Reductive Activation of Dioxygen by a Manganese(III) Porphyrin–Rhodium(III)–Formate Catalytic System

Patricia A. Gosling, Jan H. van Esch, Marion A. M. Hoffmann and Roeland J. M. Nolte*

Department of Organic Chemistry, Nijmegen SON Research Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

A two-phase system employing a Mn/Rh redox couple is capable of catalysing the epoxidation of olefins by molecular oxygen.

The reductive activation of dioxygen by cytochrome P-450 has been the subject of intense investigation in the last decade because of its complex reaction mechanism and potential use in synthetic applications including the epoxidation of alkenes [eqn. (1)]. Various synthetic model systems have been

$$\text{Alkene} + 2H^+ + 2e + O_2 \rightarrow \text{Epoxide} + H_2O \qquad (1)$$

developed to mimic the enzymatic reactions of cytochrome P-450 with molecular oxygen, most of which involve the use of a metallo-porphyrin as catalyst, in combination with a reducing agent such as sodium borohydride, ascorbate, zinc or molecular hydrogen/Pt as cocatalyst.[2,3] In the course of our studies on membrane-bound cytochrome P-450 mimics,[3] we recently observed that the rhodium complex $[\mathrm{Rh^{III}}(\eta^5\text{-}C_5Me_5)(\mathrm{bipy})Cl_2]$ (bipy = 2,2′-bipyridyl) is an efficient catalyst for the reduction of manganese(III) porphyrins by sodium formate. Here we report that a two-phase system consisting of an aqueous sodium formate solution and a trichloroethane solution of manganese(III) tetraphenylporphyrin, $[\mathrm{Mn^{III}(tpp)}]$, together with $[\mathrm{Rh^{III}}(\eta^5\text{-}C_5Me_5)(\mathrm{bipy})Cl_2]$ as a redox-active phase transfer catalyst (Fig. 1) is able to epoxidise olefins under an atmospheric pressure of oxygen.

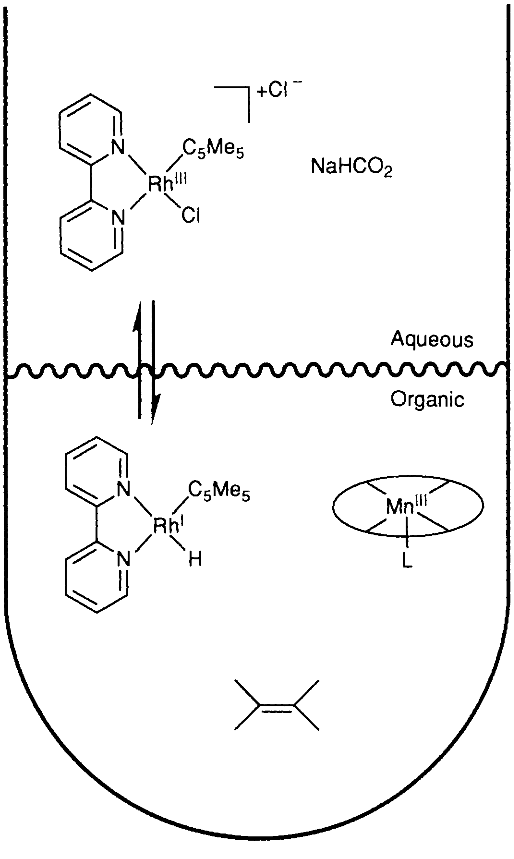

Fig. 1 Schematic representation of the catalytic system illustrating the role of the cationic $[\mathrm{Rh}(\eta^5\text{-}C_5Me_5)(\mathrm{bipy})Cl_2]$ as phase-transfer catalyst

When a solution of $[\mathrm{Mn^{III}(tpp)}]$ (2 mmol dm^{-3}; 2 ml) in dichloromethane was placed in a quartz cuvet and treated with 1.0 ml of an aqueous solution of sodium formate (0.1 mol dm^{-3}) and $[\mathrm{Rh}(\eta^5\text{-}C_5Me_5)(\mathrm{bipy})Cl_2]$ (5.0 mmol dm^{-3}) (pH 8.5) at 40 °C under an atmosphere of nitrogen, we observed an intense green colouring in the organic 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 (Fig. 2). This new absorption band is characteristic of an $[\mathrm{Mn^{II}(tpp)}]$ complex. In the absence of the rhodium complex or sodium formate no reduction took place. Presumably, the rhodium complex catalyses the reduction of

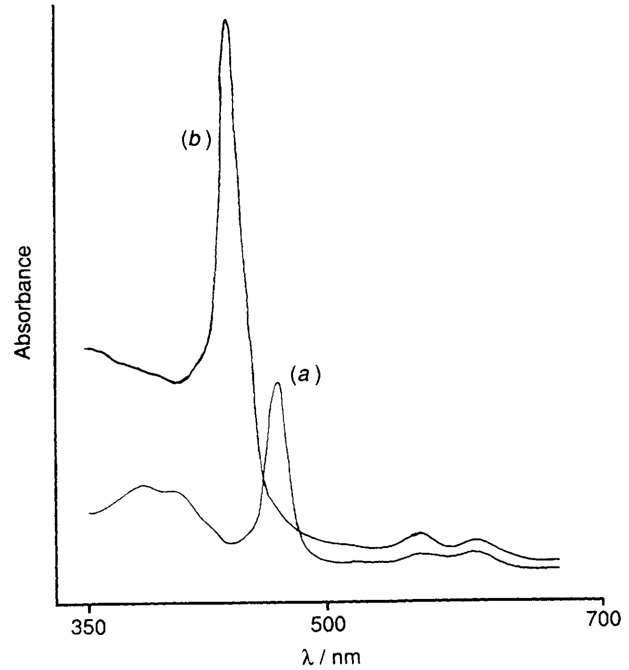

Fig. 2 UV-VIS absorption spectrum of solution of $Mn^{III}(tpp)$ (10^{-3} mol dm^{-3}) in dichloromethane after being treated with a sodium formate solution (0.1 mol dm^{-3}) without $[Rh(\eta^5\text{-}C_5Me_5)(bipy)Cl_2]$ (*a*), and with $[Rh(\mu^5\text{-}C_5Me_5)(bipy)Cl_2]$ (*b*). T = 40 °C, pH = 8.5

$[Mn^{III}(tpp)]$ in the organic phase by the formate ions in the aqueous phase. The presence of 5.0 mmol dm^{-3} of imidazole in the aqueous phase almost completely inhibited the reduction of $[Mn^{III}(tpp)]$, whereas the presence of 5.0 mmol dm^{-3} of *N*-decylimidazole in the organic phase had no effect on the reduction. It has been proposed[4] that the reduction of the rhodium complex proceeds *via* binding of formate ion to the rhodium centre. It is therefore reasonable to assume that inhibition of the reduction by imidazole is caused by competitive coordination of imidazole to the rhodium(III) centre. Since this inhibition is only observed when imidazole is present in the aqueous phase, reduction of the rhodium(III) complex must have already occurred before it diffuses to the organic phase since we observed no competitive inhibition on the reduction of $[Mn^{III}(tpp)]$ by *N*-decylimidazole.

In a subsequent series of experiments we tested whether this two-phase redox system was capable of catalysing the oxidation of olefins by molecular oxygen. In a typical reaction 1.0 ml of a trichloroethane solution of $[Mn^{III}(tpp)]$, (0.1 mmol dm^{-3}) *N*-decylimidazole (10.0 mmol dm^{-3}), benzoic anhydride (50.0 mol dm^{-3}) and substrate (0.285 mol dm^{-3}) was rapidly stirred with 1.0 ml of an aqueous solution of $NaHCO_2$ (0.1 mol dm^{-3}) and $[Rh(\eta^5\text{-}C_5Me_5)(bipy)Cl_2]$ (5.0 mmol dm^{-3}) (pH 8.5 titrated with Et_3N) at 40 °C under an atmospheric pressure of oxygen. Analysis of the organic phase by GLC showed that oxidation of the substrates had occurred (Table 1). The substrate α-pinene is selectively oxidised to the epoxide. Nerol gave a mixture of the 2,3-epoxide and the 6,7-epoxide in a molar ratio of approximately 1 : 2. Other oxidation products were only formed in trace amounts. In the absence of any one of the components, [Mn(tpp)], $[Rh(\eta^5\text{-}C_5Me_5)(bipy)Cl_2]$, sodium formate or oxygen no oxidation products were formed, and carrying out the reaction under an atmosphere of pure oxygen did not improve product yields. In the absence of benzoic anhydride the turnover numbers were much lower. Attempts to improve the efficiency of the reaction by changing the concentrations of the various reactants were unsuccessful. This result is probably due to the fact that $[Mn^{III}(tpp)]$ is almost completely degraded after 20 min as shown by the disappearance of the 470 nm Soret band in the UV-VIS spectrum.

Table 1 Activity of the bimetallic two-phase catalytic system in the epoxidation of α-pinene, nerol and *cis*-stilbene

Substrate	$[(PhCO)_2O]$/ mol dm^{-3}	p_{O_2}/mmHg[a]	Turnover no.[b]
Nerol	0.05	760	17
	0.05	160	18
	0.05	0	<1
	0.0	160	8
cis-Stilbene	0.05	760	42
	0.05	160	30
	0.0	160	2
α-Pinene	0.05	160	30

[a] The partial pressure of dioxygen was applied by stirring the reaction mixtures under an atmosphere of nitrogen (p_{O_2} = 0 mmHg), under air (p_{O_2} = 160 mmHg) or under 1 atmosphere of oxygen (p_{O_2} = 760 mmHg). [b] Turnover no. is $[epoxide]/[Mn^{III}(tpp)]$; reaction time = 1 h.

These results show that the present system is able to catalyse the epoxidation of olefins. We suggest that this reaction occurs by interaction of the olefin with a high-valent managanese–porphyrin–oxo-complex. This species is probably formed by reaction between the reduced manganese(II) porphyrin, and molecular oxygen. The higher turnover numbers achieved in the presence of benzoic anhydride are in favour of this explanation, since this compound is known to assist in the cleavage of the oxygen bond after it has bound to the manganese centre of the porphyrin ring.[5] We cannot, however, exclude the formation of peroxy acids or hydrogen peroxide as a result of autooxidation. So far, attempts to improve the yield of epoxide by using more stable derivatives of $[Mn^{III}(tpp)]$ {*e.g.* $[Mn^{III}(t_{2,6}\text{-diClpp})]$ and $[Mn^{III}(t_{penta}\text{-Clpp})]$}† have not increased product yields and similar degradation of the Mn^{III} porphyrins was observed. This rather puzzling result leads us to believe that a strongly oxidising species is formed during the course of the reaction, which is capable of rapidly degrading otherwise stable Mn^{III} porphyrins. Based on previous evidence described in the literature,[6] we tentatively suspect the formation of a rhodium–superoxo species that is capable of further reacting with the manganese porphyrins in such a way as to catalyse their degradation. Further experiments are being carried out to elucidate the reasons behind the rapid decay of the porphyrin ligand and to improve the efficiency of the catalytic system.

Received, 16th November 1992; Com. 2/06092B

References

1 B. Meunier, *Chem. Rev.*, 1992, **92**, 1411.
2 I. Tabushi and N. Koga, *J. Am. Chem. Soc.*, 1979, **101**, 6456; D. Mansuy, M. Fontecave and J. F. Bartoli, *J. Chem. Soc., Chem. Commun.*, 1983, 253; P. Battioni, J. F. Bartoli, P. Leduc, M. Fontecave and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1987, 791; I. Tabushi and K. Morimitsu, *J. Am. Chem. Soc.*, 1984, **106**, 6871.
3 J. v. Esch, M. F. M. Roks and R. J. M. Nolte, *J. Am. Chem. Soc.* 1986, **108**, 6093.
4 R. Ruppert, S. Herrmann and E. Steckhan, *J. Chem. Soc., Chem. Commun.*, 1988, 1150.
5 I. Tabushi, *Coord. Chem. Rev.*, 1988, **86**, 1.
6 A. W. Addison and R. D. Gillard, *J. Chem. Soc., A*, 1970, 2523.

---

† $Mn^{III}(t_{2,6}\text{-diClpp})$ = 5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrin manganese(III) chloride; $Mn^{III}(t_{penta}\text{-Clpp})$ = 5,10,15,20-tetrakis(pentachlorophenyl)porphyrin manganese(III) chloride.