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Lanthanide Porphyrins as Styrene Oxidation Catalysts

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It has been found that lanthanide porphyrins catalyse the oxidation of styrene with various oxidants.

Over the last few years porphyrin complexes with various transition metals have been of great interest to chemists investigating cytochrome P450-type processes, because of their ability to catalyse the oxidation of hydrocarbons under mild conditions. However, the spectrum of catalysts has been limited to complexes of the d-elements,[1] primarily iron[1a] and chromium.[1b]

We have found the first example to our knowledge of lanthanide porphyrin catalysis in the oxidation of styrene with various oxidants (PhIO, KOCl, pyridine *N*-oxide, Bu^{t}OOH). We selected the lanthanide ions because of their high coordination abilities and the existence of high oxidation states for some of them.

The tetraphenylporphyrin complexes were synthesised in boiling imidazole using the method of Horrocks.[2] For all the oxidants mentioned above, reaction (1) takes place in the presence of the catalysts.

$$PhCH{=}CH_2 \xrightarrow{\text{oxidant}} PhCH{=}O + \underset{\backslash\;/ \atop \text{O}}{PhCH{-}CH_2} + PhCH_2CH{=}O \qquad (1)$$

The products were identified by GC–MS. In a typical oxidation experiment with KOCl, the metalloporphyrin and a phase transfer agent, Bu_4NBF_4, were dissolved in 1 ml of carefully purified styrene in a Schlenk-type flask and a 10 μl sample was extracted in order to determine the concentration of the complex. Then n-pentadecane was added as an internal standard (10 μl), together with the oxidant (1 ml or 0.2 mol dm^{-3} aqueous KOCl). The mixture was degassed under vacuum and the flask was filled with argon. The reaction was run with stirring. A sample of the reaction mixture was extracted every hour and analysed by GLC. The reaction rate was determined as the rate of increase of product concentration. The stability of the products to further oxidation had been checked previously.

We measured the catalytic effect of metalloporphyrins (with lanthanide, Y, Sc, Al and Mn^{III} ions) as the difference between the reaction rates with and without the catalyst under the same conditions. The rate of styrene conversion is slightly dependent on the nature of the central ion (see Table 1). Mn^{III} porphyrin has been included to facilitate comparison of the catalytic activities of the d- and f-element porphyrins. An antibatic relationship is observed between the first oxidation potentials of the investigated complexes, which were determined by us in acetonitrile solution, and the relative rates of styrene conversion.

The epoxidation selectivity was highest for the dysprosium complex. We also investigated the influence of various factors on the reaction rate, in order to determine the characteristics of our catalytic system. We found that under the experimental conditions the reaction was first order in each of the reagents involved and in the catalyst. The presence of either hypochlorite or *tert*-butyl hydroperoxide with oxygen leads to a synergetic acceleration of the oxidation rate by a factor of 2–3. The main product is benzaldehyde.

The catalytic oxidation of styrene with potassium hypochlorite is also greatly accelerated by the addition of aliphatic alcohols. As a result, 1-alkoxy-2-chloro-1-phenylethane appears preferentially (up to 80% selectivity). This product is formed only in anaerobic conditions. We presume that the rate acceleration is related to an increase in the degree of extraction of the oxidant into the organic phase. No formation of new oxidants such as alkoxyhypochlorites was detected at pH 12–13.

Mechanistic investigations of the elaborated catalytic system are currently in progress, but we can propose some principal steps of the reaction. (*i*) Styrene is transformed into a carbon radical intermediate by the oxidant. This is consistent with the effect of oxygen on the rate and with the selectivity of benzaldehyde formation for the aerobic reaction. (*ii*) The carbon radicals are precursors of the epoxide and 1-alkoxy-2-chloro-1-phenylethane, which are not formed under aerobic conditions. (*iii*) In its catalytically active form the lanthanide porphyrin appears to be a cation radical. The appearance of the porphyrinatolutetium hydroxide radical was confirmed using low temperature EPR measurements in degassed reaction mixtures. Since the lutetium ion cannot be oxidised, the porphyrin ring must be responsible for the one-electron transfer from the metal complex to the oxidant. In this way oxidant

Table 1 The results of styrene oxidation with KOCl in the presence of various porphyrin complexes (20 °C)

Catalyst[a]	Conditions	Relative conversion rate [cat] = 10^{-3} mol dm^{-3}	Epoxide selectivity (%)	Oxidation potential in MeCN/V *vs.* SCE[b]
GdTPP(OH)	Air	2.5	0	1.46
	Argon	0.93	40	
TbTPP(OH)	Air	2.25	0	1.30
	Argon	0.78	54	
DyTPP(OH)	Air	6.9	25	1.00
	Argon	2.9	69	
YbTPP(OH)	Air	19	5	1.0
	Argon	8.2	50	
LuOEP(OH)	Argon	12	60	0.84[d]
LuTPP(OH)	Argon	8.3	50	1.06[d]
YTPP(OH)	Argon	7	—	—
ScTPP(OH)	Argon	10	12	—
AlTPP(OH)	Argon	7	40	—
MnTPP(Cl)	Argon	46[c]	90	—
H_2TPP	Argon	1.0	10	1.08[e]

[a] TPP: dianion of 5,10,15,20-tetraphenylporphyrin, OEP: dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin. Activity of YbTPP(OH) 80 cycles h^{-1}; [ClO$^-$] = 0.2 mol dm^{-3}, [Bu_4NBF_4] = 2 × 10^{-2} mol dm^{-3}, pH = 12.0. [b] SCE: saturated calomel electrode. Supporting electrolyte sodium perchlorate. [c] Rate constant 230 × 10^{-6} mol dm^{-1} s^{-1} for [cat] = 2.5 × 10^{-3} mol dm^{-3}; the data in ref. 5 give 600 × 10^{-6} mol dm^{-1} s^{-1}. [d] Ref. 3. [e] Ref. 4.

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molecules can be transformed into radicals, which initiate the ensuing reaction of styrene.

With the exception of the last feature, our catalytic system is like that of Kinneary, which involves nickel(II) complexes.[6] According to Kinneary, electron transfer occurs from the central metal ion to the oxidant. Furthermore, Kinneary's scheme would require some modification in order to explain the formation of 1-alkoxy-2-chloro-1-phenylethane in the styrene–hypochlorite–alcohol system.

Hence, a new catalytic oxidation system has been found, which appears to allow catalytic single electron activation of two-electron oxidants.

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