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A manganese(III) porphyrin/rhodium(III) bipyridine/formate catalyst system for the reductive activation of molecular oxygen

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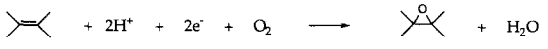
Abstract

A two-phase system utilizing a rhodium(III) bipyridine complex and a manganese(III) porphyrin in the presence of sodium formate for the reductive activation of molecular oxygen and the subsequent epoxidation of alkenes is described. In this system, the reducing equivalents for the conversion of Mn^{III} to Mn^{II} are obtained from the rhodium-catalyzed oxidation of formate to carbon dioxide.

Keywords: Manganese(III) porphyrin; Rhodium(III) bipyridine; Reductive activation; Molecular oxygen

1. Introduction

The structure and function of a class of enzymes called monooxygenases have been the inspiration for the design of some synthetic catalytic systems capable of the reductive activation of molecular oxygen [1–8]. Monooxygenases are responsible for the enzymatic transformation of many endogenous substrates as well as xenobiotics. Organic substrates are functionalized by these enzymes to increase their solubility and to facilitate their excretion from the body. Cytochrome P-450 is a monooxygenase that, among other reactions, catalyzes the epoxidation of alkenes [9,10]. In general terms this process can be described by Eq. (1).



In the case of cytochrome P-450, the two electrons are provided by NAD(P)H which reduces cytochrome P-450 reductase [10,11]. The exquisite control rendered by the enzyme system which delivers precisely two electrons to the Fe^{III} center at the right time during the catalytic cycle, is difficult to mimic in the laboratory, but it is this step, i.e., the reduction of the Fe^{III} or Mn^{III} center (in the case of enzyme mimics) to the corresponding Fe^{II} or Mn^{II} ion that is one of the crucial steps in the catalytic cycle [1]. Attempts described in the literature to utilize molecular oxygen as the oxidant in conjunction with a reductant have only been marginally successful, largely due to the inability to control the number of reducing equivalents [4–8]. Too many reducing equivalents in the vicinity of the $Mn^{V}=O$ species will reduce

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it to Mn^{III} and water, with the result that no oxidation products are formed (Fig. 1).

Previous investigations in our laboratory made use of vesicle preparations for modeling the complete catalytic cycle of cytochrome P-450 and for controlling the electron flow to the Mn^{III} porphyrin [8]. In a vesicle preparation, the reactants are kept separated from one another by the nature of the bilayer structure. In the course of these investigations it was discovered that the rhodium complex $[Rh^{III}bipyCp^*Cl]Cl$ (bipy = 2,2′-bipyridine, $Cp^* = \eta^5\text{-}C_5Me_5$) was able to catalyze the reduction of Mn^{III} porphyrin to Mn^{II} porphyrin by sodium formate efficiently [12]. Because our goal was to develop a laboratory scale synthetic method for the epoxidation of alkenes using molecular oxygen as the oxidant it was desirable to simplify the reaction conditions without decreasing the reactivity of the catalyst.

We chose a system that imposed some order on the components of the reaction, but did not require the use of vesicles. The two-phase reaction system with both hydrophilic and hydrophobic regions separates the catalyst from the electron source. The rhodium bipyridyl complex with the rhodium ion in the 3^+ state is ionic and soluble in the aqueous phase while the alkene substrate and $Mn^{III}TPP$ catalyst are soluble in the organic phase. The reduced (neutral) rhodium(I) complex migrates into the organic layer where it can subsequently reduce the Mn^{III} porphyrin. By exploiting the different partitions

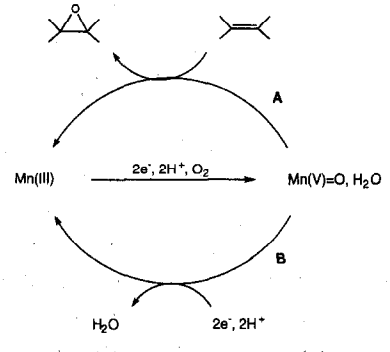


Fig. 1. Productive (A) and unproductive (B) pathways in the reaction of the $Mn^V{=}O$ species.

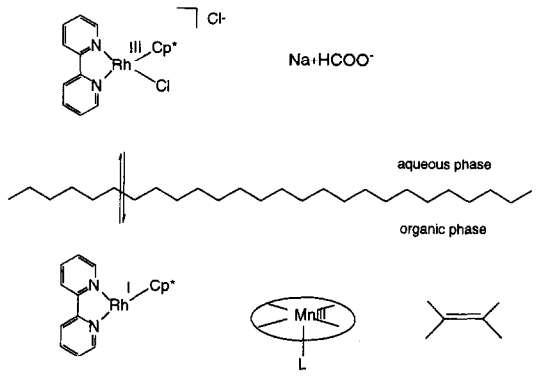


Fig. 2. Representation of the two-phase catalytic system with $Mn^{III}TPP$ as catalyst and the cationic $Rh^{III}bipyCp^*Cl$ acting as a co-reductant and as a phase-transfer catalyst.

of the oxidized and reduced rhodium species we are able to achieve a degree of separation between the electron source and the manganese porphyrin. In the two-phase system described here, Mn^{III}tetraphenylporphyrin (MnTPP) is the catalyst and $Rh^{III}bipyCp^*Cl$, in conjunction with sodium formate, is the source of electrons. Because of different solubilities in the oxidized and reduced states, the $Rh^{III}bipyCp^*Cl$ complex acts as a phase-transfer catalyst (Fig. 2). Preliminary results with this system were described in a previous communication [13].

2. Results

2.1. Reduction of Mn^{III}tetraphenylporphyrin under two-phase conditions

In order to determine the optimal reaction conditions for epoxidation, we investigated the efficacy of the $Rh^{III}bipyCp^*Cl$/formate couple to reduce $Mn^{III}TPP$ to $Mn^{II}TPP$ under two-phase conditions.

When a 10^{-5} mol dm^{-3} solution of $Mn^{III}TPP$ in dichloromethane was placed in a quartz cuvet and treated with an aqueous solution of sodium formate (0.5 mol dm^{-3}) and $Rh^{III}bipyCp^*Cl$ (5.0 mmol dm^{-3}) (pH 8.0) at 40°C under an atmosphere of argon, we observed, after several minutes, an intense green coloring in the or-

ganic phase. The UV-vis. spectrum of this solution showed that the Soret band at 470 nm had disappeared and that a new absorption band at 441 nm had formed. This new absorption band is characteristic of a $Mn^{II}TPP$ complex. In the absence of the rhodium complex or sodium formate, no reduction took place.

The proposed mechanism for the reduction of $Mn^{III}TPP$ by the $Rh^{III}bipyCp^*Cl$/formate couple is shown in Scheme 1.

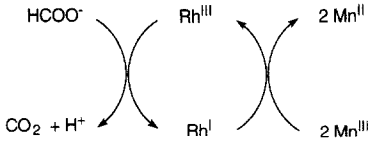
Although the reduced Rh^{I} species is potentially a two-electron reductant, it is capable of reducing $Mn^{III}TPP$, a one-electron substrate. The Rh^{II} species thus formed is able to reduce another molecule of $Mn^{III}TPP$, or form dimeric Rh^{II} species which would disproportionate into the more stable Rh^{I} and Rh^{III} forms [14].

The two-phase system precluded carrying out kinetic studies on the reduction of $Mn^{III}TPP$, but the efficacy of the reduction could be measured by determining the percentage of $Mn^{II}TPP$ formed after a predetermined period of time. The effect of the concentration of $Rh^{III}bipyCp^*Cl$ on the reduction of $Mn^{III}TPP$ to $Mn^{II}TPP$ is shown in Fig. 3.

The reduced rhodium complex must cross the aqueous/organic interface, therefore, a large excess of the rhodium complex is necessary for an efficient reduction of $Mn^{III}TPP$. From Fig. 3, it can be seen that a linear relationship exists between the concentration of $Rh^{III}bipyCp^*Cl$ and the rate of formation of $Mn^{II}TPP$ from $Mn^{III}TPP$. It can also be seen that a minimum amount of 0.5×10^{-3} mol dm^{-3} of the rhodium complex is required for the reaction to take place.

2.2. Effect of additives on the reduction reaction

A number of components are present during the actual epoxidation reaction, and the effect of each of these additives on the reduction of $Mn^{III}TPP$ was investigated. The alkene substrates themselves did not affect the reduction reaction, nor did the presence of benzoic acid anhydride, [1,15] which is used to facilitate the



Scheme 1.

splitting of the oxygen–oxygen bond to form the $Mn^{V}=O$ species. A marked effect, however, was observed on the reduction reaction in the presence of imidazole, which acts as an axial ligand that binds to the manganese center of the tetraphenylporphyrin macrocycle. An axial ligand is needed to favor heterolytic cleavage of the oxygen–oxygen bond and to stabilize the $Mn^{V}=O$ species that is formed as the result of the reductive activation of dioxygen [15,16]. As can be seen from Fig. 4, however, the presence of even a small amount of imidazole in the aqueous phase severely inhibits the reduction of $Mn^{III}TPP$.

Forty equivalents of imidazole (with respect to the amount of $Mn^{III}TPP$) are sufficient to completely inhibit the reduction of $Mn^{III}TPP$ to $Mn^{II}TPP$. This inhibition is most likely due to the fact that imidazole competes for the coordination site on the rhodium atom which must be occupied by formate to obtain reduction of the rhodium atoms (Scheme 2).

To avoid this complication, other imidazoles, modified with long alkyl chains, were tested for

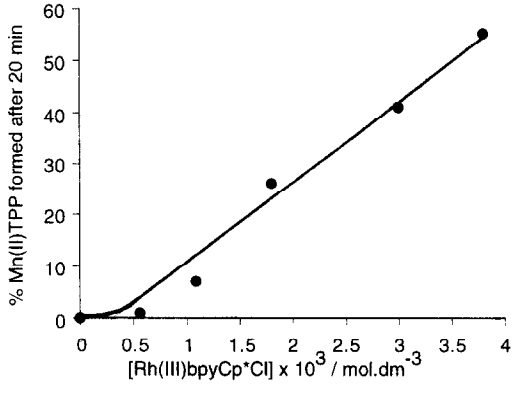


Fig. 3. Effect of $Rh^{III}bipyCp^*Cl$ concentration on the reduction of $Mn^{III}TPP$. $[Mn^{III}TPP] = 1.0 \times 10^{-5}$ mol dm^{-3}, $T = 40°C$, 2.0 cm^3 trichloroethane, 1.0 cm^3 of an aqueous solution (0.5 mol dm^{-3}) sodium formate, pH 7.5, argon atmosphere.

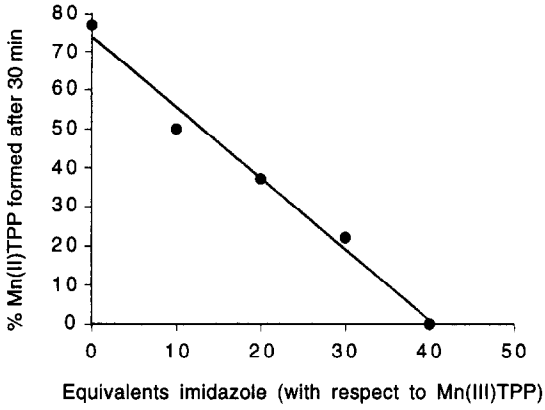


Fig. 4. Inhibition of the reduction of $Mn^{III}TPP$ to $Mn^{II}TPP$ by imidazole under two-phase conditions, under an argon atmosphere. For reaction conditions see Fig. 3. $[Rh^{III}bipyCp^*Cl] = 4.0 \times 10^{-3}$ mol dm^{-3}.

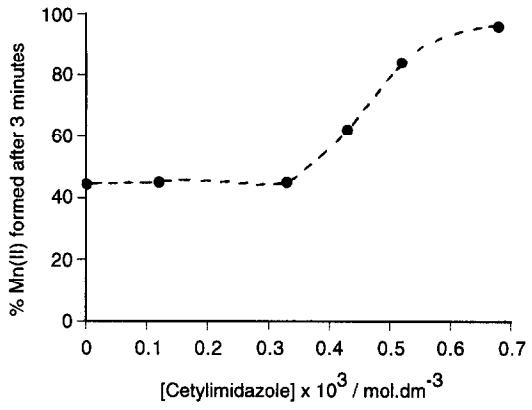


Fig. 5. Percent $Mn^{II}TPP$ formed after 3 min vs. the concentration of *N*-cetylimidazole. For reaction conditions see Fig. 3. $[Rh^{III}bipyCp^*Cl] = 4.0 \times 10^{-3}$ mol dm^{-3}.

their effect on the reduction reaction. These imidazoles are only soluble in organic media. They are, therefore, not present in the aqueous layer and are unable to inhibit the formation of the Rh^{III}hydride. Both *N*-cetylimidazole (C_{16} alkyl chain) and *N*-decylimidazole (C_{10}) had no inhibiting effect on the reduction of Mn^{III} to Mn^{II} not even in amounts as high as 100 eq. (with respect to $Mn^{III}TPP$) (Fig. 5).

Once the hydride is formed, competing coordinating ligands appear not to inhibit the reduction of $Mn^{III}TPP$. This result is in agreement with the proposed mechanism for the formation of the rhodium–hydride as illustrated in Scheme 2. In fact, as can be seen from Fig. 5, the presence of long-chain imidazoles increased the rate of the reduction of $Mn^{III}TPP$. At low concentrations, between zero and 0.32 mol dm^{-3} *N*-cetylimidazole, no enhancement of the reduction of $Mn^{III}TPP$ to $Mn^{II}TPP$ was observed, but at higher concentrations, there appears to be a linear correlation between the concentration of cetylimidazole and the efficiency at which the

$$[Rh^{III}]^{2+} + HCOO^- \rightleftharpoons [Rh^{III}—HCOO]^+$$

$$[Rh^{III}—HCOO]^+ \longrightarrow [Rh^{III}—H]^+ + CO_2$$

Scheme 2.

Mn^{III} central metal atom was reduced to Mn^{II}. The unexpected effect of cetylimidazole can be explained if the orientation of the $Mn^{III}TPP$ molecules at the water/dichloromethane interface is assumed to be as depicted in Fig. 6.

Previous work by Kölle [17] and Steckhan and co-workers [18,19] has demonstrated that the reduction of rhodium bipyridyl complexes by formate is dependent on the pH of the aqueous solution. Kölle found that in acidic pH

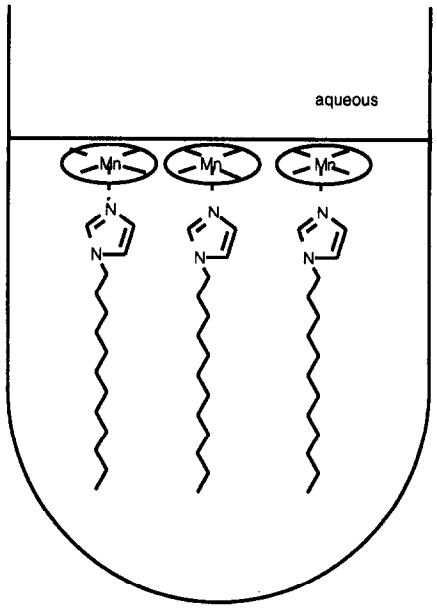


Fig. 6. Proposed orientation of the complex between $Mn^{III}TPP$ and *N*-cetylimidazole at the water/dichloromethane interface.

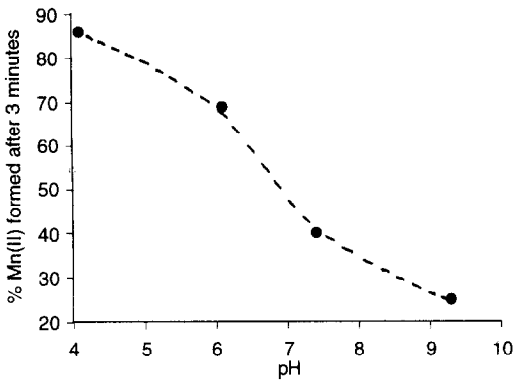


Fig. 7. Amount of $Mn^{II}TPP$ formed (shown as percentage) after 3 min at various pH values of the aqueous layer. For reaction conditions see Fig. 3. $[Rh^{III}bipyCp^*Cl] = 4.0 \times 10^{-3}$ mol dm^{-3}.

(< 7.5), the reduction of the Rh^{III} complex to Rh^{I} was irreversible, presumably because the Rh^{I} species are protonated.

To study the effect of the pH of the aqueous layer on the reduction of $Mn^{III}TPP$ to $Mn^{II}TPP$, we looked at the amount of $Mn^{II}TPP$ that was formed in the organic layer after 3 min at varying pH. The results are shown in Fig. 7.

At pH 4.0, almost 90% of $Mn^{III}TPP$ was reduced to $Mn^{II}TPP$ after three minutes. At pH 9.4 only 22% of $Mn^{II}TPP$ was formed after the same period of time. Previous work in our laboratory on $Rh^{III}bipyCp^*Cl$ complexes that were anchored in vesicle systems showed a decrease in activity at lower pH [13,12], whereas in the two-phase system described here we found that at low pH the reduction of $Mn^{III}TPP$ to $Mn^{II}TPP$ was enhanced. This result can be explained by the fact that the pH strongly influences the nature of the rhodium species that are formed in aqueous solution.

To investigate the rhodium species that are present in solution at varying pH, UV–vis. spectra were taken of $Rh^{III}bipyCp^*Cl$ and formate in water at different pH values. At low pH (pH 4.0), the UV–vis. spectrum initially showed a peak at 530 nm which gradually disappeared and was replaced by a peak at 610 nm. Due to the acidic conditions, the peak at 610 nm can most probably be ascribed to the protonated Rh^{I} complex (which is identical to the Rh^{III}hydride). In basic solution, (pH 7.5–9.5) the λ_{max} was at 511 nm which corresponds to the Rh^{I} complex that has been reported in the literature [17]. The Rh^{III}hydride, which is present in acidic solution appears to be more efficient at reducing $Mn^{III}TPP$ to $Mn^{II}TPP$ than the Rh^{I} complex which is formed in basic solution. Both species, however, are able to reduce the Mn^{III} atom, albeit at varying degrees of efficiency as illustrated in Fig. 7.

Using UV–vis. spectroscopy, we attempted to observe the presence of the Rh^{I} species in the organic layer under two-phase conditions. Only after all of the $Mn^{III}TPP$ had been reduced to $Mn^{II}TPP$ did a band at 520 nm appear, which is characteristic of the Rh^{I} complex, taking into account the differences in the solvent.

Although the rhodium bipyridyl complex itself acts as a phase transfer catalyst under the two-phase system described here, we were interested in determining the influence of a standard phase-transfer-catalyst such as a quaternary ammonium salt on the reduction of $Mn^{III}TPP$. The effect of a catalytic amount of benzyltributylammonium chloride to the two-phase solution is shown in Fig. 8.

A small amount of phase transfer catalyst had no effect on the rate of reduction $Mn^{III}TPP$ to $Mn^{II}TPP$. In a 3.0 mmol dm^{-3} solution of

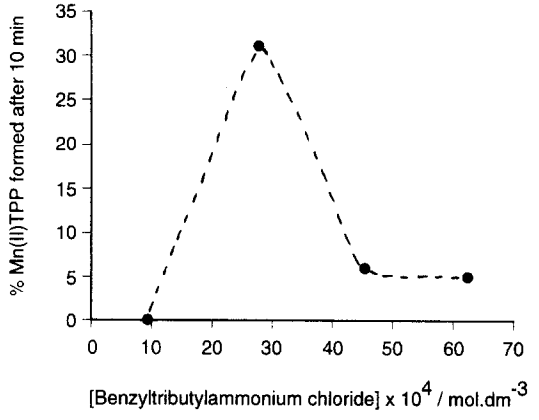


Fig. 8. Effect of a phase transfer catalyst (benzyltributylammonium chloride) on the reduction of $Mn^{III}TPP$ to $Mn^{II}TPP$. For reaction conditions see Fig. 3. $[Rh^{III}bipyCp^*Cl] = 4.0 \times 10^{-3}$ mol dm^{-3}.

phase transfer catalyst, however, the amount of $Mn^{II}TPP$ formed after 10 min was markedly enhanced. More concentrated solutions of benzyltributylammonium chloride inhibited the reduction of $Mn^{III}TPP$ to $Mn^{II}TPP$, probably due to the increased concentration of the chloride ion in solution which will shift the equilibrium of the formation of the Rh^{III}–HCOO species to the left (see Scheme 2). The reason for the positive effect of benzyltributyl ammonium chloride is not yet clear. A possible explanation may be the formation of benzyltributyl ammonium formate which can enter the organic phase and immediately reduce any rhodium(III) species that is formed from the reaction of Rh^{I} and $Mn^{III}TPP$.

2.3. Epoxidation

Once the appropriate reaction conditions for the efficient reduction of $Mn^{III}TPP$ had been determined it was possible to carry out epoxidation reactions under two-phase conditions. Epoxidation reactions were carried out with several alkene substrates under different oxygen pressures and in the presence or absence of benzoic anhydride. The results are summarized in Table 1.

The highest turnover numbers were obtained in the presence of benzoic anhydride. Benzoic anhydride has been shown to assist in the splitting of the oxygen–oxygen bond, as reported in the literature [1,15]. The oxygen pressure did not appear to have a large influence on the reaction, with approximately equal amounts of nerol epoxide being formed under 1.0 atm of oxygen and under air. In all cases, the formation of epoxide stopped after 30–60 min. Even running the reaction from several hours to overnight did not result in an increase in epoxide yield. We presumed that the $Mn^{III}TPP$ was still viable due to the characteristic dark green/brown color of the reaction mixture indicative of $Mn^{III}TPP$. Spectral evidence, however, showed that the $Mn^{III}TPP$ catalyst was completely degraded after 1 h of reaction. The characteristic Soret band at 470 nm in the UV–vis. spectrum had disappeared, indicating complete decay of the complex. The degradation of the $Mn^{III}TPP$ catalyst was followed over time and the results are shown in Fig. 9.

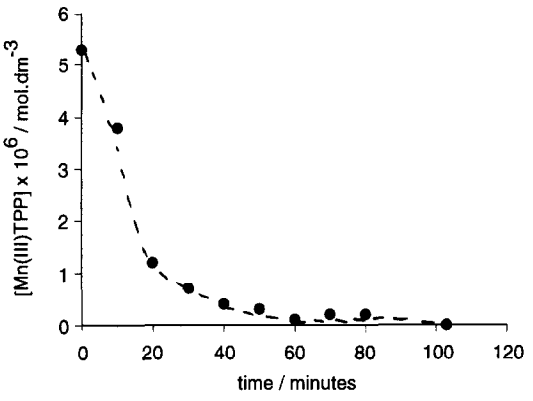


Fig. 9. Decay of $Mn^{III}TPP$ under the reaction conditions (Table 1) used for epoxidation.

This rapid degradation of the Mn^{III}porphyrin catalyst is quite remarkable in view of the fact that $Mn^{III}TPP$ has been shown to be stable under a variety of oxidizing conditions [20,21]. We hoped to improve the number of turnovers and increase the yield of epoxide formed by replacing the $Mn^{III}TPP$ with a more robust catalyst. We chose $Mn^{III}TPP$ complexes that are modified with electron-withdrawing substituents at the *ortho* positions in the phenyl rings as well as porphyrins with completely substituted

Table 1
Epoxidation results with $Mn^{III}TPP/Rh^{III}bipyCp*Cl$/formate in a two-phase system [a]

Substrate	$[(PhCO)_2]/M^{-1}$	P_{O_2}/mmHg	Turnover number [b]
α-Pinene	0.05	160	30
Nerol	0.05	0	< 1
Nerol	0.05	160	18
Nerol	0.05	760	17
Nerol	0	160	8
cis-Stilbene	0.05	160	42

[a] Reaction conditions: 0.285 mol dm^{-3} alkene, 0.1 mmol dm^{-3} MnTPP, 5.0 mmol dm^{-3} $Rh^{III}bipyCp^*Cl$, 10.0 mmol dm^{-3} *N*-decylimidazole, 0.5 mol dm^{-3} sodium formate; 2.0 cm^3 trichloroethane/H_2O, 1:1 v/v, 40°C, pH 8.0.
[b] Total turnovers during the course of the reaction.

phenyl rings. These so-called 'second generation' porphyrins [22–26] are less susceptible to attack at the *meso*-positions due to both steric effects from the substituents and the electron-withdrawing effect which makes the *meso*-position less favorable to electrophilic degradation. The results of epoxidation reactions carried out with these catalysts are shown in Table 2.

Turnover numbers were not improved for two reasons. All of the catalysts shown in Table 2 except for $MnTF_5PP$ decayed within a short period of time (ca. 1 h) in a similar manner to that of $Mn^{III}TPP$. $Mn^{III}TF_5PP$ appeared to be stable under the reaction conditions, but the affinity for oxygen of this complex was severely reduced, probably as a result of the extreme electron-withdrawing effect of the penta-fluorinated phenyl rings [27,28].

Clearly a strongly oxidizing species is formed during the course of the reaction which is responsible for the degradation of the porphyrin catalysts. It is known that rhodium bipyridyl complexes are capable of forming per- or superoxo rhodium species in the presence of a reducing agent under basic conditions [29–32]. Furthermore, these rhodium–superoxo complexes are able to oxidize Fe^{II} to Fe^{III}. Because our epoxidation system includes a rhodium(III) bipyridyl complex in the presence of a reducing agent, we attempted to establish a relationship

Table 2
Epoxidation results using substituted manganese porphyrins as catalysts [a]

Porphyrin catalyst	Substrate	Total turnover
$MnTCl_2PP$	α-Pinene	3
$MnTCl_2PP$	Styrene	4
$MnTCl_5PP$	α-Pinene	0
$MnTF_5PP$	α-Pinene	8

[a] Reaction conditions: 0.285 mol dm^{-3} alkene, 0.1 mmol dm^{-3} Mn^{III}porphyrin, 5.0 mmol dm^{-3} Rh^{III}bipyCp*Cl, 10.0 mmol dm^{-3} *N*-decylimidazole, 0.2 mol dm^{-3} benzoic anhydride, 1.0 cm^3 0.5 mol dm^{-3} sodium formate, pH 8.0, 2.0 cm^3 trichloroethane/H_2O, 1:1 v/v; P_{O_2} = 160 mmHg, 40°C. $MnTCl_2PP$ = 5,10,15,20-[tetrakis-2,6-dichlorophenyl)porphyrin]-Mn^{III}; $MnTCl_5PP$ = 5,10,15,20-[tetrakis(pentachlorophenyl)porphyrin]Mn^{III}; $MnTF_5PP$ = 5,10,15,20-[tetrakis(pentafluorophenyl)porphyrin]Mn^{III}.

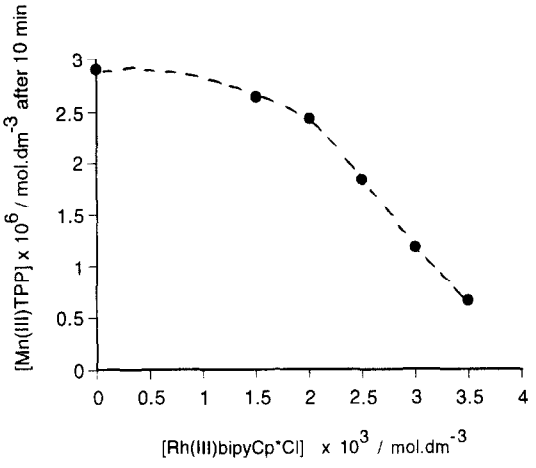


Fig. 10. Decay of $Mn^{III}TPP$ vs. Rh^{III}bipyCp*Cl concentration. For reaction conditions see Fig. 3.

between the concentration of rhodium complex present in solution and the rate of degradation of the $Mn^{III}TPP$. The results are shown in Fig. 10. It is clear from Fig. 10 that increasing the amount of rhodium in the reaction mixture increases the degree to which the $Mn^{III}TPP$ catalyst is degraded. Control reactions determined that the Rh^{III}bipyCp*Cl complex in its unreduced state is not responsible for the decay of the porphyrin.

There is also some spectral evidence for the presence of a rhodium-superoxo species that forms due to the interaction of the reduced rhodium species in the presence of oxygen. Two different spectral traces were observed when samples of water (pH 8.0) containing Rh^{III}bipyCp*Cl and formate ion were measured using UV–vis. spectroscopy either under argon or in the presence of oxygen. The spectrum of the solution containing oxygen also showed after several minutes the appearance of a peak at 600 nm which is indicative of rhodium–superoxo species according to results reported by Addison and Gillard [29].

If we assume that a rhodium–superoxo species is responsible for the fairly rapid degradation of the $Mn^{III}TPP$ catalyst we can try to alter the reaction conditions to prevent the formation of this highly oxidizing species. Control

Table 3
Epoxidation results with α-pinene at various pH [a]

pH of aqueous phase	Total turnover
4.0	0
5.0	0
6.0	6
7.0	10
8.0	30
9.0	3

[a] Reaction conditions: 0.285 mol dm^{-3} alkene, 0.1 mmol dm^{-3} MnTPP, 5.0 mmol dm^{-3} Rh^{III}bipyCp*Cl, 10.0 mmol dm^{-3} *N*-decylimidazole, 0.2 mol dm^{-3} benzoic anhydride, 1.0 cm^3 0.5 mol dm^{-3} sodium formate, pH 8.0, 2.0 cm^3 trichloroethane/H_2O, 1:1 v/v; P_{O_2} = 160 mmHg, 40°C.

experiments showed that in the absence of Mn^{III}TPP, no epoxides were formed. Therefore, the oxidizing rhodium species that is presumably generated is not capable of epoxidizing the substrate. Because evidence described in the literature [29] states that rhodium bipyridyl superoxo species are formed under basic conditions, we investigated the epoxidation of α-pinene under varying pH. The results are shown in Table 3.

These results suggest that the ideal conditions for the reduction of Mn^{III} may not translate into ideal conditions for the epoxidation of alkenes. While Mn^{III} is more easily reduced to Mn^{II} at pH 4, shown in Fig. 7, no epoxide was formed at this pH. At higher pH, epoxide is formed, but with concurrently faster degradation of the catalyst. At pH 4.0, the Mn^{III}TPP is not degraded, while at pH 9.0, the Mn^{III}TPP is degraded after approximately 30 min of reaction.

3. Discussion

We have shown that it is possible to carry out the reductive activation of molecular oxygen (and subsequent epoxidation of alkenes) using Rh^{III}bipyCp*Cl and formate ion as the source of electrons for the reduction of Mn^{III}porphyrin to Mn^{II}porphyrin. The epoxidation reactions were run in a two-phase system which was chosen to provide some separation of the Mn^{III}TPP catalyst from the reductant. Separation of the electron source from the porphyrin catalyst is necessary to avoid the unproductive pathway, that of the reduction of the active Mn^{V}=O species to water, as illustrated in Fig. 1. We were able to exploit the different solubilities of the oxidized and reduced forms of the rhodium bipyridyl complex so that it could behave as a phase-transfer catalyst. The rhodium species in the 3^+ state is ionic and soluble in the aqueous phase. As the neutral Rh^{I} species, the complex migrates into the organic layer where it reduces Mn^{III}TPP to Mn^{II}TPP. This slow diffusion of the reduced rhodium complex limits the amount of reducing equivalents in the immediate environment of the Mn^{III} porphyrin. Which reduced rhodium species, either the Rh^{I} or the Rh^{III}–hydride, is present in solution is dependent upon the pH of the aqueous layer. At high pH (9), the Rh^{I} species is predominant, and reduction of Mn^{III}TPP to Mn^{II}TPP is slower. At low pH (4), the Rh^{III}hydride species is predominant, and the reduction of Mn^{III} to Mn^{II} of the porphyrin molecule is faster. Because the reduced rhodium complex must cross the organic solvent/water interface, a 200-fold excess of Rh^{III}bipyCp*Cl respective to the amount of Mn^{III}TPP is necessary for efficient reduction of Mn^{III}TPP to occur.

We were also able to show that coordinating ligands such as imidazoles, which are used as axial ligands for Mn^{III}TPP, could compete for the site on the rhodium atom that must be occupied by formate ion for the formation of the rhodium hydride to occur. This competition by imidazole inhibits the reduction of Mn^{III}TPP to Mn^{II}TPP. Long chain imidazoles, such as *N*-cetylimidazole, that are only soluble in the organic phase, enhanced the rate of reduction, probably by positioning the Mn^{III}porphyrin molecules closer to the dichloromethane/water interface (Fig. 6).

Although we were able to show that Mn^{III}TPP can be efficiently reduced to Mn^{II}TPP under

two-phase conditions in the presence of Rh^{III}bipyCp*Cl and sodium formate, the subsequent epoxidation of alkene substrates proceeded less smoothly. Turnover numbers of 30 were achieved for α-pinene and 42 for *cis*-stilbene at pH 8.0. Despite their low values, these turnover numbers are in fact some of the highest reported in the literature for Mn^{III}porphyrin catalysts that use molecular oxygen as the terminal oxidant [2–8]. For an epoxidation system, however, these numbers are quite low and attempts to improve them were not successful for a number of reasons. The Mn^{III}TPP catalyst itself was not stable under the reaction conditions. Within 1 h of reaction time, the Mn^{III}TPP molecule was completely degraded. Even more robust porphyrins [22–26] such as the 'second-generation' *ortho*-substituted chloro-porphyrins, and the penta-substituted chloro- and fluoro-porphyrins were either completely degraded during the course of the reaction or, in the case of $Mn^{III}T_{penta}FPP$, were unreactive. The reason for this fast oxidative degradation of the Mn^{III} porphyrin catalysts is most likely due to a rhodium–superoxo species that forms as a result of the interaction between the reduced rhodium bipyridyl complex and molecular oxygen. These complexes have been reported in the literature as occurring when Rh^{III} complexes are in the presence of a reducing agent and a base [29]. The structure of these rhodium-superoxo complexes has been shown to be *trans*-dimers [29,32,33].

Varying the pH of the aqueous layer did not improve catalyst turnovers. Mn^{III}TPP was rapidly reduced to Mn^{II}TPP at pH 4.0, but no epoxide was formed at this pH. At higher pH, in contrast, i.e., pH 9.0, epoxide was formed, but the Mn^{III}TPP catalyst degraded rapidly. In fact, the more basic the aqueous layer was, the faster the porphyrin molecule was degraded. The optimum pH for the epoxidation reactions, or that which gave the highest turnover numbers was a pH between 7 and 8. In order to improve the turnover numbers and thus the yield of epoxide produced in the two-phase system, it is necessary to inhibit the interaction between the reduced rhodium complex and molecular oxygen. The rhodium complex in the 3^+ state appears to be inert to oxygen, so that increasing the rate of the electron transfer from reduced rhodium species to manganese(III) porphyrin may be suitable for increasing catalyst turnover rate and the overall efficiency of the reaction. Work on improving this system is in progress.

4. Experimental section

4.1. Materials

Unless indicated otherwise, all reagents were purchased from Aldrich and used as received. Trichloroethane and dichloromethane were distilled from $CaCl_2$ and stored over 4 Å molecular sieves. The water used in the two-phase epoxidation reactions was doubly distilled. Alkenes were purified by column chromatography over basic alumina gel (eluent = CH_2Cl_2).

4.2. Instrumentation

IR spectra were taken on a Perkin Elmer 1720-X Infra-red Fourier Transform spectrometer. GC-analyses were carried out on a Varian 3700 gas chromatograph equipped with a flame ionization detector, (column: CP-sil fused silica, 25 m, 25 μm diameter) coupled to a Hewlett Packard 3395 integrator. UV–vis. spectra were taken on a Perkin Elmer Lambda 5 spectrometer. Elemental analyses were determined with a Carlo Erba Ea 1108. Melting points were determined on a Jeneval polarization microscope THMS 600 hot stage and are uncorrected.

4.3. Syntheses

The porphyrins [34,35] and [Rh^{III} bipy Cp*Cl]Cl [36,37] were synthesized as reported in the literature.

4.4. Epoxidation reactions

A Schlenk tube (2.0 cm × 10.0 cm) was charged with 2.0 cm^3 of trichloroethane. To the solvent was added in the following order, 78 mm^3 (0.60 mmol) alkene, and benzoic anhydride (0.60 mmol). *N*-Cetylimidazole and Mn^{III} porphyrin were added to give a solution of 10.0 mmol dm^{-3} and 0.1 mmol dm^{-3}, respectively. Sodium formate (1.0 cm^3, pH 8.0) and Rh^{III}bipyCp*Cl_2 were added to the reaction mixture to give a final concentration of 0.5 mol dm^{-3} and 5.0 mmol dm^{-3}, respectively. The Schlenk tube was placed in a 40°C water bath and the two-phase solution was stirred vigorously in air. Stirring speeds for each reaction were kept constant at 1100 rpm, to ensure equivalent oxygen diffusion rates. At appropriate intervals the stirring was stopped and an aliquot of the organic layer was taken and analyzed by gas chromatography.

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