Manganese Complexes of 1,2-Naphthoquinone Mono-oximes (2-Nitrosophenols) as Catalysts for Alkene Epoxidation

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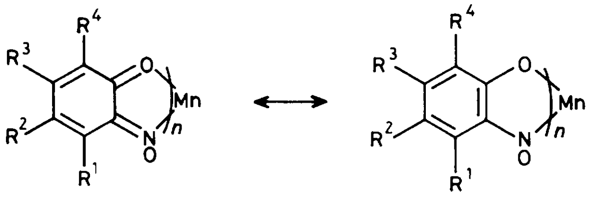
Epoxides are the major products of the catalytic oxidation of alkenes (cyclohexene, styrene, oct-1-ene, and methyl oleate) with dioxygen using the complexes Mn(1-nqo)$_n$ and Mn(2-nqo)$_n$ as catalysts (n = 2 or 3, 1- and 2-nqoH = 1,2-naphthoquinone 1- and 2-oxime).

Catalytic epoxidation of alkenes is commercially important[1] and synthetically significant as it allows the simultaneous functionalisation of two adjacent carbon atoms.[2] Most of the catalytic systems reported to date are based on the use of metalloporphyrins as catalysts and oxygen sources such as iodosylbenzene, hydroperoxides, and sodium hypochlorite.[3] These methods avoid the important problem of activation of dioxygen and also have the drawback of stoicheiometric co-product formation.[4] Recently, catalytic systems based on the nitroso/nitro redox couple have been used for the aerobic oxidation of alkenes to aldehydes and ketones.[5] Complexes of type M(nqo)$_n$ (n = 2 or 3; nqoH = 1,2-naphthoquinone 1- or 2-oxime) can prove to be potent oxidation catalysts as they have, in addition to the metal's ability to activate dioxygen, features of the nitroso/nitro redox couple (Figure 1). We have thus investigated the catalytic potential of readily obtainable Mn(nqo)$_2$ and Mn(nqo)$_3$ complexes,† as manganese is known to be crucial for oxygen evolution in the photosynthetic process,[6] and now report on the first successful application of non-porphyrin manganese complexes for the aerobic epoxidation of alkenes.



$R^1 = R^2 = H, R^3, R^4$ = benzo or $R^3 = R^4 = H, R^1, R^2$ = benzo

Figure 1

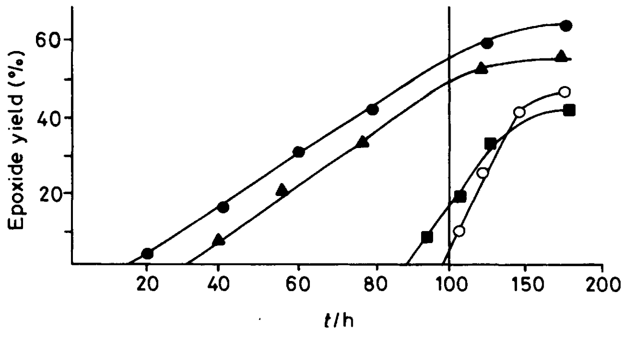


Figure 2. Reaction profile of cyclohexene epoxidation with dioxygen and the complexes Mn(nqo)$_n$ as catalysts: ●, Mn(1-nqo)$_2$; ○, Mn(2-nqo)$_2$; ■, Mn(1-nqo)$_3$; ▲, Mn(2-nqo)$_3$.

Catalytic epoxidations were performed by stirring catalyst, alkene, and toluene (internal standard) at 60 °C in an oxygen atmosphere. Periodically, samples were taken and analysed by g.l.c. (Carbowax 20M on Chromosorb W-HP). Oxidations of cyclohexene, styrene, and oct-1-ene gave the corresponding epoxides as the major products (Table 1). In contrast, the bulk of the epoxide from the reaction involving methyl oleate decomposed to give carboxylic acids. Reaction profiles indicated an initial induction period followed by a linear rise in epoxide yield and levelling-off of yield after ca. 175 h (*e.g.* Figure 2). Each catalyst gave a different induction period which was independent of catalyst concentration. This shows that the manganese bis- and tris-chelates are not the active catalytic species. Addition of pyridine to the epoxidation mixtures was found to reduce the induction periods for all the catalytic systems and increase the rate of epoxidation. However, the overall yield was unaffected. The levelling-off

Table 1. Oxidation of alkenes with dioxygen catalysed by the complexes Mn(1-nqo)$_n$ or Mn(2-nqo)$_n$.

Catalyst	Alkene (mmol)	Epoxide yield, %[a]; Turnover[b]	Induction time/h; reaction time/h
Mn(1-nqo)$_2$[c]	Cyclohexene (300.1)	65; 260	19; 150
Mn(2-nqo)$_2$[c]		46; 184	99; 150
Mn(1-nqo)$_3$[c]		40; 160	89; 150
Mn(2-nqo)$_3$[c]		55; 220	33; 150
Polymer-Mn		75;—	48; 150
Mn(1-nqo)$_2$[d]	Styrene (98.4)	21; 82	32; 100
Mn(2-nqo)$_2$[d]		14; 55	110; 200
Mn(1-nqo)$_3$[d]		17; 67	95; 200
Mn(2-nqo)$_3$[d]		22; 86	39; 100
Mn(1-nqo)$_2$[e]	Oct-1-ene (89.2)	30; 53	48; 200
Mn(2-nqo)$_2$[e]		24; 43	120; 200
Mn(1-nqo)$_3$[e]		19; 34	110; 200
Mn(2-nqo)$_3$[e]		27; 48	65; 200
Mn(1-nqo)$_2$[c]	Methyl oleate (60.0)	24; 57[f]	5; 72
Mn(2-nqo)$_2$[c]		18; 43[f]	10; 72
Mn(1-nqo)$_3$[c]		23; 54[f]	8; 72
Mn(2-nqo)$_3$[c]		24; 56[f]	7; 72

[a] Yield based on alkene. [b] Turnover based on the amount of catalyst used. [c] 0.75 mmol. [d] 0.25 mmol. [e] 0.5 mmol. [f] In addition to acidic products (60—70%).

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† The complexes Mn(nqo)$_2$ were prepared by the reaction of $MnCl_2.4H_2O$ with Na(nqo) and the complexes Mn(nqo)$_3$ were synthesised by the nitrosation of the appropriate naphthol in the presence of $MnCl_2.4H_2O$; product characterisation was achieved by elemental analysis, spectroscopic, and magnetic studies.

of yield can be attributed to the formation of less active or inactive μ-oxo dimers of type $(nqo)_2MnOMn(nqo)_2$. Oxo-bridged manganese(IV) dimers have been previously reported to be formed in epoxidation reactions involving Mn–porphyrin systems.[3] In order to reduce dimer formation, $Mn(2\text{-}nqo)_2$ was anchored onto a polyvinyl pyridine/styrene copolymer support. Oxidation of cyclohexene by the polymer-mounted $Mn(2\text{-}nqo)_2$ gave a lower induction period (48 h) and a higher epoxide yield (75%) than the induction period (99 h) and epoxide yield (46%) given by $Mn(2\text{-}nqo)_2$.

The '$Mn(1\text{-}nqo)_n/Mn(2\text{-}nqo)_n$ complexes + dioxygen' mixture is a potent epoxidation system. It provides a cheap and simple alternative to model systems which are expensive and do not involve activation of dioxygen. The exact epoxidation mechanism is unclear, but it is likely that the catalytic cycle involves a high-valent oxo-manganese intermediate as in the Mn–porphyrin + sodium hypochlorite or iodosylbenzene systems[6] and the nitroso/nitro redox couple.

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