Surface Chemistry

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Oxygen Atom Transfer in the Photocatalytic Oxidation of Alcohols by TiO_2: Oxygen Isotope Studies**

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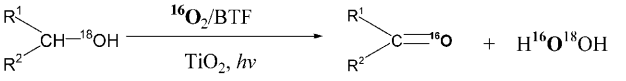
The selective oxidation of alcohols into carbonyl compounds using dioxygen in lieu of toxic or corrosive stoichiometric oxidants such as ClO^-, Cr^{IV}, and Cl_2, is one of the most challenging functional group transformations.[1,2] The oxidation of alcohols using dioxygen as the oxidant has been successfully realized by using noble-metal and transition-metal complexes for catalysis.[2] TiO_2 photocatalysis has also attracted much attention as a potential and promising strategy for this aim, because of its high oxidation ability, environmentally friendly properties, and the benefit of using O_2 as an oxidant and light as the driving force.[3] A few successful cases involving TiO_2 photocatalysis in acetonitrile, water, or solvent-free systems have recently been reported.[4]

Molecular oxygen plays a vital role in the aerobic oxidation of alcohols in all these systems. Therefore, it is significant and necessary to reveal how the dioxygen participates in the reaction process. In the noble-metal catalysis system, the role of dioxygen has been proven to oxidize the reduced noble-metal center (for example, M^0 or M^{n+} hydride species) without an O-atom transfer from dioxygen to the products.[5] In the aerobic oxidation of alcohols in the cytochrome P450 system, a *gem*-diol intermediate is formed, in which one hydroxyl group comes from the alcohol substrate (ca. 100% ^{16}O abundance) and the other from O_2 (98% ^{18}O labeled). Such a *gem*-diol intermediate leads to approximately 50% of the carbonyl product having incoorporated ^{18}O atoms.[6] Unlike these thermal catalytic systems, the essential role of dioxygen in the oxidation of alcohols by TiO_2 photocatalysis has not been completely clarified yet. Herein we disclose an unexpected phenomenon: when the photocatalytically oxidative transformation of isotope-labeled alcohols was performed over pure anatase TiO_2 in organic solvents, such as benzotrifluoride (BTF), the oxygen atom in the substrate alcohol is completely replaced by one of the oxygen atoms of dioxygen, that is, the photocatalytic process involves a selective cleavage of the C–O bond of the alcohol with concomitant formation of a new C=O bond in the product aldehyde in which the O atom comes from dioxygen. This finding adds fundamental insight to the oxidation process of alcohols on the TiO_2 surface, which is of importance for both the TiO_2 photocatalysis and the selective oxidation of alcohols.

^{18}O-enriched benzyl alcohol and cyclohexanol were used for the TiO_2 photocatalytic oxidation (Table 1). The original abundance of ^{18}O in the ^{18}O-enriched benzyl alcohol was 65% (Table 1, entries 1–2) and 90% (Table 1, entries 4–7), respectively. However, the ^{16}O abundance in the product, benzaldehyde, was approximately 100% in all these experiments when analyzed at different conversions. This result indicates that an oxygen atom transfer from the dioxygen to the product during the reaction process. Moreover, little change in the abundance of ^{18}O in the unreacted alcohols was observed, indicating no isotope exchange between the substrate and product, or between the substrate and dioxygen. In entries 2 and 7 of Table 1, the photocatalyst TiO_2 was treated with ^{18}O-enriched water (98% ^{18}O abundance) under UV irradiation for 12 hours to replace the surface H_2O/OH

Table 1: Abundance of ^{18}O in the substrates and products.[a]



Entry	Conversion [%]	Selectivity [%]	Substrate (^{18}O:^{16}O)	Product (% ^{16}O)
1	40	100	$C_6H_5CH_2OH$ (65:35)	C_6H_5CHO (>99)
2[b]	43	99		C_6H_5CHO (>99)
3[c]	10	100		C_6H_5CHO (50)
4	17	99	$C_6H_5CH_2OH$ (90:10)	C_6H_5CHO (>99)
5	42	99		C_6H_5CHO (>99)
6	65	99		C_6H_5CHO (>99)
7[b]	43	99		C_6H_5CHO (>99)
8[d]	52	99		C_6H_5CHO (17)
9	11	99	$C_6H_{11}OH$ (77:23)	$C_6H_{10}O$ (>99)
10	20	99		$C_6H_{10}O$ (>99)
11	47	99		$C_6H_{10}O$ (>99)

[a] The reactions were carried out in BTF solutions (1.5 mL) of alcohols (0.1 mmol) with TiO_2 (0.1 mmol, 5.3 g L^{-1}) under 0.1 MPa O_2, and 100 W Hg lamp irradiation. [b] TiO_2 was treated by stirring in $H_2{}^{18}O$ (98% ^{18}O) under UV irradiation for 12 h. [c] The reaction was carried out on a 1 cm × 2 cm TiO_2 electrode under UV irradiation for 12 h under Ar (>99.99%). The bias potential was 0.6 V vs. SCE. [d] The reaction was conducted under Ar, 0.1 mol% Pt/TiO_2 was used as the photocatalyst.

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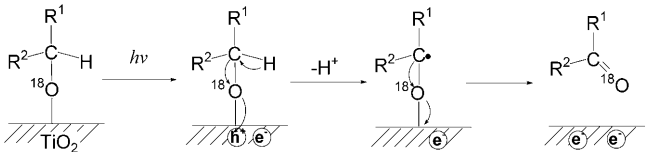
groups with ^{18}O-enriched H_2O/OH groups. When the ^{18}O-enriched TiO_2 surface was used as the photocatalyst, the oxygen atom in the product was still replaced with ^{16}O completely. This observation implies that the O atom transferred into the product did not originate from the surface-bound water or OH groups of TiO_2, also excluding the involvement of the common ·OH radicals as the active oxidizing species in the aqueous TiO_2 photocatalysis.[3a]

In a photo-electrochemical experiment under an anaerobic Ar atmosphere (Table 1, entry 3), the photo-generated electrons on the conduction band were transferred to the counter electrode, and hence the alcohol could also be oxidized into the corresponding aldehyde in the absence of O_2. In this process, a two-electron transfer (TET) process (Scheme 1) occurs,[8a] and the oxygen atom of the alcohol



Scheme 1. The two-electron transfer mechanism in the oxidation of alcohols in the absence of O_2.

should remain in the product. As shown in entry 3 of Table 1, the product was found to retain the original ^{18}O-enriched content after reacting for 12 hours. The little increase (from 35% to 50%) in the abundance of ^{16}O in the product may come from the dioxygen mixed into Ar and dissolved in the solvent (BTF). In another anaerobic experiment using Pt/TiO_2 as the photocatalyst (Table 1, entry 8), the alcohol could also be oxidized by a TET process because the electrons on Pt/TiO_2 could combine with protons to lead to the continuous production of H_2 under the catalysis of Pt clusters.[8b,c] The abundance of ^{18}O in the product was found to be 83%. These results, in comparison with those under aerobic conditions (Table 1, entries 4–6), clearly indicate that an O atom transfer is not involved in the oxidative transformation of the alcohol when the reaction is run in the absence of dioxygen, although the alcohol can still be oxidized into the corresponding aldehyde by a TET process.

A similar oxygen atom transfer phenomenon could also be observed in the photocatalytic oxidation of ^{18}O-enriched cyclohexanol (77% ^{18}O) into cyclohexanone at different conversions (Table 1, entries 9–11). In other solvents, such as CH_3CN, CH_2Cl_2, and C_6H_{14}, the oxygen atom transfer process was also observed (Table 2). These results unambiguously demonstrate a selective cleavage of the α-C–O bond of the alcohol, with the incorporation of an oxygen atom from the dioxygen to form a new C=O bond in the aerobic photooxidation of alcohols by TiO_2 photocatlysis. Such an oxygen atom transfer mechanism has not been proven either in the photocatalytic or noble-metal catalytic transformation of alcohols.

To reveal the oxygen atom transfer mechanism, some possible reaction processes can be ruled out based on our investigations:

Table 2: The oxygen atom transfer in the photocatalytic oxidation of benzyl alcohol in different solvents.[a]

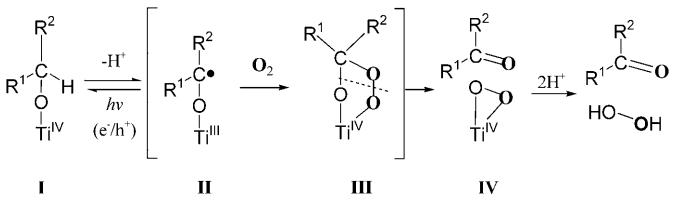
Entry	Solvent	Substrate (^{18}O: ^{16}O)	Conversion [%]	Selectivity [%]	Product (% ^{16}O)
1	BTF		51	99	>99
2	CH_3CN	$C_6H_5CH_2OH$	44	99	>99
3	CH_2Cl_2	(90: 10)	31	99	>99
4	C_6H_{14}		40	99	>99

[a] The reactions were carried out under 0.1 MPa O_2 and 100 W Hg lamp irradiation for 4 h. Benzyl alcohol (0.1 mmol), TiO_2 (0.1 mmol, 5.3 g L^{-1}), solvents (1.5 mL).

1) The TET mechanism for the oxidation of alcohols could be easily ruled out. In the TET process (Table 2, entries 3 and 8), the oxygen atom in dioxygen is not incorporated into the product and no oxygen atom transfer will occur. When dioxygen exists in the reaction system, the O_2 molecule reacts easily with the alcohol radical and therefore limits the TET process. Thus, the contribution of the TET process can be ignored under the aerobic atmosphere.

2) The photocatalytic reaction in organic solvents such as BTF was dramatically different from that in water. The ESR trapping experiments showed that the main active oxidative species in aqueous system is the ·OH radical,[9] which was, however, not detected in the BTF system (see Figure S4 in the Supporting Information). The experiments on kinetic isotope effect (KIE) were carried out for the TiO_2 photocatalytic oxidation of $C_6H_5CH_2OH$/$C_6H_5CD_2OH$ under aerobic conditions. The KIE values were 1.2 and 4.6 in BTF and the aqueous system, respectively. The significant difference in the KIE values indicates different photocatalysis mechanisms in the two systems, that is, the abstraction of the β-hydrogen atom of the alcohol by ·OH radical is the rate-determining step in the aqueous system, but not in the BTF system.[10] Therefore, in the BTF system, a broad range of alcohols including aryl, aliphatic, and enolic alcohols could be oxidized to their corresponding aldehydes or ketones with high selectivity (see Table S2 in the Supporting Information). In comparison, much poorer selectivity in the aqueous system was observed (using benzyl alcohol as a substrate, 38% selectivity and 45% conversion at 8 h; and 45% total organic carbon (TOC) was removed after 12 h of photoreaction).

We therefore propose the possible reaction mechanism as shown in Scheme 2: an alcohol molecule adsorbs onto the surface of TiO_2 to form the structure **I** via a deprotonation process. TiO_2 is excited by UV light to produce h^+/e^- pairs. The adsorbed alcohol first reacts with the photo-generated hole and subsequent deprotonation to form a carbon radical, whereas the photo-generated electron is captured by Ti^{IV} to form Ti^{III} (**II**). Both of the carbon radical and the Ti^{III} are easy to combine with dioxygen.[3] The oxygen bridge structure **III** may form through two possible routes: 1) the electron/Ti^{III} (in the conduction band) first reduces O_2 to the superoxide, which then attacks the carbon radical to form intermediate **III** or 2) the carbon radical first combines with dioxygen to form an organic superoxyl radical which additionally reacts with Ti^{III} to form structure **III**. The concerted cleavage of C–O



Scheme 2. The proposed oxygen transfer process in the TiO_2 photocatalytic oxidation of alcohols in BTF solvent in the presence O_2.

bond of the alcohol and the O–O bond of dioxygen is likely realized through such an oxygen bridged structure **III**. A similar structure was also observed when the dioxygen reacts with iron complexes such as deoxyhemerythrin.[11] The TiO_2-bound peroxide bridge structure **IV**, as one of the two products of the concerted bond-cleavage process (**III**→**IV**), may then combine with the protons to form H_2O_2, which was evidenced by iodometric titration method (see Figure S5 in the Supporting Information). An analogous side-on peroxide of Ti site (**IV**) has been reported in the tilanosilicate photocatalysis in the presence of F^- ions.[4d]

Isotope-labeled resonance Raman spectroscopy was used to detect the peroxide O–O bond formation in the photocatalytic oxidation of benzyl alcohol. Figure 1B shows the

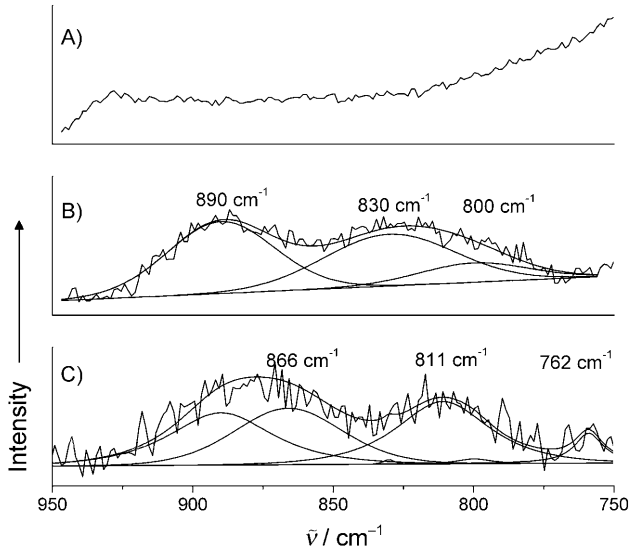


Figure 1. Low-frequency resonance Raman spectra: A) the Raman spectra of TiO_2 photocatalyst used in this work. B) Raman spectra of the TiO_2 photocatalyst with ^{16}O benzyl alcohol after three hours of photoreaction. C) Raman spectra of the TiO_2 photocatalyst with ^{18}O benzyl alcohol after three hours of photoreaction.

Raman spectrum of the TiO_2 catalyst with ^{16}O-benzyl alcohol as the substrate after the photocatalytic reaction for three hours, and Figure 1C gives the Raman spectrum of the TiO_2 catalyst with ^{18}O benzyl alcohol (90% ^{18}O abundance) after three hours of photoreaction. Comparing with the Raman spectrum of TiO_2 (Figure 1A), new peaks at 890 cm^{-1}, 830 cm^{-1}, and 800 cm^{-1} appeared in Figure 1B, respectively. The peak at 800 cm^{-1} could be assigned to the ν(O-Ti) in structure **I**. The isotopic shift (peak at 762 cm^{-1} in Figure 1C) fits the calculated value (762 cm^{-1}), and the peak at 830 cm^{-1} in Figure 1B could be assigned to the ν(C–O) stretch vibration of the adsorbed alcohol, which has an isotopic shift of 19 cm^{-1} (811 cm^{-1} in Figure 1C), very close to the calculated value of 20 cm^{-1}. The 890 cm^{-1} band in Figure 1B is assigned to the $\nu(^{16}O–^{16}O)$ of a side-on coordinate peroxide (**IV**).[12a] Similar bands have been reported for Ti complexes.[12b] In Figure 1C, the 890 cm^{-1} band of the $\nu(^{16}O–^{16}O)$ still remained, but was much weaker. The new band at 866 cm^{-1} is assigned to the $\nu(^{16}O–^{18}O)$ in structure **IV**. The isotopic shift of 24 cm^{-1} for this mode was very close to the shift of 25 cm^{-1} predicted by Hooke's law for a diatomic O–O stretch. The existence of the $^{16}O–^{18}O$ bond confirms the concerted cleavage process **III**→**IV** (Scheme 2) of the C–O bond of the alcohol and the O–O bond of the dioxygen.

In summary, it is reported for the first time that an oxygen atom transfer, from the dioxygen to the α-carbon atom of the alcohol, dominates the reaction process of the photocatalytic oxidation of alcohols by TiO_2 in organic solvents such as BTF. This new discovery helps us to better understand of the TiO_2-based photocatalysis and the selective oxidation of alcohols, and to find broad applications in the synthesis of organic compounds.

Experimental Section

Photocatalysis: The photocatalytic reactions were carried out under irradiation by a 100 W high-pressure Hg lamp (Toshiba SHL-100UVQ) with continuous stirring in a 10 mL Pyrex glass bottle (cut-off light below 300 nm, thus TiO_2 can be excited but not the substrates) under O_2 (0.1 MPa). The radiant flux received by the reactor was 12.1 mW cm^{-2}. A typical reaction system contained 0.1 mmol substrate and 0.1 mmol TiO_2 (5.3 g L^{-1}) in 1.5 mL benzotrifluoride (BTF) solvent. The products were detected by GC-MS methods (Thermo-Finingan; Trace 2000/Trace DSQ) with a DB-5MS column (30 m × 0.25 mm).

The photocatalyst TiO_2 was prepared by a hydrothermal process (see the Supporting Information). Pure anatase particles with average size of 10 nm and surface area of 210 $m^2 g^{-1}$ were obtained.

In this work, we defined the conversion and selectivity for the alcohol oxidation as:

Conversion $= (c_{r_0} - c_r)/c_{r_0}\,100\,\%$

Selectivity $= c_p/(c_{r_0} - c_r)\,100\,\%$

c_{r_0}: the initial concentration of the reactant;

c_r: the concentration of the reactant during the reaction;

c_p: the concentration of the product during the reaction.

Photo-electrochemical studies: The photo-electrochemical experiments were carried out using a potentiostat at an applied bias of 0.6 V vs. SCE, under the protection of Ar. A Pyrex glass bottle (cut-off light < 300 nm) was used as the electrochemical cell. The supporting electrolyte used was 0.05 M $(t\mathrm{Bu})_4N^+ (PF_6)^-$. A TiO_2 film electrode was prepared by coating the precursor TiO_2 gel (prepared by the hydrothermal process) onto a 1 × 2 cm^2 ITO glass slide and subsequent heating at 450 °C for 3 h. In this system, a TiO_2 film electrode was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum plate as the counter electrode. The experiments were carried out under irradiation using a 100 W Hg lamp; 0.2 mmol of the substrate was added into 10 mL BTF, and the reaction time was 12 h.

The Raman spectra were recorded in the backscattering geometry by using a Renishaw-2000 Raman spectrometer with the 514.5 nm line of an Ar ion laser as the excitation source. TiO_2

photocatalyst after photoreaction was separated with centrifuge, and then dried at room temperature. The solid samples were detected on microscope slides (25.4 mm × 76.2 mm, 0.5 mm thick).

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