Selective Electrocatalysis of Olefins by a Water-soluble Manganese Porphyrin in Acidic Solution

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Stable manganese(IV) tetrakis(*N*-methyl-2-pyridyl)porphyrin is electrochemically generated in acidic solutions at room temperature to selectively catalyse the oxidation of olefins.

Manganese complexes[1-3] are thought to play an important role in the water-splitting reaction $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$. Water-soluble manganese porphyrins have been of interest for their high oxidation states.[4] Also, manganese porphyrins have been used to mimic cytochrome P-450 as a monooxygenase. Chemical[5] and electrochemical[6] methods have been carried out to generate oxo-manganyl porphyrins,[7] which can undergo oxidations towards olefins.

However, water-soluble manganese(IV) porphyrins with *N*-methyl-4-pyridyl,[8] sulfonatophenyl,[9] or carboxyphenyl[10] substituents at the *meso* positions were not stable at pH <9.0. The electrocatalytic oxidation of olefins by the first of these was interrupted with the formation of decomposed products.[11]

Manganese tetrakis(*N*-methyl-2-pyridyl)porphyrin Mn^{III}(2-tmpyp) forms stable $O{=}Mn^{IV}$(2-tmpyp) in pH 5.5 buffer solutions. The stability against ring oxidation is probably due to the proximity of the positively charged *N*-methylpyridinium groups to the porphyrin ring. $O{=}Mn^{IV}$(2-tmpyp) exhibits different activities in oxygen transfer reactions for various water-soluble olefins containing carboxylic groups.

Fig. 1(*a*) shows the electrooxidation of Mn^{III}(2-tmpyp) in pH 5.5 buffer solution using an optically transparent thin-layer cell.[12] The equilibria at various potentials reflect the stability of the oxidized form. The formal potential ($E^{0\prime}$) is calculated[13] to be +0.95 V. At E_{appl} = +1.07 V the absorption spectrum exhibits peaks at 424 and 548 nm of $O{=}Mn^{IV}$(2-tmpyp).[14] However, in the presence of 0.05 mol dm^{-3} cyclopent-2-ene-1-acetic acid, the spectrum of Mn^{III}(2-tmpyp) at 364, 454 and 556 nm remains unchanged even at E_{appl} = +1.07 V [Fig. 1(*b*)], but the absorbance in the 230 nm region steadily increases, which is not observed in the absence of Mn^{III}(2-tmpyp). These observations indicate the formation of a new product concurrently upon the rapid reduction of $O{=}Mn^{IV}$(2-tmpyp) back to Mn^{III}(2-tmpyp). When cyclopent-2-ene-1-acetic acid was replaced by cyclopentylacetic acid, the corresponding saturated compound, the absorption spectrum of $O{=}Mn^{IV}$(2-tmpyp) was then observed. The reaction mechanism thus can be expressed by Scheme 1.

Bulk electrolysis was carried out and products were analysed. Ion chromatography shows a major product **1** and a minor one **2**. Product **1** was isolated and its absorption spectrum exhibited a broad band at 226 nm. Parallel chemical oxidation of cyclopent-2-ene-1-acetic acid by *tert*-butyl hydroperoxide in the presence of the manganese porphyrin was carried out. The product, cyclopent-2-ene-4-one-1-acetic acid, exhibits identical retention time and absorption spectrum as **1**.

Various water-soluble olefins which possess a carboxylic acid group were investigated for their activity in the Mn(2-tmpyp)-catalysed oxidation. The criterion for activity was the

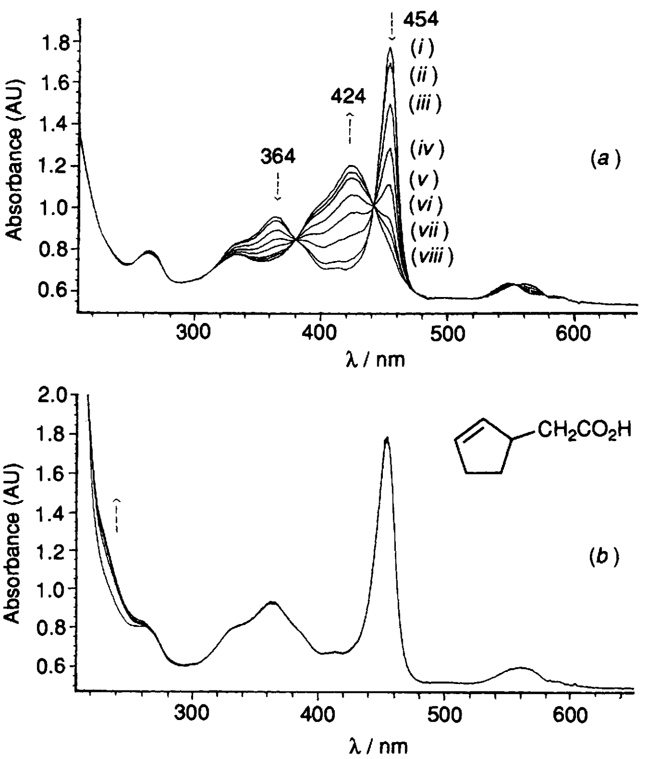
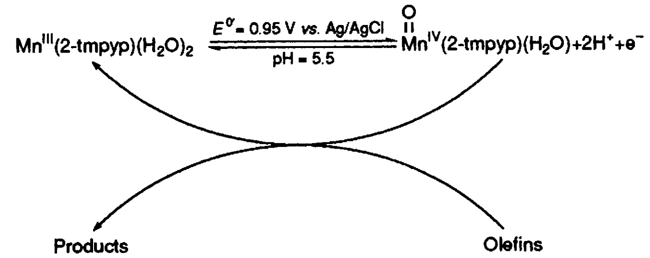
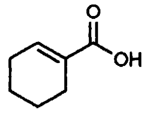


Fig. 1 (*a*) Thin-layer spectra of 1.0 × 10^{-4} mol dm^{-3} Mn^{III}(2-tmpyp) at different oxidation potentials in pH 5.5 buffer solution. E_{app} = (*i*) 0.40 (*ii*) 0.90 (*iii*) 0.93 (*iv*) 0.95 (*v*) 0.97 (*vi*) 1.00 (*vii*) 1.02 (*viii*) 1.07 V. (*b*) Thin-layer spectra of 1.0 × 10^{-4} mol dm^{-3} Mn(2-tmpyp) containing 0.05 mol dm^{-3} cyclopent-2-ene-1-acetic acid at E_{app} = 1.07 V in pH 5.5 buffer solution. Time interval = 1 h.



Scheme 1



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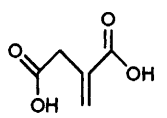

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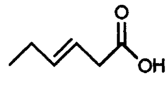

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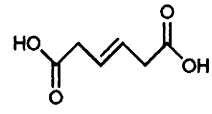

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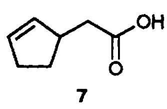

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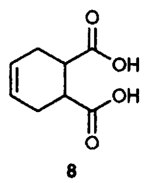

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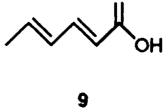

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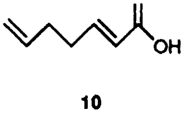

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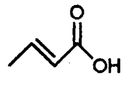
conversion of O=Mn^{IV}(2-tmpyp) back to Mn^{III}(2-tmpyp) at E_{appl} = +1.07 V as shown in Fig. 1. The relative rates of oxidation of the different alkene substrates by O=Mn^{IV}(2-tmpyp) were then estimated by the absorbances of Mn^{III}(2-tmpyp) and O=Mn^{IV}(2-tmpyp). It was found that the rate was in the order of cyclopent-2-ene-1-acetic > cyclohex-1-ene-1-carboxylic acid > itaconic acid. For these products having absorbance in 240 nm region, allylic oxidation is proposed.[15] Compounds **3**–**10** are active and **11**–**18** inactive.

It is noteworthy that there is some regularity in the results. (*i*) The 2-ene carboxylic acids cannot be oxidized by O=Mn^{IV}(2-tmpyp), except cyclohex-1-ene-1-carboxylic acid and itaconic acid. (*ii*) All 3-ene carboxylic acids can be oxidized. (*iii*) Cyclic 4-ene carboxylic acids can be oxidized while straight-chain 4-enes cannot. (*iv*) All 6-ene carboxylic acids can not be oxidized. (*v*) The 2,4-diene carboxylic acids and 2,6-diene carboxylic acids can be oxidized.



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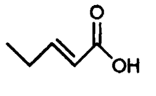

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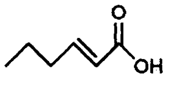

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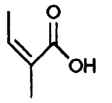

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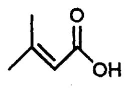

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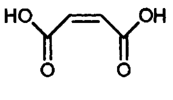

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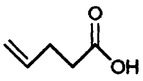

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The activity towards oxidation is probably related to the closeness of the double bond to the electron-withdrawing carboxylic group under which conditions the oxidation would be more difficult and would occur at a higher potential. Cyclic olefins appear more active and hence the stereochemistry is an important factor. Nearly all straight-chain 2-, 4- and 6-enes cannot be oxidized but 2,4-dienes and 2,6-dienes can.

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