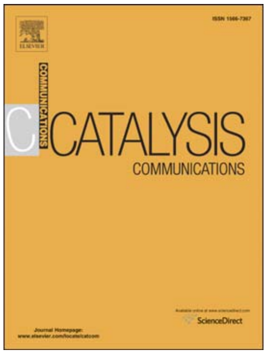

Photocatalytic deoxygenation of sulfoxides to sulfides over titanium(IV) oxide at room temperature without use of metal co-catalysts

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

Hiroshi Kominami*, Kosuke Nakanishi, Satoshi Yamamoto, Kazuya Imamura, Keiji Hashimoto

Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae, Higashiosaka, Osaka 577-8502, Japan.

E-mail: hiro@apch.kindai.ac.jp

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.

Keywords: photocatalyst, TiO_2, sulfoxide, deoxygenation, sulfide, chemoselective

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 under argon, and then photoirradiated at $\lambda > 300$ 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 Figure 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 light width of ±10 nm using SM-100 (Bunkoukeiki, Tokyo). The light was used for photocatalytic reaction instead of the mercury arc. Spectra and intensity of the monochromated light from the Xe lamp were determined using a spectroradiometer (USR-45D, Ushio, Tokyo).

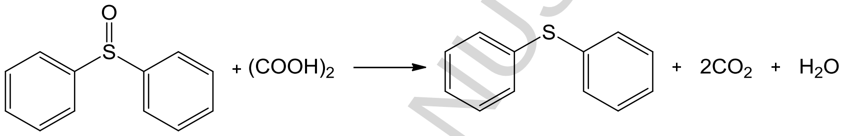
3. Results and discussion

3.1. Photocatalytic deoxygenation of diphenyl sulfoxide

Figure 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 Figure 1 were expressed as first-order kinetic and the rate constant was determined to be 2.15×10^{-2} 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 Equation (1):

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

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 Figure 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.



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

Figure 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 acid) were used. These organic acids, especially oxalic acid, have been shown to be efficient hole scavengers for chemoselective reduction of 3-nitrostyrene to 3-aminostyrene over a TiO_2 photocatalyst [9]. When the amount of oxalic acid was decreased, both the yield and selectivity of DPSI decreased. Decrease in the selectivity suggests that DPSI was converted to some oxidized species other than DPSO because re-oxidation of DPSI to DPSO only decreases the yield of DPSI (the selectivity being preserved). These results indicate that twice the amount of a hole scavenger is necessary to avoid consumption of DPSI due to oxidation by positive holes.

An action spectrum is a strong tool for determining whether a reaction observed occurs via a photoinduced process or a thermocatalytic process. To obtain an action spectrum in this reaction system, deoxygenation of DPSO in acetonitrile suspensions of TiO_2 (ST-01, Ishihara) was carried out at 298 K under irradiation of monochromated light from a Xe lamp with light width of ±10 nm. Apparent quantum efficiency (AQE) at each centered wavelength of light was calculated from the ratio of twice the amount of DPSI formed and the amount of photons irradiated using the following Equation (2):

$$\mathrm{AQE} = \frac{2\times \text{the amount of DPSI formed}}{\text{amount of incident photones}}\times 100. \qquad \cdots(2).$$

As shown in Figure 3, AQE was in agreement with the absorption spectrum of TiO_2. Therefore, it can be concluded that deoxygenation of DPSO in an acetonitrile suspension was induced by photoabsorption of TiO_2. As also shown in Figure 3, AQE reached 35% at 350 nm, indicating that photocatalytic deoxygenation of DPSO proceeded with high efficiency of photon utilization as well as chemical aspects such as selectivity and MB.

The expected reaction process of photocatalytic deoxygenation of DPSO to DPSI over TiO_2 is shown in Figure 4: 1) By irradiation of UV light, photogenerated electrons (e^-) and positive holes (h^+) are formed in the conduction and valence bands of TiO_2, and oxalic acid (or oxalate) is oxidized by h^+, and 2) DPSO is reduced by e^-, resulting in the formation of DPSI. However, H_2 formation by reduction of H^+ does not occur under a metal-free condition because H_2 evolution generally requires loading of co-catalysts such as platinum and Pd.

3.2. Applicability of photocatalytic deoxygenation of sulfoxide

The applicability of photocatalytic deoxygenation of sulfoxide to sulfide was investigated, and the results are summarized in Table 1. Results of entries 1-3 indicate that the TiO_2 photocatalyst can be used repeatedly for deoxygenation of DPSO to DPSI without deactivation. The reusability of TiO_2 is attributable to its stability. Since the TiO_2 photocatalyst is used without modification with a metal co-catalyst, the present reaction system is free from changes in states such as size, dispersion and oxidation states of the co-catalyst during the photocatalytic reaction. Almost quantitative deoxygenation of DPSO occurred under a ten-times concentrated condition (entry 4) as shown in Figure 1. Methyl phenyl sulfoxide was more easily deoxygenated to methyl phenyl sulfide (entry 5). We found that phenyl vinyl sulfoxide was chemoselectively reduced to phenyl vinyl sulfide without hydrogenation of a C=C double bond (entry 6). Our research group have reported that 3-nitrostyrene was chemoselectively reduced to 3-aminostyrene without reduction of a C=C double bond to 3-ethylaniline in a suspension of a TiO_2 photocatalyst in the presence of oxalic acid as hole scavengers at room temperature [32]. The high reduction potential of vinyl group accounts for the chemoselective reduction of 3-nitrostyrene and phenyl vinyl sulfoxide. The use of TiO_2 without a metal co-catalyst strongly contributed to the chemoselectivity. If TiO_2 modified with a metal co-catalyst is used, hydrogenation of a C=C double bond [35] would occur as well as deoxygenation. Photocatalytic deoxygenation was also applicable for sulfoxide of an acyclic compound (entry 7), though a longer reaction time was required.

3.3. Effects of physical properties of TiO_2

To evaluate the effects of physical properties of TiO_2, representative commercial TiO_2 samples, which were registered at the Catalysis Society of Japan as Japan Reference Catalysts (JRC-TIO series), were used for photocatalytic deoxygenation of DPSO under the same conditions. Phase of TiO_2 and specific surface area of the TiO_2 samples are summarized in Table S1. Figure 5 shows the effect of specific surface area of TiO_2 samples on yields of DPSI produced. A clear correlation was observed for most of the TiO_2 samples between specific surface area and DPSI yield, though there were some exceptions. These results also mean that TiO_2 structure (anatase or rutile) had little effect on the photocatalytic deoxygenation of DPSO; however, bi-phase of anatase and rutile in the TiO_2 sample may be effective. We are now investigating adsorption properties of these TiO_2 samples toward DPSO, DPSI and oxalic acid.

4. Conclusions

Photocatalytic deoxygenation of sulfoxides to corresponding sulfides was examined in acetonitrile suspensions of bare TiO_2 particles at room temperature without the use of a metal co-catalyst and toxic reagents. Organic acids, especially oxalic acid, worked efficiently as hole scavengers. The use of an excess of organic acids was effective for achieving high yields of sulfide and for avoiding fruitless degradation of sulfides. The present photocatalytic method can be applied for deoxygenation of various sulfoxides to corresponding sulfides. Chemoselective reduction of phenyl vinyl sulfoxide to phenyl vinyl sulfide was also achieved because the metal-free TiO_2 photocatalyst had no ability for hydrogenation of the C=C double bond.

Acknowledgements

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Figure Captions

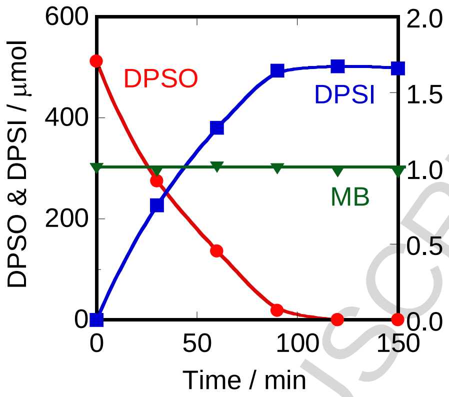
Figure 1 Time courses of DPSO remaining, DPSI formed and material balance of DPSO and DPSI in an acetonitrile suspension of TiO_2 in the presence of oxalic acid (1 mmol) under irradiation of UV light.

Figure 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.

Figure 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.

Figure 4 Expected reaction process of photocatalytic deoxygenation of DPSO to DPSI over metal-free TiO_2 in the presence of oxalic acid (OA).

Figure 5 Effect of specific surface area of TiO_2 samples on yields of DPSI produced in photocatalytic deoxygenation of DPSO (50 µmol) for 10 min in acetonitrile solutions containing oxalic acid (100 µmol). Minor form in bi-phase samples is shown in parenthesis.



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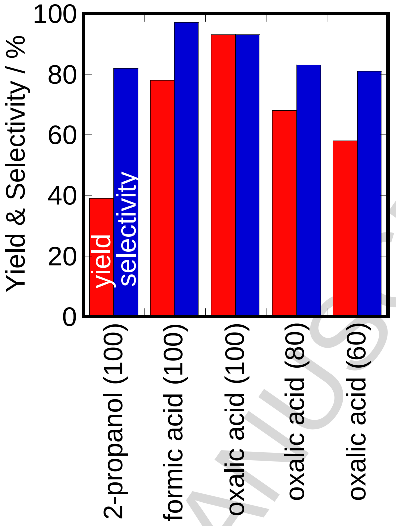

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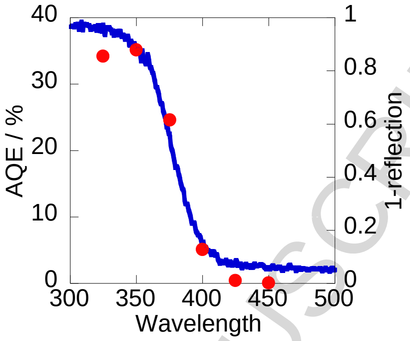

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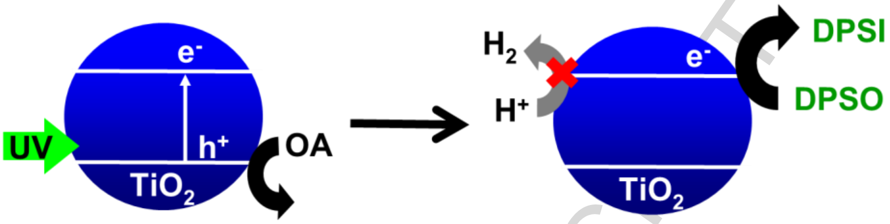

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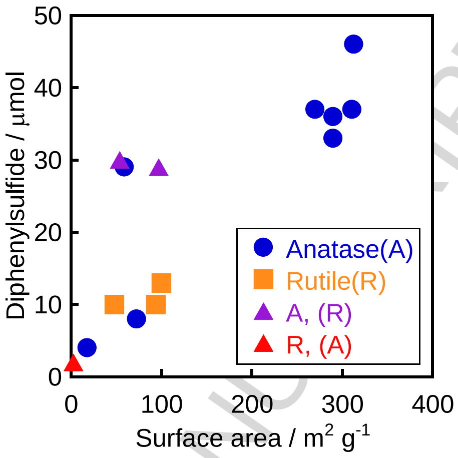
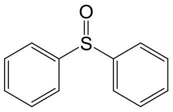
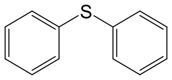
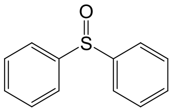
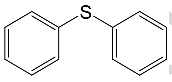
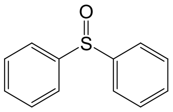
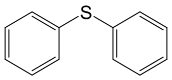
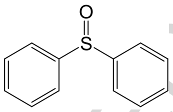
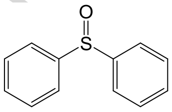
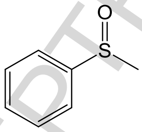
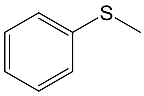
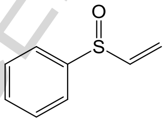
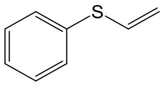
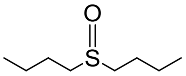
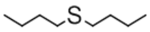
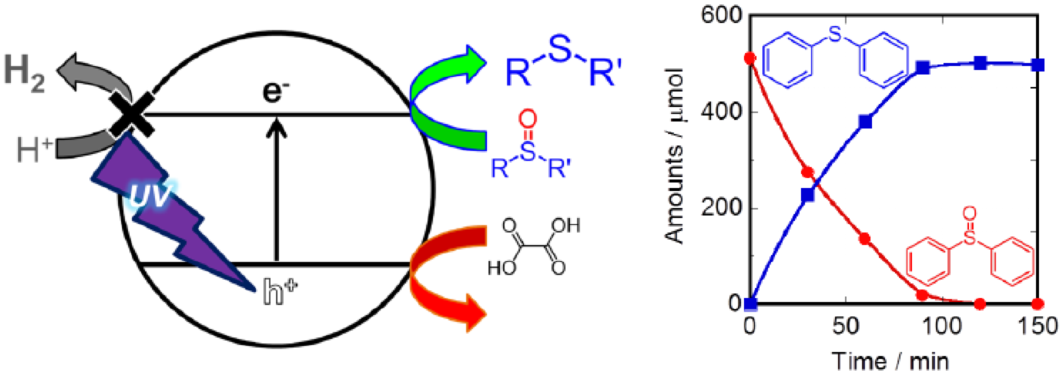


Figure 5 Effect of specific surface area of TiO_2 samples on yields of DPSI produced in photocatalytic deoxygenation of DPSO (50 µmol) for 10 min in acetonitrile solutions containing oxalic acid (100 µmol). Minor form in bi-phase samples is shown in parenthesis.

Table 1 Photocatalytic deoxygenation of sulfoxides to corresponding sulfides over TiO_2 at 298 K.[a]

Entry	Sulfoxides	Sulfides	t / min	Yield / %[b]	Sel. /%[b]
1			20	93	95
2[c]			20	98	98
3[d]			20	>99	>99
4[e]			120	98	98
5			15	99	99
6			15	82	82
7			30	91	91

[a] Reaction conditions: TiO_2 (50 mg), substrate (50 µmol), acetonitrile (5 cm^3), oxalic acid (100 µmol), room temperature, under Ar. [b] Determined by GC using an internal standard. [c] Second use. [d] Third use. [e] Diphenyl sulfoxide (500 µmol), oxalic acid (1 mmol).



Graphical abstract

Highlights

Photocatalytic deoxygenation of sulfoxides was examined over metal-free TiO_2.

Sulfoxides were successfully deoxygenated to corresponding sulfides with high yields.

Formic acid and oxalic acid were appropriate as hole scavengers.

The TiO_2 photocatalyst could be repeatedly used without loss of activity.

Phenyl vinyl sulfoxide was reduced to sulfide without hydrogenation of a C=C bond.