Oxidation of Alkanes by Dioxygen Catalysed by Photoactivated Iron Porphyrins

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Cycloalkanes were oxidized by O_2 itself under mild conditions (22 °C; 200 Torr of O_2) in the presence of catalytic amounts of a polyhalogenated porphyrin–iron(III)–hydroxo complex irradiated with light of wavelength between 350 and 450 nm; these oxidations occurred without consumption of a reducing agent, selectively transformed cyclohexane into cyclohexanone under appropriate conditions (about 0.2 turnover per min), and did not involve Fe^V=O active species but, more probably, iron-alkylperoxo intermediates.

Iron porphyrins have been found to be efficient biomimetic catalysts for alkene epoxidation and alkane hydroxylation, by use of either various oxygen atom donors or of O_2 itself in the presence of a reducing agent, according to the monooxygenase reaction [eqn. (1)].[1] From a chemical point of view, it would be particularly interesting to find catalytic systems able to perform alkane oxidation by O_2 without the need for and consumption of a reducing agent. Iron polyhalogenated porphyrins have recently been found to catalyse the oxidation of alkanes into alcohols and ketones under an O_2 pressure of *ca.* 10 atm, and temperatures of *ca.* 80 °C.[2]

$$RH + O_2 + 2e^- + 2H^+ \rightarrow ROH + H_2O \qquad (1)$$

This communication describes results showing for the first time that cycloalkanes are efficiently oxidized by O_2 itself under mild conditions (22 °C; 1 atm: 200 Torr of O_2) in the presence of catalytic amounts of iron(III) complexes of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin, Fe^{III}(tdcpp), under irradiation with light of wavelength between 350 and 450 nm. These oxidations occur without consumption of a reducing agent and, under appropriate conditions, cyclohexane is selectively transformed into cyclohexanone. Their mechanism is discussed in relation to the mechanism of oxidations catalysed by cytochrome P-450 and model systems.

Photoirradiation at 365 nm of deaerated solutions of Fe^{III}(tdcpp)(OH) in cyclohexane led to its reduction into Fe^{II}(tdcpp) as shown by visible spectroscopy. The quantum yield of this photoreduction of Fe^{III}(tdcpp)(OH) was determined by a previously reported method[3] and found to be 10^{-4}. Upon introduction of O_2 into the solution, the spectrum of Fe^{III}(tdcpp)(OH) was restored. Identical irradiation of Fe(tdcpp)(OH) in the cavity of an ESR spectrometer but in the presence of 5,5-dimethylpyrroline *N*-oxide (dmpo) as a spin trap[4] led to an ESR spectrum exhibiting the typical signals of the adduct between dmpo and ˙OH radicals.[5] These results indicate that, upon irradiation, (tdcpp)Fe^{III}–OH undergoes a homolytic cleavage of its iron-axial ligand bond [eqn. (2)], a type of reaction already observed for many other porphyrin–Fe^{III}-L complexes.[6–12]

$$(\mathbf{P})\mathrm{Fe^{III}\text{-}OH} \xrightarrow{h\nu} (\mathbf{P})\mathrm{Fe^{II}} + {}^{\bullet}\mathrm{OH} \qquad (2)$$

Irradiation (350–450 nm) of Fe(tdcpp)(OH) in cyclohexane under a pressure of 200 Torr of O_2 led to the progressive appearance of cyclohexanone as a function of the irradiation time. Cyclohexanone formation followed zero-order kinetics allowing us to calculate a quantum yield of 1.7×10^{-3} for this reaction and a rate of 0.14 turnover per min (Table 1). Fe(tdcpp)(OH) slowly disappeared during this reaction but 80 moles of product were obtained per mole of consumed catalyst. Interestingly, cyclohexanol was only formed in very minor amounts in this reaction ($\Phi_{ox} < 10^{-5}$). Replacement of Fe(tdcpp)(OH) by Fe(tdcpp)(Cl) or Fe(tdcpp)(OEt) led to a much less efficient oxidation of cyclohexane and to a completely different cyclohexanol : cyclohexanone ratio [2 : 1 instead of 0.02 : 1 in the case of Fe(tdcpp)(OH)] (Table 1). Under identical conditions, Fe^{III} complexes of porphyrins less resistant towards oxidative degradation, like Fe(tpp) (tpp = *meso*-tetraphenylporphyrin) or Fe(tmp)(OH) [tmp = *meso*-tetrakis-(2,4,6-trimethylphenyl)porphyrin] led to the formation of both cyclohexanol and cyclohexanone with very low yields ($\Phi_{ox} < 10^{-4}$).†

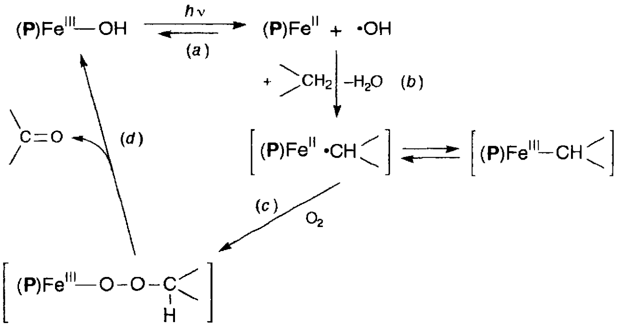
Table 1 Oxidation of cycloalkanes by O_2 catalysed by photoirradiated iron porphyrins[a]

Catalyst	Products[b]	$10^3\Phi_{ox}$[c]	Initial[d] rate	Turnover[e]
Substrate = cyclohexane				
Fe(tdcpp)(OH)	one	1.7	0.14	80
	ol	<0.1		<2
Fe(tdcpp)(Cl)	one	0.25	0.02	3
	ol	0.55	0.04	7
Fe(tdcpp)(OEt)	one	0.45	0.03	10
	ol	0.75	0.06	18
Fe(tpp)(Cl)	one	<0.1		<2
	ol	<0.1		—
Fe(tmp)(OH)	one	<0.1		—
	ol	<0.1		—
Substrate = cyclooctane				
Fe(tdcpp)(OH)	one	6.3	0.55	150
	ol	1.0	0.08	25
Fe(tdcpp)(Cl)	one	1.0	0.08	170
	ol	0.35	0.03	60

[a] In a typical experiment, a 3×10^{-5} mol dm^{-3} solution of iron porphyrin in aerated cyclohexane (200 Torr O_2) was irradiated in a 1 cm spectrophotometric cell with light of wavelength between 350 and 450 nm at 22 ± 1 °C as reported previously.[3] (Hanau Q400 mercury lamp; selection of required wavelength range by use of a glass cut-off filter.) Under these conditions, incident light was completely absorbed. Reaction products were determined by GC by comparison of their retention times with those of authentic samples, using iodobenzene as internal standard. Reported values are ±10%. [b] One = cyclohexanone for cyclohexane and cyclooctanone for cyclooctane; ol = cyclohexanol for cyclohexane and cyclooctanol for cyclooctane. [c] Moles of product per mole of absorbed photons. [d] Moles of products formed per mole of iron catalyst and per min, at the beginning of the reaction. [e] Moles of product formed per mole of consumed iron porphyrin.

Irradiation of Fe(tdcpp)(OH) in cyclooctane also led to the major formation of cyclooctanone with a relatively good quantum yield (6.3×10^{-3}) with 150 turnovers of the catalyst before its disappearance. However, in contrast to what was observed for cyclohexane, the alcohol : ketone ratio obtained with Fe(tdcpp)(OH) was higher (0.17 : 1 instead of 0.02 : 1) and the alcohol and ketone yields did not markedly change upon replacement of Fe(tdcpp)(OH) by Fe(tdcpp)(Cl) (Table 1).

The following experiments have been done in order to discover whether the high-valent iron–oxo (formally Fe^V=O) species, which are the active species in iron porphyrin-catalysed monooxygenations of substrates either by single oxygen atom donors or by O_2 and a reducing agent,[1] were also involved in the above described photoassisted oxidations. These active Fe^V=O species are very efficient for the epoxidation of alkenes like cyclohexene or *cis*-stilbene,[1] even in the presence of an excess of alkane.[13] However, irradiation of Fe(tdcpp)(OH) either in pure cyclohexene or in CH_2Cl_2 containing 5% of *cis*-stilbene,‡ under conditions identical to those used for cyclohexane, failed to give detectable amounts of the corresponding epoxides, whereas large amounts of allylic oxidation products were formed in the case of cyclohexene (5000 and 4500 turnovers after 30 min reaction for the formation of cyclohexenol and cyclohexenone, respectively). These results indicate that the major active species involved in the observed photoassisted oxidation of cycloalkanes catalysed by Fe^{III}(tdcpp)(OH) is not a (tdcpp)Fe^V=O complex. A likely mechanism for cyclohexanone formation in this reaction involves ˙OH radicals formed by photocleavage of the Fe–OH bond of Fe(tdcpp)(OH) [eqn. (2)] as a reactive species. This radical should easily abstract a hydrogen atom of cyclohexane, leading to the formation of an Fe^{II}–cyclohexyl radical pair (Scheme 1). Reaction of O_2 with this pair of free radicals (which could exist as an Fe^{III}–σ-alkyl complex[1c]) could lead to an Fe^{III}–peroxoalkyl complex. Such complexes



Scheme 1

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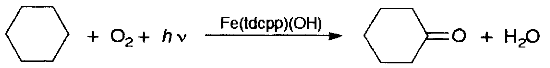
† Oxidation of cumene by O_2 and photoirradiated Fe(tpp)(Cl) has been reported;[12] these authors mentioned that other substrates more difficult to oxidize were not hydroxylated by this Fe(tpp)(Cl) system.

‡ In the case of reactions performed on *cis*-stilbene, irradiations were carried out at λ > 400 nm to avoid direct photochemistry of this aromatic alkene.

were found rapidly and selectively to decompose with formation of the corresponding ketone and the starting $\mathrm{Fe^{III}}$ complex.[14] Under the conditions used, this reaction would regenerate $\mathrm{(tdcpp)Fe^{III}{-}OH}$. The mechanism of Scheme 1 would explain the selective formation of cyclohexanone from cyclohexane and irradiated Fe(tdcpp)(OH) in catalytic amounts with the stoichiometry of eqn. (3). It would also



(3)

explain why this system is not able to epoxidize alkenes, as its active •OH species is very prone to abstract hydrogen atoms from alkanes or alkenes (in allylic position) but not to add to alkene double bonds. It is noteworthy that step (*a*)[11] and steps (*c* + *d*)[14] have already been reported. The minor formation of alcohols from cyclohexane and cyclooctane and Fe(tdcpp)(OH) could derive from secondary reactions due to the formation of ROO•[12] or ROOH (after steps *b* and *c*) and their further decomposition catalysed by Fe(tdcpp).[15]

This photoassisted oxidation of cyclohexane into cyclohexanone catalysed by Fe(tdcpp)(OH) is a new kind of selective activation and functionalization of alkanes by O_2 under mild conditions, as it does not need any consumption of a reducing agent in contrast with most of the previously described comparable iron porphyrin-based systems and as its mechanism better corresponds to a dioxygenase rather than to a monooxygenase reaction.

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