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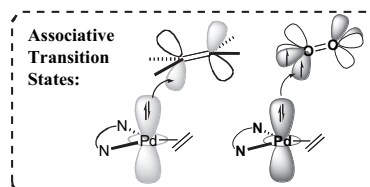
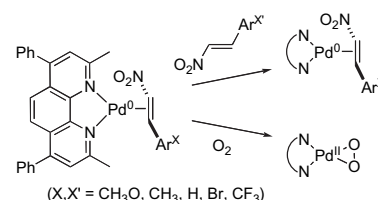
Articles

**Brian V. Popp, Joseph L. Thorman,
Shannon S. Stahl**

*Journal of Molecular Catalysis A: Chemical 251
(2006) 2*

Similarities between the reactions of dioxygen and alkenes with palladium(0): Relevance to the use of benzoquinone and molecular oxygen as stoichiometric oxidants in palladium-catalyzed oxidation reactions

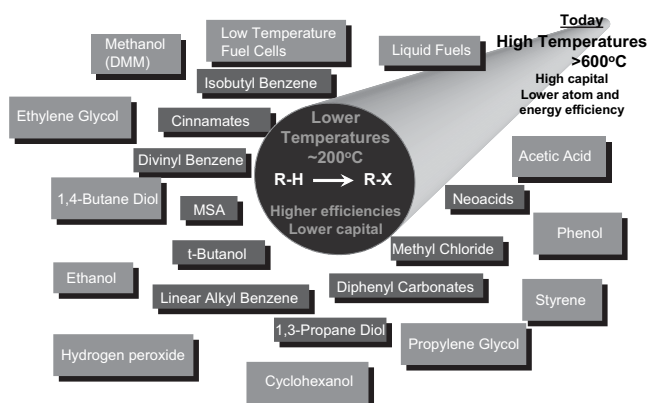
Reactions of palladium(0)-alkene complexes with exogenous alkenes and dioxygen have been explored. Kinetic studies of these reactions indicate that they proceed through associative substitution pathways with similar transition states that feature charge transfer from the palladium(0) to the incoming substrate. These mechanistic results provide a framework for understanding the similarity reactivity of benzoquinone and dioxygen in palladium-catalyzed oxidation reactions.



**Brian L. Conley, William J. Tenn III,
Kenneth J.H. Young, Somesh K. Ganesh,
Steven K. Meier, Vadim R. Ziatdinov,
Oleg Mironov, Jonas Oxaard, Jason Gonzales,
William A. Goddard III, Roy A. Periana**

*Journal of Molecular Catalysis A: Chemical 251
(2006) 8*

Design and study of homogeneous catalysts for the selective, low temperature oxidation of hydrocarbons

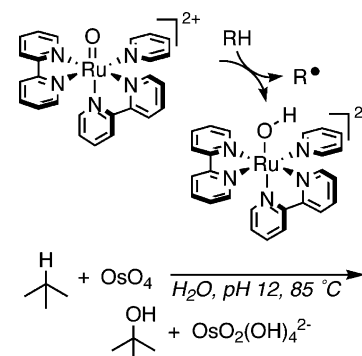


**James M. Mayer, Elizabeth A. Mader,
Justine P. Roth, Jasmine R. Bryant,
Takashi Matsuo, Ahmad Dehestani,
Brian C. Bales, Eric J. Watson, Takao Osako,
Karine Valliant-Saunders, Wai Han Lam,
David A. Hrovat, Weston Thatcher Borden,
Ernest R. Davidson**

*Journal of Molecular Catalysis A: Chemical 251
(2006) 24*

Stoichiometric oxidations of σ -bonds: Radical and possible non-radical pathways

Oxidizing transition metal complexes can abstract hydrogen atoms from C–H and O–H bonds. Examples reviewed here include oxidations of alkylaromatics and hydroxylamines by ruthenium-oxo and iron(III) complexes. Rate constants for such reactions can often be predicted from the reaction driving force and intrinsic barriers. Novel OsO₄ oxidations of H₂ and alkanes, in contrast, may not occur by a radical mechanism.

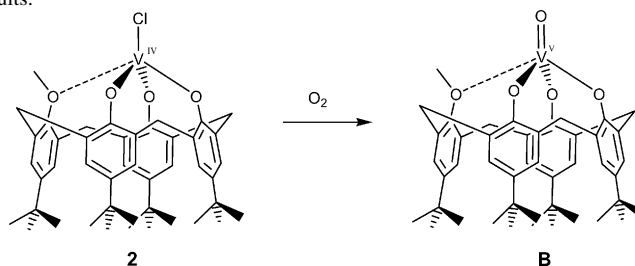


**Elke Hoppe, Christian Limberg,
Burkhard Ziemer, Clemens Mügge**

Journal of Molecular Catalysis A: Chemical 251
(2006) 34

Vanadium calixarene complexes as molecular models
for supported vanadia

The calixarene vanadium (IV) chloro complex, **2**, has been synthesised via a surprising reaction sequence and shown to react with dioxygen to give the vanadium(V)oxo complex **B** which is conformationally flexible and crystallises in the cone or partial cone conformation. The first step leading to the formation of **B** certainly represents the binding of O₂ to the V^{IV} centre. The O–O bond cleavage probably involves a second molecule of **2**. This type of reactivity is not restricted to **2**: replacement of chloride by triphenylsiloxide leads to the same results.

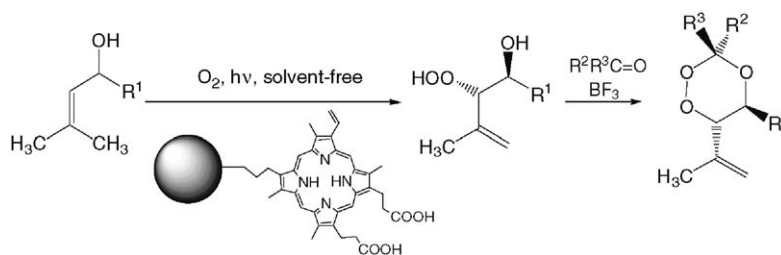


**Axel G. Griesbeck, Anna Bartoschek,
Tamer T. El-Idreesy, O. Höinck, Claus Miara**

Journal of Molecular Catalysis A: Chemical 251
(2006) 41

Type II photooxygenation in polymer matrices for
the synthesis of new antimalarial peroxides

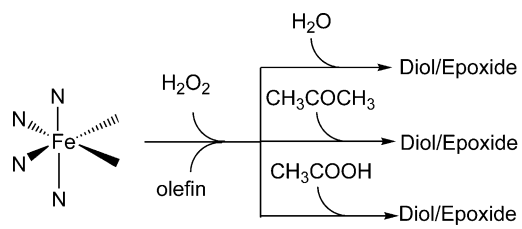
The singlet oxygen ene reaction with allylic alcohols was developed as a route to mono- and spirobicyclic 1,2,4-trioxanes, molecules which showed moderate to high antimalarial properties similar to the naturally occurring sesquiterpene-peroxide *artemisinin*. As sensitizing materials tetraarylporphyrins embedded in polystyrene (PS) beads or in polymer films were used. Alternatively, the sensitizers were covalently linked to polystyrene during emulsion polymerization.



**Rubén Mas-Ballesté, Megumi Fujita,
Carla Hemmila, Lawrence Que Jr.**

Journal of Molecular Catalysis A: Chemical 251
(2006) 49

Bio-inspired iron-catalyzed olefin oxidation.
Additive effects on the *cis*-diol/epoxide ratio

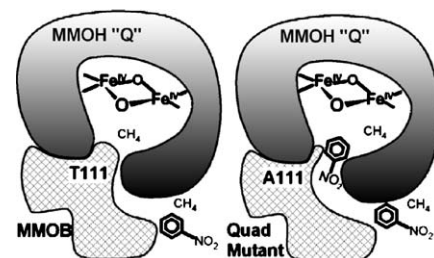


J. Zhang, H. Zheng, S.L. Groce, J.D. Lipscomb

Journal of Molecular Catalysis A: Chemical 251
(2006) 54

Basis for specificity in methane monooxygenase
and related non-heme iron-containing biological
oxidation catalysts

Biological systems activate O₂ using many mechanisms, but generally the activation process is regulated to assure specificity. The nature of this regulation must be understood before the true nature of the underlying chemistry can be described with certainty. Examples are given of regulation by second sphere amino acids in methane monooxygenase and an aromatic ring cleaving dioxygenase.

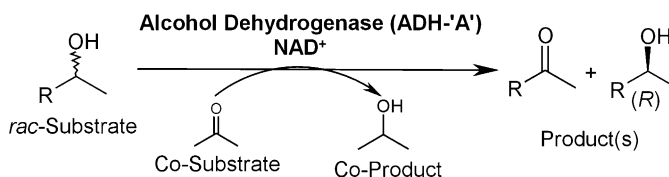


**Klaus Edegger, Harald Mang, Kurt Faber,
Johannes Gross, Wolfgang Kroutil**

Journal of Molecular Catalysis A: Chemical 251
(2006) 66

Biocatalytic oxidation of *sec*-alcohols via hydrogen transfer

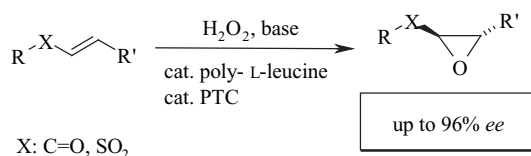
Employing acetone as hydrogen acceptor various *sec*-alcohols can be oxidized to the corresponding ketone in an asymmetric fashion. The enzyme exhibits exclusive regioselectivity for secondary alcohols, primary alcohols remain untouched. This protocol does not only provide a simple 'green' oxidation method for organic synthesis at ambient conditions, but also allows the preparation of ketones, which are labeled 'natural' for flavor and fragrance applications.



**Thomas Geller, Arne Gerlach,
Christa M. Krüger, H.-Christian Militzer**

Journal of Molecular Catalysis A: Chemical 251
(2006) 71

The Juliá-Colonna epoxidation: Access to chiral, non-racemic epoxides

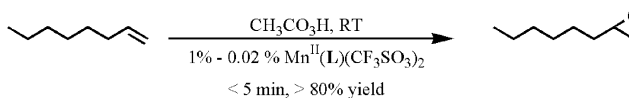


Andrew Murphy, T. Daniel P. Stack

Journal of Molecular Catalysis A: Chemical 251
(2006) 78

Discovery and optimization of rapid manganese catalysts for the epoxidation of terminal olefins

Twenty-two Mn^{II} complexes were screened for the catalytic epoxidation of terminal olefins using peracetic acid as the oxidant. Of these complexes, few are active epoxidation catalysts under strongly acidic conditions, but most can epoxidize 1-octene under less acidic conditions. Of these catalysts [Mn(phen)₂(CF₃SO₃)₂] can epoxidize terminal olefins using as little as 0.02 mol% catalyst within 5 min.

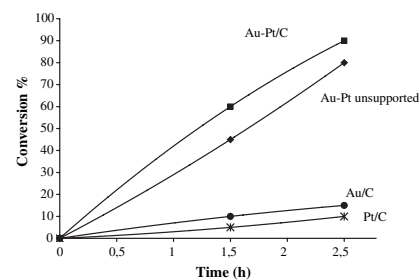


**Massimiliano Comotti, Cristina Della Pina,
Michele Rossi**

Journal of Molecular Catalysis A: Chemical 251
(2006) 89

Mono- and bimetallic catalysts for glucose oxidation

Mono- and bimetallic gold catalysts, derived from nanometric colloidal sols, have been applied to the aerobic oxidation of D-glucose to D-gluconic acid under mild conditions (pressure 300 kPa, temperature 323–363 K). A synergetic effect was discovered adding palladium and, mainly, platinum to gold: in the case of Au:Pt = 2 w/w composition, the total conversion of glucose was obtained with TOF up to 924 h⁻¹ (Fig. 1). The catalytic activity is increased more than one order of magnitude by working in the presence of alkali at pH 9.5, where monometallic Au is superior to Pd and Pt metals but no synergetic effects were detected after alloying with Pd and Pt.

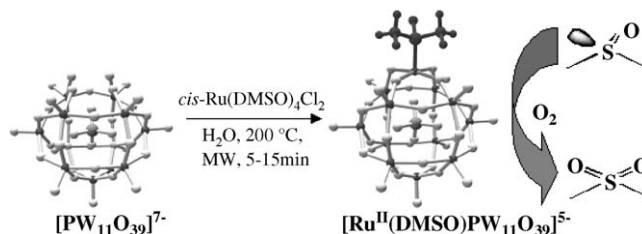


**Marcella Bonchio, Mauro Carraro,
Andrea Sartorel, Gianfranco Scorrano,
Ulrich Kortz**

Journal of Molecular Catalysis A: Chemical 251
(2006) 93

Bio-inspired oxidations with polyoxometalate
catalysts

Transition metal substituted polyoxometalates (TMS-POM) provide a redox-active metal center, (Fe, Ru, Mn or else), with a totally inorganic ligand system, featuring rigid polydentate binding sites, high electron-acceptor character, extreme robustness and interesting structural and coordination properties, in some cases, mimicking the coordination geometry of natural oxygenase enzymes.

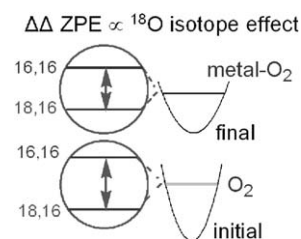


**Valeriy V. Smirnov, David W. Brinkley,
Michael P. Lanci, Kenneth D. Karlin,
Justine P. Roth**

Journal of Molecular Catalysis A: Chemical 251
(2006) 100

Probing metal-mediated O₂ activation in chemical
and biological systems

We are establishing competitive oxygen (¹⁸O) isotope fractionation techniques to probe mechanisms of chemical and biological oxidation reactions. Summarized here are isotope effects on reactions of enzymes and inorganic compounds which reflect the activation of the O–O bond upon binding O₂ to a metal center as well as the nature of transition states for inner- and outer-sphere electron transfer reactions.

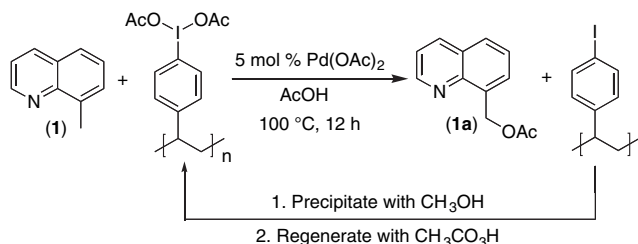


**Eric W. Kalberer, Salena R. Whitfield,
Melanie S. Sanford**

Journal of Molecular Catalysis A: Chemical 251
(2006) 108

Application of recyclable, polymer-immobilized
iodine(III) oxidants in catalytic C–H bond
functionalization

This paper describes the palladium-catalyzed oxidative functionalization of arene and alkane C–H bonds using the polymer-immobilized iodine(III) oxidant poly-4-(diacetoxyiodo)styrene (PS-I(OAc)₂) and its derivatives. These transformations have been applied to a wide variety of arene and alkane substrates, and the polymer-immobilized iodine(I) byproducts are readily recovered and recycled in these reactions.

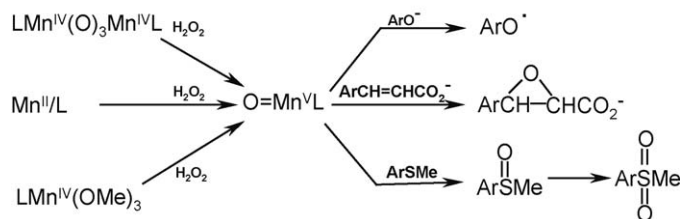


**John R. Lindsay Smith, Bruce C. Gilbert,
Antoni Mairata i Payeras, Jane Murray,
Terry R. Lowdon, John Oakes,
Roger Pons i Prats, Paul H. Walton**

Journal of Molecular Catalysis A: Chemical 251
(2006) 114

Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane
complexes: Versatile catalysts for the oxidation of
organic compounds with hydrogen peroxide

Manganese-1,4,7-trimethyl-1,4,7-triazacyclononane complexes catalyse the oxidation of phenolate and cinnamate anions and sulfides by hydrogen peroxide. The data are compatible with the active oxidant being an electrophilic oxo-manganese(V) species. In contrast, the comparable oxidation of sulfoxides involves a nucleophilic oxidant. A mechanism in which hydrogen peroxide reacts with a manganese-sulfoxide complex is proposed.



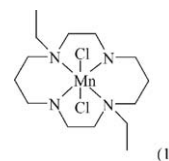
L = 1,4,7-trimethyl-1,4,7-triazacyclononane

G. Reinhardt

Journal of Molecular Catalysis A: Chemical 251 (2006) 177

Fingerprints of bleach systems

In this comparative study bleach performance, dye fading and fiber damage of eight different bleach systems are examined. The selection covers activators, transition metal complexes designed for peroxide and aerial bleaching such as (**1**), as well as oxygen transfer agents. Multi-cycle washing tests are performed under real life conditions following recently developed dye and fiber damage test protocols. The results indicate that each bleach system has its characteristic performance and damage profile.

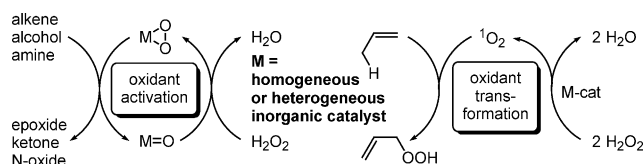


Véronique Nardello, Jean-Marie Aubry, Dirk E. De Vos, Ronny Neumann, Waldemar Adam, Rui Zhang, Johan E. ten Elshof, Peter T. Witte, Paul L. Alsters

Journal of Molecular Catalysis A: Chemical 251 (2006) 185

Inorganic compounds and materials as catalysts for oxidations with aqueous hydrogen peroxide

An overview is given of liquid-phase oxidations with aqueous hydrogen peroxide using homogeneous or heterogeneous catalysts derived from inorganic compounds.

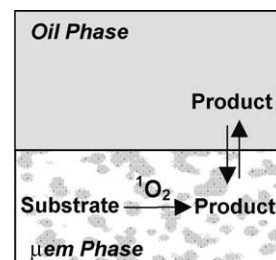


Laurent Caron, Véronique Nardello, Paul L. Alsters, Jean-Marie Aubry

Journal of Molecular Catalysis A: Chemical 251 (2006) 194

Convenient singlet oxygenation in multiphase microemulsion systems

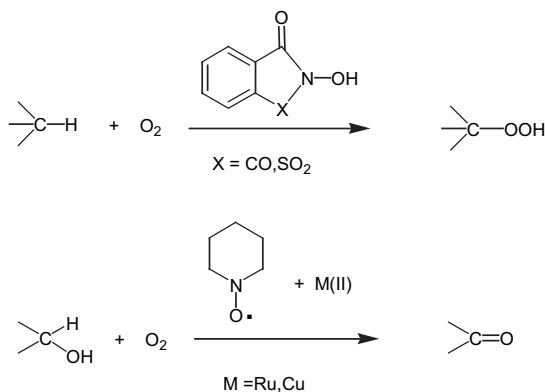
Two-phase microemulsion systems (Winsor I) may be successfully applied to the peroxidation of organic substrates by singlet oxygen chemically generated from $\text{H}_2\text{O}_2/\text{MoO}_4^{2-}$. Advantages of these reaction media are those of microemulsions plus easy work-up of the products, lower costs and lower amounts of amphiphilic compounds compared to the one-phase microemulsion systems.



Roger A. Sheldon, Isabel W.C.E. Arends

Journal of Molecular Catalysis A: Chemical 251 (2006) 200

Catalytic oxidations mediated by metal ions and nitroxyl radicals

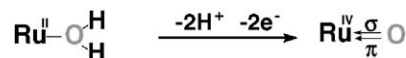


**Montserrat Rodríguez, Isabel Romero,
Cristina Sens, Antoni Llobet**

Journal of Molecular Catalysis A: Chemical 251
(2006) 215

Ru=O complexes as catalysts for oxidative transformations, including the oxidation of water to molecular dioxygen

A short review related to the chemistry of ruthenium complexes containing one and two Ru=O groups is presented. For complexes containing one Ru=O group, a special attention is addressed to describe the effect of electronic perturbations transmitted by the ligands to the mentioned Ru=O. For complexes containing two Ru=O groups, the accent is placed at the importance of the relative spatial disposition of those two Ru=O groups.

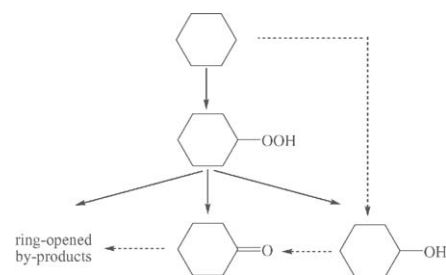


Ive Hermans, Pierre A. Jacobs, Jozef Peeters

Journal of Molecular Catalysis A: Chemical 251
(2006) 221

Understanding the autoxidation of hydrocarbons at the molecular level and consequences for catalysis

A thoroughgoing experimental and theoretical study reveals that, cyclohexylhydroperoxide is the most important precursor of all oxygenated compounds, and even ring-opened byproducts, in the free-radical autoxidation of cyclohexane. This hitherto unknown role of CyOOH is ascribed to its very fast reaction with chain-carrying peroxy radicals at its α H-atom. The enhanced hydroperoxide selectivity in *N*-hydroxyphthalimide catalysed reactions is the result of a more selective CyH chain-propagation.



Werner R. Thiel

Journal of Molecular Catalysis A: Chemical 251
(2006) 229

A DFT study on the decomposition of semiperacetals

DFT calculations provide strong evidence that the evolution of hydrogen from mixtures of aldehydes and hydrogen peroxide proceeds via a concerted mechanism.

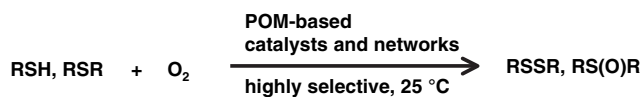


**Craig L. Hill, Travis M. Anderson,
Jong Woo Han, Daniel A. Hillesheim,
Yurii V. Geletii, Nelya M. Okun, Rui Cao,
Bogdan Botar, Djameladdin G. Musaev,
Keiji Morokuma**

Journal of Molecular Catalysis A: Chemical 251
(2006) 234

New complexes and materials for O₂-based oxidations

Polyoxometalate-based complexes and materials show selective oxidation by dioxygen of model substrates (propane thiol, 2-chloroethyl ethyl sulfide, and triphenylphosphine).

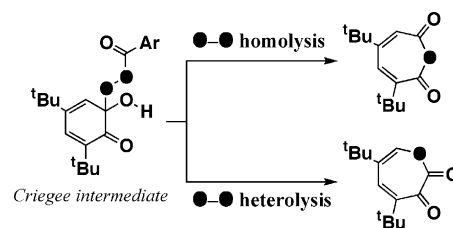


**Yutaka Hitomi, Hiroshi Yoshida,
Tsunehiro Tanaka, Takuzo Funabiki**

Journal of Molecular Catalysis A: Chemical 251
(2006) 239

Mechanistic study on regioselective oxygenation reaction of 1,2-quinones with peroxybenzoic acids: Relevant to mechanisms of catecholdioxygenases

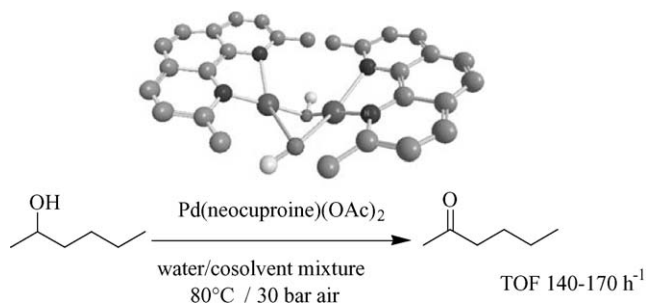
We examined the factors that determine the regioselectivity of the oxygenation reaction of 1,2-quinone by peroxybenzoic acids in order to provide mechanistic insights into the regioselective cleavage of catechols catalysed by the enzymes. The results suggest that the cleavage fashion of the O–O bond in the Criegee intermediate determines the regioselectivity of the oxygen atom insertion into 1,2-quinones.



**Isabel W.C.E. Arends, Gerd-Jan ten Brink,
Roger A. Sheldon**

Journal of Molecular Catalysis A: Chemical 251
(2006) 246

Palladium-neocuproine catalyzed aerobic oxidation of alcohols in aqueous solvents

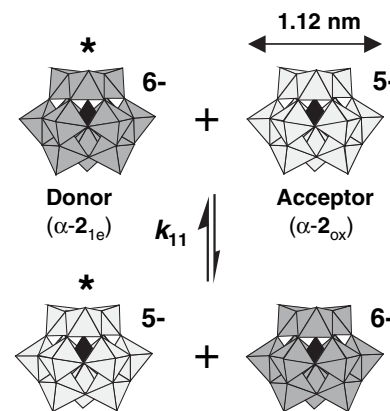


Yurii V. Geletii, Ira A. Weinstock

Journal of Molecular Catalysis A: Chemical 251
(2006) 255

Ionic-strength dependence of electron-transfer reactions of Keggin heteropolytungstates: Mechanistic probes of O₂ activation in water

Rates of electron self exchange between $\alpha\text{-AlW}_{12}\text{O}_{40}^{6-}$ ($\alpha\text{-2}_{1e}$) and $\alpha\text{-AlW}_{12}\text{O}_{40}^{5-}$ ($\alpha\text{-2}_{ox}$), as a function of ionic strength in water, comply with the extended Debye–Hückel equation. These, and related aqueous-solution studies, recommend 2_{1e} as mechanistic probe for obtaining detailed information about the first steps in reduction of O₂ to H₂O, a process of considerable importance to chemistry and biology.

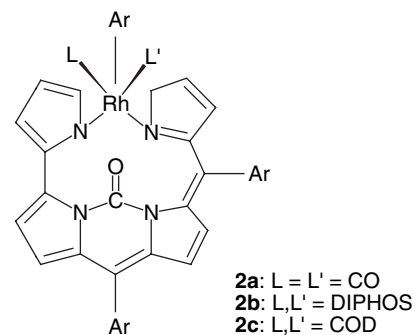


**Irena Saltsman, Yael Balazs, Israel Goldberg,
Zeev Gross**

Journal of Molecular Catalysis A: Chemical 251
(2006) 263

Synthesis, spectroscopy, and structures of chiral rhodium(I) corrole complexes

Rhodium(I) complexes of a chiral corrole were prepared with ligands of very different electronic and steric properties, all of which were characterized by multinuclear NMR methods and X-ray crystallography.

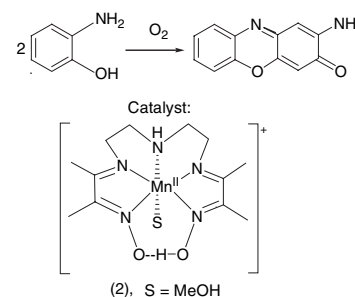


**Imola Cs. Szgyártó, Tatiana M. Simándi,
László I. Simándi, László Korecz, Nóra Nagy**

Journal of Molecular Catalysis A: Chemical 251
(2006) 270

A functional phenoxazinone synthase model based on dioximatomanganese(II)

The dioximatomanganese(II) complex $[\text{Mn}(\text{HL})]^{+}$ (2) is a functional phenoxazinone synthase model, catalyzing the oxidative dimerization of 2-aminophenol to 2-amino-3H-phenoxazine-3-one (apx) via an o-benzoquinone monoimine (bqmi) intermediate. The kinetic behavior is consistent with the rate-determining decomposition of a ternary catalyst-substrate-dioxygen intermediate to bqmi followed by non-catalytic transformation to apx.

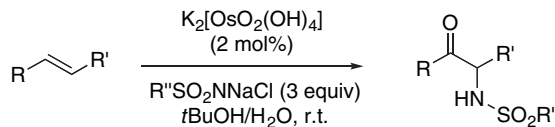


**Kilian Muñiz, Claas H. Hövelmann,
Amparo Villar, Rubén Vicente, Jan Streuff,
Martin Nieger**

Journal of Molecular Catalysis A: Chemical 251
(2006) 277

2-Amino ketones from osmium-catalysed oxidations of alkenes

The first examples of direct conversion of alkenes to yield racemic 2-amino ketone products in what represents a so-far unknown reactivity in osmium catalysis are presented. In addition, a two-step procedure, which converts alkenes into enantiomerically pure vicinal amino alcohols followed by stereoselective oxidative conversion into 2-amino ketones is described. Both pathways derive from a common mechanistic background and constitute a novel side-reaction of the original aminohydroxylation chemistry.

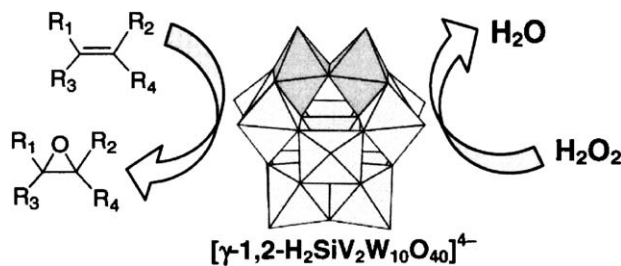


direct or stepwise protocols

**Noritaka Mizuno, Yoshinao Nakagawa,
Kazuya Yamaguchi**

Journal of Molecular Catalysis A: Chemical 251
(2006) 286

Bis(μ -hydroxo) bridged di-vanadium-catalyzed selective epoxidation of alkenes with H_2O_2



Dennis G.H. Hetterscheid, Bas de Bruin

Journal of Molecular Catalysis A: Chemical 251
(2006) 291

Open-shell rhodium and iridium species in (catalytic) oxygenation reactions

So far, mainly closed-shell intermediates have been proposed as intermediates in catalytic oxygenation at rhodium and iridium sites. Recently, however several reports have been published indicating that open-shell species may play an important role. In this article an overview of these examples is given and oxygenation at rhodium and iridium centers via open-shell species is discussed.

