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Base Acceleration of Alkane Oxidation by an Iron-porphyrin–Hypochlorite System. Activity, Selectivity and Kinetic Isotope Effect

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Addition of alkali strongly accelerates the oxidation of cyclohexane by an iron tetramesitylporphyrin–NaOCl system, the selectivity of the reaction and the H–D kinetic isotope effect also being affected; possible mechanisms of OH^- action are discussed.

The creation of efficient processes for the selective oxidation of alkanes under mild conditions remains a considerable challenge.[1] The biomimetic approach, *i.e.* using the principles of monooxygenase operation, has proved to be fruitful.[2,3] Recently, it has been found that iron porphyrins (PFeCl) can transfer an oxygen atom to alkanes from NaOCl under phase transfer conditions.[4,5] The rate and selectivity of this alkane oxidation depend on the reaction conditions, the structure of PFeCl and the medium. A characteristic feature of the PFeCl–NaOCl system in alkane oxidation is the high values of the H–D kinetic isotope effects (KIE), which depend on the structure of PFeCl.[6] In this work, we have investigated the influence of a base on alkane oxidation by an iron tetramesitylporphyrin chloride (TMPFeCl)–NaOCl system.

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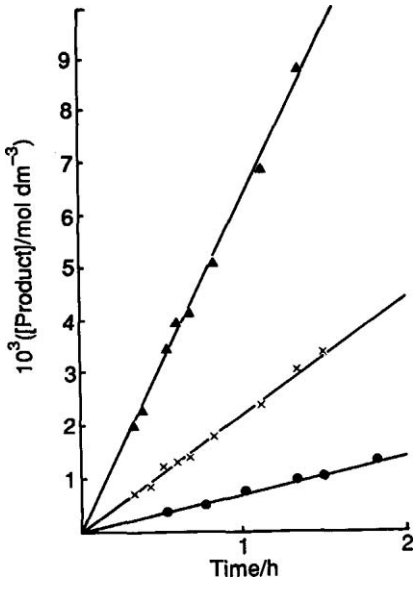


Fig. 1 Kinetics of formation of cyclohexanol (▲) and cyclohexanone (×) with $[OH^-]_{H_2O} = 12$ mol dm^{-3} and kinetics of cyclohexanol formation (●) at $[OH^-]_{H_2O} = 2.3$ mol dm^{-3}. *Experimental conditions*: $T = 20$ °C, 1 mol dm^{-3} NaOCl solution (0.2 ml), C_6H_6 (0.8 ml), C_6H_{12} (0.2 ml), TMPFeCl (0.12 μmol), CTAB (2.4 μmol).

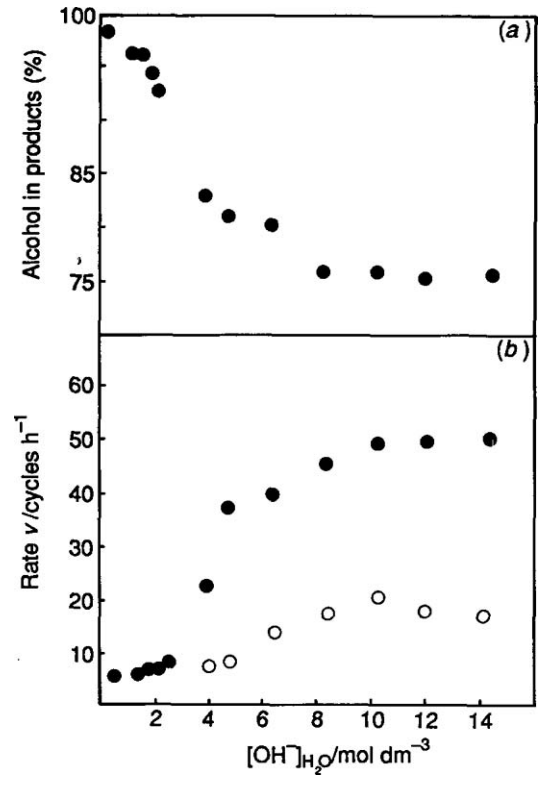


Fig. 2 Dependence of the rate and selectivity of cyclohexane oxidation by TMPFeCl–NaOCl on $[OH^-]_{H_2O}$. (*a*) Percentage of alcohol in reaction products; (*b*) initial rates of the cyclohexanol (●) and cyclohexanone formation (○). Experimental conditions as described in Fig. 1.

PFeCl catalyses cyclohexane oxidation in a biphasic medium C_6H_6–H_2O in the presence of a cetyltrimethylammonium bromide (CTAB) phase transfer agent, which transfers OCl^- into the organic phase. Other anions, such as Cl^- and OH^-, can also be transferred to C_6H_6 from the aqueous phase. The order of extraction capacity for the C_6H_6–H_2O system is $OCl^- > Cl^- > OH^-$.[7] Hence the organic phase can dissolve OH^- when a very basic solution of NaOCl is used.

Oxidation of C_6H_{12} was conducted in a reaction vessel with a magnetic stirrer. In a typical experiment, 1.5×10^{-3} mol NaOCl in 0.2 ml of alkaline solution was added to a solution of 1.2×10^{-7} mol TMPFeCl and 2.4×10^{-6} mol CTAB in 0.8 ml benzene and 0.2 ml alkane and stirred for 4 h at 20.0 ± 0.1 °C.

Analysis of the products was conducted by GLC. The kinetic isotope effect was measured in a competitive oxidation of equamolar mixtures of cyclohexane and cyclopentane ($C_6H_{12} + C_5H_{10}$) and ($C_6D_{12} + C_5H_{10}$). KIE values were determined by dividing the ratio $[C_6H_{11}OH]/[C_5H_9OH]$ by the ratio $[C_6D_{11}OH]/[C_5H_9OH]$.

The kinetics of product formation in cyclohexane oxidation by the TMPFeCl–NaOCl system with $[OH^-]_{H_2O} = 2.3$ mol dm^{-3} and 12 mol dm^{-3} is shown in Fig. 1. When $[OH^-]_{H_2O} = 2.3$ mol dm^{-3}, the initial rate of alcohol formation is equal to 7 turnovers per hour. At $[OH^-]_{H_2O} = 12$ mol dm^{-3}, two products of the C_6H_{12} oxidation have been identified, namely $C_6H_{11}OH$ and $C_6H_{10}O$ (3:1) and the turnover numbers for alcohol and ketone formation are increased to 50 and 16 h^{-1}, respectively.

The dependence of both the rate and selectivity of cyclohexane oxidation on $[OH^-]_{H_2O}$ have been investigated (Fig. 2). At base concentrations in the aqueous phase lower than 2 mol dm^{-3}, almost no ketone is formed. The rate of C_6H_{12} oxidation is markedly affected by an increase in the base concentration from 2 to 7 mol dm^{-3}. Above 7 mol dm^{-3}, $[OH^-]_{H_2O}$ changes neither the rate nor the selectivity of alkane oxidation. To our knowledge there are no literature precedents for an accelerating influence of a base on alkane oxidation in such systems.

The dependence of the KIE associated with the oxidation of C_6H_{12} by the TMPFeCl–NaOCl system at 20 °C on $[OH^-]_{H_2O}$ has also been studied [eqn. (1)].

$$\frac{C_6H_{12}}{C_6D_{12}} \xrightarrow{\text{TMPFeCl–NaOCl}} \frac{C_6H_{11}OH}{C_6D_{11}OD} \quad (1)$$

When $[OH^-]_{H_2O} < 2$ mol dm^{-3}, $k_H/k_D = 21.9 \pm 1.9$
When $[OH^-]_{H_2O} > 7$ mol dm^{-3}, $k_H/k_D = 11.2 \pm 0.5$

The difference in k_H/k_D can be attributed to a more active species, formed under strongly basic conditions, which oxidizes the C—H bond with lower k_H/k_D.

Evidently, there are two pathways for alkane oxidation by the PFeCl–NaOCl system, depending on the base concentration. Pathway (1) (when $[OH^-]_{H_2O} < 2$ mol dm^{-3}): selective oxidation of alkanes occurs at a low rate and very high KIE, $k_H/k_D = 21.9 \pm 1.9$.

An analysis of the kinetic isotope effects associated with cyclohexane oxidation was given elsewhere.[6] The unusually high values of k_H/k_D and the particularly sharp dependence of k_H/k_D on temperature suggest a tunnelling contribution to the C–H bond cleavage step.[6] Pathway (2) (when $[OH^-]_{H_2O} > 7$ mol dm^{-3}): fast oxidation of alkanes to alcohol and ketone (3:1) occurs, $k_H/k_D = 11.2 \pm 0.5$ for formation of the alcohol. There is an intermediate region where $2 < [OH^-]_{H_2O} < 7$ mol dm^{-3}.

It can be seen in Fig. 1 that the kinetics of oxidation in the presence of alkali correspond to parallel formation of alcohol and ketone. Accordingly, the rate of formation and the yield of the ketone are not affected when $C_6H_{11}OH$ is initially added to the reaction mixture and the reaction is conducted under the same conditions as for the oxidation of pure cyclohexane.

The reaction is not affected if it is performed under argon, indicating that the products do not result from interaction with molecular oxygen.

Concerning the possibility of using PFeCl with electron-withdrawing substituents other than TMPFeCl, we further studied iron tetrakis (*o*-fluorophenyl)porphyrin chloride (ToFPPFeCl) as a catalyst, and a similar influence of the base

was observed. Furthermore, when NaOCl was replaced by PhIO as an oxidant, the selectivity of the C_6H_{12} oxidation was affected by the base in the same manner. Addition of alkali (NaOH + CTAB) does not, apparently, change the reaction rate since in this case the rate-limiting step is the dissolution of PhIO,[8] but the ratio alcohol:ketone changes from 9 (in the absence of a base) to *ca.* 3 (when the base is added) *i.e.*, a similar value to that obtained using NaOCl with base.

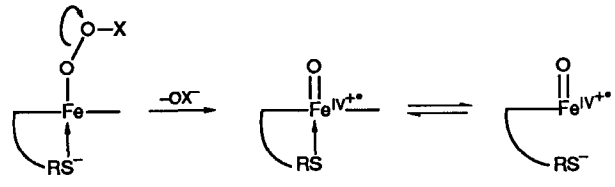
A mechanism for alkane oxidation according to Pathway (1) has previously been proposed (Scheme 1).[4]

$$RH + [PFe \cdot OCl] \rightarrow [R^{\cdot} + (HO—Fe^{IV}P)^{+} + Cl^{-}] \rightarrow ROH + PFeCl \quad (2)$$

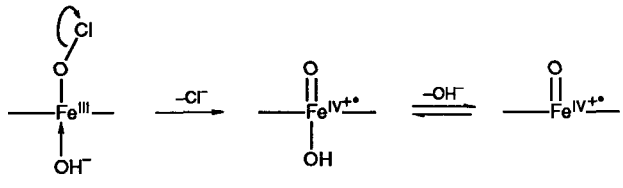
Scheme 1

This may be represented as abstraction of an H atom from the alkane by the active species, accompanied by synchronous elimination of Cl^-, followed by recombination of the alkyl radical and the iron porphyrin hydroxo complex without escape of the free radicals from the solution.

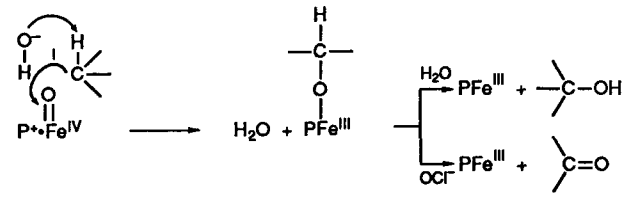
The base may accelerate the formation of active species by 'nucleophilic coaction', like that in cytochrome P-450, in which



Scheme 2 Nucleophilic coaction in cytochrome P-450



Scheme 3 Nucleophilic coaction in the PFeCl–NaOCl system



Scheme 4

the RS^- group presumably is essential for nucleophilic coaction during heterolytic cleavage of the O—O bond (Schemes 2 and 3).

An alternative mechanism might involve the participation of the base molecule in the transition state for C—H bond cleavage, since the base may be the primary acceptor of a proton from the alkane molecule (Scheme 4).

Further investigation is of course necessary to establish additional mechanistic details pertaining to the nature of this significant rate acceleration.

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