Journal of Molecular Catalysis, 36 (1986) 297 - 317

DUAL PATHWAYS FOR MANGANESE CATALYSIS OF OLEFIN OXIDATION WITH ALKYL HYDROPEROXIDES

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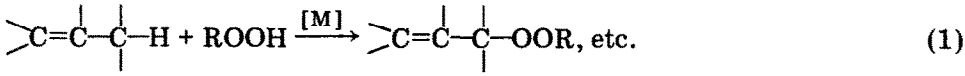
(Received September 18, 1985; accepted January 28, 1986)

Summary

The catalytic oxidation of various olefins with t-butyl hydroperoxide as the terminal oxidant is effectively carried out with cationic manganese(III) complexes of the salen ligand [*N*,*N*′-ethylenebis(salicylideneaminato)] in the presence of pyridine or imidazole as the cocatalyst. Two concurrent processes have been identified with cyclohexene as the olefinic substrate, which affords both cyclohexenyl t-butyl peroxide and cyclohexene oxide within 5 min at 25 °C in acetonitrile solutions. The pathway leading to cyclohexenyl t-butyl peroxide (allylic peroxidation) involves a free radical chain mechanism which is completely inhibited by the hindered phenol ionol. The presence of ionol allows various olefins to be cleanly epoxidized with t-butyl hydroperoxide–pyridine and catalytic amounts of salenMn^{III}. Olefin epoxidation occurs by an oxygen-rebound mechanism involving a reactive oxomanganese(V) species similar to that obtained with iodosylbenzene as the terminal oxidant. Both systems yield the same spectral transients with $\lambda_{max} \sim 550$ nm and show the same reactivity patterns of various olefins. Homolysis and heterolysis of an alkylperoxomanganese(III) intermediate is considered to be the common precursor responsible for the radical chain initiation of allylic peroxidation and for the reactive oxomanganese(V) species in olefin epoxidation.

Introduction

Alkyl hydroperoxides are useful as terminal oxidants in catalytic processes owing to their ready availability from various hydrocarbon autoxidations [1]. At least three distinctive pathways have been identified in metal catalysis of oxidation, particularly of olefinic substrates [2]. Allylic oxidation by alkyl hydroperoxides in eqn. 1 is one of the earliest examples discovered by Kharasch and coworkers [3, 4].



$$>C{=}C{-}\overset{|}{C}{-}H + ROOH \xrightarrow{[M]} >C{=}C{-}\overset{|}{C}{-}OOR, \text{ etc.} \qquad (1)$$

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Carbon–hydrogen activation in eqn. 1 involves a free radical chain mechanism in which the metal catalyst [M] serves in a redox capacity [5]. Metal complexes capable of readily undergoing 1-electron changes (*e.g.*, $Fe^{III} \rightleftharpoons Fe^{II}$, $Cu^{II} \rightleftharpoons Cu^{I}$, $Co^{III} \rightleftharpoons Co^{II}$, etc.) are among the most effective for this catalytic transformation.

Alkyl hydroperoxides also react with olefins to form epoxides, *i.e.*:

$$\text{>C=C<} + \text{ROOH} \xrightarrow{[M']} \text{>C(O)C<} + \text{ROH} \qquad (2)$$

which is the basis for the industrially important oxirane technology [6, 7]. Oxygen atom transfer in eqn. 2 is a concerted, stereospecific process in which the metal catalyst [M′] serves largely as a Lewis acid [8, 9]. Metal coordination is an important consideration for catalytic activity, and various complexes of Ti(IV), Mo(VI), V(V), etc. have been extensively utilized. Recently, a third process has been described for alkyl hydroperoxides, which is akin to the oxidations relevant to biochemical systems [10]. In the oxygen-rebound mechanism, the metal serves as a relay for the oxygen atom transfer from the terminal oxidant to the olefin substrate via an oxometal reactive intermediate [11, 12]. Indeed, such a formal two-electron change of the catalyst has been established in some chromium complexes undergoing catalytic interconversion in the form $Cr^{III} \rightleftharpoons O{=}Cr^{V}$ [13, 14]. Similar metal–oxometal couples have been proposed for the catalytic activity of iron and manganese systems [15 - 17].

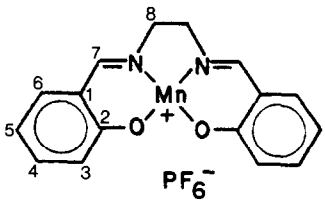
By and large, these three catalytic mechanisms have maintained their separate identity, but crossover from one pathway to another in a particular system must be considered. We report here an unambiguous example in which two pathways can be clearly delineated in the catalytic oxidation of olefins with alkyl hydroperoxide. In our studies, the catalyst consists of salen–manganese(III) which is used in conjunction with t-butyl hydroperoxide as the terminal oxidant.

Results

Synthesis of the salenmanganese(III) catalyst

Of the variety of salenmanganese(III) derivatives extant, all of them exist as neutral complexes in which the axial position is occupied by anions such as chloro, nitro, azido, etc. [18]*. However these complexes are usually insoluble in organic solvents, and they are catalytically inactive for our purposes. Accordingly, we prepared a cationic $salenMn^{III}$ salt of the non-coordinating anion hexafluorophosphate by electron transfer from $salenMn^{II}$ to the ferrocenium ion, *i.e.*

*salen = *N,N′*-ethylenebis(salicylideneaminato).

SalenMn + $Fc^+PF_6^-$ ⟶  + Fc (3)

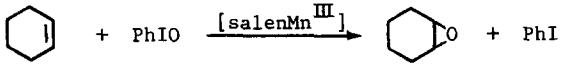
I

The salenMn^{III} salt I is readily soluble in acetonitrile. Similarly, the 5,5′-dimethoxy and 5,5′-dinitro analogs were prepared from the ferrocenium oxidation of the corresponding manganese(II) complexes.

Catalytic epoxidation of cyclohexene with iodosylbenzene

In order to test the catalytic efficacy of these salenMn^{III} cations as catalysts, we examined their effect on cyclohexene since it is a substrate which is particularly prone to allylic oxidation. Iodosylbenzene is a useful terminal oxidant for this purpose owing to its limited solubility in acetonitrile. Thus the course of oxidation is visually apparent from the gradual dissolution of iodosylbenzene. The latter coincides with the formation of iodobenzene which is readily analyzed by gas chromatography.

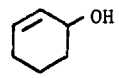
The addition of catalytic amounts of salenMn^{III} to a mixture of cyclohexene and iodosylbenzene in acetonitrile leads to complete reaction within 15 min at 25 °C. The results in Table 1 show that cyclohexene oxide is formed with unusually high selectivity, *i.e.*

 + PhIO $\xrightarrow{[salenMn^{III}]}$ + PhI (4)

Thus the competing oxidation to cyclohexenol is minor, and that leading to cyclohexenone is nonexistent. The yield of cyclohexene oxide based on the formation of the reduced iodobenzene in Table 1 is substantially improved

TABLE 1

SalenMn^{III} catalysis of cyclohexene oxidation with iodosylbenzene[a]

SalenMn^{III}	Products, 10^2 mmol (%)[b]	
		
5,5′-dimethoxy	5.3 (36)	< 0.1 (1)
unsubstituted	7.7 (53)	0.5 (3)
5,5′-dinitro	10.5 (67)	0.6 (4)

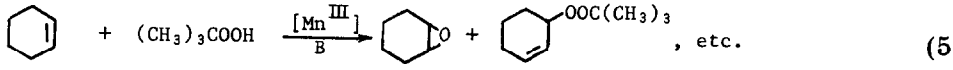
[a]In 5 ml of acetonitrile containing 0.30 mmol cyclohexene, 0.15 mmol iodosylbenzene and 0.011 mmol catalyst at 25 °C.
[b]Relative to iodobenzene formed.

by the use of 5,5′-dinitrosalenMn^{III} as the catalyst. Conversely, the presence of the electron-releasing 5-methoxy substituent in the salenMn^{III} catalyst lowers the epoxide yield. For this reason all of our subsequent catalytic studies were carried out with 5,5′-dinitrosalenMn^{III}, hereafter referred to simply as Mn^{III}.

We emphasize that olefin epoxidation under these conditions is all the more remarkable if one considers that the catalyzed reduction of iodosylbenzene to iodobenzene occurs at only slightly diminished rates in the absence of cyclohexene. (The nature of the background reaction is under separate study.)

Catalytic epoxidation of cyclohexene with t-butyl hydroperoxide

The addition of catalytic amounts of Mn^{III} to a mixture of cyclohexene and t-butyl hydroperoxide in acetonitrile had no visible effect for prolonged periods. However the addition of small amounts of pyridine bases or imidazole [B] to this solution led to a spontaneous reaction which was complete within 5 min at 25 °C. Analysis of the reaction mixture revealed the presence of cyclohexene oxide and a new product, cyclohexenyl t-butyl peroxide,

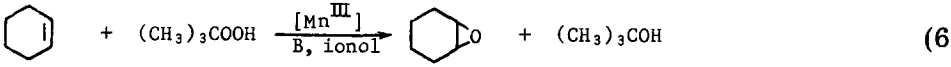


(5)

in the amounts listed in Table 2. Cyclohexenyl t-butyl peroxide was identified by comparison of its mass spectrum with that of an authentic sample [19].

The additives most effective to promote the catalytic oxidation are Brönsted bases such as imidazole, pyridine and methoxypyridine. However, the addition of the sterically hindered base 2,6-di-t-butylpyridine did not promote epoxidation. Furthermore, the presence of the donor ligand pyridine *N*-oxide (which is effective in metal coordination) was without effect in the catalytic oxidation.

The effect of radical inhibitors on the catalytic oxidation of cyclohexene with t-butyl hydroperoxide was tested with ionol (2,6-di-t-butyl-*p*-cresol), since it is known to be an effective hydrogen donor to alkylperoxy radicals [20]. The results in Table 3 show that the formation of the allylic substitution product is effectively quenched by ionol. The yield of cyclohexene oxide is singularly unaffected by the presence of ionol.



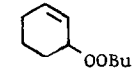
(6)

Minor amounts of cyclohexenol were also formed, but they were not analyzed quantitatively.

The generality of the catalytic oxidation with t-butyl hydroperoxide was examined with various olefins. Each olefin was converted to its epoxide,

TABLE 2

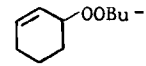
Effect of additives on the salenMn^{III} catalysis of cyclohexene oxidation with t-butyl hydroperoxide[a]

Additive	mmol (equiv)	 (mmol)[b]	Products (10^2 mmol) 	
none	— —	0.020	0	1.4[g]
imidazole	0.011 (1)	0.121	1.0	12.2
imidazole	0.044 (4)	0.191	5.1	11.8
imidazole	0.066 (6)	0.174	5.1	12.4
$CH_3COC_6H_4$imid[c]	0.066 (6)	0.162	1.7	15.0
p-MeOPy[d]	0.28 (25)	0.189	6.7	11.6
Py[e]	0.28 (25)	0.188	5.3	13.8
Py[e]	0.66 (60)	0.164	3.6	14.4
2,6-(t-Bu)$_2$Py	0.28 (25)	—	< 0.1	11.4[g]
PyO[f]	0.28 (25)		< 0.1	2.8[h]

[a]In 5 ml of acetonitrile containing 0.60 mmol cyclohexene, 0.30 mmol t-butyl hydroperoxide and 0.011 mmol 5,5′-dinitrosalenMn^{III} at 25 °C. Reaction time = 5 min, unless stated otherwise.
[b]Amount consumed (by difference) from analysis after specified reaction time.
[c]4′-(Imidazol-1-yl)acetophenone.
[d]*p*-Methoxypyridine.
[e]Pyridine.
[f]Pyridine *N*-oxide.
[g]Reaction time ≅ 30 min.
[h]Reaction time ≅ 10 min.

TABLE 3

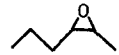
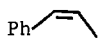
Effect of radical inhibitor on the catalytic oxidation of cyclohexene by t-butyl hydroperoxide[a]

Ionol[b] mmol (equiv)	 (mmol)[c]	Products (mmol) 	
none	0.191	0.051	0.118
0.022 (2)	0.157	0.054	0.134
0.33 (30)	0.101	0.053	0.040
0.55 (50)	0.075	0.052	0[d]

[a]In 5 ml of acetonitrile containing 0.60 mmol cyclohexene, 0.30 mmol t-butyl hydroperoxide, 0.011 mmol 5,5′-dinitrosalenMn^{III} and 0.044 mmol imidazole at 25 °C. Reaction time = 5 min.
[b]2,6-Di-t-butylcresol.
[c]Cyclohexene consumed (by difference) from analysis after reaction.
[d]Too small to detect < 0.001 mmol.

TABLE 4

Catalytic oxidation of olefins with t-butyl hydroperoxide[a]

Olefin	(mmol)[b]	Ionol[c] (mmol)	Product (10^2 mmol)			
			Epoxide		Other	
	(0.12)	0		(3.7)	t-BuOOBu-t	(0.4)
(*Z*) 	(0.19)	0	(*Z*)  (*E*)	(4.9) (d)	t-BuOOBu-t	(0.4)
(*Z*) 	(0.062)	0.55	(*Z*)  (*E*)	(4.9) (d)	t-BuOOBu-t	(0)
	(0.091)	0.55		(5.1)	t-BuOOBu-t $PhCH(CH_3)CHO$	(0) (1.5)
	(0.52)	0.55		(3.2)	$PhCH_2CHO$	(0.6)
(*Z*) 	(0.028)	0.55	(*Z*)  (*E*)	(2.4) (0.1)		
	(0.076)	0.55		(4.1)		

[a] In 5 ml of acetonitrile containing 0.60 mmol olefin, 0.30 mmol t-butyl hydroperoxide, 0.044 mmol imidazole, and 0.011 mmol 5,5′-dinitrosalenMn^{III} at 25 °C. Reaction time = 5 min.

[b] Olefin consumed (by difference) by analysis after reaction completion.

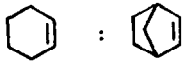
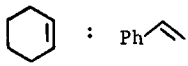
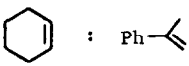
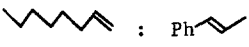
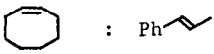
[c] 2,6-Di-t-butylcresol.

[d] Not determined, <0.2.

as listed in Table 4. Small but discrete amounts of di-t-butyl peroxide were generated during the catalytic oxidation. However, it could be eliminated by the addition of ionol to the catalytic system. Although the catalytic epoxidations of *Z*-hexene-2 and *Z*-β-methylstyrene afford high stereochemical yields of the corresponding *Z*-epoxides, they are not stereospecific. In each case, the corresponding *E*-isomers were generated in small amounts (<2%). The yields of epoxides based on the olefin consumed in Table 4 generally lay in the range of 30 - 80%. However these yields are subject to rather large experimental errors, since they were determined by difference at low olefin conversions. The yields of epoxides based on the amount of t-butyl hydroperoxide consumed were low, generally being 10 - 15%. Thus the oxidizing power in this catalytic system was diverted to other pathways including the

TABLE 5

Relative reactivity of olefins by the competition method[a]

Olefin pair A(mmol) : B(mmol)	X_f[b] (mmol)	Y_f[b] (mmol)	Rel. React.[c]
 0.303 : 0.354	0.232	0.284	1.2
 0.503 : 0.506	0.455	0.460	1.0
 0.294 : 0.296	0.259	0.259	0.95
 0.510 : 0.493	0.002[d]	0.017[e]	0.1[f]
 0.511 : 0.511	0.007[g]	0.010[e]	0.7[f]

[a]In 5 ml of acetonitrile containing 0.30 mmol t-butyl hydroperoxide, 0.044 mmol imidazole, 0.011 mmol 5,5′-dinitrosalenMn^{III} and 0.55 mmol ionol at 25 °C.
[b]Amount of olefin after reaction, unless indicated otherwise.
[c]Calculation described in the Experimental Section.
[d]Octene-1 oxide.
[e]*E*-β-methylstyrene oxide.
[f]Based on epoxides formed.
[g]Cyclooctene oxide.

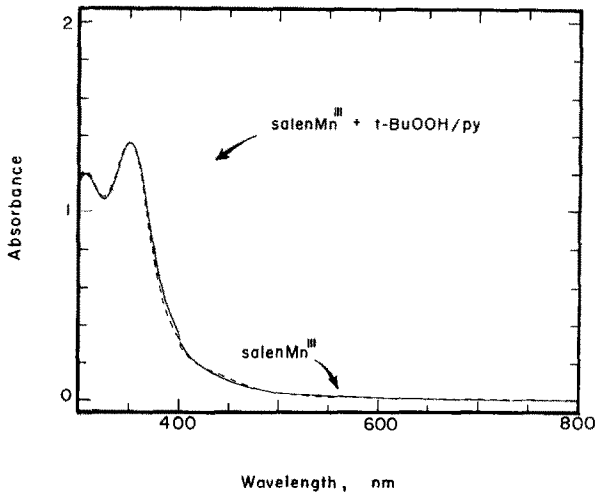
formation of dioxygen. Accordingly, we relied on the competition method to evaluate the nature of the oxygen atom transfer to olefins.

The pattern of olefin reactivity in the catalytic epoxidation with t-butyl hydroperoxide is illustrated in Table 5. The competition method ensures that each olefin in the pair is subjected in the same way to the reactive intermediate which is responsible for the oxygen atom transfer. The validity of the method was established in earlier studies [20, 21], and it provides credence to the unusual reactivity pattern. Thus a factor of only ten separates the reactivity of β-methylstyrene and octene-1.

Spectral changes during catalytic epoxidations with t-butyl hydroperoxide

When either pyridine or imidazole is added to a yellow solution of Mn^{III} containing t-butyl hydroperoxide, there is a rather rapid color change to dark brown. Upon standing, the dark brown color is slowly discharged, (30 min) and the solution returns to its original hue. However, if an olefin such as cyclohexene is added immediately, the color change occurs more rapidly. The spectral changes accompanying these transformations are illustrated in Fig. 1. The new absorption band with a partially resolved maximum at ~550 nm is related to the formation of a reactive intermediate in the catalytic epoxidation. It is important to note that the same series of color changes accompanied the catalytic epoxidation with iodosylbenzene as the terminal oxidant [21]. (However, with iodosylbenzene, the formation of the spectral band with $\lambda_{max} \sim 550$ nm is not dependent on the presence of pyridine or imidazole).

The appearance of the new, transient absorption band at λ 550 nm is dependent on the pyridine concentration. Figure 2 shows that it reaches a maximum absorbance within 2 min of mixing the components, and then disappears rapidly. The final absorption spectrum corresponds closely to that of the original cationic salenMn^{III} catalyst.



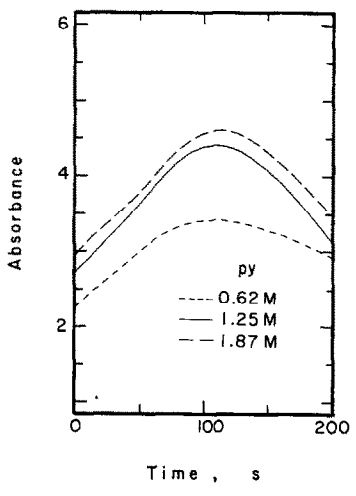


Fig. 1. Absorption spectrum of 5.5×10^{-4} M 5,5'-$(NO_2)_2$salenMn^{III} in acetonitrile with (- - - -) and without (——) 2.5×10^{-1} M pyridine. Transient absorption spectrum obtained from 2.2×10^{-3} M 5,5'-$(NO_2)_2$salenMn^{III} containing 0.06 M t-butyl hydroperoxide and 1.25 M pyridine in acetonitrile (·····).

Fig. 2. Growth and decay of the transient absorption band at λ 540 nm from 2.2×10^{-3} M 5,5'-$(NO_2)_2$salenMn^{III} and 0.06 M t-butyl hydroperoxide containing (- - - -) 0.62 M, (——) 1.25 M and (— — —) 1.87 M pyridine in acetonitrile at 25 °C.

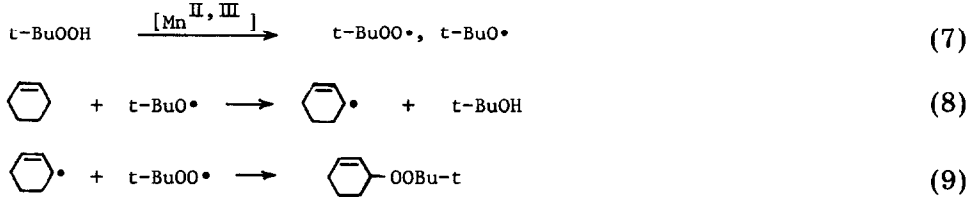
Discussion

Dual pathways for salenMn^{III} catalysis of olefin oxidation

The catalysis by salenMn^{III} of olefin oxidation with alkyl hydroperoxides leads to two concurrent processes, *viz.*, allylic peroxidation and olefin epoxidation. Thus the treatment of cyclohexene with t-butyl hydroperoxide in the presence of catalytic amounts of salenMn^{III} slowly yields cyclohexenyl t-butyl peroxide, as presented in Table 2 (entry 1). The addition of either pyridine or imidazole to the same components promotes the production of cyclohexene oxide (entries 2 - 8). The latter is also characterized by a marked increase in catalytic activity, and t-butyl hydroperoxide is completely consumed within 5 min. Furthermore, it is accompanied by a 10-fold increase in the yield of cyclohexenyl t-butyl peroxide (Table 2).

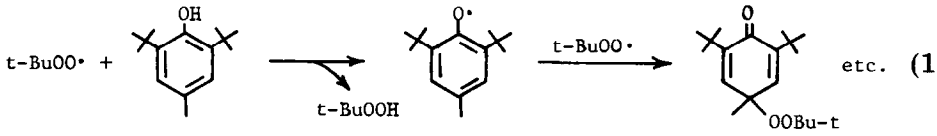
Allylic peroxidation by radical chain mechanism — inhibition by ionol

The formation of cyclohexenyl t-butyl peroxide under these conditions is akin to the cobalt catalysis of cyclohexene oxidation originally observed by Kharasch and coworkers [3, 4]. The results in Table 3 demonstrate that the hindered phenol ionol effectively quenches the production of cyclohexenyl t-butyl peroxide. Ionol is known to be an efficient antioxidant capable of suppressing free radical chain reactions by the interception of alkylperoxy radicals [22]. Thus the allylic substitution leading to cyclohexenyl t-butyl peroxide is characteristic of a large class of metal-catalyzed reactions of peroxides [23], the mechanisms of which are generally described as electron transfer chain, or ETC, catalysis [24]. As applied to the formation of allylic peroxides such as cyclohexenyl t-butyl peroxide from cyclohexene and t-butyl hydroperoxide, the principal homolytic reactions of the propagation sequence include those presented schematically below:



Scheme 1.

The initiation of the catalysis occurs as a direct consequence of the production of any one of the paramagnetic species in Scheme 1 by homolytic and/or redox reactions of the peroxide [1, 5]. Likewise, the inhibition or retardation of the chain process in Scheme 1 is achieved by the destruction of the free radicals by ionol [20], *e.g.*:



(10)

and/or the oxidation of the reduced salenMn^{II} species.

The catalytic pathway leading to olefin epoxidation is quite distinct and separate from the radical chain process described above for allylic peroxidation. Since the results in Table 3 indicate that the formation of cyclohexene oxide is by and large unaffected by ionol, free radicals of the types extant in Scheme 1 are not intermediates in epoxide formation. The same dichotomy is shown during the oxidation of octene-1 and hexene-2 in Table 4. With each substrate, the production of the corresponding olefin oxide is accompanied by the appearance of small but distinctive amounts of di-t-butyl peroxide — the formation of which is symptomatic of homolytic processes of the type described in Scheme 1. Thus t-butyl peroxy radicals are known to undergo disproportionation to di-t-butyl peroxide, *i.e.*

$$2\,\text{t-BuOO}\cdot \longrightarrow \text{t-BuOOBu-t} + O_2 \qquad (11)$$

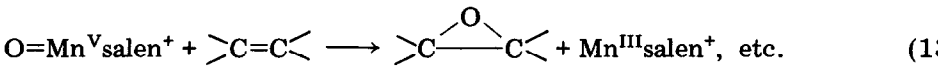
at close to diffusion-controlled rates [25]. The efficient removal of the homolytic intermediates leading to di-t-butyl peroxide by ionol (compare eqn. 10), which leaves the epoxides in Table 4 intact, is another manifestation of the dual pathways available in this system.

As different as the propagation steps are for allylic peroxidation and olefin epoxidation, they share in common the strong dependence on the properties of pyridine and imidazole as cocatalysts (Table 2). In other words, the combination of t-butyl hydroperoxide and pyridine (or imidazole) is sufficient to induce salenMn^{III} to produce the paramagnetic species required to initiate Scheme 1, and at the same time to induce epoxide formation. Before discussing how such a bifurcation of the salenMn^{III} catalyst can occur, let us consider the pathway by which olefins are converted to epoxides in this catalytic system.

SalenMn^{III} catalysis of olefin epoxidation

The catalysis of olefin epoxidation with salenMn^{III} and iodosylbenzene (Table 1) is uncomplicated by competing homolytic reactions such as those leading to cyclohexenyl t-butyl peroxide and di-t-butyl peroxide. The unique reactivity pattern obtained earlier with various olefins of different structural types accords with an oxygen-rebound mechanism for catalysis presented below [21].

$$\text{Mn}^{III}\text{salen}^+ + \text{PhIO} \longrightarrow \text{O=Mn}^{V}\text{salen}^+ + \text{PhI} \qquad (12)$$



(13)

Scheme 2.

According to Scheme 2, an oxomanganese(V) species is the reactive intermediate responsible for oxygen-atom transfer to the olefin in eqn. 13. Reactivity studies of various olefins indicate that the same oxomanganese(V) species is the reactive intermediate in the catalytic system derived from t-butyl hydroperoxide–pyridine. In order to facilitate a direct comparison of the two systems, we measured the reactivity of diverse olefins by the competition method under the same conditions. The results are summarized in Table 6. Within experimental error, there is no distinction between iodosylbenzene and t-butyl hydroperoxide–pyridine as terminal oxidants for olefin epoxidation with salenMn^{III} as the catalyst. Furthermore, the presence of pyridine has no influence on the relative reactivity of cyclohexene and octene-1 in the catalytic system derived from salenMn^{III} and iodosylbenzene [21].

Since the reactivity pattern for catalytic epoxidation with salenMn^{III} and iodosylbenzene is distinctively unique [21], we take the comparison in Table 6 to indicate that the same reactive intermediate is involved in the oxygen-atom transfer when t-butyl hydroperoxide–pyridine is the terminal oxidant. With iodosylbenzene as the terminal oxidant, the formation of the reactive oxomanganese(V) in eqn. 12 is similar to that previously established for the related chromium(III) cations [13, 14], *viz.*:

$$\text{salenCr}^{III} + \text{PhIO} \longrightarrow \text{O=Cr}^{V}\text{salen}^{+} + \text{PhI} \qquad (14)$$

Such an oxomanganese(V) species is also capable of reversibly coupling with salenMn^{III} to form a μ-oxomanganese(IV) dimer [26].

$$\text{O=Mn}^{V}\text{salen} + \text{salenMn}^{III} \rightleftharpoons \text{salenMn}^{IV}\text{OMn}^{IV}\text{salen} \qquad (15)$$

TABLE 6

Comparison of iodosylbenzene and t-butyl hydroperoxide–imidazole in olefin reactivity[a]

Olefin	Relative reactivity[b]	
	PhIO[c]	t-BuOOH–Imid.[d]
	1.0 (—)	1.0 (0.81)
	0.18 (0.1)	— (0.1)
	0.62 (0.55)	— (0.66)

[a]With 0.011 mmol 5,5′-(NO_2)salenMn$^{+}PF_6^{-}$ in 5 ml acetonitrile at 25 °C.
[b]Molar reactivity relative to *E*-β-methylstyrene consumed. Value based on epoxide yields in parentheses.
[c]0.15 mmol iodosylbenzene.
[d]0.33 mmol t-BuOOH plus 0.044 mmol imidazole and 0.55 mmol ionol at 25 °C.

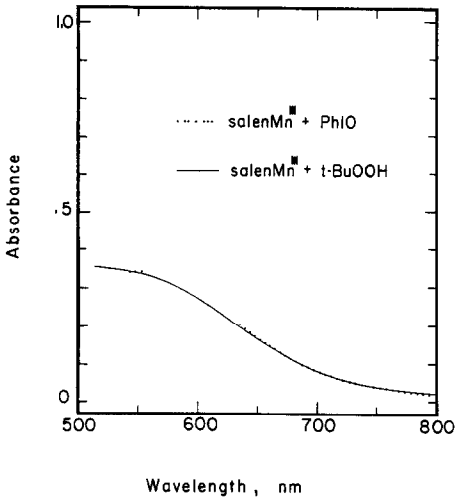


Fig. 3. Difference absorption spectra obtained from 2.2×10^{-3} M 5,5'-$(NO_2)_2$salenMn^{III} and 1.25 M pyridine in acetonitrile containing either (·····) iodosylbenzene (excess) or (——) 0.06 M t-butyl hydroperoxide.

Indeed, the latter is the predominant form under steady-state conditions owing to its somewhat greater stability. It is observed spectrally by the appearance of a new transient absorption band with $\lambda_{max} \sim 550$ nm when salenMn^{III} is treated with iodosylbenzene with or without pyridine [21].

The same transient absorption band appears during the catalytic oxidations with t-butyl hydroperoxide. For example, the absorption spectrum of a solution of salenMn^{III}, shown in Fig. 1, is essentially unchanged by the addition of either t-butyl hydroperoxide or pyridine. However, the presence of t-butyl hydroperoxide and pyridine together causes the brown solution of salenMn^{III} to darken, and a new absorption band to appear with $\lambda_{max} \sim$ 550 nm. The close similarity of this absorption band with that obtained from iodosylbenzene is shown in Fig. 3. (Since these difference spectra were obtained by spectral subtraction of the salenMn^{III} background spectrum, they are meaningful only in the region $\lambda \gtrsim 500$ nm.) The same spectral change occurs when pyridine is replaced with imidazole, but other donor ligands such as pyridine *N*-oxide and 2,6-di-t-butylpyridine are ineffective. Since the latter also do not induce the formation of epoxide (see Table 2), we associate the appearance of the new spectral band in Fig. 1 with the formation of active oxomanganese species of the type observed with iodosylbenzene. Such a reactive species can be formed from t-butyl hydroperoxide–pyridine via an alkylperoxo intermediate*, *e.g.*

*Cf. W. A. Lee and T. C. Bruice [15] and D. Mansuy *et al.* [10].

$$\text{salenMn}^{III} + \text{t-BuOOH} \xrightarrow{[py]} \text{t-BuOOMn}^{III}\text{salen} + \text{pyH}^{+} \quad (16)$$

$$\text{t-BuOOMn}^{III}\text{salen} \xrightarrow{[\text{t-BuO}^{-}]} \text{O=Mn}^{V}\text{salen}^{+} \quad (17)$$

Scheme 3.

which is followed by the reversible coupling to the oxomanganese dimer in eqn. 15. The latter is especially relevant when an olefinic substrate is absent. Under these conditions, the evolution of the transient intermediate can be observed by monitoring the appearance of the absorption band at λ 550 nm. The rate profiles in Fig. 2 reveal the rapid growth and decay of the transient intermediate. In the growth period, the *amount* of this intermediate is directly related to the pyridine concentration; but the *rate* is rather insensitive to pyridine. Such a kinetic behavior is consistent with Scheme 3 in which the rearrangement of the alkylperoxo species (eqn. 17) is rate limiting. According to Scheme 3, pyridine and imidazole function principally as Brönsted bases to promote the formation of the alkylperoxomanganese(III) species in eqn. 16. Pyridine *N*-oxide is ineffective in this capacity, owing to its limited basic properties. Moreover, metal coordination of the donor ligand by itself is insufficient to promote the formation of the transient intermediate. For example, pyridine *N*-oxide, which is ineffective with t-butyl hydroperoxide, is known to be as effective as pyridine in its ability to coordinate to the oxomanganese(V) species derived from iodosylbenzene [21]. (The latter does not lead to significant shifts in the transient spectrum.) Despite these differences however, the comparisons of the relative reactivities of olefins and the spectral transients provide strong support for a common oxomanganese(V) species as the reactive intermediate for catalytic oxygen-atom transfer with iodosylbenzene as well as with t-butyl hydroperoxide–pyridine.

Oxidative conversion of salenMn^{III} by one- and two-electron processes

Although iodosylbenzene and t-butyl hydroperoxide–pyridine share a common pathway for olefin epoxidation via oxomanganese(V) in Schemes 2 and 3, they are distinguished by their ability to effect allylic peroxidation. Since the allylic peroxidation occurs only with t-butyl hydroperoxide (and promoted by pyridine), we identify the alkylperoxomanganese(III) precursor generated in eqn. 16 as the point of departure. Indeed, homolytic scission of the oxygen–oxygen in such an intermediate would afford alkoxy radicals and oxomanganese(IV), both capable of initiating the radical process in Scheme 1, *i.e.* [27]:

$$\text{t-BuOOMn}^{III}\text{salen} \longrightarrow \text{t-BuO}\cdot + \text{O=Mn}^{IV}\text{salen} \quad (18)$$

$$\text{t-BuO}\cdot + \text{t-BuOOH} \longrightarrow \text{t-BuOH} + \text{t-BuO}_2\cdot, \text{ etc.} \quad (19)$$

$$\text{O=Mn}^{IV}\text{salen} + \text{t-BuOOH} \longrightarrow \text{HOMn}^{III}\text{salen} + \text{t-BuO}_2\cdot, \text{ etc.} \quad (20)$$

Scheme 4.

Homolysis and heterolysis of the alkylperoxomanganese(III) as represented in eqns. 18 and 17, respectively, constitute the competing pathways by which the catalytic processes for allylic peroxidation and olefin epoxidation are initiated. The evidence on hand suggests that such a competition can be controlled by the donor ligand B. For example, the results in Table 2 (entry 9) indicate that 2,6-di-t-butylpyridine does not induce epoxide formation, but it is effective in the promotion of allylic peroxidation. Such a sterically hindered base is indeed capable of proton removal from oxygen (as in eqn. 16) sufficient to generate the alkylperoxomanganese(III) precursor required for homolytic initiation in Scheme 4. However, 2,6-di-t-butylpyridine would be too sterically encumbered to bind effectively [28], if the rearrangement to oxomanganese(V) in eqn. 17 (Scheme 3) required axial coordination by a donor ligand [29]. Such a formulation is supported by the absence of the transient absorption associated with olefin epoxidation (compare Fig. 2) when 2,6-di-t-butylpyridine is employed as the donor ligand B. By contrast, pyridine and imidazole are effective both as Brönsted bases and as coordinating ligands. We hope that a more extensive search for other ligands will provide a means to quantitatively investigate this interesting dichotomy further.

Conclusions

Dual pathways leading to allylic substitution (cyclohexenyl t-butyl peroxide) and olefin epoxidation (cyclohexene oxide) have been delineated during the salenMn^{III} catalysis of cyclohexene oxidation with t-butyl hydroperoxide–pyridine. Allylic peroxidation corresponds to a homolytic chain process in which free radicals and one-electron redox changes of salenMn^{III} play important roles. Olefin epoxidation on the other hand represents the two-electron interconversion of manganese(III) and oxomanganese(V) species. The two pathways can thus be distinguished by

TABLE 7

Relative reactivity of some olefins in epoxidation with various agents[a]

Olefin	Epoxidizing agent		
	SalenMn^{III} [b]	$Mo(CO)_6$ [c]	CH_3CO_3H [d]
octene-1	1.0	1.0	1.0
styrene	6.7	1.3	2.2
cyclohexene	6.7	13	25
norbornene	7.3	14	30

[a]With the reactivity of octene-1 taken as 1.0.
[b]With either iodosylbenzene [21] or t-butyl hydroperoxide in acetonitrile at 25 °C.
[c]With t-butyl hydroperoxide in benzene at 90 °C.
[d]In acetic acid at 25 °C [31].

inhibitors such as ionol which effectively eliminate the homolytic chain important to allylic peroxidation, and leave the process leading to olefin epoxidation intact. The observation of common spectral transients in Figs. 1 and 3, together with the comparison of the relative reactivities of olefins in Table 6, indicate that the catalytic epoxidation with salenMn^{III} is the same as that observed with iodosylbenzene as the terminal oxidant. In both cases, the oxygen atom transfer to olefin occurs via an oxomanganese(V) intermediate which shows reactivity patterns in Table 7 that are differentiated from those observed in the related coordination catalysis by molybdenum(VI) [30]. The results of olefin epoxidation with peracetic acid are also included in Table 7 for comparison [31]. These differences underscore the theoretical problem which remains to quantitatively describe the nature of oxygen-atom transfer to olefins from various oxygen donors [32].

Experimental

Materials

t-Butyl hydroperoxide (Lucidol) was purified by three successive distillations under reduced pressure or via isolation of the sodium salt and found to be 97% and 99% by iodometric titration [33]. Iodosylbenzene was prepared by the hydrolysis of the corresponding diacetate (Aldrich Chemical Co.) with aqueous sodium hydroxide and stored at −20 °C. Imidazole (preparative electrophoresis grade) from Canal Industrial Corp. was used as received. 4′-(Imidazol-1-yl)acetophenone from Aldrich was recrystallized from dichloromethane. 2,6-Di-t-butylpyridine from Aldrich and 2,6-di-t-butyl-*p*-cresol (ionol) from Shell were used as received.

1-Octene, cyclohexene, cyclooctene, styrene, α-methylstyrene, *Z*-β-methylstyrene, and norbornene were all commercial samples from Aldrich Chemical Co. *o,o′*-Dimethylstyrene was obtained from Fairfield Research Chemicals, and *Z*-hexene-2 from Wiley Organics. Octene-1, *cis*-cyclooctene, norbornene, *Z*-hexene-2 were distilled from lithium aluminum hydride under argon and stored in Schlenk vessels. All the styrenes were purified by distillation from lithium aluminum hydride under reduced pressure, and stored at −20 °C in teflon-stoppered Schlenk vessels under argon. The epoxides were independently prepared by the epoxidation of corresponding alkenes with *m*-chloroperbenzoic acid (80 - 85%) from Aldrich Chemical Co. The epoxides were identified by their ^{1}H NMR spectra and confirmed by the GC–MS cracking patterns. The mass spectra were stored in the library of the GC–MS computer (*vide infra*) and retrieved when required for comparison purposes. Styrene oxide and cyclohexene oxide were commercial samples (Aldrich).

Hexane, acetonitrile, chlorobenzene, pyridine, diethyl ether, dimethyl sulfoxide and dichloromethane were reagent grade commercial solvents which were repurified by standard methods [34]. After distillation, they were stored under argon atmosphere in Schlenk flasks.

Salicylaldehyde, ethylenediamine and manganous acetate (Fisher), 5-nitrosalicylaldehyde (Eastman Kodak), and 5-methoxysalicylaldehyde (Aldrich) were used as received. The ligand salenH_2 was prepared by a literature procedure [35], as were the 5,5′-dinitro and 5,5′-dimethoxy analogs. They were recrystallized from ethanol as bright yellow solids.

General procedure for the synthesis of (salen)manganese(II) complexes

Owing to their air-sensitivity, the manganese(II)–Schiff base complexes were prepared under argon with strict exclusion of air. To a suspension of the appropriate salenH_2 ligand (4 mmol) in 40 ml of deaerated absolute ethanol, was added a solution of KOH (8 mmol) dissolved in 10 ml deaerated ethanol through a cannula needle. To the resulting yellow solution was added dropwise a solution of $Mn(OAc)_2 \cdot 4H_2O$ (4 mmol) in 10 ml deaerated methanol with the aid of a teflon cannula. The yellow solution turned dark and an orange solid began to appear. The solid suspension was stirred vigorously for 1 h at room temperature and refluxed for 3 - 4 h to ensure completion of the reaction. The solution was then cooled to room temperature, the orange precipitate Schlenk-filtered, washed with deaerated methanol and dried *in vacuo*. The yield, IR spectral data (nujol mull) and magnetic susceptibility data of the Mn(II)–Schiff base complexes are given below [36].

(Salen)Mn(II)

Yield: 62%. IR: 1620(s), 1525(s), 1340(m), 1276(m), 1234(s), 1198(s), 1140(s), 1120(m), 1086(s), 1042(m), 982(s), 940(m), 905(s), 855(s), 750(s), 732(s) cm^{-1}. μ_{eff} = 6.13 BM.

(5,5′-Dimethoxysalen)Mn(II)

Yield: 80%. IR(nujol): 1627(s), 1608(s), 1541(s), 1380(s), 1333(m), 1294(s), 1257(w), 1242(w), 1217(m), 1184(w), 1154(s), 1088(w), 1032(s), 982(m), 946(w), 933(w), 854(s), 828(s), 796(s), 776(s), 733(w) cm^{-1}.

(5,5′-Dinitrosalen)Mn(II)

Yield: 85%. IR: 1638(s), 1599(s), 1554(s), 1384(s), 1306(vs), 1248(s), 1184(m), 1135(w), 1103(s), 1078(m), 1044(m), 972(w), 950(m), 889(m), 842(m), 787(m), 756(m), 733(m), 698(s), 644(m) cm^{-1}. μ_{eff} = 5.74 BM.

General procedure for the synthesis of (salen)manganese(III)$^+PF_6^-$ salts

To a stirred suspension of 1 mmol of the salenMn(II) complex in 20 ml of deaerated CH_3CN, a solution of ferrocenium hexafluorophosphate (1 mmol) dissolved in 30 ml acetonitrile was added dropwise via a teflon cannula. The yellow suspension immediately began to turn brown. Stirring was continued for 30 min during which time the mixture became completely homogeneous. The solvent was removed under reduced pressure, and the

neutral ferrocene was removed by several ether extractions. The manganese(III) complex which remained as a brown residue was crystallized from either a mixture of acetone and water or acetone and ethanol. The brown microcrystalline product was dried *in vacuo* for 2 h. The detailed data for characterization are provided below.

[(Salen)Mn]$^+PF_6^-$

Yield: 60%. IR(nujol): 3588(br), 1618(s), 1601(s), 1551(s), 1442(s), 1391(s), 1328(m), 1281(s), 1270(s), 1247(s), 1212(s), 1156(m), 1137(s), 1090(m), 1049(m), 1032(w), 980(w), 952(w), 905(s), 836(vs, broad), 802(s), 752(s), 742(s), 647(m), 634(m) cm^{-1}. UV–vis in CH_3CN [nm, ϵ (M^{-1} cm^{-1})]: 218 (3.06×10^4), 231 (3.63×10^4), 282 (1.60×10^3), 311 (1.12×10^3), 353 (7300), 402 (4500), 494 (1000). $\mu_{eff} = 4.73$ BM. Anal. for [(salen)Mn]$PF_6(H_2O)$, $C_{16}H_{16}O_3N_2MnPF_6$. Calcd: C, 39.69%; H, 3.33%; N, 5.78%. Found: C, 39.66%; H, 3.30%; N, 5.72%.

[(5,5'-(OMe)$_2$salen)Mn]$^+PF_6^-$

The same procedure was used in the synthesis of this compound. Yield: 70%. IR(nujol): 1635(s), 1616(s), 1556(s), 1472(s), 1283(s), 1253(m), 1244(m), 1165(s), 1094(m), 1053(s), 1040(s), 972(m), 840(vs, br), 770(m), 727(w), 619(m) cm^{-1}. UV–vis in CH_3CN [nm, ϵ (M^{-1} cm^{-1})]: 241 (3.9×10^4), 283 (2.15×10^4), 367 (7.7×10^3).

[(5,5'-(NO$_2$)$_2$salen)Mn]$^+PF_6^-$

To a suspension of 5,5'-dinitrosalenMn^{II} (4 mmol) in 50 ml deaerated CH_3CN was added a solution of ferrocenium hexafluorophosphate (4 mmol) in 100 ml CH_3CN through a teflon cannula. The resulting greenish-brown suspension was stirred for 1 h. The homogeneous solution was concentrated to 20 ml and poured into a pool of ether (100 ml). The flocculent greenish-brown precipitate was dissolved in an acetone–ethanol mixture, which on slow evaporation in air gave greenish-brown needles of the product. The product was dried *in vacuo* for two hours and recrystallized. Yield: 61%. IR(nujol): 3400(br), 1631(s), 1601(s), 1560(s), 1496(m), 1440(w), 1388(s), 1330(s), 1298(vs), 1137(w), 1109(s), 989(w), 954(m), 916(w), 860(s), 845(vs), 802(s), 757(m), 701(m), 660(m) cm^{-1}. UV–vis in CH_3CN [nm, ϵ (M^{-1} cm^{-1})]: 242 (2.86×10^4), 275 (2.74×10^4), 351 (2.34×10^4). $\mu_{eff} = 4.65$ BM. Anal. for [(5,5'-$(NO_2)_2$salen)Mn]$PF_6(C_2H_5OH)_{3/2}$, $C_{19}H_{21}O_{7.5}N_4PF_6Mn$. Calcd: C, 36.42%; H, 3.35%; N, 8.94%. Found: C, 35.99%; H, 3.46%; N, 8.80%.

Instrumentation

The electronic absorption spectra were recorded with a Hewlett-Packard 8450A diode-array spectrometer. Magnetic susceptibility was measured at 25 °C by the Evans method [37] in CD_3CN [for Mn(III) complexes] and in DMSO-d_6 [for Mn(II) complexes] using a JEOL FX-90Q NMR spectrometer. Infrared spectra were obtained on a Nicolet DX-10 (Fourier transform) spectrometer.

Organic analyses were conducted on a Hewlett-Packard 5790A gas chromatograph with either a 12.5 m crosslinked dimethysilicone capillary column or a 30 m Carbowax capillary column. The GC–MS analyses were performed on a Hewlett-Packard 5890 gas chromatograph interfaced to a Hewlett-Packard 5970 mass spectrometer (E.I., 70 eV). In many instances, we found it possible to make direct comparisons with the same compounds listed in the 59973 NBS mass spectral library stored in the computer. In other cases, comparisons were made with those mass spectra of authentic samples. In every case, we found the mass spectra of *E* and *Z* isomers to be the same [21].

Epoxidations of olefins and the analysis of products

Iodosylbenzene

Epoxidations were carried out under argon in a 25 ml Schlenk tube equipped with a stirring bar and an air-tight rubber septum. A stock solution of the dinitrosalenmanganese(III) complex in acetonitrile (2.2×10^{-3} M) was prepared, and 5 ml of this solution (corresponding to 0.011 mmol of the catalyst) was placed in the reaction tube which was previously evacuated and filled with argon. The olefin (0.3 mmol) and internal standard (0.30 mmol, consisting of either chlorobenzene, n-decane or pentadecane) were added to the catalyst solution. Gas chromatographic analyses were performed by withdrawing several aliquots with the aid of hypodermic syringe. After the initial analysis, 33 mg (0.15 mmol) of iodosylbenzene was added in one lot to the reaction solution under a flow of argon. All of the iodosylbenzene usually disappeared within 5 - 15 min. GC analysis was performed approximately 30 min after the start of the reaction.

t-Butyl hydroperoxide

Epoxidations were carried out under argon in a 25 ml Schlenk tube equipped with a stirring bar and a rubber septum. A stock solution of the dinitrosalenMn^{III} complex in acetonitrile (2.2×10^{-3} M) was prepared, and 5 ml of this solution (corresponding to 0.011 mmol of the catalyst) was placed in a reaction tube which was previously evacuated and filled with argon. To this solution, 0.044 mmol of imidazole (44 μl of a 1.0 M solution in CH_3CN was added, followed by 0.6 mmol of olefin and 0.1 mmol of internal standard (either PhCl or n-decane). Gas chromatographic analysis was performed by withdrawing several aliquots with the aid of a hypodermic syringe. After the initial analysis, 35 μl (0.30 mmol) of t-butyl hydroperoxide was added dropwise over a 1 min period. The GC analysis was performed approximately 15 - 20 min after the start of the reactions. Alternatively, in a 25 ml Schlenk tube containing 120 mg of ionol (0.55 mmol) was added 5 ml of a solution of dinitrosalenMn^{III} complex in acetonitrile (2.2×10^{-3} M), 0.044 mmol of imidazole, 0.60 mmol of olefin and 0.10 mmol of internal standard. The solution was analyzed by gas chromatography as described earlier. To this solution 35 μl (0.30 mmol) of t-butyl hydroperoxide was added dropwise over a 1 min period. Gas

chromatographic analysis was performed 15 min after the commencement of reaction, which was usually complete within 5 min. Quantification of the products from these experiments was carried out in at least triplicate by the internal standard method.

The mass spectral cracking patterns (E.I, 70 eV) for some distinctive products are given separately. α-phenylpropionaldehyde, *M/z*(%): 50(8), 51(17), 77(29), 78(9), 79(29), 91(9), 103(16), 105(100), 106(9), 134(9). Phenylacetone, *M/z*(%): 39(11), 43(100), 50(3), 51(5), 63(6), 65(12), 89(3), 91(25), 92(11), 134(5). Cyclohexenyl t-butyl peroxide, *M/z*(%): 39(33), 41(47), 43(73), 57(21), 58(11), 67(9), 68(12), 79(18), 80(32), 81(100), 170(0.3). Di-t-butyl peroxide, *M/z*(%): 41(52), 43(65), 44(13), 45(26), 55(16), 57(100), 58(77), 59(11), 73(37), 146(26).

Relative reactivities of olefins by intermolecular competitions

The relative reactivities by intermolecular competition were calculated by the expression:

$$k_X/k_Y \cong \log(X_f/X_i)/\log(Y_f/Y_i)$$

where X_i and Y_i are the initial concentrations of the olefins X and Y and X_f and Y_f are the final concentrations of these olefins [38]. For applying this equation, the initial concentrations of olefins were at least five times greater than the conversion. In a typical procedure for the competitive catalytic epoxidation, 0.3 mmol of each of two olefins were mixed with a solution containing 0.011 mmol of the Mn^{III} complex, 120 mg of ionol, 0.044 mmol of imidazole and 0.2 mmol of internal standard in 5 ml CH_3CN. Before the start of the reaction the amounts of olefins were determined by GC analysis. Then, 0.30 mmol of t-butyl hydroperoxide was added, and the solution vigorously stirred. The amounts of products formed and olefins consumed were determined by GC analysis, 15 min after the commencement of reaction.

Acknowledgement

We thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

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