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Kinetic Study on the Oxidation of Trichlorophenol Using Hydrogen Peroxide and an Iron(III) Complex of Tetrasulfonatophthalocyanine Catalyst

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An oxidative decomposition of TCP, catalyzed by the title complex in the presence of hydrogen peroxide, was studied kinetically. The decrease in the initial reaction rate in an acidic solution resulted from a depression of the proton dissociation of hydrogen peroxide.

Chlorinated aromatic compounds, such as 2,4,6-trichlorophenol (TCP), are well-known recalcitrant pollutants because of their slow biodegradation by microorganisms.[1] TCP is one of the major chlorinated phenols produced by paper mils in the delignification of wood pulp by chlorine bleaching.[2]

Recently, it was reported that efficient oxidative dechlorination and aromatic cycle cleavage of TCP by hydrogen peroxide was catalyzed by (tetrasulfonatophthalocyaninato)iron(III) chloride, [Fe(S-pc)]Cl; TCP was oxidized to a mixture of chloromaleic, chlorofumaric, maleic, and fumaric acids and also to oxidative coupling products.[3—7] It is important to study the detailed mechanism of the oxidative decomposition of TCP for a further improvement of the system to efficiently decompose a pollutant. In this paper, we report on a kinetic study of the oxidative decomposition of TCP catalyzed by [Fe(S-pc)]Cl in the presence of hydrogen peroxide.

Aqueous hydrogen peroxide was poured into a solvent mixture of water and acetonitrile (7 : 3, v/v) containing TCP and [Fe(S-pc)]Cl, of which the pH was adjusted with a KH_2PO_4 and NaOH buffer solution. The absorption spectral change of the solution was monitored by a UV-vis spectrometer (Fig. 1). The initial reaction rate for the decomposition of TCP was followed by its absorbance change at 205 nm.[8] While some isosbestic points were observed during the reaction, their deviation arose around the end of the reaction.

By plotting the logarithm of the rate with that of the [Fe(S-pc)]Cl concentration, a straight line with a unit slope was obtained, which shows that the reaction proceeded via a first-order on the [Fe(S-pc)]Cl concentration. While the logarithm of the slope was one for the hydrogen-peroxide concentration, it was zero for TCP. The pH dependence of the rate shows that the rate reached the maximum around the neutral pH region, and then tended to decrease with increasing the pH of the solution (Fig. 2).

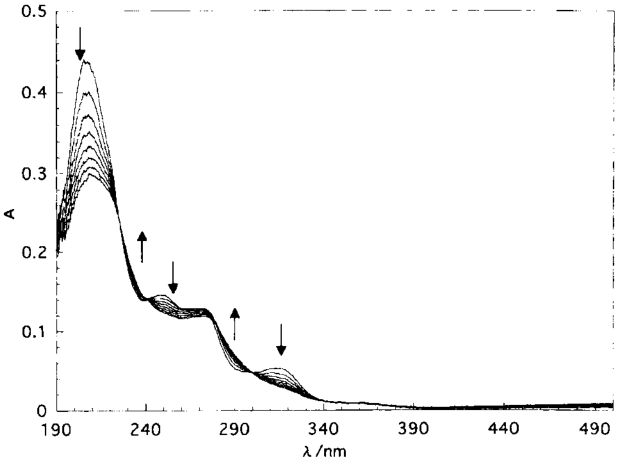

Fig. 1. Absorption spectral changes for the decomposition of TCP. [TCP] = 2×10^{-4} mol dm^{-3}, [[Fe(S-pc)]Cl] = 5×10^{-6} mol dm^{-3}, [hydrogen peroxide] = 2×10^{-4} mol dm^{-3}. pH = 7. cell length = 1 mm. The spectrum was measured in 4-min interval after the reaction.

The proposed reaction mechanism for the decomposition of TCP is shown in the Scheme 1. It was reported that the TCP degradation occurred with a nucleophilic oxidizing

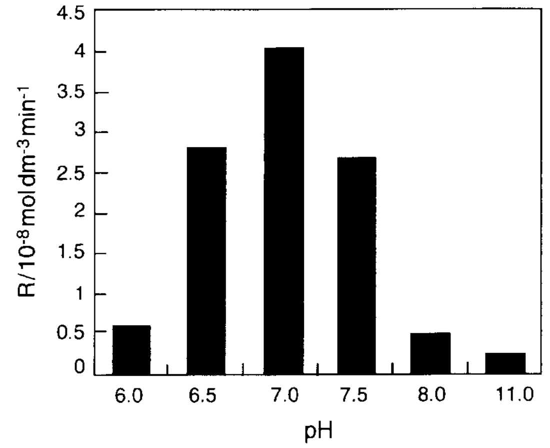

Fig. 2. Dependence of the initial rate on pH. [[Fe(S-pc)]Cl] = 5×10^{-6} mol dm^{-3}, [TCP] = 4×10^{-4} mol dm^{-3}, [hydrogen peroxide] = 7.7×10^{-4} mol dm^{-3}.

$$\mathrm{TCP} \rightleftharpoons \mathrm{H^+ + TCP^-} \tag{1}$$

$$\mathrm{H_2O_2} \rightleftharpoons \mathrm{H^+ + HO_2^-} \tag{2}$$

$$\mathrm{[Fe(S\text{-}pc)]Cl + HO_2^-} \xrightarrow{\text{slow}} \mathrm{[Fe(S\text{-}pc)]OOH} \tag{3}$$

$$\mathrm{TCP^-} \xrightarrow{\mathrm{[Fe(S\text{-}pc)]OOH}} \text{decomposed products} \tag{4}$$

Scheme 1.

species, such as the hydroperoxo intermediate, rather than an electrophilic oxo intermediate.[5,6] Based on the zero-reaction order of the TCP concentration, the formation of an active intermediate may be the rate-determining step (Eq. 3). The decrease in the rate while lowering the pH may have resulted from a decrease of hydrogen-peroxide anions, because the reaction order is zero for the TCP concentration (Eq. 2). Furthermore, the rate became slower in an alkaline solution, probably due to the formation of an inactive μ-oxo dimer by dehydration of the hydroxo complexes. Although it was reported that the slow rate in an acidic solution could be attributed to a depression of the proton dissociation of TCP ($pK_a = 6.4$),[7] based on the result of a kinetic analysis, it has been clarified that the slow rate resulted from a depression of the proton dissociation of hydrogen peroxide ($pK_a = 11.8$).

Experimental

[Fe(S-pc)]Cl was prepared by a method described in a literature,[9] and the purity of the complex was determined by the UV-vis spectrum and an elemental analysis. The UV-vis spectra were recorded on a Shimadzu UV-3100 spectrometer. The pH of the solvent mixture was measured by a F-7 Horiba pH meter. Elemental analyses were carried out using a Yanako CHN Corder MT-5.

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8 Molar absorptivity of TCP was 33000 $mol^{-1}\,dm^3\,cm^{-1}$ at 205 nm in the solvent mixture (pH = 7).

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