

Sterically hindered iron-porphyrins as catalysts in cyclohexane oxidation. Steric effect of oxygen transfer from PhIO to iron(III)-porphyrins[†]

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Six sterically hindered chloro *meso-tetra-ortho*-alkylphenylporphinato iron complexes (T(*o*-R)PPFe(III)Cl, R=Me, Et, *n*-Pr, *n*-Bu, *i*-Pr, *t*-Bu) were used to catalyse the monooxygenation of cyclohexane with PhIO. A special steric effect of these alkyl substituents R on the catalytic character is proposed on the basis of the results.

Keywords: iron-porphyrins, cyclohexane oxidation

The use of synthetic ferric porphyrin derivatives as models of cytochrome P-450 to monooxygenate alkane has now been firmly established. However, these models usually give low yields of the corresponding alcohols and rather low selectivity.¹⁻² Nappa reported that steric control of iron porphyrin complex was needed to monooxygenate hydrocarbon compounds in higher yield.³ On the other hand, Gross reported recently that aryl-chlorinated iron tetraarylporphyrins with chloro substituents at the *b*-pyrrole positions was not a better catalyst than the derivative without chloro substituents at the *b*-pyrrole positions.⁴ In order to improve our understanding of this factor in different iron porphyrin complexes which influence the monooxygenation of cyclohexane, six sterically hindered chloro *meso-tetra-ortho*-alkylphenylporphinatoirons complexes (T(*o*-R)PPFe(III)Cl, R=Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu) were prepared and their catalytic effects in terms of both the yield of cyclohexanol (and cyclohexanone) and the rate of cyclohexanol formation were studied.

All T(*o*-R)PPFeCl samples with different R groups gave higher yields of cyclohexanol (and cyclohexanone), and also gave higher rates of cyclohexanol formation than TPPFeCl when they were used to catalyse the monooxygenation of cyclohexane. Obviously, the steric effect (but not electronic effect)³ of ortho alkyl groups in T(*o*-R)PPFeCl is favourable to the catalytic process. These results are shown in Table 1 and Fig. 1.

From these results, the following orders were observed for the yields of cyclohexanol when T(*o*-R)PPFeCl was used as catalyst: R = *i*-Pr > Et > *n*-Pr > Me > *n*-Bu > *t*-Bu > H. The order of the rate of cyclohexanol formation for the above reaction is: R = *i*-Pr > Et > *t*-Bu ≥ *n*-Pr ≥ Me ≥ *n*-Bu > H. These results suggest that the medium size *ortho* alkyl groups (*i*-Pr and Et) on the phenyl groups of porphyrin periphery in T(*o*-R)PPFeCl is more favourable to the catalysed oxygen atom transfer from PhIO to

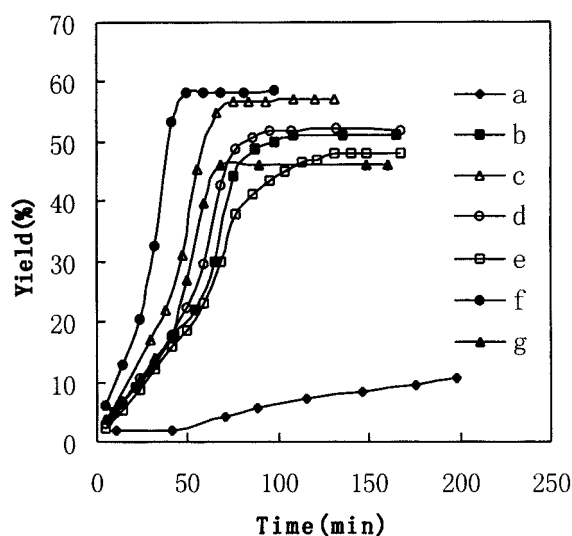


Fig. 1 Concentrations of cyclohexanol vs times in the monooxygenation of cyclohexane with PhIO catalysed by T(*o*-R)PPFeCl: (a), R=H; (b), R=Me; (c), R=Et; (d), R=*n*-Pr; (e), R=*n*-Bu; (f), R=*i*-Pr; (g), R=*t*-Bu.

cyclohexane. Except for T(*o*-*t*-Bu)PPFeCl, a parallel relationship between the catalytic rates of cyclohexanol formation and the yields of cyclohexanol is apparent.

The lifetimes of T(*o*-R)PPFeCl with different R groups were studied by monitoring the destruction of T(*o*-R)PPFeCl with PhIO in CH₂Cl₂ medium with UV-Vis spectrometer at 25°C. The results show the order of the destruction of seven different T(*o*-R)PPFeCl sample with PhIO in the first 10 min

Table 1 The results of the monooxygenation of cyclohexane with PhIO catalysed by T(*o*-R)PPFeCl

Iron porphyrins R	Yield/%		Rate constant mol/l/min ³ × 10 ⁻³	Correlation coefficient
	Cyclohexanol	Cyclohexanone		
H	35.4	10.3	0.34	0.995
Me	51.0	13.3	4.1	0.981
Et	57.0	14.8	6.1	0.982
<i>n</i> -Pr	52.0	13.8	4.4	0.982
<i>n</i> -Bu	48.1	14.4	3.4	0.991
<i>i</i> -Pr	58.4	14.1	9.2	0.983
<i>t</i> -Bu	46.0	13.7	4.9	0.980

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as: $R = H \gg Me > Et > n\text{-Pr} > t\text{-Bu} > n\text{-Bu} > i\text{-Pr}$, indicating that except for $T(o\text{-}t\text{-Bu})PPFeCl$, the more the size of the alkyl groups increased, the longer the lifetime of $T(o\text{-}R)PPFeCl$ becomes. Apparently, the *ortho* alkyl groups offer a protective effect against the destruction of $T(o\text{-}R)PPFeCl$. The lifetime of $T(o\text{-}R)PPFeCl$ does not completely parallel the yield of cyclohexanol and the rate of cyclohexanol formation. From these results we may conclude that it is not the lifetime of $T(o\text{-}R)PPFeCl$ but the rate of cyclohexanol formation which is primarily responsible for the higher yield in our experiment, and the steric effect of the *ortho* alkyl substituents in $T(o\text{-}R)PPFeCl$ should favour the catalytic process in the monooxygenation of cyclohexane.

A mechanism for the monooxygenation of cyclohexane with PhIO catalysed by $TPPFeCl$ has been proposed (Scheme 1).⁵⁻⁷ Step 2 has been suggested as the rate-determining step.⁸ Obviously, both the approach of PhIO to $TPPFeCl$ and the approach of substrate to oxo-metal species could be unfavourably influenced by the steric bulkiness of the peripheral substituents of the porphyrin ring both in step 1 and in step 3, based on the 'side-on approach' model proposed first by Groves and co-workers.^{9,10} Therefore, the steric effect of R should favour step 2. The catalysis of iron-porphyrins may be also favoured by the presence of hydroxyl groups present in alkyl substituents. However, the self-monooxygenation of the alkyl groups in the parent $T(o\text{-}R)PPFeCl$ during monooxygenation of cyclohexane was not observed in the infrared spectra of the reaction mixture of $T(o\text{-}R)PPFeCl$ with PhIO in the absence of substrate. Hence a reasonable explanation for the steric effect is that the nonbonding interaction between the *ortho* alkyl group and PhI moiety in the $PhIO\text{-}Fe(T(o\text{-}R)PP)Cl$ adduct promotes the cleavage of the I-O bond and thus the formation of the oxo- $Fe(T(o\text{-}R)PP)Cl$ intermediate (Scheme 2).

It is surprising that although *t*-butyl group is bulkier than *i*-propyl group, the $T(o\text{-}t\text{-Bu})PPFeCl$ is not only less efficient in catalysing the monooxygenation of cyclohexane than $T(o\text{-}i\text{-Pr})PPFeCl$ (in terms of both the yield and rate of cyclohexanol formation) but is also more susceptible to the destruction with PhIO than $T(o\text{-}i\text{-Pr})PPFeCl$. According to the red shift of the absorption band of $T(o\text{-}t\text{-Bu})PPFeCl$ in UV-Vis spectra as compared with other $T(o\text{-}R)PPFeCl$, we suggest that tetra *o*-*t*-butylphenyl porphyrin ring in $T(o\text{-}t\text{-Bu})PPFeCl$ is relatively flatter than that of other $T(o\text{-}R)PPFeCl$ because of the nonbonding interaction between *t*-Bu and *t*-Bu groups or *t*-Bu and phenyl groups. Under normal conditions the substituted phenyl groups in other $T(o\text{-}R)PPFeCl$ are nearly perpendicular to the porphyrin plane).³ As a result, the distance between the *t*-Bu group and PhI moiety in $T(o\text{-}t\text{-Bu})PPFeCl\text{-O-I-Ph}$ would be increased and

the nonbonding interaction between them accordingly decreased. Likewise, *t*-Bu groups in $T(o\text{-}t\text{-Bu})PPFeCl$ offer less protection against the destruction with PhIO.

Experimental

Elemental analyses were done on a U.S. Model PE-240C instrument. UV-Vis spectra were recorded on a Shimadzu Model UV-240 spectrometer and infrared spectra on a Shimadzu IR-470 spectrophotometer. Gas chromatographic analysis was performed on a Shimadzu Model GC-9A chromatographic instrument with hydrogen flame ionisation detector, and PEG-20M column.

All solvents were purified by the standard procedures before use. Iodobenzene was synthesised according to the literature method.¹¹ *p*-Dichlorobenzene was chemical grade without further purification. $TPPH_2$ and $T(o\text{-}R)PPH_2$ ($R = \text{Me, Et, } n\text{-Pr, } i\text{-Pr, } n\text{-Bu, } t\text{-Bu}$) were synthesised according to the literature method¹²⁻¹⁴ with the corresponding *ortho*-alkyl-benzaldehydes and pyrroles. Some alkylbenzaldehydes were synthesised according to the modified Klouwen method¹⁴⁻¹⁵ and identified by proton NMR and elemental analysis. $TPPFeCl$ and $T(o\text{-}R)PPFeCl$ were synthesised according to the literature¹³ with some modification.¹⁴

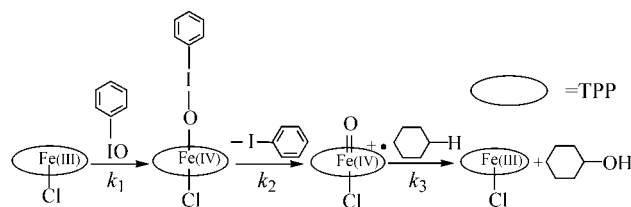
Catalytic monooxygenation of cyclohexane: $T(o\text{-}R)PPFeCl$ (0.0283 mmol), PhIO (160 mg, 0.727 mmol) and *p*-dichlorobenzene (an internal standard for GC measurement) accurately measured were added to 10 ml of cyclohexane. The reaction mixture was stirred vigorously at 25°C until cyclohexanol was no longer formed. When the reaction started, the reactant sample was withdrawn quantitatively with syringe from the reaction vessel at an interval of about 10 min for GC analysis. All reactions were repeated at least 3 times. The condition and data treatment for GC measurement and quantitative calculation were reported in our previous paper.¹⁴ The rate constants k_i for these catalytic monooxygenation of cyclohexane were calculated according to the pseudo-zero order kinetic treatment of these reaction in the first 45 minutes after the reaction started, and very good linear correlations between the quantities of the resulted cyclohexanol or cyclohexanone and reaction time were presented. The kinetic measurement of the oxidative destruction of $T(o\text{-}R)PPFeCl$ was run in UV/Vis spectrometer with the mixture of PhIO and $T(o\text{-}R)PPFeCl$ in CH_2Cl_2 at 25°C by monitoring the decline of the special absorption band (506 nm) of $T(o\text{-}R)PPFeCl$ for 10 minutes.

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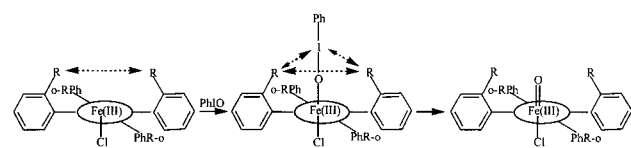
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Scheme 1



Scheme 2