Olefin Epoxidation by a Mono-oxygenase Model. Effect of Site Isolation

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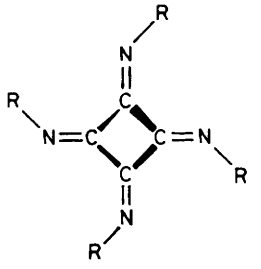
Anchoring of (tetraphenylporphinato)manganese(III) acetate to a rigid polymer support considerably enhances the rate of cyclohexene epoxidation by this catalyst.

The development of efficient oxidation catalysts after the example of the mono-oxygenase enzymes in nature has received much attention.[1] Recently, cytochrome P-450 models have been reported that epoxidize olefins under relatively mild

conditions.[2] These model systems consist of a synthetic metallo(III)porphyrin and an oxygen source, either a single oxygen donor such as iodosylbenzene or a hypochlorite, or a combination of molecular oxygen and a reducing agent. The active species in these systems is probably a highly reactive oxometallo(V)porphyrin.[3]

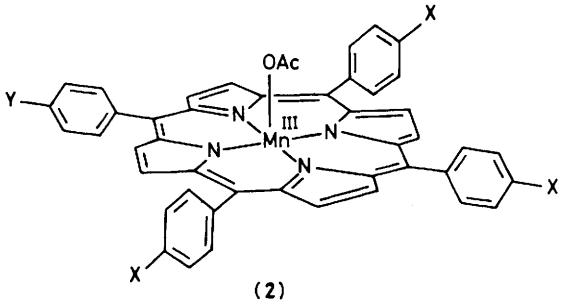
In mono-oxygenases the metalloporphyrin is surrounded by a globin, which creates site isolation of the active centre. This suggested to us that the principle of site isolation may also be applied to the above mentioned synthetic catalysts. Thus, their activity might be favourably affected since the formation of less reactive dimers, *e.g.* (μ-oxo)metallo(IV)porphyrin dimers would be prevented.[4] Site isolation can be achieved by anchoring the porphyrin onto a rigid support and we give here an example of such an anchoring.



(1)

R = $CH(CO_2H)CH_2C_6H_4OH$

(1a,b) = anchored (2a,b)



(2)

a, X = Me, Y = $O[CH_2]_3Br$ or $O[CH_2]_3O$ (after coupling)

b, X = Y = $O[CH_2]_3Br$ or $O[CH_2]_3O$ (after coupling)

c, X = Y = H

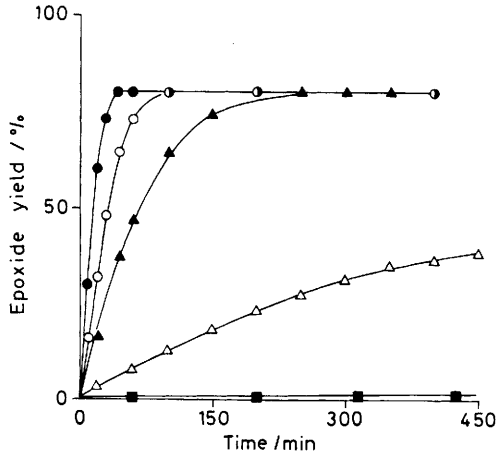


Figure 1. Cyclohexene epoxidation by (**1a**) in the presence of 4-methylpyridine (●), pyridine (○), 4-cyanopyridine (▲), imidazole (■), and without additive (△).

We used a polymer of an isocyanide, $(R\text{-}N{=}C{<})_n$ (**1**), as the support. Polymer (**1**) has a rigid 4^1 helical configuration. It was prepared by converting the α-amino group of L-tyrosine into an isocyano function and by subsequent polymerization with nickel chloride.[5,6] The molecular weight of (**1**) amounted to $\overline{M}_V$ 25 000 (100 repeating units).

(Tetra-*para*-substituted-phenylporphinato)manganese(III) acetates (**2a**) and (**2b**) were synthesized and coupled to (**1**) by means of ether linkages with the tyrosine phenyl rings.[6] The coupling products, (**1a**) and (**1b**), have a porphyrin content of 4 and 1.5 weight %, respectively, which corresponds to an average of 0.5—1.0 molecule of catalyst per polymer chain. Compound (**1b**) has a cross-linked structure, whereas (**1a**) has not.

The catalytic activity of the anchored catalysts (**1a**) and (**1b**), and the non-anchored catalysts (**2a—c**) was tested in the epoxidation of cyclohexene using a biphase or triphase (for polymer catalysts) system.† Sodium hypochlorite was used as a single oxygen donor. Reactions were followed by g.l.c. and mass spectrometry.

Pyridine and substituted pyridines considerably enhanced the catalytic activity of the anchored porphyrin, the effect decreasing in the series 4-picoline > pyridine > 4-cyanopyridine (Figure 1). Imidazole completely blocked the epoxidation of cyclohexene. The rate enhancing effect of pyridine has been reported before, in case of complex (**2c**).[7] Pyridine and the substituted pyridines probably co-ordinate to the Mn^{III} centre and facilitate the formation of the oxo-Mn^{V} species by virtue of their electron donating properties.

The effect of anchoring the porphyrin was investigated in the presence of 4-picoline† (Figure 2). The anchored catalyst (**1a**) is approximately 3 times more active than the free catalysts (**2a**)—(**c**), which show the same activity. Initial turnover numbers were 300 and 95 mol h^{-1} (mol catalyst)$^{-1}$, respectively. This rate enhancement is considerable, in particular if we take into account the insolubility of (**1a**) in the reaction medium, whereas complexes (**2a**)—(**c**) are soluble. The observed effect emphasizes the importance of site isolation of the porphyrin catalyst. The cross-linked catalyst (**1b**) shows

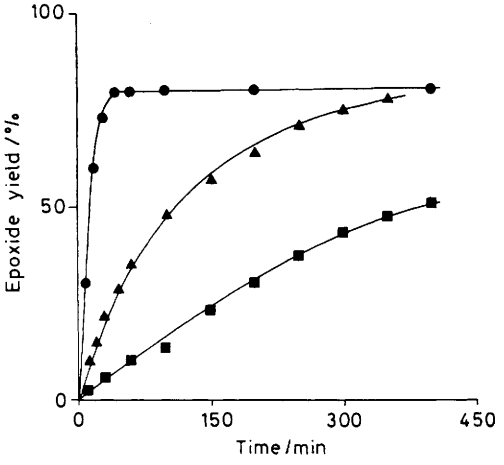


Figure 2. Effect of anchoring on the rate of cyclohexene epoxidation. Catalyst (**1a**) (●), (**1b**) (■), and (**2a**), (**b**), or (**c**) (▲).

† In a typical experiment the following components were mixed: 0.0025 mmol of porphyrin catalyst (either polymer attached or free), 1.25 mmol of 4-methylpyridine, 1 cm^3 of a solution of benzyltriethylammonium chloride (5 mmol dm^{-3}) in methylene chloride, 0.4 mmol of cyclohexene, and 2.0 cm^3 of an aqueous solution (pH 13) of sodium hypochlorite (0.35 mol dm^{-3}). Reaction temperature 25.0 °C.

a lower epoxidation rate which may be the result of diffusion limitation or shielding of the metalloporphyrin.

Anchored catalysts of the type described here, which can be recovered and retain their activity during prolonged periods of time, may become attractive alternatives to the currently employed epoxidation reagents,[8] the more so as they use inexpensive chemicals, such as dilute solutions of commercial bleach, and do not require drastic, *e.g.* anhydrous, conditions.

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