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Rhenium oxo complexes in catalytic oxidations

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The US Chemical industry is a large waste generator; it releases ~1.5 billion pounds of toxic waste into the environment each year [1]. Even though in the manufacturing of commodity chemicals waste is usually less than 0.1 lb per pound product, it is not uncommon to produce more than 100 lb of waste per pound of product in fine chemicals and pharmaceuticals. Clearly there is plenty of room for environmental improvements. The best strategy for reducing hazardous waste is through pollution prevention. Catalytic science will be central in the development of a vast repertoire of chemical reactions that are environmentally benign. For example, in the area of selective oxidations, catalyst design and development are necessary for the move towards 'Green Chemistry' in the 21st century. Noxious stoichiometric oxidants, such as permanganate and chromate, will be replaced with cleaner oxidants like hydrogen peroxide and oxygen.

Of all metals, the oxo chemistry of rhenium has been expanded the most during the last 15 years. Tremendous new information (synthetic and mechanistic) has been gained on oxorhenium complexes and their reactions [2–5]. Much of the current advancement in oxorhenium chemistry has largely been motivated by scientific curiosity and interest in high-valent organometallic oxides. The exploratory research of Herrmann et al. has led to the discovery of one of the most versatile oxidation catalysts known to date [4]. This catalyst is methylrhenium trioxide (CH_3ReO_3), or MTO for short. MTO's efficient synthesis and high catalytic utility have made it the most studied organometallic compound. All of the oxidations catalyzed by MTO make use of H_2O_2 as the stoichiometric oxidant. Several reviews have appeared on the subject [2–4,6,7]. The discovery of MTO's catalytic abilities has fueled new investigations of other oxorhenium complexes. In this review, we cover the catalytic chemistry of MTO and other oxorhenium complexes pertaining to organic and inorganic oxidations. The coverage is comprehensive and not limited to peroxide-based transformations. The use of main group oxygen donors, such as sulfoxides and amine *N*-oxides, is also included. The most recent advances from 1991 to date (May 1999) are emphasized.

1. Introduction to MTO's versatility

The ability of methyltrioxorhenium(VII), MTO, to catalyze the epoxidation of olefins with hydrogen peroxide was demonstrated initially by Herrmann and coworkers in 1991 [8]. The mechanisms of oxygen transfer in the MTO/H_2O_2 system have been fully documented by Espenson et al. [9–11]. Recent reviews have addressed the utility of MTO as an oxidation catalyst for a variety of substrates [2,4,6,7]; we include with more details many of the results contained in these reviews and recent developments since 1996. The general mechanism of oxygen transfer from hydrogen peroxide catalyzed by MTO is summarized in Scheme 1.

MTO reacts with H_2O_2 in equilibria reactions to form a monoperoxo- and a diperoxo-rhenium(VII) species, **A** and **B**, respectively. The equilibrium constants K_1 and K_2 in a number of solvents are shown in Table 1. Both peroxorhenium complexes are

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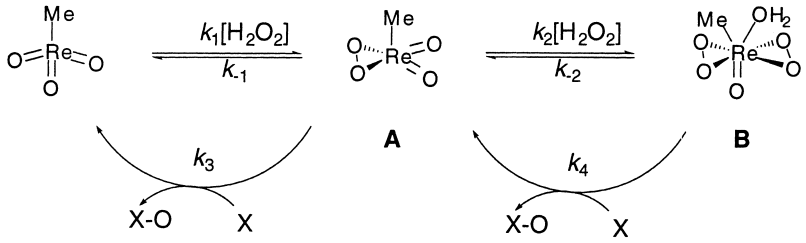
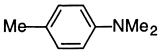
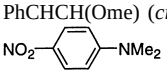
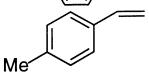
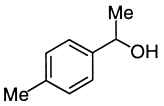
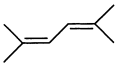
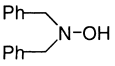


Scheme 1.

Table 1
Equilibrium constants for the MTO/H_2O_2 reactions in various media

Solvent	K_1 ($l\,mol^{-1}$)	K_2 ($l\,mol^{-1}$)	Reference
CH_3OH	261	814	[14]
CD_3CN	210	700	[15]
2.6 M H_2O in CH_3CN	2.1×10^2	6.6×10^2	[16]
0.1 M $HClO_4$ in 1 : 1 CH_3CN/H_2O	13	136	[17]
0.2 M $HClO_4$, 0.50 M H_2O	7.7	156	[9]
CD_3NO_2	–	1300	[15]

Table 2
Rate constants for substrate oxidation by **A** (k_3) and **B** (k_4)

Substrate	k_3 ($l\,mol^{-1}\,s^{-1}$)	k_4 ($l\,mol^{-1}\,s^{-1}$)	Conditions[a]	Reference
$P(C_6H_5)_3$	7.3×10^5	22×10^5	*a*	[17]
$(Me_2CH)_2S$	1.6×10^4	–	*a*	[18]
	2.65×10^3	9.65×10^2	*a*	[18]
$P(C_6F_5)_3$	1.3×10^2	3.47×10^2	*a*	[17]
	1.18×10^2	32	*a*	[18]
	24.5	–	*b*	[14]
PhCHCH(Ome) (*cis* and *trans*)	14.1	16	*a*	[19]
	1.9	–	*b*	[14]
	0.38	0.18	*a*	[19]
	–	1.02×10^6	*d*	[20]
	–	150	*b*	[21]
	–	3.92	*c*	[16]
	–	3.33	*b*	[21]
	–	0.0714	*c*	[16]

[a] *a* = 25°C in 1 : 1 CH_3CN/H_2O + 0.1 M $HClO_4$; *b* = 25°C in CH_3OH; *c* = 25°C in CH_3CN; *d* = 20% H_2O/CH_3CN with 0.1 M $HClO_4$ at 25°C.

reactive towards oxygen-accepting substrates, Table 2. Since rhenium retains its +7 oxidation state in all of these compounds, the peroxo ligand is activated electrophilically via coordination to the rhenium(VII) Lewis acid. Indeed, kinetics establish that k_3 and k_4 are directly related to the nucleophilicity of the substrate. Additionally, a water-free version of **B** has been synthesized by adding hexamethylphosphoramide to a solution of **B** [12]. This species has also been shown to an active oxidant [12].

A general rate law has been derived that is applicable to most oxidations catalyzed by MTO. Using the steady-state approximation [13] for **A** and **B** during the course of the oxidation(s), the rate law is given as in Eq. (1), where X is an oxygen-accepting substrate.

$$v = \frac{k_1k_3[\mathrm{Re}]_T[H_2O_2][X] + \left((k_1k_2k_4[\mathrm{Re}]_T[X][H_2O_2]^2)/(k_4[X]+k_{-2})\right)}{k_{-1} + k_3[X] + k_1[H_2O_2] + \left((k_1k_2[H_2O_2]^2)/(k_4[X]+k_{-2})\right)} \quad (1)$$

Although other rhenium(VII) oxides have also been found to catalyze oxidations with aqueous H_2O_2, these systems generally require harsher conditions, especially high concentrations of hydrogen peroxide and elevated temperatures [22,23]. Some of these results will be described in subsequent sections. Recent reports, however, have attested to the ability of rhenium oxides to catalyze oxidations under essentially water-free conditions using urea hydrogen peroxide or bis(trimethylsilyl)peroxide (vide infra). [24,25].

2. Olefin epoxidation

Excellent reviews have been published describing MTO's ability to catalyze the epoxidation of olefins [2,4,6,7]. Here, we present new advances in olefin epoxidation since 1996.

2.1. Ligand-accelerated catalysis

2.1.1. The MTO/pyridine/H_2O_2 system

Sharpless and coworkers have reported that the addition of catalytic amounts of pyridine to the MTO/H_2O_2 system improves olefin epoxidation [26]. A series of saturated, aliphatic tertiary amines had been found to inhibit strongly catalyst activity, an effect that is independent of amine concentration, solvent, and presence or absence of water [26]. Additionally, it had been reported earlier that the addition of pyridine to the system in fact was detrimental [22]. The Sharpless group, however, discovered that catalytic amounts of pyridine in at least 3 mol% concentration provide a three-fold benefit for olefin epoxidation: (1) rate enhancement, (2) prevention of epoxide hydrolysis to diol, and (3) promotion of catalyst lifetime. A few examples are presented in Table 3.

It is important to note the narrow range of acceptable pyridine concentrations for efficient olefin epoxidation. Over a range of pyridine concentrations from 1 to 12 mol%, the initial rates of the reaction in nitromethane or methylene chloride are nearly equivalent. Yet, the catalyst decomposes at pyridine concentrations of less than 3 mol%. The Sharpless group also has shown that much higher concentrations of pyridine are required to show enhancing effects when the reaction is carried out in *t*-BuOH. Thus, the range of pyridine concentrations that yields the best results is 3–12 mol% pyridine.

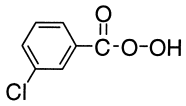
Sharpless and coworkers have also found that 3-cyanopyridine is the best pyridine ligand for epoxidation of terminal olefins [27]. The optimal conditions for the epoxidation of styrene involves a mixture of 10 mol% pyridine and 10 mol% 3-cyanopyridine, along with 0.5 mol% MTO and 2 equivalents of 30% H_2O_2 in CH_2Cl_2; this results in >97% conversion of styrene and >89% yield of styrene oxide. Other terminal olefins that have been studied are best converted using only 3-cyanopyridine instead of a mixture of two different ligands.

Until the discovery of the MTO/H_2O_2 system, epoxidations were performed almost exclusively using *m*-CPBA (*meta*-chloroperoxybenzoic acid). Sharpless outlines the following advantages of the MTO/H_2O_2/pyridine system over *m*-CPBA: (1) the MTO system is comparable in cost but safer; (2) the selectivity and scope of the epoxidation are much greater, as even acid sensitive epoxides resist ring opening or rearrangement; (3) the MTO system is more reactive, requires less solvent, and involves easier product workup and isolation; (4) the only byproduct of the MTO system is water.

Table 3
Comparison of epoxidation results obtained in the presence and absence of pyridine

Substrate	Without pyridine[a]			With pyridine[b]		
	Temperature (°C)	Time (h)	Yield (%)	Temperature (°C)	Time (h)	Yield (%)
	15	24	99	25	0.02	>99
	10	20	95	25	1	>99
	15	72	75	25	14	>99

[a] Aqueous H_2O_2 employed as oxidant in *tert*-butanol [22].
[b] 30% H_2O_2 in CH_2Cl_2 [26].



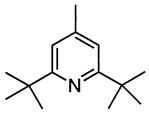
m-CPBA

Control experiments by the Sharpless group rule out two possibilities concerning the role of pyridine in the accelerated reaction rates. A homogeneous solvent system consisting of an 85 : 15 ratio of CH_3NO_2 : *t*-BuOH yields nearly identical reaction profiles to the reactions done in methylene chloride or nitromethane. This control experiment essentially rules out the possibility of a phase transfer effect between solvents. Additionally, 2-picoline was used in place of pyridine, resulting in no acceleration of the reaction rate regardless of the solvent. This indicates that simple base effects also do not explain the pyridine-mediated acceleration [26]. Excess pyridine not only results in more basic solutions, which promote catalyst deactivation [11,28], but oxidation of pyridine to the *N*-oxide becomes competitive with olefin epoxidation [15]. The range of pyridine concentrations discovered by the Sharpless group provides enough pyridine to prevent ring-opening of epoxides but not too much pyridine to retard the epoxidation. Additionally, in this concentration range, the pyridine coordinates to MTO and prevents HO_2^- from decomposing the catalyst to CH_3OH and ReO_4^-.

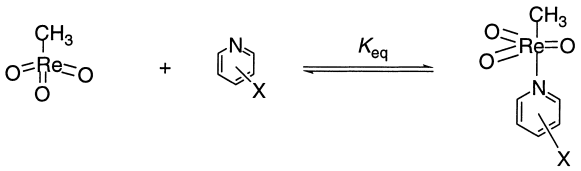
2.1.2. Pyridine's role in olefin epoxidation

The intricacies of pyridine interaction with the MTO/H_2O_2 system for olefin epoxidation have been thoroughly examined by Wang and Espenson [15]. Pyridine interactions with MTO and the peroxorhenium species can be explained in terms of sterics, electronic effects, and basicity. The equilibrium constants for the reaction given by Eq. (2), Table 4, reveal that sterically hindered pyridines, such as 2,6-di-*tert*-butyl-4-methylpyridine (entry 4), interact only slightly with MTO. Electron-rich pyridines, such as 4-methylpyridine (entry 2), exhibit relatively high equilibrium constants when reacted with MTO and thus are strongly favored over electron-withdrawing pyridines such as 3-chloropyridine (entry 3).

Table 4
Equilibrium binding constants for reaction of MTO and a variety of pyridine ligands[a]

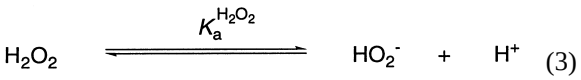
Entry	Ligand	K_{eq} ($l\,mol^{-1}$)
1		200 ± 6
2		732 ± 20
3		>1
4		>1
5		210 ± 4

[a] Reference [15]; conditions: 23°C in CD_3NO_2.



(2)

Pyridine-*N*-oxide was found to bind to MTO just as strongly as pyridine does (entries 1 and 5); however, pyridine's increased basicity ($pK_b = 8.75$ compared to $pK_b = 13.2$ for pyridine-*N*-oxide) leads to a greater accelerating effect for diperoxo complex formation. This acceleration is explained by considering the equilibrium between H_2O_2 and HO_2^-, Eq. (3). Pyridine's higher basicity pushes the equilibrium to the right, increasing the concentration of HO_2^-, which is more reactive than H_2O_2 [15].



(3)

Reactions of MTO were carried out with pyridine (Py) and with 2,6-di-*tert*-butyl-4-methylpyridine (Py*) in order to determine the role of sterics [15]. Py and Py* have similar pK_b's, but Py* is too sterically hindered to coordinate to MTO and is also nonoxidizable. MTO decomposes significantly when the sterically bulky pyridine is added to a solution of MTO and hydrogen peroxide. However, the addition of pyridine to an MTO/H_2O_2 solution protects the catalyst from rapid decomposition.

A series of experiments was performed using α-methylstyrene in acetonitrile with 0.83 M H_2O_2, and the kinetic data were analyzed using the method of initial rates [15]. It was found that the oxidation of pyridine is first-order in pyridine and zero-order in α-methylstyrene, while the epoxidation of the olefin is first-order in olefin and zero-order in pyridine. Kinetics analysis yields a higher rate constant for pyridine oxidation than for olefin epoxidation; thus, oxidation of pyridine is favored over epoxidation of α-methylstyrene. The rate of epoxidation was found to be much lower in the absence of pyridine. The epoxidation of α-methylstyrene was also performed with 4-methylpyridine, 3-chloropyridine, and pyridine-*N*-oxide in similar experiments. The electron-rich 4-methylpyridine oxidizes faster than pyridine, but the active peroxo species react at approximately the same rate in the presence of pyridine or 4-methylpyridine; the maximum epoxidation rate for this series of experiments requires a concentration of 4-methylpyridine ≥0.05 M. It was also found that pyridine-*N*-oxide does not accelerate the epoxidation reaction but does accelerate the formation of the reactive peroxorhenium species. The acceleration of peroxorhenium formation can perhaps be probed by IR spectroscopy. Coordination of an oxygen- or nitrogen-containing ligand weakens the Re=O bond [15]. This weakening could be a key element in what is believed to be the rate-controlling step for the formation of the peroxo species **A**, which is the formation of $CH_3ReO_2(OH)(OOH)$ [15].

2.1.3. Pyrazole as a ligand for the MTO/H_2O_2 system

For most starting materials, ligand oxidation is at least as fast and usually faster than olefin epoxidation. It has been found that the competing processes of olefin epoxidation and *N*-oxidation of the ligand require large excesses of pyridine in order to maintain high activity levels. The addition of pyrazole (Fig. 1) to a solution of MTO in CH_2Cl_2/H_2O_2 clearly transfers the catalyst to the organic phase, indicated by the bright yellow color of the diperoxorhenium complex [29]. This phase transfer increases the lifetime of the catalyst by preventing hydrolytic decomposition in the aqueous phase. Styrene and its derivatives, which are usually susceptible to ring-opening and rearrangement, are converted quantitatively to the corresponding epoxides within 1–3 h using MTO and 12 mol% pyrazole (Table 5) [29]. Hardly any of the ring-opening byproducts are observed. This system is the most selective oxidation system for the epoxidation of olefins known to date. The addition of 6 mol% pyrazole to a solution of MTO and styrene gives a decreased yield of styrene oxide but maintains high selectivity (>99%). *N*-alkylated pyrazole derivatives, such as *N*-methyl pyrazole, decrease both catalyst activity and lifetime. Herrmann concludes that the stability of pyrazole against oxidation seems to be responsible for the epoxidation efficiency. Apparently, the pyrazole ligand is slightly less susceptible to oxidation than pyridine or bipyridine.

2.1.4. N-oxides

Bipyridine *N*,*N*′-dioxide (Fig. 1) is also an effective ligand for preventing the formation of ring-opening

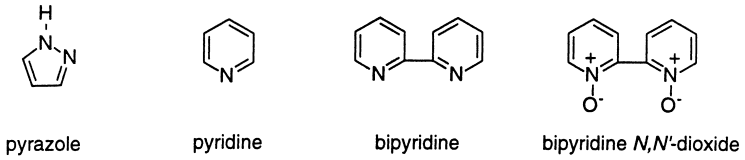
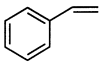
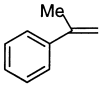
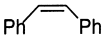
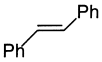


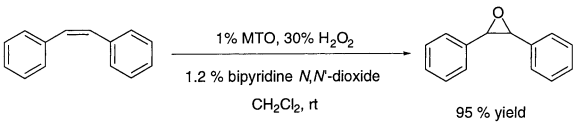
Fig. 1. Ligands for enhanced MTO-catalyzed epoxidations.

Table 5
Comparison of pyridine and pyrazole as ligands for MTO/H_2O_2 system pyrazole system

Substrate	Pyridine system[a]			Pyrazole system[b]		
	Time (h)	Conversion	Epoxide	Time (h)	Conversion	Epoxide
	3	>99	>99	16	84	>99
	1	>99	90	6	92	>98
	1	>99	>99	6	96	>99
	0.02	89	>99	2	>99	>99
	14	>99	>99	48	82	>99
	4	>99	92	30	>99	>98
	4.5	>99	98	30	85	>98

[a] Conditions: 0.5 mol% MTO, 12 mol% pyridine, 1.5 equivalent 30% H_2O_2, CH_2Cl_2, room temperature; reference [26].
[b] Conditions: 0.5 mol% MTO, 12 mol% pyrazole, 2 equivalents of 35% H_2O_2, CH_2Cl_2, room temperature; reference [29].

products in MTO-catalyzed epoxidations of olefins [30]. Bipyridine has also been used as a ligand, but its oxidation to the dioxide is much faster than oxidation of the substrate; only 20% conversion of stilbene is achieved while bipyridine *N*,*N*′-dioxide is formed in quantitative yield [30]. The use of bipyridine *N*,*N*′-dioxide appears not to have a detrimental effect on the catalyst's activity since the ligand is a weaker base than pyridine. However, the equilibrium constant for binding of bipyridine *N*,*N*′-dioxide to MTO is much lower than that for pyridine; thus, bipyridine *N*,*N*′-dioxide does not bind MTO as strongly as pyridine does. *Cis*-stilbene is converted to *cis*-stilbene oxide in 95% yield with 1.0% MTO, 30% aqueous hydrogen peroxide, and 1.2% bipyridine *N*,*N*′-dioxide in CH_2Cl_2 at room temperature, Eq. (4), [30].



(4)

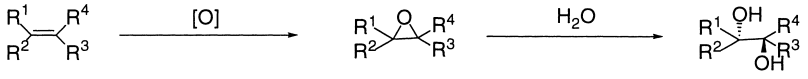
Good to high epoxide yields are obtained from the oxidation of a wide spectrum of olefins, including mono-, di-, tri-, and tetra-substituted olefins. It has been found that the MTO/H_2O_2/dioxide system works best for the oxidation of styrene with 3 M H_2O_2 in *tert*-butyl alcohol instead of aqueous hydrogen peroxide. Isoquinoline *N*-oxide and pyridine *N*-oxide are less effective at obtaining good yields of the epoxide, which may indicate that the two oxygen atoms of bipyridine *N*,*N*′-dioxide are important [30].

N-oxide adducts of MTO have also been synthesized and isolated. Herrmann and coworkers reported in 1997 the isolation of an adduct of MTO with 4-*tert*-butylpyridine *N*-oxide [31]. The complex, when applied to oxidation of cyclohexene with 10% H_2O_2, is more selective and does not lead to ring-opening of the epoxide products as seen in oxidations with the *N*-donor analogue, (4-*tert*-butylpyridine)methyltrioxorhenium [31]. Generally speaking, aromatic *N*-oxide ligand complexes of MTO are significantly more stable and are highly selective compared to *N*-donor ligand complexes [31]. However, the selectivity of the *N*-oxide complexes diminishes above room temperature [31].

2.2. Water-free olefin epoxidation

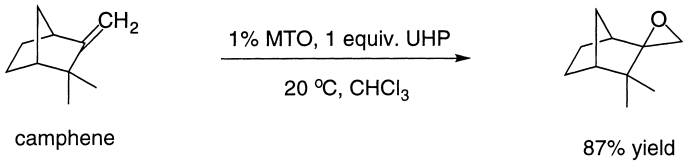
2.2.1. Urea-hydrogen peroxide (UHP) as oxidant

MTO-catalyzed epoxidations of olefins often lead to ring-opening hydrolysis products, Eq. (5).



(5)

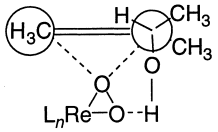
The less desirable diol product can be averted by using the urea hydrogen peroxide complex (UHP) in place of aqueous hydrogen peroxide [24,32]. When UHP is used as the primary oxidant, the reaction can be carried out in nonaqueous solvents, thereby substantially decreasing the possibility of epoxide hydrolysis. The MTO-catalyzed reaction of camphene with UHP gives 95% yields of the epoxide and none of the 1,2-diol, Eq. (6).



(6)

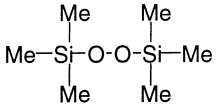
Conversely, the reaction of camphene with 85% H_2O_2 and MTO results in the formation of exclusively cleavage and rearrangement products and none of the epoxide. Thus, the UHP/MTO system is successful in preventing hydrolysis of most epoxides, which are the initial oxidation product. Yet, some substrates such as α-methylstyrene yield a considerable percentage of the hydrolysis product (∼32%). A major drawback of the UHP/MTO system is insolubility of the polymeric UHP complex, a fact that results in a kinetically slow heterogeneous system. For example, electron-poor olefins resist oxidation to the point of competing with catalyst deactivation.

Perhaps the most exciting feature of the UHP/MTO catalytic system is its ability to transform olefins to epoxides diastereoselectively. Epoxidation of chiral allylic alcohols results in high threo diastereoselectivity. This selectivity seems to indicate that the reaction proceeds through a peracid-like transition state [24].



2.2.2. Trimethylsilyl peroxide with MTO and other rhenium oxides

One of the few limitations of rhenium-oxo chemistry in catalysis is the hydrolytic instability of most oxorhenium compounds except MTO. Attempts to modify the MTO system by replacing the methyl group with other alkyl substituents have resulted in species that are poor catalysts when used with low concentrations of H_2O_2 [22]. Subsequently, it has been shown that less expensive rhenium oxides, especially Re_2O_7, $HOReO_3$, and ReO_3, exhibit high catalytic activity at safe peroxide concentrations when aqueous hydrogen peroxide is replaced by bis(trimethylsilyl)peroxide, $Me_3SiOOSiMe_3$ (BTSP) [25].



BTSP

BTSP is soluble and stable in organic solvents and hydrolyzes rapidly in water. The addition of 1 equivalent H_2O hydrolyzes BTSP within only a few minutes and results in poor olefin conversion. Additionally, catalytic epoxidation is extremely poor when 4 Å molecular sieves are added to the solution to remove all traces of water. However, the addition of 5 mol% H_2O dramatically accelerates epoxidation. The catalytic amount of water reacts with BTSP to form small amounts of hydrogen peroxide. It is important to note that slow addition of H_2O_2 does not achieve higher conversions of the olefins; MTO decomposes faster in lower hydrogen peroxide concentrations. A 'proton dependent' cycle proposed by Sharpless accounts for the success of the BTSP system when a catalytic amount of water is added [25]. A protic species X–OH is required to transfer the peroxo group from silicon to rhenium. As with the MTO/H_2O_2 system, the addition of pyridine to this MTO/BTSP system prevents ring-opening of acid-sensitive epoxides. Curiously, the necessary dose of pyridine is lowered from 12 to 0.5–1.0 mol% for both MTO and Re_2O_7-catalyzed epoxidations. When the BTSP/pyridine system is employed, Re oxides other than MTO are more efficient in some cases for the epoxidation of dienes and terminal olefins [25].

Below, we present a sample of substrates that have been efficiently oxidized using water-free epoxidation methods (Table 6).

3. Epoxidation and hydroxylation of conjugated dienes

Methylrhenium trioxide has also been shown to catalyze the oxidation of conjugated dienes by hydrogen peroxide [16]. Most of the dienes that have been studied react with hydrogen peroxide and MTO to form diols, but urea hydrogen peroxide has proven to be an effective peroxide source for the oxidation without subsequent ring-opening.

3.1. Kinetics of diene oxidation

Kinetics experiments have been performed in acetonitrile by monitoring the decrease in diene absorption in the UV region [16]. As UHP is insoluble in acetonitrile, the kinetics experiments were performed using aqueous hydrogen peroxide. Plots of absorbance versus time were analyzed using initial rates and pseudo-first-order methods. The general rate law for the reaction is the same as that given in Eq. (1). In order to simplify this into a more manageable form, the concentration of the diene was taken to be larger than the concentration of peroxide, enabling the simplification of the expression to

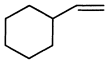
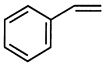
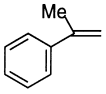
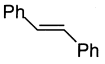
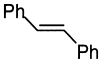
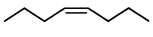
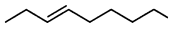
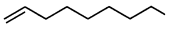
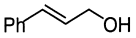
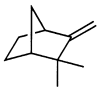
$$\nu = k_1[\mathrm{Re}]_\mathrm{T}[\mathrm{H_2O_2}] \tag{7}$$

A more meaningful expression with regard to the actual oxygen-transfer step of the reaction can be obtained by using diene concentrations that are lower than the concentration of hydrogen peroxide. The equation then reduces to

$$\nu = k_4[\mathrm{Re}]_\mathrm{T}[\mathrm{diene}] \tag{8}$$

Since the rhenium species obviously remains constant, the reaction can be said to follow pseudo-first-order kinetics. Indeed, the rate constant k_ψ shows a linear dependence on $[\mathrm{Re}]_\mathrm{T}$. The monoperoxorhenium complex, **A**, apparently contributes little to the oxidation of the dienes compared to the contribution of the diperoxorhenium complex, **B**. Thus, the reaction between **B** and the alkene was determined to be the rate-controlling step. The rate constant k_4 for converting diene to product depends on the substituents attached to the diene. Dienes with electron-donating substituents display higher k_4 values, while dienes with electron-withdrawing substituents display lower k_4 values. It follows that the more electron-rich double bond in a diene is more easily converted to the epoxide. Conjugation of the double bonds also is an important factor to consider in drawing meaningful conclusions from rate data. Systems that exhibit a greater degree of conjugation have faster oxidation rates. For example, 1,3-cyclohexadiene was found to have a much higher k_4 ($1.0\ \mathrm{l\ mol^{-1}\ s^{-1}}$) than 1,4-cyclohexadiene ($0.102\ \mathrm{l\ mol^{-1}\ s^{-1}}$). For cyclic dienes, ring size seems to be important, as the rate of oxidation decreases from six carbons to seven and then to eight. This decrease

Table 6
Oxidation of olefins using water-free methods

Substrate	Stoichiometric oxidant[a]	Catalyst	Time (h)	Epoxide yield (%)
	UHP	MTO (1%)	18	99
	BTSP	Re_2O_7 (0.5%)	7	95
	UHP	MTO (1%)	20	93
	UHP	MTO (1%)	19	96
	BTSP	Re_2O_7 (1%)	10	82
	BTSP	Re_2O_7 (1%)	13	78
	UHP	MTO (1%)	19	≥95
	UHP	MTO (1%)	21	68
	BTSP	Re_2O_7 (0.5%)	10	96
	UHP	MTO (1%)	19	≥95
	BTSP	MTO (0.5%)	15	92
	BTSP	MTO (0.5%)	9	90
	BTSP	Re_2O_7 (0.5%)	14	94
	UHP	MTO (1%)	24	≥95
	UHP	MTO (1%)	37	≥95
	UHP	MTO (1%)	30	≥95

[a] UHP work: reference [24]. BTSP work: reference [25]; conditions for MTO/UHP oxidations: 1 equivalent of UHP in $CDCl_3$ at 20°C, conditions for Re=O/BTSP oxidations: 1.5 equivalent BTSP per double bond in CH_2Cl_2 or THF at room temperature.

can actually be explained as a loss of conjugation as the dihedral angle widens for the rings with higher numbers of carbons [16].

3.2. Product formation and stability

Epoxide product yields obtained from the reaction of a series of dienes with UHP range from 58% for 2,5-dimethyl-2,4-hexadiene to 96% for *cis*,*cis*-1,3-cyclooctadiene. In the absence of water, some epoxides showed no evidence of ring opening after periods up to 1 week. Diol formation does occur over a period of several hours upon addition of 2.2 M water.

4. Reactions of allylic alcohols with MTO

4.1. Kinetics of epoxidation

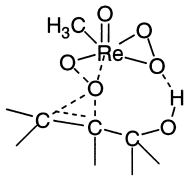
Espenson and coworkers have recently reported a wealth of kinetic data on the epoxidation of allylic alcohols by the MTO/H_2O_2 system [33].

Using Eq. (1), it has been observed that fits of the kinetic data to the equation with acceptable results can be obtained only when $k_4 \gg k_3$. This means simply that the oxidation of allylic alcohols with **A** is negligible and can be largely ignored. Knowing this and taking $k_{-2} \ll k_4$ [substrate], the rate equation reduces to

$$\nu = \frac{k_1 k_2 k_4 [\text{alcohol}][\text{Re}]_T[H_2O_2]^2}{(k_{-1} + k_1[H_2O_2])k_4[\text{alcohol}] + k_1 k_2 [H_2O_2]^2} \quad (9)$$

Rate constants for a series of allylic alcohols reveal the same general trends characteristic of most MTO-catalyzed oxidations. Substitution of the alkene carbons with electron-donating groups (such as alkyl groups) leads to higher epoxidation rates.

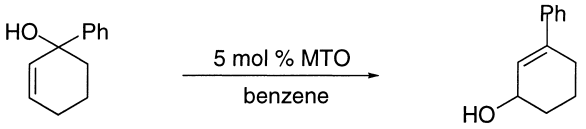
A few key results from the most recent work help toward elucidating a more definitive transition state structure. First, as mentioned above, the oxidation of allylic alcohols with **A** is negligible, which means that **A** is relatively unreactive toward 3-hydroxyalkenes but still reactive toward alkenes and alcohols. **B**, on the other hand, is reactive toward all three substrates. Second, the kinetic dependence on $[H_2O_2]$ is unusual in that most other substrates show oxidation rates that are independent of peroxide concentration, especially relatively high concentrations. Third, **B** exhibits high diastereoselectivity for the oxidation of allylic alcohols. This effect has been studied in experiments with 2-cyclohexen-1-ol; the oxidation of this allylic alcohol results in greater than >95% yield of one of the stereoisomers. All these results taken together lead to the proposal of a transition state structure that involves hydrogen bonding between the OH group of the allylic alcohol and a peroxo oxygen from **B**; the oxygen atom that is transferred is taken from the same peroxo group that is involved in hydrogen bonding. The structure of the transition state most likely to account for all these results is shown below [1].



[1] Reprinted with permission from Tetzlaff, H.R.; Espenson, J.H. Inorg. Chem. 38 (1999) 88. Copyright 1999 American Chemical Society.

4.2. 1,3-transposition of allylic alcohols

MTO catalyzes 1,3-transposition of allylic alcohols in a single step [34]. For example, 3-hydroxy-3-phenylcyclohexene undergoes 1,3-transposition, catalyzed by MTO, to form 6-hydroxy-2-phenylcyclohexene, Eq. (10). Control experiments show that the reaction does not occur in the absence of MTO.



98 %

(10)

MTO remains intact in benzene and acetonitrile solutions [34], but some allylic alcohols give poor conversions or none at all. It has been found that in some cases, the alcohols condense or are dehydrated.

4.2.1. Kinetics and mechanism of MTO-catalyzed 1,3-transpositions

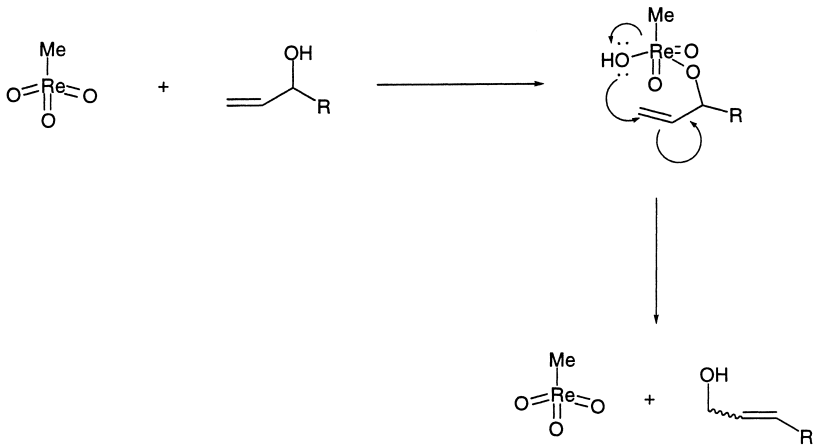
Kinetics experiments at constant alcohol concentration show first-order dependence on [MTO], and experiments at constant MTO concentration show first-order dependence on [alcohol]. However, the rate constant for experiments at constant [MTO] decreases with increasing [alcohol] [34]. Unfortunately, no kinetic scheme has been developed to account for these unusual results.

Espenson and coworkers propose the following mechanism for the 1,3-transposition of allylic alcohols catalyzed by MTO, Scheme 2.

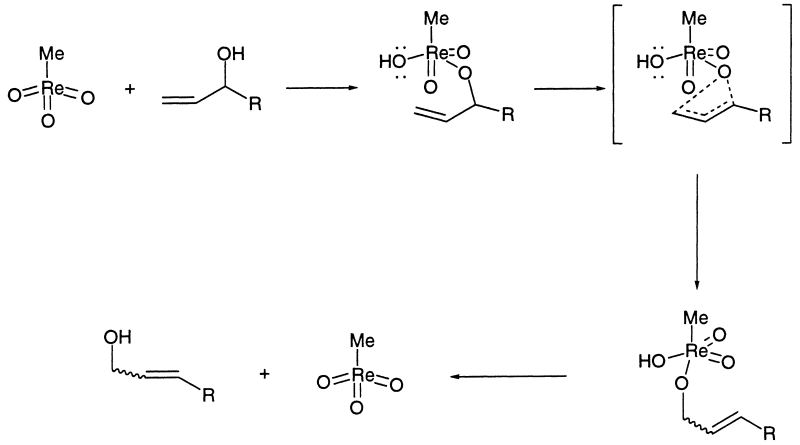
The formation of a complex between MTO and alcohols is precedented [35], as are similar mechanisms involving metal-oxo complexes [36,37]. However, ^{18}O-labeling experiments involving $CH_3Re(^{18}O)_3$ and 3-methyl-2-buten-1-ol show no incorporation of labeled oxygen into the transposed product. The mechanism shown in Scheme 3 is the most plausible mechanism to date [34].

5. Oxidation of silyl enol ethers

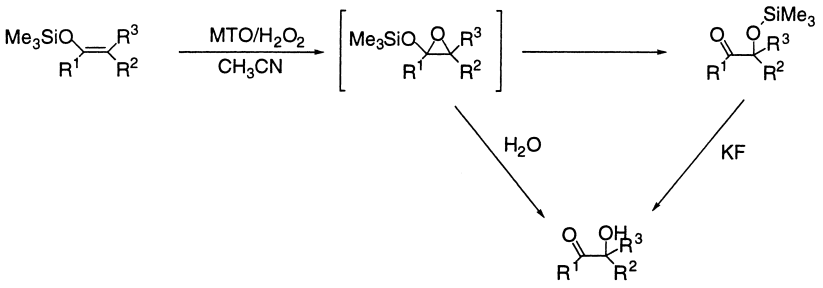
Silyl enol ethers can be converted to α-siloxy and α-hydroxy ketones using a system that combines



Scheme 2. Reprinted with permission from Jacob, J.; Espenson, J.H.; Jensen, J.H.; Gordon, M.S. Organometallics 17 (1998) 1835. Copyright 1998 American Chemical Society.



Scheme 3. Reprinted with permission from Jacob, J.; Espenson, J.H.; Jensen, J.H.; Gordon, M.S. Organometallics 17 (1998) 1835. Copyright 1998 American Chemical Society.

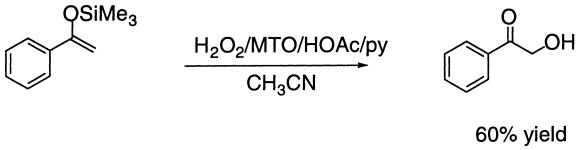


Scheme 4.

H_2O_2/MTO with acetic acid and pyridine, Scheme 4, [38]. Attempts to oxidize the ethers to the siloxy and hydroxy ketones using H_2O_2 and MTO but without acetic acid and pyridine are unsuccessful. Also, an H_2O_2/MTO/HOAc oxidation system without pyridine results only in total hydrolysis of the substrate. As discussed earlier with respect to epoxidation of olefins, pyridine prevents the formation of hydrolysis products. The acetic acid is necessary to prevent base-induced decomposition of MTO.

The reaction yields both the α-siloxy and α-hydroxy ketones, but the former can be converted to the latter by treatment with potassium fluoride. The formation of the products is thought to proceed through an epoxide intermediate, [38], Scheme 4.

Yields for most of the substrates that have been investigated are >94% (siloxy and hydroxy ketone products combined). However, conjugated systems do not give great product yields, as is the case for the reaction of 1-phenyl-1-(trimethylsiloxy)ethene, Eq. (11).



(11)

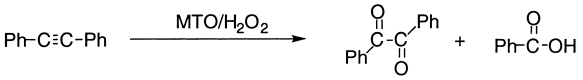
The balance of the product yield are hydrolysis products. The conjugated systems are apparently less prone to oxidation; therefore, hydrolysis occurs more readily with these substrates.

6. Oxidation of alkynes

The MTO/hydrogen peroxide system catalyzes the oxidation of both internal and terminal alkynes [39]. Historically, alkynes have been subjected to oxidation by harsh organic peracids, and some alkynes were resistant to oxidation even under those conditions. The MTO/H_2O_2 system provides a much cleaner, safer method of alkyne oxidation [39].

6.1. Oxidation of internal alkynes

The products obtained from the oxidation of internal alkynes largely depend on the solvent used. Diphenylacetylene converts (>84%) primarily to benzil and benzoic acid with MTO/H_2O_2 in homogeneous solution, Eq. (12); the highest conversion and highest yield of benzil is achieved in ethanol.



(12)

Greater yields of benzoic acid and lower yields of benzil result when a biphasic CH_2Cl_2/H_2O mixture is used; this mixture also gives lower conversions of diphenylacetylene. When dimethyldioxirane is the solvent, ketene-derived products dominate. Aromatic alkynes are less reactive than aliphatic alkynes, but aliphatic alkynes lead to more complex product mixtures [39].

6.2. Oxidation of terminal alkynes

Terminal alkynes are oxidized to give less complex product mixtures than internal alkynes give but also are solvent dependent [39]. Primary alcohols promote the formation of esters as the major products, but secondary alcohols allow little ester formation; tertiary alcohols allow none at all. Carboxylic acids are obtained as the major products when acetone is the solvent, and the biphasic CH_2Cl_2/H_2O mixture yields primarily α-keto carboxylic acids.

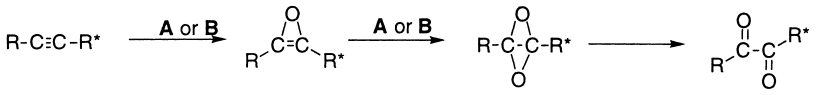
6.3. Possible mechanisms for alkyne oxidations

Alkyne oxidation is thought to proceed through an oxirene intermediate [39]. This mechanism (Scheme 5) provides a reasonable path to the diketone.

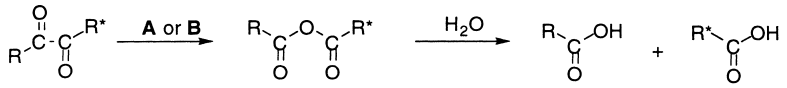
Two different pathways could account for the formation of the carboxylic acids. The first pathway is the well known conversion of an α-diketone to a pair of carboxylic acids by Baeyer–Villiger oxidation, [39], Scheme 6.

Espenson and Zhu propose another mechanism involving a reaction of the oxirene intermediate with MTO to form a ‘bisalkoxy’ complex, [39], Scheme 7.

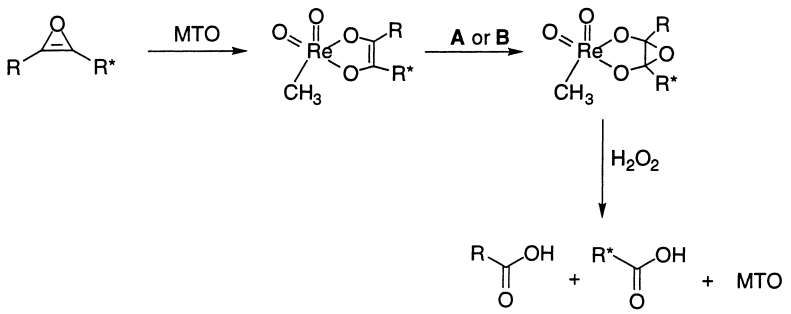
The carboxylic acid could also be formed via ketene rearrangement. The oxirene intermediate rearranges to a ketene, and the ketene subsequently adds water (or an alcohol) to form the carboxylic acid, [39], Scheme 8.



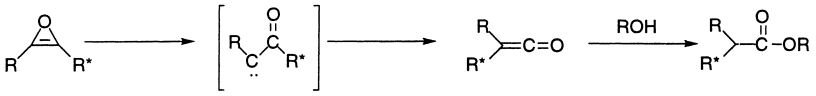
Scheme 5.



Scheme 6.



Scheme 7. Reprinted with permission from Zhu, Z.; Espenson, J.H. J. Org. Chem. 60 (1995) 7728. Copyright 1995 American Chemical Society.



Scheme 8. Reprinted with permission from Zhu, Z.; Espenson, J.H. J. Org. Chem. 60 (1995) 7728. Copyright 1995 American Chemical Society.

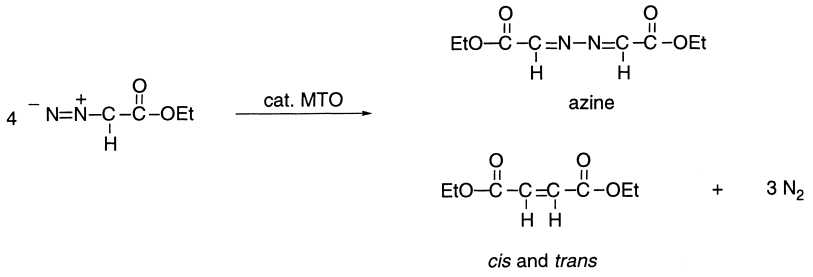
The alkyne : MTO ratio alters the alkyne conversion but not the product distribution. Hydrogen peroxide seems to be responsible for the product mixtures in different solvents, as benzil is the dominant product when peroxide is the limiting reagent in acetone, methanol, and the CH_2Cl_2–H_2O system.

7. Isoelectronic nitrene- and carbene-transfer to alkenes

Ethyl diazoacetate (EDA) has been shown to be a remarkably versatile reagent for a variety of reactions catalyzed by MTO [40,41]. These reactions range from decomposition of EDA to transfer of carbenes across double bonds. Dry benzene is the solvent of choice for most of the reactions as small amounts of water result in the formation of ethyl glycolate.

7.1. Decomposition of ethyldiazo acetate (EDA)

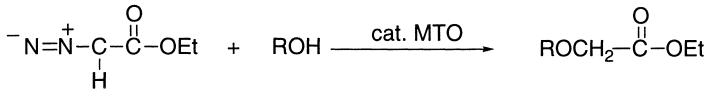
EDA decomposes to yield diethyl maleate and fumarate with a small amount of ethyl glyoxalate azine, Eq. (13). The decomposition proceeds at 60°C with 10% MTO in dry benzene and a reaction time of 6 h. The olefin *cis* : *trans* ratio for the reaction works out to 9 : 1. The amount of the azine formed during the reaction is determined by the concentrations of EDA and MTO. The azine is formed in quantitative yield when MTO is used in 0.2 mol% of EDA, but using 3 mol% MTO results in the formation of 10% azine product.



(13)

7.2. Formation of alkoxy and phenoxy esters

EDA reacts with primary, secondary, and tertiary alcohols in the presence of MTO to form alkoxy and phenoxy esters in fair to good yields, Eq. (14).



(14)

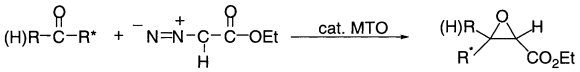
Isolated yields of ≥87% are obtained with low-molecular-weight primary alcohols and phenols; larger and more sterically hindered alcohols give yields of at least 57% (obtained from *t*-amyl alcohol). The side products of the reaction are diethyl maleate and fumarate; none of the azine is observed.

7.3. Formation of thioesters and glycine esters

Thiols and amines react with EDA in the same way as do alcohols to form thioesters and glycine esters. Yields for a series of thiols range from 89 to 96%; glycine ester yields for a series of primary and secondary amines range from 84 to 91%. Traces of diethyl maleate and fumarate are observed, but none of the azine is formed. Instead of dry benzene, the thiols and amines themselves are used as the solvents, resulting in fast reactions. The reaction of EDA with thiols in the presence of MTO runs to completion within minutes, and the reaction of EDA with amines in the presence of MTO takes only 1 h to finish.

7.4. MTO-catalyzed formation of epoxides from ketones and aldehydes

Aldehydes and ketones react with EDA in the presence of MTO to form epoxides in yields of 49–79%, Eq. (15).

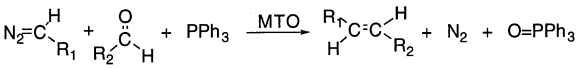


(15)

The reactions of aliphatic aldehydes with EDA and MTO show the fastest rates, followed by aromatic aldehydes and then ketones. Aldehydes react to form the epoxide in mostly *trans* stereochemistry, while ketones react to yield a mixture of both stereoisomers.

7.5. Aldehyde olefination

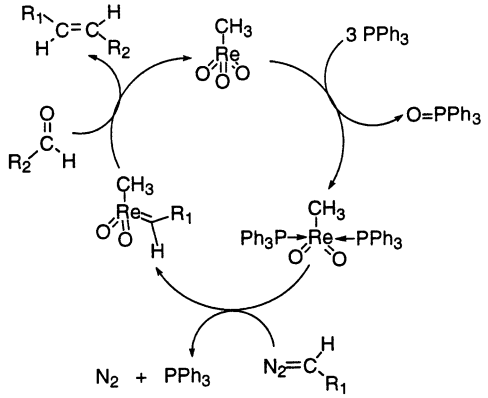
Aldehydes couple with diazoalkanes in the presence of triphenylphosphine and catalytic amounts of MTO to give olefins in 85% yield, Eq. (16), [42]. Depending on the substrate, the stereo selectivity (*trans*) ranges from 60 to 95%. *Trans* selectivity is improved at lower catalyst loadings.



(16)

A mechanism involving methylrhenium dioxide (MDO) formation followed by the formation of an oxorhenium(VII) alkylidene intermediate, Scheme 9, has been proposed by Herrmann

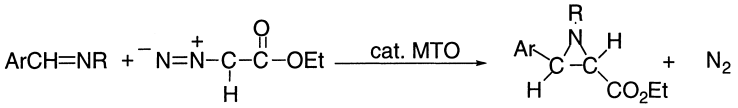
et al. Aldehyde olefination with a diazo reagent and PPh_3 is catalyzed by oxorhenium(V) complexes such as *mer,trans*-$Re(O)Cl_3(PPh_3)_2$, **I**, and *mer,cis*-$Re(O)Cl_3(Me_2S)(OPPh_3)$, **II**; olefin yields are quantitative with a *trans* selectivity >90% [43,44]. These results support the postulated mechanism in Scheme 9. However, Espenson and Zhu have shown that MTO catalyzes the formation of epoxides from the reaction of aldehydes and diazo reagents (vide supra). MTO is also known to effect deoxygenation of epoxides with PPh_3, (vide infra). Therefore, the competing mechanism described in Scheme 10 might be relevant to aldehyde olefination.



Scheme 9. Proposed mechanism of aldehyde olefination catalyzed by MTO.

7.6. Aziridine formation

Much like the epoxidations described above, aromatic imines react with EDA to form aziridines at yields ≥87%, Eq. (17).

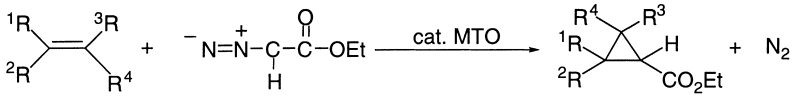


(17)

Only the *trans* isomer of the aziridine is formed, and traces of fumarate and diethyl maleate are present. The intermediate of the reaction is thought to be a rhenium oxy-carbene and will be discussed in a subsequent section.

7.7. Synthesis of cyclopropanes

Cyclopropanecarboxylic esters are obtained in 57–87% isolated yield by the reaction of alkenes with EDA and MTO, Eq. (18).



(18)

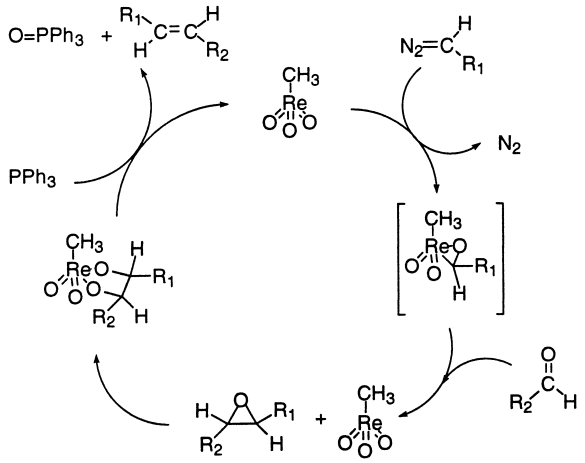
This reaction also is much faster when performed using the alkene as the solvent. The mechanism is thought to include the formation of a carbene intermediate analogous to the intermediate formed in the reaction of H_2O_2 with MTO [41].

7.8. The nitrene and carbene intermediates

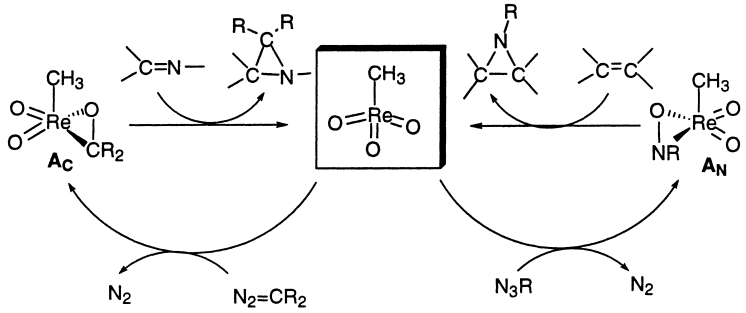
As discussed earlier, MTO forms a mono- and a diperoxo species when reacted with H_2O_2. The formation of aziridines and cyclopropanes mentioned above are proposed to proceed via 'nitrenoid' and 'carbenoid' intermediates, respectively [41]. These nitrene and carbene intermediates are isoelectronic with the monoperoxorhenium species **A**, so the intermediates are dubbed $\mathbf{A}_C$ for the carbene and $\mathbf{A}_N$ for the nitrene. The following mechanism (Scheme 11) has been proposed for the formation of the intermediates [41].

8. Sulfide oxidations

MTO has been shown in recent years to catalyze the oxidation of sulfides by H_2O_2 [18,45,46]. Adam et al.

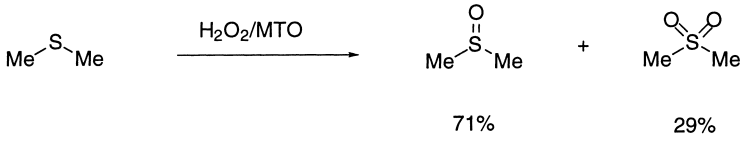


Scheme 10. Alternate mechanism for MTO-catalyzed aldehyde olefination.



Scheme 11. Proposed carbene and nitrene intermediates for MTO-catalyzed reactions of EDA and azides.

were the first to demonstrate this by oxidizing a series of organic sulfides using 1 mol% MTO with 1–2 equivalents of 85% H_2O_2 in $CDCl_3$ [45]. Diphenyl sulfide is oxidized with 91% conversion to give diphenyl sulfoxide at yields greater than 95%. Dimethyl sulfide reacts with the MTO/ H_2O_2 system to give >95% conversion and a sulfoxide : sulfone ratio of 71 : 29, Eq. (19).



71% 29% (19)

Greater concentrations of either the catalyst or the oxidant resulted in increased yields of the sulfones. It has also been shown that the monoperoxo adduct is indeed more reactive than the diperoxo adduct, and sulfoxide oxidation to sulfone proceeds with much slower rates than that of sulfide to sulfoxide [18]. The highest conversions are obtained with ethanol as the solvent [46]; the reaction times are also reduced drastically by changing the solvent from chloroform to ethanol. Oxidation of the sulfide with a 1 : 1 ratio of oxidant to substrate in ethanol results in excellent yields of sulfoxide, whereas the oxidation of the sulfide with 2 equivalents of oxidant produces the corresponding sulfone in quantitative yield.

8.1. Kinetics of sulfide oxidations

Kinetics studies show the characteristics of Michaelis–Menten kinetics, that is a kinetic trace that is zero order during the initial part of the reaction but approaching first order by the end of the reaction [18]. When the peroxide concentration is kept low, the only peroxorhenium complex that is present to any appreciable amount is **A**. Assuming steady-state for the formation and subsequent loss of **A** yields the following rate law, Eq. (20), where $[Re]_T = [MTO] + [\mathbf{A}]$, and the rate constants are those defined in Scheme 1.

$$\text{rate} = \frac{k_3[\text{Re}]_T[\text{H}_2\text{O}_2][\text{sulfide}]}{((k_{-1} + k_3[\text{sulfide}])/k_1) + [\text{H}_2\text{O}_2]} \quad (20)$$

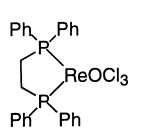
8.2. Oxidation of thiophenes

The oxidation of thiophenes proceeds slower than the oxidation of sulfides [47]. This seems reasonable when one considers that the oxidation mechanism is thought to include a nucleophilic attack by the substrate on one (or both) of the peroxorhenium complexes. The delocalization of electrons from the sulfur into the aromatic thiophene ring renders the sulfur not as reactive towards the electron-deficient peroxide on the rhenium center [47]. A comparison of rate constants k_3 and k_4 for oxidation of sulfides and thiophenes is given in Table 7. The data presented in the table is consistent with a mechanism that involves electrophilic activation of peroxide; electron-donating substituents on the thiophenes lead to an increase in rate constants.

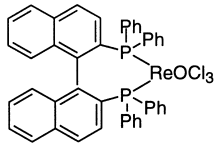
Thiophene and benzothiophene 1-oxides can also be oxidized to their corresponding dioxides [47]. Curiously, the rates of oxidation of these sulfoxides do not differ drastically from substrate to substrate. This phenomenon raises the possibility of the sulfoxide being the electrophile, which is an obvious departure in mechanism from the first oxidation step [47]. Similar observations have been made for Baeyer–Villiger oxidations and will be discussed later.

8.3. Water-free sulfide oxidations

Urea hydrogen peroxide (UHP) has recently found a use as an oxidant for sulfide oxidations [48]. It has been shown recently that MTO and *mer,trans*-$Re(O)Cl_3(PPh_3)_2$, **I**, catalyze the oxidation of sulfides to sulfoxides. As with its hydrogen peroxide oxidations, MTO is found to catalyze the oxidation of sulfides all the way to the corresponding sulfone when more than 1 equivalent of UHP is used. However, *mer,trans*-$Re(O)Cl_3(PPh_3)_2$ as well as two new Re(V) catalysts, **III** and **IV**, convert sulfides to sulfoxides without overoxidizing to the sulfones.



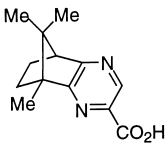
III



IV

The catalytic activity of all four rhenium catalysts is highly dependent on the solvent. The reaction rates of sulfide oxidation are much faster in acetonitrile than in chloroform or methylene chloride. Catalyst **III** requires longer reaction times for the oxidations of methyl benzyl sulfide and methyl phenyl sulfide than $Re(O)Cl_3(PPh_3)_2$, but catalyst **IV** catalyzes both oxidations faster than $Re(O)Cl_3(PPh_3)_2$. Sulfoxide yields of 80–92% have been reported for oxidation with UHP and 2–3 mol% $Re(O)Cl_3(PPh_3)_2$.

There have also been attempts at achieving enantioselectivity in sulfide oxidations catalyzed by oxorhenium compounds. It has been shown that pyrazine-2-carboxylic acid (PCA) accelerates the oxidation of certain aliphatic and aromatic hydrocarbons [49] (vide infra), a phenomenon that probably involves a Re–PCA adduct. A chiral PCA ligand **V** has been used as a co-catalyst for the oxidation of methyl phenyl sulfide, resulting in the formation of the sulfoxide with an enantiomeric excess (EE) of 15%.

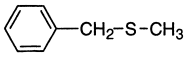
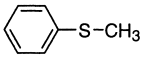
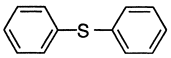
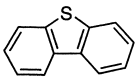
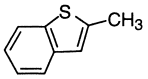
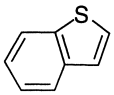


V

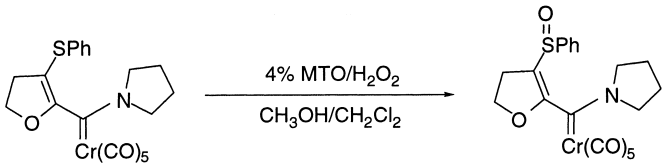
8.4. Oxidation of thioether fischer carbene complexes to sulfoxides

Sulfoxides can be made in reasonably good yields from thioether Fischer carbenes Eq. (21) using 4%

Table 7
Oxidation of sulfides and thiophenes by the MTO/H_2O_2 catalytic system

Substrate	k_3	k_4	Reference
	$(5.4 \pm 0.3) \times 10^3$	–	[18]
	$(2.65 \pm 0.08) \times 10^3$	$(9.65 \pm 0.02) \times 10^2$	[18]
	$(1.18 \pm 0.06) \times 10^2$	$(3.2 \pm 0.05) \times 10^1$	[18]
	10.2 ± 0.2	21.8 ± 0.1	[47]
	–	4.99 ± 0.05	[47]
	–	1.75 ± 0.03	[47]

MTO and hydrogen peroxide in a methanol/methylene chloride solution [50].

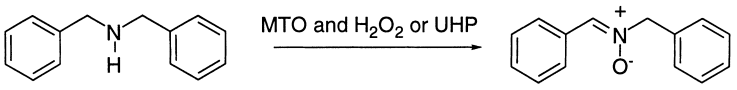


(21)

9. Amine oxidations

9.1. Synthesis of nitrones from secondary amines

Several reports have been written of MTO's ability to catalyze the oxidation of secondary amines to nitrones [21,51,52]. Dibenzylamine has been completely converted Eq. (22) to the nitrone almost exclusively (as compared to the hydroxylamine product) under two different sets of conditions: (1) 5% MTO, 4 equivalents of 35% H_2O_2 in CH_3OH, and (2) 2% MTO, 3 equivalents of UHP adduct in CH_3OH [52]. Some results for the oxidation of amines to nitrones are shown in Table 8.

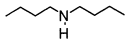
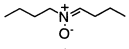
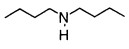
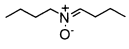
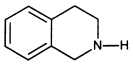
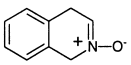
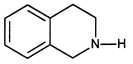
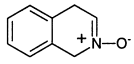
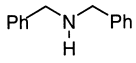
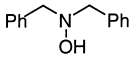
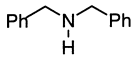
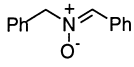
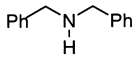
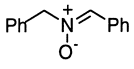


(22)

The MTO/UHP system possesses the higher utility, and the system was used to convert a number of secondary amines to nitrones in 60–95% yield. However, the oxidation of unsymmetrical secondary amines generally result in a regioisomeric mixture of products [52]. It has been reported that the diperoxo complex of MTO is the dominant form of the catalyst when high concentrations of H_2O_2 are used in the oxidation of secondary amines [21]. The amine is converted to a hydroxylamine before conversion to the corresponding nitrone.[21,52,53] In fact, the formation of the hydroxylamine is rate-controlling [21]. Similarly, it has also been shown that MTO catalyzes the oxidation of primary amines, both aliphatic and aromatic, to the corresponding nitro compounds, Eq. (23), [51].

$$R\text{–}NH_2 \xrightarrow[EtOH]{MTO/H_2O_2} R\text{–}NO_2 \quad (23)$$

Table 8
Oxidation of secondary amines to nitrones

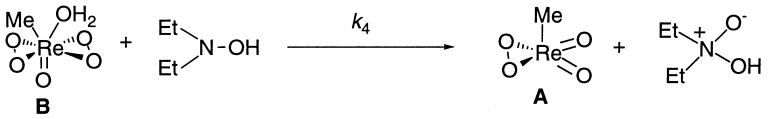
Substrate	Solvent	Conditions	Product	Yield (%)	Reference
	EtOH	25°C; 1.0 h		95	[53]
	*i*-PrOH	25°C; 0.5 h		87	[53]
	MeOH	25°C; 1 h		66	[53]
	EtOH	25°C; 0.5 h		90	[51]
	EtOH	0°C; 0.5 h		80	[53]
	EtOH	25°C; 0.5 h		85	[53]
	MeOH	25°C; 0.5 h		97	[53]

Since the oxidation of amines to nitrones is thought to proceed through a hydroxylamine intermediate, Zauche and Espenson undertook a study of the kinetics and mechanism of the oxidation of hydroxylamines to nitrones [21]. MTO, **A**, and **B** will reach equilibrium concentrations as a function of the equilibrium constants and $[H_2O_2]$ on their own, but the situation is different during the catalytic cycle. As illustrated by monitoring the absorption at 360 nm attributable to **B**, the concentration of **B** declines and then rises after addition of the hydroxylamine; the rise occurs after formation of the nitrone is complete. This phenomenon indicates that the steady-state concentrations of all the rhenium species depends on the equilibrium constants in the absence of hydroxylamine as well as the rate constants for the reactions of the peroxorhenium species with the hydroxylamine.

The kinetic data has been analyzed by two different but in this case equivalent methods. The reaction is carried out at high $[H_2O_2]$, and it is assumed that **B** is the major species reacting with, in this case, diethylhydroxylamine [21]. The method of initial rates yields the rate law $\nu_i = k_4[\mathbf{B}][Et_2NOH]_0$, which is nearly equivalent to $\nu_i = k_4[Re]_T[Et_2NOH]_0$, where k_4 is the rate constant for the reaction, Eq. (24)

The rate constant is evaluated using a least-squares fit of the line obtained from a plot of ν_i versus $[Re]_T \times [Et_2NOH]_0$ and is calculated as $k_4 = 52 \pm 1\,l\,mol^{-1}\,s^{-1}$. The method of pseudo-first-order kinetics was applied by plotting $k_\psi[Et_2NOH]_0$ versus $[Re]_T[Et_2NOH]_0$. The rate constant k_4 was calculated to be $51 \pm 1\,l\,mol^{-1}\,s^{-1}$.

The method of initial rates has been used for the bulk of the kinetic analyses performed on this system. Rate constants for a series of 11 dialkylhydroxylamines have been calculated and seem to indicate that hydroxylamines with sterically bulky substituents exhibit slower rate constants. The reaction of **B** with the hydroxylamine is apparently rate-controlling, implying a mechanism that involves nucleophilic attack of the nitrogen on one of the peroxo oxygens [21]. The intermediate of the reaction is supposed to be a dialkylhydroxylamine *N*-oxide, but this species has yet to be observed directly. The nitrone formation step occurs much more rapidly than the initial oxidation and does not contribute directly to the rate equation. Kinetic isotope effects were studied using $(CH_3)(CD_3)NOH$, and the rate constant ratio is $k_H/k_D = 2.9$. An E2 elimination mechanism involving the attack of a

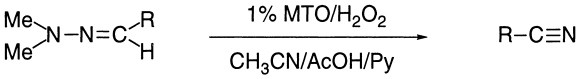


(24)

a conjugate base on the C–H proton concurrent with the attack of a conjugate acid on the OH group seems likely for the formation of the product nitrone(s) [21].

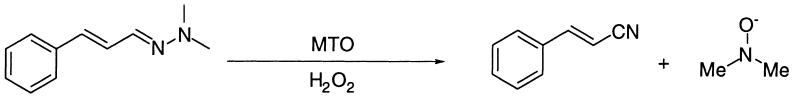
9.2. Synthesis of nitriles

The latest work on MTO-catalyzed oxidation of organonitrogen compounds describes the conversion of *N,N*-dimethylhydrazones to nitriles [54,55]. Aqueous H_2O_2 is employed as the oxidant in an acetonitrile–acetic acid–pyridine solution (94.5 : 5 : 0.5), and the substrates are converted to high yields of their respective nitriles Eq. (25) in a relatively short time (15 min).



(25)

Acetic acid is present in the solution to prevent the deactivation of MTO by the hydrazones, and pyridine has previously been shown to diminish hydrolysis by reducing the Lewis acidity of the peroxorhenium adduct (vide supra). Other functional groups present on the hydrazones are unaffected by the oxidant, as illustrated by Eq. (26). The conjugated system remains intact while the more reactive hydrazone is oxidized.



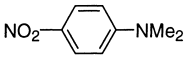
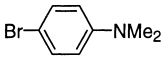
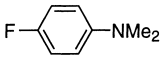
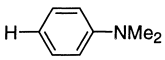
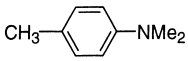
(26)

The proposed mechanism involves the formation of an oxide, which is believed to undergo a Cope-type elimination, [54], Scheme 12.

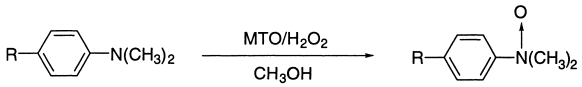
9.3. Oxidation of anilines

Anilines are oxidized at room temperature with the MTO/H_2O_2 system in methanol to yield nitrosobenzenes, Eq. (27), [14]. Zhu and Espenson have performed a series of experiments with varying substituents at the *para* position, and product yields reached or exceeded 85%, Table 9. Different substituents do not lead to drastically different product yields, but kinetics experiments show a substantial electronic effect on reaction rate.

Table 9
Rates and yields of aniline oxidations[a]

Aniline	k_3 (l mol^{-1} s^{-1})	Yield (%)
	1.9	88
	8.7	89
	12.7	85
	18.4	92
	24.5	87

[a] 5 mol% MTO, 2.5 equivalents of H_2O_2 in CH_3OH at 25°C.

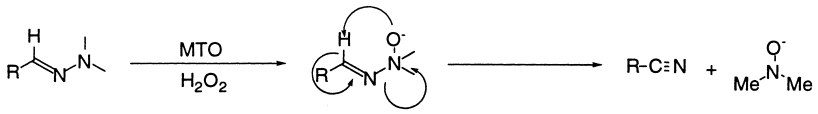


(27)

Data from kinetics experiments were evaluated using the initial rates method. The reactions were monitored by the formation of nitrobenzene and its absorbance at 320 nm. The rate law for the reaction is given in Eq. (28).

$$\nu = \frac{k_3[\mathrm{Re}]_T[\mathrm{H_2O_2}][\text{aniline}]}{((k_{-1} + k_3[\text{aniline}])/k_1) + [\mathrm{H_2O_2}]} \tag{28}$$

The rate law simplifies to $\nu = k_3[\mathrm{Re}]_T[\text{aniline}]$ when a large excess of hydrogen peroxide is used [14]. The reactivity of the peroxorhenium species toward the anilines was also evaluated. It was found that the rate constant for the oxidation of *N,N*-dimethylaniline by **A** is 18.4 l mol^{-1} s^{-1}, while the rate constant for the oxidation of the same aniline with **B** is only $(1.14 \pm 0.07) \times 10^{-2}$ l mol^{-1} s^{-1}. A series of compounds containing different *para* substituents were analyzed to reveal that electron-donating substituents increased the rate constants of aniline oxidation (Table 9), that is, the rate constants follow a linear Hammett free-energy relationship. A mechanism based on kinetics and product yields indicate a nucleophilic



Scheme 12.

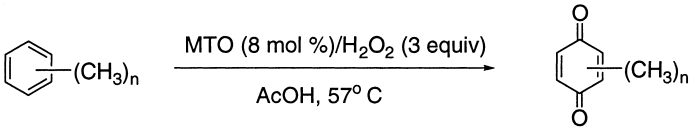
attack by the nitrogen atom on one of the peroxidic oxygens of the mono-peroxo MTO adduct.

Zhu and Espenson performed another set of experiments using *N*-phenylhydroxylamine, particularly because it is proposed to be an intermediate of the aniline oxidation. Without MTO, the rate constant is $0.78 \pm 0.04\,\mathrm{l\,mol^{-1}\,s^{-1}}$ and the product yield is 88%. Using MTO in catalytic amounts shows a rate constant of $178 \pm 11\,\mathrm{l\,mol^{-1}\,s^{-1}}$, which results in a rate enhancement of $178/0.78 \approx 2 \times 10^4$.

10. Aromatic oxidations

10.1. Oxidation of methylbenzenes

Oxidizing alkyl-substituted arenes is difficult with most oxidizers because of the non-selectivity of the oxidation, that is, oxidation of the arene ring competes with oxidation of the alkyl side-chain [56]. However it has been shown recently that the MTO/H_2O_2 oxidation system selectively oxidizes only the ring of methyl benzenes, Eq. (29), [56].



(29)

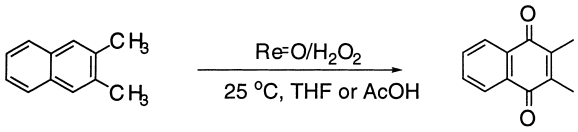
As with most oxidations catalyzed by MTO, the arenes with more methyl groups are oxidized faster because of their higher electron density. Dimethyl benzenes have poor conversion rates (Table 10, entry 1) to their respective quinones regardless of the proximity of the methyl groups to each other. However, 1,3,4-trimethyl benzene gives good conversion to the quinone (entry 2). Higher substituted arenes (entries 3 and 4) give excellent conversions and quinone yields.

Hydroquinones are the side products for reactions in Table 10 that have less than 100% quinone yield. It is presumed that the hydroquinones are intermediates between the arene starting materials and the quinone products [56]. Hydroquinones are converted to quinones at a faster rate than are arenes, so left-over hydroquinones can be converted to quinones by subjection to the same reaction conditions a second time.

For cases in which the conversion is less than 100%, it is proposed that the catalyst is deactivated during the course of the reaction [56]. The results of several test experiments with *p*-xylene substantiate this proposal [56]. It has been shown previously that highly acidic solutions prevent MTO from decomposing [11], but the addition of trifluoromethanesulfonic acid in this case does not stabilize the catalyst against decomposition. Similarly, the addition of MTO in three equal portions and the addition of the MTO/H_2O_2 solution dropwise over 1 h does not improve *p*-xylene conversion.

10.2. Oxidations of 2,3-dimethylnaphthalene with various rhenium oxides

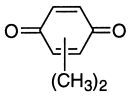
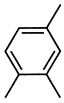
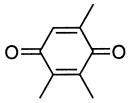
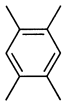
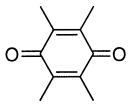
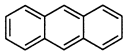
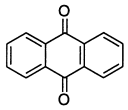
MTO is the most efficient rhenium oxide known for aromatic oxidations, but several other rhenium oxides yield at least fair conversions (Tables 11 and 12) of 2,3-dimethylnaphthalene to 2,3-dimethyl-1,4-naphthoquinone (Vitamin K_3), Eq. (30), [23].



(30)

As indicated by Tables 11 and 12, some of the Re-oxo catalysts appear to be unstable in acidic

Table 10
Conversions and yields for oxidation of methylbenzenes by the MTO/H_2O_2 system[a]

Entry	Substrate	Time (h)	Product	Conversion (%)	Quinone yield (%)
1		3.5		12–15	100
2		4		75	67
3		5		99	88
4		1.5		100	80

[a] Conditions: 8 mol% MTO, 20 equivalents of 30% H_2O_2 in glacial acetic acid at $57 \pm 2^{\circ}C$; reference [56].

media. While MTO (Tables 11 and 12, entry 1) and Re_2O_7-bpy (Table 11, entry 3 and Table 12, entry 2) give improved conversions in acidic media, ReO_3 (Table 11, entry 2 and Table 12, entry 4) gives much worse results in acidic solution. The failure of CH_3ReO_3-tpy and the perrhenate species to efficiently convert the substrate is probably also due to deactivation of the catalyst by the acid.

Oxidation of 2,3-dimethylnaphthalene can also be achieved using Lewis base adducts of halo-rhenium oxides. The bidentating ligand 4,4′-bis(*tert*-butyl)-2,2′-bipyridine has been shown to form complexes with rhenium oxides of the type $XReO_3$, where X = F, Cl, Br, CN, SCN [12]. These complexes have been shown to oxidize 2,3-dimethylnaphthalene to 2,3-dimethyl-1,4-naphthoquinone with 85% H_2O_2 at 25°C in a solution containing acetanhydride, acetic acid, diethyleneglycoldibutyl ether (as an internal standard), and THF [12]. Optimal yields of only 57–63% are obtained because of hydrolytic decomposition of the complexes to perrhenate. Oxygen-labeling experiments (^{17}O NMR) show that a diperoxorhenium complex is formed while the bidentating ligand is removed [12].

10.3. Oxidation of methoxybenzenes

Methoxybenzenes are aromatic substrates that are more electron-rich than the methylbenzenes men-

Table 11
Conversions of 2,3-dimethylnaphthalene using various Re-Oxo catalysts in non-acidic solution

Entry	Catalyst	Conversion (%)[a]
1	CH_3ReO_3	67
2	ReO_3	56
3	Re_2O_7–bpy[b]	52
4	$C_3H_5ReO_3$	46
5	Cp'ReO_3[c]	45
6	CpReO_3[d]	39
7	$ClReO_3$	32

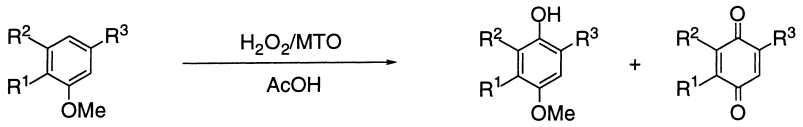
[a] Conditions: 2 mol% catalyst, 15 equivalents of 85% H_2O_2, dry THF, 25°C, 24 h.
[b] bpy = 2,2′-bipyridine.
[c] Cp' = η^5-C_5H_4Me.
[d] Cp = η-C_5H_5.

Table 12
Conversions of 2,3-dimethylnaphthalene using various Re-Oxo catalysts in acidic solution

Entry	Catalyst	Conversion (%)[a]
1	CH_3ReO_3	73
2	CH_3ReO_3-bpy[b]	66
3	Re_2O_7-bpy[b]	66
4	ReO_3	31
5	CH_3ReO_3-*p*-^{t}BuPy	26
6	[ReO_3–L][ReO_4][c]	6
7	K[ReO_4]	0

[a] Conditions: 2 mol % catalyst, 15 equivalents of 85% H_2O_2, 2 ml dry THF with 5 ml glacial acetic acid, 25°C, 4 h.
[b] bpy = 2,2′-bipyridine.
[c] L = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethyltriamine.

tioned above and have been shown to react with the MTO/H_2O_2 in acetic acid solution, Eq. (31), [57].



(31)

As in the oxidation of methylbenzenes, the acid seems to be necessary to promote efficient oxidation, but exactly how it interacts with the diperoxorhenium species is unknown. The arene shown in Table 13, entry 1, has been studied in-depth with respect to optimum oxidation conditions.

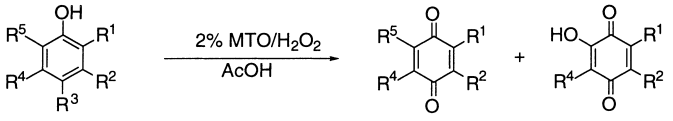
Control experiments in the absence of MTO yield no oxidation of methoxybenzene. Note also that oxidation of the substrate in the absence of acid results in very poor quinone yield (entry 5).

It has also been suggested that the catalyst decomposes during the reaction [57]. However, unlike the oxidation of methylbenzenes, increased yields are obtained when MTO is added incrementally during the course of the reaction (entry 2). It is also interesting to note that water content of the EtOH/HBF_4 solvent seems to be insignificant compared to the water content when acetic acid is the solvent. In the ethanol/HBF_4 solvent, the difference obtained between using concentrated hydrogen peroxide and using diluted hydrogen peroxide is minimal (entries 3 and 4).

The proposed mechanism allows for an arene oxide intermediate, [57], Scheme 13.

10.4. Oxidation of phenols to p-quinones

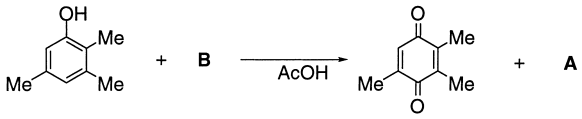
Phenols and naphthols are oxidized to *p*-quinones using 2% MTO in an H_2O_2/acetic acid solution, Eq. (32), [58].



R^3 = H or OH

(32)

Typical reaction times for a range of phenols/naphthols are 2–4 h, and the reactions proceed at temperatures of 20–40°C. The oxidation with hydrogen peroxide in the absence of MTO proceeds very slowly. Under 10% yield of quinone is obtained from 2,6-dimethylphenol in the absence of MTO after 4 h at 40°C, compared with 93% yield under the same conditions with 2% catalyst. These results effectively rule out the possibility of peroxyacetic acid acting as the primary oxidant instead of a peroxorhenium species. The diperoxorhenium complex has been shown to be the primary oxidant; 2,3,5-trimethylphenol reacts with isolated diperoxomethylrhenium oxide to give >90% quinone yield, Eq. (33).

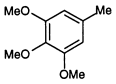
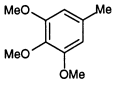
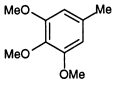
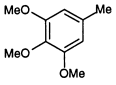
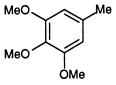
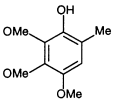
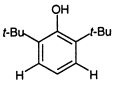
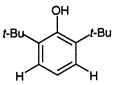
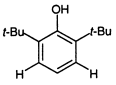


(33)

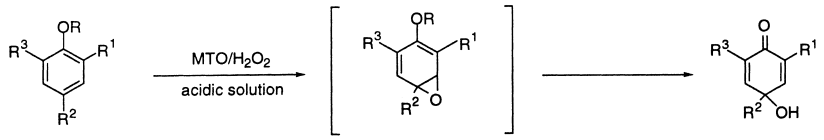
Higher temperatures result in higher conversion but lower selectivity (Table 13, entries 8 and 9). More equivalents of concentrated H_2O_2 result in better phenol conversion and increased product yield (Table 13, entries 7 and 8).

As a testament to the environmental 'friendliness' of the MTO/H_2O_2 system, it is interesting to note the differences in results achieved by this system as compared to the industrial process involved in making Vitamin-K_3 (2-methyl-1,4-naphthoquinone). The industrial process employs chromic acid, and while it makes Vitamin-K_3 in 30–60% yield, it also generates hazardous chromium waste at a rate of 18 kg per 1 kg of product. Compare that system with MTO/H_2O_2, which gives 81% conversion of the substrate and 86% selectivity toward the active isomer of Vitamin-K_3 while regenerating the original MTO.

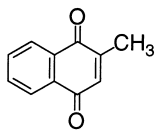
Table 13
Oxidation of phenols and methoxybenzenes

Entry[a]	Substrate	Temperature (°C)	H_2O_2 (%, equivalent)	Solvent	Conversion (%)	Yield[b]
1		25	35, 2.5	HBF_4[c]	50	67
2		25	35, 2.5	HBF_4[c]	90[d]	56
3		25	35, 2.5	AcOH	69	59
4		25	85, 5.0	AcOH	98	59
5		25	35, 2.5	EtOH	27	9
6		25	35, 2.5	HBF_4[c]	95	83
7		20	83, 5.0	AcOH	58	77
8		40	83, 5.0	AcOH	86	74
9		40	83, 10.0	AcOH	92	74

[a] Reference for entries 1, 2, and 3 is [57]; for entries 4 and 5 is [58].
[b] Yields are corrected based on conversion of starting material after 4 h in the presence of 2 mol% MTO.
[c] HBF_4 in EtOH.
[d] Additional 2 mol% MTO added after 4 h, additional 4 h reaction time.



Scheme 13. Proposed mechanism for oxidation of phenols and methoxybenzenes by MTO/H_2O_2.



Vitamin K_3

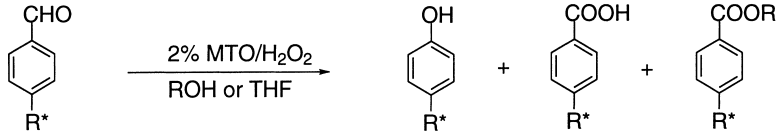
Most reports have indicated that the MTO/H_2O_2 system can be thought of as an electrophilic reagent. Accordingly, electron-rich phenols were found to undergo higher oxidation rates (higher conversion) than electron-deficient phenols. Similar to the oxidation of the methoxybenzenes, an arene oxide intermediate is

likely. Two possible intermediates are shown below [58].

Similar to this chemistry is the oxidation of biphenylene by hydrogen peroxide and MTO to the *o*-quinone [59].

10.5. Oxidation of benzaldehydes

Benzaldehydes with methoxy or hydroxyl substituents in the *ortho*- and *para*- positions are oxidized with the MTO/H_2O_2 system (Eq. (34)) to the corresponding phenols in good yields, [60], Table 14.



(34)

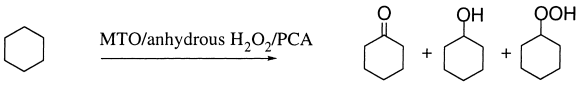
This reaction has been studied in depth by employing 4-methoxybenzaldehyde as substrate. The yield of the product phenol is highly dependent on the solvent, and it has been shown that tetrahydrofuran and alcohols, particularly ethanol, give the best yields. The yield is also temperature dependent, as temperatures of 50–70°C give the phenol in good yields (75%) while a temperature of 30°C results in only an 8% yield of the phenol (Table 14, entry 4). Varying concentrations of hydrogen peroxide also give drastically different results. Low H_2O_2 concentrations decrease both the rate of the reaction and the yield of phenol. High H_2O_2 concentrations decrease phenol yield and increase the yield of benzoic acid (entry 2). An MTO concentration of 10% results in decreased conversion of the benzaldehyde and decreased yield of the phenol (entry 5).

11. Oxidation of hydrocarbons

Oxygen atom insertion into C–H bonds of saturated hydrocarbons is catalyzed by MTO with H_2O_2 as the oxygen source [49,61]. The reaction is stereospecific with retention of configuration.

11.1. Primary and secondary hydrocarbon oxidation

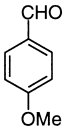
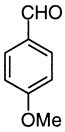
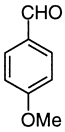
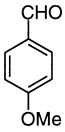
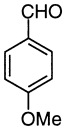
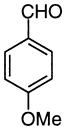
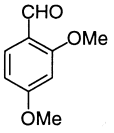
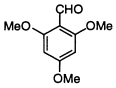
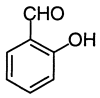
Inert alkanes lacking a tertiary C–H bond undergo oxidation with anhydrous and aqueous hydrogen peroxide (in large excess at 40–60°C in alcoholic solvents) in the presence of MTO [49]. Acetonitrile is the solvent of choice for the reactions involving anhydrous hydrogen peroxide, and the addition of pyrazine-2-carboxylic acid (PCA) accelerates the oxidations [49]. The rates of uncatalyzed autooxidation of cycloalkanes are up to 20 times slower than the MTO/H_2O_2/PCA catalyzed oxidation, and MTO/H_2O_2 in the absence of PCA oxidizes cycloalkanes at rates up to three times slower than in the presence of PCA. The total yield of oxygenated products in reactions without PCA is four times lower. The reaction of cyclohexane with anhydrous H_2O_2, MTO, and PCA in open air yields cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide in a 1.0 : 7.9 : 8.5 ratio, Eq. (35), [49].



(35)

The product distribution changes substantially when the reaction takes place under argon, yielding a cyclohexanone : cyclohexanol : cyclohexyl hydroperoxide ratio of 1.0 : 7.1 : 12.3. This result seems to indicate that atmospheric oxygen is involved in the oxidation [49]. As shown by the oxidation of *trans*-decalin, PCA accelerates the oxidation of the tertiary and the secondary C–H bonds by up to three times. Unfortunately, the yields of these reactions are quite poor. As seen in Table 15, less than 5% yield of the major product is obtained from the oxidation of cyclohexane and cyclooctane (entries 1 and 2).

Table 14
Oxidation of benzaldehydes[a]

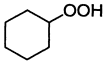
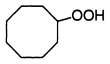
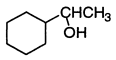
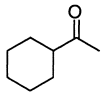
Entry	Substrate	Solvent	MTO (mol%)	Temperature (°C)	Conversion (%)	Phenol[b] (%)
1		THF	2	50	100	67
2		EtOH	2	50	100	61[c]
3		EtOH	2	50	100	74
4		EtOH	2	30	54	8
5		EtOH	10	50	68	24
6		*t*-BuOH	2	50	87	44
7		EtOH	2	25	100	86
8		EtOH	6	25	100	66
9		EtOH	2	25	> 90	71

[a] Standard oxidation solution: 4 equivalents of 1 M H_2O_2; reference: [60].
[b] Isolated yield.
[c] Four equivalent 3 M H_2O_2.

11.2. C–H bond activation in tertiary substrates

The MTO/H_2O_2 system oxidizes a variety of tertiary substrates to alcohols and ketones [61]. Good to excellent yields are obtained for most of the substrates, as shown in Table 15 (entries 3, 4, and 5). As Table 15 indicates, ketones are obtained as products from substrates that have a hydroxy group (entries 3 and 5). Oxidation of tertiary hydrocarbon substrates yields alcohols (entry 4).

Table 15
Results for C–H activation of secondary and tertiary substrates by MTO/H_2O_2

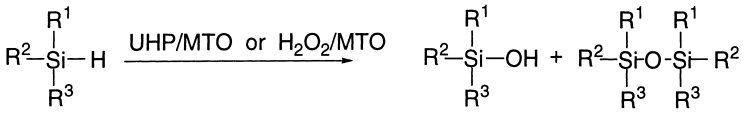
Entry	Substrate	Time (h)	Temperature (°C)	Product	Yield (%)	Reference[a]
1		6	80		1.53	[49]
2		6	80		4.36	[49]
3		10	60		52	[61]
4		48	60		60	[61]
5		24	60		95	[61]

[a] Conditions for reference [49] 0.02 mol% MTO, 83% H_2O_2 in CH_3CN with 0.08 mol% PCA; conditions for reference [61]: 16 mol% MTO, 38% H_2O_2 in ROH (EtOH or *t*-BuOH).

12. Oxidation of silanes to silanols and disiloxanes

One of the most remarkable results involving MTO-catalyzed oxidation of organic substrates has only very recently been introduced to the literature [62]. MTO-catalyzed oxygen-atom insertion into C–H bonds of aliphatic and aromatic substrates is known (vide infra), so it seems completely reasonable and not surprising that Si–H bond activation can also be accomplished with catalytic amounts of MTO and hydrogen peroxide. However, there are striking differences in the results obtained between using an MTO/UHP system and using MTO/H_2O_2.

Simply, both MTO/UHP and MTO/H_2O_2 oxidize silanes to silanols and disiloxanes, Eq. (36), [62].



(36)

Reaction times exceeding 8 h result in decomposition of both the MTO catalyst and the primary oxidant. Methylene chloride was found to be the best solvent. The conversion percentage is highly dependent on catalyst concentration; 87% conversion is obtained with 1.0 mol% catalyst, but the conversion rate falls to 50% with 20 mol% MTO. Similarly, the percent yield of silanol decreases with increasing catalyst concentration; the silanol : disiloxane ratio changes from 98 : 2 at 1.0 mol% MTO to 61 : 39 at 20 mol% MTO. Other experiments in which the oxidant is generated in situ have also been performed. Adding 1 equivalent urea to a solution containing 1 equivalent 85% H_2O_2 and 1.0 mol% MTO in CH_2Cl_2 results in 72% conversion of dimethylphenyl silane and a silanol : disiloxane ratio of 99 : 1. Under the same conditions, the addition of 0.1 equivalent urea results in 34% conversion, and the addition of 10 equivalents urea results also in a 34% conversion rate. The silanol : disiloxane ratio remains at 99 : 1 for the reaction with excess urea, while the reaction with a dearth of urea gives a 65 : 35 ratio.

12.1. Oxidations with UHP/MTO

The silane does not convert to either the silanol or the disiloxane in the absence of MTO. Yields of silanol exceed 75% for most of the silanes studied. In order to determine the best reaction conditions for yield and selectivity optimization, detailed studies have been performed with dimethylphenyl silane.

Table 16
Silane oxidation catalyzed by MTO

Substrate	Oxidant	Conversion (%)	Silanol (%)	Disiloxane (%)
$EtMe_2SiH$	85% H_2O_2	55	<5	>95
	UHP	≥95	94	6
Et_3SiH	85% H_2O_2	54	54	46
	UHP	78	≥99	<1
$PhMe_2SiH$	85% H_2O_2	26	20	80
	UHP	87	98	2
t-$BuMe_2SiH$	85% H_2O_2	70	≥99	<1
	UHP	98	≥99	<1

12.2. Oxidations with H_2O_2/MTO

Overall, the oxidation of dimethylphenyl silane with 85% hydrogen peroxide proves to be inferior to the UHP/MTO methods. The addition of 1 equivalent 85% H_2O_2 and 1.0 mol% MTO to a solution of the silane results in only 26% conversion and a silanol : disiloxane ratio of 1 : 4. Increasing the number of hydrogen peroxide equivalents (10.0) results in higher conversion (36%) and a better silanol : disiloxane ratio (31 : 69). Increasing the concentration of MTO (10 mol%) also improves the conversion (69%), but the silanol : disiloxane ratio suffers tremendously (1 : 49). Even the addition of pyridine to the 85% H_2O_2/MTO oxidant does not allow it to match the efficiency of UHP/MTO for silane oxidation. A comparison of the efficiency and selectivity of silane oxidations with H_2O_2 and UHP is presented in Table 16.

12.3. Oxidation of chiral silanes

The oxidation of the chiral (+)-(α-Np)PhMeSiH has also been studied both with UHP/MTO and H_2O_2/MTO [62]. Variation of MTO concentration (1.0–20.0 mol%) using UHP as the oxidant does not alter the conversion percentage substantially (12–15% conversion), and the silanol : disiloxane ratio remains essentially constant. However, the enantiomeric excess changes drastically from 91% with 1.0 mol% MTO to only 15% with 20.0 mol% MTO. Using 85% H_2O_2 results in even poorer conversion (2%), a 9 : 1 ratio, and an EE of 1%.

12.4. Matrices for silane oxidation

Urea is not the only matrix that has been tried for silane oxidation. Amylose and SiO_2 have also been used as additives. The use of 1.0 mol% MTO and amylose at 44 wt.% gives a dimethylphenyl silane conversion of 49% and a silanol : disiloxane ratio of only 11 : 14. Increased wt.% of amylose (445 wt.%) results in far lower conversion (9%) but a much better product ratio (49 : 1). However, using 135 wt.% SiO_2 gives a 28% conversion and a woeful product ratio of 17 : 83. It follows that much attention must be paid to the urea matrix and its ability to facilitate silane oxidation.

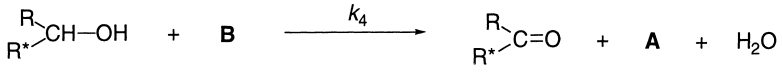
13. Oxidation of alcohols

MTO was first shown to oxidize alcohols by Murray in 1995 [61]. Zauche and Espenson have since improved the oxidation system with a couple of significant changes [20]. Alcohols react with 2 equivalents of 30% H_2O_2/4 mol% MTO at 40°C to yield ketones within 24 h at most; no solvent is required besides the alcohols. The use of the neat alcohols results in far greater yields of the ketones than were obtained using a solution of 20% water/acetonitrile. Many ketone yields exceed 80%, and most of the reactions are nearly complete after only 8 h. For the oxidation of benzyl alcohol, 2 equivalents of hydrogen peroxide yield a considerable amount of benzoic acid (21%), while 1 equivalent of the peroxide results in 40% benzaldehyde and 7% benzoic acid.

Kinetic studies on the oxidation of alcohols by the MTO/H_2O_2 system reveal a departure in mechanism from the oxidations of other substrates such as alkenes,

sulfides, and amines. The method of initial rates has been employed to determine rate constants for the oxidation of several alcohols.

The initial rate of reaction is given by $\nu_i = k_4[\mathbf{B}][R_2CHOH]_0$ where $k_4[Re]_T[R_2CHOH]_0$, where k_4 is given in Eq. (37). The highest rate constant determined was for 4-methyl-α-methylbenzyl alcohol ($10.2 \times 10^5\,l\,mol^{-1}\,s^{-1}$). Rate constants for all alcohols are within a factor of 5.



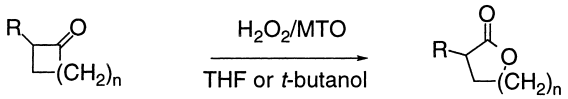
(37)

The mechanism for the MTO-catalyzed oxidation of alcohols proceeds through an intermediate that involves interactions between the peroxorhenium oxygen with the C–H bond, which is an intermediate typical of a hydride abstraction [20]. This intermediate is proposed to form along two pathways; the major pathway, accounting for 80% of the product, involves a di-hydroxy group on the rhenium center. A series of reactions involving *para*-substituted α-methylbenzyl alcohols shows that electron-donating groups at the *para*-position increase the rate of oxidation. It is interesting to note that alcohol oxidations with MTO/H_2O_2 are kinetically slow and the most convenient preparative methodology involves the use of Br^- as a cocatalyst, Scheme 14. MTO catalyzes the oxidation of bromide to the hypobromite ion, BrO^-, which combines with additional Br^- to give bromine, Br_2. Alcohols are easily oxidized to aldehydes and ketone by Br_2. The MTO/H_2O_2/Br^- catalytic system utilizes peroxide as the stoichiometric oxidant.

14. Baeyer–Villiger oxidation

For the large majority of ketones, hydrogen peroxide is not a sufficiently strong oxidant to convert ketones into lactones or esters by itself. Several different catalysts have been developed for oxidation of cyclic ketones, including catalysts that employ molybdenum and platinum [63,64]; however, these catalysts do not measure up to MTO's ability to catalyze Baeyer–Villiger oxidations [65].

The oxidative processes catalyzed by MTO/H_2O_2 are thought to occur through electrophilic activation (vide supra). However, the Baeyer–Villiger oxidation is thought to proceed via a nucleophilic attack on the carbonyl carbon. Considering this apparent paradox, one may not expect the MTO/H_2O_2 system to catalyze Baeyer–Villiger oxidations. However, it has been shown that the diperoxorhenium species is a highly effective catalyst for converting cyclic ketones to lactones [65]. In the case of cyclobutanone, butyrolactone is formed at yields greater than 99% in a matter of seconds, Eq. (38).

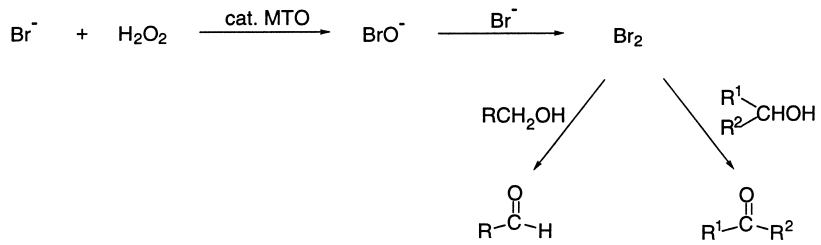


(38)

The turnover frequency (TOF) for this reaction has been calculated to be $200\,min^{-1}$, a considerable improvement over a TOF of $40\,min^{-1}$ that has been calculated for the same reaction using [(dppe)Pt(CF_3)(CH_2Cl_2)]BF_4 [66]. While the oxidation of cyclobutanone gives yields of 80% at room temperature, the oxidations of cyclopentanone and cyclohexanone give far lower yields at the same temperature. Cyclopentanone is oxidized to its lactone in only 15% yield at 25°C and a reaction time of 12 h, while the oxidation gives a 72% yield of the lactone at 70°C at a time of 1 h.

It is important to note that while the oxidation of cyclic ketones with hydrogen peroxide does occur in the absence of MTO, the process is extremely slow. Whether at 15 or 25°C, the addition of MTO to the reaction mixture (for cyclobutanone) speeds up the reaction by at least an order of magnitude. For example, when the reaction is run at room temperature, the uncatalyzed reaction gives only a 7% yield of butyrolactone, compared to the 80% yield obtained with MTO that was previously mentioned. At 15°C, 100% yield of butyrolactone is obtained after 21 h using MTO/H_2O_2 , while only 38% is yielded after 3 days in the absence of MTO.

Another series of experiments has been performed using the isolated diperoxorhenium species instead of MTO/H_2O_2. One equivalent of the diperoxorhenium



Scheme 14.

species reacts with 2 equivalents of cyclobutanone, yielding 1 equivalent of the butyrolactone in 90% yield at room temperature. As mentioned previously, the diperoxorhenium species is yellow in color and absorbs around 366 nm, so the reaction can be monitored by observing the disappearance of this absorbance. The absorption at 366 nm decays, and a new absorption at 310 nm is formed, which is indicative of the monoperoxorhenium species.

As stated earlier, the fact that MTO catalyzes Baeyer–Villiger oxidations at all is surprising in light of its electrophilic character. It has been proposed that this behavior is a result of the unsymmetric geometry of the reactive diperoxorhenium species [65]. As shown by ^{17}O NMR, the peroxo oxygen atoms are not identical; one shows at 363 ppm, while the other shows at 422 ppm. This polarity of the peroxo oxygens is further illustrated by their absorptions in the infrared region [65]. It is proposed that this polarity is responsible for both the electrophilic character of the diperoxorhenium species as well as its nucleophilic character. This proposal is further substantiated by experiments that have been performed using a mechanistic probe for oxygen transfer reagents. Thianthrene-5-oxide was used to determine the oxygen transfer parameter X_{SO} of the diperoxorhenium reagent [22]. This parameter ranges from 0 to 1, with 0 as completely electrophilic and 1 as completely nucleophilic. The parameter X_{SO} ranges from 0.45 to 0.8 for the diperoxorhenium species and is highly solvent-dependent. Reactions performed with thianthrene-5-oxide and the diperoxorhenium in chloroform yield $X_{SO} = 0.45$, indicating increased electrophilicity of the peroxo groups. The same experiment done in acetonitrile gives $X_{SO} = 0.8$. We should add that this method of determining the oxygen transfer parameter is not always reliable for transition metal peroxides.

15. Oxidation of cyclic β-diketones

MTO has been shown to catalyze the H_2O_2-mediated oxidation of cyclic β-diketones to carboxylic acids [67]. Most of the diketones studied were efficiently oxidized at conversions of >84%, and the acid products from most of the diketones reached 100%. A large excess (5.8 equivalents) of hydrogen peroxide was employed for these reactions along with a 1 : 1 acetonitrile-water solution at 25°C.

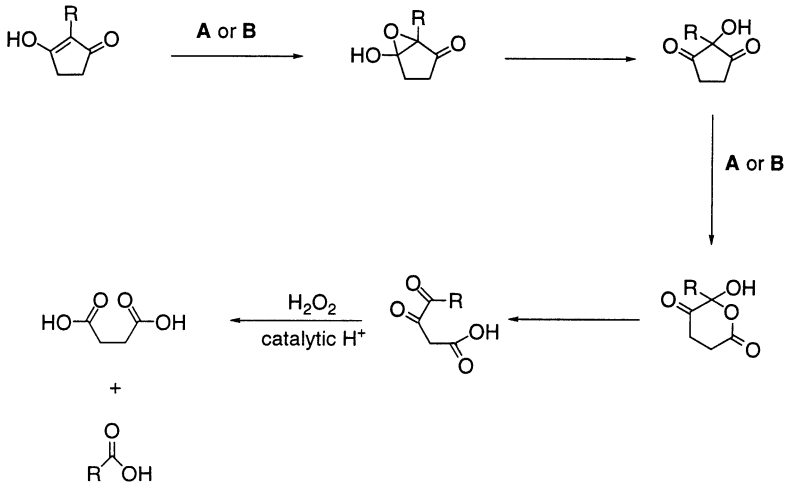
15.1. Mechanism

Espenson and Abu-Omar have proposed the following mechanism [67], Scheme 15.

In solution the cyclic β-diketones exist in their enolic forms, as illustrated in the above mechanism. The reaction proceeds first through an initial epoxidation, followed by rearrangement of the epoxide. The C–C bond is then cleaved, and an oxygen atom is inserted. Next, an α-diketone intermediate is formed, and finally, this intermediate is oxidized by hydrogen peroxide to give the carboxylic acids [67]. The α-diketone intermediate is not observed during the course of the reaction.

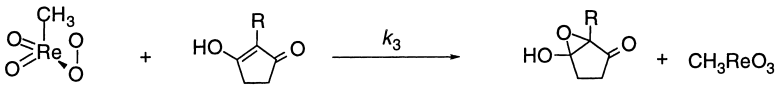
15.2. Kinetics

Kinetic studies were performed in a 1 : 1 CH_3CN–H_2O solution containing 0.01 M $HClO_4$ to minimize MTO decomposition [67]. All of the reactions except for the oxidation of monochlorodimedone followed first-order kinetics. The pseudo-first-order rate constants were evaluated using a single exponential equation fit. The method of initial rates was used to monitor the kinetics of the monochlorodimedone oxidation during the initial 5% of the reaction. In their enolic



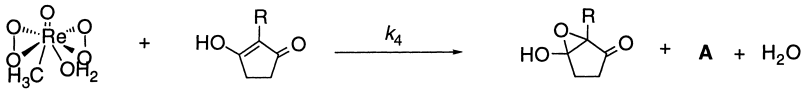
Scheme 15. Proposed mechanism for oxidation of cyclic β-diketones. Reprinted with permission from Abu-Omar, M.M.; Espenson, J.H. Organometallics, 15 (1996) 3543. Copyright 1996 American Chemical Society.

form, cyclic β-diketones exhibit strong UV absorptions, which were used to monitor the reaction of the diketones with the peroxorhenium species **A** and **B**. As the initial epoxidation step disrupts the conjugation responsible for these intense absorptions, the reactions could be monitored only as far as the first step. Acid is known to catalyze diketone oxidation in the absence of MTO and presence of hydrogen peroxide, but the MTO/H_2O_2 system catalyzes the oxidation so much faster that acid-catalyzed oxidation is negligible. Kinetic studies enabled the calculation of rate constants k_3 and k_4, shown in Eqs. (39) and (40).



(39)

A



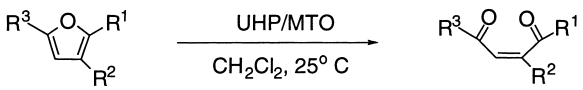
(40)

B

Applying the steady-state approximation and the fact that the equilibria for the formation of the peroxorhenium intermediates are established much faster than the oxidation of the diketones at high peroxide levels, the rate equation is given by $v = k_\psi[\beta] = k_3[\beta][\mathbf{A}] + k_4[\beta][\mathbf{B}]$ [67]. The rate constants k_3 range from 0.19 to 0.86 l mol^{-1} s^{-1}, and k_4 ranges from 0.018–0.17 l mol^{-1} s^{-1}.

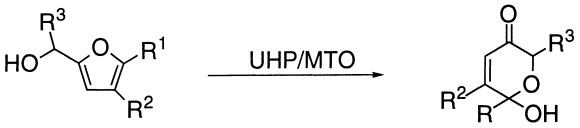
16. Conversion of furans to enediones

The scope of applicability of the UHP/MTO system for oxidation has been expanded recently to include the transformation of furans to enediones, Eq. (41), [68].



(41)

Good to excellent enedione yields (67–97%) have been observed for a variety of substrates. Substituted pyranones are obtained in 75–95% yield from the oxidation of furans with hydroxymethyl groups at the 2-position, Eq. (42).



(42)

Solvent effects on the rate of oxidation are apparent as the substrate is oxidized much faster in acetonitrile than in methylene chloride. However, the product work-up is easier in CH_2Cl_2.

17. Oxidation of [(η^5-Cp*)Re(CO)$_3$] with various rhenium oxides

MTO and other rhenium oxides catalyze the oxidation of [(η^5-Cp*)Re^{I}(CO$_3$)] to [(η^5-Cp*)Re^{VII}O$_3$) with hydrogen peroxide, [23], Eq. (43). (Cp* = η^5-C_5Me_5).

As shown in Table 17, all the rhenium catalysts give at least fair yields of the Re^{VII} product. High concentrations of hydrogen peroxide are absolutely necessary for the formation of a catalytically active Re species. Anhydrous H_2O_2 solutions in organic solvents or 85% (w/w) H_2O_2 solutions in water must be used; 30% H_2O_2 solutions in water are not successful.

The structure of the active species in the Re_2O_7/H_2O_2 system has been determined, [23], Eq. (44).

Table 17
Yields obtained for oxidation of [(η^5-Cp*)Re(CO$_3$)] catalyzed by a variety of Re oxides[a]

Entry	Catalyst	Yield (%)
1	MTO	90
2	Re_2O_7	81
3	$CH_3CH_2ReO_3$	78
4	(η^5-Cp)ReO_3	75
5	(η^5-C_5H_4Me)ReO_3	73
6	ReO_3	72
7	$ClReO_3$	69

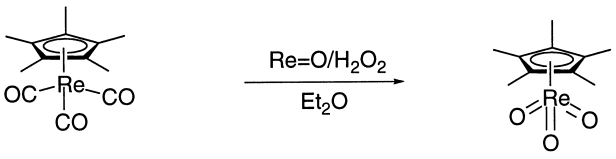
[a] Conditions: 3.5 M H_2O_2 in Et_2O, 4 mol% catalyst, initial reaction temperature at −45°C allowed to warm to 25°C, 18 h.

The peroxo complex has a red-orange color and is an explosive solid. It decomposes to perrhenate in dry organic solvents with a rate constant $k = 0.51 \times 10^{-2}\ s^{-1}$ and with excess water at $k = 4.07 \times 10^{-3}\ s^{-1}$. The crystal structure of the peroxo species with a diglyme adduct has been determined [23].

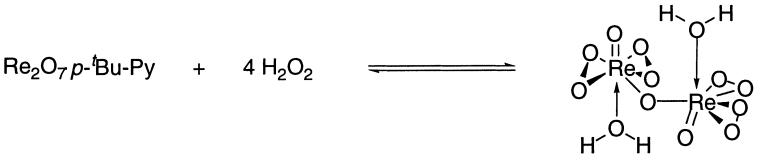
18. Cyclization reactions

18.1. Tandem cyclizations

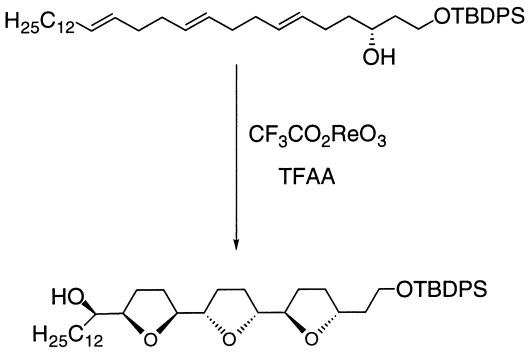
One of the more recent advances in the utility of rhenium oxides involves tandem oxidative polycyclizations, which are extremely important reactions for the total synthesis of natural products. A mixture of trifluoroacetyl perrhenate and trifluoroacetic anhydride (TFAA) has proven to be an effective reagent for promoting triple-oxidative cyclizations, Eq. (45), [69,70].



(43)

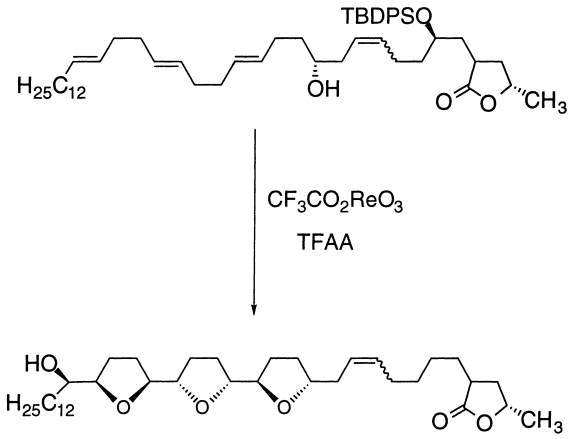


(44)



(45)

The natural product Goniocin, an Annonaceous acetogenin, has been synthesized from a 4,8,12-trienol substrate, which undergoes tandem cyclization to yield the three adjacent THF rings [69]. Goniocin is then obtained through further reaction of the tris–THF product. The oxidation is also compatible with substrates containing different functional groups, Eq. (46), [69].

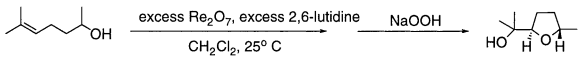


(46)

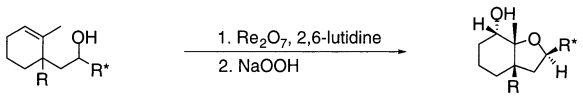
The above reaction is particularly interesting because six new stereocenters are created with high diastereoselectivity. Sinha et al. have also established a set of stereoselectivity rules for tandem oxidative polycylizations involving trifluoroacetyl perrhenate and disubstituted alkenols [70]. However, it must be emphasized that this transformation is not catalytic; the perrhenate species is used in excess (2–3 equivalents).

18.2. Cyclization of 5-hydroxyalkenes with Re_2O_7 and H_5IO_6

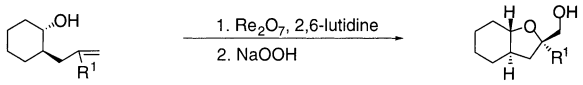
An excess of Re_2O_7 reacts with 5-hydroxyalkenes in the presence of excess 2,6-lutidine to yield 2-hydroxymethyl-tetrahydrofurans [71]. For example, 6-methyl-5-hepten-2-ol is converted to 5-methyl-2-(1-hydroxy-1-methylethyl)-tetrahydrofuran stereoselectively; as shown by Eq. (47), the *trans* isomer is the major product. The reaction is also highly stereospecific for cyclic 5-hydroxyalkenes with few exceptions, Eqs. (48) and (49).



(47)



(48)



(49)

The drawback of this chemistry is that it requires an excess amount of Re_2O_7. However, it has also been shown that 5-hydroxyalkenes can be oxidized catalytically with Re_2O_7 when a co-oxidant is employed [72]. Instead of using 3–4 equivalents of Re_2O_7, 1 equivalent of Re_2O_7 can be used in conjunction with H_5IO_6 for oxidative cyclization of 5-hydroxyalkenes [72]. Also, some substrates can be cyclized using a catalytic amount (10 mol%) of Re_2O_7 with *t*-BuOOH as oxidant [72]. Stereoselectivity and product yields for both the Re_2O_7/H_5IO_6 system and the Re_2O_7/*t*-BuOOH system are comparable to using excess Re_2O_7 in the absence of a co-oxidant.

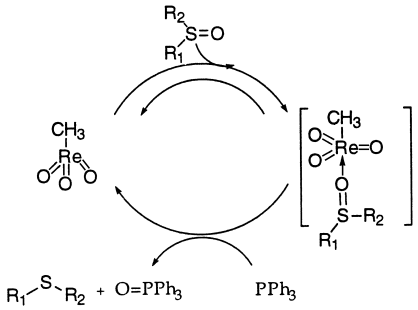
19. Oxygen-transfer reactions with sulfoxides

19.1. Oxidation of tertiary phosphines

Although the reaction between triphenylphosphine and sulfoxides, Eq. (50), is highly favorable

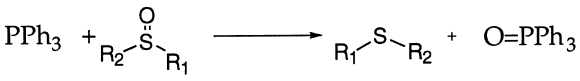
Table 18
MTO catalyzed oxidation of triphenylphosphine by several sulfoxides [73]

Sulfoxide	Sulfide product	Yield (%)
$PhS(O)CH{=}CH_2$	$PhSCH{=}CH_2$	73
Ph_2SO	Ph_2S	66
PhS(O)Me	PhSMe	71
$(Pr^i)_2SO$	$(Pr^i)_2S$	75
$(Bu^n)_2SO$	$(Bu^n)_2S$	77
$(p\text{-}CH_3C_6H_4)_2SO$	$(p\text{-}CH_3C_6H_4)_2S$	65
$(p\text{-}ClC_6H_4)_2SO$	$(p\text{-}ClC_6H_4)_2S$	59



Scheme 16. Ligand-centered oxygen transfer with sulfoxides catalyzed by MTO.

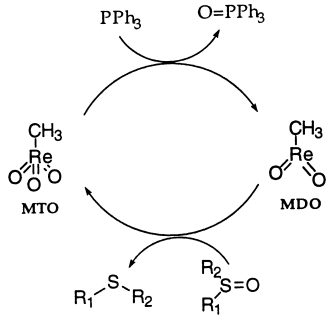
(∼−47 kcal/mol), no oxygen atom-transfer products are observed at ambient temperature in the absence of a catalyst. Several rhenium(VII) and (V) oxo complexes are effective catalysts for reactions of the type described in Eq. (50).



(50)

19.1.1. MTO-catalyzed phosphine oxidations

Deoxygenation of sulfoxides with PPh_3 catalyzed by MTO gives moderate to good yields of sulfides, 59–77% [73]. The reaction is functional group tolerant and a variety of sulfoxides are deoxygenated effectively in benzene at room temperature, Table 18, [73]. There are two possible mechanisms for oxygen atom-transfer that have been considered. The first is a ligand-centered mechanism, which involves the coordination of the sulfoxide to MTO and then attack of the phosphine on the coordinated ligand to yield phosphine oxide and sulfide, Scheme 16. The second mechanism involves a change in the oxidation state of the rhenium; MTO is reduced by PPh_3 to give methylrhenium dioxide (MDO), which is oxidized by sulfoxide to regenerate MTO completing the catalytic cycle, Scheme 17.



Scheme 17. Metal-centered oxygen transfer with sulfoxides catalyzed by MTO.

Table 19
Rate constants for the oxidation of MDO to MTO by sulfoxides [74][a]

Sulfoxide	k ($l\,mol^{-1}\,s^{-1}$)
Me_2SO	15.2
PhS(O)Me	17
$MeC_6H_4S(O)Me$	21
$PhS(O)CH{=}CH_2$	11

[a] Reprinted with permission from Inorg. Chem. 35, 7756. Copyright 1996 American Chemical Society.

Both reactions described in Scheme 17 have been studied independently. In the absence of an oxidant, triphenylphosphine reduces MTO to give a phosphine adduct of methyldioxorhenium(V) ($MDO : 2PPh_3$). Sulfoxides have been shown to oxidize MDO back to MTO [74]. Kinetic studies on MDO oxidation with sulfoxides in acetonitrile-water (1 : 1 v/v) follow pseudo-first-order kinetics, when sulfoxide is in excess, and mixed-second-order kinetics when sulfoxide concentrations are comparable to those of MDO [74]. Representative second-order rate constants for the reaction of MDO with sulfoxides are shown in Table 19.

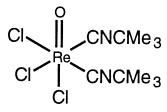
Under catalytic conditions in benzene, Scheme 16 was favored as the operating mechanism because turnover rates exceeded those observed for the reduction of MTO by PPh_3.

19.1.2. Oxorhenium(V) catalysts

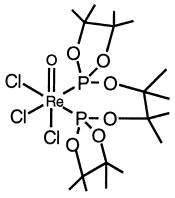
Both oxorhenium(V) complexes *mer,trans*-$Re(O)Cl_3(PPh_3)_2$, **I**, and *mer,cis*-$Re(O)Cl_3(OPPh_3)(Me_2S)$, **II**, catalyze oxygen-transfer from sulfoxides to phos-

phines. **II** is synthesized in quantitative yields by the addition of dimethylsulfoxide, DMSO, to **I** [75,76]. Therefore, catalysts **I** and **II** exhibit similar reactivities in O-transfer reactions with sulfoxides. A ligand-centered oxygen-transfer mechanism has been suggested for these catalysts. The coordinated sulfoxide is activated electrophilically; attack of the phosphine on the sulfur of the coordinated sulfoxide has been suggested in analogy to organic activating electrophiles. In support of a ligand-centered mechanism, isotope labeling experiments under stoichiometric conditions with ^{18}O-DMSO showed that the oxygen in the phosphine oxide product is mainly that of the sulfoxide [76].

In contrast to **I** and **II**, the catalytic oxidation of triphenylphosphine with *fac,cis*-$ReOCl_3(CNCMe_3)_2$, **VI**, and *fac,cis*-$ReOCl_3$(pinacop) {pinacop = ($OCMe_2CMe_2O$)$POCMe_2CMe_2$ $CMe_2OP(OCMe_2CMe_2O)$}, **VII**, involve a metal-centered oxygen-transfer mechanism. Complex **VI** reacts readily with PPh_3 to give $O{=}PPh_3$ and a paramagnetic rhenium(III) complex, Eq. (51). The π-acidic isocyanide ligand is believed to stabilize the lower valent rhenium(III) making complex **VI** a better oxo-donor than complexes **I** and **II**. The reduction of **VI** is faster than the dissociation of the isocyanide ligand. Therefore, oxygen-atom transfer does not occur through a coordinated phosphine. As for complex **VII**, the electronic and steric contributions of the bidentate ligand are believed to stabilize the rhenium(III) product [77].



VI

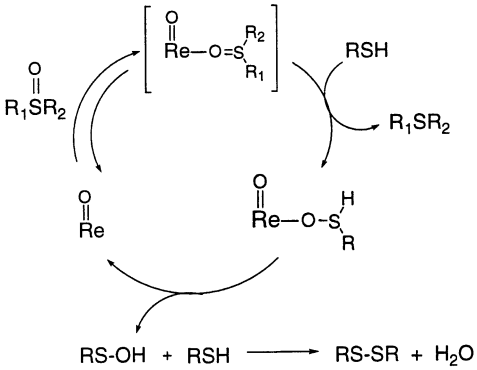


VII

$$Re(O)Cl_3(CNCMe_3)_2 + 2PPh_3 \xrightarrow{THF} ReCl_3(CNCMe_3)\ PPh_3 + O{=}PPh_3 \quad (51)$$

19.2. Oxidation of thiols

Traditionally oxidations of thiols to disulfides have been accomplished using a variety of oxidants: peroxides [78–80], periodate [81,82], dimethyldioxirane [83,84], and perborate [85]. Careful control of reaction conditions, however, is necessary to avoid overoxidation.



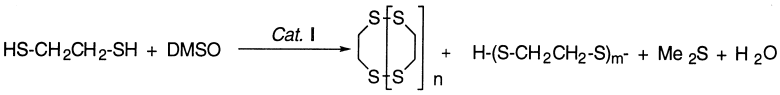
Scheme 18. Proposed mechanism for oxidation of thiols to disulfides with sulfoxide catalyzed by **I** or **II**. Reprinted with permission from Inorg. Chem. 37, 4983. Copyright 1998 American Chemical Society.

With the use of catalytic amounts of **I** or **II**, thiols are effectively oxidized to disulfides with sulfoxides under mild conditions, Eq. (52), [75,86]. Oxidations occur rapidly (within 2 h) and in high yields (>90%) at room temperature. When complex **I** is used as a catalyst, the reaction exhibits an induction period which is caused by the oxidation of the phosphine ligands of **I** prior to thiol turnover [75]. Following the induction period, the kinetics exhibited by **I** or **II** are comparable. The reaction rates are first-order in sulfoxide, and inhibited by thiol due to competition with sulfoxide for the binding site on rhenium. The proposed mechanism is oxygen-transfer from a sulfoxido ligand to afford sulfenic acid, which condenses rapidly with a second equivalence of thiol to give disulfide, Scheme 18, [75].

$$2R\text{–}SH + R_1SOR_2 \xrightarrow{Re(V)_{cat}} RS\text{–}SR + R_1SR_2 + H_2O \quad (52)$$

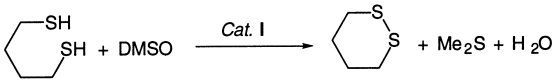
An impressive number of thiols containing a variety of functional groups undergo oxidation to the disulfide with the **I**/DMSO catalytic system [86]. Functional group tolerance include primary alcohols, carboxlyic acid, esters and protonated amines. The same catalytic system also produced a mixture of oligomeric cyclic disulfides (64%, $n = 1$–4) and in-

soluble polymeric disulfides (36%) when reacted with 1,2-ethanedithiol, Eq. (53).

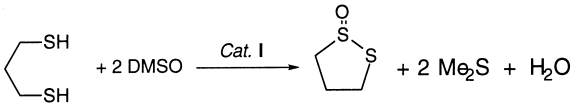


(53)

Intramolecular cyclization of 1,4-butane dithiol gave the stable six-membered 1,2-dithiane ring in yields greater than 94%, Eq. (54). 1,3-propanedithiol produced the 5-membered cyclic disulfide 1,2-dithiolane *S*-Oxide (82%), Eq. (55). This further oxidation occurs to relieve some of the ring strain, from sp (180°) to sp^2 (120°). Also, five-membered cyclic disulfides have lower oxidation potential as compared to other disulfides.

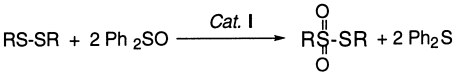


(54)



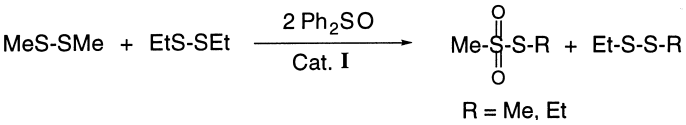
(55)

Thiosulfinate products were not detected in reaction mixtures of other thiol oxidations, acylic alkyl and aryl disulfides or the six-membered 1,2-dithiane ring, involving the 1/DMSO catalytic system. Changing the sulfoxide from DMSO to diphenylsulfoxide resulted in the oxidation of alkyl and aryl disulfides to thiosulfinates in 83% conversions for R=CH_3, Eq. (56).



(56)

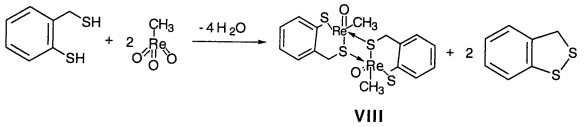
Oxidation of a 1 : 1 mixture of methyldisulfide and ethyldisulfide gave a mixture of thiosulfinate products, Eq. (57), indicating that cleavage and recombination of the disulfide occurred.



(57)

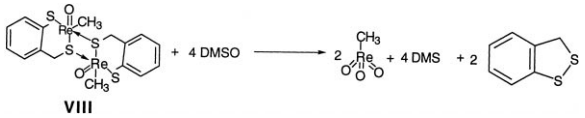
The observed differences between DMSO and diphenylsulfoxide are consistent with a ligand-centered oxygen-transfer mechanism in which the nucleophile, thiol or disulfide, attacks the coordinated sulfoxide. The electron-withdrawing ability of phenyl substituents may be responsible for the enhanced reactivity of diphenylsulfoxide.

Catalytic oxidation of thiols by DMSO can also be affected with MTO [87]. Preliminary studies suggest that the mechanism of oxidation might be different from that observed for the rhenium(V)/sulfoxide system, vide supra. The dithiolato-dirhenium(V) complex **VIII** has been isolated from the reaction of MTO with a dithiol, Eq. (58), [87].



(58)

Four equivalents of DMSO and **VIII** give dimethylsulfide, the cyclic disulfide and MTO, Eq. (59), [87]. The involvement of these rhenium(V) thiolato-complexes in the catalytic reaction remains to be established.

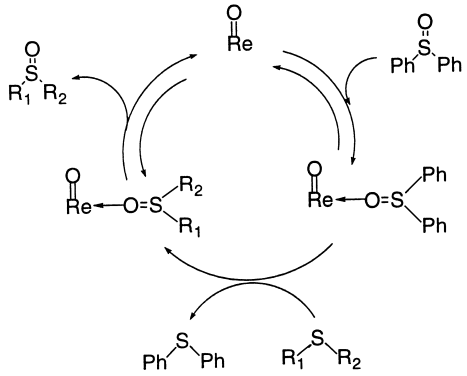


(59)

Table 20
Synthesis of sulfoxides by rhenium(V) catalyzed sulfide oxidations[a] [89]

R_1	R_2	Oxidant	Yield (%)	Time (h)
Me	Me	d_6-DMSO	86	0.5
Me	Me	Ph_2SO	96	0.1
n-Bu	*n*-Bu	d_6-DMSO	86	2.0
n-Bu	*n*-Bu	Ph_2SO	98	0.5
t-Bu	*t*-Bu	d_6-DMSO	50	2.5
t-Bu	*t*-Bu	Ph_2SO	96	1.0
Ph	Me	d_6-DMSO	10	5.0
Ph	Me	Ph_2SO	96	0.3

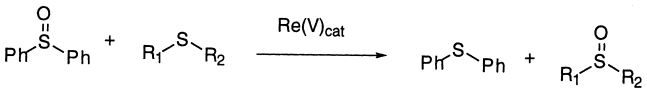
[a] Reprinted with Permission from J. Org. Chem. 61 (1996) 2261. Copyright 1996 American Chemical Society.



Scheme 19. Proposed mechanism for rhenium(V)-catalyzed oxygen-scrambling between sulfides and sulfoxides.

19.3. Oxygen-scrambling between sulfoxides and sulfides

A variety of oxidants are capable of oxidizing sulfides to sulfoxide: 30% hydrogen peroxide, $NaIO_4$, *t*-BuOCl, acyl nitrates, and peracids to name a few. When the oxidizing agent is used in excess, sulfides are converted directly to sulfones. Therefore, control of stoichiometry is necessary if sulfoxides are desired. Overoxidation of sulfides is a common problem in preparing biologically relevant sulfoxides as in the *m*-CPBA oxidation of glycosyl sulfides [88]. Oxidation of sulfides using DMSO as an oxidant is limited to a narrow range of sulfide structures, and requires high temperatures or acid catalysis. Rhenium-catalyzed oxidation of alkyl and aryl sulfides with diphenylsulfoxide is efficient and rapid under mild conditions [89]. Catalytic oxygen-atom transfer from sulfoxides provides a desirable alternative to traditional peroxide-based oxidations. The catalytic reaction is illustrated in Eq. (60). In the absence of a catalyst, the reaction does not transpire to any extent.

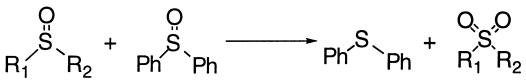


(60)

Reactions catalyzed by complexes **I** and **II** afford cleanly the desired sulfoxide without any sulfone byproducts. The formation of sulfones is kinetically slow because sulfoxides are much weaker nucleophiles than sulfides. Catalyzed oxidations with DMSO were much slower and gave lower yields in comparison to those with diphenylsulfoxide, Table 20, [89]. Attractive features of this catalytic system is its stability to air (O_2) and water; nevertheless, catalytic activity does decrease after several hours as the catalyst decomposes to inert perrhenate, ReO_4^-. Both DMSO and diphenylsulfoxide were tolerant of many functional groups such as alcohols and protonated amines.

The mechanism of oxygen-transfer involves electrophilic activation of sulfoxide via coordination to rhenium, Scheme 19. The ligand-centered mechanism is also supported by the fact that diphenylsulfoxide is more reactive than dimethylsulfoxide.

As seen previously in the MTO-catalyzed oxidation of thiols, sulfoxides are capable of oxidizing MDO back to MTO. Nevertheless, MTO has not yet been explored as catalyst for oxygen scrambling reactions between sulfoxides and sulfides. Another interesting reaction is the oxidation of sulfoxides to sulfones, Eq. (61), a reaction that is highly exoergic (−25 kcal/mol). Potential rhenium oxo complexes that catalyze reaction (61) have not yet been realized.



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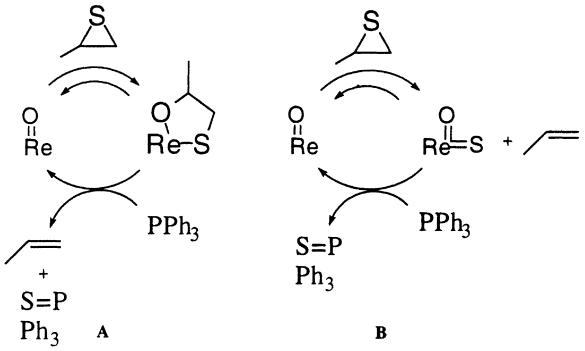
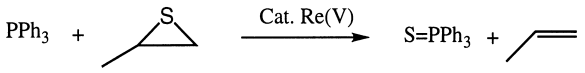


Scheme 20. Mechanism(s) of the reaction between propylene sulfide and PPh_3 catalyzed by oxorhenium(V).

20. Sulfur-atom transfer from episulfides

The isoelectronic sulfur-atom transfer to phosphine, Eq. (62), is of particular interest in the sulfurization of phosphite triesters to form phosphorothioates [90]. Both complexes **I** and **II** catalyze the sulfurization of tertiary phosphines with propylene sulfide at room temperature.



(62)

High isolated yields were obtained for these reactions (>85%) [90]. Cyclohexene sulfide is also a suitable S-atom donor for triphenyl phosphine. Two possible mechanisms for S-atom transfer have been postulated, Scheme 20. Mechanism **A** involves ring-opening of the episulfide followed by sulfur-atom abstraction by phosphine. Although the proposed metallacycle species has not been characterized, rhenium diolato (oxygen-analogs) complexes are precedented [91]. Mechanism **B** proceeds via a mixed sulfido-oxo rhenium(VII) intermediate, which then donates a sulfur atom to PPh_3. It is interesting to note that oxygen-atom transfer from epoxides to PPh_3 was not affected by complexes **I** and **II** [92].

21. Reduction of inorganic oxoanions

Periodate is commonly used in oxidation of polysaccharides for structural elucidation. The use of halo-oxoanions as oxidants has been achieved with Mn(III) and Mo(V) porphyrin complexes. The Mn(III) complex utilizes both percholorate (ClO_4^-) and periodate (IO_4^-) as oxidants [93]. The Mo(V) complex affects bromide oxidation with ClO_3^- [94]. Recently, methylrhenium(V) dioxide (MDO) has been shown to reduce at record rates a variety of inorganic oxoanions in aqueous solution at pH 0 [95,96]. The reduction of perchlorate is most intriguing because of its kinetic inertness towards reducing agents. Perchlorate is thermodynamically the weakest oxidant of the halo-oxoanions: $BrO_4^- > IO_4^- > ClO_4^-$ [97]. In general, the reduction rates of the halogen oxoanions obey the following trend: $IO_4^- > BrO_4^- > ClO_4^-$. Also, reduction rates increase as the halogen oxidation numbers decrease:

$$ClO_4^- < ClO_3^- < ClO_2^- \ll ClO^-$$
$$BrO_4^- < BrO_3^- \ll BrO^-$$
$$IO_4^- < IO_3^-$$

Ammonium perchlorate is used as a propellant in rocket fuel, explosives, and pyrotechnics. Recent health concerns about perchlorate contamination in groundwater has stimulated research in remediation methodologies [98]. Due to their high solubility in water (~8 M), perchlorates cannot be easily removed from drinking water by common precipitation technologies. Therefore, environmentally friendly and efficient catalytic remediation has to be developed and employed. The use of microorganisms to reduce perchlorates is another promising avenue. The mircobial reduction of perchlorate is a result of anaerobic respiration which yields chloride ion and molecular oxygen [99].

In aqueous solutions, MDO is made in situ from MTO and H_3PO_2, Eq. (63), [95]. As discussed in a previous section, MDO can be prepared from MTO and PPh_3 in organic media. The MDO species formed is believed to contain either a coordinated phosphine or a phosphine oxide. However, in aqueous solutions there is no evidence for the formation of a H_3PO_3–MDO species; therefore, MDO is believed to be solvated by water molecules. Upon standing, MDO reacts with MTO to give a dinuclear rhenium(VI) complex, Eq. (64), or dimerizes/oligomerizes to give a blue-black precipitate, Eq. (65), [96].

$$CH_3ReO_3 + H_2P(O)OH \rightarrow CH_3ReO_2 + HP(O)(OH)_2 \quad (63)$$

Table 21
Rate constants and stoichiometry for the reaction of MDO with several oxoanions at pH = 0 and 25°C [96][a]

Oxoanion	k_1 ($l\,mol^{-1}\,s^{-1}$)	MDO : XO_n^-
ClO_4^-	7.3	4 : 1
ClO_3^-	3.8×10^4	3 : 1
BrO_4^-	2.6×10^5	1 : 1
BrO_3^-	2.0×10^5	3 : 1
IO_3^-	1.2×10^5	3 : 1
NO_3^-	4.4×10^1	1 : 1
MnO_4^-	1.0×10^6	3 : 2
HONO	4.4×10^2	1 : 1

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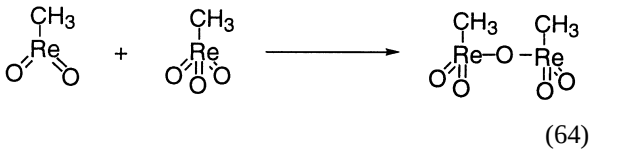
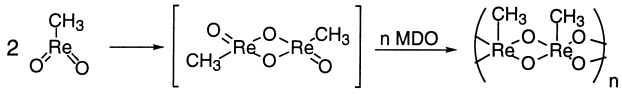


(64)



(65)

MDO is a potent oxygen-acceptor; it reacts readily with a number of oxygen donors: inorganic oxoanions (XO_n^-) (in which X = Cl, Br, I, and $n = 3$ or 4], NO_2^-, amine *N*-oxides, sulfoxides, epoxides, and $VO^{2+}_{(aq)}$. The oxygen-transfer reactions of MDO with perchlorate have been shown to involve multiple oxygen-transfer steps [95,96]. The stoichiometric reaction requires 4 molar equivalents for every mole of perchlorate ions yielding Cl^- as the final product, Eq. (66).

$$4MDO + ClO_4^- \rightarrow 4MTO + Cl^- \quad (66)$$

The reduction of ClO_4^- to ClO_3^- is the first step in reaction (66) and it is rate determining. The reduction of perchlorate by MDO is first-order in both reagents, Eq. (67), with a second-order rate constant k_1 of $7.3\,l\,mol^{-1}\,s^{-1}$. The subsequent reduction of chlorate by MDO is faster than that of perchlorate. The second-order rate constant for chlorate reduction, k_2, is $3.8 \times 10^4\,l\,mol^{-1}\,s^{-1}$ Eq. (68).

$$MDO + ClO_4^- \xrightarrow{k_2} MTO + ClO_3^-,$$

$$-\frac{d[MDO]}{dt} = 4k_1[MDO][ClO_4^-] \quad (67)$$

$$MDO + ClO_3^- \xrightarrow{k_2} MTO + ClO_2^-,$$

$$-\frac{d[MDO]}{dt} = 3k_2[MDO][ClO_3^-] \quad (68)$$

Second-order rate constants and stoichiometry for various oxoanions are presented in Table 21. Other inorganic oxoanions display similar features to those observed for the reaction of perchlorate with MDO. The reduction of oxoanions follows the general rate law given in Eq. (69) where *m* is equal to the stoichiometric equivalence of oxoanion and *k* is a second-order rate constant. The reduction of perchlorate is about five orders of magnitude slower than the reduction of perbromate. Chlorate is about four orders of magnitude faster than perchlorate. These findings follow the general trend of reactivity observed for halo-oxoanions.

$$V = mk[MDO][XO_n^-] \quad (69)$$

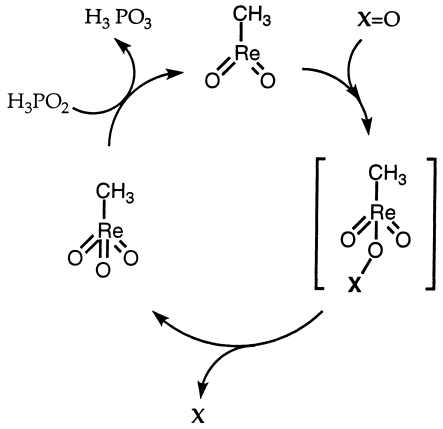
Saturation kinetics were observed for BrO_4^- and ClO_3^- anions at low concentrations (1×10^{-2} M), and NO_3^- and ClO_4^- at higher concentrations (>0.6 M). The plateau values differed depending on the oxoanion eliminating the possibility of a common steady-state intermediate. Therefore, a mechanism involving the formation of an intermediate in a prior-equilibrium step, Eq. (70), is consistent with the observed kinetics, Eq. (71).

$$XO_4^- + MDO \overset{K}{\rightleftharpoons} [MDO^{\bullet}XO] \overset{k}{\rightarrow} MTO + XO_{n-1}^- \quad (70)$$

$$v = \frac{Kk[MDO][XO_n^-]}{1 + K[XO_n^-]} \quad (71)$$

A catalytic perspective of these reactions is represented in Scheme 21. The saturation kinetics discussed above give direct evidence for the $MDO^{\bullet}XO$ adduct formation prior to oxygen transfer.

Kinetically, MDO is a more competent reductant than most transition-metal complexes that are known to reduce perchlorate and chlorate ions. Abu-Omar and Espenson report a useful table of second-order rate constants for the reduction of perchlorate and chlorate ions by several transition-metal complexes [95].



Scheme 21. Mechanism of oxygen-atom transfer from inorganic oxoanions (X=O) to H_3PO_4 catalyzed by MDO. Reprinted with Permission from Inorg. Chem. 35 (1996) 7756. Copyright 1996 American Chemical Society.

MDO, for example, is five orders of magnitude more reactive towards ClO_4^- than $V(H_2O)_6^{2+}$. The high kinetic reactivity of MDO could be attributed to its kinetic lability, high oxophilicity, and the stability of the MTO product. Studies on the relative reduction rates of ClO_4^- by several transition-metal complexes show an excellent correlation with the polarizability of the d-orbitals [100]. Therefore, it is suggested that the 5d-orbitals orbitals in rhenium play a significant role in facilitating oxygen-atom transfer.

22. Other main group oxo donors

22.1. Tertiary amine N-oxides

Of all the known *N*-oxides (nitrile oxide, azomethine oxide, diazine oxide, pyridine *N*-oxide, benzofuroxan oxide and phenazine oxide), only the oxidation chemistry of pyridine *N*-oxides is well established. Pyridine *N*-oxide and its derivatives oxidize MDO to MTO, Eq. (72). Electronic effects on the oxygen-atom transfer reaction, Eq. (72), were probed via a Hammett free-energy correlation ($\log k$ versus σ_p), Table 22, [96]. The Hammett plot yielded a reaction constant $\rho = -1.18$, which is in agreement with a nucleophilic attack by the pyridine *N*-oxide on the rhenium.

Table 22
Second-order rate constants for the oxidation of MDO by various *para*-substituted pyridine *N*-oxides [96][a]

N-Oxide	σ_p	k ($l\,mol^{-1}\,s^{-1}$)
MeO–	−0.27	7.80×10^3
Me–	−0.17	7.10×10^3
H–	0.00	4.60×10^3
Cl–	+0.23	2.67×10^3
NC–	+0.66	6.50×10^2

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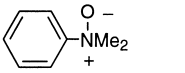
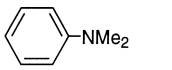
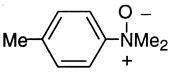
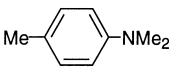
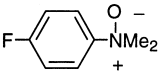
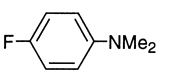
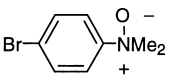
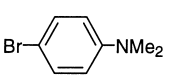
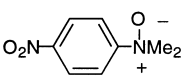
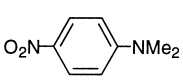
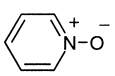
Table 23
MTO catalyzed oxidation of triphenylphosphine with various amine *N*-oxides [73]

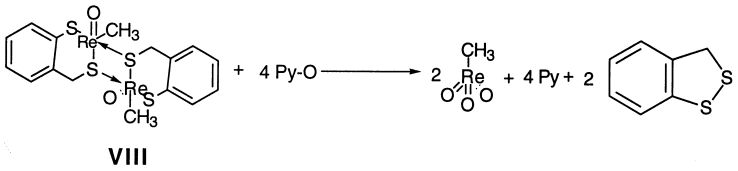
N-Oxide	Amine product	Yield (%)
		78
		81
		74
		70
		65
		77

(72)

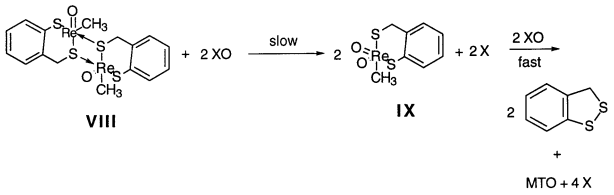
Amine oxides also oxidize triphenylphosphine to triphenylphosphine oxide under mild conditions in the presence of catalytic amounts of MTO; some representative examples are shown in Table 23, [73]. In organic media, the accepted mechanism involves a five-coordinate intermediate in which the *N*-oxide is bound to MTO; subsequently triphenylphosphine attacks the coordinated amine oxide to yield products and regenerate the catalyst [73]. This mechanism is depicted previously in Scheme 16 for the oxygen transfer from sulfoxides to triphenylphosphine. However, in aqueous solution at pH 0.0, MDO is oxidized by

pyridine *N*-oxide according to a mechanism similar to that described for the oxoanions above, Scheme 21. [96]. The acidic aqueous media is required to stabilize MDO against polymerization.

Pyridine *N*-Oxide oxidizes thiols to disulfides in the presence of stoichiometric amounts of the dithiolato-dirhenium(V) complex **VIII**, Eq. (73). These reactions were complete within 5 min (81% yield) in contrast to 1.5 days with DMSO as oxidant [87].



VIII (73)



VIII IX (76)

22.2. Tertiary arsine and stibene oxides

Tertiary arsine and stibene oxides are known to oxidize MDO to MTO by the same mechanism observed for pyridine *N*-oxide [96]. The second-order rate constants for Ph_3AsO and Ph_3SbO are comparable, 40 and 55 l mol^{-1} s^{-1}, respectively. Triphenylarsine oxide and triphenylstibene oxide are reduced catalytically by triphenylphoshine in the presence of MTO, Eqs. (74) and (75), [73]. These reactions were quantitative and complete within 30 min at room temperature in benzene. The thermodynamic driving force for reaction (75) is approximately –30 kcal mol^{-1} (gas phase) [97]. The poor solubility of Ph_3AsO and Ph_3SbO in aqueous solution, limit their use as oxidants.

$$Ph_3As{=}O + PPh_3 \overset{MTO}{\rightarrow} O{=}PPh_3 + PPh_3As \quad (74)$$

$$Ph_3Sb{=}O + PPh_3 \overset{MTO}{\rightarrow} O{=}PPh_3 + PPh_3Sb \quad (75)$$

Also, triphenyl arsine and stibene oxides oxidize thiols to disulfides in the presence of stoichiometric amounts of the dithiolato-dirhenium(V) complex **VIII** [87]. The stoichiometric reaction is similar to that seen for DMSO and pyridine *N*-oxide, Eq. (73). Reactions with Ph_3AsO were complete within 5 min while Ph_3SbO gave only 50% yield after 3 days. It is believed that the rate-controlling step is the oxidation of the dithiolato-dirhenium(V) complex to form the rhenium (VII) thiolato **IX**, which forms MTO and the disulfide rapidly, Eq. (76).

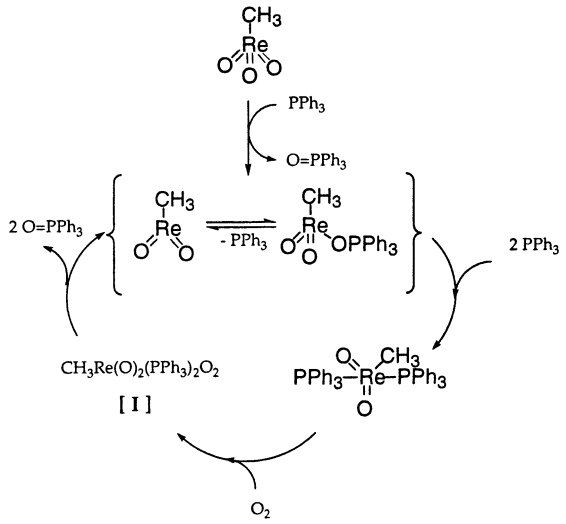
22.3. Molecular oxygen

From economic and environmental considerations, molecular oxygen is the oxidant of choice. The use of O_2 with oxorhenium complexes has been limited thus far, probably due to the fact that the most common oxidation states for oxorhenium compounds are +5 and +7, which are air-stable. Nevertheless, it has been reported that MTO catalyzes the oxidation of tertiary phosphines by molecular oxygen at room temperature [73]. Reactions employing air were complete within 2 days and those conducted with pure oxygen required less than 6 h. The control experiment, triphenylphosphine and air in the absence of MTO, did not produce any triphenylphosphine oxide after 1 week. Mechanistic studies suggest that oxygen-transfer occurs by a different pathway than the rhenium-peroxide system. The postulated mechanism contains an oxygen-containing species, [I], Scheme 22.

MTO is reduced by triphenylphosphine to form MDO or the MDO : $OPPh_3$ adduct; two additional triphenylphosphine ligands coordinate to MDO to give $CH_3Re(O)_2(PPh_3)_2$. Molecular oxygen oxidizes the phosphine via an oxygen-containing intermediate, [I], to give 2 equivalents of $O{=}PPh_3$ and regenerate MDO.

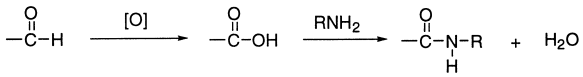
22.4. Water as an oxidant

Aldehydes can be converted to amides in two steps, oxidation to a carboxylic acid followed by condensa-

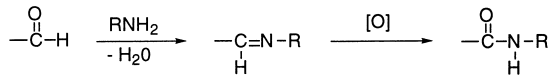


Scheme 22. Air oxidation of triphenylphosphine catalyzed by MTO.

tion with an amine, Eq. (77) This reaction could be carried out in the reverse sequence, Eq. (78), imine formation followed by oxidation. The reaction described in Eq. (78) has been accomplished with a rhenium azomethine complex and water as the oxidant [101–103].



(77)

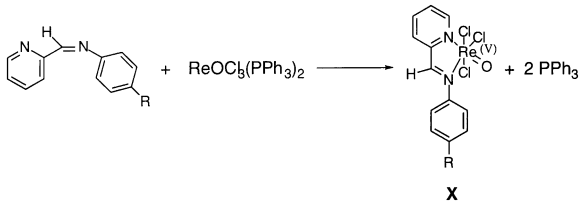


(78)

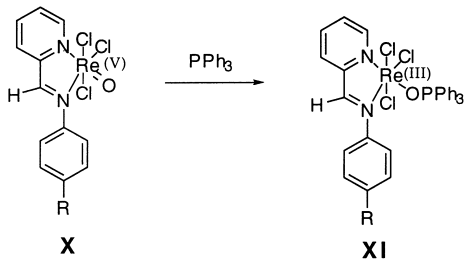
The aldimine ligand is prepared from pyridine-2-aldehyde and *p*-toluidine. The ligand is reacted with $ReOCl_3(PPh_3)_2$, **I**, in warm toluene under N_2 to give complex **X** after 2 min, Eq. (79). When the reaction is run for 10 min instead, complex **XI** is produced. Complex **X** can be converted to **XI** directly upon addition of triphenylphosphine, Eq. (80).

Table 24
Rate constants for the reactions of Eqs. (80) and (81) at 299 K [102]

R-*para*	$10^3\ k_{80}$ ($M^{-1}\ s^{-1}$)	$10^3\ k_{81}$ ($M^{-1}\ s^{-1}$)
Me	7.96	0.69
H	12.26	1.19
Cl	24.02	–

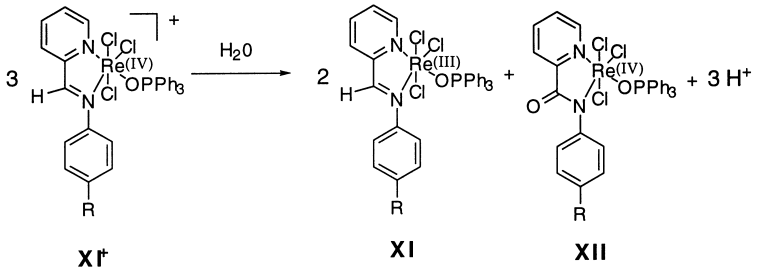


(79)

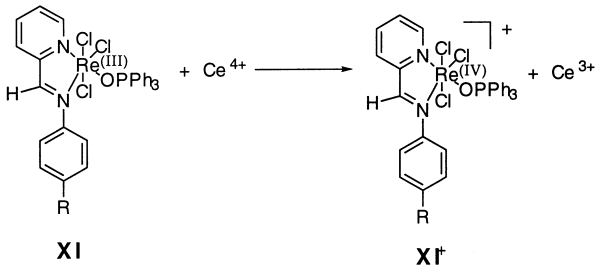


(80)

Electrochemical oxidation of **XI** in dry acetonitrile at 0.5 V versus SCE gives the cationic rhenium(IV) species $\mathbf{XI}^+$. Addition of 5% H_2O results in ligand oxidation to the amide and formation of complex **XII**, Eq. (81). **XI** can also be oxidized chemically by Ce^{4+} or H_2O_2 in aqueous solution, Eq. (82). Complex **XI** does not react with water; oxidation initially to the Re(IV) cationic complex is required. The rhenium(IV)–rhenium(III) cyclic voltammetric data shows a quasireversible one-electron redox near 0.3 V, Eq. (83). The potential increases with increasing (R-*para*) electron-withdrawing groups: Ome (0.28 V) < Me (0.30 V) < H (0.32 V) < Cl (0.35 V). A plot of $E_{1/2}$ versus σ is linear with a correlation coefficient of 0.99 and a reaction constant $\rho = 0.14$.



(81)



(82)

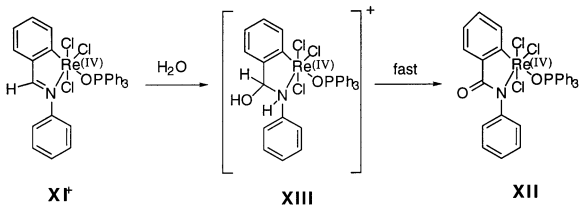
$$\mathbf{XI}^{+} + e^{-} \overset{\sim 0.3V}{\rightleftharpoons} \mathbf{XI} \tag{83}$$

Kinetics studies on reaction (81) showed that the rate is first-order with respect to $\mathbf{XI}^{+}$ and H_2O. Kinetics on reaction (80) is also first-order in [PPh_3] and [**X**]. The rate laws are given in Eqs. (84) and (85). The second-order rate constants with different R substituents on the ligands are presented in Table 24, [102]. The activation parameters for both reactions have been determined: For reaction (80) with R = Me, $\Delta H^{\ddagger} = 8.91\,\text{kcal mol}^{-1}$, and $\Delta S^{\ddagger} = -38.69\,\text{cal mol}^{-1}\,\text{K}^{-1}$; for reaction (81) with R = H, $\Delta H^{\ddagger} = 13.4\,\text{kcal mol}^{-1}$, and $\Delta S^{\ddagger} = -27.3\,\text{cal mol}^{-1}\,\text{K}^{-1}$. Large negative entropies of activation suggest strong association between the reactants in the transition-state.

$$\text{rate} = k_{\text{obs}}[\mathbf{X}] = k_{80}[\mathbf{X}][PPh_3] \tag{84}$$

$$\text{rate} = k_{\text{obs}}[\mathbf{XI}^{+}] = k_{81}[\mathbf{XI}^{+}][H_2O] \tag{85}$$

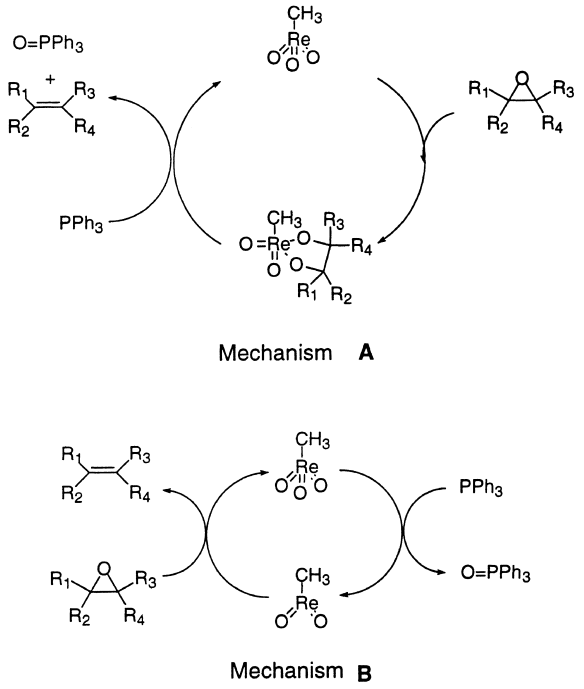
The amide oxygen in the oxidized ligand is from water. Nucleophilic attack of the water on the coordinated aldimine is consistent with the kinetics; the formation of intermediate **XIII** prior to amide formation has been proposed, Eq. (86), [102,103].



(86)

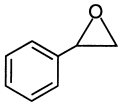
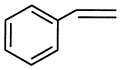
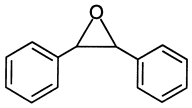
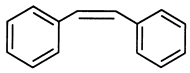
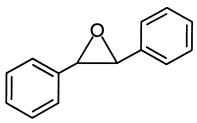
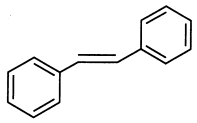
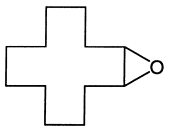
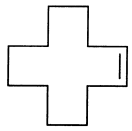
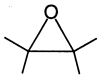
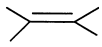
22.5. Deoxygenation of epoxides

Epoxides are known to donate an oxygen atom to oxophilic metals, Eq. (87). In benzene, epoxides can be easily converted into olefins using a catalytic amount of MTO and a stoichiometric equivalence of triphenylphosphine, Eq. (88). These reactions occur rapidly at room temperature and in high yields (>79%), [73]. The relative stereochemistry about the carbon–carbon double bond of epoxides is preserved in the product. The mechanism of O-transfer is believed to involve the formation of a dialkoxyrhenium(VII) (rhenium glycolate) complex. Dialkoxyrhenium(VII) complexes are formed in quantitative yields from the reaction of MTO with excess epoxide, Eq. (89), [91,104].

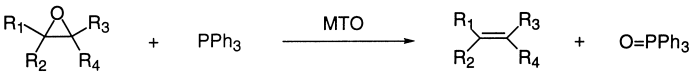


Scheme 23. The postulated mechanism of epoxide deoxygenation by triphenylphosphine catalyzed by MTO.

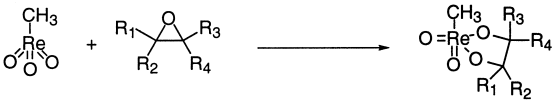
Table 25
MTO-catalyzed deoxygenation of various epoxides with PPh_3 [73]

Substrate	Olefin product	Yield (%)
		83
		71
		87
		85
		79
		81

(87)



(88)



(89)

There are two possible mechanisms for oxygen-atom transfer from an epoxide. The first involves the formation of a rhenium(VII) glycolate complex followed by phosphine attack, mechanism **A** in Scheme 23. The second mechanism proceeds through MDO followed by oxygen-transfer from epoxide, mechanism **B** in Scheme 23.

A list of different epoxides that are catalytically reduced with MTO and PPh_3 are presented in Table 25, [73]. Oxygen-atom transfer from epoxide to PPh_3 in the absence of a catalyst is non-existent.

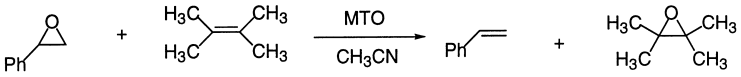
Epoxides are also capable of oxidizing olefins in the presence of MTO. The MTO catalyzed oxygen-atom transfer from styrene oxide to 2,3-dimethyl-2-butene produced styrene and 2,3-dimethyl-2-butene oxide in about 10% yield, Eq. (90), [91]. When allowed to react for 3 days, only 20% of the starting material reacted and the corresponding diol ring-opening product accounted for the remaining balance.

MTO catalyzes the disproportionation of epoxides to give olefin and diol, illustrated for cyclohexene oxide in Eq. (91), [105]. Styrene oxide and propylene oxide are capable of oxidizing azibenzil to benzil in

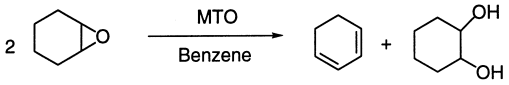
Table 26
Yields of various 1,3-dioxolanes from the reaction of epoxides with carbonyl compounds in the presence of 1% MTO [104]

Carbonyl compound	Propylene oxide	Styrene oxide	*Trans*-stilbene oxide	*Cis*-stilbene oxide
	87%	81%	89%	87%
	37%	Trace	42%	44%
	>95%	86%	>96%	90%
		88%	>96%	~100%
	>96%	94%	91%	88%
	87%	>95%		
	82%	61%		
	16% (5 days)			

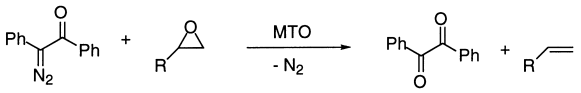
the presence of catalytic amounts of MTO, Eq. (92), [41].



(90)

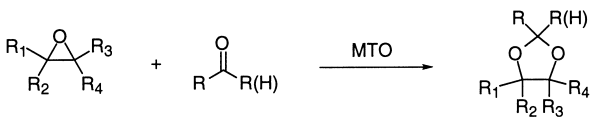


(91)



(92)

MTO catalyzes the formation of 1,3-dioxolanes in high yields from the reaction of epoxides with aldehydes or ketones, Eq. (93), [104]. Reactions of various epoxides with carbonyl compounds are summarized in Table 26.



(93)

23. Concluding remarks and future outlook

The rich catalytic chemistry of oxorhenium compounds will continue to expand and is sure to find several industrial applications in the near future. Three areas that require improvements and further investigations are (1) aromatic and aliphatic C–H oxidations with H_2O_2, (2) asymmetric oxygen-transfer, and (3) oxidative tandem cyclizations. Enantioselective epoxidations of unfunctionalized olefins are highly desirable but remain difficult to achieve. The only known catalytic system that provides optically pure unfunctionalized epoxides is the Mn(Salen)Cl/NaOCl catalyst of Jacobsen [106]. The development of an asymmetric catalytic system based on MTO or other rhenium oxo complexes is highly attractive. Stoichiometric amounts of rhenium(VII) oxide are often essential in oxidative cyclization reactions; the evolution of effective tandem polycyclizations that employ

catalytic rhenium oxide would be a milestone considering the utility of these reactions in organic synthesis. New and exciting advances are being realized in the area of employing molecular sieves in heterogeneous catalysis. Immobilization of rhenium oxide catalysts in porous materials is another area of tremendous promise.

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