Photocatalytic Homogeneous Oxidation of Organic Compounds in Aqueous Solutions Containing Iron(III) Ion: A Very Simple Method for Mineralization of Organic Pollutants in Water

Masachiyo Imanishi, Keiji Hashimoto, and Hiroshi Kominami*
Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University,
Kowakae, Higashiosaka, Osaka 577-8502

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Irradiation of UV light to aqueous solutions of various organic compounds (acetic acid, alcohols, ketones, phenol, and benzenesulfonic acid) containing a small amount of metal ions was examined under an aerated condition at room temperature. These organic compounds were quantitatively decomposed to carbon dioxide in the presence of iron(III) ion, indicating that hydrated iron(III) complex acted as an efficient homogeneous photocatalyst.

Enormous amounts of alcohols, ketones, and sulfonates are often used in the chemical industry as solvents, cleaners, and raw materials. Some of them are finally exhausted, resulting in an increase in chemical oxygen demand (COD) in waste water. A high value of COD induces heavy environmental disruption. Treatments of waste water have been required to resolve the problem of environmental pollution. Photocatalytic treatment of pollutants in water has attracted much attention because this method does not require any oxidizing and reducing agents. Two photocatalytic systems can be applied to treatment of polluted water, i.e., a heterogeneous system using a solid photocatalyst such as titanium(IV) oxide and a homogeneous system using a soluble photocatalyst. A homogeneous system is expected to have high quantum efficiency, since UV light and visible light can be incident on all of the dissolved photocatalyst. It is hence effective for practical use to apply a homogeneous photocatalyst to treatment of waste water. However, there have been few studies on treatment of water-containing pollutants in a homogeneous system[1–3] despite the fact that many studies have shown that enormous amounts of organic compounds formed by the working of nature and human activity have been oxidatively decomposed in the ocean in the presence of a small amount of metal ions by solar light.[4–8] Therefore, an alternative method for photooxidative decomposition of organic compounds should be studied for practical treatment of waste water. We studied photocatalytic mineralization of various organic compounds in aqueous solutions in the presence of various metal ions under UV irradiation and an aerated condition. We found that hydrated iron(III) complex was highly active for homogeneous photocatalytic mineralization of alcohols, ketones, carboxylic acids, phenol, and benzenesulfonic acid. In this paper, we present results showing the high activity of the hydrated iron(III) complex and quantitative photocatalytic mineralization of these compounds.

Commercial acetic acid, propanols, butanols, acetone, phenol, and benzenesulfonic acid were used without further purification. Iron(III) chloride and nitrate were commercial materials of reagent grade and used without further purification. Homogeneous photocatalytic mineralization of these organic compounds was carried out under atmospheric pressure; a test tube ($35\,cm^3$) of 15 mm in diameter made of Pyrex glass was used as the reactor. A solution ($5\,cm^3$) containing $10\,\mu mol$ of various metal ions was added to the test tube. After oxygen (O_2) had been bubbled into the solution for 20 min, the test tube was sealed with a rubber septum. Substrate ($200\,\mu mol$) was injected into the solution through the rubber septum. The resulting aerated solution was photoirradiated at a wavelength of $\lambda > 300\,nm$ ($8\,mW\,cm^{-2}$) by a high-pressure mercury arc (400 W, Eiko-sya, Japan) at 298 K. The amount of CO_2 evolved was measured every 1 h with a Shimadzu GC-8A gas chromatograph with a Porapack Q column. The amounts of inorganic and organic carbon in the liquid phase were determined by using a Shimadzu TOC Analyzer TOC-Vcs.

Activities of various metal ions were examined in homogeneous photocatalytic mineralization of acetic acid in aqueous solutions under irradiation of UV light for 5 h. The results are summarized in Table 1. Heterogeneous photocatalytic mineralization of acetic acid in an aqueous suspension of titanium(IV) oxide (TiO_2, Degussa P 25) was also investigated under the same conditions for comparison with homogeneous photocatalytic activity of the various ions. The rate of the overall photocatalytic mineralization of acetic acid was measured by summation of evolved CO_2 and inorganic carbon in the liquid phase. Iron(III) and iron(II) ions were highly active for the photocatalytic mineralization of acetic acid in the homogeneous system. In the photocatalytic mineralization of acetic acid with iron(II) ion, the time course of the concentration of iron(II) ion was determined by complexometry with *o*-phenanthroline using an absorption constant of $\varepsilon_{510} = 1.128 \times 10^4\,dm^3\,mol^{-1}\,cm^{-1}$ at 510 nm. Though little oxidation of iron(II) ion to iron(III) ion occurred for 30 min in the dark, more than 90% of the iron(II) ion was oxidized to iron(III) ion within 30 min under irradiation

Table 1. Rates of CO_2 evolution from acetic acid ($200\,\mu mol$) in aqueous solutions of metal ions ($10\,\mu mol$) under O_2 and UV light irradiation

Metal ions	CO_2 evolution rate /$\mu mol\,h^{-1}$
Fe^{3+}	64
Fe^{2+}	59
Cu^{2+}	2.8
Zr^{4+}	1.7
Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Li^+, Cs^+, Ag^+, Zn^{2+}, Al^{3+}, Ru^{3+}, Rh^{3+}, Ce^{3+}, La^{3+}, Ir^{4+}, Pd^{2+}, Pt^{4+}	<1.0
(TiO_2, $626\,\mu mol$)	70
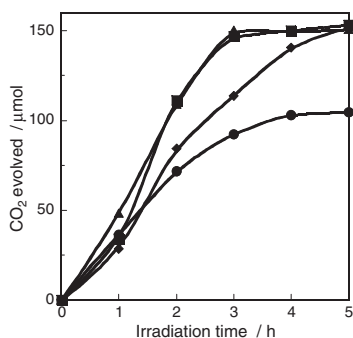
Figure 1. Evolutions of CO_2 from acetic acid (circles), 1-propanol (squares), 2-propanol (diamonds), and acetone (triangles) in aqueous solutions of Fe^{3+} (10 μmol) under O_2 and UV light irradiation.

Figure 2. Decomposition of benzenesulfonic acid (CO_2; closed circles, SO_4^{2-}; open circles) and phenol (CO_2; closed squares) (8 μmol, each) in aqueous solutions of Fe^{3+} (10 μmol) under O_2 and UV light irradiation.

of UV light. This result supports the idea that the apparent activity observed for iron(II) ion is the same as the activity of iron(III) ion. The activity of iron(III) ion at a concentration of 10 μmol was equal to that of TiO_2 (50 mg, 626 μmol). The order of the activities for various metal ions was as follows: Fe^{2+}, $Fe^{3+} \gg Cu^{2+} > Zr^{4+} > Cr^{3+}$, Mn^{2+}, Co^{2+}, Ni^{2+}, Li^+, Cs^+, Ag^+, Zn^{2+}, Al^{3+}, Ru^{3+}, Rh^{3+}, Ce^{3+}, La^{3+}, Ir^{4+}, Pd^{2+}, Pt^{4+}.

The time course of photocatalytic mineralization of acetic acid (50 μmol) in a dilute aqueous solution of iron(III) ion (10 μmol) is shown in Figure 1. Acetic acid was oxidized to 100 μmol of CO_2 under irradiation of UV light in the presence of iron(III) ion, indicating that stoichiometric and quantitative photocatalytic decomposition of acetic acid to CO_2 occurred as shown in eq 1.

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad (1)$$

As far as we know, this is the first report confirming stoichiometry of mineralization of acetic acid in a homogeneous photocatalytic reaction. However, acetic acid was not mineralized in two control experiments under irradiation of visible light ($\lambda > 400$ nm) and in the absence of O_2, suggesting that UV excited iron species and O_2 strongly concerned oxidation process(es).

The time courses of photocatalytic mineralization of 1-propanol, 2-propanol, and acetone are also shown in Figure 1, indicating that these C3 compounds (50 μmol) were mineralized stoichiometrically and quantitatively. No oxidation occurred under blank tests (iron-free and dark conditions). The initial rate of photocatalytic mineralization of the C3 compounds decreased in the following order: acetone > 1-propanol > 2-propanol. In the early stage of photocatalytic mineralization of 2-propanol, acetone was detected by GC. This result indicates that the mineralization of 2-propanol proceeded via formation of acetone.

Mineralization of C4 compounds (1-butanol, 2-butanol, 2-methyl-2-propanol, and butanone) was also examined to confirm the possibility of this homogeneous photocatalytic system. Those compounds were decomposed to CO_2 stoichiometrically and quantitatively as were C3 compounds (results not shown). Reaction rate in the photocatalytic mineralization of C4 alcohols decreased in the following order: 1-butanol > 2-butanol ≈ 2-methyl-2-propanol. The reactivity of the primary and secondary alcohols was compatible with that of C3 alcohols. The results suggest that the O–H bond of the hydroxy group was first cleaved in the photocatalytic mineralization of primary and
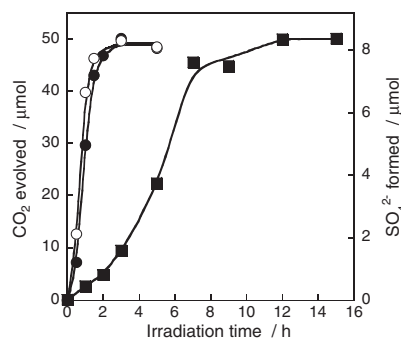
secondary alcohols; that is, oxidation of alcohols gave corresponding aldehydes and ketones as intermediates followed by further oxidation.

The time courses of photocatalytic mineralization of benzenesulfonic acid and phenol are shown in Figure 2. Oxidation of benzenesulfonic acid was negligible under iron-free conditions. Benzenesulfonic acid was easily mineralized along with stoichiometric formation of sulfonate, indicating that desulfnization and mineralization of benzenesulfonic acid occurred simultaneously. Mineralization of phenol proceeded slowly in the early stage and was accelerated at around 20% of CO_2 formation. The initial depression and acceleration of phenol mineralization can be explained as follows: A phenol molecule was photocatalytically oxidized to form some radicals, and the radicals were scavenged by other phenol molecules as inhibitors in an initial period. When phenol molecules were almost consumed, a chain propagation accelerated the oxidation of partially oxidized intermediates, resulting in quantitative mineralization of phenol.

In conclusion, various organic compounds such as alcohols, ketones, phenol, and benzenesulfonic acid dissolved in water can be mineralized by a very simple method, i.e., photocatalysis of hydrated iron complex.

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