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Kinetic investigations of oxidative degradation of aromatic pollutant 2,4,6-trichlorophenol by an iron-porphyrin complex, a model of ligninase

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Abstract

Oxidative degradation of aromatic pollutant 2,4,6-trichlorophenol to 2,6-dichloro-1,4-benzoquinone was found to be efficiently catalyzed by the iron(III) complex of *tetrakis*(3,5-disulfonatomesityl)porphyrin (FeTMPS) associated with $KHSO_5$ as an oxygen atom donor [1–3]. The kinetics of this reaction was investigated at 20°C, pH 3 by determining the dependence of the reaction rate on factors such as concentration of 2,4,6-trichlorophenol, FeTMPS and $KHSO_5$. For this reaction, the proposed mechanism involves the formation of 2,6-dichlorobenzoquinone via a peroxidase-type oxidation of the chlorinated phenol.

Keywords: Trichlorophenol oxidation; Metalloporphyrin catalyzed reaction; Kinetics

1. Introduction

There has long been a pressing need for investigations to be carried out on the degradation of environmental pollutants into less noxious, polluting or more value-added compounds using natural or engineered biological and chemical systems. A thorough understanding of the systems involved in these transformations may lead to improve the disposal processes of hazardous wastes.

Among these, dechlorination and oxidation of aromatic pollutants are of particular interest, since a large number of hazardous substances of environmental concern are chlorinated hydrocarbons. Micro-organisms in soil and water convert many man-made organic compounds into inorganic products [4] and can adapt to degrade mixtures of aromatic pollutants [5]. Among the pollutants which are the most widely present in the environment, halogenated aromatic compounds are resistant to microbial destruction [4,6]. Ligninase, an extracellular peroxidase which is present in *Phanarochaete Chrysosporium*, a white rot fungus, is able to degrade lignin [7–13]. This enzyme is also able to degrade chlorinated phenols [14–16].

The catalytic oxidation and dechlorination of 2,4,6-trichlorophenol by chemical ligninase models such as manganese oxides [17,18], iron

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or manganese porphyrin complexes [1–3,19], or metallophthalocyanines [20] has been reported in recent years. Chemical biomimetic ligninase models using water-soluble iron or manganese porphyrin complexes were found to be highly efficient for the oxidation of 2,4,6-trichlorophenol to 2,6-dichloro-1,4-benzoquinone in the presence of potassium monopersulfate or hydrogen peroxide [1–3]. Potassium monopersulfate $KHSO_5$ is an efficient oxidant for several catalytic oxidations in aqueous media [21,22]. In view of such a highly efficient catalytic system, the mechanism for and the parameters affecting the kinetics of oxidation of 2,4,6-trichlorophenol by the metalloporphyrin/$KHSO_5$ system is a subject of current investigation. This article presents a kinetic study and a mechanistic proposal of the oxidative degradation of 2,4,6-trichlorophenol by the iron(III) complex of *tetrakis*(3,5-disulfonatomesityl)porphyrin (FeTMPS) associated with $KHSO_5$ [23] as oxygen atom donor.

2. Experimental section

2.1. Materials and methods

The stock solution of 2,4,6-trichlorophenol (TCP) was 0.5 mM in acetonitrile. FeTMPS was prepared by the reported method [24] and the stock solutions were 10^{-1} mM and 10^{-2} mM in doubly distilled water. The pH of the reaction mixture was maintained at 3 using a citrate-phosphate buffer (0.1 M).

2,6-Dichloro-1,4-benzoquinone was identified by HPLC on a C18–10 μm Bondapak analytical column (eluent: methanol/water 1 : 1, v/v, flow rate: 1 ml/min). Its formation was monitored spectrophotometrically at 260 nm ($\epsilon = 15\,500\ l \cdot mol^{-1} \cdot cm^{-1}$). The initial reaction rate, v, was the number of moles of quinone produced per liter of reaction mixture in 1 s ($mol \cdot l^{-1} \cdot s^{-1}$), measured on the first minute of the reaction.

2.2. Reaction mixture for kinetic measurements [3]

For each experiment, the appropriate amounts of the stock solutions of TCP and FeTMPS were taken and diluted in 0.5 ml of acetonitrile; 1 ml of citrate-phosphate buffer was added (solution A). The required amount of $KHSO_5$ was weighed and diluted separately in 0.5 ml of buffer (solution B). The total volume of both solutions was always 2 ml. Each run was started by mixing thoroughly solutions A and B. The oxidation of TCP at 20°C was followed spectrophotometrically by monitoring the formation of quinone (absorption at 260 nm).

3. Results and discussion

3.1. Variation of the catalyst concentration

The oxidation of TCP to quinone was studied by conducting the experiments at different concentration of FeTMPS (from 8 nM to 120 nM, corresponding to 0.04 mol% to 0.6 mol% vs. TCP), the concentrations of substrate (20 μM) and $KHSO_5$ (100 μM) being constant.

A linear increase of the quinone formation rate with increasing initial concentration of the catalyst was observed. The plot of the rate (v)

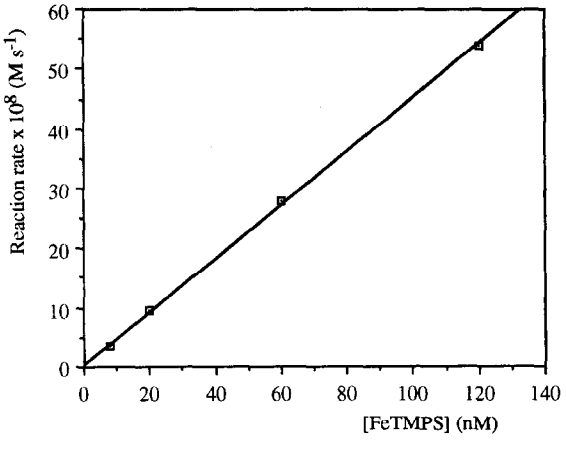


Fig. 1. Determination of the reaction order with respect to the catalyst (20°C, [2,4,6-TCP] = 20 μM and [$KHSO_5$] = 100 μM).

Table 1
Effect of TCP and $KHSO_5$ concentration on the rate of quinone formation [a]

Run	10^6 [TCP](M)	10^6 [$KHSO_5$](M)	10^8 v($M\ s^{-1}$)
1	4	100	4.5
2	8	100	10.2
3	20	100	28.0
4	25	100	35.7
5	20	40	9.5
6	20	60	16.0
7	20	150	41.9
8	20	200	55.1

[a] Experiments were performed at 20°C, [FeTMPS] = 60 nM.

of the quinone formation vs the concentration of FeTMPS (Fig. 1) passes through the origin, indicating that the catalyst is required for the reaction to proceed under these experimental conditions. The plot of log v vs. log[FeTMPS] is linear, with a slope equal to one, indicating that the oxidation of 2,4,6-trichlorophenol is first-order with respect to the catalyst.

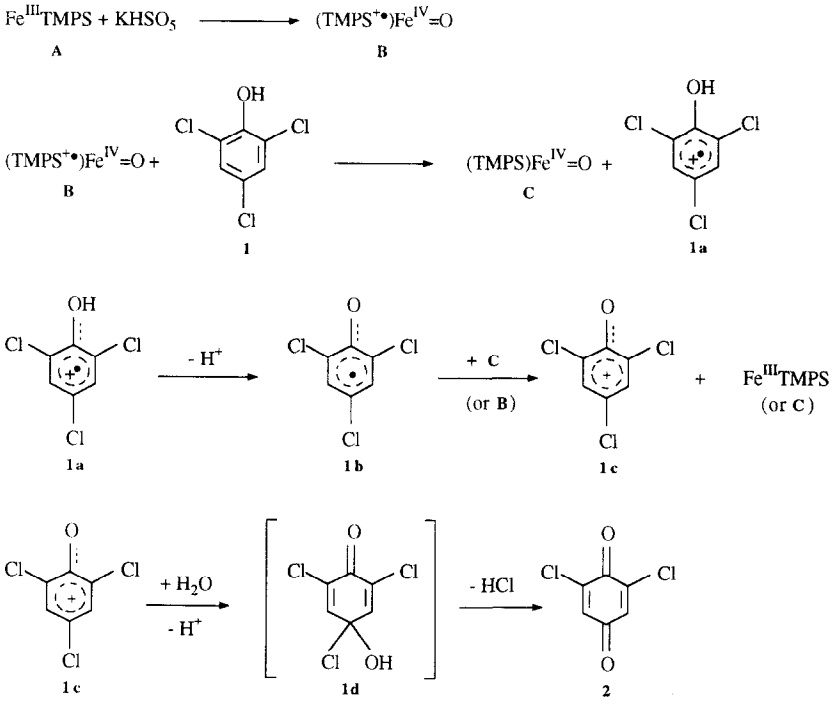
3.2. Variation of the substrate concentration

The kinetic measurements were made at different initial concentrations of TCP, in the range 4 to 25 μM (Table 1, runs 1–4), the FeTMPS concentration being 60 nM.

The rate of quinone formation was found to increase with increasing concentration of trichlorophenol and showed a first-order dependence on its concentration: the slope of log v vs. log[TCP] = 1.12.

3.3. Variation of the concentration of oxidant

The effect of the concentration of the oxidant on the rate of quinone formation was studied by varying the concentration of $KHSO_5$ from 40 μM to 200 μM, the catalyst and substrate concentrations being 60 nM and 20 μM, respectively. The amount of oxidant was therefore 2 to 10 equivalents per mole of substrate.



Scheme 1. Proposed mechanism for the oxidation of 2,4,6-TCP by the FeTMPS/$KHSO_5$ catalytic system.

The kinetic results, reported in the Table 1 (runs 3, 5–8), indicate a first-order dependence of the reaction rate on the oxidant concentration: $d(\log v)/d(\log[KHSO_5]) = 1.03$. Hence, the quinone formation is first-order with respect to TCP, FeTMPS and oxidant.

Under these conditions, the formation of the quinone is very rapid. Catalytic activity previously reported for quinone formation under identical conditions ([TCP] = 20 μM, $[KHSO_5]$ = 100 μM, [FeTMPS] = 60 nM) was 20 cycles per second [3].

The oxidation reaction of trichlorophenol involves a multistep mechanism and the determination of the rate constant of each independent step was not performed (For an example of a detailed kinetic study involving a similar multistep mechanism, namely the hydrogenation of olefins catalyzed by hydrido-iridium complexes, see Ref. [25].) It is therefore not possible to deduce from the present kinetic results a theoretical rate equation taking in account the relative rates of the different elemental reactions.

Based on the known reactivity of metalloporphyrins activated with $KHSO_5$ [21], the mechanism proposed for the oxidation of 2,4,6-trichlorophenol **1** to 2,6-dichloro-1,4-benzoquinone **2** catalyzed by the FeTMPS/$KHSO_5$ system is given in Scheme 1. In the proposed mechanism, from the catalyst Fe(III)TMPS **A**, $KHSO_5$ generates a high-valent iron-oxo species $(Por^{+\cdot})Fe(IV) = O$ **B**. This intermediate **B** reacts with substrate **1** and gives the iron-oxo species $(Por)Fe(IV) = O$ **C** and the radical-cation of trichlorophenol **1a**. Removal of a proton from **1a** yields the radical species **1b**. This species, being highly reactive, interacts with **C** (or **B**) to produce the cationic species **1c** and regenerate the catalyst **A** (or **C**). Intermediate **1c** reacts with water to produce the intermediate **1d** which can release HCl to produce the quinone **2**. The quinone formation involves a peroxidase-type two-electron oxidation of the chlorinated phenol, followed by the nucleophilic addition of a water molecule as previously observed in the **O**-demethylation of methoxylated aromatic products catalyzed by horseradish peroxidase [26,27]. The electron abstraction step is an outer-sphere electron transfer pathway as recently reported for phenol oxidation [28].

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