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Letter

Hydroxylation of cyclohexane catalyzed by porphyrinatoiron(III) with molecular oxygen: the effect of the photochemical stability of porphyrinatoiron(III) in various solvents

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Abstract

The hydroxylation of cyclohexane catalyzed by 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride (TPPFeCl) with molecular oxygen in various solvents have been preliminarily studied in the case when the catalytic reaction was not carried out in lighttight. The catalytic activity of TPPFeCl in various solvents was found to increase in the following order: acetone < benzene < methyl-cyanide, which is consistent with the order of the photochemical stability of TPPFeCl in various solvents. It seems these results are helpful to the choice of solvents in the research of the model of cytochrome *P*450.

Keywords: Porphyrinatoiron(III); Hydroxylation; Cyclohexane; Photochemical stability

As we know, biomimetic systems based on metalloporphyrins are able to perform alkane hydroxylation and alkene epoxidation using either single oxygen atom donors or molecular oxygen by mechanism of cytochrome *P*450. The challenge of closely reproducing the activity of cytochrome *P*450 focussed the attention of chemists to the use of molecular oxygen; and a sizable effort has been made regarding the increase in catalytic efficiency of metalloporphyrins. The effect of chemical stability of metalloporphyrins on their catalytic activity has also attracted the attention of everybody working on this field. Some possible pathways of deactivation of metalloporphyrin are suggested [1–5]. Recently, we found that the catalytic activity of TPPFeCl in different solvents is related to its photochemical stability in the case when the catalytic reaction is not carried out in lighttight. We now report here the preliminary results.

TPPFeCl was prepared by our laboratory and identified by elemental analyses, UV–Vis, IR, ^{1}H NMR, and mass spectroscopies. All solvents used were of analar grade and were further purified by standard procedures before use. Hydroxylation reaction using 5,10,15,20-tetraphen-

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Table 1
The results of hydroxylation of cyclohexane catalyzed by TPPFeCl in various solvent systems

Solvent	Product amount ($mol \times 10^{-5}$)		Catalyst turnover
	Cyclohexanol	Cyclohexanone	
Benzene	8.19	7.61	7.56
Acetone	8.05	6.85	7.22
Methyl-cyanide	19.30	16.35	17.40

ylporphyrinatoiron(III) chloride (TPPFeCl) as catalysts were carried out in specially constructed glass vessels, which were not in light-tight at 35 ± 0.1°C for 4 h. The catalytic system consists of TPPFeCl (0.02 mmol), coreducing agents (1.0 mmol ascorbic acid, 0.5 mmol thiosalicylic acid), substrate (5.55 mmol cyclohexane) and corresponding solvent (10 cm^3). Pure oxygen (101.325 kPa) was posed into the solution through the inlet valve of the vessel with magnetic stirring. The products were detected and analyzed by GC (Shimadzu GC-9A). The results (Table 1) show that cyclohexane was hydroxylated to cyclohexanol and cyclohexanone catalyzed by TPPFeCl with molecular oxygen. It is very interesting that the turnover numbers were very much dependent on the properties of solvents. For different solvent systems, the catalytic activity of TPPFeCl was found to increase in the following order:

acetone < benzene < methyl-cyanide.

As mentioned above, the catalytic conditions of all systems except solvent were the same, and all catalytic experiments were not carried out in lightproof case. Various metalloporphyrins, as well as porphyrins, are known to decompose under certain conditions by light and molecular oxygen [6,7]. So, we conclude that the difference of catalytic activity of TPPFeCl may be related to the difference of photochemical stability of TPPFeCl in different solvent systems.

In order to examine the photochemical stability of TPPFeCl in various solvents, the experiment of photooxygenation of TPPFeCl has been performed. The solution of TPPFeCl ($5–10 \times 10^{-5}$ $mol \cdot dm^{-3}$) was poured into a quartz reaction tube with graduation and irradiated by a Hg lamp (150 W). During irradiation, a slow stream of pure oxygen was passed through the solution. The concentration changes of TPPFeCl upon irradiation were measured by monitoring its absorbance at Soret band in the condition of fixed volume using UV–Vis spectrophotometer(Shimadzu MPS-2000). The spectral changes in various solvents observed during photooxygenation are depicted in Figs. 1–3. As shown in Figs. 1 and 2, the absorption at Soret band attributed to TPPFeCl was weakened with the increase of irradiation time in acetone and benzene (the slightly difference of spectral shape may have resulted from the difference of the photooxygenated products). These indicate that the decomposition of TPPFeCl was present in these solutions upon irradiation. It is surprising that the Soret band of TPPFeCl was blue shift and was intensified instead of weakened with the increase of irradiation time in methyl-cyanide (Fig. 3). This may be caused by the interaction between TPPFeCl and methyl-

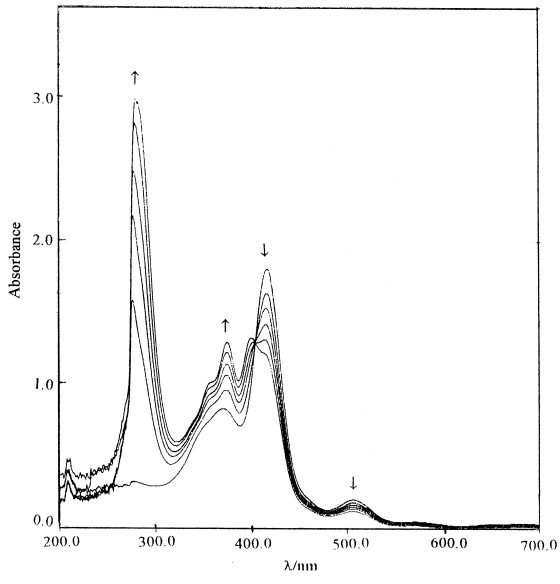

Fig. 1. Spectral change during photooxygenation of TPPFeCl in benzene. The arrows indicate the direction of change with time: 0, 30, 60, 90, 120, 150 and 180 min.

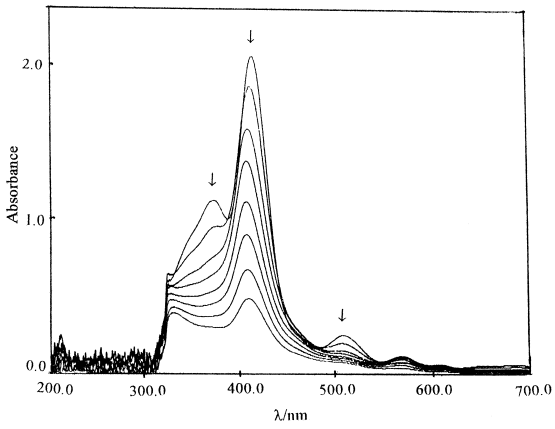

Fig. 2. Spectral change during photooxygenation of TPPFeCl in acetone. The arrows indicate the direction of change with time: 0, 15, 30, 45, 60, 75, 90 and 105 min.

cyanide under illumination. The values of the time needed to decompose 5%, 10%, and 25% of the original TPPFeCl in various solvents are listed in Table 2. Considering the photochemical behavior and the data of Table 2, the order

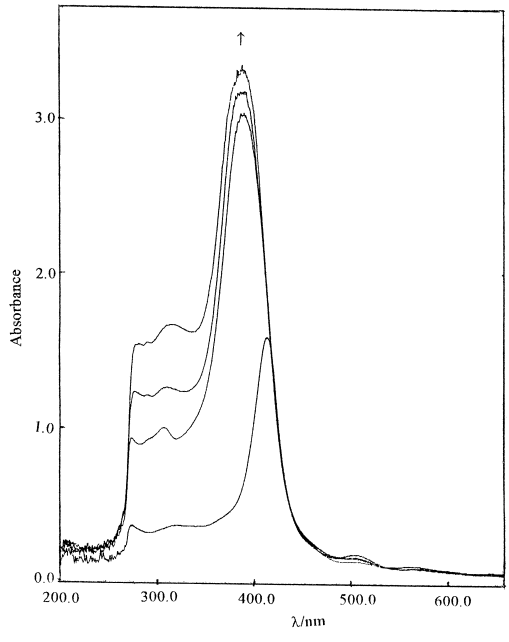

Fig. 3. Spectral change during photooxygenation of TPPFeCl in methyl-cyanide. The arrows indicate the direction of change with time: 0, 30, 60 and 90 min.

Table 2
Stability of TPPFeCl in various organic solvents under illumination in oxygen

Solvent	Decomposition time/min		
	5%	10%	25%
Benzene	27	54	142
Acetone	5	12	65
Methyl-cyanide	unable to determine		

of the photochemical stability of TPPFeCl in various solvents can be found to be:

acetone < benzene < methyl-cyanide,

and is consistent with that of the catalytic activity of TPPFeCl in various solvents described above.

The mechanism of the photooxidation of metalloporphyrins by molecular oxygen has been suggested [8,9]. The process involves generation of singlet dioxygen $^1O_2$ from triplet dioxygen $^3O_2$ by porphyrin sensitization, singlet dioxygen addition to the macrocylic ring followed by cleavage at meso-position. That is, TPPFeCl is not only a sensitiser, but also a substrate oxidized by singlet dioxygen because no other quenchers are present in our systems. The photochemical stability of TPPFeCl in our photooxygenation experiments may be related to a solvent polarity effect [10,11]. Low polarity solvents would not stabilize an adduct produced from the addition of singlet dioxygen to porphyrin ring as effectively as high polarity solvents. This may be the reason why the photochemical stability of TPPFeCl in benzene system is higher that that in the acetone system at the same condition.

In summary, photochemical stability of TPPFeCl is dependent on the properties of solvents that metalloporphyrins are dissolved in, and led to the difference of its catalytic activity in hydroxylation of cyclohexane with molecular oxygen in the case when the catalytic reaction was not carried out in lighttight. It seems these results are helpful to the choice of solvents in the research of the models of cytochrome *P*450.

Acknowledgements

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