

Photocatalytic Oxygenation of Strained Alicyclic Alkenes with μ -Oxo-bis[tetraphenylporphyrinatoiron(III)] and Molecular Oxygen

Lutz Weber,* Günter Haufe, Detlef Rehorek and Horst Hennig

Department of Chemistry, Karl Marx University, Talstr. 35, 7010 Leipzig, Germany

Iron(III) porphyrins are active catalysts for the photocatalytic epoxidation of strained cyclic alkenes and their methyl substituted derivatives with molecular oxygen.

Oxygenase enzymes play an important role in biogenesis and metabolism of xenobiotics in living organisms. Monooxygenases like cytochrome P-450 are thus reported to hydroxylate and to epoxidize unsaturated hydrocarbons. The oxidizing species of these cytochrome P-450 isozymes is assumed to be formally an oxoiron(V) porphyrin, reactions of which are reproduced by synthetic analogues in a wide variety of catalytic systems.¹ However, little is known about the chemistry of the alternative enzymic intermediate, the one-electron reduction product, the oxoiron(IV) ('ferryl') porphyrin, which is believed to hydroxylate hydrocarbons *via* a peroxy radical-chain mechanism² rather than to epoxidize alkenes.³ This communication reports for the first time that the oxoiron(IV) tetraphenylporphyrin (tpp) complex is capable of epoxidizing and/or hydroxylating cycloalkenes depending on the structure of the alkene, eqn. (2).

The oxoiron(IV) complex is formed *via* the known photodisproportionation of μ -oxo-bis[tetraphenylporphyrinatoiron(III)] upon irradiation in the wavelength range 350–440 nm, eqn. (1).² The initial μ -oxoiron complex is regenerated from

the reduced iron(II) porphyrin in the presence of dioxygen.^{2a} Contrary to the reported⁴ catalysed thermal autoxidation of various alkenes by $[\text{Fe}(\text{tpp})]_2\text{O}$ and the photoinduced autoxidation of the alkenes (Table 2), we found different product compositions and higher yields of oxygenated compounds under our photocatalytic conditions, Table 1.

Typical radical-chain autoxidation products were obtained in the case of 1-methylcyclopentene and the cyclohexenes with an up to tenfold enhancement of the reaction rate compared to autoxidation.

In contrast with these less strained alkenes the epoxide is the main product in the catalysed reaction with methylcycloheptene, while epoxides have been obtained even as the sole products starting from strained cyclooctenes. This result is of particular interest with respect to the autoxidation of 1,5-dimethylcycloocta-1,5-diene which yields with high turnover rates only 11% of the monoepoxide and a broad spectrum of allylic oxygenation products.

The following types of oxygenation reactions seem to operate in iron porphyrin photocatalysed oxygenations

Table 1 Photocatalytic oxygenation of cyclic alkenes by tetraphenylporphyrinatoiron^a

Alkene	Catalyst turnover ^b	Time/h	Products (mol %) ^c			
			Epoxide	ROH	ROOH	Ketone(s)
1-Methylcyclopentene	1236	4	26 (2)	21	17	36
Cyclohexene	625	4	4	28	—	68
1-Methylcyclohexene	4026	8	10	46 (4)	—	44 (2)
Cycloheptene	28	8	34	26	—	40
1-Methylcycloheptene	1503	8	61	—	—	39 (2)
Cyclooctene	52	8	100	—	—	—
1-Methylcyclooctene	300	8	100	—	—	—
1,5-Dimethylcycloocta-1,5-diene	986	8	100 (2)	—	—	—

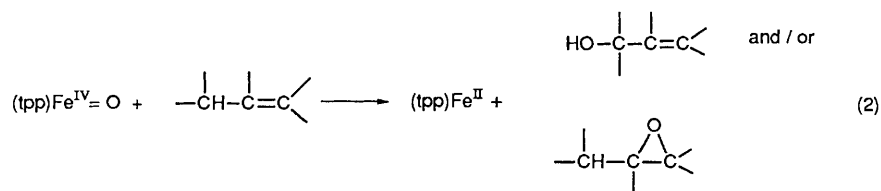
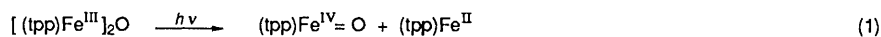
^a The photocatalytic oxygenation reactions were performed in a 50 ml thermostated, stirred photoreactor, equipped with a 55 W tungsten immersion lamp at 40°C and passing a stream of dry air (2 l h⁻¹) through the solution over the reaction period of 8 h. $[\text{Fe}(\text{tpp})]_2\text{O}$ (10 μmol) was used as catalyst with 0.1 mol of substrate dissolved in benzene (30 ml). ^b Moles of product formed per mole of catalyst.

^c Product analysis was performed by quantitative ¹³C NMR spectroscopy and computer analysis of the reaction mixtures.⁷ The number of different isomeric epoxides, allylic alcohols, hydroperoxides and ketones are given in parentheses. Products below 0.1 mol% were neglected.

Table 2 Photoinduced autoxidation of cyclic alkenes^a

Alkene	Catalyst turnover ^b	Time/h	Products (mol %)			
			Epoxide	ROH	ROOH	Ketone(s)
1-Methylcyclopentene	309	4	28	72	—	—
Cyclohexene	64	4	21	35	—	44
1-Methylcyclohexene	420	8	12	40 (4) ^c	46 (3)	2
Cycloheptene	45	8	29	33	—	38
1-Methylcycloheptene	101	8	53	11	25	11
Cyclooctene	0	8	—	—	—	—
1-Methylcyclooctene	49	8	—	100 (2)	—	—
1,5-Dimethylcycloocta-1,5-diene	4233	8	11	35 (6)	49 (3)	5 (3)

^a Conditions as in Table 1, but without catalyst. ^b Turnovers were calculated on the basis of an imaginary amount of 10 μmol of catalyst to allow comparison with results in Table 1. ^c Number of products.



depending on the nature of the alkene. (i) Abstraction of an allylic hydrogen from the substrate by either recombination of hydroxyl with the alkyl radical in the radical cage or/and diffusion of alkyl radicals from the porphyrin and reaction with dioxygen leading to a product spectrum close to autoxidation. Epoxides are formed *via* O-transfer from intermediary hydroperoxyl radicals. (ii) 'Direct' epoxidation of strained alkenes by the ferryl complex.

Only few data have been reported comparing the reactivity of different alkenes with cytochrome P-450 and iron porphyrin models.⁶ However, product selectivities obtained in the photocatalytic reaction allow ferryl species to be considered as a reasonable intermediate in P-450 and peroxidase enzymes. Furthermore, the reported^{3b} formation of epoxycyclooctane under conditions of the homolytic O-O bond fission of an acylperoxoiron(III) porphyrin may be also explained in terms of an oxoiron(IV) porphyrin intermediate.

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