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Olefin Oxygenation by the Hydroperoxide Adduct of a Nonheme Manganese(IV) Complex: Epoxidations by a Metallo−Peracid Produces Gentle Selective Oxidations

Guochuan Yin,† Maria Buchalova,† Andrew M. Danby,† Chris M. Perkins,‡ David Kitko,‡
John D. Carter,‡ William M. Scheper,‡ and Daryle H. Busch*,†

Department of Chemistry, The University of Kansas, Lawrence, Kansas 66045, and
The Procter and Gamble Company, Cincinnati, Ohio 45202

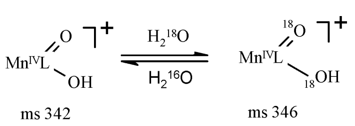
Received August 8, 2005; E-mail: busch@ku.edu

In this communication, we report the first example in which a high valent manganese compound, a pseudo-octahedral manganese(IV) derivative, catalyzes epoxidation, not by way of the familiar manganese oxo intermediate, but by a Lewis acid pathway involving the manganese/hydrogen peroxide complex. Reflecting on the history of epoxidation catalysis by manganese, our results now demonstrate that all three catalytic pathways well-known for epoxidation reactions by high valent metal ions are utilized by manganese, the metal atom redox pathway often called the *rebound mechanism*, the peroxy radical pathway, and the Lewis acid promoted oxygen atom transfer catalysis, most simply typified by Ti(IV).

Epoxidation of olefins has long been important in commercial applications, in addition to being of fundamental mechanistic interest.[1] The epoxide is commonly a minor product in relatively nonselective radical pathways.[2] For catalysis or stoichiometric reactions based on compounds of iron, manganese, cobalt, and chromium, metal oxo species are the established intermediates.[3] The metal ion undergoes two-electron reduction, and an oxygen atom is transferred from the metal coordination sphere to the substrate, a process strongly supported by studies using isotopic oxygen labels. The epoxide may be the dominant but often not the sole product. In contrast, hydrogen peroxide or alkyl peroxide adducts of metal complexes have long been recognized as intermediates in epoxidations mediated by high valent compounds of titanium, vanadium, tungsten, molybdenum, and rhenium, in processes in which the metal ion is assigned the role of a Lewis acid[5] in a mechanism believed to proceed by concerted oxygen atom transfer.[6] Despite the association of specific mechanisms with specific kinds of catalyst, a growing literature indicates that some transition metal ions participate in two or more epoxidation mechanisms.[2b,7] For example, studies indicate that, in addition to the rebound mechanism, an iron adduct of hydrogen peroxide and a manganese adduct of iodosylbenzene also serve as Lewis acids in certain oxygen transfer processes, including epoxidation. Previous to our work, peroxide adducts of high oxidation state manganese have not been implicated in the Lewis acid mechanism of epoxidation.

The catalyst in this work is [$Mn^{II}(Me_2EBC)Cl_2$], the manganese(II) complex of a cross-bridged cyclam ligand, 4,11-dimethyl-1,4,8,-11-tetraazabicyclo[6.6.2]hexadecane. Its well characterized higher valent complexes, [$Mn^{III}(Me_2EBC)Cl_2$]PF_6 and [$Mn^{IV}(Me_2EBC)(OH)_2$]$(PF_6)_2$, were synthesized as reported.[8] Direct reaction between olefins, such as norbornylene and *cis*-stilbene, and either the manganese(III) or the manganese(IV) complex does not occur in solution even after standing for days at room temperature. Clearly the Mn^{IV} complex alone is not capable of epoxidation of olefins even though substantial amounts of the compound would be expected to exist as the oxo complex (pK_a of [$Mn^{IV}(Me_2EBC)(OH)_2$]$^{2+}$ = 6.86).[8b]

Scheme 1



Because the manganese(IV) complex is unstable in base, slowly degrading to $Mn^{III}(Me_2EBC)$ species, a disproportionation mechanism for decomposition was suspected.[8b]

$$2\ \mathrm{Mn(IV)} \leftrightarrow \mathrm{Mn(III)} + \mathrm{Mn(V)}$$

Mn^{IV}oxo[3c] and Mn^{V}oxo[3b,d,4b] are frequently proposed as active intermediates in epoxidation reactions. Although we had shown that [$Mn^{IV}(Me_2EBC)(OH)_2$]$^{2+}$ does not epoxidize olefins, the possibility remained that a Mn^{V}oxo derivative might be produced by disproportionation in basic media, subsequently epoxidizing a substrate. Despite numerous attempts, no epoxide product could be detected and no conversion of olefin could be found upon degradation of the manganese(IV) complex to the manganese(III) derivative in base in the presence of olefins, such as norbornylene.

^{18}O tracer experiments have proven that the epoxide formed in catalysis by [$Mn^{II}(Me_2EBC)Cl_2$ does not come from a high valent manganese complex; the rebound mechanism is not involved in the process. First, it was necessary to show that the oxo and hydroxo groups of [$Mn^{IV}(Me_2EBC)(O)(OH)$]$^{+}$ equilibrate with the solvent $H_2{}^{18}O$.[4] When [$Mn^{IV}(Me_2EBC)(OH)_2$]$^{2+}$ was dissolved in $H_2{}^{18}O$ (95% ^{18}O), the original ms peak for [$Mn^{IV}(Me_2EBC)(O)(OH)$]$^{+}$ at m/z = 342, observed for normal aqueous solutions, disappeared, and a new ms peak for [$Mn^{IV}(Me_2EBC)(^{18}O)(^{18}OH)$]$^{+}$ appeared immediately at m/z = 346 (Scheme 1).

Second, it was necessary to show that the oxygen in the epoxide comes from oxidant, not the catalyst or solvent. The ^{18}O tracer experiment for catalytic epoxidation of *cis*-stilbene used 50% H_2O_2 in 4:1 acetone:$H_2{}^{18}O$ (95% ^{18}O atom). The product analysis by GC−MS shows that the amount of ^{18}O introduced into the epoxide product from $H_2{}^{18}O$ is identical to that obtained in the control experiments; therefore, all oxygen in the epoxide is ^{16}O from H_2O_2 (1.7 ± 0.4% incorporation of ^{18}O from $H_2{}^{18}O$ vs 1.7 ± 0.3% incorporation of ^{18}O from normal water in *cis*-stilbene oxide, and 3.8 ± 0.4% vs 2.6 ± 1% in *trans*-stilbene oxide). It is concluded that *oxygen transfer from a manganese oxo species is not responsible for epoxidation in this manganese complex catalyzed reaction*. This is consistent with the failure (above) of [$Mn^{IV}(Me_2EBC)(OH)_2$]$^{2+}$ to react directly with olefins and with the absence

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† The University of Kansas.
‡ The Procter and Gamble Company.

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Table 1. Epoxidation of Various Olefins by $Mn(Me_2EBC)Cl_2$ with H_2O_2[a]

substrate	product	yield (%)
cyclohexene	cyclohexene oxide	18.0
	cyclohexen-1-one	13.3
styrene	styrene oxide	45.5
	benzaldehyde	2.8
norbornylene	norbornylene oxide	32.0
cis-stilbene	*cis*-stilbene oxide	17.5
	trans-stilbene oxide	2.0
	benzaldehyde	2.6

[a] Reaction conditions: solvent, acetone/water (4:1), catalyst (1 mM), olefin (0.1 M), 50% H_2O_2 (1 mL), added stepwise by 0.2 mL/0.5 h, rt, yield determined by GC with internal standard.

of any products from a possible transient Mn(V) (from disproportionation of Mn(IV) in base, also above).

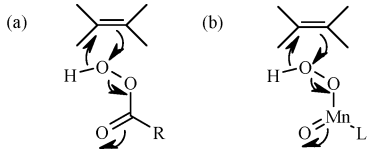
Catalytic epoxidation of various olefins by $Mn^{II}(Me_2EBC)Cl_2$, using 50% H_2O_2, gave substantial yields of epoxide (Table 1). Greater yield of cyclohexene oxide (18%) versus cyclohexen-1-one (13%) supports multiple, or at least dual, mechanisms of oxidation by this catalyst. Further, the dominant *cis*-stilbene oxide (17.5%) (vs minor *trans*-stilbene oxide (2.0%)) could not be the product of oxidation by a peroxy radical.[2a] The similarly high yield of styrene oxide (45.5%), with little benzaldehyde, also suggests a nonradical mechanism.

To substantiate the origin of the oxygen in the epoxide, *cis*-stilbene was oxidized catalytically with 2% H_2O_2 under an atmosphere of $^{18}O_2$. For the *cis*-stilbene oxide product, the deviation in the ^{16}O content from 100% approximates experimental error (3.6 ± 0.5 vs 1.7 ± 0.3% in the blank); essentially, all of the *cis* product derives its oxygen from sources other than O_2, ruling out a peroxy radical pathway for the dominant product. The small amount of *trans*-stilbene oxide (~2%) contained a substantial fraction (16 ± 3%) of oxygen from $^{18}O_2$, implicating the expected radical pathway. The small value of the fraction of ^{18}O in the *trans* isomer may reflect the abundance of hydrogen peroxide in this experiment.

In the complementary experiment in which the label resides on the peroxide, epoxidation of *cis*-stilbene with 2% $H_2{}^{18}O_2$ (90% ^{18}O; used as received due to cost) under air, incorporation of ^{18}O in *cis*-stilbene oxide is 89.9 ± 0.8% (reproducible, but no standard), while ^{18}O in *trans*-stilbene oxide is 72.5 ± 2.4%. Even assuming an optimistic overall error of ±5%, these values are essentially the same as those obtained using labeled O_2. That is, for labeling experiment with $^{18}O_2$ and with $H_2{}^{18}O_2$, the oxygen in *cis*-stilbene oxide comes exclusively from the hydrogen peroxide (est. 95 ± 5%), and that in *trans*-stilbene oxide has two sources, 80 ± 5% from hydrogen peroxide and 20 ± 5% from dioxygen. *cis*-Stilbene oxide is the dominant product over *trans*-stilbene oxide, and in the dominant reaction, *cis*-stilbene is converted to the corresponding epoxide by a nonradical pathway in which the oxygen comes directly from hydrogen peroxide, not via a rebound mechanism from a manganese oxo complex. However, the manganese atom is a critical element in the mechanism.

It is well-known that high oxidation state metal species, such as rhenium(VII), tungsten(VI), molybdenum(VI), vanadium(V), and even titanium(IV), catalyze epoxidations through formation of complexes that have been called inorganic peracids because they resemble the organic peracids in epoxidation reactions.[5] Since, here, the tetravalent manganese is the dominant moiety under the oxidation conditions and the manganese(IV) oxo species is incapable of transferring oxygen directly to olefins, we conclude that a parallel mechanism is operative for manganese(IV). We propose that a "peroxo manganic acid", $Mn^{IV}L(O)(OOH)^+$, is formed by ligand exchange between $Mn^{IV}(Me_2EBC)(O)(OH)^+$ and H_2O_2. The high charge of manganese(IV) and the associated proton polarize the O−O bond, jointly promoting the electrophilic epoxidation of the olefin.[6] As has been described by others, similar mechanisms almost certainly apply in the epoxidations of olefins by organic peracids and such inorganic analogues (Scheme 2).[5]

Scheme 2



To capture the expected main reactive intermediate, $[Mn^{IV}(Me_2EBC)(O)(OOH)]^+$, for the epoxidation reaction described here, the mass spectra were studied for solutions in which $[Mn^{II}(Me_2EBC)(OH_2)_2]^{2+}$ was actively catalyzing the oxidation reaction. Indeed, those mass spectra show the presence of the HO_2^- complex, $[Mn^{IV}(Me_2EBC)(O)(OOH)]^+$, via a moderate ms peak at $m/z = 358$. Accurate mass measurement is definitive (M^+ calcd 358.1777; found 358.1761).

In conclusion, this is the first demonstration that the hydrogen peroxide adduct of a high valent manganese complex serves as the key active intermediate in an epoxidation reaction. This conclusion extends the expectation of oxidations by manganese catalysts to include Lewis acid catalyzed peroxide oxidations.

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Supporting Information Available: Experimental procedures for epoxidations; mass spectrum of $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$ under oxidative conditions; GC/MS graphs for olefin epoxidation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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