Determination of Oxygen Sources for Oxidation of Benzene on TiO$_2$ Photocatalysts in Aqueous Solutions Containing Molecular Oxygen

Thuan Duc Bui,[†,‡] Akira Kimura,[†] Shigeru Ikeda,[†] and Michio Matsumura*,[†]

Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan, and Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

Received March 18, 2010; E-mail: matsu@chem.es.osaka-u.ac.jp

Abstract: Photocatalytic oxidation of benzene to CO$_2$ was studied in aqueous solutions using different kinds of TiO$_2$ powders, and isotopic oxygen tracers (H$_2$^{18}O and ^{18}O$_2$) 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 CO$_2$ 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. TiO$_2$, 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] TiO$_2$ 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 TiO$_2$ particles have been studied.[9−12] Photocatalytic reaction of benzene on TiO$_2$ 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 TiO$_2$ 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 (^{18}O) included in H$_2$^{18}O and ^{18}O$_2$. The movement of these isotopic atoms was traced in phenol, which is the most important intermediate, and CO$_2$

† Osaka University.

‡ Vietnam Academy of Science and Technology.

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Table 1. Characteristics of Some TiO$_2$ Powders and Contents of Labeled Phenol in the Phenol Produced from Benzene by Photocatalysis in ^{18}O-Enriched Water (10% H$_2$^{18}O)

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 TiO$_2$ 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% H$_2$^{18}O was from Cambridge Isotope Laboratories, Inc. Oxygen gas containing 99% ^{18}O$_2$ 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 TiO$_2$ 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 TiO$_2$ 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% H$_2$^{18}O containing water or ^{18}O$_2$ 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.

CO$_2$ evolution and amount of oxygen in the gas phase were monitored with Shimadzu GC-8A gas chromatographs. Contents of ^{18}O to the total amounts of oxygen included in phenol, CO$_2$, and O$_2$ were determined with a GCMS-QP2010S system.

3. Results

Product Analysis. Benzene is decomposed into CO$_2$ and water as a result of photocatalytic reaction on TiO$_2$. 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
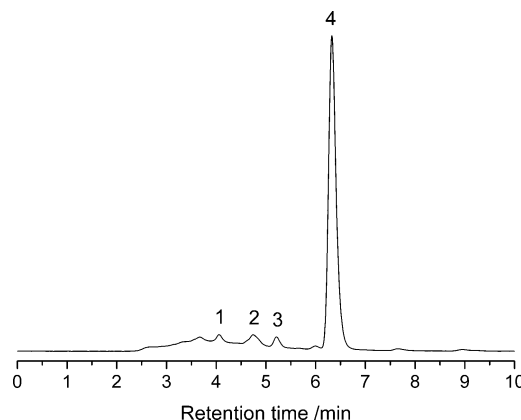
Figure 1. Typical HPLC chromatogram obtained from liquid phase analysis. Peaks 1−4 are assigned to hydroquinone, muconaldehyde, *p*-benzoquinone, and phenol, respectively.

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 TiO$_2$ 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 TiO$_2$ by a photogenerated hole.[1−5,10−12] However, there are some reports against the production of HO• radical on photoirradiated TiO$_2$.[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 TiO$_2$ photocatalysts. In the present study, we examined the origin of the oxygen introduced into phenol by using ^{18}O-enriched water (10% H$_2$^{18}O) as the solvent and analyzed the content of ^{18}O in the phenol. As a complementary study, we also used labeled dioxygen (99% ^{18}O$_2$) as the electron acceptor.

In the series of experiments using ^{18}O-enriched water, normal air was filled in the gas phase of the test tube. The production of phenol in solution, evolution of CO$_2$ and amount of remaining O$_2$ in the gas phase were determined by means of HPLC and GC, and the inclusion of ^{18}O 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]

HPLC peaks   4   1   3   2
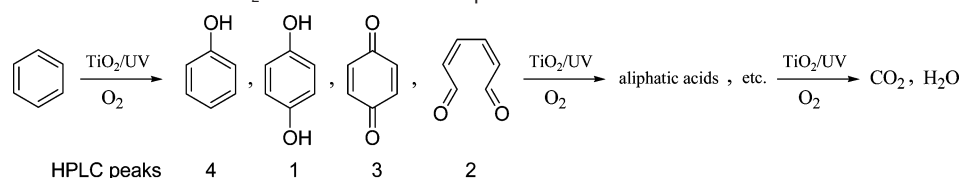
[a] The numbers under the molecular structures correspond to the peak numbers in Figure 1.
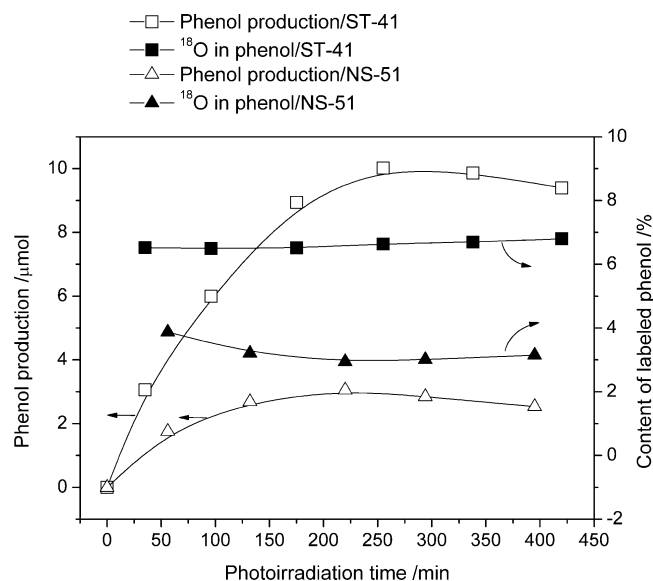

Figure 2. Time courses of photocatalyzed production of phenol from benzene and contents of phenol containing ^{18}O. Photocatalyses were carried out in ^{18}O-enriched water (10% $H_2^{18}O$) using ST-41 and NS-51 powders.

Figure 3. Amounts of phenol produced from benzene by photoirradiation for 100 min in ^{18}O-enriched water (10% $H_2^{18}O$) 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.

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 ^{18}O 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 $H_2^{18}O$ in water used, and 0.2%, which is the content of ^{18}O 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 H_2O and O_2 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
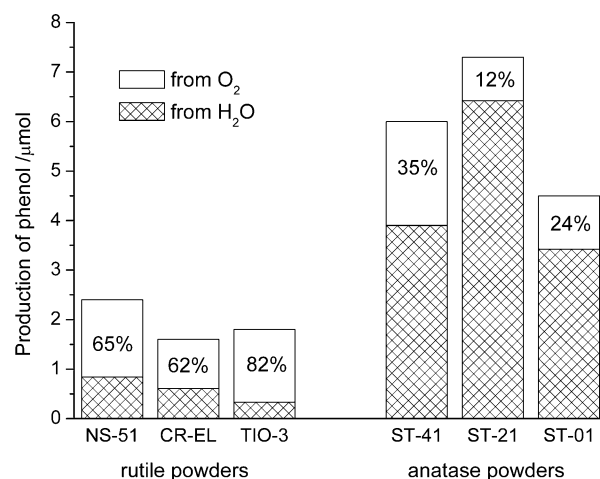
showing that antase powders are more active as photocatalysts for oxidizing organic compounds.[1–3] From simple calculation based on the contents of labeled oxygen in phenol produced, we can determine the ratio of the oxygen sources for producing phenol by the photocatalytic reaction. The contributions of H_2O and O_2 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 form O_2 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 CO_2 evolution from benzene using ST-41 (anatase) and NS-51 (rutile) powders are compared in Figure 4. CO_2 evolution started upon photoirradiation and continued with photoirradiation time. The immediate evolution of CO_2 suggests that the intermediate species produced from benzene are decomposed more easily than benzene. The content of ^{18}O in oxygen atoms of CO_2 reached 10%, which is the same as the content of $H_2^{18}O$ in the water used as the solvent. However, this does not mean that the oxygen source for CO_2 production is solely water, but it means that the content is determined by the oxygen exchange between CO_2 and H_2O because this exchange is a considerably fast process.[16] The lower contents of ^{18}O in oxygen atoms of CO_2 seen at short irradiation (less than 25 min) in Figure 4 are due to the contribution of O_2 as

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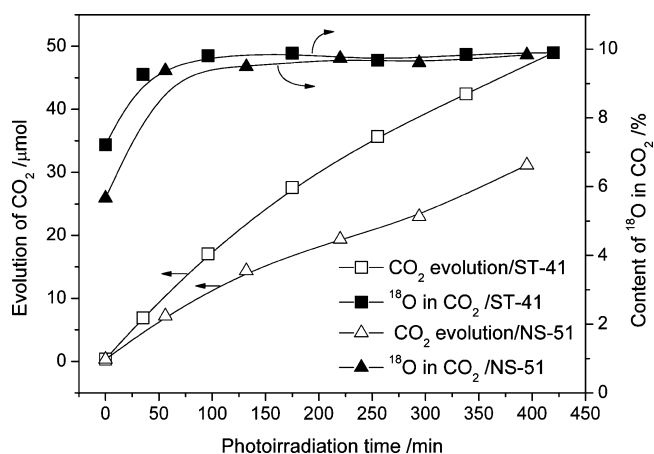
Figure 4. Time courses of CO_2 evolution from benzene and contents of ^{18}O in oxygen atoms of the CO_2. Photocatalyses were carried out in ^{18}O-enriched water (10% $H_2^{18}O$) using ST-41 and NS-51 powders.
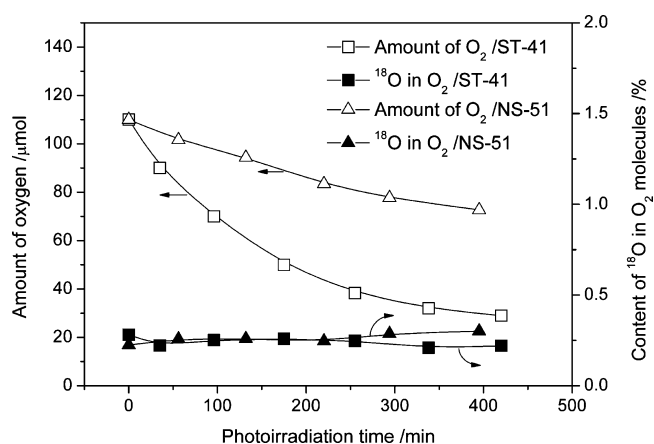

Figure 5. Time courses of the amount of O_2 in the gas phase of test tubes during photocatalyses of benzene in O-enriched water (10% $H_2^{18}O$) using ST-41 and NS-51 powders and contents of ^{18}O in O_2 molecules.

the oxygen source for producing CO_2, as discussed later. The content gradually approaches the content of ^{18}O in water with elapse of time as a result of oxygen exchange.

The production of CO_2 is accompanied by decrease in the amount of oxygen in the gas phase, as shown in Figure 5. The rate of O_2 consumption is nearly the same or even slightly faster than the rate of CO_2 evolution, as shown in Figure 4. This stoichiometric relationship apparently indicates that only O_2 is consumed as the oxidant by accepting electrons from TiO_2 even when water is used as the oxygen source for oxidation of benzene and the intermediates. The slightly larger consumption of O_2 than the amount of CO_2 observed is due to the accumulation of some intermediate species in the reaction system.

The content of ^{18}O 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 H_2O and O_2 molecules nor evolution of O_2 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 $^{18}O_2$, which was filled in the gas phase of the test tube, using normal water as the solvent. The results
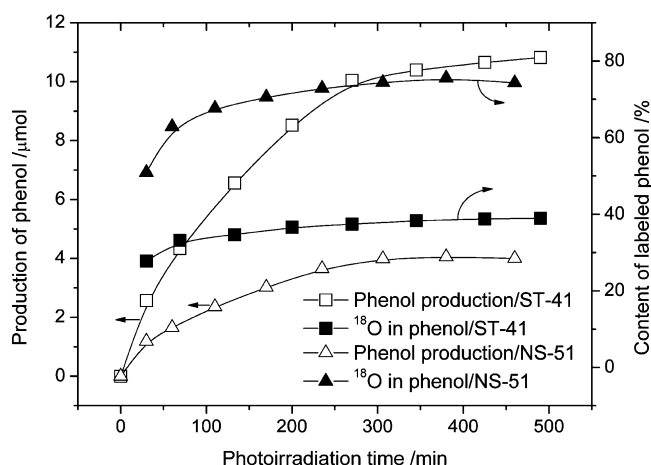

Figure 6. Time courses of photocatalyzed production of phenol from benzene and contents of phenol containing ^{18}O. Photocatalyses were carried out in normal water under $^{18}O_2$ atmosphere using ST-41 and NS-51 powders.

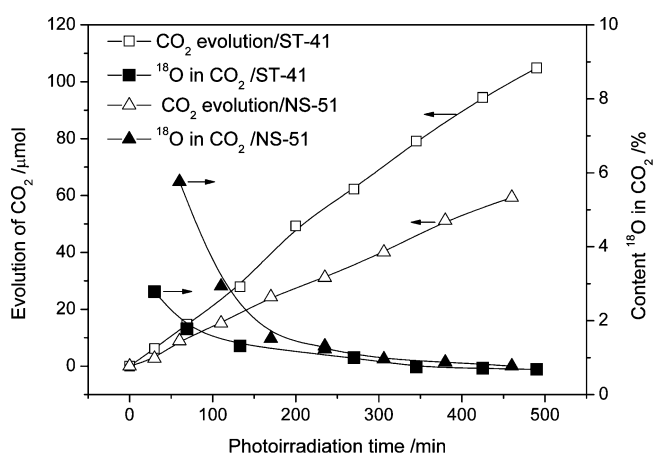**Figure 7.** Time courses of CO_2 evolution from benzene and contents of ^{18}O in oxygen atoms of the CO_2. Photocatalyses were carried out in normal water under $^{18}O_2$ atmosphere using ST-41 and NS-51 powders.

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 $^{18}O_2$ 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 TiO_2 particles due to the increased concentration of the electron acceptor, i. e., O_2 or $^{18}O_2$. Except this point, other tendencies were nearly equivalent to those observed in the reaction carried out in normal air. The contents of ^{18}O in phenol produced in $^{18}O_2$ atmosphere were 40% and 75% for ST-41 and NS-51, respectively, as shown in Figure 6. These percentages mean that the contributions of O_2 (or $^{18}O_2$) 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 ^{18}O in CO_2 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 O_2 (or $^{18}O_2$). However, the content decreased with time and finally reached the value of ^{18}O in water due to the exchange of O atoms between CO_2 and water, as discussed above concerning the results shown in Figure 4. In the initial period, the ^{18}O contents in oxygen atoms of CO_2 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 O_2 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 O_2 for the oxidation of benzene to CO_2 takes place only in the production of phenol, the content of ^{18}O in CO_2 should be about 3% because 12 oxygen atoms are used for oxidation of benzene to CO_2 molecules. The much higher content of ^{18}O in CO_2 in the initial period suggests that O_2 plays the role of oxygen-atom supplier not only to benzene but also to the successive intermediate species. In addition, the higher content of ^{18}O in CO_2 for rutile powders than for anatase powders suggests that the contribution of O_2 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 CO_2 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 TiO_2 to substrates. The former is often assumed to occur though $HO^{\bullet}$ radicals, although the generation of $HO^{\bullet}$ radicals on photoirradiated TiO_2 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$^{\bullet}$ shown in Scheme 2, $HO^{\bullet}$ radicals, Ti-OO$^{\bullet}$ 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 O_2 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 TiO_2 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]

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (1)$$

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 O_2 molecule can be converted to phenol through reductive pro-

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Scheme 2. Possible Mechanism for Production of Phenol from Benzene through an Oxygen Transfer Process Using Water as Oxygen Source
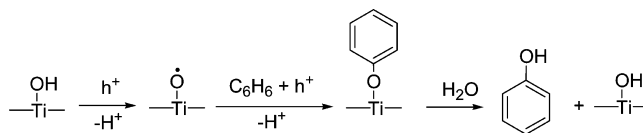
Scheme 3. Possible Mechanism for Production of Phenol from Benzene through a Hole Transfer Process Using O_2 as Oxygen Source
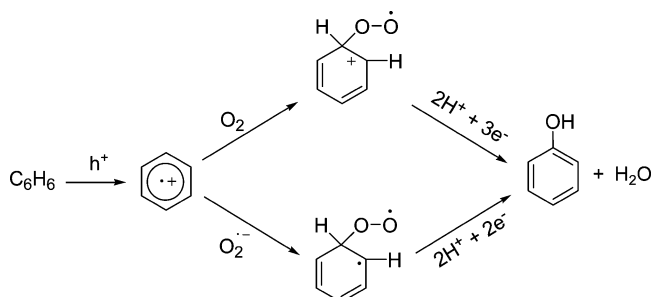
cesses, for which a variety of intermediates produced before conversion into CO_2 may be used as reductants. In addition to molecular oxygen, $O_2^{\bullet -}$ produced by reduction of O_2 on TiO_2 may also be used in the reaction with benzene cation radicals.

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 CO_2. On anatase particles, benzene is oxidized to phenol efficiently by Scheme 2 using water as the oxygen source, whereas Scheme 3 using O_2 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 CO_2. 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$^{\bullet}$, Ti-OO$^{\bullet}$, 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

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 O_2. If the HO• radicals produced from O_2 on TiO_2 contribute to the production of phenol, this provides another explanation for the contributions of water and O_2 to the production of phenol on photoirradiated TiO_2. However, this is unlikely because $O_2^{•-}$ is the chief product from O_2 on rutile powders, whereas hydrogen peroxide, which can easily be converted to HO• radicals, is the chief product from O_2 on anatase powders.[22] Therefore, if HO• radicals produced from O_2 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 $O_2^{•-}$ on rutile powders may be responsible for the large contribution of O_2 to production of phenol on rutile powders by Scheme 3 because $O_2^{•-}$ has higher reactivity with benzene cation radicals than does O_2.

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 TiO_2 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 TiO_2 photocatalyst. The results also demonstrate that ^{18}O-tracing methods are useful for clarifying the mechanism of photocatalytic reactions. However, it is difficult to apply ^{18}O-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.

Supporting Information Available: Figures demonstrating exchange of oxygen atoms between phenol and water and that between phenol and molecular oxygen and [18]O contents in CO_2 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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