

MECHANISM OF OLEFIN EPOXIDATION BY A MONO-OXYGENASE MODEL

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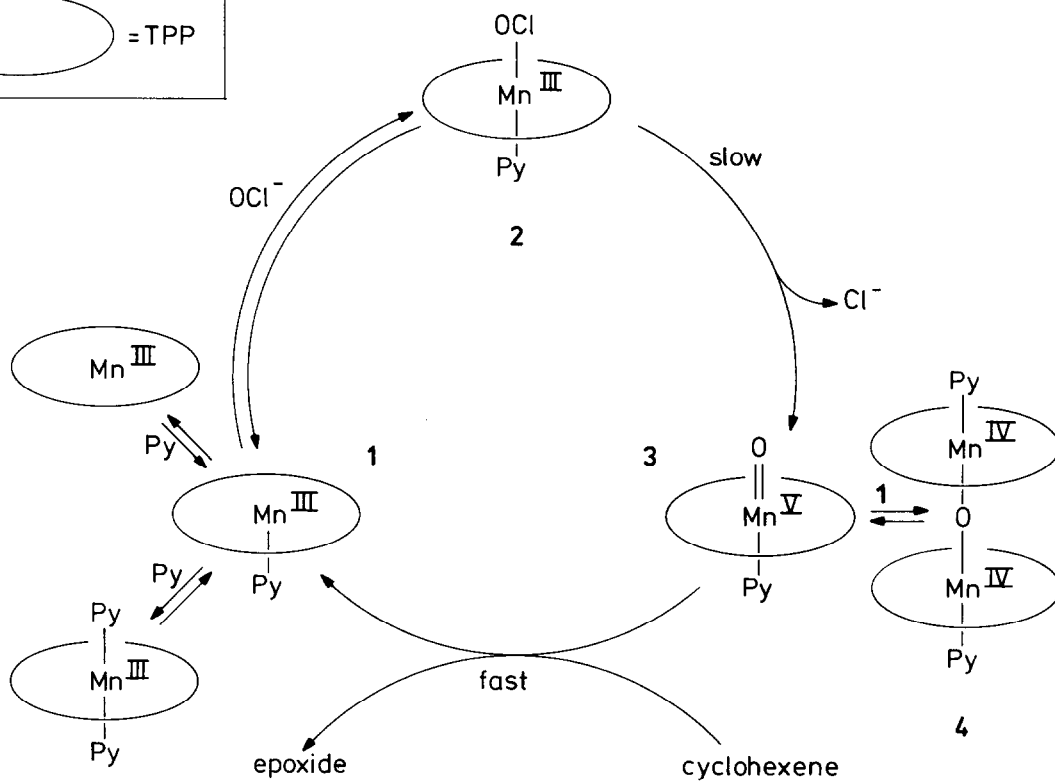
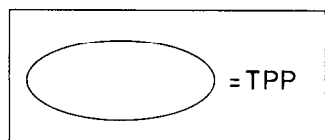
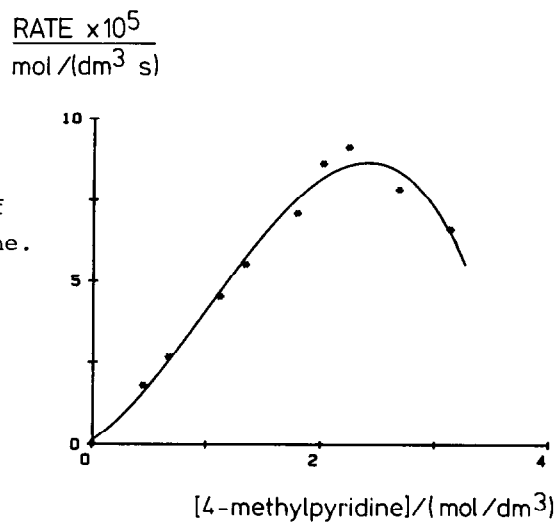
Summary: Kinetic data suggest that the rate determining step in the epoxidation of cyclohexene by Mn-TPP and sodium hypochlorite is the conversion of a Mn(III)-species into an oxo-manganese(V)-species.

Olefin epoxidation by models of cytochrome P-450 is receiving intense interest.¹ These model systems consist of a synthetic metallo(III)porphyrin and an oxygen source, either a single oxygen donor such as iodosylbenzene or hypochlorite, or a combination of molecular oxygen and a reductor.

Currently attention is focused on the mechanism of the catalytic process and in particular on elucidation of the intermediate species that are involved. In this communication we present a kinetic study of cyclohexene epoxidation by (tetraphenylporphinato)manganese(III) acetate (Mn-TPP) and sodium hypochlorite in a two phase water-dichloromethane system with benzyltriethylammonium chloride (TEBA) as phase transfer reagent.

Rates were determined by measuring the formation of 1,2-cyclohexane epoxide by GLC (Column: Carbowax 20M on Chromosorb W-HP) using toluene as an internal standard.² The following features were observed: *i.* With an excess of hypochlorite up to 90% conversion reactions are zero order in cyclohexene. *ii.* In the concentration range $0 < [\text{Mn-TPP}] < 8.26 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ of the catalyst in the organic phase the reaction order in catalyst decreases from 1 to ≈ 0 with increasing catalyst concentration. A Lineweaver-Burk plot³ of reciprocal reaction rate versus the reciprocal of Mn-TPP concentration gives a straight line with slope $K_m/v_{\text{max}} = 36.5 \pm 0.5 \text{ s}$ and intercept $1/v_{\text{max}} = (7.5 \pm 0.3) \times 10^3 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}$. *iii.* In the concentration range $0.11 < [\text{NaOCl}] < 0.45 \text{ mol} \cdot \text{dm}^{-3}$ in the aqueous phase the reaction order in sodium hypochlorite decreases from 1 to 0 with increasing hypochlorite concentration. The corresponding Lineweaver-Burk plot is linear with slope $K_m/v_{\text{max}} = (2.0 \pm 0.1) \times 10^3 \text{ s}$ and intercept $1/v_{\text{max}} = (1.05 \pm 0.05) \times 10^4 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}$. *iv.* Pyridine and substituted pyridines

Figure 1: Rate of epoxidation as a function of the concentration of 4-methylpyridine.



Scheme 1

considerably enhance the reaction rate.^{1f,4} The order of rate enhancing effect is 4-methylpyridine > pyridine > 4-cyanopyridine. Imidazole was found to block epoxidation completely. The effect of varying the concentration of 4-methylpyridine is given in Figure 1. The rate of epoxidation increases with increasing concentration of 4-methylpyridine up to a maximum value at a [4-methylpyridine]/[Mn-TPP] ratio of 650 and subsequently slows down to zero. *v.* Anchoring of the manganese-porphyrin catalyst on to a rigid support, *e.g.* a polymer of an isocyanide (RNC)_n, increases the reaction rate by a factor of at least 3.⁴

Based on these findings the following mechanism is proposed (Scheme 1). Rate determining step of the reaction is the conversion of a manganese(III) species 2 into the oxo-manganese(V) species 3. Ample literature data are now available to support the intermediate presence of such an oxo-manganese(V) complex.^{1a-c} Electron donation by coordinated pyridine will facilitate the oxidation step. Pyridine and hypochlorite molecules compete for coordination to the manganese centre. In the presence of the stronger ligand imidazole or of a high concentration of pyridine both coordination sites at manganese are blocked, and epoxidation is prevented. The fact that anchoring of the porphyrin to a support increases the rate of epoxidation strongly, suggests that anchoring prevents the formation of inactive or less active dimers. Dimerization may occur by reaction of species 3 with 1 to form the μ -oxo-manganese(IV) dimer 4. Manganese(IV)- μ -oxo-dimers have recently been isolated by Hill et al.⁵

Our observations suggest that a way of improving the epoxidation catalyst is by anchoring both the Mn-TPP species and a pyridine moiety to a rigid support, *e.g.* a rigid polymer backbone. We are currently exploiting this idea.

REFERENCES AND NOTES

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2. In a typical experiment the following components were mixed at 25°C: 37.5 × 10⁻⁵ mol cyclohexene, 12.5 × 10⁻⁵ mol toluene, 1.72 × 10⁻⁶ mol Mn-TPP catalyst, 10.08 × 10⁻⁴ mol 4-methylpyridine, and 5 × 10⁻⁶ mol TEBA in 1 cm³ of CH₂Cl₂. To this solution 2 cm³ of a solution of 0.45 mol.dm⁻³ sodium hypochlorite was added.
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