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Pathway of Oxygen Incorporation from O_2 in TiO_2 Photocatalytic Hydroxylation of Aromatics: Oxygen Isotope Labeling Studies

Yue Li, Bo Wen, Cailan Yu, Chuncheng Chen,* Hongwei Ji, Wanhong Ma, and Jincai Zhao[a]

Abstract: The hydroxylation process is the primary, and even the rate-determining step of the photocatalytic degradation of aromatic compounds. To make clear the hydroxylation pathway of aromatics, the TiO_2 photocatalytic hydroxylation of several model substrates, such as benzoic acid, benzene, nitrobenzene, and benzonitrile, has been studied by an oxygen-isotope-labeling method, which can definitively assign the origin of the O atoms (from oxidant O_2 or solvent H_2O) in the hydroxyl groups of the hydroxylated products. It is found that the oxygen source of the hydroxylated products depends markedly on the reaction conditions. The percentage of the products with O_2-derived hydroxyl O atoms increases with the irradiation time, while it decreases with the increase of substrate concentration. More intriguingly, when photogenerated valence-band holes (h_{vb}^+) are removed, nearly all the O atoms (>97%) in the hydroxyl groups of the hydroxylated products of benzoic acid come from O_2, whereas the scavenging of conduction-band electrons (e_{cb}^-) makes almost all the hydroxyl O atoms (>95%) originate from solvent H_2O. In the photocatalytic oxidation system with benzoic acid and benzene coexisting in the same dispersion, the percentage of O_2-derived hydroxyl O atoms in the hydroxylated products of strongly adsorbed benzoic acid (ca. 30%) is much less than in that of weakly adsorbed benzene (phenol) (>60%). Such dependences provide unique clues to uncover the photocatalytic hydroxylation pathway. Our experiments show that the main O_2-incorporation pathway involves the reduction of O_2 by e_{cb}^- and the subsequent formation of free $^{\bullet}OH$ via H_2O_2, which was usually overlooked in the past photocatalytic studies. Moreover, in the hydroxylation initiated by h_{vb}^+, unlike the conventional mechanism, the O atom in O_2 cannot incorporate into the product through the direct coupling between molecular O_2 and the substrate-based radicals.

Keywords: aromatic compounds · hydroxylation · isotope labeling · photocatalysis · titanium dioxide

Introduction

TiO_2 photocatalysis has attracted persistent attention due to its potential application in water purification,[1] water splitting,[2] and synthesis of chemicals.[3] During semiconductor photocatalysis, the absorption of irradiation with energy larger than the band gap leads to the formation of valence-band holes (h_{vb}^+) and conduction-band electrons (e_{cb}^-), which could initiate the oxidation and reduction reactions, respectively. For example, nearly all kinds of organic compounds could be degraded, even completely mineralized, in the air-saturated aqueous TiO_2 suspensions with UV irradiation.[4]

As a large group of organic chemicals, and due to their great effect on environmental pollution, aromatic compounds have been the most frequently used model substrates to investigate photocatalytic mechanisms[5] and to test the activity of the photocatalysts.[6] During the photocatalytic oxidation of aromatic compounds, the hydroxylated products are always among the main intermediates and the hydroxylation of the aromatics is usually regarded as the primary step,[7] and even the rate-determining step,[8] of the whole photocatalytic mineralization process. The hydroxylation is also utilized to detect the generation of $^{\bullet}OH$,[9] because the hydroxylated products of aromatics, such as coumarin and terephthalic acid, are easily detected by fluorescence emission or chromatography. Besides its great significance in photocatalysis, the hydroxylation of aromatic compounds also attracts extensive attention from scientists in a variety of disciplines and fields, such as biochemistry,[10] environmental chemistry,[11] and synthetic organic chemistry.[12]

Despite extensive attention, the detailed reaction pathway of photocatalytic hydroxylation of aromatics still eludes the understanding of the researchers. Most of the past studies mainly focused on the detection of hydroxylated products and their formation kinetics,[5b,13] while little work has been dedicated to the specific hydroxylation pathway under photocatalytic conditions so far. During the photocatalytic process, O_2 is the oxidant and the final electron acceptor.

[a] Dr. Y. Li, Dr. B. Wen, C. Yu, Dr. C. Chen, Dr. H. Ji, Dr. W. Ma, Dr. J. Zhao
Beijing National Laboratory for Molecular Sciences
Key Laboratory of Photochemistry, Institute of Chemistry
Chinese Academy of Sciences, Beijing 100190 (P.R. China)
Fax: (+86) 108-261-6495
E-mail: ccchen@iccas.ac.cn

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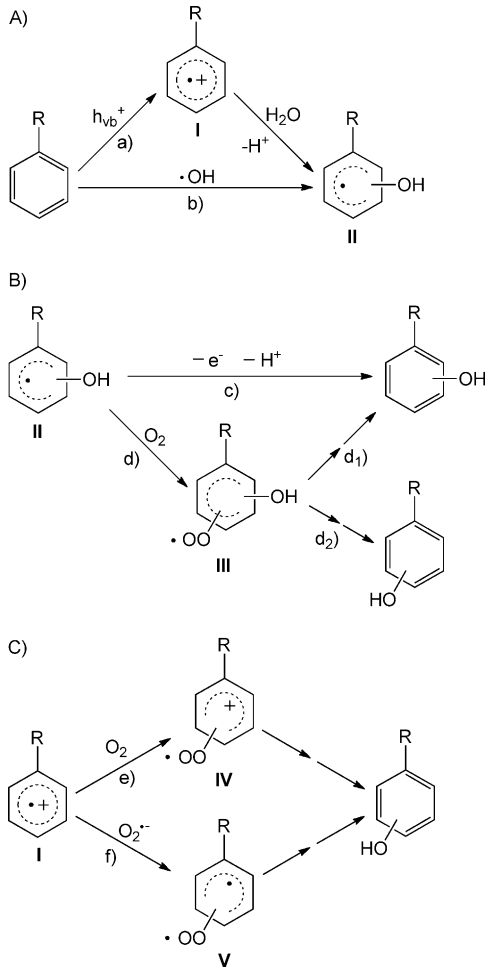
Therefore, how it takes part in the reaction is extremely important and can provide essential information on the whole hydroxylation process. Generally, the primary role of molecular O_2 is to depress the charge recombination and regenerate the photocatalyst by removing e_{cb}^-. O_2 was also considered to be able to directly participate in the oxidation process and enter the oxidized products. Recently, by using isotope-labeling methods, Matsumura, et al.[8] experimentally showed that O_2 contributes to the formation of the hydroxylated product of benzene. In the anatase and rutile systems, 10–30 and 60–80%, respectively, of the hydroxyl O atom in the formed phenol were found to be from O_2 during the photocatalytic hydroxylation of benzene. However, the detailed pathway of the O_2 incorporation is not fully understood.

It is well accepted that, as shown in Scheme 1A, the hydroxylation of aromatics is initiated by direct oxidation by h_{vb}^+ (form the cationic radical **I**) followed by hydrolysis (path a)[14] or the attack of $^{\bullet}OH$ (path b) in the photocatalytic systems. Both pathways lead to the formation of HO adduct radical **II**, which bears the O atom from H_2O/OH^- or $^{\bullet}OH$. Conventionally, $^{\bullet}OH$ is believed to be derived mainly from the H_2O/OH^- oxidation by h_{vb}^+.[5b,13a] Thus the O atom in radical **II**, formed through both pathways, would be from H_2O/OH^-. The most probable fate of radical **II** is to simply undergo one-electron oxidation and deprotonation to form the hydroxylated product (path c in Scheme 1B). By this mechanism, the hydroxyl group of the hydroxylated product would retain the O atom of radical **II**, that is, its hydroxyl O atom comes from H_2O. In principle, besides the h_{vb}^+ oxidation of H_2O/OH^-, $^{\bullet}OH$ could also be formed through the reduction of dissolved O_2 by e_{cb}^- [by means of Eqs. (1)–(5)], by which the O atom of O_2 is incorporated into radical **II** and subsequently into the product through path c. However, the importance of this pathway in the photocatalytic oxidation is usually overlooked in the literature. Most of the earlier experiments indicated that the $^{\bullet}OH$ radical from the reduction of in situ formed H_2O_2 [Eq. (5)] is generally not important for the photocatalytic oxidation of organic compounds,[15] although some reports showed that the addition of H_2O_2 could enhance the rate of the photocatalytic oxidation.[16]



Scheme 1. Traditional mechanisms of the hydroxylation of aromatics.[5b,8,13a,14,17]

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \quad (1)$$

$$O_2^{\bullet-} + H^+ \rightarrow {}^{\bullet}OOH \qquad (pK_a = 4.8) \quad (2)$$

$$2\,{}^{\bullet}OOH \rightarrow H_2O_2 + O_2 \quad (3)$$

$${}^{\bullet}OOH + e_{cb}^- + H^+ \rightarrow H_2O_2 \quad (4)$$

$$H_2O_2 + + e_{cb}^- \rightarrow {}^{\bullet}OH + OH^- \quad (5)$$

To explain the experimental observation of the incorporation of O atom from O_2 into the products, several mechanisms involving the formation of radical O_2 adducts have been proposed. Generally, these pathways are adapted from the so-called Russell mechanism ($R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$),[17] which is normally applicable to the oxidation of aliphatic substrates.[4,18] The radical HO adduct **II** was proposed to react with molecular O_2 to generate the radical O_2 adduct **III** (path d in Scheme 1B) in both photocatalytic and other oxidation systems.[19] The further reactions of radical **III** could introduce the O atom of either O_2 or H_2O into the hydroxylated product (paths d_1 and d_2). Analogously, molecular O_2 (or $O_2^{\bullet-}$) has been considered to directly couple with formed cationic radical **I** to generate radical O_2 adducts **IV** and **V** (paths e and f in Scheme 1C).[8] The products formed by the further reactions of these adducts would bear the O atoms from O_2.

Herein, as part of our mechanistic studies on the photocatalytic oxidation of organic compounds by an ^{18}O-labeling method,[18c,20] we report our experimental evidence on the origin of the hydroxyl O atom and reaction pathway in the photocatalytic hydroxylation of aromatics. We first show that, in a $^{16}O_2/H_2{}^{18}O$ system, the ^{16}O (from $^{16}O_2$) percentage in the hydroxylated product depends markedly on reaction conditions and changes with irradiation time. Further detailed examination on the oxygen source of the hydroxylation shows that a pathway involving the reduction of O_2 by

e_{cb}^- and the subsequent formation of free $^{\bullet}OH$ via H_2O_2, which was usually overlooked in the past photocatalytic studies, is the main O_2-incorporation mechanism. Such a mechanism can interpret perfectly all our experimental observations. In our study, no experimental evidence supports that the radical O_2 coupling mechanisms (paths d–f in Scheme 1) can play a significant role in the incorporation of O_2. These results help to deepen our understanding on the photocatalytic hydroxylation of aromatic compounds.

Results and Discussion

Oxygen source of the hydroxylated products formed in the photocatalytic oxidation of aromatic compounds: The photocatalytic reaction of benzoic acid (BA) was first carried out in ^{18}O-enriched water ($H_2{}^{18}O$) using $^{16}O_2$ in the air as oxidant. The measured isotope abundance[21] was corrected to determine the proportion of the origination of the hydroxyl O atom. In blank experiments, a TiO_2–$H_2{}^{18}O$ suspension containing BA or hydroxylbenzoic acid (BA-OH) was stirred for 10 h, with and without UV irradiation, and no change in the isotope abundance in the remaining BA or BA-OH was detected. These experiments indicate that the exchange of the O atoms in the carboxyl groups of BA and BA-OH and the hydroxyl group of BA-OH with $H_2{}^{18}O$ is rather slow and can be ignored under the present experimental conditions. The percentages of ^{16}O in the hydroxyl group of BA-OH are shown in Figure 1.[22] At an initial substrate concentration of 3 mM, the proportion of ^{16}O hydroxylbenzoic acid (BA-^{16}OH) was 33.0% after 1 h of irradiation, which means that about one-third of the O atoms in the hydroxyl group originates from oxidant O_2, while the other two-thirds comes from solvent H_2O (^{18}O). More interestingly, we found that the isotope abundance of the hydroxyl O atom of the product was markedly dependent on the reaction conditions, such as the irradiation time and substrate concentration. The proportion of BA-^{16}OH increased with the irradiation time. For example, the ^{16}O abundance increased from 33.0 to 40.1%, when the irradiation time increased from 1 to 2 h at a BA initial concentration of 3 mM. A similar trend was observed when higher substrate concentrations were used (Figure 1). It was also observed that the proportion of BA-^{16}OH decreased as the initial concentration of the substrate increased. For example, when a saturated solution of BA (ca. 25 mM) was applied, only 13.4% (vs. 33.0% at 3 mM BA) of the hydroxyl O atom was derived from aerial O_2 after 1 h of irradiation. Such a dependence of the proportion of O_2-derived hydroxyl O atoms on the reaction time and initial substrate concentration were also confirmed by using $H_2{}^{16}O$ as solvent and $^{18}O_2$ as oxidant (Figure S2 in the Supporting Information). The O_2 incorporation and the enhancement of its proportion with the irradiation time were also observed in the photocatalytic hydroxylation of nitrobenzene and benzonitrile (Table S1 in the Supporting Information).

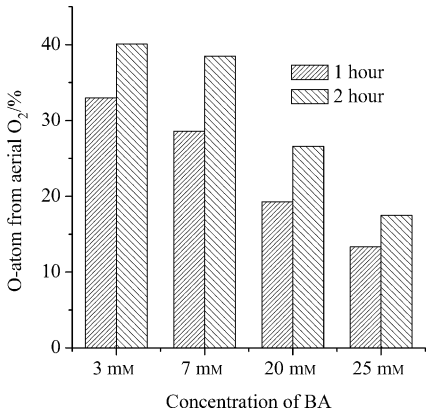


Figure 1. Percentages of O_2-derived hydroxyl O atom in BA-OH, using aerial $^{16}O_2$ as oxidant and $H_2{}^{18}O$ as solvent. TiO_2 (P25; 2 g L^{-1}), $H_2{}^{18}O$ (1 mL), irradiation time: 1 and 2 h.

Another interesting observation was that the oxygen isotope abundance of the hydroxylated product was also affected by the adsorption ability of the substrate. As shown in Table 1, when BA and benzene, which have different adsorption abilities on TiO_2,[23] coexisted in the same dispersion, the ^{16}O abundance (from $^{16}O_2$) in the formed BA-OH was much lower than that in phenol (the hydroxylated product of benzene). For example, in the dispersion with 20 mM BA and 23 mM (saturated) benzene, BA-^{16}OH accounted for only 22.3% of the hydroxylated product of BA, whereas up to 67.9% of the O atoms in phenol was from O_2 (Table 1, entry 1). Further, the addition of benzene slightly lowered the proportion of ^{16}O in BA-OH (for example, from 38.5 to 32.9% at initial BA concentration of 7 mM), while the presence of BA notably increased the ^{16}O abundance in phenol from 47.1% (Table 1, entry 3) to 60–70%.

Table 1. Percentages of ^{16}O in the hydroxyl groups of BA-OH and phenol.[a]

Entry	$c_{BA}{}^0$	BA	BA + benzene	
	[mM]	BA-OH [%]	BA-OH [%]	phenol [%]
1	20	26.6	22.3	67.9
2	7	38.5	32.9	62.9
3	0	—	—	47.1

[a] The $H_2{}^{18}O$ solution of BA (1 mL) containing TiO_2 (2 g L^{-1}), with or without the addition of benzene (50 μL), under aerated ($^{16}O_2$) conditions, irradiation time: 2 h.

The time-dependence of the ^{16}O abundance gives us a hint that the O_2 incorporation might be determined by some intermediate formed during the photoreaction, while the difference in isotope distribution of the hydroxylated product between BA and benzene suggests that the adsorption of the substrate might have an influence on the O_2 incorporation. In the following study, by detailed isotope-labeled experiments, we will identify the intermediate that controls the O_2-incorporation process, and reveal the oxygen sources of the hydroxylated product and the corresponding hydroxylation pathways.

Contribution of h_{vb}^+ and e_{cb}^-: Since the photocatalytic reaction is initiated by photogenerated h_{vb}^+ and e_{cb}^-, we first examined their effects on the isotope distribution of the hydroxylated product. To this end, we designed some special experiments, in which h_{vb}^+ or e_{cb}^- was selectively removed, and then the oxygen isotope abundance in BA-OH was analyzed. The results are summarized in Table 2. The role of h_{vb}^+ was first examined by adding formic acid (FA) to remove it selectively.[24] In the presence of only 2 mM of FA, which was 10% of the BA concentration, the abundance of ^{16}O (from $^{16}O_2$) in the hydroxylated product increased remarkably (Table 2, entry 2, for example, from 18.2 to 38.3% for 1 h of irradiation), which means that the incorporation of the O atom from solvent H_2O was greatly suppressed. Further increase of the FA concentration could make nearly all the O atoms in the hydroxyl group of the product come from O_2 (Table 2, entries 3 and 4). When $^{18}O_2$ was used, and the solvent water was in its natural isotope abundance ($H_2{}^{16}O$), almost all the hydroxyl O atoms in BA-OH were ^{18}O if 700 mM of FA was added (Table 2, entry 5). The suppression of the oxygen incorporation from H_2O by FA indicates that h_{vb}^+ is indispensable for the H_2O incorporation, that is, H_2O cannot participate directly in the hydroxylation of aromatic compounds initiated by e_{cb}^-. In addition, most of the earlier studies seemed to indicate that the hydroxylation of aromatic compounds is directly related to h_{vb}^+ or $^{\bullet}OH$ generated from it.[8,13a,14] In our study, however, h_{vb}^+ was expected to be completely scavenged, when the concentration of FA was high enough (for example, 700 mM as shown in Table 2, entries 4 and 5). The formation of BA-OH under these conditions suggests the presence of another hydroxylation pathway, which incorporates the O atom of oxidant O_2 into the hydroxylated product (see below), but does not involve h_{vb}^+.

Table 2. Abundance of ^{16}O in the hydroxyl group of BA-OH formed in the photocatalytic oxidation with the addition of the scavenger of h_{vb}^+ or e_{cb}^-.[a,b]

Entry	Scavenger (c [mM])	Abundance of ^{16}O [%] 1 h	2 h
1[c]	none	18.2	26.6
2[c]	FA (2)	38.3	33.2
3[c]	FA (40)	97.7	97.5
4[c]	FA (700)	97.8	97.7
5[d]	FA (700)	1.9	0.6
6[c]	BQ (1)	10.0	19.2
7[c]	BQ (10)	0.1	0.3
8[c]	BQ (40)	ca. 0	ca. 0
9[d]	BQ (40)	95.8	94.8

[a] TiO_2 (P25; 2 g L^{-1}), $c_{BA}{}^0 = 20$ mM, irradiation time: 1 and 2 h. [b] The additives inhibit the degradation of BA. For example, the addition of 700 mM FA reduced the consumption rate of BA from 1.86 μM min^{-1} to 0.23 μM min^{-1}. [c] In $H_2{}^{18}O$ (1 mL), under aerated ($^{16}O_2$) conditions. [d] In $H_2{}^{16}O$ (5 mL), 1 atm $^{18}O_2$.

In contrast, after benzoquinone (BQ) was employed to scavenge e_{cb}^- and/or oxidize $O_2^{\bullet-}$ back to O_2[25] to hinder the activation of O_2 by e_{cb}^-, the percentage of O_2-derived hydroxyl O atoms in BA-OH was lowered significantly, for example, from 18.2 to 10.0%, in the presence of 1 mM BQ ($c_{BQ}{}^0 : c_{BA}{}^0 = 1:20$) after 1 h of irradiation (Table 2, entry 6). Nearly all the hydroxyl O atom was found to originate from solvent H_2O and the oxygen incorporation from O_2 into the hydroxyl group was completely inhibited when a large amount of BQ was added (Table 2, entries 7 and 8). By using $^{18}O_2$ as the oxidant and $H_2{}^{16}O$ as solvent, BA-^{16}OH was nearly the exclusive hydroxylated product in the presence of 40 mM BQ (Table 2, entry 9). After e_{cb}^- is removed and the activation of O_2 by e_{cb}^- is inhibited, the hydroxylation process should be initiated only by h_{vb}^+. The complete inhibition of the O_2 incorporation under such conditions suggests that, in the hydroxylation pathway initiated by h_{vb}^+, molecular O_2 without activation by e_{cb}^- cannot enter the product. Therefore, the mechanisms involving the direct reactions between substrate-based radicals and O_2 (paths d and e in Scheme 1)[8,19] are not likely to be the main pathways for the O_2 incorporation during the hydroxylation of aromatic compounds.

It is also noted that FA is much less competitive for $^{\bullet}OH$ than BA, since the rate constant of the reaction between FA and $^{\bullet}OH$ ($k_{FA} = 1.3 \times 10^8$ M^{-1} s^{-1})[26] is much less than that of BA ($k_{BA} = 4.3 \times 10^9$ M^{-1} s^{-1}).[27] For example, in the presence of 2 mM of FA and 20 mM of BA (Table 2, entry 2), only 0.3% of the $^{\bullet}OH$ is estimated to be captured by FA. Therefore, the hydroxylation reaction of BA could still occur through the reaction between BA and $^{\bullet}OH$, if generated, even in the presence of a high concentration of FA. On the other hand, in the BQ system, the reaction between BQ and $^{\bullet}OH$ has a rate constant of 1.2×10^9 M^{-1} s^{-1}.[26] Even at the highest addition concentration (40 mM), BQ can only capture about 36% of the free $^{\bullet}OH$ in the competition with BA (20 mM). Because of the strong adsorption of BA on the surface of TiO_2, the competitiveness of BQ for h_{vb}^+ and surface $^{\bullet}OH$ should be much less than that of BA. Therefore, h_{vb}^+ and $^{\bullet}OH$ can still initiate the hydroxylation of BA in the presence of BQ.

In another experiment, $^{\bullet}OH$ was produced by the photolysis of H_2O_2 [Eq. (6)][6a,25a] to model the reaction initiated by $^{\bullet}OH$. When the photochemical reaction was carried out in $H_2{}^{16}O/H_2{}^{16}O_2$ solution but $^{18}O_2$ atmosphere, no incorporation of the ^{18}O atom of $^{18}O_2$ was observed (Table 3, entry 1). In $H_2{}^{18}O/H_2{}^{16}O_2$ solution and $^{16}O_2$ atmosphere, almost all the O atoms in the hydroxyl group was ^{16}O (Table 3, entry 2). It clearly indicates that the hydroxyl O atom is predominantly derived from H_2O_2, that is, $^{\bullet}OH$ is generated from H_2O_2 in

Table 3. Percentages of the hydroxyl O atom of BA-OH originating from ^{18}O enriched reagent in the H_2O_2/UV and $S_2O_8{}^{2-}$/UV systems.[a]

Entry	System	Abundance of ^{18}O [%] 1 h	2 h
1	$^{18}O_2/H_2{}^{16}O_2/H_2{}^{16}O$	ca. 0	ca. 0
2	$^{16}O_2$(air)/$H_2{}^{16}O_2/H_2{}^{18}O$	3.3	2.9
3	$^{16}O_2$(air)/$S_2{}^{16}O_8{}^{2-}/H_2{}^{18}O$	98.4	98.4

[a] The solution (1 mL) containing 10 mM H_2O_2 or $K_2S_2O_8$ and 20 mM BA, irradiation time: 1 and 2 h.

this system. This experiment also suggests that the hydroxylation process initiated by $^{\bullet}OH$ cannot insert the O atom of molecular O_2 into the product, which further implies that path d in Scheme 1B may play a minor role in the O_2 incorporation. Another implication of this experiment is that the isotope exchange between $^{\bullet}OH$ or the $^{\bullet}OH$ adduct **II** and H_2O is rather slow under the present experimental conditions, and hence the ^{18}O isotope labeling is a reliable technique to study the hydroxylation process.

$$H_2O_2 \rightarrow 2^{\bullet}OH \quad (6)$$

The direct oxidation process of h_{vb}^+ was modeled by the oxidation of BA by the one-electron oxidant $SO_4^{\bullet-}$.[28] It was reported that $SO_4^{\bullet-}$ reacts with aromatic compounds through one-electron transfer [Eq. (7)], rather than adding to it.[29] Also, $SO_4^{\bullet-}$ is stable in acidic and neutral aqueous solutions and cannot oxidize solvent H_2O to $^{\bullet}OH$.[30] In our study, $SO_4^{\bullet-}$ was generated by the photolysis of $S_2O_8^{2-}$ [Eq. (8)].[31] The hydroxylated product formed from the one-electron oxidation of BA by $SO_4^{\bullet-}$ had the hydroxyl O atom dominantly from $H_2{}^{18}O$ and the incorporation of $^{16}O_2$ was in the range of measurement error (Table 3, entry 3). This result is similar to the case in which BQ was used to block the activation of O_2 in the TiO_2 photocatalytic system (Table 2, entries 6–9). Together with the above FA- and BQ addition and H_2O_2/UV experiments, we can exclude safely the earlier proposed possibility that the O atom of O_2 incorporates into the hydroxylated product by the direct addition of molecular O_2 to the formed radical species (paths d and e in Scheme 1),[8,19] because according to these pathways, the O_2 incorporation should always be observed no matter how the reaction is initiated. However, it should be pointed out that we cannot rule out the formation of these radical O_2 adducts, because the further reactions of theses high-energy peroxyl radicals lead to the cleavage of aromatic ring,[32] which is not considered in the present study. ,

$$BA + SO_4^{\bullet-} \rightarrow BA^{\bullet+} + SO_4^{2-} \quad (7)$$

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \quad (8)$$

Roles of reactive oxygen species: After clarifying the importance of O_2 activation by e_{cb}^- and excluding the pathways through organic radical O_2 adducts, we decided to follow the pathway of the activation of O_2 by e_{cb}^- to identify the reactive oxygen species that is responsible for the O_2 incorporation. Superoxide species ($O_2^{\bullet-}$/$^{\bullet}OOH$) are the first reactive oxygen species formed by the one-electron reduction of O_2 by e_{cb}^- [Eqs. (1) and (2)]. The addition of superoxide dismutase (SOD), which catalyzes selectively the disproportionation of $O_2^{\bullet-}$/$^{\bullet}OOH$ to form H_2O_2 and O_2 [Eq. (3)],[33] caused a slight enhancement of the ^{16}O percentage in the hydroxyl group of BA-OH (Table 4, entry 2, for example, from 18.2 to 25.9% after 1 h of irradiation). The facilitation of the $^{16}O_2$ incorporation indicates that $O_2^{\bullet-}$/$^{\bullet}OOH$ is not a necessary species that directly introduces the O atom from O_2 into the hydroxylated product, which excludes path f in Scheme 1C as the main O_2-incorporation pathway.[8] Moreover, although both the addition of SOD and BQ could remove the formed superoxide species, the change in ^{16}O abundance of the hydroxylated product exhibited completely opposite trends, that is, the O_2 incorporation was slightly facilitated by SOD, while it was markedly suppressed in the presence of BQ (Table 1, entries 6–9). In the BQ system, $O_2^{\bullet-}$/$^{\bullet}OOH$ is oxidized back to O_2, while the superoxide species disproportionates catalytically to H_2O_2 and O_2 in the SOD system.[25] The contrastive effects between SOD and BQ on the oxygen isotope abundance suggest that H_2O_2 might play an important role in the O_2 incorporation.

Table 4. Abundances of ^{16}O in the hydroxyl group of BA-OH formed in photocatalysis with different additives.[a]

Entry	Additive	Abundance of ^{16}O [%]	
		1 h	2 h
1	none	18.2	26.6
2[b]	SOD	25.9	32.7
3[c]	POD	4.9	4.9
4[d]	$H_2{}^{16}O_2$	48.8	41.9
5[e]	$^{18}O_2/H_2{}^{16}O_2$	34.8	23.3
6[f]	$Ar/FA/H_2{}^{16}O_2$	98.0	97.7

[a] TiO_2 (P25; 2 g L^{-1}), $H_2{}^{18}O$ (1 mL), $c_{BA}{}^0 = 20$ mM, under aerated ($^{16}O_2$) conditions, irradiation time: 1 and 2 h. [b] SOD (500 U initially and 40 U per 5 min during the reaction) was added. [c] POD (34 μg initially and 3.4 μg per 5 min after the beginning of irradiation) was added. [d] $c_{H_2O_2}{}^0 = 5.2$ mM. [e] $c_{H_2O_2}{}^0 = 5$ mM, 1 atm of $^{18}O_2$. [f] $c_{FA}{}^0 = 0.7$ M, $c_{H_2O_2}{}^0 = 20$ mM, in Ar atmosphere.

H_2O_2 is the two-electron reduction product of O_2. Its role was further examined by the addition of horseradish peroxidase (POD) to decompose H_2O_2 selectively to H_2O and O_2 [Eq. (9)].[34] It was found that POD quenched H_2O_2 completely (curve c in Figure S4 in the Supporting Information), and hindered remarkably the incorporation of the O atom of O_2 into BA-OH (Table 4, entry 3). For example, the ^{16}O percentage decreased from 18.2 to 4.9% after the addition of POD for the 1 h irradiated system. On the other hand, adding $H_2{}^{16}O_2$ to the $TiO_2/H_2{}^{18}O$ system increased significantly the ^{16}O abundance in the hydroxyl group of the product (Table 4, entry 4). For instance, after 1 h of irradiation, the addition of $H_2{}^{16}O_2$ increased the ^{16}O percentage of the product from 18.2 to 48.8%. Similarly, in the SOD system, which also generated the product with higher ^{16}O abundance, the accumulation of H_2O_2 was observed to be enhanced to some extent (curve b in Figure S4 in the Supporting Information, probably because the rapid conversion of $O_2^{\bullet-}$/$^{\bullet}OOH$ into H_2O_2 and O_2 suppresses the charge recombination[35]). The correlation between the $^{16}O_2$ incorporation and the concentration of H_2O_2 in all above systems suggests again that H_2O_2, which is generated primarily from the reduction of O_2 by e_{cb}^- [Eqs. (1)–(4)],[36] plays a key role in the incorporation of O_2 into the hydroxylated product. To verify this, $H_2{}^{16}O_2$ was added into the $TiO_2/H_2{}^{18}O/^{18}O_2$ system. It was found that a significant proportion of the O atom in the hydroxyl group of the product was ^{16}O from $H_2{}^{16}O_2$ (for example, 34.8% after 1 h of irradiation, Table 4,

entry 5). It definitely proves that the O atom in H_2O_2 could be incorporated into the hydroxylated product in the photocatalytic systems.

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2 \qquad (9)$$

It is well-known that both the further reduction and photolysis of H_2O_2 could lead to the formation of $^{\bullet}OH$ [Eqs. (5) and (6)]. Spin-trapping electron spin resonance (ESR) was used to detect the formation of $^{\bullet}OH$ in the photocatalytic systems (Figure 2). The addition of SOD enhanced the intensity of the signal of trapped $^{\bullet}OH$ slightly, while POD dramatically suppressed its signal, which is in good agreement with their effects on the isotope distribution of the hydroxylated product (Table 4, entries 2 and 3) and the concentration of formed H_2O_2 (Figure S4 in the Supporting Information). These results suggest that the $^{\bullet}OH$ generated from H_2O_2 may be an important intermediate in the oxygen incorporation from O_2 into the hydroxylated product. In the present photocatalytic system, because the UV absorption of TiO_2 is much stronger than that of H_2O_2, the photolysis of H_2O_2 should be much slower than the e_{cb}^- reduction process.[36,37] Therefore, the formation of $^{\bullet}OH$ from H_2O_2 should be mainly ascribed to the surface reduction of H_2O_2 by e_{cb}^-, but the direct photolysis of H_2O_2 cannot play a significant role in the $^{\bullet}OH$ formation under the photocatalytic conditions.

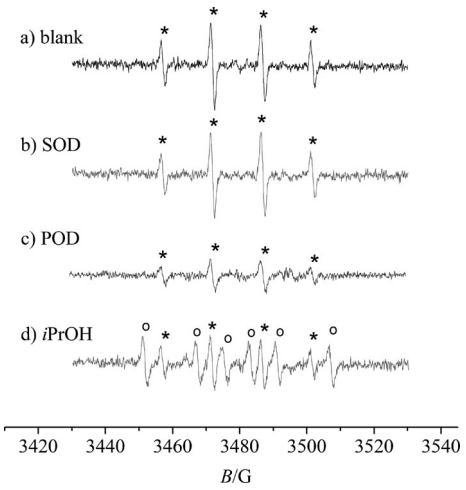


Figure 2. The ESR signals of the BA/TiO_2/UV systems with different additives. TiO_2 (2 g L^{-1}), BA (20 mM) and DMPO (50 mM), H_2O (1 mL), with the addition of a) none, b) SOD (500 U), c) POD (40 μg) and d) *i*PrOH (0.6 mmol), respectively, under aerated conditions, irradiation time: 5 min. (Fourfold peaks with intensity of 1:2:2:1 labeled by "*" are attributed to DMPO-OH, sixfold peaks labeled by "o" are due to DMPO-C(OH)Me_2.)

To further study the role of H_2O_2 and the $^{\bullet}OH$ from H_2O_2, we used $H_2{}^{16}O_2$ to replace $^{16}O_2$ as oxidant to capture e_{cb}^- (in Ar atmosphere) in the $TiO_2/H_2{}^{18}O$/UV systems. The results are shown in Figure S3 in the Supporting Information. It is evident that the O atom of H_2O_2 incorporated into the hydroxylated product, and the ^{16}O proportion of the product formed (60–90 %) was higher than that using aerial $^{16}O_2$ as oxidant (10–40 %, Figure 1). Further, the addition of FA lead to nearly all the hydroxyl O atoms in the product (ca. 98 %) arising from H_2O_2 (Table 4, entry 6). These results suggest that the oxygen incorporation from H_2O_2 into the hydroxylated product is initiated by e_{cb}^-, while the H_2O incorporation is triggered by h_{vb}^+, which is similar to the case of O_2 as oxidant. However, because three electrons are needed for the reduction of O_2 (via H_2O_2) to $^{\bullet}OH$, while the reduction from H_2O_2 to $^{\bullet}OH$ needs only one electron [Eqs. (1)–(5)], more $^{\bullet}{}^{16}OH$ should be generated from the direct capture of e_{cb}^- by $H_2{}^{16}O_2$ than by $^{16}O_2$. Therefore, the system using H_2O_2 as oxidant formed the hydroxylated product with much higher ^{16}O abundance.

Next, we will show that our experimental observations of the O_2-incorporation dependence on the reaction conditions can be well interpreted by the mechanism in which the oxygen incorporation from O_2 into the hydroxylated product is attributed to the reduction of O_2 by e_{cb}^- and the subsequent formation of $^{\bullet}OH$ (via H_2O_2). Unlike other reactive oxygen species such as $^{\bullet}OOH$ and $^{\bullet}OH$, H_2O_2 is so stable that its accumulation in the solution can be quantitatively measured by the steady-state technique. As shown in Figure 3, at all the tested substrate concentrations, the concentration of H_2O_2 increased with the reaction time, which is consistent with the increase of the ^{16}O abundance of the hydroxylated product with irradiation time (Figure 1; see also Figure S2 and Tables S1 and S2 in the Supporting Information). By the addition of $H_2{}^{16}O_2$ to the $H_2{}^{18}O$ system at the beginning of the reaction, however, the ^{16}O abundance of the product was observed to decrease with prolonged irradiation time (Table 4, entry 4), and the concentration of H_2O_2 declined from 5.2 mM to 2.4 mM during 2 h of irradiation. All these facts indicate that the accumulation of H_2O_2 during the reaction is responsible for the increase of the ^{16}O abundance with the irradiation time.

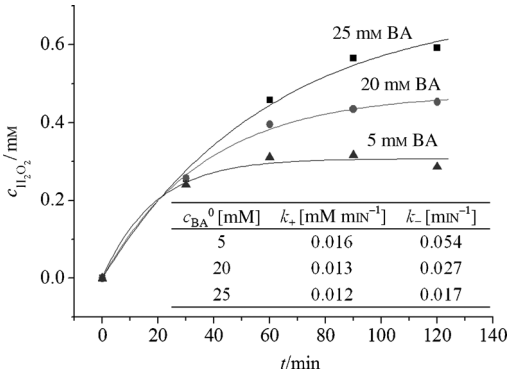
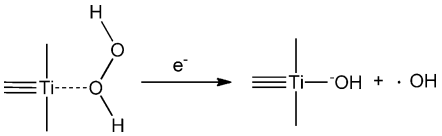


Figure 3. The change of H_2O_2 concentration along with the irradiation time at different initial substrate concentrations. TiO_2 (P25; 2 g L^{-1}), H_2O (1 mL), under aerated conditions. The inset tabulates the corresponding apparent formation and consumption rate constants.

In addition, the formed H_2O_2 accumulation was observed to be dependent on the concentration of the substrate. At the beginning stage of the photocatalytic reaction (0–30 min), the concentration of H_2O_2 was not seriously affected by the substrate concentration. However, after 30 min of irradiation, the concentration of H_2O_2 increased with the initial BA concentration at the same irradiation time. The concentrations of H_2O_2 were 0.29, 0.45, and 0.59 mM for the systems with initial BA concentration of 5, 20, and 25 mM, respectively, at irradiation of 120 min. The accumulation of H_2O_2 is determined by its formation and consumption during the photocatalytic reaction. The formation and consumption of H_2O_2 are fitted by zero-order and first-order reactions, respectively.[36,38] The apparent formation rate constants of H_2O_2 were 0.016, 0.013, and 0.012 mM min^{-1} for these systems with increasing BA concentration (inset in Figure 3), indicating that the formation rate of H_2O_2 does not change significantly among these systems. By contrast, the consumption rate constants were found to be greatly dependent on the concentration of the substrate (0.054, 0.027, and 0.017 min^{-1}, respectively), that is, the higher concentration of BA leaded to the slower consumption of H_2O_2. As stated above, in the photocatalytic system, H_2O_2 decomposes mainly by means of the e_{cb}^- reduction process on the surface of TiO_2 [Eq. (5)]. Therefore, the inhibitory effect of substrate on the consumption of H_2O_2 could be rationalized by the competitive adsorption on TiO_2 between H_2O_2 and BA.[5c,39]

To validate that, the effect of BA on the adsorption of H_2O_2 on TiO_2 was examined (Figure S6 in the Supporting Information). The inhibitory effect of BA on the adsorption of H_2O_2 was significant. For instance, with a total concentration of 0.15 mM H_2O_2, the adsorbed amount of H_2O_2 decreased from 5 μmol g^{-1} in the presence of 5 mM BA to 3 μmol g^{-1} for 25 mM BA solution (saturated). As a result, the presence of BA markedly hindered the degradation of H_2O_2 (Figure S7 in the Supporting Information). These experiments also corroborate that the direct photolysis of H_2O_2, compared with its surface reduction, is not important in the photocatalytic systems. Since the reductive degradation of H_2O_2 by e_{cb}^- is the major pathway by which the O atom from O_2 incorporates into the hydroxylated product, the inhibition of the adsorption and degradation of H_2O_2 at high BA concentration will hinder the O_2 incorporation. On the other hand, at high substrate concentration, the adsorbed amount of BA will increase. The surface oxidation process initiated by h_{vb}^+, which incorporates the O atom of H_2O into the hydroxylated product, will play a more important role. All these facts favor the oxygen incorporation from water ($H_2{}^{18}O$), and block the pathway from $^{16}O_2$, so the hydroxylated product with lower ^{16}O proportion is formed.

Finally, we will explain the difference in oxygen source between the hydroxylated products of BA and benzene according to our H_2O_2 reduction mechanism. It was reported that H_2O_2 binds in a monodentate fashhion to the surface Ti atom through its O atom.[39a,b] As shown in Scheme 2, the



Scheme 2. Surface reduction of H_2O_2.

one-electron reduction of H_2O_2 by e_{cb}^- leads to the breaking of O–O bond and formation of OH^- and $^{\bullet}OH$.[40] Because of the stronger coordination ability of OH^- with surface Ti sites, surface adsorbed OH^- and free $^{\bullet}OH$, which may diffuse to some extent away from the surface, should be formed. This argument was corroborated by earlier studies.[41] For example, Choi found that the $^{\bullet}OH$ generated from the reduction of H_2O_2 on the TiO_2 surface can be released into the gas phase and initiate remote photocatalytic oxidation.[41a] Salvador concluded that the free $^{\bullet}OH$ may only be generated by the electroreduction of dissolved O_2 via H_2O_2.[41b] On the other hand, the hydroxylation could also be initiated by h_{vb}^+, or the $^{\bullet}OH$ from it, and generates the product with H_2O-derived hydroxyl O atoms, as shown in Scheme 1. In the first process, h_{vb}^+ can only oxidize the substrate adsorbed on the surface of TiO_2. In the second process, the $^{\bullet}OH$ formed by h_{vb}^+ oxidation of H_2O/OH^- should be adsorbed on the TiO_2 surface, and its desorption proved to be difficult.[42] Thus, in both processes, the h_{vb}^+-initiated hydroxylation takes place only on the surface of TiO_2. Accordingly, the reaction on the surface tends to incorporate the O atom from H_2O into the product, while the hydroxylation of the unadsorbed substrate leads to the formation of the product containing O_2-derived O atoms. Because the adsorption of BA is much stronger than that of benzene,[23] the surface process would take a higher proportion in the hydroxylation of BA than in that of benzene, while the reaction of unadsorbed substrate is more important for benzene. Therefore, BA-OH has lower ^{16}O (from aerial $^{16}O_2$) abundance than phenol. Furthermore, in the presence of benzene, the competition of benzene for free $^{\bullet}{}^{16}OH$ with BA could lower slightly the proportion of ^{16}O in BA-OH (Table 1, entries 1 and 2), since BA and benzene have similar reaction rate constants with $^{\bullet}OH$ ($k_{BA}=(4.3\pm0.8)\times10^9$ M^{-1}s^{-1} and $k_{benzene}=(4.3\pm0.9)\times10^9$ M^{-1}s^{-1}).[27,43] Similarly, the presence of BA could enhance strongly the abundance of ^{16}O in phenol, because of the competition of BA with benzene for the surface $h_{vb}^+/^{\bullet}{}^{18}OH$.

Further, if the hydroxylation processes of BA and benzene occurred only on the surface of TiO_2, the adsorption ability of substrates, which affects their distribution among surface and bulk solution, could not have an effect on the contribution fractions of diverse pathways in the whole hydroxylation process. The only possible explanation to the oxygen isotope abundance difference between BA-OH and phenol would be the different relative importance of the direct h_{vb}^+ oxidation pathway (only from $H_2{}^{18}O$, path a in Scheme 1) and the $^{\bullet}OH$ addition pathway (from both $H_2{}^{18}O$ and $^{16}O_2$, path b in Scheme 1). Because BA and benzene have nearly identical rate constants for their reactions with

$^{\bullet}OH$ (see above), and benzene is more easily oxidized than BA (one-electron oxidation potential: $E_{BA}{}^{0}=2.6$ V and $E_{benzene}{}^{0}=2.1$ V vs. NHE),[44] the direct oxidation pathway should be more important for benzene than for BA. It means that the ^{18}O abundance of phenol (from $H_2{}^{18}O$) would be higher than that of BA-OH, which is completely contradictory to our experimental observations shown in Table 1. On the other hand, if the hydroxylation processes of BA and benzene only took place away from the surface of TiO_2 (in the bulk solution), no difference in isotope abundance between BA-OH and phenol would be measured (i.e., $^{16}O\%_{BA-OH}=^{16}O\%_{phenol}=^{16}O\%_{\cdot OH}$). It is not consistent with our experimental results either. Therefore, to explain the observed isotope abundance difference between BA-OH and phenol, both the surface reaction and bulk solution reaction should be considered at the same time.

Other supports for the different oxygen sources of the photocatalytic hydroxylation between the surface reaction and bulk solution reaction came from the free $^{\bullet}OH$ quenching experiments (Table S2 in the Supporting Information). Both *tert*-butyl alcohol (*t*BuOH) and isopropanol (*i*PrOH) were reported to capture preferably free $^{\bullet}OH$,[5a,45] because their low adsorption on TiO_2 makes them unfavorable to compete with BA for $h_{vb}{}^{+}$ or surface-bound $^{\bullet}OH$ (details of the estimation and discussion about the proportions of the $^{\bullet}OH$ captured by *t*BuOH or *i*PrOH on the TiO_2 surface and in the bulk solution are shown in Tables S3 and S4 in the Supporting Information). In the spin-trapping ESR experiment, the addition of *i*PrOH markedly weakened the trapped $^{\bullet}OH$ signal with the appearance of the signal of DMPO-C(OH)Me_2 (Figure 2; DMPO = 5,5-dimethyl-1-pyrroline-*N*-oxide, a spin-trapping reagent used in the ESR measurements), indicating the quenching effect of *i*PrOH on $^{\bullet}OH$. Accordingly, the isotope labeled experiments showed that the presence of *t*BuOH and *i*PrOH decreased the proportion of ^{16}O in the hydroxyl group of BA-OH from 18.2% to 13.9% and 11.8%, respectively, for the 1 h irradiated systems (Table S2, entries 2 and 3), indicating again the important role of free $^{\bullet}OH$, which mainly initiates the hydroxylation of unadsorbed substrates, in the oxygen incorporation from O_2.

Conclusion

We studied the photocatalytic hydroxylation of aromatics by ^{18}O-labeling method. The experiments show that ^{18}O-isotope labeling is a powerful method to identify the oxygen incorporation pathway in the photocatalytic hydroxylation. Our experimental results do not support the mechanism that the addition of molecular O_2 onto the cationic radical or a radical HO adduct of the substrate could incorporate the O atom of O_2 into the hydroxylated product. In contrast, we show that the reduction of O_2 by $e_{cb}{}^{-}$ is indispensable for the O_2 incorporation. The formed intermediate H_2O_2 plays an essential role in the O_2 incorporation process. The $^{\bullet}OH$ generated from the reduction of H_2O_2 is the final active species that introduces the O_2-derived O atoms into the hydroxylated product. The findings in the present study also reveal that, during the photocatalytic oxidation, $h_{vb}{}^{+}$ is not the only active species that initiates the oxidation. Even in the absence of $h_{vb}{}^{+}$, the substrate can still be oxidized by the $^{\bullet}OH$ formed from the reduction of O_2 by $e_{cb}{}^{-}$. The contribution of this pathway cannot be neglected for the photocatalytic oxidation, and its proportion is comparable to that of $h_{vb}{}^{+}$, at least for the hydroxylation of aromatic compounds. Our experiments also show that the photocatalytic oxidation products of the adsorbed substrates bear less oxygen from oxidant O_2 than those of the unadsorbed ones.

Experimental Section

Materials: TiO_2 (P25, ca. 80% anatase, 20% rutile; surface area, ca. 50 $m^2 g^{-1}$) was kindly supplied by the Degussa Company (Clausthal-Zellerfeld, Germany). $H_2{}^{18}O$ was purchased from Jiangsu Changshu Chemical Limited (Changshu, Jiangsu, P.R. China), the isotope abundance of which was 98%. $^{18}O_2$ (^{18}O: 97%) was purchased from Cambridge Isotope Laboratories, Inc (Andover, USA). The mass spectrometry analysis of the post-reaction solvent/atmosphere showed that the oxygen isotope abundance of the ^{18}O-enriched reagent did not change significantly (< 2%) in all the reactions. Benzoic acid (BA), benzene, nitrobenzene, benzonitrile, and their hydroxylated products were all of analytical grade, and obtained from the Beijing Chemical Company (Beijing, P.R. China). 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO), a spin trapping reagent for ESR measurements, was supplied by Sigma–Aldrich Co. (Shanghai, P.R. China). Horseradish peroxidase (POD), which was used in the measurement of H_2O_2, was purchased from the Huamei Biologic Engineering Co. (Luoyang, Henan, China), while *N*,*N*-dialkyl-*p*-phenylenediamine (DPD) was from Merk (p.a.) (Whitehouse Station, NJ, USA). Chlorotrimethylsilane (TMSCl) and 1,1,1,3,3,3,-hexamethyldisilazane (HMDS) were purchased from Acros Organics (Beijing, P.R. China). All reagents were used as received without further purification.

Photocatalytic reactions: A 100 W Hg Lamp (ToshibaIn SHL-100UVQ) was used as the light source for the photocatalytic reaction. In a typical $H_2{}^{18}O$-isotope-labeled reaction, TiO_2 (P25, 2 mg) was dispersed in $H_2{}^{18}O$ (1 mL) with a given concentration of BA under aerated conditions ($^{16}O_2$). Prior to irradiation, the suspension was magnetically stirred in the dark for about 30 min to ensure the establishment of an adsorption/desorption equilibrium. After irradiation for a definite time, the oxygen isotope abundance of the hydroxylated product was analyzed by HPLC-ESI method (Agilent LC 1200/Ion Trap 6310) with C-18 column (250 mm × 2.1 mm). Each measurement was repeated at least three times to assure the accuracy. The standard deviation of MS analysis is estimated to be ca. 0.6%. To minimize the disturbance caused by the change of substrate concentration and the formation of intermediates, only the initial stage (0–2 h, <7% of substrate conversion) of photocatalytic oxidation was studied. Figure S1 in the Supporting Information gives the typical HPLC chromatograms (acquired by UV and MS detectors) and ESI-MS spectra. The measured isotope abundance of the product was corrected with the oxygen isotope abundance of solvent H_2O and the natural isotope abundance of the product [Eqs. (10) and (11)] in which C_p, C_n, and C_w are the ^{18}O percentages of the measured isotope abundance of the product, natural isotope abundance of the product, and measured isotope abundance of solvent H_2O, respectively.

$$H_2O\% = \frac{C_p - C_n}{C_w - C_n} \times 100 \quad (10)$$

$$O_2\% = \frac{C_w - C_p}{C_w - C_n} \times 100 \quad (11)$$

In the experiments using $^{18}O_2$ as oxidant, the photocatalytic oxidation of

BA was performed in Pyrex vessels (10 mL) with $H_2{}^{16}O$ suspension (5 mL) containing BA (20 mM) and TiO_2 (P25; 2 g L^{-1}). Before the $^{18}O_2$ reaction, the suspension in the vessel underwent twenty cycles of pumping to vacuum and then purging with argon to remove the air, followed by saturation with 1 atm of $^{18}O_2$. After reaction, the oxygen isotope abundance of the hydroxylated product was measured with the same method as that of $H_2{}^{18}O$ labeled experiments, and the correction was also applied [Eqs. (12) and (13)] in which C_O is the ^{18}O abundance of ^{18}O-enriched O_2.

$$H_2O\% = \frac{C_O - C_p}{C_O - C_n} \times 100 \quad (12)$$

$$O_2\% = \frac{C_p - C_n}{C_O - C_n} \times 100 \quad (13)$$

In the measurement of the isotope abundance of the hydroxyl O atoms of the hydroxylated products formed in the photocatalytic oxidation of benzene, nitrobenzene, and benzonitrile, the reacted suspension was extracted with ethyl ether (5 mL). The organic phase was dried with anhydrous Na_2SO_4, and evaporated to about 0.1 mL by Ar purging. The concentrated sample was treated with HMDS (100 μL) and TMSCl (50 μL), and then centrifuged. The TMS derivations of phenols were analyzed by GC-MS (Thermo-Finingan; Trace 2000/Trace DSQ) with a DB-5MS column (30 m × 0.25 mm).[7a] The MS peaks corresponding to $[M-CH_3]^+$ were used to calculate the oxygen isotope abundance.

The concentration of H_2O_2 formed during the reaction was measured by the spectrophotometric DPD method.[46] Electron spin resonance (ESR) signals of the radicals trapped by DMPO were detected at ambient temperature with a Brucker ESP 300 E spectrometer, under the reaction conditions that were the same as those in the isotope labeled reactions except the addition of DMPO. A given amount of suspension (30 μL) was collected at a given time and filled into a quartz capillary for ESR measurement. The settings for the ESR spectrometer were as follows: center field, 3443 G; sweep width, 100 G; microwave frequency, 9.64 GHz; modulation frequency, 100 kHz; power, 10.05 mW.

Acknowledgements

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[21] The photocatalytic reactions of aromatics involve a series of rather complicated processes, such as cleavage of the aromatic rings, decarboxylation, and hydroxylation. In the present study, we only focus on the hydroxylation process, but other processes are not considered.
[22] It should be pointed out that three (*ortho*-, *meta*-, and *para*-) positions on BA are available for the hydroxyl to add on. Depending on the adding position, the isotope abundance of the hydroxylated products differs slightly from each other. For example, 31.7, 30.8, and 36.8% of ^{16}O-hydroxyl were measured after 1 h of irradiation in the *para*-, *meta*-, and *ortho*-hydroxylbenzoic acids, respectively, when the initial concentration of BA was 3 mM. In this paper, only the general incorporation amount, which reflects the origin of hydroxyl oxygen in the products, is considered. This slight difference cannot affect the discussion. Accordingly, the incorporation is represented by the average isotope ratios among the three isomers.
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