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EFFECT OF CARBONYL COMPOUNDS ON THE EPOXIDATION OF ALKENES BY THE MONOOXYGENASE MODEL MANGANESE(III) PORPHYRIN-SODIUM HYPOCHLORITE

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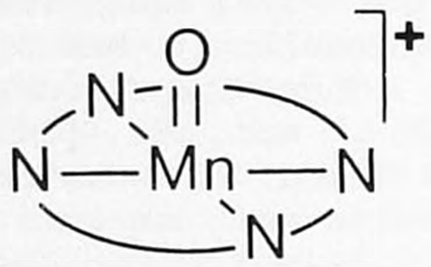
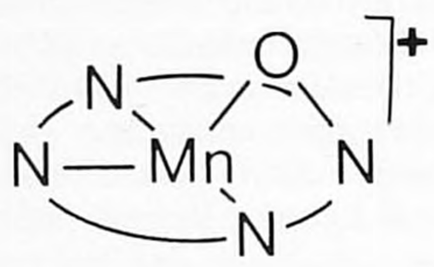
Synthetic systems that mimic the oxygen transfer properties of monooxygenases are currently receiving much attention. [1,2]. In previous papers [2,3] we reported on the kinetics of alkene epoxidation by the Cytochrome-P450 model manganese(III) porphyrin and sodium hypochlorite as oxygen donor (Meunier system [4]). The active catalyst in this model system is a high-valent manganese complex that may have structure **1a** or **1b**.



1a



1b

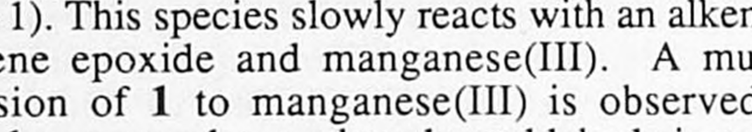
We observed that styrene increases the rate and changes the kinetics of epoxidation of aliphatic alkenes. This effect was traced back to phenyl acetaldehyde which is formed as a by-product in the styrene epoxidation reaction. In the present communication we show that other carbonyl compounds induce similar rate enhancements.

Addition of triethylbenzylammonium hypochlorite to a solution of a manganese(III) porphyrin in methylene chloride at -40°C produces a stable oxomanganese(V) species **1** (Figure 1). This species slowly reacts with an alkene to form an alkene epoxide and manganese(III). A much faster conversion of **1** to manganese(III) is observed when a carbonyl compound, e.g. phenylacetaldehyde is present (see Figure 1). The same acceleration of the process is obtained with a mixture of an alkene and a carbonyl compound in which case GLC shows that epoxide is formed. The rate enhancing effect of various carbonyl compounds was determined in the epoxidation of cyclohexene by (tetraphenylporphyrinato)manganese(III) chloride [Mn(TPP)Cl] using the two phase water-dichloromethane system previously described [2,4]. The results are presented in Table I. Both aldehydes and ketones show a rate enhancing effect. The rate enhancing factor lies in the range between 1.6 to 3.5. Based on our previous kinetic studies [2,3] we explain this result as follows.

In the rate determining step complex **1** is formed from manganese(III) porphyrin and OCl^- (eq. 1)

$$Mn^{III+} + OCl^- \rightleftharpoons Mn^{III}OCl \xrightarrow{r.d.s.} \mathbf{1} + Cl^- \qquad (1)$$

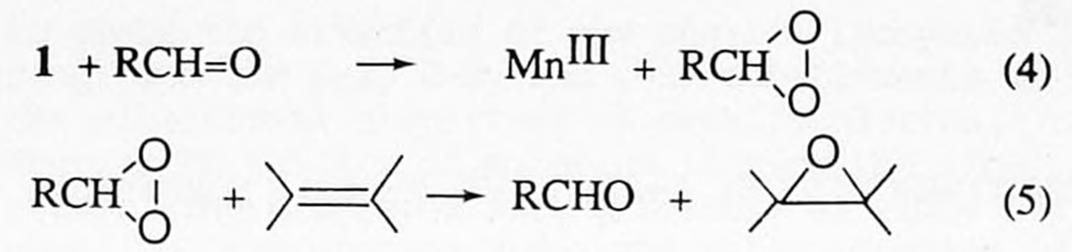
Compound **1** has two decomposition routes: one with substrate to form epoxide (eq. 2) and a second one with Mn^{III} to form an unreactive dimer (eq. 3)



$$\mathbf{1} + \rangle{=}\langle \rightarrow Mn^{III} + \qquad (2)$$

$$\mathbf{1} + Mn^{III} \rightleftharpoons Mn^{IV}\text{-O-}Mn^{IV} \qquad (3)$$

In the presence of a carbonyl compound the oxygen transfer from **1** to the alkene probably proceeds via a dioxirane intermediate (eq. 4) Dioxiranes are known to be effective epoxidizing agents (eq. 5). As a consequence, the dimerization reaction (eq. 3) is suppressed which causes the epoxidation rate to increase.



$$\mathbf{1} + RCH{=}O \rightarrow Mn^{III} + RCH(O)O \qquad (4)$$

$$RCH(O)O + \rangle{=}\langle \rightarrow RCHO + \qquad (5)$$

Table I. Rate enhancing effect of carbonyl compounds on the epoxidation of cyclohexene[a] catalysed by [Mn(TPP)Cl]

Carbonyl Compound	Rate enhancement[b]
Phenylacetaldehyde	3.5
Benzaldehyde	2.5
Propanal[c]	1.6
Hexanal	1.9
Cyclopentanon	3.3
Cyclohexanon	2.0

[a] [Mn(TPP)Cl] 2.2 x 10^{-3} mol.dm^{-3}; [4-methylpyridine] 1.26 x 10^{-3} mol. dm^{-3}; [cyclohexene] 0.6 mol.dm^{-3}; [TEBA] 0.005 mol.dm^{-3}; [carbonyl compound] 0.2-0.3 mol.dm^{-3}; T = 25.0°C.

[b] Ratio of rate with and without carbonyl compound.

[c] This aldehyde is rapidly oxidized to propionic acid.

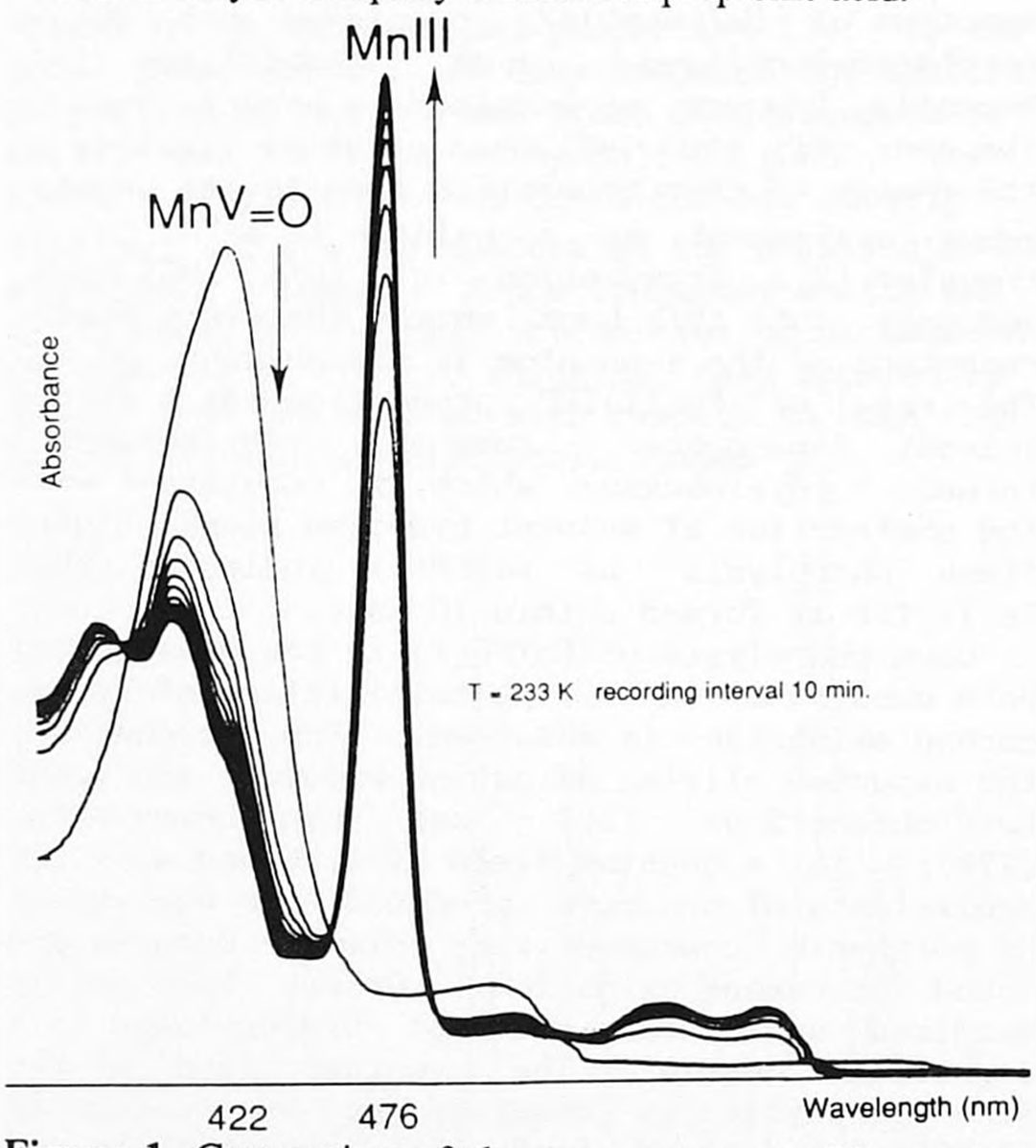


Figure 1. Conversion of the oxo-manganese(V) species into the manganese(III) complex on addition of phenylacetaldehyde

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[2] R.J.M. Nolte, J.A.S.J. Razenberg, and R. Schuurman, Ibid.**108**, 2751 (1986) and references cited.

[3] A.W. van der Made, M.J.P. van Gerwen, W. Drenth and R.J.M. Nolte, J. Chem. Soc. Chem. Commun., in the press.

[4] B. Meunier, E. Guilmet, M.E. De Carvalho, and R. Poilblanc, J. Am. Chem. Soc. **106**, 668 (1984).

[5] G. Cicala, G.R. Curci, M. Fiorentino, and O. Laricchiuta, J. Org. Chem. **47**, 2670 (1982).