In the Presence of Imidazole, Iron- and Manganese-porphyrins catalyse the Epoxidation of Alkenes by Alkyl Hydroperoxides

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In the presence of imidazole, Mn(TPP)(Cl) and Fe(TPP)(Cl) (TPP = tetraphenylporphyrin) catalyse the epoxidation of styrene, cyclohexene, 2-methylhept-2-ene, and stilbene by cumyl hydroperoxide; in the case of Mn(TPP)(Cl), a transient species, characterized by a Soret peak at 426 nm similar to that of a previously described high-valent Mn-oxo species, is detected at −37 °C.

Cytochrome P-450,[1] and also simple iron(III)-porphyrins,[2] catalyse the hydroxylation of alkanes and the epoxidation of alkenes by iodosylbenzene; the active species is probably a high-valent iron-oxo complex.[1,2] However, whereas cytochrome P-450 also catalyses both types of oxidation by alkyl hydroperoxides,[3] simple Fe^{III}- or Mn^{III}-porphyrins fail to catalyse epoxidations by these oxidants and only catalyse alkane hydroxylations.[4] The active species involved in the latter reactions is presumably the RO$^\bullet$ radical derived from homolytic scission of ROOH.[4] These results suggest that, whereas cytochrome P-450 leads to heterolytic cleavage of the O–O bond of ROOH with formation of a Fe^{V}=O hydroxylating and epoxidizing species, simple Fe^{III}- and Mn^{III}-porphyrins give a 'Fenton-like' homolytic cleavage of this bond leading to RO$^\bullet$ which is unable to epoxidize alkenes.

We report here that in the presence of imidazole, Fe(or Mn)-porphyrins catalyse the epoxidation of alkenes.

Cumyl hydroperoxide($PhCMe_2OOH$ = CumOOH) is only slowly decomposed in CH_2Cl_2 in the presence of catalytic amounts of Mn^{III}(TPP)(Cl)[5] (TPP = tetraphenylporphyrin) ($t_{\frac{1}{2}}$

Table 1. Epoxidation of alkenes by cumyl hydroperoxide in the presence of Mn(or Fe)(TPP)(Cl) and imidazole (ImH).[a]

		% Yields[b]			
Alkene	Products	Mn(TPP)(Cl)	Mn(TPP)(Cl) + ImH	Fe(TPP)(Cl)	Fe(TPP)(Cl) + ImH
Cyclohexene	Cyclohexene oxide	tr[c]	27	tr	3
	Cyclohex-2-enol	2	3	2	4
	Cyclohex-2-enone	2	2	2	5
Styrene	Styrene oxide	*ca.* 1	18	*ca.* 1	6
2-Methylhept-2-ene	2-Methylhept-2-ene oxide	*ca.* 1	41	*ca.* 1	17
cis-Stilbene	*cis*-Stilbene oxide	tr (35[d])	39 (56[d])	tr	$13\left\{\begin{array}{l}90\%\\10\%\end{array}\right.$
	trans-Stilbene oxide	tr (55[d])	4 (4[d])	tr	
trans-Stilbene	*trans*-Stilbene oxide		tr (*ca.* 1[d])		

[a] Conditions as given in the text (dropwise addition of CumOOH over 5 min). [b] Based on starting CumOOH (after 5 min at 20 °C). [c] tr = trace (<1%). [d] Identical conditions but with PhIO instead of CumOOH.

in CH_2Cl_2 = *ca.* 5 h), but it was completely decomposed within a few minutes in the presence of imidazole [10 equiv. relative to Mn(TPP)(Cl)]. When the latter reaction was performed in the presence of cyclohexene under anaerobic conditions [cyclohexene–CumOOH–Mn(TPP)(Cl)–imidazole 50:5:1:10], CumOOH was completely decomposed within 5 min, mainly into CumOH, and cyclohexene oxide (27% based on CumOOH) was formed together with small amounts of cyclohexenol and cyclohexenone (Table 1). Similar results were obtained with various alkenes (Table 1) such as styrene, 2-methylhept-2-ene, and *cis*-stilbene (yields 20—45%) under identical conditions. In the absence of either imidazole or Mn(TPP)(Cl) only traces of epoxide are formed. As shown in Table 1, similar results are obtained with Fe(TPP)(Cl) as catalyst but the epoxide yields are lower than those obtained with Mn(TPP)(Cl).

It is noteworthy that 1-methylimidazole is almost as efficient as imidazole in the epoxidation of 2-methylhept-2-ene by the Fe(TPP)(Cl)–CumOOH system whereas 2-methylimidazole and pyridine lead only to very low yields of epoxide.

The characteristics of stilbene oxidation by the CumOOH–Mn(TPP)(Cl)–imidazole system are very similar to those of the PhIO–Mn(TPP)(Cl)–imidazole system: (i) *trans*-stilbene is not very reactive giving only traces of the *trans*-epoxide in both systems; (ii) *cis*-stilbene is much more reactive and gives the *cis*-epoxide predominantly. It was previously reported that the Mn(TPP)(Cl)–PhIO system oxidized *cis*-stilbene giving a 39:61 mixture of *cis*- and *trans*-epoxides.[6a] We found that addition of imidazole [10 equiv. relative to Mn(TPP)(Cl)] greatly modified this ratio in favour of the *cis*-epoxide (93:7).† The similar characteristics of the CumOOH- and PhIO-systems in the presence of imidazole suggest a common active species. The addition of CumOOH to a PhCl solution of Mn(TPP)(Cl) at −37 °C does not lead to the appearance of any new Mn complexes, but the same reaction performed in the presence of imidazole leads to the immediate appearance of a new species, characterized by peaks at 426 and 523 nm in the visible spectrum (Figure 1). This species is very similar to that formed upon reaction of PhIO with Mn(TPP)(Cl) which has been described as a high-valent Mn-oxo complex.[6] Upon warming to 20 °C, the Mn^{III}-porphyrin is recovered quantitatively.

These results show that imidazole dramatically affects the activation of CumOOH by Mn(TPP)(Cl) or Fe(TPP)(Cl). The lack of similar effects in the oxidation of 2-methylhept-2-ene with hindered 2-methylimidazole which has a very low binding constant to Fe-porphyrins[8] suggests that the effect of imidazole is at least in part due to its co-ordination to iron and the corresponding change in the Fe^{III} reactivity.[9] Our results do not allow us to determine a detailed mechanism for alkene epoxidation by the Mn(or Fe)(TPP)(Cl)–CumOOH–imidazole system. However the similar characteristics observed for the CumOOH- and PhIO-systems in the presence of imidazole, suggest that imidazole favours the heterolytic cleavage of the O–O bond of CumOOH rather than the homolytic cleavage which appears to occur with Mn(or Fe)(TPP)(Cl) alone.[4] In addition to its effect on the mode of activation of ROOH by Mn(or Fe)(TPP)(Cl), imidazole accelerates CumOOH decomposition and controls the reactivity of the Mn^{V}=O species formed upon reaction of PhIO with Mn(TPP)(Cl) since it increases the *cis*:*trans* epoxide ratio from 39:61 to 93:7 in the epoxidation of *cis*-stilbene (Table 1).

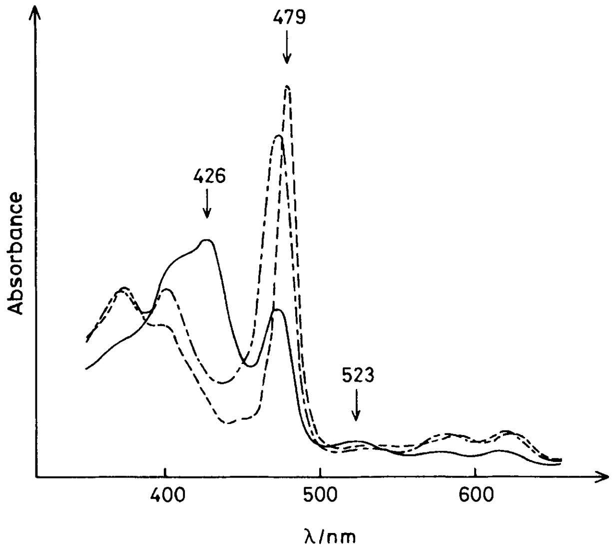

Figure 1. Visible spectrum of the intermediate formed upon reaction of CumOOH with Mn(TPP)(Cl) in the presence of imidazole: (—·—·) Mn(TPP)(Cl) (1.8×10^{-5} M) + imidazole (1.8×10^{-3} M) in PhCl at −37 °C; (——) after addition of CumOOH (1.25×10^{-3} M): (– – –) Mn(TPP)(Cl) + CumOOH alone under identical conditions [spectrum identical to that of Mn(TPP)(Cl)].

These results suggest that the endogenous cysteinate ligand of cytochrome P-450, which is even more electron-donating

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† Similarly, it was reported that in the presence of pyridine, the Mn(TPP)OAc)–PhIO system gave a *cis*- to *trans*-stilbene oxide ratio of 57:43 (42:58 without pyridine) (ref. 7).

than imidazole, may favour the heterolytic cleavage of the O–O bond not only of hydroperoxides but also of dioxygen. Finally, they give the first indication that mono-oxygenase-type efficient epoxidation of alkenes can be performed by alkyl hydroperoxides under very mild conditions.

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