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Metal Complex-Catalyzed Epoxidation of Olefins by Dioxygen with Co-Oxidation of Aldehydes. A Mechanistic Study

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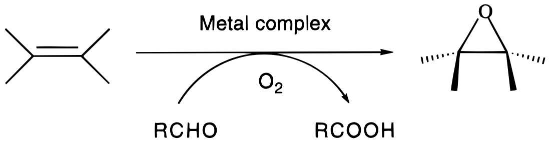
Mechanistic studies of the oxidation of olefins by dioxygen plus aldehyde in the presence of metal complexes such as metalloporphyrins and metal cyclam complexes have been carried out. Epoxides were the predominant products, with trace amounts of allylic oxidation products. *cis*-Stilbene was oxidized to a mixture of *cis*- and *trans*-stilbene oxides. It is concluded from this study that the principal role of the metal complexes is to aid in the initiation step for the free radical autoxidation of the aldehyde and that acylperoxy radicals generated in the autoxidation reaction (or metal complexes formed by complexation of the acylperoxy radicals) are the active epoxidizing agents.

Introduction

Biomimetic oxygenations of organic substrates using soluble metal coordination complexes as catalysts ideally should use dioxygen, O_2, as the source of oxygen atoms, since O_2 is used directly by oxygenase enzymes.[1] In most cases, however, the successful catalysts that have been developed for such reactions, i.e. metalloporphyrins and metal complexes of non-porphyrin ligands, require alternative oxidants,[2] e.g. hydrogen peroxide, organic peroxides, or iodosylbenzene, since reactions using dioxygen itself either give no reaction or give predominantly the undesirable side products of free-radical autoxidation. An apparent exception to this rule occurs when an aldehyde is added to the reaction mixture. In this case, it has been observed that olefins are epoxidized by dioxygen, in the presence of aldehydes and transition metal-containing catalysts, to give epoxides in high yield, with concomitant co-oxidation of aldehydes to carboxylic acids (eq 1).[3,4]



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The mechanism that has been proposed for the metal complex-catalyzed oxygenation of substrates by O_2 and aldehydes is given in Scheme 1.[5] In this mechanism, the metal complex is assumed to play two roles. First, the metal complex reacts with the aldehyde to generate an acyl radical (RC(O)$^\bullet$). The acyl radical then reacts with dioxygen to give an acylperoxy radical (RC(O)OO$^\bullet$). The acylperoxy radical acts as a carrier in a chain mechanism by reacting with another aldehyde molecule to give the peroxyacid, thereby generating another acyl radical. Oxygenation of substrate is assumed by this mechanism to occur via reactive high-valent metal oxo intermediates, which are produced by the reaction of the peroxyacid with the metal catalysts and which then react with the olefin in a fashion analogous to that observed previously for metal complex-catalyzed reactions of peroxy acids with olefins.

Scheme 1

$$
\begin{aligned}
(L_n)M^{n+} + RCHO &\longrightarrow (L_n)M^{(n-1)+} + R\dot{C}O + H^+ \\
R\dot{C}O + O_2 &\longrightarrow RCO_3{}^\bullet \\
RCO_3{}^\bullet + RCHO &\longrightarrow RCO_3H + R\dot{C}O \\
(L_n)M^{n+} + RCO_3H &\longrightarrow (L_n)M^{(n+2)+}{=}O + RCO_2H \\
(L_n)M^{(n+2)+}{=}O + \text{Substrate} &\longrightarrow (L_n)M^{n+} + \text{Product(O)}
\end{aligned}
$$

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Table 1. Epoxidation of Cyclohexene by O_2 plus Aldehyde in the Presence of Metalloporphyrins and Metal Cyclam Complexes[a]

metalloporphyrins		metal cyclams	
catalyst	cyclohexene oxide product (yield, mmol)	catalyst	cyclohexene oxide product (yield, mmol)
Cr(TPP)Cl	1.0		
Mn(TPP)Cl	1.0	$Mn(cyclam)^{2+}$	1.0
Fe(TPP)Cl	1.0	$Fe(cyclam)^{2+}$	1.4
Co(TPP)	1.0	$Co(cyclam)^{2+}$	1.6
Co(TPP)[b]	0.0	$Co(cyclam)^{2+}$[b]	0.0
Ni(TPP)	1.2	$Ni(cyclam)^{2+}$	0.0
Cu(TPP)	0.2	$Cu(cyclam)^{2+}$	0.9
Zn(TPP)	0	$Zn(cyclam)^{2+}$	0.4
no metal complex	0.6	no metal complex	0.4

[a] Reaction conditions: Metal complex (0.02 mmol), cyclohexene (3 mmol), and isobutyraldehyde or cyclohexanecarboxaldehyde (1 mL, 10 mmol) in $ClCH_2CH_2Cl$ (5 mL) for metalloporphyrins and CH_3CN (5 mL) for metal cyclam complexes. O_2 was bubbled through the reaction solution for 8 h for the metalloporphyrin reactions and for 4 h for the metal cyclam complex reactions. Data represent values averaged from three independent reactions. See Experimental Section for detailed experimental procedures and product analyses. [b] Same conditions were used except that the free radical inhibitor *N*-phenyl-1-naphthylamine (0.1 mmol) was added.

We also have sought catalysts that would function with O_2 itself as the oxidant, in our attempts to develop biomimetic systems for substrate oxygenation by non-porphyrin metal complexes such as metal cyclam complexes. We were therefore interested in assaying our catalysts in the O_2 plus aldehyde system. For this reason, we have investigated the epoxidation of olefins by O_2 in the presence of aldehydes using metal cyclam complexes and, for comparison, some metalloporphyrin complexes as catalysts. As described below, we observed olefin epoxidation in high yield in this system, but further investigation produced results that suggested that the reactions often did not proceed by the high-valent metal oxo mechanism described in Scheme 1, but rather by direct oxygen atom transfer from acylperoxy radicals. These results and our interpretation are described below.

Results

Dioxygen was bubbled through either a dichloroethane or an acetonitrile solution of cyclohexene and isobutyraldehyde containing a metalloporphyrin or a metal cyclam complex catalyst (see Table 1). High yields of cyclohexene oxide were obtained as the predominant product, with only small amounts of the allylic oxidation product cyclohexenone, i.e. less than 5% of the cyclohexene oxide product. These results are thus similar to those obtained by previous investigators using other metal complexes, both porphyrin and non-porphyrin, as catalysts.[3,4] A wide variety of metal tetraphenylporphyrin (TPP) and metal cyclam complexes were found to be effective; Zn(TPP) and $Ni(cyclam)^{2+}$ were the exceptions (see Table 1). The observation that so many different transition metal complexes were effective as catalysts in this reaction caused us to question whether this reaction actually proceeded via metal oxo intermediates, since such reactivity had not been seen for several of these complexes, e.g., Co(TPP) or Ni(TPP), with single oxygen atom donors such as iodosylbenzene. We therefore carried out the reaction in an otherwise identical fashion but without any metal complexes added, and we observed very similar results, i.e. high yields of epoxide with only small amounts of allylic oxidation products (see last entries of Table 1). We also studied the effect of addition of the free radical inhibitor *N*-phenyl-1-naphthylamine[6] and found that the reaction was indeed inhibited by its presence (see Table 1). These results suggested to us that a free radical chain mechanism was occurring in each case and that reaction pathways that produced epoxide in high yield were present, whether or not the metal complexes were present.

Table 2. Epoxidation of Various Olefins by O_2 plus Aldehyde in the Presence of $Fe(cyclam)(CF_3SO_3)_2$[a]

substrate	product (yield, mmol)	ratios
cyclohexene	cyclohexene oxide (0.6) cyclohexenol (0) cyclohexenone (0.04)	oxide/(ol + one) = 15
cis-stilbene	*cis*-stilbene oxide (0.034) *trans*-stilbene oxide (0.13) benzaldehyde (0.01)	*cis*-oxide/*trans*-oxide = 0.26
norbornene	1,2-epoxynorbornane (0.78)	exo-/endo-oxide = >200
(+)-limonene	1,2-epoxide (0.56) 1,8-epoxide (0.087)	1,2-/8,9-oxide = 6.4

[a] Reaction conditions: $Fe(cyclam)(CF_3SO_3)_2$ (0.02 mmol), substrate (3 mmol for cyclohexene, 1 mmol for *cis*-stilbene, and 2 mmol for norbornene and (+)-limonene), and isobutyraldehyde (1 mL, 17 mmol) in CH_3CN (5 mL). O_2 was bubbled through the reaction solution for 2 h.

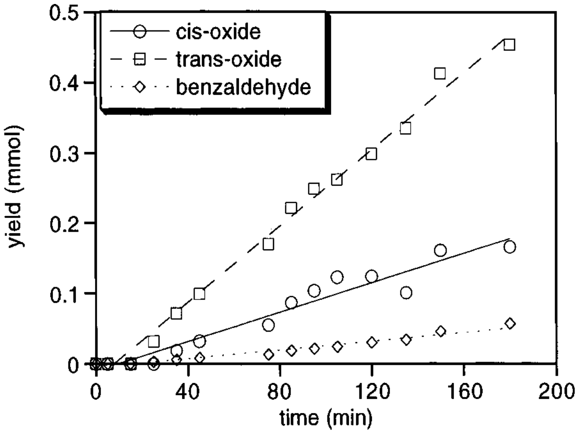

Figure 1. Time course for the formation of *cis*-stilbene oxide, *trans*-stilbene oxide, and benzaldehyde in the oxidation of *cis*-stilbene by O_2 plus aldehyde in the presence of the iron cyclam complex.

Iron(II) cyclam was then chosen for further study of its ability to act as a catalyst for reactions of other olefins using the O_2 plus aldehyde system. Results obtained for reactions of cyclohexene, *cis*-stilbene, norbornene, and (+)-limonene are given in Table 2. In the case of *cis*-stilbene, the O_2 plus aldehyde reaction gave *trans*-stilbene oxide as the predominant product, and a time course study of the reaction (see Figure 1) demonstrated that the ratio of *cis*-stilbene oxide to *trans*-stilbene oxide remained essentially constant throughout the reaction. Moreover, control reactions established that *cis*-stilbene oxide was stable under these reaction conditions, suggesting that *cis*-stilbene reacted to give *trans*-stilbene oxide directly. We had earlier studied the ferrous cyclam-catalyzed epoxidations of *cis*-stilbene by peracids and found that they gave predominantly *cis*-stilbene oxide.[7] Therefore, our results with the O_2 plus aldehyde system appeared to proceed by a different mechanism. Similar results were observed for reactions of norbornene and (+)-limonene, i.e. product distributions obtained for ferrous cyclam-catalyzed reactions in the O_2 plus aldehyde system were different from those obtained for the ferrous cyclam-catalyzed

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Table 3. Oxidation of *cis*- and *trans*-Stilbenes by O_2 plus Aldehyde in the Presence of Metalloporphyrins[a]

		products (yield, mmol)			
metal complex	stilbene	*cis*-oxide	*trans*-oxide	benzaldehyde	ratio of *cis*-/*trans*-oxide
Cr(TPP)Cl	*cis*-	0.07	0.25	0.01	0.28
	trans-	0.07	0.39	0.02	0.18
Mn(TPP)Cl	*cis*-	0.29	0.33	0.01	0.88
	trans-	0.10	0.40	0.01	0.25
Fe(TPP)Cl	*cis*-	0.15	0.50	0.02	0.30
	trans-	0.12	0.64	0.02	0.19
Co(TPP)	*cis*-	0.09	0.32	0.03	0.28
	trans-	0.07	0.37	0.01	0.19
Ni(TPP)	*cis*-	0.13	0.43	0.01	0.30
	trans-	0.08	0.62	0.02	0.13

[a] Reaction conditions: Metal complex (0.02 mmol), *cis*-stilbene or *trans*-stilbene (1 mmol), and isobutyraldehyde (1 mL, 17 mmol) in $ClCH_2CH_2Cl$ (5 mL). O_2 was bubbled through the reaction solution for 18 h.

Table 4. Oxidation of *cis*- and *trans*-Stilbene by O_2 plus Aldehyde in the Presence of Metal Cyclam Complexes[a]

		products (yield, mmol)			
$M(cyclam)^{2+}$	stilbene	*cis*-oxide	*trans*-oxide	benzaldehyde	ratio of *cis*-/*trans*-oxide
$Mn(cyclam)^{2+}$	*cis*-	0.20	0.22	0.02	0.91
	trans-	0.04	0.54	0.02	0.07
$Fe(cyclam)^{2+}$	*cis*-	0.03	0.13	0.01	0.23
	trans-	0.07	0.67	0.02	0.10
$Co(cyclam)^{2+}$	*cis*-	0.06	0.29	0.01	0.21
	trans-	0.08	0.70	0.02	0.11
$Cu(cyclam)^{2+}$	*cis*-	0.07	0.27	0.01	0.26
	trans-	0.04	0.93	0.02	0.04
no metal complex[b]	*cis*-	0.12	0.74	0.02	0.16
	trans-	0.07	0.86	0.05	0.08

[a] Reaction conditions: $M(cyclam)(CF_3SO_3)_2$ (0.02 mmol), *cis*-stilbene or *trans*-stilbene (1 mmol), and isobutyraldehyde (1 mL, 17 mmol) in CH_3CN (5 mL). O_2 was bubbled through the reaction solution for 2 h. [b] O_2 was bubbled through the reaction solution for 18 h.

reactions of MCPBA.[7] These results also suggested that the two types of reactions proceeded by different mechanisms.

Table 5. Reactivities of *Para*-Substituted Styrenes to That of Styrene in the Reactions of O_2 plus Aldehyde[a]

	para-X-styrene			
metal complex	Cl	H	CH_3	OCH_3
$Co(cyclam)^{2+}$	0.74	1.0	1.6	3.8
$Mn(cyclam)^{2+}$	0.91	1.0	1.3	2.3
Mn(TPP)Cl	0.89	1.0	1.6	2.7
no metal complex	0.78	1.0	1.6	3.5

[a] Reaction conditions: Metal complex (0.02 mmol), styrene (0.15 mmol), *para*-substituted styrene (0.15 mmol), and isobutyraldehyde (1 mL, 17 mmol) in $ClCH_2CH_2Cl$ (5 mL) for Mn(TPP)Cl and CH_3CN (5 mL) for metal cyclam complexes and no metal complex reactions. See Experimental Section for detailed experimental procedures and product analyses.

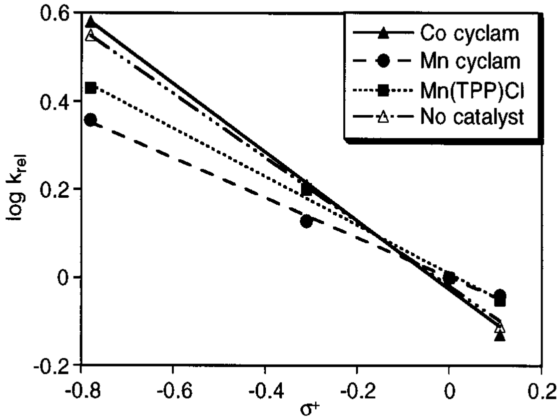

Figure 2. Hammett plot for the relative rates of disappearance of *para*-substituted styrenes in the reactions of dioxygen plus aldehyde.

The results of oxidation of *cis*- and *trans*-stilbenes with metalloporphyrins and metal cyclam complexes are summarized in Tables 3 and 4. All of the reactions yielded mixtures of *cis*- and *trans*-stilbene oxides with a trace amount of benzaldehyde. The ratios of *cis*- to *trans*-stilbene oxide in the product mixtures depended on the specific metal complex used. The reaction with Mn(TPP)Cl gave higher ratio of *cis*- to *trans*-stilbene oxide products than with other metalloporphyrins such as Cr(TPP)-Cl, Fe(TPP)Cl, Co(TPP), and Ni(TPP). With the metal cyclam complexes in acetonitrile, only the manganese cyclam complex gave a comparable yield of *cis*-stilbene oxide relative to that of *trans*-stilbene oxide; other cyclam complexes of iron, cobalt, and copper yielded less *cis*-stilbene oxide than *trans*-stilbene oxide as in the metalloporphyrin systems. We also tested manganese(II) acetylacetonate and manganese(II) phthalocyanine in the *cis*-stilbene oxidations in dichloroethane. The ratio of *cis*- to *trans*-stilbene oxides obtained in the reactions was 1.0, implying that the product ratios were not seriously influenced by the types of ligands bound to manganese. Even in the absence of metal complexes in acetonitrile solution, the oxidation of *cis*-stilbene gave the mixture of *cis*- and *trans*-stilbene oxides with a low ratio of the *cis*- to *trans*-stilbene oxide products. In a control reaction, MCPBA (0.8 mmol) was added to a solution containing *cis*-stilbene (1 mmol) and isobutyraldehyde (1 mL) in CH_3CN (5 mL). The reaction was stirred for an hour under Ar. Only the *cis*-stilbene oxide (10% based on MCPBA) and not *trans*-stilbene oxide was detected in the products.

The reactivities of *para*-substituted styrenes relative to that of styrene were determined in the O_2 plus aldehyde reactions in the presence of cobalt or manganese cyclam complexes or a manganese porphyrin complex or in the absence of any metal complexes. The relative rates for various substituents, X, are listed in Table 5. Hammett treatments of the relative reactivities of various substituents against σ^+ gave ρ values of -0.78, -0.73, -0.45, and -0.55 for the cobalt cyclam complex, no metal complex, manganese cyclam complex, and manganese porphyrin complex, respectively (see Figure 2). The ρ values obtained with the cobalt cyclam complex and with no catalyst were the same within experimental error, whereas the manganese cyclam complex gave a different ρ value. The Hammett ρ value of -0.45 with Mn(TPP)Cl was the same as the ρ values obtained in the epoxidation of 4-X-styrenes with NaOCl−Mn(TPP)OAc and with NaOCl−Mn(TMP)Cl.[8]

Discussion

It has often been assumed that high-valent metal oxo species are the most likely active intermediates when olefins are selectively oxidized to the corresponding epoxides in metal complex-catalyzed oxygen atom transfer reactions. Thus, when epoxides were observed to be formed as the major products in the reactions of O_2 plus aldehyde in the presence of metal complexes, it was suggested that high-valent metal oxo complexes were the active intermediates for oxygen atom transfer.[4] By contrast, we and others have reported recently that other species such as metal-iodosylbenzene complexes[9] and metal−OOR complexes[2d,10,11] ($R = H$, CR'_3, $C(O)R'$), which are the

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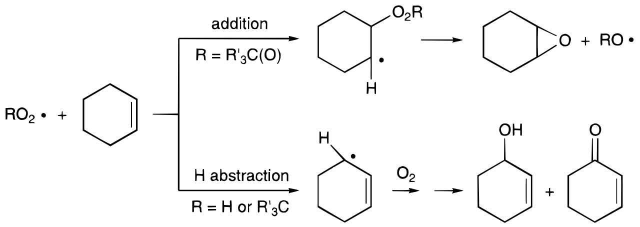
(8) Bortolini, O.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1967.

Scheme 2



precursors to the high-valent metal oxo complexes, are sometimes themselves competent as epoxidizing agents that can react directly with olefins. Therefore, we have studied the epoxidation of olefins by O_2 plus aldehyde in order to determine whether or not species other than high-valent metal oxo species might be implicated.

When epoxidations of cyclohexene were carried out using various kinds of metal complexes, all of the reactions gave cyclohexene oxide as the predominant product, and the product distributions were not dependent on the identity of the individual metal complexes. In addition, we discovered that the reaction proceeded without any metal complexes at all. The product distributions were the same whether or not a metal complex was added, leading us to conclude that high-valent metal oxo complexes are not required for the epoxidation reaction to take place. We therefore conclude that this reaction proceeds by a mechanism different from that previously proposed and, since the reaction proceeds readily in the absence of any metal complex, that the acylperoxy radical, which is generated *in situ* during the reaction of dioxygen and aldehyde, is the most plausible epoxidizing agent in this system. It has been previously shown that the acylperoxy radical generated in the radical reaction of dioxygen and aldehyde is a competent oxidizing agent for olefin epoxidations.[12] The acylperoxy radical has a greater tendency to yield epoxides by addition to the double bond of olefins rather than to abstract an allylic hydrogen atom of the olefins to give allylic oxidation products, whereas hydroxy and alkylperoxy radicals tend to abstract an allylic hydrogen (Scheme 2).[13]

Another possible epoxidizing agent in this system, i.e. percarboxylic acids, must also be evaluated as potential epoxidizing intermediates since such peracids can be formed from reaction of acylperoxy radicals with aldehydes (see Scheme 1). Peroxy acids are known to epoxidize *cis*-stilbene stereoselectively to give only the *cis*-oxide as product. We therefore studied the oxidation of *cis*-stilbene in the O_2 plus aldehyde reactions in the absence of metal complexes, and we found that *trans*-stilbene oxide was the predominant product. By contrast, we found that only *cis*-stilbene oxide was produced when MCPBA was reacted with *cis*-stilbene under our reaction conditions in the presence of isobutyraldehyde. Therefore, we can conclude that the epoxidizing intermediate is not the peroxyacid, presumably because the rate of the reaction of the acylperoxy radical with *cis*-stilbene is faster than that of its reaction with aldehyde under our reaction conditions (see Scheme 3).[13]

The ratios of *cis*- to *trans*-stilbene oxide obtained in the dioxygen plus aldehyde system have been determined using various kinds of metal complexes. In the Fe(TPP)Cl-catalyzed oxidation of *cis*-stilbene by single oxygen atom donors such as PhIO and MCPBA, *cis*-stilbene oxide was formed as the major product.[14] In these reactions, a high-valent iron oxo complex is believed to be the active intermediate for the oxygen atom transfer. Comparing these results to that of the O_2 plus aldehyde reaction, we can conclude again that the active oxidizing agent generated in the O_2 plus aldehyde reactions is not the high-valent iron oxo complexes. Instead, we propose an acylperoxy radical as a more plausible epoxidizing agent. However, if the acylperoxy radical is the sole oxidizing agent, then the ratios of *cis*- to *trans*-stilbene oxides should not depend on the kind of metal complex. Since the product ratios varied with the metal complexes used, particularly in the case of manganese complexes, we suggest that, under some conditions, there may be another intermediate in addition to the acylperoxy radical that is responsible for some fraction of the oxidation of olefins in our system. One possibility that appears reasonable to us is that the acylperoxy radical interacts with the metal complex.[3b] The epoxidizing intermediate may then be either a metal−peracid complex or a metal oxo complex generated from it.

The results discussed above have been further confirmed by studying competitive reactions between *para*-substituted styrenes and styrene. The negative ρ values obtained in all of the reactions of O_2 plus aldehyde and the better correlation against σ^+ indicate the electrophilic character of the transferred oxygen atom of intermediates. The ρ values for the cobalt cyclam complex and for no metal complex were the same, suggesting that an identical intermediate, which may be an acylperoxy radical, was generated in both reactions. In the case of the manganese cyclam-mediated reaction, a different ρ value was obtained, indicating that the mechanism is changed in some way by the presence of the manganese complexes.[3b] This observation is similar to that made in the case of the *cis*-stilbene oxidation described above.

Finally, we discuss the role that the metal complexes may play in the initiation step of this radical chain process. Two different suggestions for the formation of a radical species from an aldehyde have been made in the literature: (1) Transition metals may function as oxidizing agents to produce acyl radicals from an aldehyde as shown in eq 2.[5]

$$M^{n+} + RCHO \rightarrow M^{(n-1)+} + RC(O)^{\bullet} + H^{+} \qquad (2)$$

In this case, transition metals with high reduction potentials [$M^{n+} + e^{-} = M^{(n-1)+}$] should initiate the radical reaction readily. In our systems, we consider that this possibility is unlikely since our metal complexes are not good oxidizing agents, i.e. have low reduction potentials. (2) The second suggestion is that transition metals bind O_2 to form $M{-}OO^{\bullet}$ species which have sufficient radical character to abstract a hydrogen atom from an aldehyde to yield an acyl radical (eq 3).[15]

$$M^{n+} + O_2 \rightarrow (M{-}OO^{\bullet})^{n+} \xrightarrow{RCHO} (M{-}OOH)^{n+} + RC(O)^{\bullet} \qquad (3)$$

This mechanism may be operating in our systems, but, alternatively, the metal complexes may be simply catalyzing

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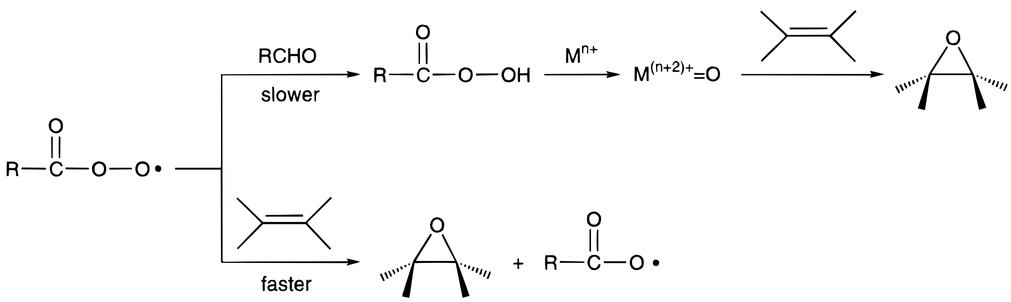
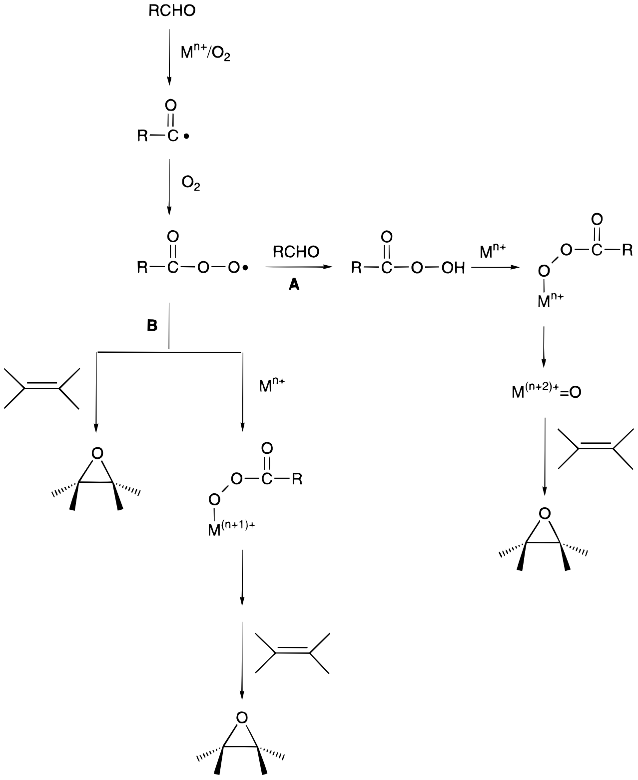
Scheme 3



Scheme 4



the formation of free radicals from traces of peroxidic impurities in the solvents or reagents. In any case, our observation of similar reactivity in the absence of any added metal complex suggests that the nature of the initiation reactions has little influence on the overall course of the reaction.

In summary, a mechanism for the epoxidation of olefins by dioxygen plus aldehyde in the presence of metal complexes has been proposed (see Scheme 4). The evidence described above suggests that pathway **B** is usually favored over pathway **A** under the conditions of our experiments. In pathway **B**, the acylperoxy radical reacts either with olefins to yield epoxides directly or with metal complexes to form metal−peroxy complexes, depending on the kind of metal ions. The metal−peroxy species, then, transfers an oxygen atom directly to olefins or forms metal oxo species by the oxygen−oxygen bond cleavage of the peroxy group. As discussed above, we conclude that several reaction pathways are operating concurrently for the epoxidation of olefins by dioxygen plus aldehyde. We also suggest that the formation of epoxide is not an adequate evidence for the intermediacy of high-valent metal oxo complexes for oxygen atom transfer reactions, since organic peroxy radicals[12,16,17] as well as metal complexes such as metal−iodosylbenzene complex,[9] metal−hydroperoxide,[2d] metal−alkylperoxide,[10] and metal−peroxyacid[11] have a tendency to yield epoxides.

Experimental Section

Materials. Acetonitrile and 1,2-dichloroethane were refluxed over CaH_2 and distilled under argon. Acetonitrile for HPLC was purchased from Fisher Scientific Co. (HPLC grade) and filtered before use. HPLC water was triply deionized. All other reagents were purchased from Aldrich Chemical Co. and used without further purification unless otherwise indicated. Metal (Mn^{2+}, Co^{2+}, Fe^{2+}) triflates were prepared by refluxing appropriate metal salts and vacuum-distilled trifluoromethanesulfonic acid.[18] Metal cyclam complexes were prepared by reacting metal triflates with cyclam ligand in acetonitrile.

Instrumentation. UV/vis spectra were recorded on a Hewlett Packard 5890 spectrophotometer. Product analyses were performed on a Donam Systems DS6200 gas chromatograph equipped with an HP-1 capillary column. The products of *cis*- and *trans*-stilbene reaction were analyzed by Waters Model 440 High Performance Liquid Chromatography equipped with a C18 column.

General Epoxidation Reactions. In a typical procedure, metal complex (0.02 mmol), olefin (3 mmol for cyclohexene, 1 mmol for *cis*- and *trans*-stilbenes, 2 mmol for (+)-limonene and norbornene), an appropriate aldehyde (1 mL), and an inert internal standard were dissolved in CH_3CN (5 mL) for metal cyclam complexes or $ClCH_2CH_2Cl$ (5 mL) for metalloporphyrins. Dioxygen (2 mL/min) was bubbled through the reaction solution, and then the products were analyzed by either GC or HPLC.

For the competitive reactions between *para*-substituted styrenes and styrene, dioxygen was bubbled through the reaction solution containing styrene (0.15 mmol), *para*-substituted styrene (0.15 mmol), isobutyraldehyde (1 mL), and metal complex (0.02 mmol). The amounts of olefins before and after reactions were determined by GC. The relative reactivities were determined using eq 4, where X_i and X_f are the initial

$$k_x/k_y = (\log(X_f/X_i))/(\log(Y_f/Y_i)) \qquad (4)$$

and final concentrations of *para*-substituted styrenes, and Y_i and Y_f are the initial and final concentrations of styrene.

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