Metallo-porphyrin Catalysed Epoxidations with Molecular Oxygen

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Summary Molybdenum and vanadium complexes quench the peroxidation of olefins by molecular oxygen in the presence of cobalt or iron porphyrins; addition of cumene to these bis-metallic systems leads to epoxidation of olefins.

IRON(III) and cobalt(III) porphyrins (*e.g.* octaethylporphyrin or protoporphyrin dimethylester) in nitrobenzene solution catalyse the peroxidation of cyclohexene.† Porphyrins with cobalt(II) and iron(III) central ions initiate the reactions only after a lag time of *ca.* 1 h, whereas with cobalt(III) porphyrins the reaction takes place immediately. The activity of the cobalt(III) porphyrins, which are diamagnetic and do not form adducts with oxygen, indicates that the catalysis does not involve the activation of oxygen.[1] Polarization and a partial electron transfer from the olefin to the metal ion are probably involved. This could be observed by a spin-trapping experiment with nitrosodurene.[2] A strong e.s.r.-signal from the nitroxide adduct of nitrosodurene and presumably the cation radical of cyclohexene, in which each of the three lines was split into a doublet by interaction with a proton, was observed,

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† Olefinic substrates which could be peroxidized included cyclohexene, 3-methylindole (M. N. Dufour-Ricroch and A. Gaudemer, *Tetrahedron Letters*, 1976, 4079), 2-methylpent-2-ene, and 2-methylpent-1-ene. 4-Methylpent-2-ene, methyl oleate, and methyl vinyl ketone did not react under these conditions.

when cobalt(III) porphyrins were added to cyclohexene solutions in the absence of oxygen ($g = 2{\cdot}0060$, $a_N = 14, 33$, $a_H = 8{\cdot}5$).

Average yields of 10^3 molecules of oxidized olefin (*e.g.* cyclohexenone and cyclohexenol[3]) per molecule of metalloporphyrin were obtained. Oxygen consumption was high in hydrophobic solvents such as benzene, nitrobenzene, and methylene chloride, whereas all protonated and water-miscible solvents, *e.g.* methanol, dimethylformamide, and dimethyl sulphoxide, quenched the reaction. Thereafter the porphyrin was decomposed into colourless oxidation products by interaction with the peroxides formed (*e.g.* cyclohexene peroxide). The yields of oxidized olefins could be increased by a factor of three when copper acetylacetonate was added to the solutions in concentrations similar to those of the porphyrins. The copper complex presumably decomposed the primary peroxides before they could react with the porphyrin periphery.[4] Attempts to optimize this system by an iron(III) or cobalt(III)porphyrin synthesized for this purpose, to which a copper(II) ion was intramolecularly bound, failed; *e.g.* 5,10,15,20-tetrakis(9-diethylaminononyl)dichlorobiscopper(II)-chlorohemin‡ was catalytically inactive towards cyclohexene and oxygen.

When equimolecular amounts of vanadium(III,IV) or molybdyl(IV,V) complexes (*e.g.* acetylacetonates or octaethylporphyrinates) were added to the iron(III) porphyrin, catalytic reactions between olefins (*e.g.* cyclohexene) and oxygen were completely inhibited (Figure). Addition of 5% cumene to the benzene–cyclohexene mixture, however, led to an immediate uptake of oxygen (Figure). The yield of cyclohexene oxidation products was again *ca.* 5×10^3 molecules per molecule of the porphyrin catalyst pair. The products, however, were now cyclohexenol and cyclohexene epoxide in a molar ratio of 1 : 1; no cyclohexenone was produced. The addition of both vanadium or molybdyl complexes and cumene was necessary in order to produce epoxides. Cumene addition alone yielded no epoxides.

From these observations we conclude that vanadium and molybdyl complexes form 1 : 1 adducts with redox-active metalloporphyrins. Experiments to detect metal–metal interactions by e.s.r. spectroscopy failed. The spectrum of a deoxygenated solution of equimolar amounts of *e.g.* iron(III) porphyrins and vanadium(III) acetylacetonates in toluene–cyclohexene at 80 K showed only the superposition of the isolated metal complexes. No effects of spin–spin interactions as observed in dimers of paramagnetic metalloporphyrins[5] were found. Semi-quantitative comparisons with solutions of the pure components showed that no detectable electron transfer between the metal complexes had taken place. Addition of oxygen to the bismetallic mixture did not produce any spectroscopic changes. Nevertheless we conclude from the results summarized in the Figure that bismolecular adducts are formed, in which the iron(III) ion, for example, is too weak an electrophile to activate cyclohexene. Cumene hydroperoxide, however, is rapidly formed at room temperature in the presence of iron(III) porphyrins. This peroxide is then decomposed by the vanadium and molybdyl complexes producing 'electrophilic' oxygen which is transferred to the olefin.

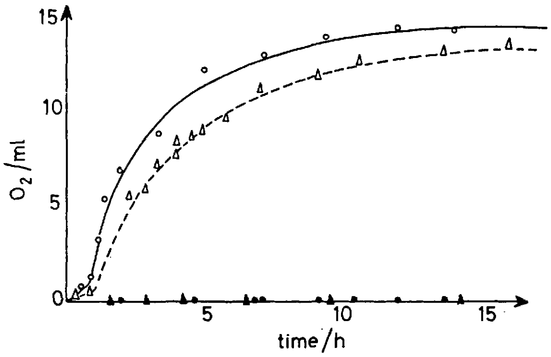

FIGURE. Oxygen consumption of a mixture of 5 ml cyclohexene and 5 ml benzene in the presence of: ▲ 0·5 mg iron(III)-octaethylporphyrin chloride (Fe^{III} OEP-Cl), 0·5 mg molybdyl(V)-octaethylporphyrin-hydroxide (MoO-OEP-OH). ● 0·5 mg Fe^{III} OEP-Cl; 0·3 mg vanadium(III)-acetylacetonate [V(acac)$_3$]. ○ 0·5 mg Fe^{III} OEP-Cl; 0·5 mg MoO-OEP-OH; 0·5 ml cumene. △ 0·5 mg Fe^{III} OEP-Cl; 0·3 mg [V(acac)$_3$]; 0·5 ml cumene.

If advantage is taken of the formation of rather stable molecular complexes of metalloporphyrins (*e.g.* with steroids),[6] regiospecific oxidations of olefins with several double bonds are possible. Preliminary experiments with squalene indicate that the inner bonds can be epoxidized in good yield with molecular oxygen. No allylic peroxidation, as with the oxidation by oxygen at 1 atm and 55 °C,[7] was observed.

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‡ Characterized by quantitative atomic absorption analysis, molecular weight determination by ultracentrifugation, and e.s.r. spectroscopy. The porphyrin without the axial copper ions has been described by J.-H. Fuhrhop and M. Baccouche, *Annalen*, 1976, 2058.

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