Catalytic and Asymmetric Oxidation of Sulphides with Iron Complexes of Chiral 'Twin Coronet' Porphyrins

Yoshinori Naruta,* Fumito Tani and Kazuhiro Maruyama*

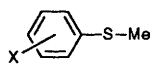
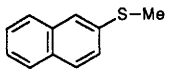
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Iron porphyrins that are modified on both faces by chiral binaphthalenes catalysed asymmetric oxidation of sulphides in fair to good enantiomeric excesses and excellent turnover numbers of the catalysts in the presence of 1-methylimidazole.

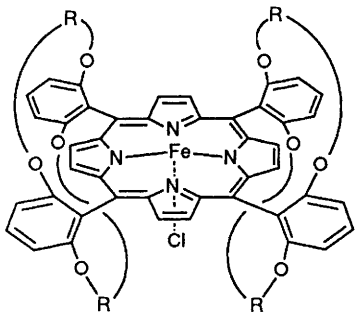
Several cytochrome P-450 models[1] for enantioselective oxygenation have been reported so far.[2] We recently designed and synthesised C_2 symmetric 'twin coronet' porphyrins that bear chiral binaphthalene auxiliaries rigidly linked by ethereal bonds on both faces to form chiral substrate binding sites and are expected to be sufficiently robust against oxidative catalyst deactivation. It was found that the iron complexes **1** and **2** catalysed asymmetric epoxidation of styrene derivatives with high enantioselectivity.[3] To the best of our knowledge, however, there is no example of a highly efficient synthetic metalloporphyrin catalyst for asymmetric oxidation of sulphides. Oxidation of prochiral sulphides to chiral sulphoxides is very important in forming chiral synthons that are useful for asymmetric induction upon C–C bond formation.[4] The enantioselective oxidation of sulphides in high enantiomeric excess (e.e.) was only achieved by means of stoichiometric reaction with a Sharpless-type reagent.[5] Moreover, isolated cytochrome P-450 enzymes exhibited low enantioselectivity in the mono-oxygenation of sulphides,[6] in contrast to flavin-dependent oxygenases.[7] We, therefore, applied 'twin coronet' porphyrins to asymmetric oxidation of prochiral sulphides.

Oxidation of sulphides by the catalyst (**1** or **2**) with iodosobenzene was performed according to the following procedure: PhIO (200 μmol) was added quickly to catalyst (1 μmol), a sulphide (500 μmol), and a GLC internal standard with or without 1-methylimidazole (1-MeIm, 100 μmol) in CH_2Cl_2 (1 ml); under an Ar atmosphere, in the dark and in a temperature-regulated reaction vessel (Scheme 1). The total turnover numbers were determined from the isolated yields of the sulphoxides produced. The enantiomeric excesses were determined by ^1H NMR spectroscopy in the presence of optically active 1,1′-bi-2-naphthol. The higher magnetic-field methyl signals of aryl methyl sulphoxides were attributed to those of the (*R*)-isomers in the presence of (*R*)-bi-naphthol.[8]

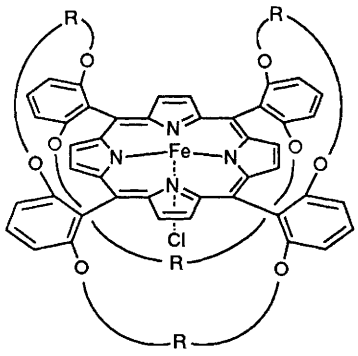
Table 1 Asymmetric oxidation of sulphides catalysed by **1** or **2**

Sulphide	Catalyst	1-MeIm(μmol)	*T*/°C	Time/h	Turnover number[a]	e.e. (%)	Configuration[b]
							
X = H	**1**	0	0	4	180	17	*S*
	1	100	−15	7.5	139	46	*S*
	2	100	−15	22	85	19	*S*
2-NO_2	**1**	100	−5	12.5	88	24	(*S*)
3-NO_2	**1**	100	−15	8	128	45	(*S*)
4-NO_2	**1**	0	0	3	173	27	(*S*)
		100	0	8	120	53	(*S*)
F_5	**1**	0	0	3	82	31	(*S*)
		100	−15	9	55	73	(*S*)
4-Me	**1**	100	−15	18	144	54	(*S*)
	**1**[c]	100	−15	22	168	34	(*R*)

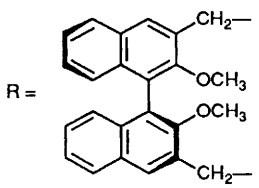
[a] Based on the amount of isolated sulphoxides. [b] The configurations in parentheses were estimated from analogy with the spectroscopic behaviour of (*S*)-methyl phenyl sulphoxide. [c] Fe(*R*)-eclipsed was used as a catalyst.



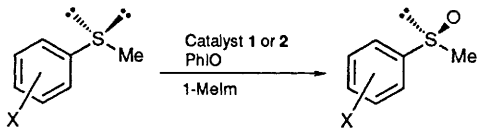
1 : Fe(*S*)-eclipsed



2 : Fe(*S*)-staggered



(*S*)



Scheme 1

In the absence of catalysts (**1** or **2**), the substrates were hardly oxygenated by iodosobenzene under the same conditions. However, the sulphoxides were produced in the presence of **1** or **2** with total turnover numbers of 55 to 180 dependent upon the substrates.† When methyl phenyl sulphide was used as a substrate with an excess of PhIO, the maximum turnover number of catalyst **1** reached 290. The iron porphyrin complexes **1**, **2** appear to act as oxidizing catalysts.

When 1-methylimidazole was added as an axial ligand, the optical yields were noticeably improved, for example from 31 to 73% (the highest value) for methyl pentafluorophenyl sulphide. These results can be attributed to the following two effects caused by the coordination of the imidazole to the active metal centre,‡ (*i*) change of the porphyrin structure in the vicinity of the iron and (*ii*) suppression of the oxidative decomposition of the catalysts.

From the results we can conclude that the steric hindrance around the sulphur atom of the substrates rather than the electronic character of the substituents appears to be dominant for prochiral face recognition on the catalyst at the transition state of oxygen transfer. These results exhibit marked contrast to those of the oxidation of the styrene derivatives, the substituent σ values of which finely correlate with the observed e.e. of product epoxides. The recognition of the alkene prochiral face would be dominated by π–π interaction between the substrate and the naphthalene moiety of the catalysts.[9]

† Accompanied by trace amounts of the corresponding sulphone (<3%).

‡ At the applied concentration of 1-methylimidazole, the Fe porphyrin **1** forms **1**·1-$MeIm_2$, **1**·1-MeIm, and **1** (in a ratio of 69:28:3) at −15 °C, determined by means of photometric titration.

Thus styrene derivatives with electron-withdrawing substituents are epoxidized in higher e.e. than those with electron-donating ones. In the oxidation of sulphides, these CT type π–π interactions between the substrate and the catalyst auxiliary π systems are expected. From CPK model study, however, the substrate sulphides at the oxo transfer stage would be required to penetrate more deeply into the cavity on the catalyst than for the case of alkenes. At this stage, two π systems cannot take proximal position enough to cause π–π interaction, but a bulky substituent on the sulphur atom only hinders this approach to the reaction centre iron atom.

It has been shown primarily that chiral iron porphyrins can be effective catalysts for asymmetric oxidation of sulphides in the presence of imidazole axial ligands. Further investigations on asymmetric and catalytic oxidation systems based on the present complexes with high activity and selectivity are currently under way.

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