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Intermetal Oxygen, Sulfur, and Selenium Atom Transfer Reactions Involving Titanium Porphyrin Complexes

Abstract

Metalloporphyrin complexes are extremely versatile reagents for a wide variety of inner-sphere redox processes involving intermetal halogen-, oxygen-, and nitrogen-atom transfers. Of particular interest is the fact that the number of redox equivalents exchanged during an atom-transfer process can be varied by changing the nature of the reducing agent. In addition, inner-sphere redox reactions can involve what Holm has termed complete vs incomplete atom transfer. We have utilized metalloporphyrin complexes to address fundamental issues which dictate the redox changes and the course of the reaction. For the $(\text{POR})\text{Cr}=\text{O} \text{ I } (\text{POR})\text{Cr}^{\text{III}}$ and $(\text{POR})\text{Cr}=\text{O} \text{ I } [(\text{POR})\text{Cr}^{\text{III}}] + \text{redox couples}$, we recently suggested that electronic factors dictate the nature of the reaction. When $\text{Cr}(\text{II})$ is the reductant, incomplete oxygen atom transfer occurs to yield a μ -oxo- $\text{Cr}(\text{III})$ dimer. However, when $\text{Cr}(\text{III})$ is the reductant, reversible oxygen atom transfer occurs between the two chromium porphyrin complexes. Correspondingly, $\text{Ti}(\text{III})$ porphyrins also undergo reversible oxygen atom transfer with oxotitanium(IV) porphyrins. From these observations and earlier work, metalloporphyrin chemistry is clearly relevant to the fundamental issue of dioxygen activation by metal ions. For example, the reaction of ferrous porphyrins with O_2 produces a μ -oxo complex, $(\text{POR})\text{Fe}-\text{O}-\text{Fe}(\text{POR})$. This reaction is thought to proceed through a μ -peroxy species, $(\text{POR})\text{Fe}-\text{O}-\text{O}-\text{Fe}(\text{POR})$ which homolytically cleaves to form a ferryl intermediate ($\text{Fe}=\text{O}$). In addition, treatment of chromous porphyrin with oxygen yields $(\text{POR})\text{Cr}=\text{O}$ or $(\text{POR})\text{Cr}-\text{O}-\text{Cr}(\text{POR})$ under conditions of excess or limiting O_2 , respectively. However, the reaction of the titanium porphyrin complex, $(\text{POR})\text{Ti}-\text{F}$, with oxygen affords an O_2 product, $(\text{POR})\text{Ti}(\text{O})_2$. These examples indicate that the role of transition metals in the activation of oxygen is complicated by the many different reaction pathways that are possible. As a continuation of our atom-transfer chemistry and our interest in oxygen activation, we have examined the intermetal oxygen atom transfer capabilities of titanium peroxo complexes and the related sulfur and selenium analogs with $(\text{TTP})\text{Ti}(\text{O})_2\text{RO}=\text{CR}$.

Disciplines

Chemistry

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Intermetal Oxygen, Sulfur, and Selenium Atom Transfer Reactions Involving Titanium Porphyrin Complexes

L. Keith Woo* and J. Alan Hays

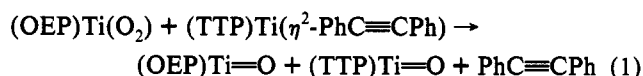
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Metalloporphyrin complexes are extremely versatile reagents for a wide variety of inner-sphere redox processes involving intermetal halogen-,¹ oxygen-,² and nitrogen-atom transfers.^{3,4} Of particular interest is the fact that the number of redox equivalents exchanged during an atom-transfer process can be varied by changing the nature of the reducing agent.^{3,5} In addition, inner-sphere redox reactions can involve what Holm has termed complete vs incomplete atom transfer.⁶ We have utilized metalloporphyrin complexes to address fundamental issues which dictate the redox changes and the course of the reaction. For the (POR)Cr=O/(POR)Cr^{II} and (POR)Cr=O/[(POR)Cr^{III}]⁺ redox couples,⁷ we recently suggested that electronic factors dictate the nature of the reaction.^{2b} When Cr(II) is the reductant, incomplete oxygen atom transfer occurs to yield a μ -oxo-Cr(III) dimer.⁸ However, when Cr(III) is the reductant, reversible oxygen atom transfer occurs between the two chromium porphyrin complexes. Correspondingly, Ti(III) porphyrins also undergo reversible oxygen atom transfer with oxotitanium(IV) porphyrins.^{2a} From these observations and earlier work, metalloporphyrin chemistry is clearly relevant to the fundamental issue of dioxygen activation by metal ions. For example, the reaction of ferrous porphyrins with O₂ produces a μ -oxo complex, (POR)Fe–O–Fe(POR).⁹ This reaction is thought to proceed through a μ -peroxo species, (POR)Fe–O–O–Fe(POR) which homolytically cleaves to form a ferryl intermediate (Fe=O).¹⁰ In addition, treatment of chromous porphyrin with oxygen yields (POR)Cr=O or (POR)Cr–O–Cr(POR) under conditions of excess or limiting O₂, respectively.^{8b} However, the reaction of the titanium porphyrin complex, (POR)Ti–F, with oxygen affords an η^2 -O₂ product, (POR)Ti(η^2 -O₂).¹¹ These examples indicate that the role of transition metals in the activation of oxygen is complicated by the many different reaction pathways that are possible. As a continuation of our atom-transfer chemistry and our interest in oxygen activation, we have examined the intermetal oxygen

atom transfer capabilities of titanium peroxo complexes and the related sulfur and selenium analogs with (TTP)Ti(η^2 -RC≡CR).¹²

When (OEP)Ti(O₂)¹³ (7.78 mM) is treated with (TTP)Ti(η^2 -PhC≡CPh) (4.53 mM) in C₆D₆ under anaerobic conditions, diagnostic changes in the ¹H NMR spectrum of the reaction sample are observed. For example, the meso-proton resonance (10.44 ppm) for the peroxo complex diminishes, the β -pyrrolic proton signal (9.06 ppm) for the acetylene complex completely disappears, and signals for free diphenyl acetylene appear. A new meso-proton signal (10.54 ppm) and a new β -pyrrolic proton resonance (9.24 ppm) emerge which signify the formation of the terminal oxo complexes, (OEP)Ti=O and (TTP)Ti=O,¹⁴ respectively (eq 1). The time scale for the reaction to reach

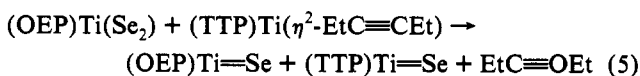
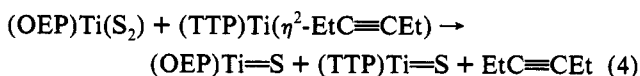


completion at ambient temperatures is on the order of minutes. Integration of the NMR signals indicates that the products form quantitatively in a 1:1 ratio and that mass balance is maintained. Thus, formation of the oxo complexes cannot be due to a reaction with adventitious dioxygen or water. Equation 1 is analogous to the product-forming step in a mechanism proposed by Marchon and Guillard to explain the formation of (TPP)Ti=O from the photolysis of (TPP)Ti(O₂) as shown in eqs 2 and 3.¹⁵ The



postulated (TPP)Ti^{II} intermediate was not detected but implicated by ¹⁸O-labeling studies. Equation 1 formally involves a two-electron reduction and O–O bond cleavage of bound O₂²⁻ to 2 O²⁻ by titanium(II) mediated by oxygen atom transfer. It is clear that this type of reaction must be given serious consideration in processes which involve metal ion activation of dioxygen.

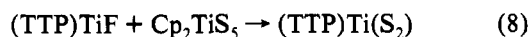
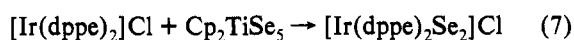
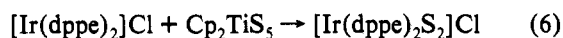
In a similar manner, the persulfido and perselenido complexes, (OEP)Ti(S₂)¹⁶ and (OEP)Ti(Se₂)¹⁶ undergo related atom transfer processes (eqs 4 and 5). In these examples, an η^2 -3-hexyne



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complex¹⁷ was used as the reductant. ¹H NMR spectroscopy was a convenient method for monitoring these reactions also. For example, in eq 5 new signals which are diagnostic for (TTP)Ti=Se¹⁷ (9.30 ppm, β-pyrrolic H) and (OEP)Ti=Se¹⁷ (10.64 ppm, meso-H) are observed with an integrated intensity ratio of 1:1. Equations 4 and 5 represent rare examples of intermetal sulfur or selenium atom-transfer reactions. Other known intermetal sulfur- or selenium-transfer reactions involve the use of Cp₂TiS₅ and Cp₂TiSe₅ as transfer reagents. In general these typically deliver S₂ or Se₂ fragments as shown in reactions 6–8.^{16,18} The exception is shown in reaction 9 in which a single selenium atom has been transferred from Cp₂TiSe₅ to a vanadium(II) complex.¹⁹



Activation of molecular oxygen is a multistep process involving the transfer of several electrons and cleavage of the O–O bond. No single metal species is capable of accomplishing these tasks by itself. Due to the intricacies involved, detailed mechanisms for the activation of oxygen by transition metal complexes are generally not known. Furthermore, elaborate schemes are often needed to account for the observed behavior. For example, in the outer-sphere reduction of (TPP)Ti(η²-O₂), a series of one-electron steps have been proposed to explain the observed cyclic voltammetry results.²⁰ The first reduction involves the porphyrin ligand, forming an anion radical complex, Ti^{IV}(η²-O₂)(TPP^{•-}). Presumably, protonation of the η²-O₂ ligand weakens the Ti-peroxo bonding and allows internal electron transfer to occur, leading to (TPP)Ti^{III}(OOH). Subsequent addition of an electron to the hydroperoxo complex is relatively easier than the first

reduction of the initial η²-O₂ complex. The overall reaction involves an ECEC mechanism in the two-electron reduction of the peroxo ligand. In reaction 1, the Ti(II) complex can serve as the Lewis acid which activates the peroxo ligand of (OEP)Ti(η²-O₂) toward reduction. Furthermore, the ability of Ti(II) to supply both electrons in the reduction step is also crucial. Thus, reactions such as that represented in eq 1 are essential in understanding fundamental steps involved in the activation of O₂.

Frequently, coordinated superoxide or peroxide intermediates are implicated in the reduction of dioxygen. The lifetimes of these intermediates can depend dramatically on the metal and ancillary ligands. Porphyrins have an especially strong stabilizing effect on such intermediates.²¹ In the work discussed here, the utility of porphyrin ligands in atom-transfer chemistry is clearly apparent from an inorganic functional group aspect. The porphyrin is an innocent ligand in these examples. It essentially serves as a spectator group and allows only reaction at the axial ligand to take place. In this manner, it should be possible to examine, in detail, one step in the reduction of O₂ to O²⁻. Few systems are known in which such a study can be undertaken. Moreover, reactions 1, 4, and 5 should enable a systematic comparison of the relative intrinsic tendencies for intermetal oxygen, sulfur, or selenium atom transfer to occur in an isoelectronic and isostructural series of complexes without complications arising from unwanted side reactions or structural reorganization. To date, the only other intragroup comparison of atom-transfer capability has been done on the halogens. Further aspects of these novel intermetal group 16 atom processes are under study.

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