Photocatalytic Reduction of Nitrobenzene to Aniline in an Aqueous Suspension of Titanium(IV) Oxide Particles in the Presence of Oxalic Acid as a Hole Scavenger and Promotive Effect of Dioxygen in the System

Hiroshi Kominami,*[1] Shin-ichi Iwasaki,[1] Tsuyoshi Maeda,[1] Kazuya Imamura,[1]
Keiji Hashimoto,[1] Yoshiya Kera,[1] and Bunsho Ohtani[2]
[1]*Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Higashiosaka, Osaka 577-8502*
[2]*Catalysis Research Center, Hokkaido University, Sapporo 001-0021*

(Received January 5, 2009; CL-090004; E-mail: hiro@apch.kindai.ac.jp)

Nitrobenzene was effectively and selectively reduced to aniline in an acidic aqueous suspension of titanium(IV) oxide photocatalyst in the presence of oxalic acid as a hole scavenger and the aniline yield was improved in the presence of a small amount of dioxygen.

One of the most promising applications of photocatalysis is mineralization (or degradation) of toxic organic compounds in air and water.[1–3] Since photocatalytic reaction satisfies several of the 15 proposed requirements for green chemistry,[4] organic synthesis of various compounds using photocatalysis has been studied by many researchers.[2] However, less attention has been paid to the photocatalytic reduction of organic compounds by photogenerated electrons (e^-). Although e^- are potentially a useful reagent, e^- have been removed from the system using sacrificial electron acceptors such as silver ion and dioxygen (O_2) in most photocatalysis studies. Photocatalytic reduction of organic acceptors such as nitroaromatics can be carried out in the presence of a large excess of an electron donor, such as methanol, and in the absence of O_2.[5–8] The purpose of the electron donor is to scavenge holes (h^+), thereby reducing the degree of recombination within the particle. Removal of O_2 from the system has been thought to improve reduction efficiency by removing this competitive electron scavenger. As far as we know, photocatalytic reductions have been carried out under deaerated conditions.

From the point of view of eco-friendly production of chemicals,[4] we should pay attention to the choice of solvent and sacrificial reagents. Methanol has been used as both a solvent and a sacrificial reagent for photocatalytic reduction of organic compounds such as nitrobenzene (NB). Since formaldehyde is formed as the oxidized species of methanol, a "greener" sacrificial reagent converting to a nontoxic compound is preferable. Oxalic acid (OA) is a "greener" sacrificial reagent because it is easily oxidized and converts into carbon dioxide (CO_2), which is separated from the solvent under acidic conditions.[9–11] It is obvious that water (H_2O) is the "greenest" among all solvents. Here we briefly describe the photocatalytic reduction of NB to aniline (AN) in an aqueous suspension of titanium(IV) oxide (TiO_2) particles in the presence of OA as a hole scavenger and the improvement in yield of AN in the presence of a small amount of O_2.

Degussa P25 TiO_2 was used because it is known to be one of the most active photocatalysts. Bare TiO_2 powder (50 mg) was suspended in an aqueous solution (5 cm^3) containing NB (13 µmol) and OA (100 µmol) in a test tube. Using a 3 mol L^{-1} HCl solution, pH of the suspension was adjusted to ca. 1. The tube was sealed with a rubber septum and then photoirradiated at a wavelength >300 nm by a high-pressure mercury arc (400 W) under argon (Ar) or mixtures of dinitrogen (N_2) and O_2 with magnetic stirring at 298 K. The amounts of NB and product(s) were determined with a Shimadzu HPLC (ODS column). Quantitative analyses of the gas phase were performed using a Shimadzu GC-8A gas chromatograph equipped with Porapak QS (CO_2) and MS-5A (dihydrogen (H_2) and O_2) columns. The blank reaction without TiO_2 gave no product.

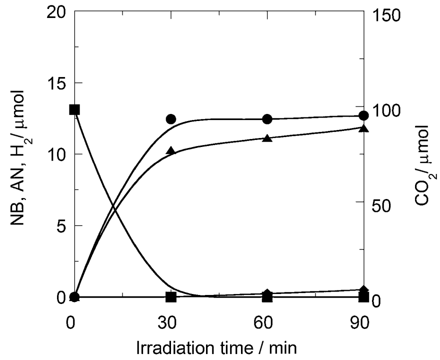

Figure 1. Time courses of the amounts of NB (squares), AN (circles), H_2 (diamonds), and CO_2 (triangles) in photocatalytic reduction of NB in the presence of OA under 5%O_2–95%N_2.

Figure 1 shows the time courses of yields of AN, H_2, and CO_2 in the photocatalytic reaction of the aqueous mixture of NB, OA, and TiO_2 powders under 5%O_2–95%N_2. After photoirradiation for 30 min, NB was almost completely consumed and AN was obtained in a high yield (95%), which was also identified by GC-MS [GC-17A, GCMS-QP5050 (Shimadzu); column = DB-1, 0.25 mm × 30 m (J&W), MS: m/z 93]. This result indicates that photocatalytic reduction of NB to AN occurred even in the presence of O_2. Reduction of NB to AN consists of several steps[6] (eq 1), and the probable stoichiometry of the reaction in the presence of OA is shown below (eq 2).

$$\text{Ph–NO}_2 \rightarrow \text{Ph–NO} \rightarrow [\text{Ph–NHOH}] \rightarrow \text{Ph–NH}_2 \qquad (1)$$

$$\text{Ph–NO}_2 + 3(\text{COOH})_2 \rightarrow \text{Ph–NH}_2 + 6\text{CO}_2 + 2\text{H}_2\text{O} \qquad (2)$$

In this study, nitrosobenzene and hydroxylamine intermediates were not detected, indicating that the rates of reduction of these species might be larger than that of NB or that these species are strongly adsorbed on the surface of TiO_2. As the oxidized product, 77 µmol of CO_2 was formed by photoirradiation for 30 min. Assuming that all of the CO_2 originated from OA, efficiency of OA utilization as a hole scavenger (EOU) was calculated by using eq 3.

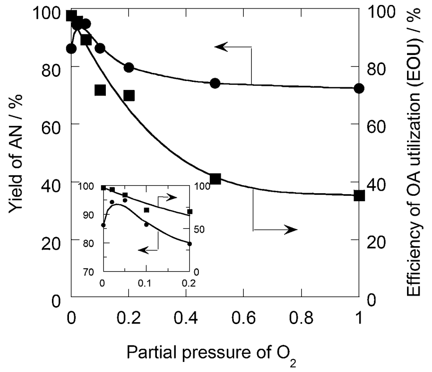

Figure 2. Effect of partial pressure of O_2 on AN yield (circles) and EOU (squares) in photocatalytic reduction of NB in the presence of OA.

$$EOU = 6 \times (n_{AN}/n_{CO_2}) \times 100 \quad (3)$$

where n_{AN} and n_{CO_2} are amounts of AN and CO_2 formed, respectively. Even in the presence of 5% O_2, EOU under these conditions was as high as 97%, indicating that OA worked effectively as a hole scavenger and fruitless mineralization of OA by O_2 (eq 4) scarcely occurred.

$$(COOH)_2 + 1/2O_2 = 2CO_2 + H_2O \quad (4)$$

It should be noted that AN was not reoxidized by further photoirradiation after 30 min, though a small amount of CO_2 was formed owing to mineralization of OA. Under acidic conditions, anilinium ion (AN^+) was eliminated from the TiO_2 surface. This mechanism for removal of the product from the surface of TiO_2 also accounts for the high yield of AN.

Figure 2 shows the effects of content of O_2 in the gas phase on AN yield and EOU in photocatalytic reduction of NB under the same conditions of photoirradiation for 60 min. When photocatalytic reaction was carried out in the absence of O_2, a high yield of AN (82%) and a high EOU (99%) were obtained. OA was almost quantitatively used as the hole scavenger for reduction of NB. The electrons have sufficient potential [flat band potential $E_{fb} = -0.52$ V vs. standard hydrogen potential (SHE) at pH 6.8][12] to reduce NB (half-peak potential $E^{red}{}_{1/2} = +0.16$ V vs. SHE).[13] Oxalate ions are oxidized by h^+, resulting in the formation of CO_2 and $CO_2^{\bullet -}$ (eq 5):

$$C_2O_4^{2-} + h^+ = CO_2 + CO_2^{\bullet -} \quad (5)$$

It has been reported that $CO_2^{\bullet -}$ has a strong reducing ability [$E^0(CO_2/CO_2^{\bullet -}) = -1.8$ V][14] and is able to reduce NB. Therefore, NB might be reduced to AN by both e^- and $CO_2^{\bullet -}$ in the present system.

It is interesting that the yield of AN in the presence of 2% and 5% O_2 in the gas phase was larger than that in the absence of O_2 as shown in Figure 2. The difference between the two reaction conditions is only whether a small amount of O_2 is present or not. The results obtained indicate that a small amount of O_2 caused rapid reduction of NB to AN in the presence of a sacrificial reagent. Photocatalytic oxidation (or mineralization) of organic compounds is generally carried out in the presence of O_2 because O_2 is a good electron-capturing reagent accelerating oxidation of organic compounds by h^+ or hydroxyl radicals. In fact, further increase in O_2 content in the gas phase decreased both AN yield and EOU (Figure 2). The decrease in AN yield was probably caused by reoxidation of AN^+ owing to large consumption of OA under large O_2 content. When O_2 captures e^-, superoxide anion ($O_2^{\bullet -}$) is formed under neutral conditions (eq 6) and $O_2^{\bullet -}$ is protonated, yielding $HO_2^{\bullet}$ radicals, under acidic conditions (eq 7). Further reduction of these one-electron-reduced products of O_2 yields hydrogen peroxide (H_2O_2) (eq 8), which is believed to cause oxidation of organic compounds.

$$O_2 + e^- = O_2^{\bullet -} \quad (6)$$

$$O_2^{\bullet -} + H^+ = HO_2^{\bullet} \quad (7)$$

$$HO_2^{\bullet} + e^- + H^+ = H_2O_2 \quad (8)$$

Active species other than e^- and $CO_2^{\bullet -}$ should exist and cause rapid reduction of NB in the presence of O_2. It is well known that $O_2^{\bullet -}$ (or $HO_2^{\bullet}$) acts as a one-electron reductant.[15] Therefore, $O_2^{\bullet -}$ (or $HO_2^{\bullet}$) is a candidate for active species for reduction of NB in the presence of a small amount of O_2. Since H_2O_2 has both reduction ability and oxidation ability depending on the type of target compound, H_2O_2 formed in this reaction process may reduce NB. However, no homogeneous reduction of NB by H_2O_2 in an aqueous solution (pH ca. 1) occurred. Therefore, all experimental results suggest an additional mechanism to increase the yield of AN in the presence of a small amount of O_2. O_2 was reduced to $O_2^{\bullet -}$ by e^- and then a part of NB was reduced by thus-formed $O_2^{\bullet -}$. Some mediators, such as IO_3^-–I^-[16] and Fe^{2+}–Fe^{3+},[17] have been reported to improve quantum efficiency in photocatalytic water splitting (H_2O) to hydrogen and O_2. O_2 works in the same manner as these mediators in an H_2O decomposition system, as a mediator in the photocatalytic reduction of BN to AN.

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) and for Scientific Research (No. 16560679) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

References

1 T. Wakanabe, A. Kitamura, E. Kojima, C. Nakayama, K. Hashimoto, A. Fujishima, in *Photocatalytic Purification and Treatment of Water and Air*, ed. by D. E. Olis, H. Al-Ekabi, Elsevier, **1993**, p. 747.
2 M. A. Fox, M. T. Dulay, *Chem. Rev.* **1993**, *93*, 341.
3 M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69.
4 P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, **1998**.
5 F. Mahdavi, T. C. Bruton, Y. Li, *J. Org. Chem.* **1993**, *58*, 744.
6 J. L. Ferry, W. H. Glaze, *Langmuir* **1998**, *14*, 3551.
7 O. V. Makarova, T. Rajh, M. C. Thurnauer, A. Martin, P. A. Kemme, D. Cropek, *Environ. Sci. Technol.* **2000**, *34*, 4797.
8 H. Tada, T. Ishida, A. Takao, S. Ito, *Langmuir* **2004**, *20*, 7898.
9 Y. Li, F. Wasgestian, *J. Photochem. Photobiol., A* **1998**, *112*, 255.
10 H. Kominami, A. Furusho, S. Murakami, H. Inoue, Y. Kera, B. Ohtani, *Catal. Lett.* **2001**, *76*, 31.
11 H. Kominami, T. Nakaseko, Y. Shimada, A. Furusho, H. Inoue, S. Murakami, Y. Kera, B. Ohtani, *Chem. Commun.* **2005**, 2933.
12 M. Graetzel, *Energy Resources Through Photochemistry and Catalysis*, Academic Press, New York, **1983**.
13 L.-J. Fan, C. Wang, S. Chang, Y. Yang, *J. Electroanal. Chem.* **1999**, *477*, 111.
14 D. M. Stanbury, *Adv. Inorg. Chem.* **1989**, *33*, 69.
15 D. T. Sawyer, J. S. Valentine, *Acc. Chem. Res.* **1981**, *14*, 393.
16 K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, *Chem. Commun.* **2001**, 2416.
17 H. Kato, Y. Sasaki, A. Iwase, A. Kudo, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2457.