Synergistic Effects in the Epoxidation of Mixtures of Styrene and Aliphatic Alkenes catalysed by a Cytochrome P-450 Model

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In competitive experiments styrene increases the rate of epoxidation of aliphatic alkenes by the mono-oxygenase model ([meso-tetraphenylporphyrinato)manganese(III) chloride–sodium hypochlorite; this effect is caused by phenylacetaldehyde, which is formed as a side-product of styrene epoxidation.

Biomimetic oxidation by single oxygen donors catalysed by synthetic metalloporphyrins is an area of active research.1–3 Recently, we reported on the mechanism of alkene epoxidation by the cytochrome P-450 model ([meso-tetraphenylporphyrinato)manganese(III) chloride with sodium hypochlorite as oxidant (Meunier system)2).3 In competitive experiments we observed that styrene increases the rate of epoxidation of aliphatic alkenes.3c We now present evidence that this rate enhancing effect is caused by aldehydes, which are formed as by-products in the epoxidation reaction.

Experiments were performed in a two phase water–di­chloromethane system with triethylbenzylammonium chloride (TEBA) as phase transfer catalyst.† Rates were determined by measuring the formation of epoxide by g.l.c. Under the experimental conditions used, the order in alkene is 0. For aliphatic alkenes in non-competitive experiments the order in ([meso-tetraphenylporphyrinato) Mn(III) chloride (MnTPP)] varies between 1 and 0 (Figure 1).

In competitive experiments with styrene (molar ratio of aliphatic alkene to styrene 1:1) the epoxidation rate of the aliphatic alkene increases and the order in catalyst changes from less than one to first order. In order to trace the origin of this phenomenon we tested the effect of various additives. We found that phenylacetaldehyde, which is formed from styrene as a by-product (ca. 20%1a,2d), induces a similar change in kinetics. Other aldehydes (benzoic acid, propionaldehyde, hexanal) also showed this behaviour, although the effects are less pronounced (Figure 1). Ketones, e.g. cyclohexanone and cyclopentanone, also accelerate the epoxidation reaction. Further experiments were performed using phenylacetaldehyde or benzaldehyde as additive. The following observations were made: (i) Without TEBA, no epoxidation takes place. The reaction cannot be induced by adding aldehyde, indicating that the aldehyde does not act as a phase transfer catalyst for OCl–. (ii) Experiments performed with cyclohexene (0.626 mol dm–3) to which various concentrations of benzoic acid (0–0.623 mol dm–3) were added, reveal that the epoxidation rate is first order in aldehyde (k1: 4.2 ± 0.1 × 10–4 s–1; Figure 1 inset). Substitution (4-NO2, 4-F, 4-Me, 4-MeO) of the phenyl ring of benzoic acid has virtually no influence on the rate of epoxidation of cyclohexene. (iii) The rate enhancing effect of the aldehyde depends on the steric environment of the porphyrin catalyst and decreases in the series MnTPP > ([meso-tetramesityl­porphyrinato) Mn(III) chloride (MnTMP) > [meso-tetra(2,6­dichlorophenyl)porphyrinato) Mn(III) chloride (MnTDCP) (Table 1). (iv) The aldehyde is partly converted into carboxylic acid; for the combination benzaldehyde (0.156 mol dm–3) and cyclohexene (0.626 mol dm–3) the rates of benzoic acid formation and cyclohexene oxide formation are 1.62 ± 0.05 × 10–5 and 17.4 ± 0.1 × 10–5 mol dm–3 s–1, respectively. In separate experiments we found that benzoic acid has no rate enhancing effect on the epoxidation of cyclohexene.

We explain these results as follows. In a rate determining step, manganese(III) porphyrin reacts with hypochlorite to form an oxomanganese(V) porphyrin complex (1).3d Without aldehyde, this complex has two decomposition routes: one with alkene to give an epoxide, equation (1), and a second one with manganese(III) to form an unreactive dimer, equation (2).

\[
\text{Mn}^{\text{V}}=\text{O} + >\text{C} = \text{C}< \rightarrow \text{Mn}^{\text{III}} + >\text{C} = \text{C}< \quad (1)
\]

\[
\text{Mn}^{\text{V}}=\text{O} + \text{Mn}^{\text{III}} \rightleftharpoons \text{Mn}^{\text{IV}}\text{OMn}^{\text{IV}} \quad (2)
\]

As we have shown previously3d equation (2) is much more important for sterically unhindered porphyrins (MnTPP) than for experimental conditions used, the order in alkene is 0. For aliphatic alkenes in non-competitive experiments the order in ([meso-tetraphenylporphyrinato) Mn(III) chloride (MnTPP)] varies between 1 and 0 (Figure 1).

In competitive experiments with styrene (molar ratio of aliphatic alkene to styrene 1:1) the epoxidation rate of the aliphatic alkene increases and the order in catalyst changes from less than one to first order. In order to trace the origin of this phenomenon we tested the effect of various additives. We found that phenylacetaldehyde, which is formed from styrene as a by-product (ca. 20%1a,2d), induces a similar change in kinetics. Other aldehydes (benzoic acid, propionaldehyde, hexanal) also showed this behaviour, although the effects are less pronounced (Figure 1). Ketones, e.g. cyclohexanone and cyclopentanone, also accelerate the epoxidation reaction. Further experiments were performed using phenylacetaldehyde or benzaldehyde as additive. The following observations were made: (i) Without TEBA, no epoxidation takes place. The reaction cannot be induced by adding aldehyde, indicating that the aldehyde does not act as a phase transfer catalyst for OCl–. (ii) Experiments performed with cyclohexene (0.626 mol dm–3) to which various concentrations of benzoic acid (0–0.623 mol dm–3) were added, reveal that the epoxidation rate is first order in aldehyde (k1: 4.2 ± 0.1 × 10–4 s–1; Figure 1 inset). Substitution (4-NO2, 4-F, 4-Me, 4-MeO) of the phenyl ring of benzoic acid has virtually no influence on the rate of epoxidation of cyclohexene. (iii) The rate enhancing effect of the aldehyde depends on the steric environment of the porphyrin catalyst and decreases in the series MnTPP > ([meso-tetramesityl­porphyrinato) Mn(III) chloride (MnTMP) > [meso-tetra(2,6­dichlorophenyl)porphyrinato) Mn(III) chloride (MnTDCP) (Table 1). (iv) The aldehyde is partly converted into carboxylic acid; for the combination benzaldehyde (0.156 mol dm–3) and cyclohexene (0.626 mol dm–3) the rates of benzoic acid formation and cyclohexene oxide formation are 1.62 ± 0.05 × 10–5 and 17.4 ± 0.1 × 10–5 mol dm–3 s–1, respectively. In separate experiments we found that benzoic acid has no rate enhancing effect on the epoxidation of cyclohexene.

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\[
\text{RR'C} \rightarrow \text{O} - \text{O} \quad (2)
\]

\[
\text{RR'C} \rightarrow \text{O} - \text{O} \quad (3)
\]

† Unless otherwise indicated the following reaction conditions were used: [MnTPP] 2.5 × 10–3, [TEBA] 5 × 10–3, [alkene] 0.626, [4-methylpyridine] 1.5 mol dm–3 in CH2Cl2 (volume organic phase 0.63 ml), aqueous NaOCl (2 ml, 0.35 mol dm–3, pH 12.7). For experimental procedures see ref. 3b.

Figure 1. Rate of cyclohexene epoxidation as a function of [MnTPP] in the presence of styrene (0.315 mol dm–3), phenylacetaldehyde (0.156 mol dm–3, ●), benzaldehyde (0.156 mol dm–3, ■), and without additive (○). Inset: rate of cyclohexene epoxidation as a function of [benzaldehyde]. For reaction conditions see footnote †.
A Pentuply-bridging Carbonyl Group: Crystal and Molecular Structure of a Salt of the 1-Oxo-2-phenyl-1,2-dicarbadodecaborate(12) Anion, [LH]+[O(Ph)C2B10H10]− (L = 1,8-N,N′,N′-tetramethylnaphthalenediamine)

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Deprotonation of the C-hydroxy ortho-carborane 1,2-HO(Ph)C2B10H10 by 1,8-N,N′,N′-tetramethylnaphthalenediamine gives a salt whose anion, [O(Ph)C2B10H10]−, effectively consists of a nido-shaped [PhCB12H10]− residue capped by a pentuply-bridging carbonyl group whose C−O distance of 1.245(3) Å and position over the open carborane face, 2.001(3) Å from the cage carbon atom, are readily rationalized by frontier orbital considerations.

Although the derivative chemistry of icosahedral carboranes C2B12H12 is now extensive,1−3 C-hydroxy species HO(R)C2B10H10 (1) have received surprisingly little attention, and none has been structurally characterised. In one of the few reported studies of such compounds,4 it was noted that they are acidic, though the potential interest of the anions [O(R)C2B10H10]− (2) generated on deprotonation of (1) went unremarked. The delocalization of anionic charge into the carborane cage expected in (2) allows such anions to be regarded as nido-shaped residues [RCB5H10]− stabilised by pentuply-bridging carbonyl groups (3), an environment consistent with the cluster-forming potential of CO units as an aldehyde or a ketone to form a carbonyl oxide species (2) or a dioxirane (3). Compounds of type (3) are known to be effective epoxidizing agents.4

Recently a number of studies have appeared in which mechanistic conclusions are drawn from competitive experiments with styrene and aliphatic alkenes.1b,2b,3c In view of the results presented here, a re-evaluation of these experiments may be required.

Received, 6th January 1987; Comm. 020

References

Table 1. Rate of cyclohexene epoxidation by manganese porphyrin catalysts in the presence and absence of phenylacetaldehyde.a

<table>
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<tr>
<th>Catalyst</th>
<th>with aldehyde</th>
<th>without aldehyde</th>
<th>Ratio of rate constants</th>
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<tr>
<td>MnTPP</td>
<td>4.0</td>
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<td>4.1</td>
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<tr>
<td>MnTMP</td>
<td>5.7</td>
<td>3.4</td>
<td>1.68</td>
</tr>
<tr>
<td>MnTDCP</td>
<td>1.5</td>
<td>1.33</td>
<td>1.15</td>
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[a] [PhCH2CHO] 0.156 mol dm−3. For reaction conditions, see footnote t. b Estimated error 5%.