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Chemoselective reduction of nitrobenzenes to aminobenzenes having reducible groups by a titanium(IV) oxide photocatalyst under gas- and metal-free conditions[†]

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m-Nitrovinylbenzene was chemoselectively reduced to *m*-aminovinylbenzene in a suspension of a TiO_2 photocatalyst in the presence of a hole scavenger at room temperature under atmospheric pressure without the use of a precious metal or reducing gas, and nitrobenzenes having other reducible groups were also chemoselectively reduced to corresponding aminobenzenes.

Aminobenzenes synthesized by reduction of corresponding nitrobenzenes are important compounds as intermediates of agrochemicals, medicines, dyes and various useful compounds.¹ However, it is difficult to selectively reduce the nitro group of nitrobenzenes having other reducible groups such as a vinyl group.¹ Catalytic hydrogenation over a metal catalyst such as nickel (Ni) or copper (Cu) is the main method for reduction of a nitro group. However, this method cannot be applied for selective reduction of the nitro group of nitrobenzenes having a vinyl group because both nitro and vinyl groups are reduced. Chemoselective reduction of the nitro group is achieved by using a large excess of a reducing agent such as tin (Sn), 2^{2a} zinc (Zn), 2^{2b} iron (Fe)^{2c} or sodium hydrosulfite. 2^{2d} However, these reaction systems give harmful wastes. Although catalytic chemoselective reduction of nitrobenzenes is important, there have been only a few reports on chemoselective reduction of a nitro group in the presence of C=C bonds³ and their yields were low. Recently, chemoselective reduction of m-nitrovinylbenzene (NVB) to m-aminovinylbenzene (AVB) has been achieved by many researchers.^{1,4} However, these (thermo)catalytic systems require precious metals, high temperature and high pressure of reducing reagents such as hydrogen (H₂) and carbon monoxide (CO) (Table S1, ESI[†]). Reduction of NVB to AVB would be more attractive if reducing reagents other than gaseous H₂ and CO are applied and the reaction is catalyzed by common elements having a simple component and structure under mild conditions such as room temperature and atmospheric pressure.

When titanium(IV) oxide (TiO₂) is irradiated by UV light, charge separation occurs and thus-formed electrons (e⁻) in the conduction band and holes (h⁺) in the valence band cause reduction and oxidation, respectively. Titanium is a common

and inexpensive element because titanium has the tenth largest Clarke number. Although various oxides of titanium exist, TiO_2 in which the oxidation state of titanium is +4 is most stable under the atmosphere and is easily formed without any extra effort. Photocatalytic reaction proceeds at room temperature and under atmospheric pressure, and the TiO₂ photocatalyst is easily separated from the reaction mixture after the reaction. In addition, TiO₂ has been used for a long time as an indispensable inorganic material such as a pigment and UV absorber because it is inexpensive and non-toxic for humans and the environment. Most of the applications of photocatalysis are mineralization (or degradation) of toxic organic compounds in air and water.⁵ Since photocatalytic reaction satisfies almost all of the 12 proposed requirements for green chemistry,⁶ organic synthesis of various compounds using photocatalysis has recently been studied by many researchers.^{5b,7} However, less attention has been paid to the photocatalytic reduction of organic compounds by photogenerated electrons because a deaerated condition is needed to achieve reduction of substrates.^{7b} Photocatalytic reduction for organic synthesis can be carried out in the presence of a large excess of an electron donor, such as methanol, and in the absence of dioxygen (O_2) .⁸ The purpose of the electron donor is to scavenge holes and to reduce recombination of holes and electrons in and/or on the particles. From the point of view of environmentally-friendly production of chemicals, attention must be paid to the choice of sacrificial reagents for photocatalytic reduction of organic compounds. Alcohols such as methanol have been used as both a solvent and a hole scavenger.⁸ However, since toxic aldehvdes are formed as the oxidized species of alcohols, a sacrificial reagent converting to a non-toxic compound is preferable. We have reported photocatalytic reduction of nitrobenzenes to corresponding aminobenzenes in an aqueous suspension of TiO₂ in the presence of oxalic acid (OA) or formic acid (FA) as a hole scavenger.9 These hole scavengers are "greener" sacrificial reagents because they are easily oxidized to carbon dioxide (CO₂) and thus-formed CO₂ molecules are removed from the liquid phase in the presence of organic acids.

In this study, we examined the photocatalytic reduction of nitrobenzenes having other reducible groups using a simple photocatalyst, TiO_2 , in the presence of OA as a hole scavenger at room temperature and atmospheric pressure, and we found that only the nitro group was chemoselectively reduced to an amino group and that aminobenzenes with reducible groups

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Fig. 1 Time courses of the amount of NVB remaining (squares) and the amount of AVB formed (circles) in a 10% water–ACN suspension of TiO_2 (50 mg) in the presence of OA (200 µmol) as a hole scavenger under deaerated conditions.

were obtained in high yields without using precious metals or high-pressure gaseous reducing reagents.¹⁰

Fig. 1 shows time courses of the amounts of NVB remaining and AVB formed in the photocatalytic reduction of NVB in a 10% (v/v) water–ACN suspension of TiO₂. The amount of NVB monotonously decreased along with photoirradiation time and NVB was almost completely consumed after 2 h, while AVB was obtained in a high yield (93%). The high yield of AVB indicates that none of the reaction of the benzene ring, reduction of the vinyl group or re-oxidation of the amino group of AVB occurred in the present system. It is notable that there are no reports on photocatalytic chemoselective reduction of a nitro group having a C=C double bond. Eqn (1) shows the probable stoichiometry of photocatalytic chemoselective reduction of NVB to AVB in the presence of OA.¹¹

$$\begin{array}{c} \mathsf{NO}_2 \\ + 3 (\mathsf{COOH})_2 \end{array} \xrightarrow{\mathsf{NH}_2} + 2 \mathsf{H}_2 \mathsf{O} + 6 \mathsf{CO}_2 \end{array} (1)$$

The yield of the present photocatalytic system was as high as that in thermocatalytic reduction of NVB to AVB systems using precious metals such as platinum, ^{1,4a,c,d} gold, ^{4b,c,e} silver, ^{4d,g,h,k} ruthenium^{4c} and rhodium.⁴ⁱ The present photocatalytic reduction required no co-catalyst such as a precious metal and occurred under conditions (298 K, atmospheric pressure and H₂-free) milder than those of thermocatalytic systems (Table S1, ESI†). The value of AQE at 366 nm calculated from the ratio of the amount of AVB and amount of photons irradiated using eqn (2) reached 15%.

$AQE = (6 \times \text{amount of AVB/number of incident photons}) \times 100$ (2)

For comparison, AQE for photocatalytic H_2 formation from 2-propanol (200 µmol) in an aqueous suspension of platinized TiO₂ was also examined and determined to be 4.1% under the same irradiation conditions. This reaction has often been used as a model reaction to evaluate the activity of a photocatalyst for H_2 evolution. The value of AQE in the present reaction larger than that of 2-propanol dehydrogenation shows that OA efficiently works as hole scavenger for photocatalytic reduction of NVB to AVB.

Photocatalytic reduction of NVB in some alcohols was examined because alcohols, mainly methanol, have often been used as solvents in photocatalytic reduction of nitrobenzenes. In this case, alcohols also work as hole scavengers. Results are summarized in Table 1. After 2 h photoirradiation, NVB was

 Table 1
 Photocatalytic chemoselective reduction of various nitrobenzenes to corresponding aminobenzenes^a



Entry	Position	Reducible group: X	Solvent	Time/ h	Conversion (%)	Selectivity (%)
1	m-	-CH=CH ₂	ACN	6	>99	88
2	<i>m</i> -	$-CH = CH_2$	10% W-ACN	2	>99	93
3	m-	$-CH = CH_2$	10% W-ACN	2	96 ^b	95^{b}
4	m-	$-CH = CH_2$	10% W-ACN	2	96 ^c	85 ^c
5	<i>m</i> -	-CH=CH ₂	Methanol ^d	2	>99	15
6	<i>m</i> -	-CH=CH2	Ethanol ^d	2	>99	20
7	0-	-Cl	ACN	2	>99	>99
8	<i>m</i> -	-Cl	ACN	2	>99	95
9	<i>m</i> -	-Cl	10% W-ACN	1	>99	97
10	<i>p</i> -	-Cl	ACN	2	>99	54
11	0-	-Br	ACN	2	>99	>99
12	<i>m</i> -	-Br	ACN	2	>99	>99
13	<i>p</i> -	-Br	ACN	2	>100	88
14	0-	-COOH	ACN	2	>99	98
15	<i>m</i> -	-COOH	ACN	2	>99	>99
16	<i>p</i> -	-COOH	ACN	2	>99	98
17	m-	-COCH ₃	10% W-ACN	1.5	>99	99
18	<i>p</i> -	-COCH ₃	ACN	2	>99	88

^{*a*} Substrate: 50 µmol, TiO₂: 50 mg, solvent: 5 cm³, oxalic acid: 200 µmol, light source: Hg arc ($\lambda > 300$ nm), temperature: 298 K, atmosphere: Ar (1 atm), conversion and selectivity were based on results of HPLC. ^{*b*} Second use. ^{*c*} Third use. ^{*d*} No oxalic acid was added because these solvents also work as hole scavengers.

almost completely consumed in alcohols; however, many unidentified by-products were formed probably due to side reaction(s) of amino and vinyl groups with alcohols. As a result, AVB selectivity was much smaller than that obtained in the reaction system using 10% (v/v) water–ACN and OA as solvent and hole scavenger, respectively. These results indicate that the combination of 10% (v/v) water–ACN and OA is effective for photocatalytic reduction of NVB.

The effect of water content of solvents on yields of AVB was investigated and the results are shown in Fig. 2. The yield of AVB in water-free ACN was lower than that in ACN containing a small amount of water, and longer photoirradiation was required for complete consumption of NVB (Fig. S1, ESI⁺). When a small amount of water was added to ACN, yields of AVB after 2 h photoirradiation increased and maximum yield was obtained at 10% (v/v) of water content. A positive effect of addition of water to ACN was also reported in photocatalytic epoxidation of alkenes, although the reason was not clarified.¹² Further addition of water, however, decreased the yield of AVB. To understand the effect of water content on reduction of NVB in the presence of OA, another photocatalytic reaction using OA, *i.e.*, photocatalytic decomposition of OA along with H₂ formation ((COOH)₂ \rightarrow H₂ + 2CO₂) in a water-ACN suspension of platinized TiO2 (P 25) under deaerated conditions was examined. This reaction system is simple because only OA is dissolved as a substrate in the liquid phase. Since the OA decomposition was carried out under deaerated conditions as well as the NVB system, the effect of oxygen on the reaction can be eliminated. Therefore, hole trapping by OA would be important in the OA decomposition system, and the results are shown



Fig. 2 Effect of water content of solvents (water–ACN) on yields of AVB formed by photocatalytic reduction of NVB for 2 h.

in Fig. S2 (ESI[†]). A tendency similar to that in the NVB system was observed in the OA decomposition system and there was a clear correlation between them as shown in Fig. S3 (ESI[†]), indicating that water added to ACN affected the two photocatalytic reactions in a similar way, though the reduced products (AVB and H₂) and photocatalysts (bare TiO₂ and platinized TiO_2) are different. These results suggest that hole trapping by OA was important in the NVB reduction as well as the OA decomposition. Addition of water seems to have various effects on the surface properties and suspending state (stability) of TiO₂ particles as well as on the stabilities, solubilities and adsorption behaviors of NVB and OA. These factors would affect each other and change complexly depending on the amount of water added. For example, a small amount of water would increase the stability of TiO₂ particles and the surfaces of TiO₂ particles would become more hydrophilic. The experimental results suggest that various factors affecting photocatalytic efficiency were highly balanced when 10% (v/v) water was added.

To examine the durability of the TiO₂ photocatalyst in this reaction system, TiO₂ was used repeatedly. After reaction in 10% (v/v) water–ACN for 2 h, TiO₂ particles were recovered by a simple filtration from the reaction mixture and were re-used. As shown in Table 1, TiO₂ photocatalysts were reusable without notable loss of activity.

The high chemoselectivity of this method for reduction of NVB was further investigated in the intermolecular competitive reaction of nitrobenzene (NB) and styrene (ST). As expected, NB (50 μ mol) was reduced to give aniline (AN, 50 μ mol) with over >99% yield, while ST (49 μ mol) was not reduced at all (eqn (3)). These results clearly demonstrate that the photocatalytic system showed complete chemoselectivity for the nitro group in the presence of inter- and intra-molecular vinyl groups.

$$\bigcup_{i=1}^{NO_2} + \bigcup_{i=1}^{NH_2} + \bigcup_{i=1}^{NH_2} + 0$$

$$(3)$$

$$>99\% \quad Not detected$$

Applicability of the photocatalytic chemoselective reduction was investigated using various nitro compounds having other reducible groups (chloro, bromo, carboxyl and acetyl groups), and Table 1 shows results of the photocatalytic chemoselective reduction of various nitrobenzenes in ACN or a mixture of water and ACN suspension of TiO₂ particles under deaerated conditions. Only the nitro group of these compounds was chemoselectively reduced even in the presence of chloro, bromo, carboxyl and acetyl groups, resulting in the formation of corresponding amino compounds with high yields. These results indicate wide applicability of this photocatalytic method for chemoselective reduction of a nitro group to an amino group without using precious metals and H₂.

We succeeded in a photocatalytic chemoselective reduction of various nitro compounds having other reducible groups to corresponding aminobenzenes in an ACN suspension of TiO_2 in the presence of OA. Addition of 10% (v/v) water to ACN increased the reduction rate and improved the yield of AVB.

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