# Unusual Kinetic Role of a Water-Soluble Iron(III) Porphyrin Catalyst in the Oxidation of 2,4,6-Trichlorophenol by Hydrogen Peroxide

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ABSTRACT: The oxidation of 2,4,6-trichlorophenol (TCP) to 2,6-dichloro-1,4-benzoquinone (DCQ) by hydrogen peroxide using iron(III) meso-tetra(4-sulfonatophenyl) porphine chloride, Fe(TPPS)Cl, as a catalyst was studied with stopped-flow UV–vis spectrophotometry and potentiometry using a chloride ion selective electrode. The observations are interpreted by a three-step kinetic model: the initial reaction of the catalyst with the oxidant (Fe(TPPS)<sup>+</sup> + H<sub>2</sub>O<sub>2</sub>  $\rightarrow$  Cat') produces an active intermediate, which oxidizes the substrate (Cat' + TCP  $\rightarrow$  Fe(TPPS)<sup>+</sup> + DCQ + Cl<sup>-</sup>) in the second step. The third step is the transformation of the catalyst into a much less active form (Cat'  $\rightarrow$  Cat") and is responsible for the unusual kinetic phenomena observed in the system. © 2004 Wiley Periodicals, Inc. Int J Chem Kinet 36: 449–455, 2004

# INTRODUCTION

Chlorinated phenols are in widespread use as wood preservatives, pesticides, fungicides, herbicides, insecticides, or disinfectants, and they are also present in the waste of paper mills. These compounds are highly

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toxic, persistent, and regarded as priority pollutants for which efficient chemical treatment processes are needed. Oxidative degradation is probably the most advantageous reaction type for this purpose and several different chemical methods have been reported. [1–17]. These methods usually use  $H_2O_2$  or KHSO<sub>5</sub> as the stoichiometric oxidant and iron complexes as catalysts. The most successful reported catalysts have ligands with a set of four N-donor atoms in either a planar or nonplanar geometry [1–6,9,12,13]. In addition to  $H_2O_2$ -dependent oxidation, TiO<sub>2</sub>-based systems for photodegradation [8,10,11,14] and ozonization [7] have also been thoroughly studied.

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2,4,6-Trichlorophenol (TCP) is one of the most significant pollutants among chlorinated phenols and is often used to test the efficiency of different oxidation methods [2,3,13]. In this paper, we report our unusual kinetic observations using iron(III) meso-tetra(4-sulfonatophenyl) porphine chloride, Fe(TPPS)Cl (structure shown in Scheme 1), as a catalyst in the initial stage of the  $H_2O_2$ -dependent oxidation of TCP. This initial process is the transformation of TCP to 2,6-dichloro-1,4-benzoquinone (DCQ) as shown in Eq. (1):



#### Materials

2,4,6-Trichlorophenol purchased from Aldrich was purified by vacuum sublimation. Iron(III) meso-tetra(4-sulfonatophenyl) porphine chloride was used as received from Frontier Scientific (www.porphyrin.com). Ion exchanged and ultrafiltered water from a Millipore MILLI-Q purification system was used to prepare the solutions. The concentrations of hydrogen peroxide stock solutions were determined iodometrically.

### Instrumentation and Computation

A Shimadzu UV-3101PC scanning spectrophotometer and an Applied Photophysics SX-18MV stopped-flow instrument were used in this study. In potentiometric experiments, a Weiss Research CL3005 combination chloride ion selective electrode and a Hanna





Instruments HI 1131 combination pH electrode were used connected to a Hanna Instruments pH302 pHmeter. The electrodes were calibrated daily with standard NaCl solutions and standard buffers, respectively. Kinetic experiments with the chloride ion selective electrode were always carried out with a small amount of NaCl added prior to the experiment (referred to as  $[Cl^-]_0$  in the figure captions) in order to avoid badly defined voltage readings at the beginning of the kinetic curves. Constant ionic strength was maintained with 0.1 M NaNO3; the same medium was used in spectrophotometric studies. All experiments were carried out in the dark because light (even fluorescent room light) accelerates further oxidation processes significantly [17]. Our experience showed that the monochromatic analyzing light beam of a scanning spectrophotometer or stopped-flow instrument is not intense enough to influence the reaction, but the white light used in a diode-array spectrophotometer corrupts the measurements. Nonlinear least squares fitting was carried out by the software package Scientist [18].

## **RESULTS AND DISCUSSION**

Our observations on the stoichiometry of the reaction (1) in water were in agreement with an earlier report which described the preparative use of reaction (1) in acetonitrile [1]. The kinetics of the process was monitored by two independent methods: potentiometry using a chloride ion selective electrode and UV–vis spectrophotometry. Typical kinetic curves are shown in Figs. 1 and 2. The reactions were carried out in air, a comparison with air-free experiments revealed no significant differences. No reaction was observed in a sample containing  $H_2O_2$  and TCP in the absence of the catalyst after a week.

As shown in Eq. (1), the oxidation reaction produces acid. This was confirmed by measurements with pHpotentiometry. The initial pH of the unbuffered TCP solution used in the experiments shown in Fig. 1 was about 4.7 because of the acidity of TCP. The  $pK_a$  of TCP was measured to be 6.15  $\pm$  0.01 at 25.0°C by combined pH-potentiometric and UV-vis spectrophotometric experiments. This value is an agreement with the consideration that the electron-withdrawing effect of the three chloro substituents makes TCP a much stronger acid than unsubstituted phenol ( $pK_a = 9.86$  $\pm$  0.01 was measured under the same conditions). The pH was shown to decrease during the oxidation reaction (see Supplementary Material). In the experiment shown as curve b in Fig. 1, the pH was 3.6 after 15 min. A further, much slower decrease was detected and a



**Figure 1** Change of chloride ion concentration during the catalytic oxidation of TCP. Line: best fits to exponential functions.  $[H_2O_2] = 47.3 \text{ mM}; [TCP] = 1.61 \text{ mM}; [Fe(TPPS)^+] = 1.4 \mu M (a), 2.8 \mu M (b); [Cl^-]_0 = 10 \mu M; 0.1 M NaNO_3; 25.0°C.$ 

final pH of about 2.8 was reached in 15 h. As seen from the very end of curve b in Fig. 1, chloride ion formation also continued on longer time scales, but its rate was much slower than in the initial phase. These observations are consistent with further oxidation on extended time scales. Only results on the first phase (up to about 10 min) are reported in this paper as they revealed an unusual kinetic role of the catalyst. The first phase was always reasonably separated from later, slower processes.

When attempts were made to study reaction (1) at pH  $\sim$  7 in phosphate buffer, no formation of chloride ion was detected in an hour and no oxidation of TCP was confirmed at all. The probable reason for this observation is that Fe(TPPS)<sup>+</sup> quite rapidly forms the  $\mu$ -oxo dimer (TPPS)Fe–O–Fe(TPPS) at pH 7, [19,20] which seems to be catalytically inactive. Thermodynamic data show that the dimer is not formed in significant concentrations below pH 6 [19,20].

The rise in the concentration of chloride ion during the first 10 min was an exponential function of time even in the absence of buffers, as shown in Fig. 1. This strongly suggests that the pH change in the initial phase (from about 5 to 3.5) does not have a significant effect. A set of experiments was also carried out with the prior addition of gradually increasing amounts of nitric acid. Figure 3 shows that the pseudo first-order rate constant did not depend on the concentration of acid added. Consequently, the reaction rate is not influenced by the pH in this range and conclusive experiments can be done without using buffers. The pH-independence is not very surprising as TCP, H<sub>2</sub>O<sub>2</sub>, and Fe(TPPS)<sup>+</sup> do not have known pH-dependent equilibria in this range.

It is notable that the pseudo first-order rate constant  $k_{\psi}$  of the two traces shown in Fig. 1 is practically the same for the two experiments having different catalyst



**Figure 2** Stopped flow kinetic traces detected during the catalytic oxidation of TCP.  $[H_2O_2] = 49.8 \text{ mM}; [TCP] = 0$  (a), 0.055 mM (b), 0.110 mM (c);  $[Fe(TPPS)^+] = 4.1 \mu$ M; 0.1 M NaNO<sub>3</sub>; 25.0°C; path length: 1 cm.



**Figure 3** Pseudo first-order rate constant as a function pH during the catalytic oxidation of TCP.  $[H_2O_2] = 48.3 \text{ mM};$ [TCP] = 1.60 mM;  $[Fe(TPPS)^+] = 3.1 \mu$ M;  $[Cl^-]_0 = 10 \mu$ M; 0.1 M NaNO<sub>3</sub>; 25.0°C.

concentrations, but the concentration of chloride ion produced increases with increasing catalyst concentration. This unexpected finding is consistent with the catalyst being the limiting reagent in some way. However, it is also clear that the concentration of chloride ion formed in the reaction, although only about 10-20% of the initial TCP concentration, is more than a factor of 100 larger than the initial catalyst concentration, which excludes the possibility that a stoichiometric reaction of the catalyst is being monitored rather than a catalytic process. Detailed experiments showed that  $k_{\psi}$ is independent of the concentration of Fe(TPPS)<sup>+</sup>, and directly proportional to the concentration of H<sub>2</sub>O<sub>2</sub> (see Supplementary Material at http://www.interscience. wiley.com/jpages/0538-8066/suppmat). The dependence on the concentration of TCP is shown in Fig. 4. Values of  $k_{\psi}$  could not be obtained at lower TCP concentrations because the detected curve was not exponential under those conditions.

UV–vis measurements with the stopped flow technique were also carried out to monitor the kinetics of the reaction. The absorbance was followed at 395 nm, which is the very intense Soret band of the porphyrin catalyst ( $\varepsilon = 1.2 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). TCP and DCQ do not have significant absorption at this wavelength, so these measurements gave information on the state of the catalyst. Figure 2 shows that a decrease in absorbance was detected during the process even in the absence of TCP. With increasing concentrations of TCP, the absorbance decrease became slower. In fact, when the TCP concentration was larger (~1.5 mM), the reaction could also be followed by a scanning spectrophotome-



**Figure 4** Pseudo first-order rate constant as a function of TCP concentration during the catalytic oxidation of TCP. Line: best fit to Eq. (5).  $[H_2O_2] = 48.5 \text{ mM}; [Fe(TPPS)^+] = 3.1 \ \mu\text{M}; [Cl^-]_0 = 10 \ \mu\text{M}; 0.1 \text{ M NaNO}_3; 25.0^{\circ}\text{C}.$ 

ter using manual mixing. It is also notable that the range of TCP concentrations used in the UV–vis experiments was larger than in the potentiometric study because useful experiments could be done at low TCP concentrations. It is known that Fe(TPPS)<sup>+</sup> reacts with H<sub>2</sub>O<sub>2</sub> directly resulting in multistep oxidative damage of the porphyrin [21,22]. This is consistent with our findings without TCP present. However, the absorbance change is much slower (Fig. 2) because the presence of oxidizable TCP inhibits the overall reaction between Fe(TPPS)<sup>+</sup> and H<sub>2</sub>O<sub>2</sub>, but not its first step.

The spectrum of the parent complex features the usual Soret band of iron porphyrins,  $\lambda_{max}$  295 nm ( $\epsilon$ =  $1.2 \times 10^5 \text{ L} \text{mol}^{-1} \text{ cm}^{-1}$ ). The intermediates Cat' and Cat" remain undetectable, consistent with the application of the steady-state approximation for their concentrations. The initial rate of absorbance change was used to study the reaction quantitatively. The full kinetic curves could not be fitted reasonably well to an exponential function or other explicit integrated rate equations used frequently in chemical kinetics. The initial rate of absorbance change was first order with respect to both  $H_2O_2$  and  $Fe(TPPS)^+$  (see Supplementary Material). The dependence of the initial rate on the concentration of TCP is shown in Fig. 5. As noted earlier, the presence of TCP slowed down the absorbance change quite significantly.

We found that a simple three-step kinetic model could interpret all the experimental observations. The model is shown in Scheme 2.



**Figure 5** Initial rate of absorbance change (395 nm) as a function of TCP concentration during the catalytic oxidation of TCP. Line: best fit to Eq. (7).  $[H_2O_2] = 23.8 \text{ mM}$ ;  $[Fe(TPPS)^+] = 3.6 \mu\text{M}$ ; 0.1 M NaNO<sub>3</sub>; 25.0°C; path length: 1 cm.

$$Fe(TPPS)^{+} + H_2O_2 \rightarrow Cat' \qquad v_1 = k_1[Fe(TPPS)^{+}][H_2O_2]$$
$$Cat' + TCP \rightarrow Fe(TPPS)^{+} + DCQ + Cl^{-} \qquad v_2 = k_2[Cat'][TCP]$$
$$Cat' \rightarrow Cat'' \qquad v_3 = k_3[Cat']$$

Scheme 2

In the first step, the reaction of the catalyst with  $H_2O_2$  produces intermediate Cat'. Cat' is the actual reactive oxidizing species that reacts directly with the substrate TCP in step 2, which also regenerates the original form of the catalyst. Step 3 is a self-decay of the species Cat', which accounts for the deactivation of the catalyst. In this model, standard steady-state treatment [23] for the concentration of Cat' yields

$$[\operatorname{Cat}'] = \frac{k_1 \cdot [\operatorname{H}_2 \operatorname{O}_2] \cdot [\operatorname{Fe}(\operatorname{TPPS})^+]}{k_2 [\operatorname{TCP}] + k_3}$$
(2)

Then the steady-state differential equation for  $Fe(TPPS)^+$  is

$$\frac{\mathrm{d}[\mathrm{Fe}(\mathrm{TPPS})^+]}{\mathrm{d}t} = -k_3[\mathrm{Cat'}]$$
$$= -k_3 \frac{k_1 \cdot [\mathrm{H}_2\mathrm{O}_2] \cdot [\mathrm{Fe}(\mathrm{TPPS})^+]}{k_2[\mathrm{TCP}] + k_3} \quad (3)$$

Assuming that the concentration of TCP remains constant throughout the process, which is not an unjustifiable approximation based on the experimental data (this will be discussed later in more detail), the differential equation can be solved for the concentration of the catalyst:

$$[Fe(TPPS)^+] = [Fe(TPPS)^+]_0 \times e^{-k_{\psi}t}$$
(4)

where  $k_{\psi}$  is a pseudo first-order rate constant defined as

$$k_{\psi} = \frac{k_1 \cdot k_3 \cdot [\text{H}_2\text{O}_2]}{k_2 \cdot [\text{TCP}] + k_3} \tag{5}$$

In turn, the concentration of chloride ion as a function of time can also be calculated:

$$[Cl^{-}] = \frac{k_2}{k_3} \times [TCP]_0 \cdot [Fe(TPPS)^{+}]_0 \times (1 - e^{-k_{\psi}t})$$
(6)

Finally, differentiation of Eq. (4) gives the initial rate for the concentration of  $Fe(TPPS)^+$ :

$$\left(\frac{d[\text{Fe}(\text{TPPS})^+]}{dt}\right)_{t=0} = -k_{\psi} \cdot [\text{Fe}\text{TPPS}^+]_0$$
$$= -\frac{k_1 \cdot k_3 \cdot [\text{H}_2\text{O}_2]_0}{k_2 \cdot [\text{TCP}]_0 + k_3} [\text{Fe}\text{TPPS}^+]_0 \tag{7}$$

The formulas derived for  $k_{\psi}$  and the initial rate of the concentration change of the catalyst derived on the basis of Scheme 2 agree with the experimental observations. The best fit is indicated by solid lines in Figs. 4 and 5. The following parameters were determined with least-squares fitting:  $k_1 = 6.0 \pm 0.7 \text{ L mol}^{-1} \text{ s}^{-1}$  and  $k_2/k_3 = (1.4 \pm 0.2) \times 10^5 \text{ L mol}^{-1}$ . The rate constants  $k_2$  and  $k_3$  could not be resolved independently, as is typical for steady-state conditions [23]. It is reasonable to ask whether  $k_3$  might be evaluated directly from experiments in the absence of TCP. Given that the parent catalyst provides the monitored absorption that decreases over time, and that intermediates Cat' and Cat'' are undetectably low concentrations, such experiments would provide  $k_1$  only.

The essence of the model given in Scheme 2 is that the catalyst is transformed to a less active form (Cat") while the catalyzed oxidation reaction reaches only about 10–20% conversion. As the reaction was confirmed to proceed further on extended time scales, Cat" is probably not completely inactive as an oxidation catalyst, but its catalytic effect is certainly negligible in the first phase of the reaction studied here. On the basis of this model, an interesting prediction can be made: adding a second portion of catalyst solution to a reaction mixture in a potentiometric experiment after 10 min should give rise to a second round of chloride ion formation that is similar to the initial one. Figure 6 shows that the experimental observations are in full agreement with the predictions.

At this point it is necessary to explain why the measured absorbance traces, unlike the rise in chloride ion concentration, were not exponential. The third reaction in Scheme 2 is only the first step in a sequence of decomposition reactions [21,22]. Therefore Cat" is in fact an intermediate and its concentration does not change in the same exponential fashion the concentration of Fe(TPPS)<sup>+</sup> does. The non-zero final absorbance in Fig. 2 clearly indicates that Cat" and further decomposition products also have some contribution to the absorbance signal at this wavelength. Consequently, the detected signal, which is the sum of all contributions, does not change exponentially. These complications are not present in the potentiometric experiments because chloride ion is monitored selectively.



**Figure 6** Sequential addition of catalyst during the catalytic oxidation of TCP.  $[H_2O_2] = 94.8 \text{ mM}; [TCP] = 1.42 \text{ mM}; [Fe(TPPS)^+] = 3.1 \mu M$  (after starting the reaction), 6.1  $\mu M$  (total after the addition of the second portion of catalyst);  $[Cl^-]_0 = 25 \mu M; 0.1 \text{ M NaNO}_3; 25.0^{\circ}\text{C}.$ 

It should also be noted that the pseudo first-order derivation from Scheme 2 depends on the assumption that the concentration of TCP does not change significantly during the process. The maximum yield of chloride ion was about 20% in the potentiometric experiments used for the kinetic study, this implies that the decrease in the TCP concentration during the process is about 20% at most. One might argue that this is too high to be considered as constant. However, there is another reason why the approximation works well. The actual rate of chloride ion formation can be calculated from Scheme 2 as follows:

$$\frac{d[Cl^{-}]}{dt} = k_2 \cdot [Cat'] \cdot [TCP]$$
$$= \frac{k_1 \cdot k_2 \cdot [H_2O_2] \cdot [FeTPPS^+] \cdot [TCP]}{k_2 \cdot [TCP] + k_3} \quad (8)$$

This rate shows saturation with increasing concentration of TCP. Thus, the rate is insensitive to the change in TCP concentration at high initial concentrations and the pseudo first-order approximation works well even with a substantial change in the TCP concentration. These observations also explain why the detected curves were not exponential at low initial TCP concentrations.

Cat' is a reactive, steady-state intermediate present at very low concentration levels and one can only speculate about its chemical identity. Three hints suggest that Cat' may be the end-on hydroperoxide (TPPS)Fe—OOH. First, this is not an unlikely product of the reaction between Fe(TPPS)<sup>+</sup> and H<sub>2</sub>O<sub>2</sub> with the release of a single proton. Second, end-on hydroperoxides are very often the key catalytic oxidants in different catalytic systems with iron complexes [24]. Finally, the deactivation described in the third reaction of Scheme 2 does not involve any H<sub>2</sub>O<sub>2</sub> or TCP. If H<sub>2</sub>O<sub>2</sub> or TCP were reactants in that step, the rate law would surely have a different form. End-on hydroperoxides have a well-known heterolytic bond cleavage giving iron(V) oxo species and a hydroxide ion [24]. Thus the reaction (TPPS)Fe—OOH  $\rightarrow$  (TPPS)FeO<sup>+</sup> + OH<sup>-</sup> is not unreasonable in our system, and it does not involve H<sub>2</sub>O<sub>2</sub> or TCP.

The second reaction of Scheme 2 almost certainly does not happen as a single kinetic step. Based on the known mechanisms of phenol oxidations [25-28], it seems likely that the reaction produces a phenoxide radical via hydrogen atom abstraction from TCP in the rate-determining step. The phenoxide radical is then likely to react with hydrogen peroxide present in large excess and release chloride ion forming the product quinone in subsequent fast steps. If Cat' is indeed (TPPS)Fe-OOH, it may give water and the iron(IV) oxo species (TPPS)FeO as the direct products of the second reaction in Scheme 2. (TPPS)FeO may abstract a hydrogen atom from another TCP giving (TPPS)Fe<sup>+</sup>, thus completing the catalytic cycle in steps fast relative to the rate-determining step. However, because kinetics does not yield information on reactions after the rate-determining step, the previous considerations serve only to show that it is possible to have a complete catalytic cycle with chemically plausible steps assuming that Cat' is the end-on hydroperoxide.

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