

Reactivity and mechanisms of metalloporphyrin-catalyzed oxidations

JOHN T. GROVES*

Department of Chemistry, Princeton University, Princeton, NJ 08544, USA

Accepted 22 December 1999

ABSTRACT: Effective systems for the catalytic oxygenation of hydrocarbons have been developed based on metalloporphyrins containing iron, manganese and ruthenium. These metalloporphyrin catalysts were inspired by studies of the mechanism of the heme oxygenase cytochrome P450 and related enzymes. Oxometalloporphyrins, which have now been spectroscopically characterized, have very high reactivity as oxygen transfer agents. A combination of experimental and computational methods has begun to provide an understanding of the structure and reactivity of these oxometalloporphyrin complexes and the mechanisms of oxygen transfer reactions they catalyze. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: iron; manganese; ruthenium; oxo complexes; oxygenation; oxygen rebound

INTRODUCTION

The controlled oxygenation of alkanes, alkenes and aromatic hydrocarbons is one of the most important technologies for the conversion of petroleum products to valuable commodity chemicals [1, 2]. Many of these processes utilize metal catalysts to promote both the rate of reaction and product selectivity [3, 4]. There is considerable pressure to replace old technologies with more efficient alternatives using dioxygen, hydrogen peroxide or other easily accessible and environmentally friendly oxidants.

The heme-containing protein cytochrome P450 catalyzes these intrinsically difficult reactions quite effectively under mild conditions using the oxygen from air [5, 6]. It is not surprising that significant efforts have been directed toward these remarkable enzymes and their artificial mimics. Effective catalytic systems for hydrocarbon oxidation based on metalloporphyrin catalysts with iron, manganese and ruthenium complexes have been developed [6–10]. The purpose of this overview is to summarize recent progress in the field of metalloporphyrin-catalyzed oxidations.

SYNTHETIC OXOMETALLOPORPHYRINS AS MODELS FOR CYTOCHROME P450

Studies using synthetic metalloporphyrins as models for cytochrome P450 have afforded important insights into the nature of the enzymatic processes [11, 12]. The consensus

mechanism involves hydrogen atom abstraction from the substrate (R—H) by a reactive iron-oxo intermediate followed by rapid transfer of the metal-bound oxygen atom to an intermediate caged alkyl radical. This so-called *oxygen rebound* mechanism [13] is consistent with the stereochemical, regiochemical and allylic scrambling results observed in the hydroxylation of diagnostic substrates by cytochrome P450 and rules out *freely* diffusing radicals [14] and direct oxygen insertion processes.

Important insights into the nature of such oxoiron intermediates (Fig. 1) have come from the study of genetically engineered heme proteins and model systems. Thus Watanabe and co-workers have shown that mutants of myoglobin have accelerated rates of oxoiron intermediate formation using hydrogen peroxide as an oxidant [15], and Weiss and co-workers have incorporated manganese microperoxidase into a molecular sieve architecture [16, 17]. Further, DFT computational approaches by Shaik and co-workers have afforded an important new tool for assessing the roles of axial ligation, spin state crossings and charge distribution [18].

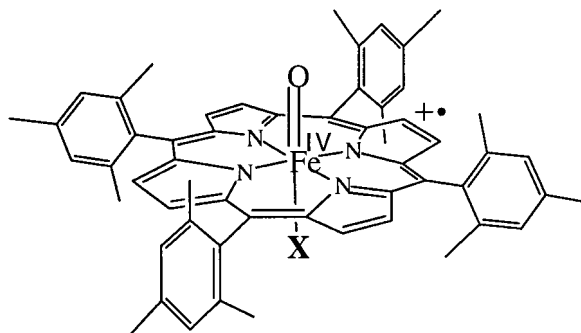


Fig. 1. Oxoiron(IV) TMP cation radical.

*Correspondence to: J. T. Groves, Department of Chemistry, Princeton University, Princeton, NJ 08544, USA.
E-mail: jtgroves@princeton.edu

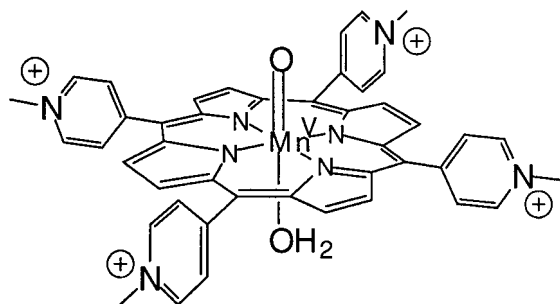


Fig. 2. A water-soluble oxomanganese(V) porphyrin.

MANGANESE PORPHYRINS IN CATALYTIC OXIDATIONS

Manganese porphyrins have been shown to have unusually high reactivity toward olefin epoxidation and alkane hydroxylation [19, 20]. The reaction of the water-soluble tetra-*N*-methyl-4-pyridylporphyrinatomanganese(III) (Mn^{III} (TMPyP)) with a variety of oxidants, *m*-CPBA, HSO_3^- and ClO^- , was first deduced by Meunier and co-workers to produce a manganese-oxo intermediate which underwent rapid oxo-aqua interconversion [21–23]. Recently, the detection of an oxomanganese(V) porphyrin intermediate (Fig. 2) under ambient catalytic conditions by using rapid-mixing stopped-flow techniques has allowed a direct assessment of its reactivity [24].

Surprisingly, the 2-*N*-methylpyridyl isomer oxo Mn^{V} (TM-2-PyP) was found to be unusually stable, allowing its characterization by ^1H NMR [25]. Reaction rate constants for oxo Mn^{V} (TM-2-PyP) toward electron transfer, hydrogen atom abstraction and epoxidation were all *several orders of magnitude slower* than the corresponding 4-*N*-methylpyridyl species. This unusual effect, which did not appear in the corresponding reactions of the Mn(IV) and Mn(III) states, was ascribed to the low-spin, d^2 electronic configuration of oxo Mn^{V} .

RUTHENIUM PORPHYRINS IN OXIDATIVE CATALYSIS

Ruthenium porphyrins have been found to catalyze the *aerobic* epoxidation of olefins under mild conditions [26]. Murahashi and co-workers have studied the aerobic oxidation of alkanes catalyzed by polyfluorinated metalloporphyrins including Ru^{II} (TPFPP)(CO) in the presence of

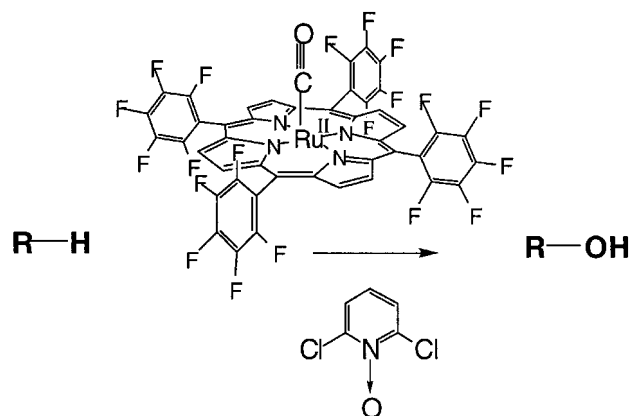


Fig. 3. Alkane hydroxylation by Ru^{II} (TPFPP)CO.

acetaldehyde [27, 28]. The catalytic oxygenation of cyclohexane and adamantane at 70°C under 1 atm dioxygen gave *ca* 200 turnovers in 24 h. More recently, Labinger and co-workers [29] have investigated the catalysis of aerobic olefin oxidation by a highly electron-deficient perhalogenated ruthenium porphyrin complex Ru^{II} (TPFPCL₈)(CO). For this system a radical autoxidation mechanism has been suggested [30–32].

Hirobe and co-workers were the first to use 2,6-disubstituted pyridine *N*-oxides in conjunction with ruthenium porphyrins for the oxidation of olefins, alcohols and sulfides [33–36]. The epoxidation of styrene with 2,6-dichloropyridine *N*-oxide was efficiently catalyzed by Ru^{VI} (TMP)(O)₂ or Ru^{II} (TMP)(CO) to afford styrene oxide with high selectivity and nearly quantitative yields based on substrate used [36].

A highly active system for hydrocarbon oxygenation using electron-deficient polyhalogenated ruthenium porphyrins with 2,6-dichloropyridine *N*-oxide has been reported recently [37, 38] (Fig. 3). The oxidations with this system were characterized by high rates (up to 800 turnovers per minute and up to 15000 turnovers) and selectivity even under mild conditions and could be carried out in non-acidic reaction media. Metastable Ru(III) and oxoRu(V) species have been proposed as key intermediates in the catalytic cycle.

Acknowledgement

The author is grateful for financial support from the National Science Foundation.



John T. Groves received a Ph.D. at Columbia in 1969. He was Professor of Chemistry at the University of Michigan before moving to Princeton in 1985. Groves was appointed Hugh Stott Taylor Professor of Chemistry in 1991, elected to the American Academy of Arts and Sciences in 1993 and received the Alfred Bader Award in Bioorganic and Bioinorganic Chemistry in 1996.

REFERENCES AND NOTES

- Shilov AE, Shul'pin GB. *Chem. Rev.* 1997; **97**: 2897–2932.
- Groves JT, Shalyaev KV, Lee J. In *The Porphyrin Handbook*, vol. 4. Kadish KM (ed.). Academic Press: San Diego, CA, 1999; 17.
- Sheldon RA, Kochi JK. *Metal-catalyzed Oxidations of Organic Compounds*. Academic Press: New York, 1981.
- Simandi LI. *Dioxygen Activation and Homogeneous Catalytic Oxidation*. Elsevier: Amsterdam, 1991.
- Ortiz de Montellano PR. *Cytochrome P450. Structure, Mechanism and Biochemistry* (2nd edn). Plenum: New York, 1995.
- Groves JT, Han Y-Z. In (2nd edn). Ortiz de Montellano PR (ed.). *Cytochrome P-450. Structure, Mechanism and Biochemistry* Plenum: New York, 1995; 3.
- Moro-oka Y, Akita M. *Catal. Today* 1998; **41**: 327.
- Collman JP, Zhang X, Lee VJ, Uffelman ES, Brauman JI. *Science* 1993; **261**: 1404.
- Sheldon RA. *Metalloporphyrins in Catalytic Oxidations*. Marcel Dekker: New York, 1994.
- Meunier B. *Chem. Rev.* 1992; **92**: 1411.
- McLain J, Lee J, Groves JT. In *Biomimetic Oxidations*. Meunier B (ed.). ICP Publishers, 2000; in press.
- Davies JA. *Selective Hydrocarbon Activation: Principle and Progress*. VCH: New York, 1994.
- McClusky GA, Groves JT. *J. Am. Chem. Soc.* 1976; **98**: 859.
- Ingold KU, MacFaul R. In *Biomimetic Oxidations*. Meunier B (ed.). ICP Publishers, 2000, in press.
- Matsui T, Ozaki S, Watanabe Y. *J. Am. Chem. Soc.* 1999; **121**: 9952.
- Schunemann V, Trautwein AX, Rietjens IMCM, Boersma MG, Veeger C, Mandon D, Weiss R, Bahl K, Colapietro C, Piech M, Austin RN. *Inorg. Chem.* 1999; **38**: 4901.
- Primus JL, Boersma MG, Mandon D, Boeren S, Veeger C, Weiss R, Rietjens IMCM. *J. Biol. Inorg. Chem.* 1999; **4**: 274.
- Filatov M, Harris N, Shaik S. *J. Chem. Soc., Perkin Trans. 2* 1999; 399.
- Groves JT, Kruper WJ, Haushalter RC. *J. Am. Chem. Soc.* 1994; **102**: 377.
- Meunier B. *Bull. Soc. Chim. Fr.* 1986; **4**: 578.
- Bernadou J, Fabiano A-S, Robert A, Meunier B. *J. Am. Chem. Soc.* 1994; **116**: 9375.
- Pitie M, Bernadou J, Meunier B. *J. Am. Chem. Soc.* 1995; **117**: 2935.
- Bernadou J, Meunier B. *J. Chem. Soc., Chem. Commun.* 1998; 2167.
- Groves JT, Lee J, Marla SS. *J. Am. Chem. Soc.* 1997; **119**: 6269.
- Groves JT, Jin N. *J. Am. Chem. Soc.* 1999; **121**: 2923.
- Groves JT, Quinn R. *J. Am. Chem. Soc.* 1985; **107**: 5790.
- Murahashi S-I, Naota T, Komiya N. *Tetrahedron Lett.* 1995; **36**: 8059.
- Murahashi S-I, Komiya N. *Catal. Today* 1998; **41**: 339.
- Birnbaum ER, Labinger JA, Bercaw JE, Gray HB. *Inorg. Chim. Acta* 1998; **270**: 433.
- Labinger JA. *Catal. Lett.* 1994; **26**: 95.
- Grinstaff MW, Hill MG, Labinger JA, Gray HB. *Science* 1994; **264**: 1311.
- Birnbaum ER, Grinstaff MW, Labinger JA, Bercaw JE, Gray HB. *J. Mol. Catal. A* 1995; **104**: L119.
- Higuchi T, Ohtake H, Hirobe M. *Tetrahedron Lett.* 1989; **30**: 6545.
- Higuchi T, Ohtake H, Hirobe M. *Tetrahedron Lett.* 1991; **32**: 7435.
- Ohtake H, Higuchi T, Hirobe M. *Tetrahedron Lett.* 1992; **33**: 2521.
- Ohtake H, Higuchi T, Hirobe M. *Heterocycles* 1995; **40**: 867.
- Groves JT, Bonchio M, Carofiglio T, Shalyaev K. *J. Am. Chem. Soc.* 1996; **118**: 8961.
- Groves JT, Shalyaev KV, Bonchio M, Carofiglio T. *Stud. Surf. Sci. Catal.* 1997; **110**: 865.