

CATALYSIS BY METALLOPORPHYRINS OF OXIDATIVE DESULPHURISATION
AT PENTACOVALENT PHOSPHORUS BY CUMYL HYDROPEROXIDE

R Stephen Davidson and Martin D Walker

Department of Chemistry, The City University
Northampton Square, LONDON, EC1V 0HB

Summary - Cumyl hydroperoxide causes oxidative desulphurisation at pentacovalent phosphorus with retention of configuration in the presence of various manganese (iii) and iron (ii) mesotetraphenylporphyrins provided imidazole is present, the yields of oxidised phosphorus compounds being influenced by the rate of destruction of the hydroperoxide by parasitic side reactions.

We recently reported that certain manganese (iii) porphyrins in the presence of imidazole and tetra butylammonium periodate induce oxidative desulphurisation at pentacovalent phosphorus¹. We now report that cumyl hydroperoxide can be used in place of the periodate and upon the stereochemical course of the reaction.

RESULTS AND DISCUSSION

(i) EFFECT OF VARYING THE METAL ION AND PORPHYRIN STRUCTURE.

(a) PRODUCT STUDIES

As can be seen from the Table both iron (iii) and manganese (iii) porphyrins catalyse the oxidation of organophosphorus compounds (i) to (iv) provided imidazole is present (optimal concentration 5-10 equivalents). For the unhindered meso-tetraphenylporphyrins (TPP) the manganese (iii) species gives slightly higher yields of oxidation products than the iron (iii) species. Use of hindered porphyrins-meso-tetrapentafluorophenylporphyrin (TPFPP) and meso-tetramesitylporphyrin (TMP) was explored since these compounds are less likely to undergo oxidative degradation^{2,3} and the formation of unproductive u-oxo species². The iron (iii) and manganese (iii) derivatives of these porphyrins led, in general, to slightly lower yields oxidised organophosphorus compounds.

(b) KINETIC STUDIES

The lower yield of oxidation products obtained with the hindered porphyrins was attributed to there being greater steric inhibition in the transition state for oxygen transfer from the oxo-species $M=O$ ($M=Mn^V, Fe^V$) of the hindered porphyrins compared with the unhindered porphyrin¹. Surprisingly, it was found that Mn (iii) TPFPP catalyses oxidation of triphenylphosphine sulphide more rapidly than Mn (iii) TPP. Clearly electronic as well as steric effects are important in these reactions. The kinetic studies also showed that in all the cases examined that at the end of the reactions unconsumed phosphine sulphide was present. Addition of a further amount of hydroperoxide initiated further consumption of the sulphide.

It is clear that the desired oxidation reaction is in competition with parasite side reactions ⁴, which lead to the destruction of reagents thereby making it difficult to obtain a stricture activity relationship for (i)-(iv).

(ii) STEREOCHEMISTRY OF OXIDATIVE DESULPHURISATION

Manganese (iii) tetraphenylporphyrin chloride in conjunction with imidazole and cumyl hydroperoxide was used to oxidise an enantiomerically enriched sample of 0-isopropyl-0-1-menthyl methylphosphonothioate and the reaction followed by ³¹Pnmr. The starting material showed resonances at 91.88&91.00ppm (ratio 1:2.07) and the products at 28.00 and 27.53ppm (ratio 1:2.04) (H_3PO_4 used as internal standard). These results show that the reaction occurs with retention at phosphorus and reinforces the view that these reactions are occurring via the $Mn^V=O$ and $Fe^V=O$ species and not via a radical process ^{3,5}. That mixed function oxidases also induce oxidation with retention points to similarity between the course of the enzyme mimic induced reactions and those of the enzyme ⁶.

TABLE YIELDS (%) OF OXIDATION PRODUCTS OBTAINED BY OXIDATIVE DESULPHURISATION AT PHOSPHORUS INDUCED BY CUMYL HYDROPEROXIDE^a AND CATALYSED BY PORPHYRINS

PORPHYRIN	ORGANOPHOSPHORUS COMPOUND OXIDISED			
	$Ph_3P=S^b$	$Ph_2P(S)(OEt)^b$	$Ph P(S)(OEt)_2^b$	$(EtO)_3PS^b$
MnTPPCL _c	82	81	60	34
FeTPPCL _c	95	62	22	13
MnTPPFPPCL _c	43	49	48	54
MnTMPCL _c	44	46	35	36
FeTMPCL _c	41	28	20	17

A 10 equivs. cumyl hydroperoxide in the presence of 5 equivalents of imidazole dichloromethane as solvent, reaction time 6 hr. b 1 equivalent c 0.02 equivalents.

REFERENCES

1. R.S. Davidson, M.D. Walker and R.K. Bhardwaj, Tet. Letts, 1987 28 2981
2. P.S. Traylor, D. Dolphin and T.G. Traylor, J.C.S. Chem. Comm, 1984, 279
3. B.R. Cook, T.J. Reinert and K.S. Suslick, J. Amer. Chem Soc., 1986 108
4. P.N. Balasubramanian, A. Sinha and T.C. Bruice, J. Amer. Chem. Soc, 1987, 109 1456, B. Meunier, E Guilmet, M.E.D. Carvalho and R. Poilblanc J. Amer. Chem Soc, 1984, 106, 6668
5. Some reactions of metalloporphyrins with hydroperoxides have been shown to involve radical processes. J.R. Lindsay Smith and D.N. Mortimer, J.C.S. Chem. Comm, 1985 64.
6. T.R. Fukuto Pure and Appl. Chem. 1978, 50, 1015.

Acknowledgements: We thank the SERC for a maintenance grant (to MDW), the MoD (CDE Est.) for participating in a CASE award, Professor McFarlane (City of London Polytechnic) for ³¹P spectra and D R Hall (CDE) for stimulating discussions.

(Received in UK 17 February 1988)