Interaction of Mono-oxygen Donors with Porphinatoiron(III)-complexes Bearing Electron-releasing *meso*-Substituents

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Summary Formation of complexes between tetra(*p*-methoxyphenyl)- and tetra(*p*-tolyl)-porphinatoiron(III) chlorides are reported.

RECENT reports[1–3] suggest that cytochrome P 450-catalysed oxygen transfer reactions utilizing peroxy-compounds may occur *via* an oxidant–P 450 complex (equation 1) rather than the oxoiron intermediates $(FeO)^+$ heretofore assumed to be the activated species common to oxidations involving either mono-oxygen donors,[4–6] or O_2 and coenzymes.[6–8] Our

$$Fe^{III} + ROOH \rightarrow [Fe^{III} \cdot \text{oxidant}] \xrightarrow{R'SH} Fe^{III} + R'SOH + ROH \quad (1)$$

investigations into the nature of the intermediates in tetra-arylporphinatoiron(III)-catalysed oxidations demon-

strate that peroxy-compounds form complexes consistent with equation (1), and provide additional evidence that oxoiron complexes may not be intermediates common to all porphinatoiron-catalysed oxygen transfer reactions.

We have attempted, by appropriate substitution of the porphyrin ring, to stabilize electrophilic oxygen donor–porphinatoiron complexes and have determined the products of oxygen transfer to cyclohexene. Molecular orbital calculations[9] indicate that electron-releasing substituents on the porphyrin *meso* positions place electron density in the axial orbital of iron. Hence, tetra(*p*-methoxyphenyl)- and tetra(*p*-tolyl)-porphinatoiron(III) chlorides (FeTAPCl and FeTTPCl, respectively) were selected as oxygen transfer catalysts.

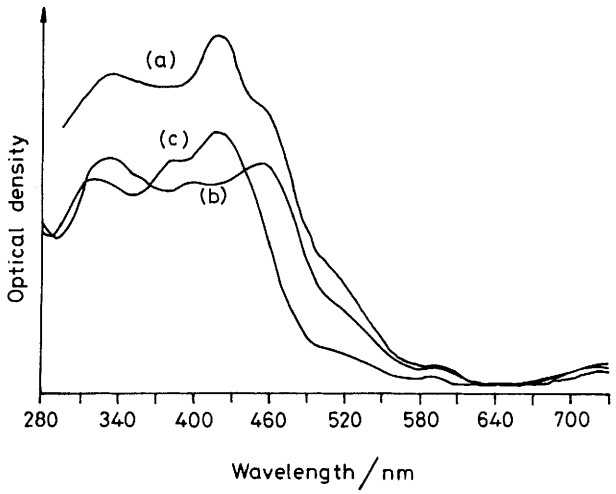

FIGURE. Electronic spectra in CH_2Cl_2 of the intermediates generated from (a) FeTAPCl with PNPBA; (b) FeTAPCl with excess of CHP; (c) FeTPPCl with excess of CHP.

FeTAPCl (5 mg, 6·1 μmol) in CH_2Cl_2 (2·5 ml) reacts with *m*-chloroperbenzoic acid (MCPBA, 1·2 mg, 7 μmol) in CH_2Cl_2 (1·3 ml) at room temperature, or with *p*-nitroperbenzoic acid (PNPBA, 1·3 mg, 7 μmol) in CH_2Cl_2 (1·3 ml) at 10 °C within 15 min, yielding an intermediate with the electronic spectrum shown in Figure (a). With excess of peracid, the intensity of the band at 420 nm decreases, but destruction of porphyrin occurs before complete disappearance of the band. Addition of a solution of cumenyl hydroperoxide (CHP; 2·5 μl, 15 μmol) in CH_2Cl_2 (1 ml) to FeTAPCl (5 mg) produced the electronic spectrum shown in Figure (b) in which the 420 nm band is absent.

Generation of the intermediate and decay to starting porphinatoiron occur with 1 : 1 correspondence, as shown by the isosbestic points in the spectra obtained by repetitive scanning of reaction mixtures. Addition of aqueous dithionite to the intermediate, with the two-phase mixture shaken vigorously, immediately regenerates the starting porphinatoiron.

Reaction of FeTTPCl with 5 equiv. of CHP in CH_2Cl_2 (0·5 ml) at room temperature resulted in an intermediate with an electronic spectrum [Figure (c)] having the same features as those of the FeTAPCl intermediates but with a smaller red shift of the Soret band. The Soret region of the spectrum resembles that of the complex generated with P 450 and MCPBA.[1] Shaking with aqueous dithionite immediately regenerates the starting compound.

Conversion into intermediate occurs to a considerable extent with stoicheiometric amounts of the perbenzoic acids, but an excess of CHP is required for complete reaction. The electronic spectra of the peroxy-intermediates are unusual, having features similar to those of hypermetalloporphyrins[10] or metalloporphyrin π-cation-radicals.[11] The marked decrease in the red shift of the Soret band from the FeTAP complex to that of the FeTTP complex suggests formation of a hyperporphinatoiron(III)–peroxide complex. The magnetic moment of the intermediate generated with FeTAPCl and CHP was determined by the Evans method[12] to be 5·7 B.M., a value inconsistent with high-spin Fe^{4+} expected for an oxo-complex.[11,13]

Addition of freshly distilled cyclohexene (1 ml) to intermediates generated under N_2 in degassed solution results in slow decay of the intermediate with concomitant regeneration of starting complex and formation of cyclohexene oxidation products in yields and proportions as shown in the Table. Product distributions differ markedly from control reactions in the absence of the iron complex. In the presence of oxygen, the reactions proceed rapidly but do not terminate after formation of 1 equiv. of products and yield increased ratios of oxide and ketone to alcohol, akin to those reported for the tetraphenylporphinatoiron chloride-catalysed oxidation of cyclohexene by O_2.[14]

Oxygen transfer proceeds through a different intermediate when the oxygen donor is iodosobenzene. Addition of iodosobenzene (8 mg) to FeTAPCl (5 mg) in CH_2Cl_2 (2 ml) at room temperature resulted in catalytic turnover ($t_{\frac{1}{2}}$ 10 min, iodobenzene production monitored by g.l.c.). Changes in the electronic spectrum accompanied iodosobenzene turnover (weak band at 650 nm, increase in absorbance at 450—500 nm), but the absolute spectrum of an immediate could not be resolved, even at low temperature. Rapid filtration of the reaction mixture under

TABLE

Oxidant	Product yield/%[a]	Product composition/% Cyclohexene oxide	Cyclohex-2-enone	Cyclohex-2-enol	Catalyst
MCPBA	60	<1	59	40	FeTAPCl
PNPBA	56	<1	51	49	
CHP	21	<1	18	81	
Iodosobenzene	2	20	12	67	
MCPBA	63	92	3	4	None
PNPBA	86	82	9	8	
CHP	30	1	50	49	
Iodosobenzene	100	22	10	68	

[a] Yields based on amount of oxidant.

N_2 into cyclohexene resulted in a low yield of oxidation products (Table).

The oxidant dependence of the product distributions (Table and ref. 3) of the porphinatoiron-catalysed oxidations indicates that a free oxoiron intermediate may not be common to all oxygen transfer reactions.

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[1] M. J. Coon, R. C. Blake, D. D. Oprian, and D. P. Balloc, *Acta Biol. Med. Ger.*, 1979, **38**, 449.
[2] R. C. Blake and M. J. Coon, *J. Biol. Chem.*, 1980, **255**, 4100.
[3] J. Capdevila, R. W. Estabrook, and R. A. Prough, *Arch. Biochem. Biophys.*, 1980, **200**, 186.
[4] J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, 1979, **101**, 1032.
[5] C. K. Chang and M.-S. Kuo, *J. Am. Chem. Soc.*, 1979, **101**, 3415.
[6] For a recent review of P 450 oxidations see Microsomes and Drug Oxidations,' eds. V. Ullrich, I. Roots, A. Hildebrandt, R. W. Estabrook, and A. H. Conney, Pergamon, New York, 1977, pp. 202 and 218.
[7] A. D. Rahimtula and P. J. O'Brien, *Biochem. Biophys. Res. Commun.*, 1974, **60**, 440.
[8] E. G. Hrycay, J. A. Gustafsson, M. Engelman-Sundberg, and L. Ernster, *Eur. J. Biochem.*, 1976, **61**, 43.
[9] G. H. Loew, C. J. Kert, L. M. Hjelmeland, and R. F. Kirchner, *J. Am. Chem. Soc.*, 1977, **99**, 3534.
[10] M. Gouterman in 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1978, Vol. 3, pt. A, pp. 59—77.
[11] R. H. Felton, G. S. Owen, D. Dolphin, A. Forman, D. C. Berg, and J. Fajer, *Ann. N.Y. Acad. Sci.*, 1973, **206**, 504.
[12] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
[13] I. Morishima and S. Ogawa, *Biochem. Biophys. Res. Commun.*, 1978, **83**, 946.
[14] D. R. Paulson, R. Ullman, R. B. Sloane, and G. L. Closs, *J. Chem. Soc., Chem. Commun.*, 1974, 186.