Photo-Fenton effect of 4-chlorophenol in ice

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HIGHLIGHTS

- Photo-Fenton effect occurs in ice.
- $^\bullet$OH concentration is determined by the molecular probe technique.
- $^\bullet$OH has an important effect on 4-chlorophenol photoconversion.
- 4-Chlorophenol photoconversion in ice is affected by the quasi-liquid layer in ice.

ARTICLE INFO

ABSTRACT

The photoconversion of 4-chlorophenol (4-CP) in a simulated sunlight-Fenton system was investigated in ice and aqueous solution. It was found that the hydroxyl radical ($^\bullet$OH) had an important effect on the photoconversion of 4-CP in both phases, but the effects of Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^- were different. In aqueous solution, the photoconversion efficiency of 4-CP was proportional to the $^\bullet$OH concentration, and hence, Cl^- and HCO_3^- as $^\bullet$OH scavengers prohibited the photoconversion; SO_4^{2-} had little effect; NO_3^- promoted the process under certain conditions owing to $^\bullet$OH being generated by the photolysis of NO_3^-. In ice, however, the photoconversion efficiency of 4-CP was not proportional to the concentration of $^\bullet$OH. The photoconversion efficiency of 4-CP increased with increasing concentrations of all ions, although the $^\bullet$OH remained almost constant, only increasing or decreasing slightly. This provides new evidence for the presence of a quasi-liquid layer (QLL). Hydroxylation products were detected in both phases. All photoproducts in aqueous solution contained only a single benzene ring, whereas in ice, dimers were also detected.

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1. Introduction

Organic pollutants in snow and ice pose threats to both wildlife and human beings [1]. Although there has been extensive research on organic pollutants in the atmosphere, natural water, and soil, relatively little has been conducted for snow and ice, which are an important part of frigid and temperate ecosystems in winter. In snow and ice, physical migration of organic pollutants, and their microbiological and chemical reactions play relatively unimportant roles, whereas photochemical reactions, which are not affected strongly by temperature, are more significant in the migration and transformation of organic pollutants [2]. Organic pollutants in snow and ice can be transformed by photochemical reactions to form photoproducts. Some of the photoproducts, some of which are different to those formed in aqueous solutions [3–6], are more toxic than their parent substances [7] when the snow and ice melt and the photoproducts are released into the environment [8].

H_2O_2 exists not only in the atmosphere [9] but also in natural snow and ice as a common trace constituent. Research on summits and in Greenland has indicated that the concentration of H_2O_2 in snow and ice has increased by 50% in the past 200 years, and especially so in the last 20 years [10]. In snow and ice, the photolysis of H_2O_2 is the main source of the hydroxyl radical ($^\bullet$OH) [11], which can cause the degradation of organic pollutants. Dolinová found that the photoproducts of aromatic hydrocarbons (benzene, anthracene, and naphthalene) in ice in a UV/H_2O_2 system were mainly hydroxylation products [12]. Our prior work also showed that the photoproducts of 4-CP in ice in a UV/H_2O_2 system included not only coupling products but also hydroxylation products [13].

Iron is commonly present in air, water, soil, plants, and animals and is involved in many chemical and biological processes [14]. The catalytic decomposition of H_2O_2 by Fe^{2+} to produce $^\bullet$OH, the so-called Fenton effect, has been used widely to remove refractory organic pollutants from wastewater [15].

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Actually, the Fenton effect also exists in the natural environment when H_2O_2 and Fe^{2+} co-exist. Prior work on the photochemical reaction of phenolic compounds in the presence of H_2O_2 in ice showed that Fe^{2+} or Fe^{3+} strongly promoted the photoconversion of phenolic compounds [16], which suggests that the photo-Fenton effect also occurs in ice. Until now, research on the photochemical reaction of organic pollutants in snow and ice has mainly focused on the direct photolysis of organic pollutants [3,17,18] and indirect photolysis in the presence of $^\bullet OH$ precursors such as nitrite, nitrate, and H_2O_2 [15,19,20]. The photo-Fenton effect in ice has not yet been reported. To understand this new phenomenon, we investigated the photoconversion of 4-CP in the presence of the Fenton reagent (H_2O_2 and Fe^{2+}) both in ice and in aqueous solution under simulated sunlight irradiation ($\lambda > 300$ nm). The concentration of $^\bullet OH$ generated during the photo-Fenton reaction was determined by the molecular probe technique. The results further confirm the role of the quasi-liquid layer (QLL) in the ice phase reaction by comparing the relationship between the concentration of $^\bullet OH$ and the photoconversion efficiency of 4-CP.

2. Experimental

2.1. Chemicals

See the Supporting Information.

2.2. Photoconversion experiments

A 125-W high-pressure mercury lamp (Shanghai Philips Co., China) with a hard Pyrex glass outer shade ($\lambda > 300$ nm) was used to simulate sunlight. Two kinds of solutions were prepared. One was used for the photoconversion of 4-CP, containing 4-CP, H_2O_2, and $FeCl_2$. The other was used for the analysis of the $^\bullet OH$ concentration, containing H_2O_2, $FeCl_2$, benzoic acid (BA), and BA–Na. Each kind of the solution was separately divided into different quartz tubes (15 mm × 150 mm, 10 mL in each tube).

For the ice phase experiment, the quartz tubes containing the mixed solution were put into a cryostat box (Henan Xinfei Electric Co., Ltd. China) and the solution was solidified at $-20\,^\circ C$ to obtain the ice sample. Comparison of freezing in slow and fast way shows that the way making ice didn't affect the photoconversion. Then, the ice samples were irradiated for 3 h in the cryostat box (-12 to $-14\,^\circ C$). The ice samples were guaranteed not to melt during irradiation. Two parallel samples were taken out every 0.5 h, thawed to room temperature ($20\,^\circ C$), and analyzed.

For the water-phase experiment, the quartz tubes containing the mixed solution were put into the cryostat box and irradiated for 3 h (3–$5\,^\circ C$). Two parallel samples were taken out every 0.5 h and analyzed.

The data in figures are the average of the two parallel samples.

2.3. Analysis of 4-CP and $^\bullet OH$

The concentration of 4-CP was analyzed by high performance liquid chromatography (HPLC).

The solution containing BA and BA-Na mentioned in 2.2 was used to capture $^\bullet OH$ generated in the system [11]. After $^\bullet OH$ had been captured, p-hydroxybenzoic acid (p-HBA) was formed, and thus, the concentration of p-HBA, which was determined by the HPLC instrument, was proportional to the $^\bullet OH$ concentration. The initial rate of $^\bullet OH$ formation was obtained by a linear fitting of [$^\bullet OH$]-t data. The details of the analysis for 4-CP and p-HBA are given in the Supporting Information.
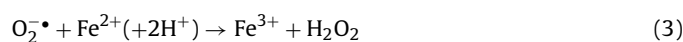
2.4. Enrichment and analysis of the photoproducts

Two extraction methods were respectively used for the enrichment of the photoproducts. In the direct extraction method, a 300-mL solution obtained from the water or ice samples after irradiation for a given time was transferred to a 1-L separating funnel and extracted with 70 mL of dichloromethane, and the extracts were concentrated to 1.5 mL using a rotary evaporator, and then quantified by gas chromatograph–mass spectrometer (GC–MS) (Finnigan Corporation U.S.). In the derivatization method, a 300-mL solution obtained from the water or ice samples after irradiation for a given time was transferred to a 1-L separating funnel, adjusted to neutral pH value with solid K_2CO_3, and extracted with 20 mL of petroleum ether (30–$60\,^\circ C$) for 1 min. The petroleum ether phase was discarded to separate alkaline and neutral organic interfering substances. Next, the solution was added 1.5 mL acetic anhydride and shaken for 1 min, then extracted for 3 min using 10 mL of toluene. The toluene phase was collected, dehydrated with Na_2SO_4 [21], and then analyzed by GC–MS after being concentrated to 1.5 mL by nitrogen sparging. The GC–MS analysis conditions for the photoproducts are listed in the Supporting Information.

3. Results and discussion

3.1. Effect of light

As shown in Fig. 1a and b, the concentration of 4-CP was unchanged under dark conditions, no matter whether in ice or aqueous solution, and when no other substances presence. However, under simulated sunlight irradiation, 4-CP was photolyzed directly because it absorbs light of wavelength greater than 300 nm ($\lambda_{max} = 280$ nm), and both H_2O_2 and Fe^{2+} slightly promoted the conversion of 4-CP. This is because the photolysis of H_2O_2 in the presence of light generates $^\bullet OH$ (Eq. (1)), and Fe^{2+} produces a little H_2O_2 (Eqs. (2) and (3)).

$$H_2O_2 + hv \rightarrow 2^\bullet OH \tag{1}$$

$$e_{aq}^- + O_2 \rightarrow O_2^{-\bullet} \tag{2}$$

$$O_2^{-\bullet} + Fe^{2+}(+2H^+) \rightarrow Fe^{3+} + H_2O_2 \tag{3}$$

When Fe^{2+} and H_2O_2 were both present, 4-CP decomposed in the aqueous solution, even under dark conditions, owing to the Fenton effect, but the conversion efficiency was lower. In ice, however, 4-CP was not significantly degraded in the dark (actually, the slow reaction of the Fenton reagent with 4-CP during the freezing process resulted in less than 5% loss of 4-CP, which must be deducted from all conversion efficiencys in ice). For H_2O_2 and Fe^{2+} together in the presence of light, 4-CP was clearly degraded in both phases, which confirms that the photo-Fenton effect occurs in ice and in aqueous solution.

Fig. 1c and d shows the change in the $^\bullet OH$ concentration during the photo-Fenton reaction in both phases. It can be seen that, under the dark condition, no $^\bullet OH$ was detected in the BA + BA − Na system in either phase, while for the BA + BA − Na + H_2O_2 + Fe^{2+} system, no $^\bullet OH$ was detected in the ice, but a little $^\bullet OH$ was detected in the aqueous solution. Under the light condition, the $^\bullet OH$ concentration clearly increased in both phases, and was higher in the aqueous solution than in the ice. This is because in the ice the free movement of molecules is restricted and then the probability of collision is decreased. The change in $^\bullet OH$ in the systems was consistent with the photoconversion of 4-CP, which shows that $^\bullet OH$ also is an important factor in the photo-Fenton reaction of 4-CP in ice.