

Novel reactivity of photoexcited iron porphyrins caged into a polyfluoro sulfonated membrane in catalytic hydrocarbon oxygenation

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Heterogenization of iron porphyrins inside Nafion creates new photocatalytic systems which can be used to oxidize cyclohexene and cyclohexane with sunlight and O₂ under mild conditions (room temperature, atmospheric pressure); the polymeric matrix makes the iron porphyrin a good photocatalyst for the monooxygenation of the substrate and increases both its photocatalytic efficiency (about ten times) and its stability (turnover values > 1000).

As a development of an important field of research dealing with photoexcited iron porphyrins in the catalytic oxygenation of hydrocarbons,¹ we have recently investigated photocatalytic composite systems in which the porphyrin complexes are confined inside cross linked polystyrene,² bound on semiconducting transition metal oxides such as TiO₂³ or interacting with polyoxotungstates.⁴ Generally speaking, the use of heterogeneous media or organized systems is a suitable means to control the reaction environment in order to promote specific processes of interest in biomimetic catalysis by iron porphyrins.⁵

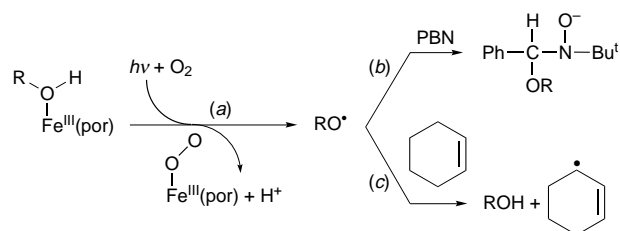
This work deals with composite systems in which iron porphyrin complexes are caged inside Nafion,⁶ a commercial polyfluorosulfonated membrane consisting of sulfonic groups connected to a polymeric structure of polytetrafluoroethylene. We have chosen this support because (i) it is chemically inert also in strong oxidizing media; (ii) it is totally transparent to the light of interest in metal porphyrin photochemistry; (iii) it is expected to cage the monocationic porphyrin complexes inside its large anionic cavities where the SO₃⁻ groups are located; and (iv) dioxygen concentration inside Nafion is more than ten times higher than in organic solvent.⁷

The photocatalytic activity of these composite systems is demonstrated in the oxygenation of cyclohexene and cyclohexane by O₂ and sunlight under mild conditions (20 °C, 760 Torr of O₂). A comparison with the photocatalytic properties of the same iron porphyrins in homogeneous solution reveals that the polymeric matrix strongly affects the chemoselectivity of the oxidation process and increases both the photochemical efficiency and the stability of the iron porphyrin.

The following iron(III) porphyrins have been chosen on the basis of their well known¹ behaviour in homogeneous solution: iron(III) *meso*-tetraphenylporphyrin [Fe^{III}(tpp)]⁺, iron(III) *meso*-tetrakis(2,6-dichlorophenyl)porphyrin [Fe^{III}(tdcpp)]⁺, iron(III) *meso*-tetrakis(pentafluorophenyl)porphyrin [Fe^{III}(tf₅pp)]⁺. Their absorption into Nafion was carried out in CH₂Cl₂-alcohol at 40 °C after swelling the membrane in EtOH or PrⁱOH. Typically the uptake of 0.5–0.8 μmol of complex in 1 g of resin occurs in a few minutes.

The UV–VIS spectra of the modified resin after swelling with EtOH or PrⁱOH are exactly those of the starting iron porphyrin dissolved in acidified alcohol media, which an extensive literature⁸ ascribes to the monocationic species having an alcohol molecule bound to the axial position.† We then infer that heterogenization does not affect the nature of the iron porphyrin axial ligand. In support of this conclusion, an EPR spin-trapping investigation indicates that heterogenization does not affect even the primary photochemical process consisting of the homolytic cleavage of the Fe^{III} axial ligand bond according

to step (a) in Scheme 1, which is a type of reaction already observed for many other iron porphyrin complexes in homogeneous solution.^{1a,b,8,9} In fact, photoirradiation‡ of the iron porphyrin/Nafion composite systems in alcohol in the presence of the spin trap phenyl-*tert*-butylnitron (PBN) inside the cavity of an EPR spectrometer yields spectra exhibiting the typical signals of the adducts between PBN and alkoxy radicals [step (b)].¹⁰



Scheme 1

Since the substituents on the *meso*-aryl groups of [Fe^{III}(tdcpp)]⁺ and [Fe^{III}(tf₅pp)]⁺ prevent the formation of a μ-oxo dimer complex,¹¹ the very fast reaction of the iron(II) porphyrin with O₂ is expected to restore the starting Fe^{III} complex, so inducing the reductive activation of O₂ itself^{1b,12} (Scheme 1). In this way, using dioxygen and sunlight, the iron porphyrin/Nafion systems are able to form, in a cyclic way, reactive intermediates which are expected to induce the oxidation of hydrocarbons. The results obtained in the oxidation of cyclohexene and cyclohexane are summarized in Table 1.

Table 1 shows that irradiation of [Fe^{III}(tdcpp)]⁺ in EtOH-cyclohexene (25% v/v) results in the formation of cyclohex-2-en-1-one, cyclohex-2-en-1-ol and *trans*-cyclohexane-1,2-diol monoethyl ether. Interestingly, if the same experiment is carried out using PrⁱOH instead of EtOH, the ether represents about 90% of the overall oxidized alkene, and allylic oxidation products are formed only in very minor amounts. The presence of the ether indirectly reveals the formation of cyclohexene epoxide which, in the strong acidic environment inside Nafion, likely undergoes a nucleophilic attack by the alcohol, leading to the epoxide ring opening.§ Oxidation of cyclohexene is also observed with Fe^{III}(tf₅pp)/Nafion even though the ratio of allylic oxidation products increases significantly in PrⁱOH. For the latter system we obtain the maximum initial oxidation rate of ca. 8.5 turnovers min⁻¹.

Photoexcitation of [Fe^{III}(tdcpp)]⁺ in homogeneous alcoholic solution gives totally different results: (i) the photooxidation is slower than in heterogeneous conditions; (ii) no ether is obtained; (iii) in addition to allylic oxidation products, cyclohexanol and cyclohexanone are formed, as we discussed earlier.¹³

The turnover values reported in Table 1 indicate that heterogenization significantly increases (about ten times) the stability of [Fe^{III}(tdcpp)]³⁺. The Nafion matrix does not undergo any degradation and can be utilised several times. [Fe^{III}(tpp)]⁺ is much less stable inside Nafion than both [Fe^{III}(tdcpp)]⁺ and [Fe^{III}(tf₅pp)]⁺. This indicates that, as in homogeneous sol-

Table 1 Photocatalytic^a oxygenation of cyclohexene and cyclohexane

Photocatalytic system	Substrates	Products ^b and related turnover ^c			
Fe ^{III} (tdcpp)/Nafion EtOH		 1700	 380	 520	
Fe ^{III} (tdcpp)/Nafion Pr ⁱ OH		 52	 5	 750	
Fe ^{III} (tf ₅ pp)/Nafion EtOH		 550	 280	 310	
Fe ^{III} (tf ₅ pp)/Nafion Pr ⁱ OH		 1100	 200	 1800	
Fe ^{III} (tpp)/Nafion Pr ⁱ OH		 22	 30	 31	
Fe ^{III} (tdcpp)/EtOH (homogeneous solution)		 79	 100	 32	 44
Fe ^{III} (tdcpp)/Nafion Pr ⁱ OH		< 10 ⁻⁵ mol dm ⁻³			
Fe ^{III} (tdcpp)/Nafion Pr ⁱ OH		 11	 4	 80	 22

^a Six hours photoirradiation, see footnote ‡. ^b Reaction products were determined by gas chromatography and gas mass analyses. Reported values are ±10%. Cyclohexane-1,2-diol monoethers have been separated on an SiO₂ column and characterised by proton NMR spectroscopy. ^c Mol of product formed per mol of consumed iron porphyrin.

utions,^{1c,9} halogen substituents on the *meso* aryl groups play a fundamental role in restoring the starting iron porphyrin during the photocatalytic cycle, avoiding both a too fast oxidative degradation of the porphyrin ring and the formation of μ-oxo-dimers.

Upon irradiation of Fe^{III}(tdcpp)/Nafion in PrⁱOH containing cyclohexane (25% v/v) the concentration of oxidation products was < 10⁻⁵ mol dm⁻³, on the same timescale as for cyclohexene. On the other hand, the alkane undergoes hydroxylation when cyclohexene is present as a co-substrate (cyclohexane 12.5% v/v, cyclohexene 12.5% v/v). This suggests that cyclohexene plays a dominant role in the formation of active monooxygenating species during the photocatalytic process.

Cyclohexene is expected to capture efficiently alkoxy radicals originating from the photochemistry of iron porphyrins through an allylic hydrogen abstraction process [step (c) in Scheme 1].¹⁴ This hypothesis is confirmed by experiments in which the intensity of the EPR signal of the adduct between PBN and alkoxy radicals is followed as a function of irradiation time. We observed that the signal intensity is unchanged in the presence of cyclohexane, while it is reduced by about 75% if cyclohexene is present. Apparently, the latter is able to compete efficiently with PBN in the reaction with the radical intermediates giving relatively stable cyclohexenyl radicals. Reaction of O₂ with these radicals in the presence of the iron porphyrin can give efficient monooxygenating species^{1b} as in the catalytic cycle of cytochrome P450.¹⁵ As a tentative

explanation, the polymeric matrix may favour the above reactions in the proximity of the metal centre and, at the same time, inhibit the escape of radical intermediates that initiate autooxidation processes.[¶] Our previous work in the homogeneous phase shows that photoexcited porphyrins under aerobic conditions can oxidise cyclohexane even in the absence of cyclohexene.^{1c} However, in that case, the active species are OH· radicals which are more reactive than alkoxy radicals in extracting hydrogen atom from hydrocarbons.¹⁶

Notes and References

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† Exchange of the acid membrane with NaCl causes a red shift of the Soret band, in keeping with the deprotonation of the coordinated alcohol molecule and the formation of a neutral porphyrin complex. In fact, in this case we observe experimentally that the complex is released by the membrane after a few hours in alcohol. The spectral variations described are exactly the same as those for the starting iron porphyrin in alcohol with added CF₃SO₃H or HClO₄. In the acidified alcohol medium one should reasonably have an equilibrium among more species, with the anions or the alcohol molecules as axial ligands in the porphyrin complex.

‡ Irradiation was carried out at 20 ± 1 °C with a Hanau Q 400 mercury lamp (15 mW cm⁻²), under oxygen at 760 Torr. Selection of wavelength between 330 and 400 nm was performed by use of a glass cut-off filter.

§ This statement is confirmed by the observation that the epoxide in acidic solution undergoes a nucleophilic attack with the formation of the same *trans*-cyclohexane-1,2-diol monoalkyl ether during the photocatalytic oxidation.

¶ The effect of the matrix is not just that of providing an acid environment. In fact, photooxidation of the cycloalkenes by [Fe^{III}(tdcpp)]⁺ dissolved in EtOH or PrⁱOH acidified with trifluoromethanesulfonic acid leads to the formation of a mixture of various oxygenation products which, on the other hand, does not include the ethers.

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