

Determination of Oxygen Sources for Oxidation of Benzene on TiO₂ Photocatalysts in Aqueous Solutions Containing Molecular Oxygen

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Abstract: Photocatalytic oxidation of benzene to CO₂ was studied in aqueous solutions using different kinds of TiO₂ powders, and isotopic oxygen tracers (H₂¹⁸O and ¹⁸O₂) were used to investigate the oxidation process. Phenol was produced as a main intermediate in solution. When anatase powders, which showed high activity for oxidation of benzene, were used, 70–90% of oxygen introduced into phenol was from water. On the other hand, when rutile powders were used, only 20–40% of the oxygen was from water. The rest was from molecular oxygen in both cases. The rate of phenol production by using molecular oxygen was nearly the same between anatase and rutile powders. Hence, the high activity of anatase powders for oxidation of benzene to CO₂ is attributed to their high activity for oxidation of benzene to phenol, which is considered to be the rate-determining step, using water as the oxygen source. The processes using water and molecular oxygen as the oxygen sources are ascribed, respectively, to oxygen transfer and hole transfer processes in the initial step of benzene oxidation.

1. Introduction

Photocatalysis based on the utilization of solar energy has been considered to be green chemistry. TiO₂, a well-known and most applicable photocatalyst, has been used in many applications in environmental treatments because of its chemical and physical durability, high activity, nontoxicity, and low cost.^{1–3} TiO₂ photocatalytic reactions have also attracted attention in the field of organic synthesis.^{4,5}

In photocatalysis, absorption of photons with energy larger than the band gap of a semiconductor produces holes in the valence band and electrons in the conduction band. Some of the photogenerated holes and electrons migrate to the semiconductor surface and initiate simultaneous oxidation and reduction reactions or chains of redox reactions. Much effort has been made to deepen the understanding of this complex reaction system and to make use of it efficiently. Several mechanism models have been proposed on the basis of experimental results obtained by chemical and physical methods.^{1–5} The higher catalytic activity of anatase particles compared with rutile particles in decomposition of organics has been mostly attributed to its higher conduction band level (larger band gap).^{1,6}

However, the photocatalytic reaction mechanism is still unclear, because for example rutile particles are more active than anatase particles in oxidation of water, which necessitates very strong oxidation power.^{7,8}

Benzene is an essential solvent and starting material in the chemical industry. However, it is also a highly toxic and carcinogenic compound. Therefore, the clearance of benzene and its derivatives is a major problem in environmental treatment, and photocatalytic reactions of benzene on TiO₂ particles have been studied.^{9–12} Photocatalytic reaction of benzene on TiO₂ is also interesting for deepening the understanding of the mechanism of photocatalytic reactions, because it is one of the most fundamental organic materials. Hence, clarification of the mechanism of this reaction is very important from both theoretical and practical aspects.

The aim of this study was to clarify the processes of benzene photooxidation on TiO₂ in aqueous solution. The initial products from benzene were carefully studied, and the photocatalytic reaction mechanism was studied by isotopic tracing methods using a stable isotope of oxygen (¹⁸O) included in H₂¹⁸O and ¹⁸O₂. The movement of these isotopic atoms was traced in phenol, which is the most important intermediate, and CO₂

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Table 1. Characteristics of Some TiO₂ Powders and Contents of Labeled Phenol in the Phenol Produced from Benzene by Photocatalysis in ¹⁸O-Enriched Water (10% H₂¹⁸O)

powders	content of rutile (%)	specific surface area (m ² /g)	content of labeled phenol (stationary value) (%)
ST-41	<0.1	8.2	6.7
ST-21	<0.1	56.1	9.0
ST-01	<0.1	192	8.6
NS-51	98.6	6.5	3.0
CR-EL	>99.9	7.1	3.2
TIO-3	>99.9	48.1	1.7

evolved. From the results, we obtained useful insights into the difference between activities of rutile and anatase particles as photocatalysts.

2. Experimental Section

Six kinds of TiO₂ powders were used as photocatalysts. They were NS-51 from Toho Titanium Co. Ltd.; TIO-3 from Catalysis Society of Japan; and CR-EL, ST-41, ST-21, and ST-01 from Ishihara Sangyo Ltd. The contents of rutile and specific surface areas of these powders are shown in Table 1. Benzene, phenol, *p*-hydroquinone, and *p*-benzoquinone were obtained from Wako Pure Chemical. Pure water containing 10% H₂¹⁸O was from Cambridge Isotope Laboratories, Inc. Oxygen gas containing 99% ¹⁸O₂ was from Isotec Co. All of the chemicals were guaranteed reagents and used without further purification.

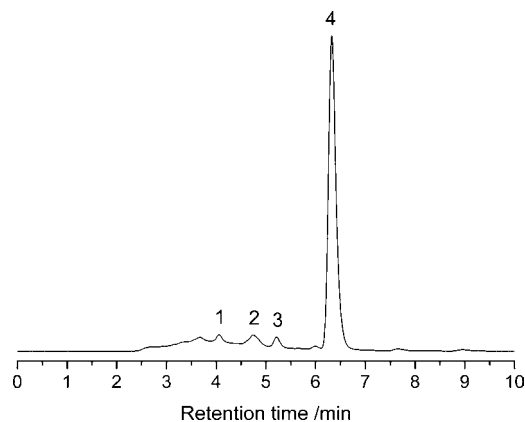
All of the photooxidation reactions were carried out in a closed Pyrex tube containing 20 mg of TiO₂ powder, 0.1 mL of benzene, 2 mL of water, and 14 mL of gas phase at atmospheric pressure. The gas phase was either air or oxygen. The reaction solution was stirred with a magnetic stirrer to suspend the TiO₂ powder and photoirradiated with UV–vis light from a 500 W high-pressure mercury lamp (Wacom BMO-500DY). The reaction temperature reached a stable temperature of about 40 °C after 30 min of photoirradiation. To make an aqueous reaction solution saturated with benzene, 0.1 mL of benzene was added to the reaction system. The dissolved part of benzene in the reaction solution was in equilibrium with the vaporized part in gas phase. To trace an oxygen isotope in the products, either 10% H₂¹⁸O containing water or ¹⁸O₂ was used as the oxygen isotope source.

Intermediate products in reaction solutions were analyzed with an HPLC system equipped with a Hitachi L-7400 UV detector and 4.6 mm × 150 mm columns (GL-Sciences, Intersil ODS-3). The HPLC mobile phase was a mixture of acetonitrile and water (1:1 v/v), which was flowed at a rate of 0.5 mL/min. The products were identified from the HPLC results by comparing retention times and UV–vis absorption spectra of the products with those of corresponding authentic compounds.

CO₂ evolution and amount of oxygen in the gas phase were monitored with Shimadzu GC-8A gas chromatographs. Contents of ¹⁸O to the total amounts of oxygen included in phenol, CO₂, and O₂ were determined with a GCMS-QP2010S system.

3. Results

Product Analysis. Benzene is decomposed into CO₂ and water as a result of photocatalytic reaction on TiO₂. However, some intermediate species must be produced before complete mineralization. To monitor the intermediate products, small amounts of the solution were periodically sampled during photocatalytic reaction with a microsyringe and analyzed by means of HPLC and GC–MS. A typical HPLC chromatogram obtained is shown in Figure 1. By comparing retention times and UV–vis absorption spectra of the products in the samples with those of authentic compounds, the main peaks seen in the chromatogram are assigned to *p*-hydroquinone (peak 1), muconaldehyde (peak

**Figure 1.** Typical HPLC chromatogram obtained from liquid phase analysis. Peaks 1–4 are assigned to hydroquinone, muconaldehyde, *p*-benzoquinone, and phenol, respectively.

2), *p*-benzoquinone (peak 3), and phenol (peak 4). The HPLC chromatogram shows that there are some other unidentified products, which have a broad band in the retention time from 2.5 to 4 min and small peaks after the peak of phenol. The broad band probably comprises peaks of aliphatic carboxylic acids. On the other hand, the peaks appearing after the peak of phenol are probably due to biphenol and polyphenol compounds. We have also found that some intermediate species, catechol and polymerized products, are present only on the surface of TiO₂ powders.⁹ Some of the main products are summarized in Scheme 1 and have already been reported.^{9–12} Of these intermediates, phenol is the largest in quantity.

Photooxidation of Benzene in Labeled Water. Since the amount of phenol is much larger than the amounts of other products and is the only product containing one oxygen atom, phenol is often considered to be the initial product of the photocatalytic oxidation of benzene.^{10–12} It has been proposed that phenol is produced as a result of reaction between benzene and an HO• radical, which is produced by oxidation of an OH group on TiO₂ by a photogenerated hole.^{1–5,10–12} However, there are some reports against the production of HO• radical on photoirradiated TiO₂.^{13,14} It is therefore important to identify the origin of the oxygen atom introduced into phenol, which will also give insights into the mechanism of oxidation of organic compounds on TiO₂ photocatalysts. In the present study, we examined the origin of the oxygen introduced into phenol by using ¹⁸O-enriched water (10% H₂¹⁸O) as the solvent and analyzed the content of ¹⁸O in the phenol. As a complementary study, we also used labeled dioxygen (99% ¹⁸O₂) as the electron acceptor.

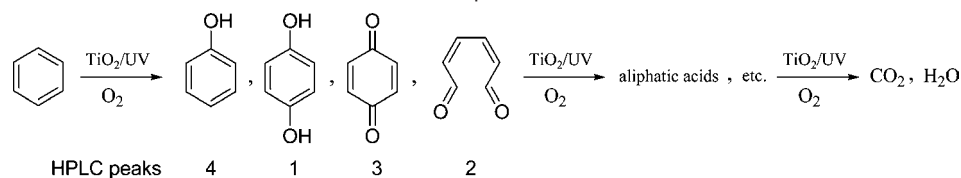
In the series of experiments using ¹⁸O-enriched water, normal air was filled in the gas phase of the test tube. The production of phenol in solution, evolution of CO₂ and amount of remaining O₂ in the gas phase were determined by means of HPLC and GC, and the inclusion of ¹⁸O in them was traced by GC–MS.

Figure 2 shows that the concentration of phenol initially increases with photoirradiation time. The rate of phenol production is higher for ST-41 (anatase) than for NS-51 (rutile). Similar results were obtained using other anatase and rutile powders, the characteristics of which are shown in Table 1. This result is

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Scheme 1. Photooxidation of Benzene on TiO₂ Surface in Aerated Aqueous Solution^a

^a The numbers under the molecular structures correspond to the peak numbers in Figure 1.

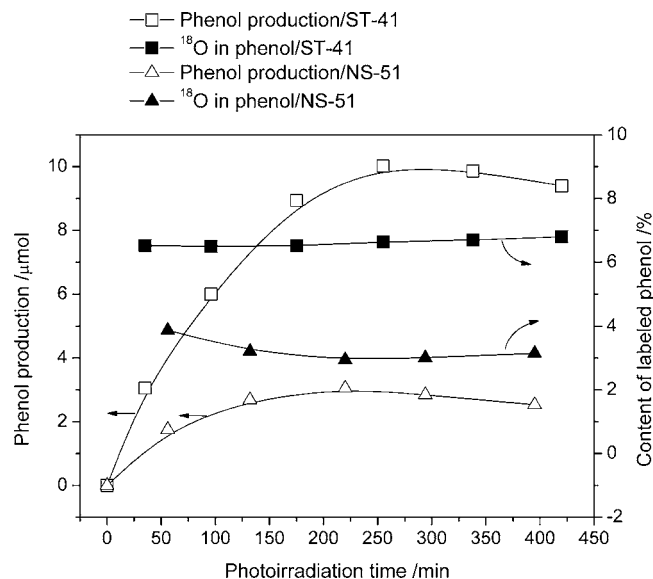


Figure 2. Time courses of photocatalyzed production of phenol from benzene and contents of phenol containing ¹⁸O. Photocatalyses were carried out in ¹⁸O-enriched water (10% H₂¹⁸O) using ST-41 and NS-51 powders.

consistent with the results of previous studies showing that anatase powders show higher photocatalytic activity than that of rutile powders.^{1–3} After reaching maximum values at about 250 min, the concentration of phenol gradually decreases. This decrease is due to the photocatalytic decomposition of phenol and decrease in the concentration of dissolved benzene in the aqueous solution and the decrease in the amount of oxygen added to the reaction tube. The contents of labeled phenol (phenol with an ¹⁸O atom) are about 6.7% for ST-41 and about 3.0% for NS-51. These contents are almost constant, although the initial value for NS-51 is slightly higher than the stationary value. It is important that these contents are between 10%, which is the content of H₂¹⁸O in water used, and 0.2%, which is the content of ¹⁸O included in normal air. The stationary contents of labeled phenol for experiments using several TiO₂ powders are shown in Table 1. The results show that the content of labeled phenol is between 1.7% and 9.0% and that the content is lower for rutile powders than for anatase powders.

The oxygen-exchange rate between phenol and water and that between phenol and molecular oxygen were experimentally confirmed to be slow, as shown in Figures S1 and S2, respectively, in Supporting Information. Therefore, the results showing that the content of labeled phenol is between 1.7% and 9.0% indicate that oxygen atoms are introduced into phenol from both H₂O and O₂ during phenol formation. The results also indicate that contribution of water is larger for anatase powders than for rutile powders.

Anatase powders produce larger amounts of phenol than do rutile powders after photoirradiation for 100 min, as shown in Figure 3. This result is consistent with results of previous studies

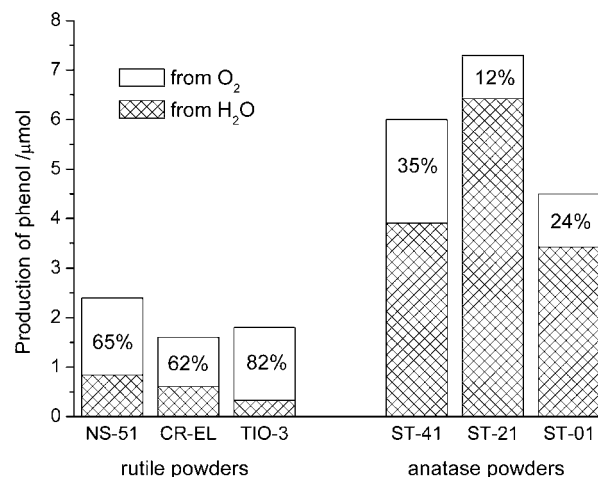


Figure 3. Amounts of phenol produced from benzene by photoirradiation for 100 min in ¹⁸O-enriched water (10% H₂¹⁸O) using several TiO₂ powders and percentage of phenol produced using water as the oxygen source, which was calculated on the basis of the results shown in Table 1.

showing that anatase powders are more active as photocatalysts for oxidizing organic compounds.^{1–3} From simple calculation based on the contents of labeled oxygen in phenol produced, we can determine the ratio of the oxygen sources for producing phenol by the photocatalytic reaction. The contributions of H₂O and O₂ to the production of phenol for these rutile and anatase powders are also shown in Figure 3. The marked difference between anatase and rutile powders is that anatase powders produce very large amounts of phenol using water as the oxygen source compared with rutile powders. On the other hand, the amounts of phenol produced using oxygen from O₂ are nearly the same between anatase and rutile powders. Hence, the high efficiency of phenol production using water as the oxygen source is attributed to the high photocatalytic activity of anatase powders.

The rates of CO₂ evolution from benzene using ST-41 (anatase) and NS-51 (rutile) powders are compared in Figure 4. CO₂ evolution started upon photoirradiation and continued with photoirradiation time. The immediate evolution of CO₂ suggests that the intermediate species produced from benzene are decomposed more easily than benzene. The content of ¹⁸O in oxygen atoms of CO₂ reached 10%, which is the same as the content of H₂¹⁸O in the water used as the solvent. However, this does not mean that the oxygen source for CO₂ production is solely water, but it means that the content is determined by the oxygen exchange between CO₂ and H₂O because this exchange is a considerably fast process.¹⁶ The lower contents of ¹⁸O in oxygen atoms of CO₂ seen at short irradiation (less than 25 min) in Figure 4 are due to the contribution of O₂ as

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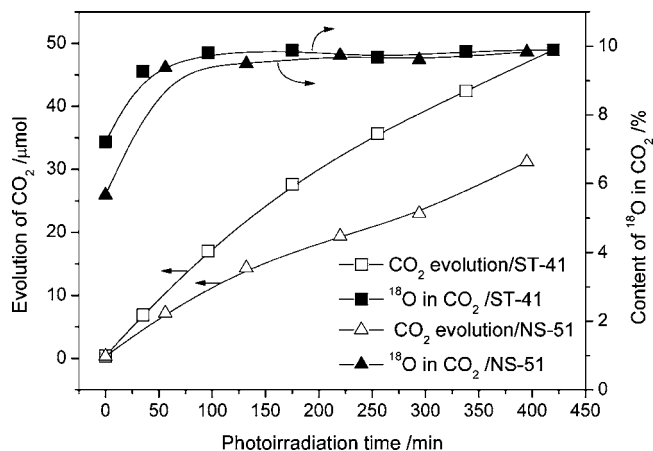


Figure 4. Time courses of CO₂ evolution from benzene and contents of ¹⁸O in oxygen atoms of the CO₂. Photocatalyses were carried out in ¹⁸O-enriched water (10% H₂¹⁸O) using ST-41 and NS-51 powders.

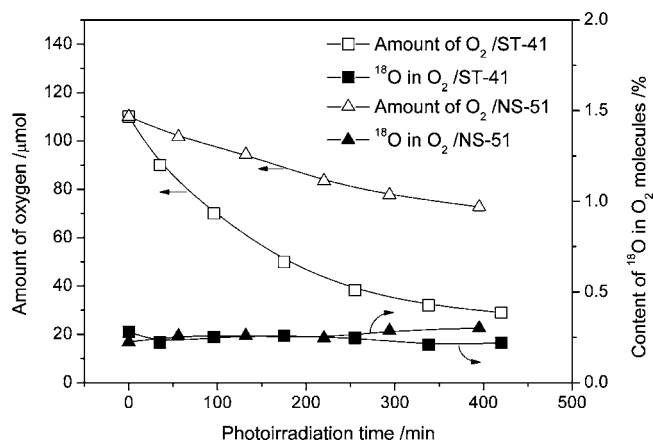


Figure 5. Time courses of the amount of O₂ in the gas phase of test tubes during photocatalyses of benzene in O-enriched water (10% H₂¹⁸O) using ST-41 and NS-51 powders and contents of ¹⁸O in O₂ molecules.

the oxygen source for producing CO₂, as discussed later. The content gradually approaches the content of ¹⁸O in water with elapse of time as a result of oxygen exchange.

The production of CO₂ is accompanied by decrease in the amount of oxygen in the gas phase, as shown in Figure 5. The rate of O₂ consumption is nearly the same or even slightly faster than the rate of CO₂ evolution, as shown in Figure 4. This stoichiometric relationship apparently indicates that only O₂ is consumed as the oxidant by accepting electrons from TiO₂ even when water is used as the oxygen source for oxidation of benzene and the intermediates. The slightly larger consumption of O₂ than the amount of CO₂ observed is due to the accumulation of some intermediate species in the reaction system.

The content of ¹⁸O in oxygen molecules during photooxidation of benzene over both rutile and anatase hardly changed during photoirradiation (Figure 5). This result indicates that neither O-exchange between H₂O and O₂ molecules nor evolution of O₂ from photooxidation of water took place.

Photooxidation of Benzene in Labeled Oxygen Atmosphere.

To further confirm the above results about the origin of O atoms introduced into phenol, we carried out the reaction in an atmosphere of pure ¹⁸O₂, which was filled in the gas phase of the test tube, using normal water as the solvent. The results

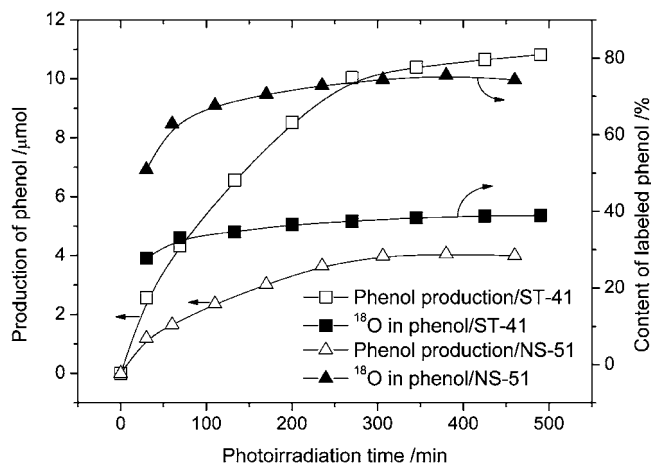


Figure 6. Time courses of photocatalyzed production of phenol from benzene and contents of phenol containing ¹⁸O. Photocatalyses were carried out in normal water under ¹⁸O₂ atmosphere using ST-41 and NS-51 powders.

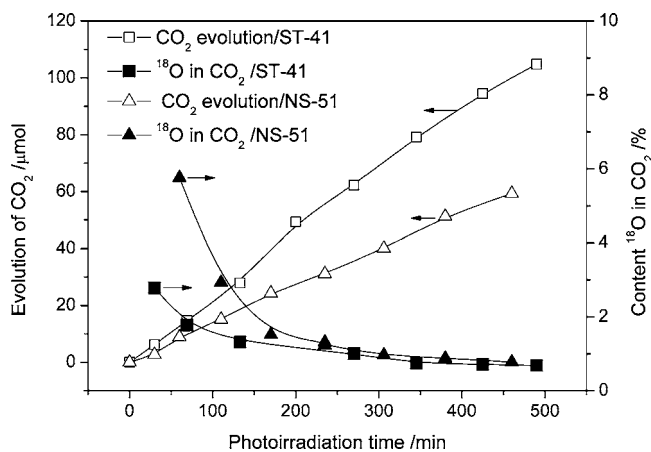


Figure 7. Time courses of CO₂ evolution from benzene and contents of ¹⁸O in oxygen atoms of the CO₂. Photocatalyses were carried out in normal water under ¹⁸O₂ atmosphere using ST-41 and NS-51 powders.

obtained using ST-41 (anatase) and NS-51 (rutile) powders as the photocatalysts are shown in Figures 6 and 7.

When the reaction was carried out under the ¹⁸O₂ atmosphere instead of normal air, the mineralization rate was increased almost twice the rate obtained in air, which is shown in Figure 4. This is ascribable to the enhanced electron removal from the photoirradiated TiO₂ particles due to the increased concentration of the electron acceptor, i. e., O₂ or ¹⁸O₂. Except this point, other tendencies were nearly equivalent to those observed in the reaction carried out in normal air. The contents of ¹⁸O in phenol produced in ¹⁸O₂ atmosphere were 40% and 75% for ST-41 and NS-51, respectively, as shown in Figure 6. These percentages mean that the contributions of O₂ (or ¹⁸O₂) to the production of phenol are 40% and 75% for ST-41 and NS-51, respectively, which are closed to the percentages determined for the reactions in air.

The high content of ¹⁸O in CO₂ in the initial period of the reaction, as shown in Figure 7, suggests that a large amount of oxygen atoms used for the oxidation of benzene is supplied from O₂ (or ¹⁸O₂). However, the content decreased with time and finally reached the value of ¹⁸O in water due to the exchange of O atoms between CO₂ and water, as discussed above concerning the results shown in Figure 4. In the initial period, the ¹⁸O contents in oxygen atoms of CO₂ are 3% for ST-41 and

6% for NS-51, as shown in Figure 7. By sampling at a shorter time period, we found that the initial value for ST-41 reaches as high as 10%, as shown in Figure S3 in the Supporting Information. On the other hand, the contribution of O₂ as the source of oxygen to the production of phenol using ST-41 was about 35%, as shown in Figure 3. If the contribution of O₂ for the oxidation of benzene to CO₂ takes place only in the production of phenol, the content of ¹⁸O in CO₂ should be about 3% because 12 oxygen atoms are used for oxidation of benzene to CO₂ molecules. The much higher content of ¹⁸O in CO₂ in the initial period suggests that O₂ plays the role of oxygen-atom supplier not only to benzene but also to the successive intermediate species. In addition, the higher content of ¹⁸O in CO₂ for rutile powders than for anatase powders suggests that the contribution of O₂ is larger for rutile powders than anatase powders in different kinds of organic species. However, quantitative analysis is difficult because of the considerably fast exchange of O atoms between CO₂ and water.

4. Discussion

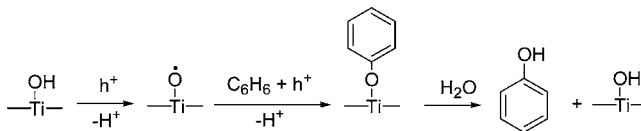
In general, the initial photooxidation of organic compounds has been considered to be due to either oxygen transfer^{1–5,11,12} or hole transfer^{10,15} from TiO₂ to substrates. The former is often assumed to occur through HO• radicals, although the generation of HO• radicals on photoirradiated TiO₂ is still controversial.^{13,14} In the case of benzene photooxidation, it has been widely considered that the oxygen transfer is the only way to produce phenol.^{4,5,11,12} The results showing that, although not at 100% efficiency, phenol is produced by using water as the oxygen source, as can be seen in Figure 3, suggest that the oxygen transfer process does exist in the phenol production, especially on anatase particles. A possible process is shown in Scheme 2. Besides Ti–O• shown in Scheme 2, HO• radicals, Ti–OO• or more complicated surface peroxides can be the source of oxygen to be transferred to benzene.^{1–3,17–21}

Importantly, however, the experimental results show that phenol can also be produced using O₂ as the oxygen source, as can be seen in Figure 3. This indicates that phenol can be produced by a route different from the oxygen transfer process. The contribution of oxygen molecules as the oxygen source to oxidation of organic compounds on photoirradiated TiO₂ has been proposed in some kinds of oxidation reactions. They are mostly observed for the reactions between aliphatic radicals and an oxygen molecule.^{1–4,10}

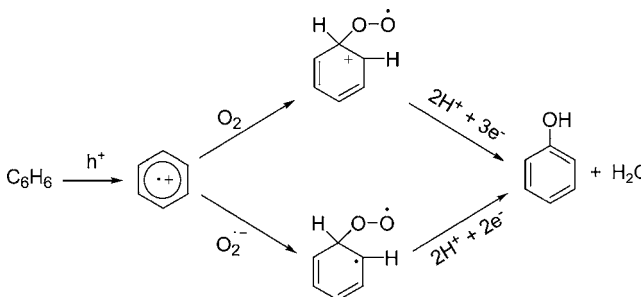


In the case of benzene, it seems more reasonable to consider that benzene cation radicals, which are formed by the hole transfer mechanism, are the species to react with oxygen, as shown by Scheme 3. The peroxide radical formed as a result of the reaction between the benzene cation radical and an O₂ molecule can be converted to phenol through reductive pro-

Scheme 2. Possible Mechanism for Production of Phenol from Benzene through an Oxygen Transfer Process Using Water as Oxygen Source



Scheme 3. Possible Mechanism for Production of Phenol from Benzene through a Hole Transfer Process Using O₂ as Oxygen Source



cesses, for which a variety of intermediates produced before conversion into CO₂ may be used as reductants. In addition to molecular oxygen, O₂^{•−} produced by reduction of O₂ on TiO₂ may also be used in the reaction with benzene cation radicals.

We speculate that the marked difference in photocatalytic activity for the oxidation of benzene between rutile and anatase powders, as shown in Figure 3, is due to the different activities of anatase and rutile powders for the oxidation of benzene to phenol, which is considered to be the rate-determining step of the whole process of the oxidation of benzene to CO₂. On anatase particles, benzene is oxidized to phenol efficiently by Scheme 2 using water as the oxygen source, whereas Scheme 3 using O₂ as the oxygen source contributes to a lesser degree, as shown in Figure 3. On the other hand, on rutile particles, the contribution of Scheme 2 to benzene oxidation is much smaller. Hence, the ease in oxidation of benzene to phenol by Scheme 2 on anatase particles is attributed to its high photocatalytic activity for oxidizing benzene to CO₂. We speculate that the energy levels and/or the atomic configuration on the surface of the anatase particles are the reason for their efficient production using water as the oxygen source, as has been discussed in relation to the higher photocatalytic activity of anatase particles.⁶ As for the surface atomic arrangement, we speculate that anatase particles have a more irregular structure on the surface than do rutile particles because they are manufactured at lower temperatures than are rutile particles. These irregular sites may contribute to the formation of Ti–O•, Ti–OO•, or more complicated surface peroxides on the surface, which are then used for forwarding the process represented by Scheme 2.

Rutile powders are known to be good photocatalysts for oxidizing water into molecular oxygen in the presence of good electron acceptors such as Fe(III) ions.^{7,8} However, we found that in the oxidation of benzene using molecular oxygen as the electron acceptor, the route using water as the oxygen source (Scheme 2) is not efficient on rutile powders, as shown in Figure 3. The difference probably arises from the difference in the mechanisms of these two processes. In the case of oxidation of water, a pool of holes (or accumulation of peroxides) and strong electron acceptors are necessary to enable the 4-electron transfer process for liberating molecular oxygen, whereas oxidation of

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benzene is driven by a 1-electron transfer process that does not need a pool of holes.

Finally, it should be noted that HO• radicals can be produced by reduction of O₂. If the HO• radicals produced from O₂ on TiO₂ contribute to the production of phenol, this provides another explanation for the contributions of water and O₂ to the production of phenol on photoirradiated TiO₂. However, this is unlikely because O₂^{•-} is the chief product from O₂ on rutile powders, whereas hydrogen peroxide, which can easily be converted to HO• radicals, is the chief product from O₂ on anatase powders.²² Therefore, if HO• radicals produced from O₂ contribute to phenol production, this process must be advantageous for anatase powders. This contradicts the experimental results shown in Figure 3. The ease in producing O₂^{•-} on rutile powders may be responsible for the large contribution of O₂ to production of phenol on rutile powders by Scheme 3 because O₂^{•-} has higher reactivity with benzene cation radicals than does O₂.

5. Conclusions

By using isotope-tracing methods we successfully determined the origin of the oxygen atom introduced into phenol that is produced from benzene by photocatalyzed reaction on TiO₂ particles. For efficient oxidation of benzene, the path using water as the oxygen source is considered to be important. However,

it was also found that molecular oxygen can be a source of oxygen introduced into phenol, which is more important on rutile powders than on anatase powders. Since benzene is one of the most basic organic compounds, the results are useful for deepening the understanding of photocatalytic reactions of organic materials on a TiO₂ photocatalyst. The results also demonstrate that ¹⁸O-tracing methods are useful for clarifying the mechanism of photocatalytic reactions. However, it is difficult to apply ¹⁸O-tracing methods to carbonyl compounds because the rates of oxygen exchange between water and carbonyl compounds are too fast to identify the source of oxygen atoms introduced into them.

Acknowledgment. T.D.B. is very grateful to Vietnam International Education Development (VIED), Ministry of Education and Training (MOET), Vietnam, and Graduate School of Engineering Science, Osaka University, Japan for financial support.

Supporting Information Available: Figures demonstrating exchange of oxygen atoms between phenol and water and that between phenol and molecular oxygen and ¹⁸O contents in CO₂ produced from benzene in the initial stage of the reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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