

## Sensitized Photodegradation of Benzene in Water

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The photodegradation of benzene was studied in an aqueous solution using a medium pressure Hg-lamp. In this study, persulfate, nitrate, nitrite, chloride, and sulfate ions were all tested as sensitizers. The persulfate, nitrate, and nitrite ions exhibited a sensitizing effect in the photodegradation of benzene, whereas no detectable effects were observed with the sulfate and chloride ions. When nitrite ions were used as the sensitizer, the photodegradation of benzene ran through a maximum value and thereafter decreased with an increasing nitrite concentration. The resulting build-up of nitrite ions seemed to scavenge the hydroxyl radicals. When nitrite ions were present along with persulfate ions, the photodegradation of benzene was inhibited.

Key words : Photodegradation, Benzene, Persulfate, Nitrate, Nitrite, Chloride, Sulfate, Sensitizer, Hydroxyl radical

### 1. Introduction

As a result of urbanization and industrialization, water sources have become contaminated with anthropogenic organic compounds. One such group of compounds, which has attracted special interest because of their occurrence in water, is aromatic hydrocarbons, specifically, benzene, toluene and xylene<sup>1)</sup>. The prevalence of these compounds in the environment is due to their high production and use worldwide. In particular, these compounds are important constituents of gasoline and other commercial fuels that have an aromatic content of up to 45%. Known mechanisms that contaminate the environment include inadvertent dumping, leakage from underground storage tanks, landfill leachate, and entry into the hydrosphere by volatilization<sup>2)</sup>.

The photochemical transformation of organic pollutants in water can be accomplished by either direct or indirect routes. In direct photolysis, the photochemical reactions are initiated by the absorption of light by the substrates which is then electronically excited. Since the electronically excited molecules become energetically unstable, they undergo a rearrangement or even fragment.

However in indirect photolysis, other chemical species, or a sensitizer, is present that is capable of absorbing light. This chemical species or sensitizer becomes electronically excited by light absorption, then the excitation energy is either transferred to the substrates or produces a variety of transient oxidants such as singlet oxygen(<sup>1</sup>O<sub>2</sub>)<sup>3)</sup>, alkyl peroxy radicals(ROO·)<sup>4)</sup>, and hydroxyl radicals(HO·)<sup>5)</sup> through the interaction with water or dissolving oxygen.

In general, indirect photolysis, so-called sensitized photolysis, proceeds more rapidly than direct photolysis, therefore, sensitized photolysis would appear to be a viable method for treating toxic and refractory organic pollutants in water.

Accordingly, this study focused on applying sensitized photolysis to the treatment of benzene in water. Persulfate, sulfate, nitrate, nitrite, and chloride ions were all tested as sensitizers, and the resulting effects of the various sensitizers on the photolysis of benzene were then investigated.

### 2. Experimental

#### 2.1. Materials

Analytical grade benzene was obtained from

Junsei Chemicals and potassium salts of persulfate, sulfate, nitrate, nitrite and chloride ions were supplied by Shinyo Pure Chemical Co.. All chemicals were used as received without further purification. The water was initially distilled by a pure water system and then purified with an ultrapure water system(Barnstead D4744) to above  $18\text{M}\Omega\text{-cm}$ .

## 2.2. Equipment

The photochemical reactions were performed in a 1L conical batch photoreactor(Ace Glass Inc. 7840). A quartz tube was immersed in the center of the reactor to house a medium pressure mercury lamp(450W, HANOVIA PC 451050) which had a dominant wavelength of 254nm. The benzene concentration was measured using a Hewlett Packard 6890 gas chromatograph(column: HP-VOC, carrier gas: He(1mL/min), Initial temp.:  $90^\circ\text{C}$ , initial time: 5min, final temp.:  $220^\circ\text{C}$ , temp. rate:  $5^\circ\text{C}/\text{min}$ , detector: FID) which was connected to a purge & trap concentrator(Tekmar 3000, transfer line temp.:  $150^\circ\text{C}$ , purge time: 8min, desorb. temp.:  $175^\circ\text{C}$ , carrier gas: He(40mL/min)).

## 2.3. Sample Preparation

Aqueous solutions of benzene were prepared in volumetric flasks to give an initial concentration of 1mg/L. Aqueous solutions of the sensitizers were prepared by dissolving the potassium salts of the anions in ultrapure water. The anion concentrations in the experiments ranged as follows: persulfate, 0 mg/L-16 mg/L, sulfate 0 mg/L-10 mg/L, nitrate 0 mg/L-20 mg/L, nitrite 0 mg/L-16 mg/L, and chloride 0 mg/L-10 mg/L. A sample of lake water was obtained from Chinyang lake located by Chinju City, Korea. The lake water sample was centrifuged and filter-sterilized by passing it through a  $0.22\ \mu\text{m}$  millipore filter under a vacuum.

The samples for irradiation were shaken vigorously to saturate then with air before being poured into the photoreactor, which was completely filled to remove any headspace. Each experiment was performed in duplicate, with one set of dark controls.

## 3. Results and Discussion

### 3.1. Photodegradation in Lake Water

Under UV irradiation, the photodegradation of

benzene in Chinyang lake water and ultrapure water is shown in Fig. 1.

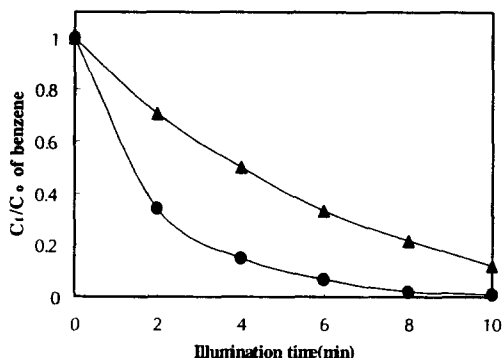


Fig. 1. Photodegradation of benzene in lake water(●) and ultrapure water(▲).  
( $C_t$ : initial concentration,  $C_0$ : concentration after t min)

The transformation of benzene in the ultrapure water was much slower than that in the lake water. Semi log plots of the residual benzene concentration versus time exhibited a linear relationship, demonstrating that the photodegradation of benzene was pseudo first-order(Fig. 2).

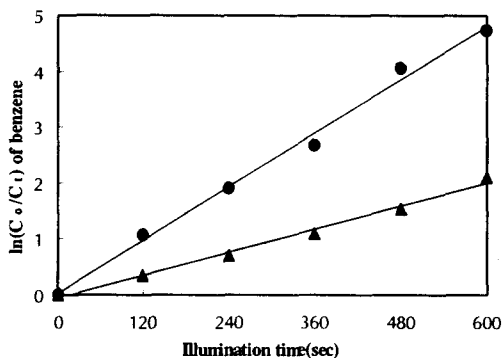


Fig. 2. Semi log plots of residual benzene concentration versus illumination time.  
(●: lake water, ▲: ultrapure water)

The experimental rate constants for the transformation of benzene under UV irradiation were calculated from the data in Fig. 2. The rate constant in the lake water was  $7.9 \times 10^{-3}\text{sec}^{-1}$  which was about 2 times higher than that in the distilled water,  $3.4 \times 10^{-3}\text{sec}^{-1}$ . The actual concentrations of sulfate, nitrate, nitrite and chloride ions in the lake water



percentage of benzene was clearly increased, thereby indicating that nitrite enhances the photodegradation of benzene. However, since a subsequent significant decrease occurred when the nitrite concentration was above 2 mg/L, it would appear that nitrite is both sensitizing and scavenging hydroxyl radicals. Some other studies have indicated that nitrate photolysis leads to the formation of nitrite ions<sup>9)</sup>. Russi et al<sup>10)</sup> also found that hydroxyl radicals do not appear to increase linearly with a nitrate concentration above approximately 3mg/L. Accordingly, the decrease in the photodegradation percentage of benzene when the nitrate concentration was above 4 mg/L would seem to be related to the nitrite ions that were produced from the nitrate photolysis(eq. (3) ~ (5)). The build-up of nitrite ions with an increasing nitrate concentration then also results in the scavenging of hydroxyl radicals(eq (9))<sup>8)</sup>.



### 3.3. Interactions of Sensitizers

The relative importance of the anions in the transformation of benzene was investigated by combining the anions at environmental concentrations(Fig. 5). When persulfate and chloride ions were both present at a concentration of 2mg/L and 2mg/L, respectively(Fig. 5-e), the time dependence of the photodegradation of benzene coincided exactly with that obtained from the test in the presence of persulfate by itself(Fig. 5-c). A similar result was observed when sulfate ions were tested together with persulfate ions(Fig. 5-g). It is also worth noting, although not shown in Figure 5, that the photodegradation of benzene in the presence of three anions, persulfate, sulfate, and chloride ions, also exhibited the same curve of photodegradation as that with persulfate by itself. Therefore, these results indicate that there is no interaction between persulfate ions and chloride ions or between persulfate ions and sulfate ions. In contrast, the transformation of benzene was accelerated when persulfate and nitrate ions were combined together(Fig. 5-f). However, when all the anions were present together(Fig. 5-b) or when nitrite ions were present together with persulfate ions (Fig. 5-d), the photodegradation of benzene was reduced.

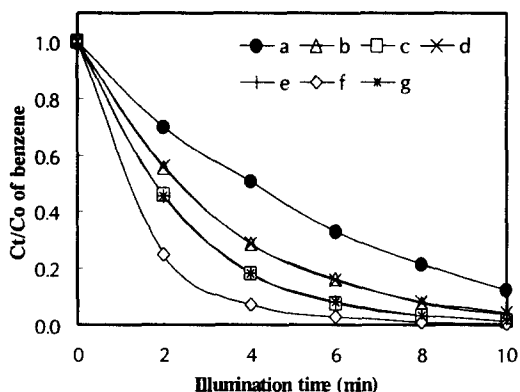


Fig. 5. Interaction of anions in photodegradation of benzene.

(a: no ions, b: total ions, c: persulfate ions, d: persulfate ions+nitrite ions, e: persulfate ions + chloride ions, f: persulfate ions + nitrate ions, g: persulfate ions + sulfate ions)

This result would seem to suggest that the hydroxyl radicals are effectively quenched by a particular ion, possibly, nitrite. Figs. 6 and 7 illustrate the effects of nitrite ions on the photodegradation of benzene in the presence of persulfate and nitrate ions, respectively. Undoubtedly, the nitrite ions inhibited the sensitized photodegradation of benzene.

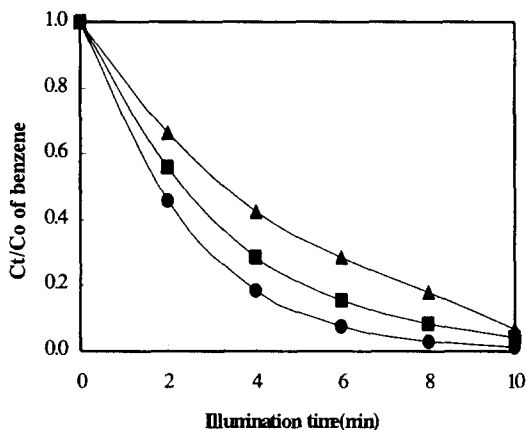


Fig. 6. Photodegradation of benzene in the presence of nitrite and persulfate ions.

(●: persulfate ions, ■: persulfate ions + persulfate ions(2mg/L), ▲: persulfate ions + nitrite ions(6mg/L))

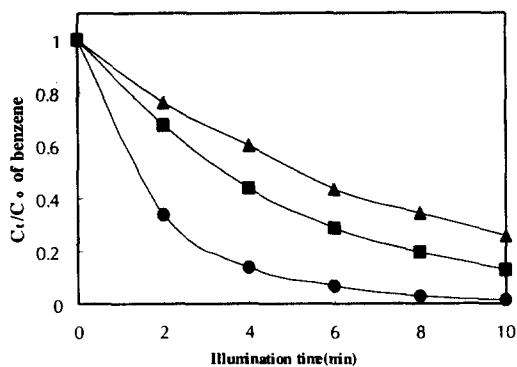


Fig. 7. Photodegradation of benzene in the presence of nitrite and nitrate ions.

(● : nitrate ions, ■ : nitrate ions + nitrite ions (2mg/L), ▲ : nitrate ions + nitrite ions (6mg/L))

In the photocatalytic degradation of benzene<sup>11)</sup>, in which the principal oxidant is a hydroxyl radical, the degradation products were phenol, biphenyl, catechol, hydroquinone, muconic acid, carbon dioxide, and so on (Fig. 8).

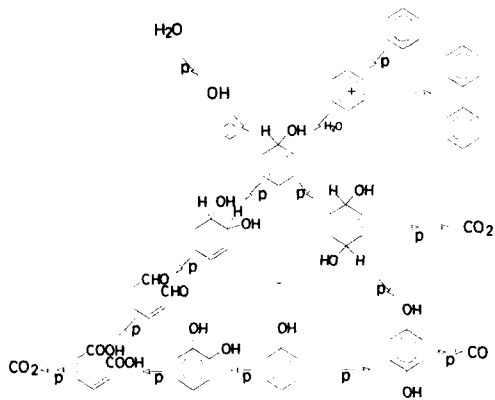


Fig. 8. Pathways of photocatalytic degradation of benzene.

In this study, phenol was identified and quantified (Fig. 9). Therefore, in the first stage of the sensitized photodegradation, benzene was degraded to phenol. When nitrite ions were added, the production of phenol in the sensitized photodegradation of benzene diminished, however, in the cases of persulfate and nitrate ions, the phenol production increased. These results indicate that nitrite ions inhibit the sensitized photodegradation of benzene.

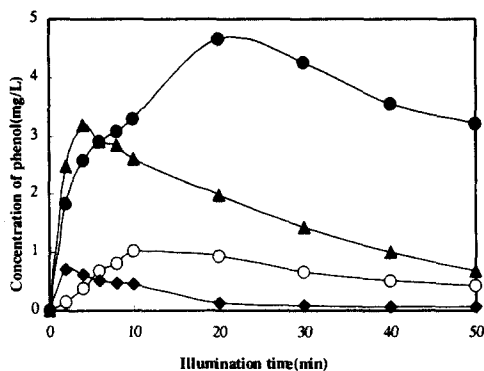


Fig. 9. Production of phenol in sensitized photodegradation of benzene (50mg/L).

(○ : no anions, ▲ : persulfate ions, ● : nitrate ions, ◆ : nitrite ions)

Based on the above results, it can be concluded that persulfate and nitrate ions can sensitize the photodegradation of benzene in an aqueous solution, whereas sulfate and chloride ions are unable to sensitize the reaction. Furthermore, nitrite ions can also be used as a sensitizer, however, a high concentration will inhibit the photodegradation of benzene.

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