Atom-transfer reactions catalyzed by methyltrioxorhenium(VII)—mechanisms and applications

James H. Espenson

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011, USA.
E-mail: espenson@ameslab.gov

Received (in Cambridge, UK) 25th November 1998, Accepted 23rd December 1998

Methyltrioxorhenium activates hydrogen peroxide by an electrophilic mechanism, transferring a single oxygen atom to many substrates without the intervention of free-radical intermediates. The reactions proceed without by-products, unlike those of most chemical (stoichiometric) oxidizing agents. In separate chemistry, the rhenium catalyst brings about the transfer of oxygen atoms between a pair of closed-shell molecules.

Introduction

This review focuses on the catalytic chemistry of the compound methyltrioxorhenium, CH_3ReO_3, abbreviated as MTO. With but eight atoms, the small MTO molecule functions as a versatile catalyst for a considerable breadth of reactions. The essence of its chemistry is the transfer of an oxygen atom from one species to another. The oxygen source is often hydrogen peroxide; molecular oxygen is not activated. Oxygen transfer between two other substrates, as in $X + YO \rightarrow XO + Y$, is a separate process catalyzed by MTO.

Our research has been directed toward two aspects of the catalytic chemistry: gaining an understanding of the mechanisms by which different MTO reactions occur and using that understanding to predict and carry out other useful transformations. These two outlooks reinforce one another. The solubility of MTO in aqueous and most organic media adds to its versatility; the solvent can be chosen to meet requirements of the substrates, to facilitate product isolation, to enable kinetics studies, or as a matter of convenience. MTO is air-stable also, which enhances its general usefulness in catalytic systems; on the other hand, with but rare exception it does not catalyze autoxidation reactions.

The MTO molecule is isoelectronic and isostructural with the dangerously explosive permanganic acid, $HMnO_4$. MTO is rather more like perrhenic acid, $HReO_4$ or $HO–ReO_3$, in that both are quite mild oxidants. Indeed, with one known exception, the catalytic chemistry of MTO does not involve its redox reactivity; the rhenium atom remains in oxidation state VII. An exception, to be dealt with in due course, involves the intermediacy of the rhenium(V) compound $CH_3ReO_2{\cdot}L_2$, with L = solvent or incidental ligand. Let us note at the outset that the methyl group of MTO, or an aspect it confers on the system, is somehow essential. The isoelectronic perrhenic acid does not catalyze the reactions presented here, likely because ReO_4^- is anionic.

This review divides the reactions of MTO and its derivatives into these groups: (1) interactions with hydrogen peroxide, (2) O-atom transfer from hydrogen peroxide, leading to simple and complex transformations, (3) reactions proceeding by C–H activation, (4) non-oxidative rearrangement and coupling reactions, (5) the use of bromide ions as a co-catalyst, and (6) extensions to some nitrene and carbene chemistry.

The MTO catalyst

MTO remains the premier member of a now-sizable family of compounds $R–ReO_3$ in which the organic group R may be alkyl, vinyl, aralkyl, allyl, alkynyl, or cyclopentadienyl. MTO shows the greatest thermal stability ($T_{dec} > 300$ °C) of any member of the series, aside perhaps from $(\eta^5\text{-}C_5Me_5)ReO_3$, a catalytically-inactive compound with an 18e electronic configuration. The preparative aspects and the structural chemistry of MTO and numerous derivatives have been thoroughly reviewed recently,[1] and thus need be dealt with only cursorily here. MTO has the expected $\psi\text{-}T_d$ structure of a four-coordinate compound of a d^0 metal center.[2] Coordination compounds, such as MTO·L and $MTO{\cdot}L_2$, where L is an anionic or uncharged Lewis base, have been characterized.[3–5] They have five- and six-coordinate structures. MTO–ligand systems are highly labile, and the ^1H NMR signals for the methyl protons of MTO and MTO·L coalesce to a singlet owing to the lability of the system on the NMR timescale. At 298 K in acetonitrile, the first binding constant of pyridine to MTO is 200 L mol^{-1} whereas that of the better donor 4-picoline is 730 L mol^{-1} and that of the sterically encumbered 2,6-di-*tert*-butyl-4-methylpyridine is < 1 L mol^{-1}.[6] Under the conditions studied, binding of a second pyridine in solution was not detected.

MTO is not prone to decomposition in solvents containing water by pathways involving acid. If this appears remarkable, then it is useful to recall that this feature is common to many

---

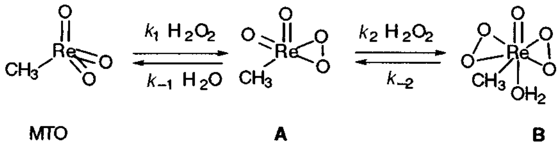
James Espenson was born in Los Angeles, California and attended school there and in its environs. He entered the California Institute of Technology, obtaining his B.S. degree in 1958. He enrolled for graduate study in the University of Wisconsin and wrote his PhD thesis under the supervision of Edward L. King in 1962. Following that he was a postdoctoral associate at Stanford University with Henry Taube during 1962–63. He was appointed Instructor of Chemistry at Iowa State University in 1963 and jointly Assistant Chemist at the Ames Laboratory of the (then) US Atomic Energy Commission. Promotions followed in due course: to Assistant Professor (1965), Associate Professor (1967), Professor (1971). He was named Distinguished Professor in 1988, and continues to hold a joint appointment at the Ames Laboratory, where he is Program Director.

Espenson has been named the John A. Wilkinson teaching award winner, Fellow of the Alfred P. Sloan foundation, Fellow of the Japan Society for the Promotion of Science, and Fellow of the American Association of the Advancement of Science. He is the author of more than 300 research publications and of the book Chemical Kinetics and Reaction Mechanisms *(2nd edn., 1995).*

other methyl–metal compounds and ions. Solutions of $HgCH_3^+$, $TlCH_3^{2+}$, $CH_3AuOH_2^{2+}$, to cite a few heavy metal derivatives, are stable toward strong acid.[7] Certain methylated first-row metals are also stable in strongly acidic solutions, such as $CH_3Co(dmgH)_2{\cdot}L$ and its relatives, including methylcobalamin. This aspect suggests, correctly, that MTO might be stabilized during catalytic turnovers by the addition of acid in semi-aqueous and aqueous media, and by the use of aprotic solvents in other instances. It is rarely useful to insist upon dry solvents for MTO-catalyzed reactions, especially since the family of reactions for which MTO is most often used, activation of hydrogen peroxide, forms water as a stoichiometric product.

Peroxorhenium compounds—structure, equilibrium, kinetics

Key to the activation of hydrogen peroxide is its interaction with MTO, yielding an equilibrium mixture of two peroxorhenium compounds, denoted **A** and **B**, both η^2-peroxo complexes of rhenium(VII). The existence of the η^2-peroxo groups comes as no surprise. This is the prevalent mode of coordination between peroxide and many d^0-metal centers.[8] The structural formulas of **A** and **B** are shown in Scheme 1.



Scheme 1

The structure of the diperoxo complex **B** has been determined crystallographically. Rhenium adopts the structure of a pentagonal bipyramid, with axial oxo (167 pm) and aqua (225 pm) groups. In the equatorial positions are the methyl group (213 pm) and the four peroxo oxygens (191 pm).[9] The water molecule is also coordinated to **B** in solution; its ^{1}H signal can be seen below −55 °C in d_8-THF.[9,10] No such signal was found for **A**, however, implying the absence of a coordinated water molecule or its exceptional lability.[10]

Both **A** and **B** have been detected by their methyl resonances in the ^{1}H and ^{13}C NMR spectra, and by their optical signals. Of these, the easier to locate is **B**, since it more readily builds to appreciable concentrations. The binding of peroxide to rhenium is cooperative, as will be explained two paragraphs hence. As a consequence, except for particular concentrations of hydrogen peroxide, **A** does not rise to levels comparable to those of MTO and **B** at equilibrium, although the NMR and optical signals of **A** can easily be seen if the peroxide concentration is not so high as to favor **B** exclusively. Because the reactions between MTO and hydrogen peroxide are equilibrium processes, it is not permitted to evaluate properties of **B**, such as its absorption spectrum, by dissolving the isolated solid. Certain erroneous values, such as absorption coefficients, have been reported as a result. Partial dissociation of **B** will occur, depending on the concentration of total rhenium and peroxide. Instead, one must obtain the spectrum of **B** by determinations in solutions containing some excess of peroxide, or by extrapolation from the least-squares fitting of the mathematical expression relating absorbance and the individual molar absorptivities:

$$\bar{\varepsilon} = \frac{\text{Absorbance}}{b[\mathrm{Re}]_\mathrm{T}} = \frac{\varepsilon_{\mathrm{MTO}} + \varepsilon_{\mathbf{A}}K_1[\mathrm{H_2O_2}] + \varepsilon_{\mathbf{B}}K_1K_2[\mathrm{H_2O_2}]^2}{1 + K_1[\mathrm{H_2O_2}] + K_1K_2[\mathrm{H_2O_2}]^2}$$

That is not to say that the equilibria in Scheme 1 are instantaneously established. In fact, the four rate constants defined therein have been evaluated under different conditions of solvent and temperature. One such experiment showing time-resolved spectral changes accompanying this reaction is shown on the cover.[11]

These steps play an important role in governing the rate of catalytic turnovers. Table 1 summarizes the values of the equilibrium and rate constants for the two reaction steps in aqueous solution[12] and in acetonitrile, and Table 2 presents the molar absorptivities and chemical shifts of compounds **A** and **B**.[13]

Table 1 Equilibrium and rate constants at 298 K for the formation of the peroxorhenium compounds **A** and **B** in aqueous solution and in acetonitrile containing 2.6% water

	K	k_f/L mol^{-1} s^{-1}	k_r/s^{-1}
Step 1:	16.1 (aq.)	80 (aq.)	10 (aq.)
	209 (AN)	0.81 (AN)	3.9×10^{-3} (AN)
	261 (MeOH)		
Step 2:	132 (aq.)	5.2 (aq.)	4×10^{-2} (aq.)
	660 (AN)	4.5×10^{-2} (AN)	6.8×10^{-5} (AN)
	814 (MeOH)		

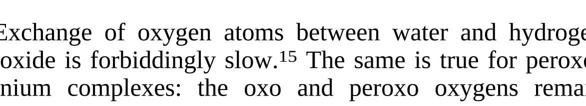
Table 2 Values of molar absorptivities and chemical shifts for MTO, **A**, and **B**

		NMR: δ	
Compound	$\lambda_{\max}$ (log ε)	^{1}H	^{13}C
MTO	206 (3.78) 228 (3.56)[a,b]	2.1[d]	19.09[e]
A	320 (2.85)[c]	2.4[d]	
B	360 (3.08)[c]	2.7[d]	31[f]

[a] In aqueous solution. [b] Ref 55. [c] In CH_3CN. [d] In THF; Ref 13. [e] In $CDCl_3$ at 28 °C; Ref 56. [f] In D_2O at 20 °C; Ref 9.

The unusual features of the data in Table 1 are these: (1) the second peroxide has a larger binding constant than the first, that is to say, they show cooperativity; (2) the step with the greater driving force is the slower. Both of these trends also hold in other solvents. Cooperativity is perhaps the consequence of an increasing Re–O bond order as the number of oxo groups decreases; **B** is favored as a consequence. The slowness of the second binding step compared to the first may reflect both the increased crowding of the coordination positions and the decreased electrophilic character of rhenium once the first peroxide has been added. In organic solvents the binding constants are generally larger than in water, and the rate constants smaller; indeed, the step represented by k_2 often poses a significant kinetic barrier to product formation by the path in which **B** is the intermediate.

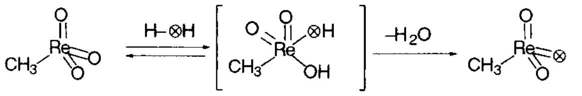
Activation parameters have been reported for the first step. The values in aqueous solution for k_1 are: $\Delta H_1^\ddagger$ = 24.5 kJ mol^{-1}, $\Delta S_1^\ddagger$ = −212 J K^{-1} mol^{-1}, $\Delta V_1^\ddagger$ = −10.6 cm^3 mol^{-1}.[14] These values have been interpreted according to Scheme 2.



Scheme 2

Exchange of oxygen atoms between water and hydrogen peroxide is forbiddingly slow.[15] The same is true for peroxorhenium complexes: the oxo and peroxo oxygens remain distinct. Oxygen atoms are, however, rapidly exchanged between MTO and water. At first this seems anomalous, in that the Re=O bonds are short and robust. However a process analogous to that just shown for peroxide easily provides a pathway for facile exchange (Scheme 3).

These reactions are the prelude to the activation of H_2O_2 by MTO. In all of this, there is no indication that organic hydroperoxides associate with MTO or are activated by it.



Scheme 3

Evidently the formation of the η^1-O_2^{2-} structure is crucial. Over very long times, MTO does decompose in the presence of alkyl hydroperoxides, such as Bu^{t}OOH and Am^{t}OOH. These reactions occur by radical pathways involving RO$^\bullet$ and ROO$^\bullet$ intermediates, among others.[16] They stand alone as examples of single-electron reactivity of MTO.

Catalyst deactivation

The decomposition of MTO is strongly accelerated by increases in the concentration of hydroxide ions. Even in strongly acidic media, $pH < 3$, the rate law shows a pH-dependence that implicates a first-order kinetic dependence on $[OH^-]$.[17] The full rate–pH profile, shown in Fig. 1, is consistent with this net reaction showing the evolution of methane:

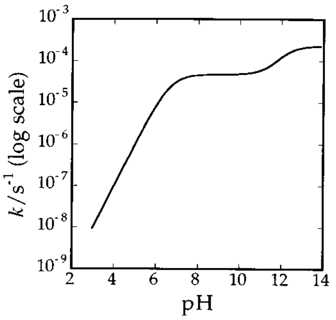


Fig. 1 The pH–rate profile for the decomposition of MTO with numerical values referring to 298 K. The reaction is strongly base-catalyzed, with two plateaus corresponding to the stepwise acid ionization of MTO_{aq}.

$$CH_3ReO_3 + H_2O = CH_4 + ReO_4^- + H^+$$

The two plateaus seen in the pH profile correspond to the successive acid ionization reactions of MTO_{aq}, corresponding to $CH_3ReO_3(OH)^-$ and $CH_3ReO_3(OH)_2^{2-}$. The respective equilibrium constants, expressed as pK_a values, lie in the ranges 6.7–7.5 and 11.7–11.9 at 298 K.[10,17,18] The rate equation for the reaction at $pH < \approx 6$ is $v = k[\mathrm{MTO}][OH^-]$, with $k = 8.6 \times 10^2$ L mol^{-1} s^{-1} at 298 K ($\Delta H^\ddagger = 15.9$ kJ mol^{-1}).[17]

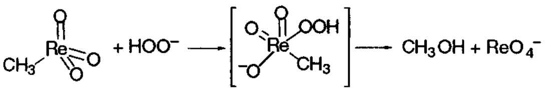
These reactions are slow enough that they tend not to cause difficulty in catalysis, although their instability toward base generally precludes the use of an alkaline medium. As will be shown, the decomposition of MTO in the presence of hydrogen peroxide occurs more rapidly and usually comprises the greater problem. Irreversible decomposition of MTO in peroxide-containing solutions forms methanol primarily, according to these net reactions:[10]

$$CH_3ReO_3 + H_2O_2 = CH_3OH + ReO_4^- + H^+$$

The rate law can be written

$$\frac{d[ReO_4^-]}{dt} = k\frac{[CH_3ReO_3][H_2O_2]}{[H^+]}$$

from which one infers that the reaction can be represented by any of these bimolecular partners: **A** + OH^- ($k_{298} = 3.1 \times 10^9$ L mol^{-1} s^{-1}), CH_3ReO_3 + HO_2^- ($k_{298} = 2.0 \times 10^8$ L mol^{-1} s^{-1}), or, improbably, $CH_3ReO_3(OH)^-$ + H_2O_2. The first two are in principle resolvable by isotopic labeling, but oxygen exchange between H_2O and ReO_4^- occurs too rapidly to permit a definitive experiment.[19] Because HO_2^- is a more potent nucleophile than OH^-, it seems likely that their reactions with MTO are analogous. We therefore describe the reaction as shown below.



Concurrently, oxygen is evolved as a consequence of the MTO-catalyzed decomposition of hydrogen peroxide ($2H_2O_2 \rightarrow 2H_2O + O_2$), which we infer takes place from **B**:[10,13]

$$CH_3Re(O)(\eta^2\text{-}O_2)_2 \rightarrow CH_3ReO_3 + O_2$$

Photochemical deactivation

Irradiation of **B** by light filtered so as to allow only $\lambda > 400$ nm, to prevent direct photolysis of hydrogen peroxide itself, leads to the slow fading of its yellow color. In acetonitrile this process gives a quantitative yield of perrhenic acid and principally methyl hydroperoxide.[13] The main photoreaction is:

$$CH_3Re(O)(\eta^2 - O_2)_2 + H_2O \xrightarrow{h\upsilon} ReO_4^- + CH_3OOH + H^+$$

A small concentration of methanol was formed as well; the higher the concentration of hydrogen peroxide, the lower the yield of methanol. In methylene chloride and THF at higher energies, with monochromatic light between 365 and 248 nm, $^3O_2$ was formed.[20] The conclusion was reached that the coupling of initially formed oxygen atoms, ^3O, was responsible.

Peroxide activation by MTO: reaction kinetics

Hydrogen peroxide will oxidize certain electron-rich substrates, but the reactions are generally rather slow without the MTO catalyst. In a few cases both the uncatalyzed and the MTO-catalyzed rate constants have been determined. The catalytic enhancements for MTO often amount to a factor of 10^5–10^6. Many other substrates, ones that seem not to react with hydrogen peroxide, do so quite successfully once MTO has been added. In this section certain aspects of the chemical kinetics will be presented, and the subject of the chemical mechanisms will be taken up in the next section.

The reaction scheme is simply described: **A** and **B** separately react with substrate **X**, converting it to the product **XO**. In so doing, **A** is converted to MTO and **B** to **A**. The respective rate constants are designated k_3 for **A** and k_4 for **B**. These steps couple with those in Scheme 1, which enter as kinetic or sometimes equilibrium reactions depending on the various values pertaining to a given substrate and solvent, and to the concentrations employed. The analysis of the kinetic data has many features in common with that for enzyme-catalyzed reactions and the Michaelis–Menten formalism. This approximation has been termed the 'improved steady-state' method.[21] To illustrate the difference between it and the ordinary steady-state treatment, we show a simple case, the conversion of starting material S to product P *via* intermediate I. The expressions for the reaction rates are:

Reaction Scheme

$$S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} I \xrightarrow{k_2} P$$

Steady-state

$$v = \frac{d[P]}{dt} = \frac{k_1k_2[S]}{k_{-1} + k_2}$$

Improved steady-state

$$v = \frac{d[P]}{dt} = \frac{k_1k_2[S]}{k_{-1} + k_2 + k_1[S]}$$

The improved steady-state mathematics affords the advantage that the intermediate need not be maintained at a small fraction of the concentration of S, as it must in the ss formalism. That E·S may attain a concentration comparable to E is a vital feature of the Michaelis–Menten equation in that it provides a model to account for the experimentally observed phenomenon that the reaction rates rise initially with [S] and then tend toward a plateau. This effect, known as saturation kinetics, is not found in the ss analysis.[22]

For MTO it is also not valid to adopt the ss model in that it would require that [**A**] and [**B**] always << [MTO]. The improved ss treatment gives this result:

$$-\frac{d[X]}{dt}=\frac{k_1k_3[\mathrm{Re}]_T[H_2O_2][X]+\dfrac{k_1k_2k_4[\mathrm{Re}]_T[X][H_2O_2]^2}{k_4[X]+k_{-2}}}{k_{-1}+k_3[X]+k_1[H_2O_2]+\dfrac{k_1k_2[H_2O_2]^2}{k_4[X]+k_{-2}}}$$

This equation appears to be more formidable than it really is. With the rate constants k_1, k_{-1}, k_2, and k_{-2} known from studies of the MTO–H_2O_2 reactions in the absence of substrate, only k_3 and k_4 remain as unknowns.

Under certain conditions this form simplifies. The parameters involved may be ones the experimenter can control to some extent, such as concentrations, but the parameter list also includes rate constants that will, of course, differ relatively among substrates, often by a large amount. Thus the conditions needed for simplification need to be scrutinized individually for different substrates and concentration ranges. Two of the useful simplifications are these:

(a) at the relatively low concentrations of hydrogen peroxide, such that **B** is not significant,

$$-\frac{d[X]}{dt}=\frac{k_1k_3[\mathrm{Re}]_T[H_2O_2][X]}{k_{-1}+k_3[X]+k_1[H_2O_2]}$$

This form has been useful at times mostly because **A** and **B** usually (but not always) are quite comparable in their reactivity (*i.e.*, k_3 and k_4 are of the same magnitude, as illustrated later).

(b) at quite high peroxide concentrations, where **B** is the only significant form,

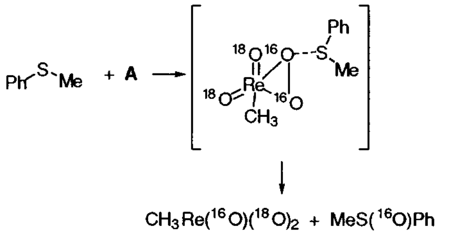
$$-\frac{d[X]}{dt}=k_4[X][\mathrm{Re}]_T$$

This approach has proved useful when the parameters permit its application. One test, but not the only one, is that the reaction rates are peroxide-independent when this form applies.

This is an outline of the kinetics analysis. The reader is referred to the referenced publications for further detail.[23] In the balance of this review, rate constants will be given without further explanation as to their origin.

Peroxide activation by MTO: isotopic tracer

Isotopic labeling was carried out to define the source of the oxygen atom transferred to the substrate. It consisted of the use of MTO and water labeled with oxygen-18 (recall that this pair rapidly exchanges) and hydrogen peroxide labeled with oxygen-16. GC–MS determinations showed that only PhS(^{16}O)Me was formed, implying that the catalytic reaction transfers a peroxo oxygen to the substrate. As **A** (shown here) or **B** reacts, we have Scheme 4.



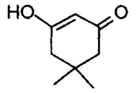
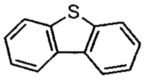
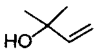
Scheme 4

As the cycle repeats, $CH_3Re(^{16}O)(^{18}O)_2$ continues to revert to $CH_3Re(^{18}O)_3$ by exchange with water. The repeated recycling with $H_2{}^{16,16}O_2$ generates **A** and **B** with $^{16,16}O_2{}^{2-}$ groups that then transfer oxygen-16. The necessary control experiments were carried out to verify that this was a valid experiment.[23]

Peroxide activation by MTO: reactivity of different substrates

In order to present and discuss the structure–reactivity relationships, it is desirable first to examine the relative magnitudes of k_3 and k_4. Values of these rate constants for selected substrates are presented in Table 3. These are by no means all of the data, but they are representative of the substrates. Save for the special case of the allylic alcohol to which we return in a later section, the numerical values presented make the case quite emphatically: k_3 and k_4 are of the same magnitude. Sometimes the one is a little larger, sometimes the other. A factor of three in either direction encompasses all of the variations. The similarity of the values for a given substrate is particularly striking in that the rate constants themselves span a factor of 10^8. The proof we have advanced for the comparable reactivity has been verified repeatedly; it rests on the quantitative interpretation of the kinetic effects of the concentrations of hydrogen peroxide and substrate. This demonstration has included epoxidation reactions.[24] This method has been commented on and accepted by others.[25] Despite this, certain statements and diagrams persist in identifying **A** as inactive and **B** as the only active form of the catalyst; see, for example, Fig. 1 in a 1996 reference.[20]

Table 3 Comparisons of the rate constants k_3 for **A** and k_4 for **B** in their reactions with different substrates

Substrate	k_3/L mol^{-1} s^{-1} ^{a}	k_4/k_3 ^{a}	Ref.
PhSMe	2.65×10^3	0.36	23
Ph_2S	1.18×10^2	0.27	23
PPh_3	7.3×10^5	3.0	57
$P(C_6F_5)_3$	1.30×10^3	2.7	57
trans-PhCH=CHOMe	14.2	0.90	24
trans-PhCH=CHMe	0.51	0.43	24
Cl^-	5.6×10^{-2}	2.3	12
Br^-	3.5×10^2	0.49	42
 HO O	0.19	0.58	58
 S	10.2	2.1	59
 HO	$k_3 \approx 0$ $k_4 = 7.6 \times 10^{-3}$	>>1	28

^{a} The solvent is 1 : 1 acetonitrile–water at pH 1 except for the halide ions in aqueous solution at pH 0 and the allylic alcohol where 4 : 1 acetonitrile–water was used.

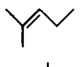
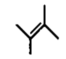
The inductive effect of substituents within a family of related substrates allows one to probe the electron demand in the transition state. Several such results are summarized in Table 4. In every case, the rate increases with electron-donating substituents on an aryl group and *vice versa*. These effects are regular, but mild. The four reactions in the series have Hammett reaction constants in the range −0.63 to −1.19. Each of them displays the trend that electron-donating substituents increase the rate of reaction with **A**, and *vice versa*. In keeping with that, it is instructive to examine the kinetic effects of substituting methyl groups on the double bond of aliphatic alkenes. Table 5 presents a subset of the data, which clearly show that the more alkyl groups on the double bond, the greater the reaction rate. Because of the substituent effects, and supported by the isotopic labeling, we propose a transition state for this reaction in which the nucleophilic reagent **X** (including electron-rich alkenes) attacks a peroxo-oxygen of the rhenium catalyst.

Table 4 Effect of substituents on the aryl group of different substrates on the relative rate constants (k_3/k_{3H}) for the reactions with **A**

Substituent:	4-MeO	4-Me	3-Me	H	4-F	4-Cl	4-Br	4-CF_3	4-NH_3^+	4-NO_2
σ:	−0.27	−0.17	−0.069	0	0.06	0.23	0.23	0.54	0.73	0.78
Substrate										
$ArNMe_2$		1.33		1.00 [a]	0.69		0.47			0.10
ArSMe		1.6		1.00 [b]		0.61			0.22	
Ar_3P		1.29		1.00 [c]		0.66		0.47		
$ArCH{=}CH_2$	5.45	1.59	1.09	1.00 [d]						

[a] Relative to k_{3H} = 18.4 L mol^{-1} s^{-1} at 25.0 °C in methanol; $\rho = -1.19$.[60] [b] Relative to $k_{3H} = 2.65 \times 10^3$ L mol^{-1} s^{-1} in 1:1 acetonitrile–water at pH 1 and 25.0 °C; $\rho = -0.98$.[23] [c] Relative to $k_{3H} = 7.3 \times 10^5$ L mol^{-1} s^{-1} in 1:1 acetonitrile–water at pH 1 and 25.0 °C; $\rho = -0.63$.[57] [d] Relative to $k_{3H} = 1.1 \times 10^{-1}$ L mol^{-1} s^{-1} in 1:1 acetonitrile–water at pH 1 and 25.0 °C; $\rho = -0.93$.[24]

Table 5 Kinetic effects on k_4/L mol^{-1} s^{-1} at 298 K in two solvents for epoxidation reactions arising from the substitution of alkyl groups on the double bond.[61]

Structural formula	No. Alkyl groups	MeOD	CH_3CN-H_2O
	1	0.013	0.098
	2	0.048	0.25
	3	0.26	3.92
	4	1.33	8.93

In keeping with those results, it is instructive to examine the k_3 values themselves for different types of nucleophilic reagents **X**. The most reactive group are the phosphines, the least the alkenes. A display of these values is presented in Fig. 2. The rate constants span eight orders of magnitude, roughly 10^6–10^{-2} L mol^{-1} s^{-1}. An inspection of the entries in this figure confirm that this is a general trend.

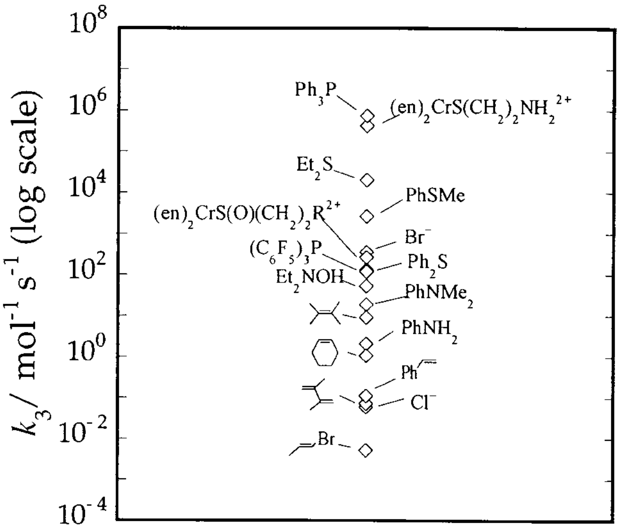
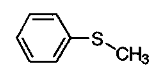
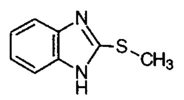


Fig. 2 A display of selected compounds showing the value of each rate constant k_3 at 298 K. Note that the reactivity spans a factor of ≈ 10^8; note that the axis has a logarithmic scale.

A further manifestation of these effects is seen in a different variation of the substituent effects. Substitution of electronegative substituents into the molecule greatly reduces its reactivity. For example, compare these rate constants:[23]



$k_3 = 2.65 \times 10^3$
L mol^{-1} s^{-1}

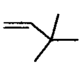


$k_3 = 4 \times 10^{-1}$
L mol^{-1} s^{-1}

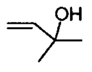
When successive oxidation steps are found, as with this conversion: $R_2S \rightarrow R_2SO \rightarrow R_2SO_2$ for which the successive rate constants are in an approximate 35:1 ratio.[26] Likewise, once a 1,3-diene has been converted to the epoxide (preferentially, at the more alkylated double bond) there is little tendency to form the di-epoxide.

From these various approaches, it is possible to argue that the role of MTO is to polarize the normally nucleophilic peroxide anion to the extent that it can itself be attacked by nucleophiles. Other high-valent metal complexes from such elements as Mo(VI), W(VI), Os(VIII), Cr(VI), and V(V), often oxo species themselves and possessed of a d^0 electron configuration, can activate peroxide by a similar mechanism.[27]

This brings us to the rather special case of allylic alcohols, represented by the last entry to Table 3. A comparison of these rate constants at first suggests the same effect, save that the electronegative hydroxy group gives rise to a remarkably small kinetic deceleration by comparison with other examples. But the allylic alcohols constitute the seemingly unique instance (see Table 3) in which k_3 is negligible compared with k_4, implying a special mechanism open only to catalyst **B**.[28]

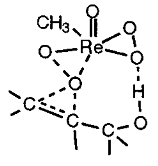


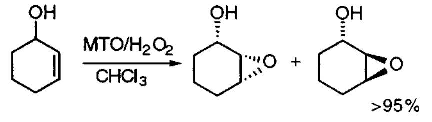
$k_3 = 8.7 \times 10^{-3}$
L mol^{-1} s^{-1}

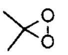


$k_4 = 7.6 \times 10^{-3}$
L mol^{-1} s^{-1}

We suggest that these findings manifest the overriding importance of hydrogen bonding in this transition state, a point of view reinforced by data on stereoselectivity in the same system.[28b] We have concluded that the transition state features hydrogen bonding to a *different* peroxo group than that transferring the oxygen atom. This transition state is depicted below, along with one reaction showing that diasteroselectivity can consequently be realized with allyl alcohols.





Peroxide activation by MTO: comparisons to dimethyldioxirane 

Aside from the obvious structural analogy between **A**, **B**, and DMDO, the similarities in reactivity are notable. To cite just a few points, DMDO reacts *stoichiometrically* with many of the same substrates that **A** and **B** do, such as *N*,*N*-dimethylanilines,[29] alkenes,[30,31] and thioethers.[32] Beyond that, the correlation between the rate constant k_4 for **B** and that for DMDO is striking. Fig. 3 presents on a log–log scale the one set of values against another. The slopes of these lines are 0.84 for aliphatic alkenes and 1.18 for styrenes. Were it not for this, no reason would arise to question the previously given explanation that catalysis by MTO arises from the ability of Re(VII) to polarize the coordinated peroxide anion. But surely the saturated carbon center of DMDO is incapable of activating its peroxide group in the same fashion. The remarkable correlations between the MTO and DMDO reactions require that attributes common to both reagents be sought. Features such as bond and angle strain are, qualitatively, common to both groups of peroxides. The final accounting for the electronic structures remains to be made, and speculation at this point is unnecessary.

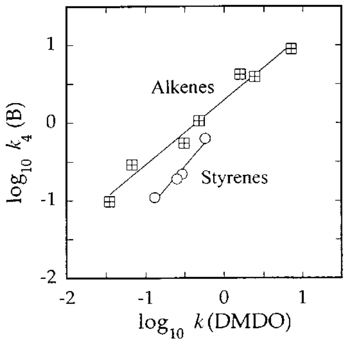


Fig. 3 The rate constants for the epoxidation of styrenes and of aliphatic alkenes by two reagents, dimethyldioxirane and the diperoxorhenium complex **B**, are shown as a linear free-energy correlation. The slopes of the lines are 1.18 ($R = 0.982$) and 0.84 ($R = 0.987$).

Peroxide activation by MTO: stabilization of epoxides

Some of the reactions that can follow epoxide formation are deleterious, the most notorious of which is loss of epoxides to acid-catalyzed ring-opening. Generally, but not universally, this is considered an undesirable event. The addition of acid to the solutions, in an effort to stabilize the catalyst, is not allowed. The acidity of the water molecule coordinated to **B**, which has been given as $pK_A = 3.8$,[9] provides a built-in method for loss of the epoxide. If one attempts to circumvent this effect by the use of a Brønsted base or a buffer, then the inherent base-sensitivity of **B** (especially) immediately prevails, and the catalytic reaction ceases.[10,17,18] A Lewis base such as pyridine serves to stabilize the catalyst against decomposition at the same time eliminating the acidity of the medium and thus preserving the epoxide.[33,34] Representative values of the equilibrium constants (L mol^{-1}) at 298 K for binding Lewis bases to MTO are as shown here for nitrogen bases in acetonitrile[6] and for the phosphorus derivatives in benzene.[35]

(p-Tol)$_3$P	2.0
3-NCC$_5$H$_4$N	7.2
(p-Tol)$_3$PO	5.3×10^1
C$_5$H$_5$N	2.0×10^2
C$_5$H$_5$NO	2.1×10^2
4-MeC$_5$H$_4$N	7.3×10^2

Coordination of a Lewis base to MTO evidently prevents its being attacked by HOO$^-$, which is the most serious pathway for its loss. [10] The coordination is not so tight, however, as to preclude the necessary formation of the peroxorhenium compounds. A further helpful effect of the Lewis base, if it is also a Brønsted base, is to accelerate the conversion of MTO to **A** and to **B**, which greatly reduces the time the system needs to maintain its integrity. If the epoxide-stabilizing reagent is, for example, a pyridine, then it will be oxidized concomitantly. For example, for α-methyl styrene in acetonitrile at 296 K, the competing reaction rates are: [6]

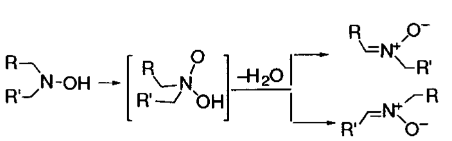
$$v_i^{\text{Py-NO}} = k[\text{MTO}]_0[\text{Py}]_0 \qquad k = 0.42 \pm 0.01 \text{ L mol}^{-1}\text{ s}^{-1}$$
$$v_i^{\text{Epox}} = k[\text{MTO}]_0[\alpha\text{-MeSty}]_0 \qquad k = 0.22 \pm 0.04 \text{ L mol}^{-1}\text{ s}^{-1}$$

The development of methods to prevent catalyst deactivation continues to be an active area, owing to the importance of transforming alkenes to epoxides, and the last work still remains incomplete.

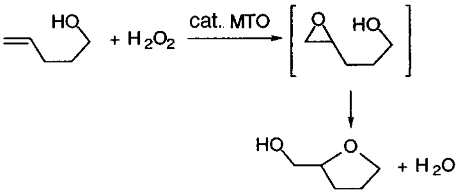
Peroxide activation by MTO: reactions with steps subsequent to O-atom addition

Certain other reactions that follow oxygen-atom transfer from **A** or **B** to the substrate are an inherent part of the process. Here are some examples:

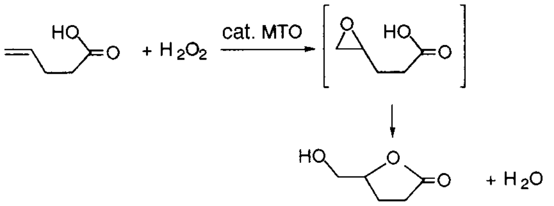
Secondary hydroxylamines yield an intermediate that is converted to the final nitrone product in a rapid elimination reaction following the first step:



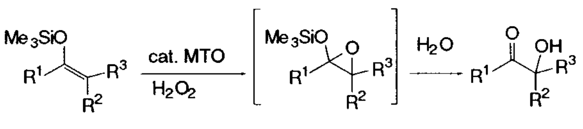
4-Hydroxyalkenes, following epoxide formation undergo cyclization to form substituted tetrahydrofurans;[36] with related molecules the cyclization rates are seen to fall in the expected order favoring these ring sizes 5 > > 6 > 3 > 7 > 8:[37]



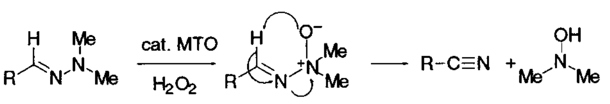
δ,γ-Unsaturated hydroxycarboxlyic acids, again following epoxidation, yield hydroxy lactones:[38]



Silyl enol ethers provide a convenient an efficient route to α-hydroxy ketones by way of an epoxide; the product yields are generally ⩾95%:[39]



Particularly useful is the MTO-catalyzed oxidation of *N*,*N*-dimethylhydrazones derived from aldehydes which produces nitriles in > 90% yield.[40] This reaction begins in the usual manner, with the transfer of an oxygen atom from **A** or **B** to the more basic (amine) nitrogen. Following that, a Cope-type elimination reaction[41] yields the nitrile and dimethylhydroxylamine. The latter is independently oxidized to the nitrone, $CH_3N(=CH_2)O$, as described previously.

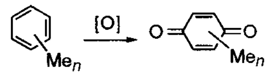


During the course of these studies we have developed a particular solvent formulation that preserves the catalyst quite well. It consists of a mixture of acetonitrile, acetic acid, and pyridine (94.5 : 5 : 0.5). The role of pyridine is to accelerate the cycling of MTO and its peroxides, as in Scheme 1, with acetic acid preventing the mixture from becoming so basic that the catalyst is irreversibly deactivated.

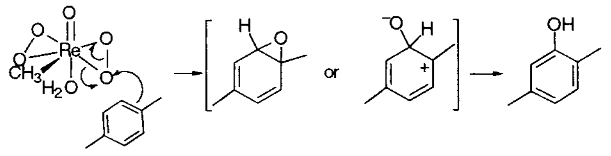
Peroxide activation by MTO: reactions involving the breaking of C–H bonds

In every one of the reactions presented to this point, an oxygen atom was transferred from a peroxorhenium complex to an electron-rich atom or center. In contrast, arenes and secondary alcohols are oxidized by a different mechanism.

MTO–hydrogen peroxide converts methyl arenes to quinones, yielding preferentially the *para* isomer:

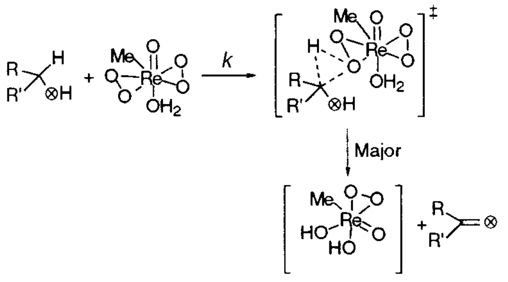


These tend to be sluggish reactions. A higher level of MTO is employed, typically 10% of the arene, and a temperature of 57 °C in glacial acetic. The yields are high, but the conversions not, since the catalyst is gradually deactivated. *o*-, *m*-, and *p*-Dimethylbenenes gave the quinones in 12–15% conversion after 3.5 h; 1,2,4-trimethylbenzene gave 75% conversion in 4 h, along with 33% of the hydroquinone. The data are scant, but a plausible mechanism for the first and most difficult step, phenol formation, is as given in Scheme 5.



Scheme 5

The oxidation of secondary alcohols by hydrogen peroxide is also catalyzed by MTO; again the reaction faces a substantial kinetic barrier. Representative rate constants at 298 K for the reaction between **B** and the alcohols are 1.02×10^{-4} L mol^{-1} s^{-1} for 4-methyl-α-methylbenzyl alcohol and 4.9×10^{-5} L mol^{-1} s^{-1} for 4-chloro-α-methylbenzyl alcohol. There was a kinetic isotope effect of 3.2 for the α C–H bond of 1-phenylethanol (1,2,2,2-D_4). When the same alcohol was labeled with ^{18}O, 80% of the oxygen was retained in the ketone. Tests for the possible intervention of a free radical intermediate were carried out; the evidence was entirely negative. A mechanism featuring hydride abstraction is proposed, the first time for the H_2O_2/MTO system (Scheme 6)



Scheme 6

Peroxide activation by MTO: bromide ions as co-catalyst

The ability of the MTO/H_2O_2 system to oxidize Br^- to BrO^- (ref. 42) (see Table 3) affords a means of developing a different oxidizing species in solution, one capable of adopting a different mechanism. Actually, the useful species is Br_2, not BrO^-/HOBr, since the reaction between HOBr and Br^- is exceptionally rapid.[43] This approach offers two advantages: it opens a new mechanism in place of oxygen-atom transfer and accomplishes what amounts to a bromine reaction without using any substantial concentration of that element, obviating waste disposal costs for bromide solutions.

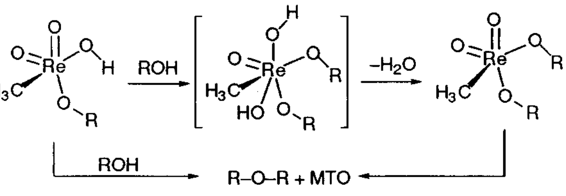
Sec-phenylethanol, for example, is oxidized by MTO/H_2O_2 42-times more rapidly when a catalytic concentration of bromide is present (1.1 mM HBr and 200 mM alcohol) as compared to the same reaction in its absence. The reason is that Br_2 carries out hydride abstraction, which **A** and **B** do not.[44] The sequence is the following:

$$Br^- \xrightarrow{A/B} BrO^- \xrightarrow{Br^-,\, H^+} Br_2 \xrightarrow{R_2CHOH} 2Br^- + R_2CO$$

MTO-catalyzed reactions not involving hydrogen peroxide

Rearrangement reactions of a single substrate

Alcohols to ethers. MTO is the first transition metal complex in trace quantity to catalyze the direct formation of ethers from alcohols. These reactions occur in various aprotic solvents (benzene, toluene, dichloromethane, acetone, *etc.*) and in the alcohols themselves. Aromatic alcohols react best; for example benzyl alcohol is converted in 30% yield to the ether; the conversion is 36%, the balance being comprised of 3% PhCHO and 3% $PhCH_3$. This required 2 d at room temperature; after that time none of the catalyst remained. The intermediates characterized and inferred for the reaction of MTO with hydrogen peroxide and for its exchange with water indicate the following mechanism (Scheme 7) from which the ether can be formed by reductive elimination.[45]

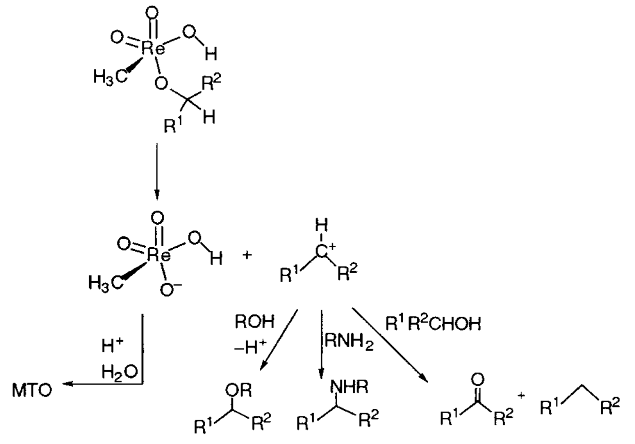


Scheme 7

We noted that (a) no reaction occurred with alcohols containing an electron-withdrawing group at the *para* position such as NO_2, Br, and Cl, (b) an olefin was formed from 2,2-dimethyl-1-phenylpropan-1-ol, and (c) alcohols underwent disproportionation catalyzed by MTO. It seems that these reactions occur through a carbocation intermediate (Scheme 8).

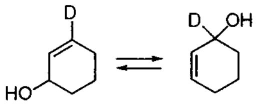
This scheme further reports that MTO catalyzes the reactions between amines, aryl and alkyl, and alcohols, leading to amine products.[45]

1,3-Transposition of allylic alcohols.[46] MTO catalyzes the approach to equilibrium in reactions such as those shown in Table 6. Yields of the isomerized alcohol are often less than

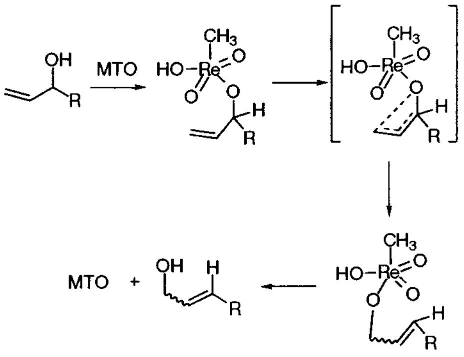


Scheme 8

100%, due to the reverse reaction. This equilibrium was confirmed by the use of deuterium labeling; the isotopomers of 2-cyclohexen-1-ol are interconverted by this degenerate reaction:

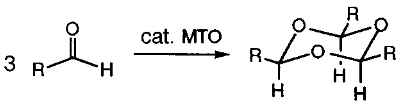


The equilibrium constant was found to be 1.20 ± 0.02 in benzene at ~23 °C, demonstrating an appreciable equilibrium isotope effect. The reaction is sharply inhibited by traces of water. The use of $CH_3Re(^{18}O)_3$ resulted in no incorporation of oxygen-18 into the alcohol product. Because of that we must discard a mechanism related to that presented for ether formation. A mechanism to account for the various lines of evidence, including the inhibition of water that competes with the allyl alcohol and leads to the dead-end species $CH_3Re(O)_2(OH)_2$, is depicted in Scheme 9.



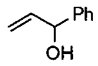
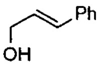
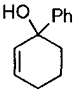
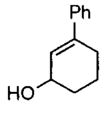
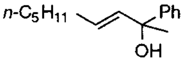
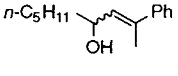
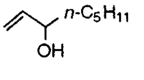
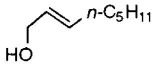
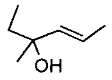
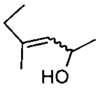
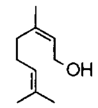
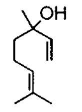
Scheme 9

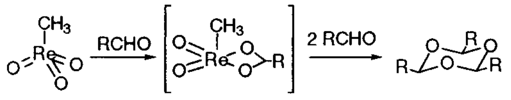
MTO-catalyzed cyclotrimerization of aldehydes. This reaction yields 1,3,5-trioxanes:



This reaction was carried out successfully for nineteen anhydrous aldehydes.[47] The stereochemistry was established by NMR and by X-ray crystallography in one instance; oxygen-18 labeling of MTO showed that just one of the three oxygen atoms in the product derived from MTO. Yields are generally high, >90%. Although many trioxanes can be isolated at room temperature, several of the reactions need to be carried out at −30 °C, lest the products revert to the parent aldehyde. Indeed, all of the trimeric products revert to the aldehyde thermally. The mechanism has not been established, but the structures shown for several of the reactions are suggestive of a sequence in which an adduct with four-membered ring, derived from the interaction of MTO and one aldehyde, is further homologated (Scheme 10).

Table 6 Equilibrium reactions for the 1,3-transposition of allylic alcohols.[62]

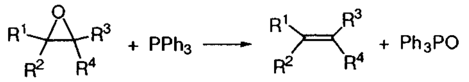
Substrate	Product	Time	% Product at equilibrium
		5 d	63
		10 h	98
		3 d	52
		1 d	33
		2 d	30
		2.5 d	86



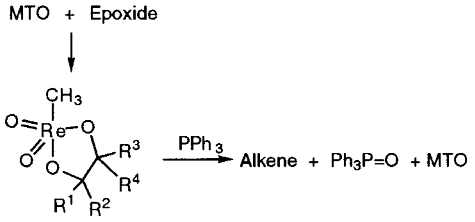
Scheme 10

Atom transfer reactions not involving hydrogen peroxide

The reactions referred to in this section are of the general form YO + X → Y + XO. One example is the reaction between epoxides and triphenylphosphine. Without MTO no reaction occurs despite its spontaneity ($\Delta G^\circ \approx -230$ kJ mol^{-1}). The catalyst causes this general transformation:[48]



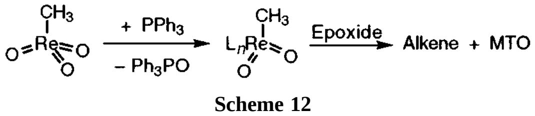
The reaction gives high yields ($\geq 79\%$) in benzene at room temperature, seems to be quite general, and proceeds with preservation of the relative stereochemistry about the C–C bond of the epoxide. Two distinctly different, plausible mechanisms can be suggested from other results. In the first, the epoxide and MTO form a dialkoxyl (glycolato) rhenium complex. This reaction has been well established independently.[49] Following that the phosphine abstracts an oxygen, leading to the products and the regeneration of the catalyst (Scheme 11).



Scheme 11

A certain level of support for this scheme is afforded by the determination that the independently-prepared dialkoxylrhenium complex reacts with triphenylphosphine in the required manner.

The second plausible explanation starts with the reaction between triphenylphosphine and MTO. Methyldioxorhenium(V) is formed; the Re(V) is coordinated by phosphine (L) to an extent dependent on their concentrations; a compound in which Re(VII) is present in the molecular unit has been characterized: $CH_3Re(O)_2L_2 \cdot MTO$.[50] This species is known to abstract an oxygen atom from substrates that have a bond to oxygen weaker than that present in MTO, 465 kJ for MTO(aq) = CH_3ReO_2(aq) + O(aq).[51] Based on these ideas, this alternative reaction scheme can be proposed, in which L represents phosphines or other ligands coordinated to Re(V) (Scheme 12).



Scheme 12

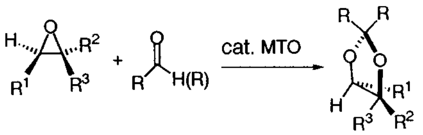
It would be premature at this stage to decide between the two. Several related transformations have also been found. Thus MTO is an effective catalyst, when accompanied by triphenylphosphine, for converting tertiary amine oxides [*e.g.*, $ArN(O)Me_2$ and C_5H_5NO] to amines, triphenylphosphine oxide being formed concomitantly. These reactions were studied in benzene, but there is no reason to believe other solvents would not serve as well.[48]

Sulfoxides are converted into sulfides in high yield (65–77%) by the same procedure. Reactions have been carried out in benzene at room temperature for aryl and alkyl sulfoxides.[48] On the other hand, attempts to excise an oxygen atom from a sulfone have failed. Among other factors, one notes that sulfoxides have an S–O bond enthalpy of ≈ 330 kJ mol^{-1}, whereas for sulfones this is ≈ 440 kJ mol^{-1}.

The bond enthalpies along the series Ar_3EO (E = P, As, Sb) are such that oxygen is preferentially bound to phosphorus. Uncatalyzed oxygen exchange is not significant. With MTO catalytic reactions occur, converting ArAs(Sb)O and Ar_3P to ArAs(Sb) and Ar_3PO. The involvement of the Re(V) complex, CH_3ReO_2 or its ligated derivatives, seems likely.

Coupling reactions using the MTO catalytic template

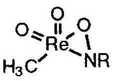
Ketones and aldehydes do not react with epoxides in the absence of MTO. With the MTO catalyst, 1,3-dioxolanes are formed, often but not invariably in high yields from reactions carried out for two days in chloroform.[52] The net equation is shown below.



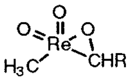
The reaction proceeds in two steps: in the first, as described in the preceding section, a dialkoxylrhenium complex is formed, and then attacked by the carbonyl compound. Each step proceeds with inversion of configuration, the resultant being that the dioxolane retains the structure of the parent epoxide.

Carbene and nitrene transfer reactions

As one examines the structures of **A** and **B**, it is natural to inquire whether one (both?) of the oxygen atoms of the coordinated peroxide might be replaced with isoelectronic nitrene (NR) or carbene (CR_2) equivalents. Taking **A** for example, might the intermediates $\mathbf{A_N}$ or $\mathbf{A_C}$ be made? And, if successful, would these species transfer a group (presumably the less electronegative nitrene or carbene fragment) to a suitable substrate? Attempts to prepare $\mathbf{A_N}$ by the reactions of MTO with hydroxylamines, this being the example from isoelectronic substitutions in Scheme 1, have met with no success. Not only that, but such mixtures showed no evidence of catalytic activity toward substrates that react with MTO/H_2O_2.



$\mathbf{A_N}$



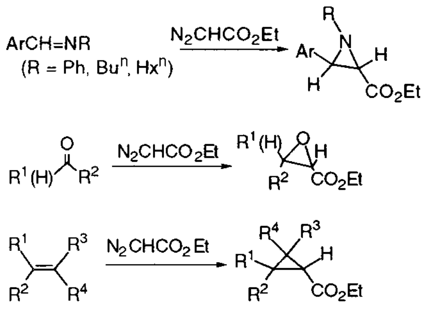
$\mathbf{A_C}$

We consequently turned to organic azides and diazoalkanes as sources of the putative NR and CR_2 groups for incorporation into an active form of MTO. A certain level of success has been realized, as represented by the subsequent MTO-catalyzed conversions, when ethyl diazoacetate was used. Aryl imines were transformed to aziridines, carbonyl compounds to epoxides, and alkenes to epoxides (Scheme 13)[53,54]

The model in terms of an $\mathbf{A_C}$-like carbene donor holds some appeal, but attempts to identify such species have not been successful. It may be that MTO releases a free carbene to carry out this chemistry, an idea that finds credence in the sensitivity of these reactions to moisture, a feature not found in most MTO-catalyzed reactions.

In summary

The catalyst methyltrioxorhenium has proved its abilities and its versatility. It seems assured of a useful place in the repertoire of



Scheme 13

catalysts that activate hydrogen peroxide and also provide other pathways for oxygen atom transfer. The fact that MTO is soluble in different media, and retains its catalytic activity therein, enhances its usefulness. Other substances act as catalysts for peroxide reactions, among them molybdates, tungstates, and other Mo(VI) and W(VI) complexes.[27] But MTO, advantageously, does not engage in any oligomerization or pH-dependent equilibria, unlike molybdate and tungstate, greatly simplifying the characterization of its reaction mechanisms.

Acknowledgements

I am grateful to my coworkers in this area, whose names are given in the referenced publications. Support is acknowledged from the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-7405-Eng-82 for research concerning the MTO catalyst, particularly selective oxidation reactions, and the development and study of catalytic organic reactions; to the National Science Foundation (CHE–9007283) for support of research in the area of O-atom transfer, and to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of research concerning organic transformations.

References

1 C. C. Romão, F. E. Kühn and W. A. Herrmann, *Chem. Rev.*, 1997, **97**, 3197.
2 W. A. Herrmann, P. Kiprof, K. Rydpal, J. Tremmel, R. Blom, R. Alberto, J. Behm, R. W. Albach, H. Bock, B. Solouki, J. Mink, D. Lichtenberger and N. E. Gruhn, *J. Am. Chem. Soc.*, 1991, **113**, 6527.
3 W. A. Herrmann, J. G. Kuchler, G. Weichselbaumer, E. Herdtweck and P. Kiprof, *J. Organomet. Chem.*, 1989, **372**, 351.
4 J. Takacs, M. R. Cook, P. Kiprof, J. G. Kuchler and W. A. Herrmann, *Organometallics*, 1991, **10**, 316.
5 W. A. Herrmann, J. G. Kuchler, P. Kiprof and J. Riede, *J. Organomet. Chem.*, 1990, **395**, 55.
6 W.-D. Wang and J. H. Espenson, *J. Am. Chem. Soc.*, 1998, **120**, 11335.
7 R. S. Tobias, *Organomet. Chem. Rev.*, 1966, **1**, 93–129.
8 G. Strukul, R. Ros and R. A. Michelin, *Inorg. Chem.*, 1982, **21**, 495.
9 W. A. Herrmann, R. W. Fischer, W. Scherer and M. U. Rauch, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1157.
10 M. Abu-Omar, P. J. Hansen and J. H. Espenson, *J. Am. Chem. Soc.*, 1996, **118**, 4966.
11 Dr P. D. Metelski is acknowledged for preparing this experiment and display.
12 P. J. Hansen and J. H. Espenson, *Inorg. Chem.*, 1995, **34**, 5839.
13 W.-D. Wang and J. H. Espenson, *Inorg. Chem.*, 1997, **36**, 5069.
14 O. Pestovsky, R. van Eldik, P. Huston and J. H. Espenson, *J. Chem. Soc., Dalton Trans.*, 1995, 133.
15 H. Taube, *Rec. Chem. Prog.*, 1956, **17**, 277.
16 K. A. Brittingham and J. H. Espenson, *Inorg. Chem.*, in press.
17 G. Laurenczy, F. Lukács, R. Roulet, W. A. Herrmann and R. W. Fischer, *Organometallics*, 1996, **15**, 848.
18 J. H. Espenson, H. Tan, S. Mollah, R. S. Houk and R. D. Eager, *Inorg. Chem.*, 1998, **37**, 4621.
19 R. K. Murmann, *J. Phys. Chem.*, 1967, **71**, 974.
20 I. Hatzopulos, H.-D. Brauer, M. R. Geisberger and W. A. Herrmann, *J. Organomet. Chem.*, 1996, **520**, 201.
21 J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill Inc., New York, 2nd edn. 1995.
22 It is this author's opinion that certain disagreements about steady-state kinetics trace to the failure to make a clear distinction between ss and improved-ss treatments: see R. Breslow, *J. Chem. Educ.*, 1990, **67**, 228; D. B. Northrop, *J. Chem. Educ.*, 1993, **70**, 999; R. Breslow, *J. Chem. Educ.*, 1993, **70**, 999.
23 K. A. Vassell and J. H. Espenson, *Inorg. Chem.*, 1994, **33**, 5491.
24 A. Al-Ajlouni and J. H. Espenson, *J. Am. Chem. Soc.*, 1995, **117**, 9243.
25 K. P. Gable, *Adv. Organomet. Chem.*, 1997, **41**, 127.
26 D. W. Lahti and J. H. Espenson, unpublished results.
27 G. Strukul, *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic Publishers, Dordrecht, 1992.
28 (*a*) H. A. Riley and J. H. Espenson, *Inorg. Chem.*, in press; (*b*) W. Adam, A. Corna, A. Martinez, C. M. Mitchell, T. I. Ready, M. Renz and A. K. Smerz, *J. Mol. Catal. A*, 1997, **117**, 357.
29 P. C. Buxton, J. N. Ennis, B. A. Marples, V. Waddington and T. R. Boehlow, *J. Chem. Soc., Perkin Trans. 2*, 1998, 265.
30 A. L. Baumstark, E. Michelena-Baez, A. M. Navarro and H. D. Banks, *Heterocycl. Commun.*, 1997, **3**, 393.
31 A. L. Baumstark and L. Vasquez, *J. Org. Chem.*, 1988, **53**, 3437.
32 W. A. Schenk, J. Frixch, W. Adam and F. Prechtl, *Angew. Chem., Int. Ed. Engl.*, 1994, **106**, 1699.
33 J. Rudolph, K. L. Reddy, J. P. Chiang and K. B. Sharpless, *J. Am. Chem. Soc.*, 1997, **119**, 6189.
34 C. Coperet, H. Adolfsson and K. B. Sharpless, *Chem. Commun.*, 1997, 1565.
35 M. D. Eager and J. H. Espenson, unpublished information.
36 H. Tan and J. H. Espenson, submitted for publication.
37 F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry*, Plenum Press, Part A, 3rd edn., New York, 1990, p. 163.
38 H. Tan and J. H. Espenson, in press.
39 S. Stanković and J. H. Espenson, *J. Org. Chem.*, 1998, **63**, 4129.
40 S. Stanković and J. H. Espenson, *Chem. Commun.*, 1998, 1579.
41 R. Fernandez, C. Gasch, J. Lassaletta, J. Llera and J. Vazquez, *Tetrahedron Lett.*, 1993, **34**, 141.
42 J. H. Espenson, O. Pestovsky, P. Huston and S. Staudt, *J. Am. Chem. Soc.*, 1994, **116**, 2869.
43 A. Mohammed and H. A. Liebhafsky, *J. Am. Chem. Soc.*, 1934, **56**, 1680.
44 R. Stewart, in *Oxidation Mechanisms: Applications to Organic Chemistry*, W. A. Benjamin Inc., New York, 1964.
45 Z. Zhu and J. H. Espenson, *J. Org. Chem.*, 1996, **61**, 324.
46 J. Jacob, J. H. Espenson, J. H. Jensen and M. S. Gordon, *Organometallics,* 1998, **17**, 1835.
47 Z. Zhu and J. H. Espenson, *Synthesis* 1998, 417.
48 Z. Zhu and J. H. Espenson, *J. Mol. Catal.*, 1995, **103**, 87.
49 Z. Zhu, A. Al-Ajlouni and J. H. Espenson, *Inorg. Chem.*, 1996, **35**, 1408.
50 W. A. Herrmann, P. W. Roesky, M. Wang and W. Scherer, *Organometallics*, 1994, **13**, 4531.
51 M. M. Abu-Omar, E. H. Appleman and J. H. Espenson, *Inorg. Chem.*, 1996, **35**, 7751.
52 Z. Zhu, J. H. Espenson, *Organometallics*, 1997, **16**, 3658.
53 Z. Zhu and J. H. Espenson, *J. Org. Chem.*, 1995, **60**, 7090.
54 Z. Zhu and J. H. Espenson, *J. Am. Chem. Soc.*, 1996, **118**, 9901.
55 I. A. Begnan, J. Behm, M. R. Cook and W. A. Herrmann, *Inorg. Chem.*, 1991, **30**, 2165.
56 W. A. Herrmann, J. G. Kuchler, J. K. Felixberger, E. Herdtweck and W. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 394.
57 M. M. Abu-Omar and J. H. Espenson, *J. Am. Chem. Soc.*, 1995, **117**, 272.
58 M. M. Abu-Omar and J. H. Espenson, *Organometallics*, 1996, **15**, 3543.
59 K. N. Brown and J. H. Espenson, *Inorg. Chem.*, 1996, **35**, 7211.
60 Z. Zhu and J. H. Espenson, *J. Org. Chem.*, 1995, **60**, 1326.
61 A. Al-Ajlouni and J. H. Espenson, *J. Org. Chem.*, 1996, **61**, 3969.
62 J. Jacob, J. H. Espenson, J. H. Jensen and M. S. Gordon, *Organometallics*, 1998, **37**, 1835.

Paper 8/09222B