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Short Communication

Photocatalytic deoxygenation of sulfoxides to sulfides over titanium(IV) oxide at room temperature without use of metal co-catalysts

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ABSTRACT

Deoxygenation of sulfoxides was examined in acetonitrile suspensions of metal-free titanium(IV) oxide (TiO_2) under irradiation of UV light at room temperature. Experimental results indicate that deoxygenation was induced by the TiO_2 photocatalyst and that organic acids such as formic acid and oxalic acid are appropriate as hole scavengers in the photocatalytic reaction. Diphenyl sulfoxide was successfully deoxygenated to diphenyl sulfide with high yields, and the TiO_2 photocatalyst could be repeatedly used for deoxygenation without loss of activity. The present photocatalytic method could be applied for deoxygenation of various sulfoxides to corresponding sulfides, and phenyl vinyl sulfoxide was chemoselectively reduced to phenyl vinyl sulfide without hydrogenation of a C=C double bond.

1. Introduction

Deoxygenation of sulfoxides is an important reaction in both organic synthesis and biochemistry [1–3]. However, conventional deoxygenation requires stoichiometric reagents such as phosphines, halogens, and metal hydrides [4–8] and yields a large amount of undesirable waste, although many efforts have been devoted to improve reaction conditions and to minimize the use of toxic reagents by using catalytic systems [9–11]. Recently, excellent catalysts for deoxygenation of sulfoxides, i.e., gold (Au) and ruthenium (Ru) supported on hydroxyapatite (HAP), were reported [12,13]. However, even the Au/HAP and Ru/HAP catalysts required temperatures higher than 383 K and dimethylphenylsilane as a reducing agent yielding by-product residues such as siloxanes. Therefore, a more environmentally friendly catalytic reaction system for deoxygenation of sulfoxides working at lower temperatures with “greener” reducing agents giving no residue is keenly desired.

When titanium(IV) oxide (TiO_2) is irradiated by UV light, charge separation occurs and thus-formed electrons in the conduction band and positive holes in the valence band cause reduction and oxidation, respectively. Photocatalytic reaction proceeds at room temperature and under atmospheric pressure, and the TiO_2 photocatalyst is easily separated from the reaction mixture after the reaction and can be used repeatedly without a re-activation or re-generation process. In addition, TiO_2 has been used for a long time as an indispensable inorganic material such as a pigment and UV absorber because it is inexpensive and not toxic for humans and the environment. Since photocatalytic reaction satisfies almost all of the 12 proposed requirements for green chemistry [14], organic synthesis of various compounds using photocatalysts has recently been studied by many researchers [15] and the number of reports on photocatalytic reduction of organic compounds by using photogenerated electrons has been increasing [16, 17]. However, most of the reports deal with reduction (hydrogenation) of nitrobenzenes to aminobenzenes [18–32]. In this study, we examined a new photocatalytic reduction system, i.e., deoxygenation of sulfoxides (reduction of sulfoxides to sulfides) in a suspension of metal-free TiO_2 in the presence of hole scavengers such as oxalic acid and formic acid. In this reaction, these organic acids also work as stoichiometric reagents for deoxygenation. However, oxalic acid and formic acid are recently used as green hole scavengers for photocatalytic reduction and hydrogenation because these oxalic acids are converted to carbon dioxide, which is easily separated from the solvent under acidic conditions [33, 34]. Here we report that corresponding sulfides were successfully produced at room temperature without the use of toxic or undesirable reagents.

2. Experimental

All of the reagents were commercial materials of reagent grade and used without further purification. Ishihara ST-01 was mainly used as the TiO_2 photocatalyst in this study. In a typical run, TiO_2 (50 mg) was suspended in 5 cm^3 of acetonitrile containing diphenyl sulfoxide (DPSO) and oxalic acid in a test tube, sealed with a rubber septum

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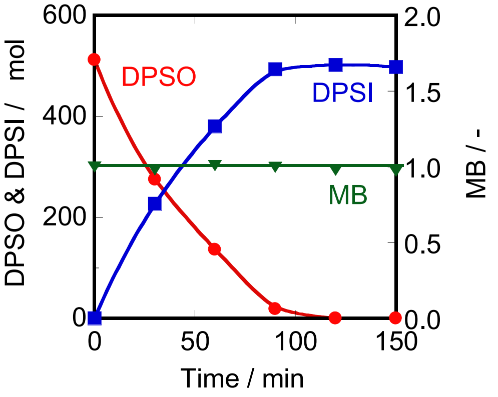


Fig. 1. Time courses of DPSO remaining, DPSI formed and material balance of DPSO and DPSI in an acetonitrile suspension of TiO_2 in the presence of oxalic acid (1 mmol) under irradiation of UV light.

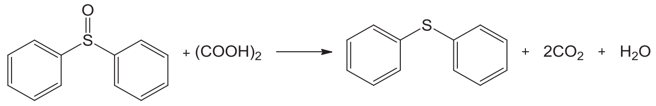
under argon, and then photoirradiated at λ > 300 nm by a 400-W high-pressure mercury arc (Eiko-sha, Osaka) with magnetic stirring in a water bath continuously kept at 298 K. The amounts of DPSO unreacted and diphenyl sulfide (DPSI) formed were determined with an FID-type gas chromatograph (GC-2014, Shimadzu, Kyoto) equipped with a DB-1 column. The example of the gas chromatogram output is shown in Fig. S1. The amount of hydrogen gas (H_2) as the reduction product of protons (H^+) was determined with a TCD-type gas chromatograph (GC-8A, Shimadzu, Kyoto) equipped with an MS-5A column. To obtain an action spectrum, the full arc from a xenon (Xe) lamp (Optiplex, Ushio, Tokyo) was monochromated with a light width of ±10 nm using SM-100 (Bunkoukeiki, Tokyo). The light was used for photocatalytic reaction instead of the mercury arc. The spectra and intensity of the monochromated light from the Xe lamp were determined using a spectroradiometer (USR-45D, Ushio, Tokyo).

3. Results and discussion

3.1. Photocatalytic deoxygenation of diphenyl sulfoxide

Fig. 1 shows time courses of DPSO remaining and DPSI formed in an acetonitrile suspension of TiO_2 in the presence of oxalic acid under deaerated conditions. Just after photoirradiation, DPSO monotonously decreased, while DPSI was formed as the deoxygenation (reduction) product of DPSO. After 120 min, DPSO was almost completely consumed and DPSI was obtained in a high yield (98%). The results shown in Fig. 1 were expressed as first-order kinetic and the rate constant was determined to be $2.15 \times 10^{-2}\ \mathrm{min}^{-1}$. Other reduced products such as H_2 were not formed, indicating that photogenerated electrons (in other words, oxalic acid) were selectively used for reduction of DPSO. No H_2 formation in the present reaction system is attributed to the use of bare (metal-free) TiO_2. This H_2-free system is attractive because there is no need to remove H_2 from the reaction system. To evaluate stoichiometry and selectivity of the reaction and side-reactions occurring under the present conditions, a new indicator, i.e., material balance (MB), was calculated by Eq. (1):

$$\mathrm{MB} = \frac{n(\mathrm{DPSO}) + n(\mathrm{DPSI})}{n_0(\mathrm{DPSO})}, \tag{1}$$



Scheme 1. Photocatalytic deoxygenation of DPSO to DPSI in the presence of oxalic acid as a hole scavenger.

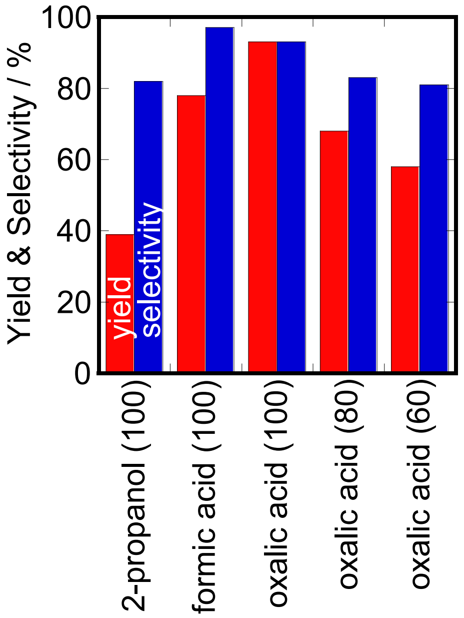


Fig. 2. Effects of the kind and amount of hole scavengers on yield and selectivity of DPSI produced in photocatalytic deoxygenation of DPSO (50 μmol) in acetonitrile suspensions of TiO_2 for 15 min. The values in parentheses are the amounts of hole scavengers in μmol.

where n(DPSO) and n(DPSI) are the amounts of DPSO and DPSI during the photocatalytic reaction, respectively, and n_0(DPSO) is the amount of DPSO before the photocatalytic reaction. As shown in Fig. 1, the values of MB were almost unity during the reaction, indicating that no other intermediates were produced under the present conditions. We noted that 1) the amount of DPSI was unchanged, 2) the color of TiO_2 became blue (Ti^{3+} species formed), and 3) no H_2 was evolved, under excessive photoirradiation after complete consumption of DPSO. These results indicate that DPSI was not consumed by successive reactions such as re-oxidation and degradation under the present conditions and that oxalic acid remaining was not consumed any more due to rapid recombination between photogenerated electrons and positive holes over Ti^{3+} species. From these results, the reaction, i.e., deoxygenation of DPSO to DPSI, would be shown in Scheme 1, although we did not determine the amount of CO_2.

Fig. 2 shows the effect of the kind and amount of hole scavenger on yield and selectivity of DPSI produced in photocatalytic deoxygenation of DPSO in acetonitrile suspensions of TiO_2 for 15 min. Use of a typical alcoholic hole scavenger, 2-propanol, resulted in a low yield due to the small reaction rate. On the other hand, large yields were obtained with sufficient selectivities when organic acids (formic acid and oxalic

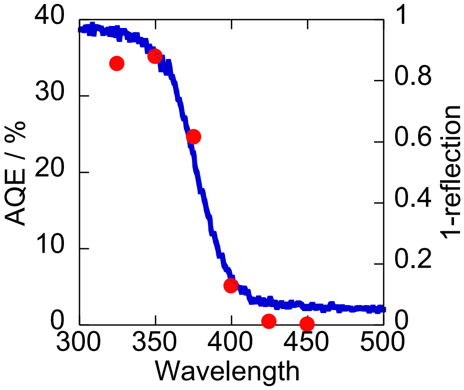


Fig. 3. Absorption spectrum (right axis) and action spectrum of TiO_2 in the deoxygenation of DPSO (left axis). DPSO: 50 μmol, oxalic acid: 100 μmol.