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Photocatalytic degradation of sulfonated aromatics in aqueous TiO_2 suspension

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Abstract

Sodium benzenesulfonate and its substituted compounds were degraded photocatalytically. Several factors influencing the degradation rate, such as the initial concentration, temperature and substituent group, were examined. The activation energy (15.65 kJ mol^{-1}) is comparable with the values reported for other aromatic compounds. The degradation rate decreases with Hammett's constant, which indicates the electrophilic nature of the degradation reaction. One major and two minor intermediate products were identified. The reaction mechanism was proposed on the basis of the formation of these intermediate products.

Keywords: Photocatalytic degradation; Sulfonated aromatics

1. Introduction

Many organic compounds are photocatalytically oxidized in UV-illuminated TiO_2 suspensions. This process has been applied to wastewater treatment. There has been an increasing number of studies [1,2] on this new method in recent years. It has been shown that the photocatalytic process is a practical method for water purification [3].

Sulfonated aromatics are a constituent of many industrial and pharmaceutical products, such as detergents, medicines, agrochemicals and coloring agents. They are water soluble and hence often found in aqueous effluent. Most of them are not biodegradable, and alternative methods of degradation are required by various industries. In the present work, the photocatalytic degradation of sodium benzenesulfonate and its substituted compounds [4] was studied. The photocatalytic degradation rate depends on various parameters, such as the type of photocatalyst [5], temperature [6,7], initial concentration of the reactant [7–9], adsorbability of the solutes to the catalyst [10] and the substituent group of the reactant. These parameters were examined for sodium benzenesulfonate.

2. Experimental details

The TiO_2 samples used were obtained from Aldrich (anatase and rutile), Katayama Chemicals Company (rutile) and Fujititan Company Ltd. (anatase TP-2). The surface area and crystal characteristics of each TiO_2 sample have been described previously [5]. Platinization of TiO_2 was performed following the method reported by Kraeutler and Bard [11]. Sulfonated aromatics were in the form of either the sodium or potassium salt, except nitrobenzenesulfonic acid. All chemicals and solvents were of reagent or spectrophotometric grade.

In typical experiments, 70 mg of TiO_2 powder was suspended in 25 ml of water (10^{-3} mol l^{-1}) in a Pyrex glass cell by stirring. The cell was illuminated for a specific period using a 500 W super-high-pressure mercury lamp through a water filter with Pyrex glass windows; stirring was continued during irradiation. IR and UV light below 310 nm were thus eliminated. The light intensity after the water filter was 18 mW cm^{-2} in the 330–390 nm region. For the study of the temperature effect, a water-jacketed Pyrex glass cell was used. The cell was controlled at a specific temperature during illumination. Subsequently, the suspension was filtered through a 0.45 μm Millipore membrane, and the filtrate was subjected to analysis by reverse-phase high performance liquid chromatography (HPLC). SO_4^{2-} was analyzed by ion chromatography. To monitor the evo-

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lution of CO_2, the cell was covered with a butylgum septum and further sealed with an aluminum cap. CO_2 was analyzed by gas chromatography (GC) with a flame ionization detector (FID) after catalytic conversion to methane. Total organic carbon (TOC) was determined by a Shimadzu TOC-500.

3. Results and discussion

The degradation rates of sodium benzenesulfonate were measured with different TiO_2 samples. The initial rates and half-lives obtained from these experiments are compared in Table 1. Of these samples, TP-2 is the best catalyst. However, the degradation with TP-2 is too fast for studying the kinetics; therefore Aldrich anatase was used in further experiments. A blank experiment in the dark in the presence of TiO_2 showed that the adsorption of sodium benzenesulfonate is negligibly small for the purposes of the kinetic study. The illumination ($\lambda > 310$ nm) in the absence of TiO_2 resulted in only slow direct degradation. Approximately 5% of sodium benzenesulfonate was degraded after 30 min of illumination and 18% after 180 min. The rate was accelerated significantly in the presence of TiO_2. Similar results in blank experiments were obtained with substituted benzenesulfonates.

The effect of the initial concentration of sodium benzenesulfonate on the degradation rate is shown in Fig. 1. The results were analyzed by following the Langmuir–Hinshelwood equation [7–9]

$$r_0 = 1/kKC_0 + 1/k$$

where k is the rate constant and K is the adsorption coefficient. In Fig. 2, r_0^{-1} is plotted against C_0^{-1}. From this curve, $k = 66$ μmol h^{-1} and $K = 1.79$ l $mmol^{-1}$ were obtained. The value of K is comparable with that reported for 3-chlorophenol (1.6) [12] and smaller than those of 4-chlorophenol (1.9) [13] and oxalic acid (4.3) [14] adsorbed on P25 TiO_2, but larger than those of inorganic ion species (0.87 for $PtCl_6^{2-}$ and 0.32 for I^-) [15]; this indicates moderate adsorbability of benzenesulfonate on Aldrich anatase at pH 5.4.

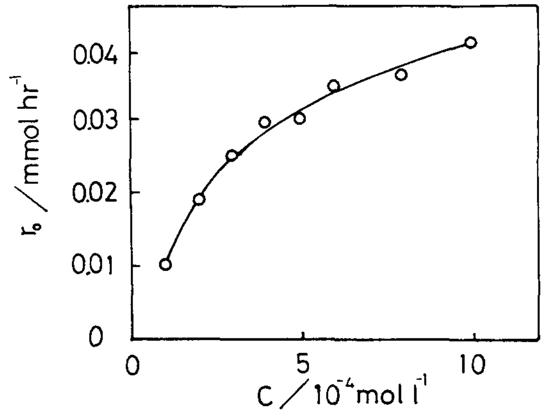

Fig. 1. Initial degradation rate as a function of the initial concentration of sodium benzenesulfonate.

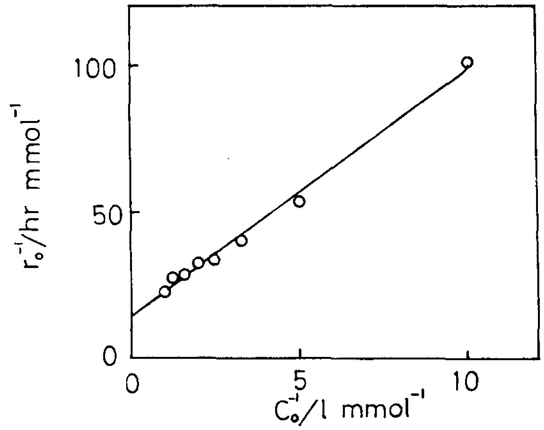

Fig. 2. Reciprocal initial rate vs. reciprocal initial concentration of sodium benzenesulfonate.

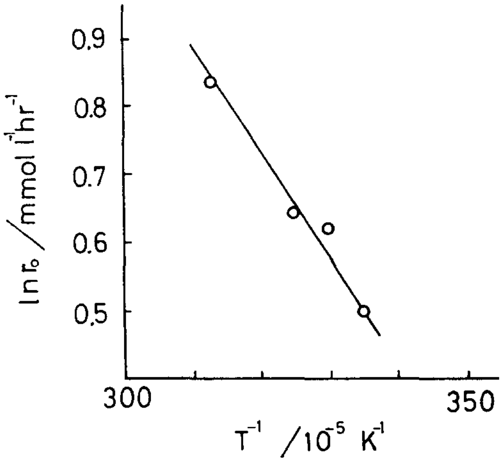

Fig. 3. Arrhenius plot for sodium benzenesulfonate.

Table 1
Photocatalytic activity of TiO_2

TiO_2	$t_{1/2}$ (min)	r_0 (μmol h^{-1})
Aldrich (rutile)	72.0	15
Aldrich (anatase)	35.0	42
Platinized Katayama (rutile)	66.0	17
TP-2 (anatase)	15.0	58

The degradation rate increased with temperature. An increase in temperature from 25 to 38 °C resulted in about a 25% increase in the initial degradation rate. Figure 3 shows the Arrhenius plot, where $k_1 = r_0/C_0$ was assumed. The activation energy obtained from this plot is 13.4 kJ mol^{-1}. This value is slightly larger than the values reported for phenol [6] and salicylic acid

[7] (10 and 11 kJ mol^{-1} respectively). Mathews [7] reported that these values are close to that for an OH radical reaction. It is therefore suggested that the photocatalytic degradation rate of benzenesulfonate is governed by an OH radical reaction. On the other hand, a smaller value (6.7 kJ mol^{-1}) has been reported for the photocatalytic cleavage of H_2S on vanadium sulphide [16] and a larger value (35.3 kJ mol^{-1}) for the catalytic reaction of H_2S on V_2O_5–Al_2O_3 [17].

The degradation of sodium benzenesulfonate was accompanied by the formation of SO_4^{2-}, H^+ and CO_2. Figure 4 shows the formation curve of SO_4^{2-} and the variation of pH. After 5 h of illumination, the concentration of SO_4^{2-} is close to the amount of sulfur contained in the initial solution. The TOC elimination rate is somewhat similar to the formation rate of SO_4^{2-}. After 5 h, approximately 90% of the TOC is lost. Thus it is demonstrated that sodium benzenesulfonate is totally mineralized by photocatalytic degradation.

Intermediate products were identified from a comparison of their retention times in HPLC with those of standard samples. In the case of sodium benzenesulfonate, one major and two minor intermediate products were identified: *p*-phenolsulfonic acid, hydroquinone and *p*-quinone (Fig. 5). The concentration of *p*-quinone increases with illumination time and is about 10^{-6} mol l^{-1} after 120 min. This is considered to be formed by the oxidation of hydroquinone. The formation of the hydroxylated intermediate compounds indicates that attack by the OH radical is the principal reaction pathway. On the basis of the intermediate compounds detected, possible degradation processes are tentatively proposed in Fig. 6, although several other reaction pathways are also involved.

The degradation rates of several para-substituted benzenesulfonates were compared to estimate the effect of the substituent group. The pH of the solution was not adjusted except for nitrobenzenesulfonic acid. The order of the degradation rate for the different substituents is $CH_3 > H > OH > Cl > NO_2$. This order indicates that the rate is accelerated by electron-donating substituents and retarded by electron-accepting substituents. The degradation rate is also affected by the

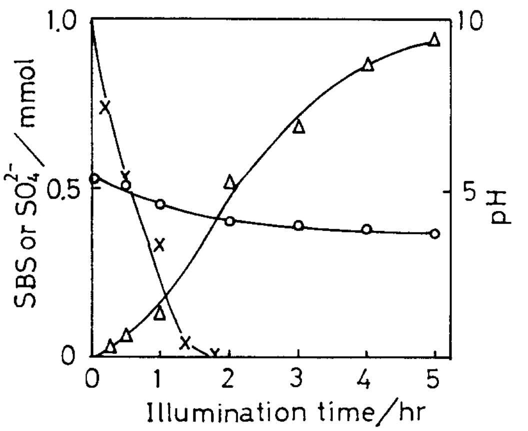

Fig. 4. Formation of SO_4^{2-} and variation of pH on degradation of sodium benzenesulfonate: ×, degradation of sodium benzenesulfonate; △, SO_4^{2-}; ○, pH.

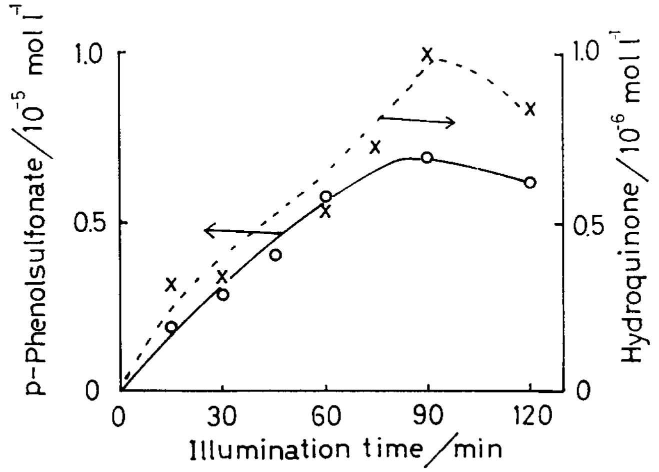

Fig. 5. Formation of intermediate compounds by the degradation of sodium benzenesulfonate: ○, *p*-phenolsulfonate; ×, hydroquinone.

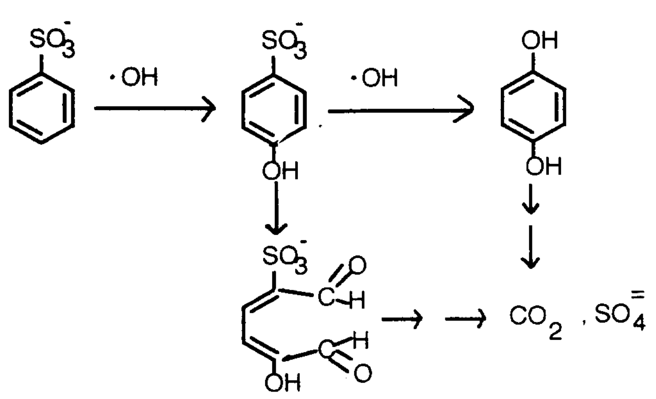

Fig. 6. Possible degradation pathway of sodium benzenesulfonate.

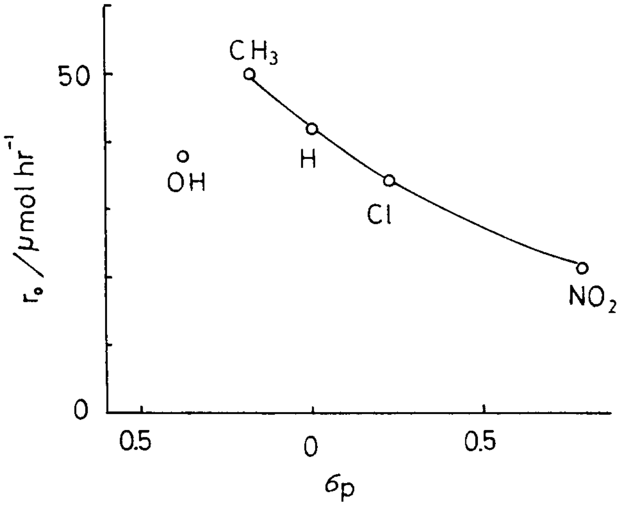

Fig. 7. Initial rate vs. Hammett's substituent constant.

adsorbability of the compound to TiO_2. The difference in the adsorbability between the different substituted compounds was assumed to be negligibly small in the present pH range (pH 5.4–5.9). With this assumption, the influence of the substituent on the degradation rate can be interpreted in terms of Hammett's relationship [18,19]. The approximately proportional relationship shown in Fig. 7 confirms the electrophilic nature of the photocatalytic reaction.

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