (TTP)Cr-Cl, and (CAP)Cr-Cl were recrystallized from benzene/pentane. (OEP)Cr-Cl was recrystallized from dichloromethane/pentane. The concentrations of stock solutions were determined by UV-vis spectroscopy prior to use.

Equilibrium Measurements. Samples for equilibrium determinations for the chromium oxo-chloro exchange were prepared by adding known volumes of stock solutions of known concentrations of all components of the equilibrium: (OEP)Cr-Cl, (OEP)Cr=O, (TTP)Cr-Cl, (TTP)Cr=O, and an internal standard, anthracene. The solvent was evaporated on a high-vacuum line. The NMR solvent, benzene- d_6 , was transferred under reduced pressure, and the tube was flame-sealed under approximately 600 Torr of nitrogen. The equilibrium constant was determined by integrating the methyl signal of (TTP)Cr=O and the methyl signal of (OEP)Cr=O. These signals were compared to the integrated signal of the 9,10-hydrogens of anthracene to verify that mass balance was maintained. The spectrum was monitored in a temperature-controlled probe until no further change was observed. T_1 values of the (porphyrinato)chromium oxo complexes and anthracene were obtained by standard NMR techniques.²⁷ The values are given in Table I. Relaxation delays for the NMR integrations were set at greater than 5 times the longest T_1 .

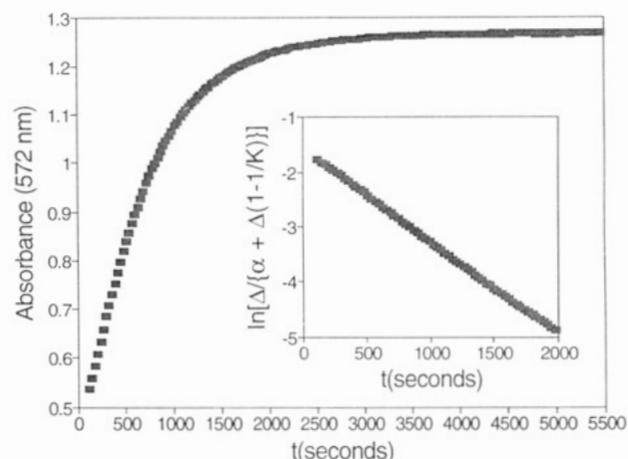
Kinetic Measurements. Rate data for the (POR)Cr=O/(POR)Cr-Cl systems were obtained on a UV-visible spectrometer equipped with a thermally regulated cell holder. Solutions of the oxo and the appropriate chloride complexes were loaded in a 1-mm cuvette under a nitrogen atmosphere. The capped cuvette was placed in the cell holder, and the

Table III. Equilibrium Constants for Eq 4 in Benzene- d_6

T ($^{\circ}C$)	K	T ($^{\circ}C$)	K
10	3.7 ± 0.1	30	2.7 ± 0.1
20	3.1 ± 0.1	40	2.6 ± 0.1

Table IV. Forward Rate Constants for Eq 4 in Benzene

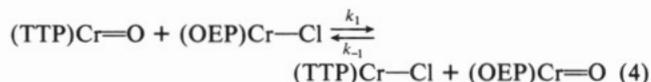
T ($^{\circ}C$)	k_1 ($M^{-1} s^{-1}$)	T ($^{\circ}C$)	k_1 ($M^{-1} s^{-1}$)
30	0.14 ± 0.01	50	0.70 ± 0.06
40	0.28 ± 0.06	60	1.51 ± 0.14

**Figure 1.** Representative absorption (572 nm) vs time plot for eq 4 at 50 $^{\circ}C$. [(TTP)Cr=O]₀ = 1.12×10^{-3} M, and [(OEP)Cr-Cl]₀ = 4.63×10^{-4} M. Inset: plot of $\ln[\Delta/(\alpha + \Delta(1-1/K))]$ vs t .

run was monitored at 572 nm. Molar absorptivities of the metalloporphyrins at 572 nm are given in Table II. A final spectrum from 500 to 700 nm was taken to verify that decomposition of the oxo complex did not occur during the course of the run. Typical initial concentrations ranged from 4.64×10^{-4} [(OEP)Cr-Cl] to 1.12×10^{-3} M [(TTP)Cr=O]. Kinetic runs were also done in the presence of excess chloride in the form of bis(triphenylphosphoranylidene)ammonium chloride. Rate constants were obtained using an integrated rate law for second-order equilibrium reactions as derived by King.²⁸

Results

Reduction of Oxochromium(IV) Porphyrin with Chromium(III) Porphyrin. Treatment of (TTP)Cr=O with (OEP)Cr-Cl in benzene results in spectral changes which are consistent with the transfer of a terminally bound oxygen ligand between two metal complexes shown in eq 4. The UV-vis spectrum of the resulting



mixture contains two new Soret bands indicating the formation of (TTP)Cr-Cl (450 nm) and (OEP)Cr=O (416 nm). The band centered at 434 nm is a combination of the Soret bands of (TTP)Cr=O (430 nm) and (OEP)Cr-Cl (436 nm) and does not completely disappear, indicating that eq 4 is an equilibrium process. Throughout the reaction, well-defined isosbestic points are observed at 531 and 559 nm. The reversibility of eq 4 can be confirmed by the complementary experiment in which (OEP)Cr=O is treated with (TTP)Cr-Cl. This generates a final UV-vis spectrum that has peak positions identical to those observed for the forward process.

Since the Cr(IV) oxo complexes are low-spin d^2 and diamagnetic, it is also possible to independently establish the extent of reaction by ¹H NMR spectroscopy. This is most conveniently accomplished by monitoring the methyl proton signal of (TTP)Cr=O (2.38 ppm) and the methyl resonance of (OEP)Cr=O

(17) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(18) Rousseau, K.; Dolphin, D. *Tetrahedron Lett.* **1974**, *48*, 4251.

(19) Almog, J.; Baldwin, J. E.; Crossley, M. J.; Debernardis, J. F.; Cyer, R. L.; Huff, J. R.; Peters, M. K. *Tetrahedron* **1981**, *37*, 3589.

(20) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(21) Summerville, D. A.; Jones, R. D.; Hoffman, B. M.; Basolo, F. *J. Am. Chem. Soc.* **1977**, *99*, 8195.

(22) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C.; Butler, W. M. *Inorg. Chem.* **1982**, *21*, 1363.

(23) UV-vis (toluene): λ_{max} (log ϵ) 544 (4.25), 434 (5.25), 376 nm (4.35). ¹H NMR (CDCl₃): δ 9.08 (s, 8 H, β -H), 8.11 (d, 8 H, α -H), 7.55 (d, 8 H, m -H), 2.69 (s, 12 H, CH₃).

(24) Büchler, J. W.; Lay, K. L.; Castle, L.; Ullrich, V. *Inorg. Chem.* **1982**, *21*, 842.

(25) UV-vis (toluene): λ_{max} (log ϵ) 572 (4.43), 534 (4.20), 416 nm (4.94). ¹H NMR (CDCl₃): 10.89 (s, 4 H, m -H), 4.13 (m, 16 H, CH₂), 1.95 (t, 24 H, CH₃).

(26) Woo, L. K.; Goll, J. G.; Czapl, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478.

(27) Martin, M. L.; Delpuech, J.-J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden and Son, Inc.: Philadelphia, PA, 1980; pp 254-259.

(28) King, E. L. *Int. J. Chem. Kinet.* **1982**, *14*, 1285. For a second-order reversible reaction, $A + B \rightleftharpoons C + D$, Δ is the displacement of any species from its equilibrium value. $\Delta = [A] - [A]_{eq} = [B] - [B]_{eq} = [C]_{eq} - [C] = [D]_{eq} - [D]$ and $\alpha = [A]_{eq} + [B]_{eq} + ([C]_{eq} + [D]_{eq})/K$.

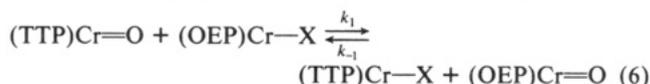
(1.84 ppm) against an internal standard, the 9,10-protons of anthracene (8.15 ppm) in benzene- d_6 . Flame-sealed NMR tubes containing mixtures of (TTP)Cr=O, (OEP)Cr—Cl, (OEP)Cr=O, (TTP)Cr—Cl, and anthracene in benzene- d_6 maintain mass balance during the course of the experiment in terms of total oxo complex concentration. The equilibrium constants for eq 4 over a 30-deg range were measured by ^1H NMR spectroscopy and are listed in Table III. The thermodynamic parameters, $\Delta H^\circ = -2.0 \pm 0.4$ kcal/mol and $\Delta S^\circ = -4.6 \pm 1.2$ cal/(mol·K), were derived from this temperature dependence.

The forward rates of eq 4 in benzene were examined spectrophotometrically by following the absorbance changes at 572 nm, as shown in Figure 1. All of the compounds involved, (OEP)Cr—Cl, (OEP)Cr=O, (TTP)Cr—Cl, and (TTP)Cr=O, obey Beer's law over the concentration range 1.0×10^{-4} to 4.0×10^{-3} M. This indicates that self-association does not complicate the mechanistic analyses. In all kinetic runs, the data were found to obey an integrated rate law for reversible second-order reactions (eq 5).²⁸ Plots of $\ln[\Delta/(\alpha + \Delta(1 - 1/K))]$ vs t are linear for

$$\ln \left[\frac{\Delta}{\alpha + \Delta(1 - 1/K)} \right] = -\alpha k_1 t + \text{constant} \quad (5)$$

more than 3 half-lives. A typical plot is shown in the inset of Figure 1. Table IV summarizes forward rate constants as a function of temperature for eq 4.

Effect of Axial Ligands. Axial-ligand effects were studied in these systems by varying the monoanionic ligand on the starting chromium(III) porphyrin complexes as shown in eq 6. A com-



parison of two different axial ligands, pivalate and chloride, was made at 50 °C in benzene. Rates for eq 6 were found to have very little dependence on the nature of the axial ligand ($k_{\text{piv}} = 1.5 \pm 0.5$ and $k_{\text{Cl}} = 0.70 \pm 0.06$ M⁻¹ s⁻¹). Examination of other bulky ligands such as 2,6-diisopropylphenoxide and 1-adamantylxide were not possible due to solubility problems of the resultant chromium(III) porphyrin complexes.

Kinetics of Oxygen Atom Transfer as a Function of Added Axial Chloride. The rate of oxygen atom transfer between Cr^{IV}=O and Cr^{III}—Cl was studied as a function of added chloride ion. The source of Cl⁻ was particularly important. Tetra-*n*-butylammonium chloride salts react with (POR)Cr=O to produce Cr(III) complexes. This is presumably due to the hydrogen-abstrating ability of the chromium oxo complex.²⁴ Consequently, bis(triphenylphosphoranylidene)ammonium chloride, (PPN)Cl, was used as the external source of chloride. Because of the poor solubility of (PPN)Cl in benzene, these experiments were done in CH₂Cl₂ solutions. (PPN)Cl dissolves in CH₂Cl₂ to yield solutions having a molar conductance of $\Lambda = 101 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.²⁹ The dissociation constant for (PPN)Cl at 30 °C in CH₂Cl₂ is 4.58×10^{-4} .³⁰

The rate data from all CH₂Cl₂ experiments were found to follow second-order reversible kinetics (eq 5) for more than 3 half-lives. In the absence of Cl⁻, the rate constant for oxygen atom transfer between (TTP)Cr=O (1.15×10^{-3} M) and (OEP)Cr—Cl (4.84×10^{-4} M) in CH₂Cl₂ is 25.1 ± 3.6 M⁻¹ s⁻¹ at 30 °C. Under similar conditions except with 2.42×10^{-3} M (PPN)Cl present, the amount of free Cl⁻ in solution is 8.48×10^{-4} M and the [Cl⁻]/[(OEP)Cr—Cl] ratio is 1.8. In this case, the rate constant drops to 16.2 ± 0.08 M⁻¹ s⁻¹. When 4.84×10^{-3} M (PPN)Cl is used, the [Cl⁻]/[(OEP)Cr—Cl] ratio is $1.28 \times 10^{-3}/4.84 \times 10^{-4} = 2.6$ and the rate falls to 10.2 ± 0.9 M⁻¹ s⁻¹. Additionally, these experiments also allow a comparison of rates in two solvents. Rates were found to increase on changing solvents from benzene to CH₂Cl₂. A similar solvent effect has been observed for an analogous atom-transfer reaction between (OEP)Mn≡N and (TPP)Cr—Cl.³¹

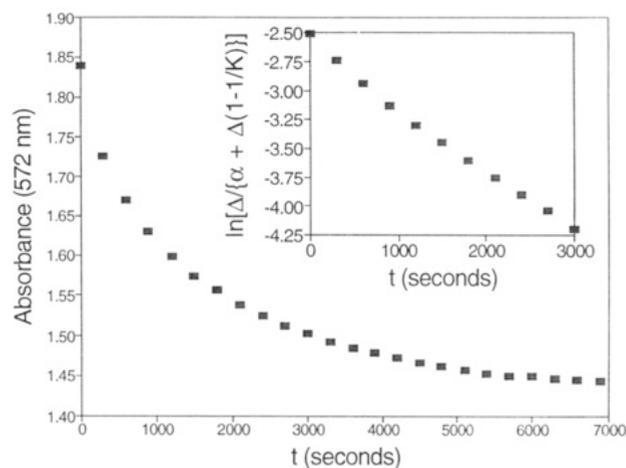


Figure 2. Representative absorption (572 nm) vs time plot for reaction 7 at 30 °C. [(OEP)Cr=O]₀ = 5.75×10^{-4} M, and [(CAP)Cr—Cl]₀ = 4.85×10^{-4} M. Inset: plot of $\ln[\Delta/(\alpha + \Delta(1 - 1/K))]$ vs t .

Reactions Involving a Sterically Encumbered Ligand. As a mechanistic probe, the chromium(III) complex of Baldwin's C₂-capped porphyrin, (CAP)Cr—Cl, was used in place of (TTP)Cr—Cl. In the capped complex, a pyromellitoyl group blocks the position trans to the chloride.³² When (CAP)Cr—Cl (2.16×10^{-3} M) was treated with (OEP)Cr=O (1.48×10^{-3} M) in C₆D₆, formation of (CAP)Cr=O and (OEP)Cr—Cl was observed by ^1H NMR spectroscopy at 50 °C as shown in eq 7. This is (CAP)Cr—Cl + (OEP)Cr=O ⇌ (CAP)Cr=O + (OEP)Cr—Cl (7)

clearly illustrated by the decrease in the meso-proton signal (10.59 ppm) of (OEP)Cr=O and the appearance of the two pyrrole β-proton signals (9.16 and 9.05 ppm) of (CAP)Cr=O.

The kinetic behavior of eq 7 in CH₂Cl₂ at 30 °C was monitored by UV-vis spectroscopy. A typical absorption decay curve at 572 nm for eq 7 is shown in Figure 2. As in all previous cases, the second-order integrated rate law, eq 5, was followed for more than 3 half-lives. A plot of $\ln[\Delta/(\alpha + \Delta(1 - 1/K))]$ vs t for reaction 7 is shown in the inset of Figure 2. The observed rate constant at 30 °C is $k = 0.26 \pm 0.05$ M⁻¹ s⁻¹. When a 10-fold excess of (PPN)Cl per chromium chloride is added, the rate of oxygen atom transfer between (OEP)Cr=O and (CAP)Cr—Cl drops to 0.010 ± 0.001 M⁻¹ s⁻¹.

Discussion

We have found that complete oxygen atom transfer between two metalloporphyrins can be achieved. It is possible to observe this process by using different porphyrin ligands as UV-vis and ^1H NMR spectroscopic labels. An additional benefit derived from the use of metalloporphyrins arises from the structural integrity maintained by these complexes throughout the reaction, eliminating complications due to ligand loss. Furthermore, stereochemical rearrangements found in other systems that undergo complete atom transfer are not possible here.^{6,9} Rate constants for reaction 4 have been measured in the forward direction over a 30-deg temperature span. These rate constants range between 0.14 and 1.51 M⁻¹ s⁻¹. The temperature dependence of the forward rate yields activation parameters of $\Delta H^\ddagger = 15.4 \pm 0.7$ kcal/mol and $\Delta S^\ddagger = -12 \pm 2$ cal/(mol·K).

Electrochemical studies on chromium porphyrins provide evidence which indicates that eq 4 does not involve an outer-sphere mechanism. For example, the half-wave reduction potential for the [(TTP)Cr—Cl]⁺/(TTP)CrCl couple occurs at $E_{1/2} = 0.80$ V vs SCE in CH₂Cl₂.^{33,34} The corresponding potential for reducing

(29) Algra, G. P.; Balt, S. *Inorg. Chem.* **1981**, *20*, 1102.

(30) Calculated from eq 1 in ref 29.

(31) (a) Neely, F. L. Ph.D. Dissertation, Georgia Institute of Technology, 1989. (b) Bottomley, L. A.; Neely, F. L. *Inorg. Chem.*, submitted for publication.

(32) Sabat, M.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 3715.

(33) Creager, S. E.; Murray, R. W. *Inorg. Chem.* **1985**, *24*, 3824.

(34) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 342.

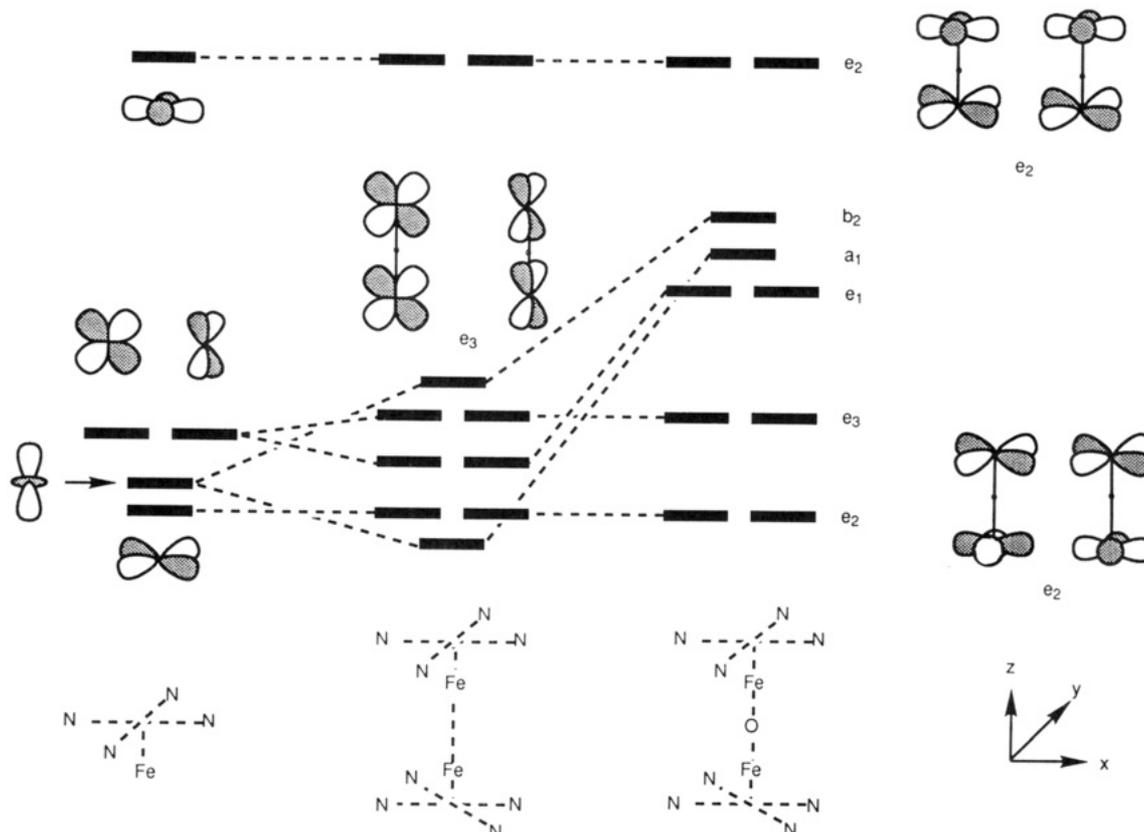
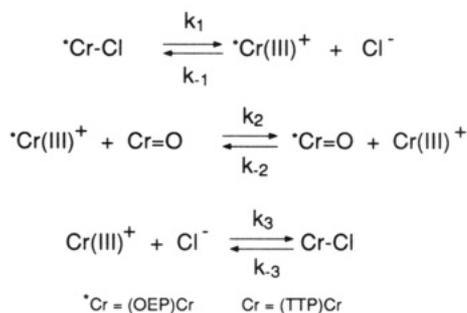


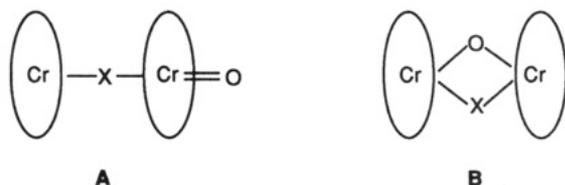
Figure 3. Building up of the orbitals of $[(\text{NH}_2)_4\text{Fe}-\text{O}-\text{Fe}(\text{NH}_2)_4]^{4+}$. From left to right: the orbitals of the pyramidal N_4Fe in which the Fe is displaced 0.5 Å out of the N_4 plane; the orbitals of two N_4Fe units brought to 3.526-Å separation between the irons; the orbitals of the composite oxo complex.

Scheme I

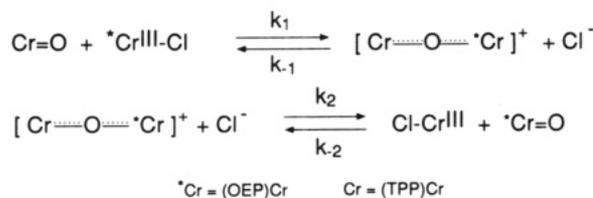


$(\text{TTP})\text{Cr}=\text{O}$ to $[(\text{TTP})\text{Cr}=\text{O}]^-$ occurs at $E_{1/2} = -1.12$ V vs SCE.³³ Thus, $(\text{TTP})\text{Cr}-\text{Cl}$ is not thermodynamically capable of reducing the chromium oxo porphyrin complex in an outer-sphere pathway.

Although eq 4 proceeds by an inner-sphere process, mechanistic aspects of this reaction are complicated by the bridging abilities of both the chloro and the oxo ligands. In order to address this issue, we have compared the reduction of $(\text{TTP})\text{Cr}=\text{O}$ with that of both $(\text{OEP})\text{Cr}-\text{Cl}$ and $(\text{OEP})\text{Cr}-\text{O}_2\text{CC}(\text{CH}_3)_3$. The rate constants for these two reactions are very similar, regardless of whether chloride ($k_{\text{Cl}} = 0.70 \text{ M}^{-1} \text{ s}^{-1}$) or pivalate ($k_{\text{piv}} = 1.5 \text{ M}^{-1} \text{ s}^{-1}$) is the axial ligand on chromium(III). Because pivalate is a much bulkier ligand, this rate comparison serves to rule out a binuclear intermediate in which the monoanionic ligand is involved in bridging the two metals. Thus the μ -chloro-bridged adduct, A, and the doubly bridged species, B, must not be important intermediates along the reaction pathway.



Scheme II



It is very likely that the redox reaction between $(\text{TTP})\text{Cr}=\text{O}$ and $(\text{OEP})\text{Cr}-\text{Cl}$ involves a μ -oxo intermediate. Formation of this intermediate can occur either by an $\text{S}_{\text{N}}1$ -type mechanism (Scheme I) or by an $\text{S}_{\text{N}}2$ -type mechanism (Scheme II).

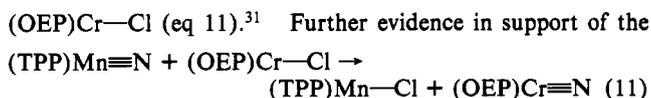
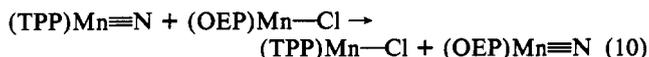
These two processes can be distinguished by their chloride ion dependencies. The $\text{S}_{\text{N}}1$ mechanism has a forward rate constant which has an inverse dependence on the chloride ion concentration (eq 8). However, the forward rate constant for the $\text{S}_{\text{N}}2$ mech-

$$k_f = \frac{k_1 k_2}{k_{-1}[\text{Cl}^-] + k_2[(\text{TTP})\text{Cr}=\text{O}]} \quad (8)$$

anism is independent of the chloride concentration (eq 9). Since

$$k_f = \frac{k_1 k_2 [\text{Cl}^-]}{k_{-1}[\text{Cl}^-] + k_2[\text{Cl}^-]} = \frac{k_1 k_2}{k_{-1} + k_2} \quad (9)$$

the observed oxygen/chloride exchange rates between $(\text{TTP})\text{Cr}=\text{O}$ and $(\text{OEP})\text{Cr}-\text{Cl}$ are inhibited by added Cl^- , the lowest energy pathway for eq 4 must involve an initial dissociation of Cl^- from the chromium(III) complex. Conductivity measurements by Kadish have established that chlorochromium(III) porphyrin complexes do dissociate in CH_2Cl_2 to a measurable extent.³⁵ The $\text{S}_{\text{N}}1$ -type mechanism for reaction 4 is analogous to the process proposed for the N/Cl exchange between $(\text{TTP})\text{Mn}\equiv\text{N}$ and $(\text{OEP})\text{Mn}-\text{Cl}$ (eq 10)²⁶ and between $(\text{TTP})\text{Mn}\equiv\text{N}$ and



chloride dissociation path is apparent when the trans position of the chlorochromium(III) complex is sterically blocked using a pyromellitoyl cap. Even though an S_N2 process is no longer possible, the oxygen atom transfer reaction between $(OEP)Cr=O$ and $(CAP)Cr-Cl$ (eq 7) is still found to proceed. In the capped system, the reaction rate is comparable to that for the uncapped analog. As evidence for the preequilibrium chloride dissociation step, we find that added chloride strongly inhibits oxygen atom transfer from $(OEP)Cr=O$ to $(CAP)Cr-Cl$.

The reduction products of oxochromium porphyrins are strongly dependent on the nature of the reducing agent.¹³ When a chromium(II) porphyrin is the reductant, the reaction stops at μ -oxo formation (eq 12).³⁶ However, use of chromium(III) porphyrins

$$(TPP)Cr=O + (TPP)Cr \rightarrow (TPP)Cr-O-Cr(TPP) \quad (12)$$

results in reversible oxygen atom transfer. An examination of the electronic structure of μ -oxometalloporphyrin dimers provides a possible rationale for the stark contrast in these processes. The d-orbital energy level for $[Fe(TTP)]_2O$ shown in Figure 3 was derived by Tatsumi and Hoffmann³⁷ using extended Hückel calculations on $[(NH_2)_4Fe-O-Fe(NH_2)_4]^{4-}$ as a computational model. To a first approximation, this energy level diagram should apply to the $[(POR)Cr-O-Cr(POR)]^{0,+}$ system. When Cr(II) is the reductant, the neutral μ -oxo product has six d-electrons. The magnetic moment for this complex at 300 K was found to be $1.61 \mu_B$ per Cr atom.^{36b} This is consistent with an $S = 2$ electronic state arising from an $(e_2)^4(e_3)^2$ configuration. However, when Cr(III) is the reductant, the cationic $d^5 \mu$ -oxo species must have an $(e_2)^4(e_3)^1$ (low spin) or $(e_2)^2(e_3)^2(e_1)^1$ (high spin) ground state. Either configuration is electronically degenerate and Jahn-Teller destabilized, leading to cleavage of the μ -oxo intermediate. No such electronic destabilization exists for the neutral $d^6 \mu$ -oxo dimer, in accord with its relative stability toward complete oxygen transfer.

Examples in which single-atom-bridged binuclear complexes appear to exhibit distorted bridge linkages have been reported. The dianion $[Cl_5W-N-WCl_5]^{2-}$ serves to illustrate this point. The

single-crystal X-ray structure of this complex consists of isolated ions with inequivalent W-N bond distances of 1.71 (7) and 2.03 (7) Å.³⁸ Directly related to the case of incomplete oxygen atom transfer is the complex $[(S-peida)OV_A-O_b-V_BO(S-peida)]^-$ where $S-peida^{2-}$ is $(S)-[1-(2\text{-pyridyl})ethyl]imino$ diacetate. The V_A-O_b bond distance (1.875 (4) Å) is significantly longer than the V_B-O_b bond length (1.763 (4) Å).³⁹ Both of these bridged complexes (W^V-N-W^{VI} and V^V-O-V^{IV}) possess a single d-electron. Correspondingly, the MO scheme in Figure 3 suggests that each complex should have an electronically degenerate $(e_2)^1$ configuration.

Finally, it is interesting to note that the electronic rationale proposed above appears to correctly explain the stability of $(\mu\text{-oxo})$ titanium porphyrin dimers. Thus, when $(TTP)Ti=O$ is treated with $(OEP)Ti-Cl$, oxygen atom transfer occurs to produce $(TTP)Ti-Cl$ and $(OEP)Ti=O$.¹³ The presumed cationic intermediate in this process, $[(TTP)Ti-O-Ti(OEP)]^+$, should have an electronically degenerate $(e_2)^1$ configuration. However, the neutral μ -oxo dimer, $(TTP)Ti-O-Ti(TTP)$, is a stable d^1-d^1 complex which has been characterized structurally by single-crystal X-ray diffractometry.⁴⁰ The MO scheme in Figure 3 predicts that it should have an electronically nondegenerate $(e_2)^2$ ground-state configuration.

Concluding Remarks

A number of new results have evolved from this study. Of particular interest is the observation that complete inter-metal oxygen atom transfer is possible and facile for chromium porphyrins. The reversible processes reported here are the first such examples involving chromium porphyrins. The inhibition of reaction 4 and capped porphyrin reaction by excess chloride strongly supports a primary reaction pathway that involves an initial chloride dissociation from the chromium(III) reductant. Moreover, mechanistic studies indicate that the oxo ligand is the preferred bridging species despite the presence of other good bridging ligands (e.g. chlorides and carboxylates). Finally, a simplified molecular orbital analysis suggests that the complete oxo transfer between $(POR)Cr=O$ and $(POR)Cr-Cl$ is promoted by electronic factors. This electronic rationale is further supported by the chemistry of titanium porphyrin complexes.

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(36) (a) Liston, D. J.; Murray, K. S.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1982**, 1109. (b) Liston, D. J.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1568.

(37) (a) Tatsumi, K.; Hoffmann, R.; Whangbo, M.-H. *J. Chem. Soc. Chem. Commun.* **1980**, 509. (b) Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328.

(38) Weller, V. F.; Liebelt, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1982**, *484*, 124.

(39) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168.

(40) Woo, L. K.; Hays, J. A.; Young, V. G., Jr.; Day, C. L. Manuscript in preparation.