Dihydroxylation of Naphthalene by Molecular Oxygen and Water Using TiO₂ Photocatalysts

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TiO₂-catalyzed photo-reaction of naphthalene was investigated in mixed solutions of acetonitrile and water. The main products were confirmed to be 1,8- and 1,3-dihydroxynaphthalene, without any 1- or 2-naphthol being detected. Both O₂ and H₂O were essential to yield the products. The quantum efficiency of the 1,8- and 1,3-dihydroxynaphthalene products reached about 10% at 365 nm after irradiated for 1 h.
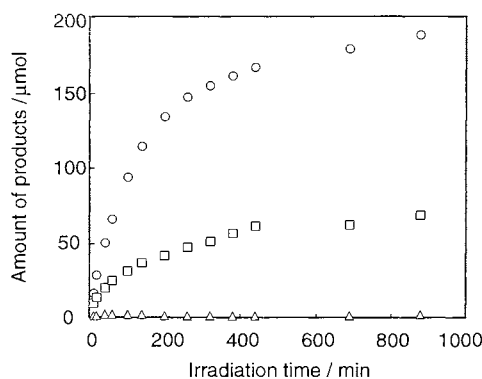

During the past two decades, much attention has been paid to the semiconductor photocatalysts because of their potential application to decomposition of wide range of harmful chemicals in air and in water,[1,2] and to chemical conversion and storage of light energy.[3,4] In addition, syntheses of useful compounds on photoirradiated semiconductor photocatalysts have also been explored. Up to now, many organic compounds, both aliphatics and aromatics, have been synthesized using semiconductor photocatalysts, such as TiO₂, CdS, ZnS and silica-supported metal oxides.[5-14]

Here, we report a new method for the synthesis of dihydroxynaphthalene using TiO₂ as photocatalyst under UV illumination. The hydroxylation reaction needs only water and molecular oxygen as the reactants. The reaction conditions are in marked contrast to conventional methods, where strong oxidants, high temperature, and strong alkaline medium are necessary. The most striking feature of the photocatalyzed reaction of naphthalene is that 1,8- and 1,3-dihydroxynaphthalenes were produced selectively.
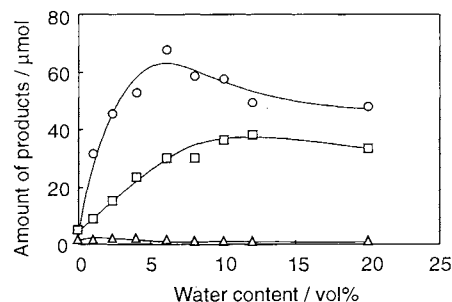
The photocatalytic reactions were carried out in Pyrex glass tubes (φ 15 mm) filled with a mixture of acetonitrile and water at room temperature. Different kinds of TiO₂ powders, which were obtained from the Catalysis Society of Japan (TiO-2, 3, 5) and commercial sources (P25, CR-EL, ST-11, ST-01, PT-101), were suspended in the reaction solution. The solution was magnetically stirred, bubbled with O₂, and externally photoirradiated. A 500 W high-pressure mercury lamp was employed as the light source, and UV34-filter (Kenko Co.) was used to remove deep UV light (λ < 340 nm). Under the conditions, only TiO₂ particles absorb the light quanta. The light intensity was controlled using fine stainless-steel meshes. Reaction products were analyzed with a high-performance liquid chromatograph (HPLC) using an ODS or ODS-3V column. The products were identified by comparing the retention times of the products with those of authentic compounds. Although authentic 1,8-dihydroxynaphthalene was not available, it was isolated from the products and confirmed by 500 MHz ¹H NMR and liquid-chromatograph-mass spectroscopy.[15] Quantum efficiencies of the reactions were determinted at around 365 nm, which were selected using UV34 and U340 glass filters (Kenko Co.). The number of irradiated photons per second was determined to be 5.85 × 10¹⁶ s⁻¹ using a potassium tris(oxalato)-ferrate chemical actinometer in the same glass tube used for the photocatalytic reaction. After photo-irradiation for 1 h, the

quantum efficiencies were determined to be 7.3% and 2.9% for the production of 1,8- and 1,3-dihydroxynaphthalene, respectively, by assuming that 2 photons were necessary for producing one molecule and that all the irradiated photons were adsorbed by TiO₂.

Irradiation of the TiO₂ (Degussa P25) photocatalyst, which was suspended in the acetonitrile : water (94:6 in volume) mixed solution of naphthalene, led to the formation of 1,8- and 1,3-dihydroxynaphthalene and a very small amount of 1,4-dihydroxynaphthalene, as shown in Figure 1. The reaction rate was lowered as photoirradiation continued, as seen in Figure 1, probably because of the competitive adsorption of the reactants and the products on the photocatalyst. Among the TiO₂ powders investigated, Degussa P25, which contains a 30% rutile phase and has a 43 m²/g surface area, showed the highest activity. The main products did not depend on the powders. It should be emphasized that the di-hydroxylated compounds were obtained,

Figure 1. TiO₂-photocatalyzed production of 1,8-dihydroxynaphthalene (○), 1,3-dihydroxynaphthalene (□), and 1,4-dihydroxynaphthalene (△). The reaction was carried out in a mixed solution (5 ml) of CH₃CN and H₂O (6% in volume) containing TiO₂ (P25, 0.015 g) and naphthalene (0.78 mmol). The solution was bubbled with O₂ and irradiated with a 500 W Hg lamp (λ > 340 nm).

Figure 2. Effect of water content in the mixed solution (acetonitrile-water) on the amount of products obtained after photoirradiation for 1 h. Reaction conditions are the same as those shown in Figure 1.

whereas no mono-hydroxylated compounds, i.e. 1- and 2-naphthol, were detected in the reaction products. The high selectivity of the products is very striking, because 1,8- and 1,3-dihydroxy-naphthalen are hardly obtained from naphthalene by the conventional methods. Besides the dihydroxylated naphthalenes, an undefinable peak appeared in the HPLC, which had a retention time shorter than those of mono- and di-hydroxylated naphthalenes. The mass balance between the amounts of consumed naphthalene and produced dihydroxylated naphthalenes indicated that the content of the unidentified species in the products is about 10%. No products were generated in the dark, or under irradiation without TiO_2 powder.

The presence of water in the solution is essential to the production of dihydroxynaphthalenes. As shown in Figure 2, only a little amount of products was obtained when no water was added, while the reaction rate increased with the content of water and reached the maximum at a water-content of about 6%. Oxygen is also essential, because no products were obtained in the absence of O_2. Using Fe^{3+} ion as the electron acceptor instead of oxygen, we obtained only a little amount of the products. These results indicate that both molecular oxygen and water are essential to the hydroxylation of naphthalene. In other words, the intermediate species formed from O_2 and H_2O as the result of the reactions with photogenerated electrons and holes are considered to play essential roles in the reaction.

When we reacted benzene under the same conditions, the main product was phenol. Fujihira et al. have also studied the TiO_2-photocatalyzed reaction of benzene and toluene in water, and reported that the main products were corresponding mono-hydroxyl compounds.[16] These results are in contrast to the reaction of naphthalene in solutions containing water. When we carried out the hydroxylation reaction of naphthalene using Fe^{3+} and H_2O_2 (the Fenton reaction), which produce •OH radical, the main products were mono-hydroxylated naphthalenes. The production of dihydroxylated compounds is, therefore, concluded to be unique to the photocatalytic reaction of naphthalene on TiO_2.

All the results suggest that a unique mechanism is involved in the photocatalytic reaction of naphthalene on TiO_2 particles. Fox et al. studied the photocatalytic reaction of naphthalene and its derivatives on TiO_2 in anhydrous acetonitrile.[7] To explain the photooxidation of naphthalene derivatives, they assumed the formation of the endoperoxide intermediates. This mechanism can explain the yield of ring-cleaved products as well as the hydroxylation of one benzene ring, which were the main

products in their cases. However, it cannot explain the yield of 1,8-dihydroxynaphthalene, which was the main product in our case. The details of the mechanism are not clear at the present stage. However, the interaction between the intermediate species generated from oxygen and water, which are supposed to be bound to the surface, and the naphthalene molecules adsorbed on the TiO_2 surface is considered to be the key of the reaction. Since dihydroxynaphthalenes are useful intermediates for the syntheses of specialty chemicals, this reaction is meaningful from a viewpoint of applications.

References and Notes

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