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Photocatalytic Oxidation of Alcohols on TiO_2

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The reaction mechanisms of the photocatalytic oxidation of several different alcohols on TiO_2 were investigated by three experimental techniques: spin trapping, photocurrent measurement, and product analysis. The results are interpreted according to the band model of a semiconductor and current doubling. It was found that alcohols with α-hydrogens gave low concentrations of spin adducts since their photoproduced radicals have short lifetimes on TiO_2 due to a current-doubling process. Also, it was found that oxygen participated in a radical chain mechanism in the photocatalytic oxidation of ethanol to acetaldehyde.

The application of photoelectrochemistry and photocatalysis to organic synthesis has been recently reviewed.[1-3] In these reviews many kinds of organic reactions on photocatalysts have been introduced. Principally, reactions on photocatalyst are understood to be short-circuited electrolytic reactions. However, there are some reactions which afford different products from those obtained in electrolysis on metal electrodes or in chemical reactions with redox reagents. For example, the photocatalytic oxidation of diphenylethylene on TiO_2 gives diphenylketone, while the electrolysis on Pt attains oxidative dimerization.[4] Many attractive reactions, such as phenol formation from benzene[5] and N-alkylation of amines,[6] have also been reported. In some cases alcohols are involved in these reactions. Therefore, it is necessary to understand how alcohols react on a photocatalyst. In this work we investigated the reaction mechanism of the photocatalytic oxidation of several different alcohols on TiO_2 by correlating the results from three experimental techniques: spin trapping, photocurrent measurement, and product analysis.

In the current study, TiO_2 was used as the semiconductor since it is stable; a wealth of information has been developed concerning photocatalysis on its surface. Different alcohols were chosen for the reactants in order to obtain information on the effect of the molecular structure on the reaction mechanism.

Information on the reaction of organic substances on the irradiated surface of semiconductors was obtained by the spin-trapping technique.[7,8] This technique involves the reaction of a diamagnetic spin-trapping reagent with short-lived radicals to produce relatively stable paramagnetic spin adducts which can be detected and identified by electron spin resonance (ESR). For example, a spin-trapping reagent such as 5,5-dimethyl-4,5-dihydro-3*H*-pyrrole *N*-oxide (DMPO) reacts with various radicals to give spin adducts whose ESR spectra have hyperfine structures. From the hyperfine structure, information concerning the structure of the trapped radical can be deduced. In this way, we can obtain information about the kind of radicals involved in the reactions. Recent investigations concerning photocatalytic oxidations of alcohols on semiconductor powder using the spin-trapping method were reported by this laboratory[9] and Leaustic et al.[10]

Photocurrent doubling is another important technique[11] for investigating photocatalytic reaction mechanisms on semiconductors. This type of reaction on an n-type semiconductor is illustrated as follows. A photon ($h\nu$) whose energy is equal or larger than that of the band gap of semiconductor produces an electron-hole pair. The current-doubling reagent (R_{cd}) donates an electron to the valence band and the resultant radical species($R^{\bullet}_{cd}$) is then converted into species ($R^{\bullet}_{cd}{}^{*}$), which has a sufficiently high electronic potential that another electron is injected from $R^{\bullet}_{cd}{}^{*}$ into the conduction band. The whole reaction is that R_{cd} donates two electrons to the semiconductor electrode; as a result, the photocurrent is theoretically double that which is usually observed when only the first electron is injected. Current-doubling reactions have been investigated using many different semiconductors and substances.[11-18] For alcohols on TiO_2, Miyake et al. reported that alcohols with α-hydrogens react as current-doubling reagents, but those without α-hydrogens do not.[13]

Since oxygen may play a significant role in photocatalytic reactions, we studied this effect under air and nitrogen.

Experimental

Spin Trapping Experiment. Slurries of TiO_2 were prepared in pure alcohols since the presence of water, even at a 50% level, causes losses in the ESR sensitivity and, hence, very weak ESR spectra result. Titanium dioxide powder (10 mg; P-25 Nippon Aerosil, 30 nm diameter) was dispersed in one of six alcohols (1 ml), and mixed ultrasonically for more than 20 min in order to produce a slurry that was stable during the course of the experiments. To remove dissolved oxygen, the slurry was freeze-pumped at least three times and back-filled with dry nitrogen. A spin-trapping reagent (DMPO 5 μl, Sigma, used as-received) was added to the slurry, an aliquot of which was introduced into a quartz ESR flat cell (volume 0.52 cm^3, spacing 0.3 mm) by means of a rubber squeeze bulb. To prevent oxygen from entering the slurry, preparations were made under flowing nitrogen gas. The cell was placed in a TM_{110} cavity of an X-band electron spin resonance spectrometer (JEOL, JES-PE-1X). The microwave power was 10 mW and the modulation amplitude was 1.0 Gauss for all experiments. ESR measurements were made immediately after irradiation for 30 s and 1 min was required to scan the spectrum. Ultraviolet irradiation was directed to the window of the cavity using a 500 W high-pressure mercury lamp with a glass filter which cut off wavelengths shorter than 390 nm and a water filter which absorbed infrared radiation. Light with wavelengths <390 nm caused a decomposition of DMPO or its spin adducts to give a complicated ESR spectra. All alcohols used in these experiments were at least of 98% purity.

Current Doubling Experiment. The photocurrent was measured in a solution containing 0.05 M HCl in an alcohol-water mixture (1 : 1 in volume). The usual three-electrodes method[13] was employed, where a single crystal of TiO_2 was the working electrode, Pt was the counter electrode, and a saturated calomel electrode (S.C.E.) was the reference electrode, respectively. The light source was a 500 W Xe-lamp with a water filter to decrease infrared radiation.

Photoelectrochemical Oxidation of Ethanol and Product Analysis. The electrolyte for the photoelectrolysis was a mixture of aqueous HCl solution (0.1 M, 2 ml) and ethanol (2 ml). The working electrode (W.E.) was thin-layer TiO_2, deposited on tin oxide-coated glass by spray pyrolysis using titaniumoxy acetylacetonate. A Pt counter electrode and an S.C.E. reference electrode were incorporated in the cell. Irradiation to the TiO_2 was performed through the glass and the tin oxide. Quantitative analyses of a small aliquot of the solution were performed periodically by gas chromatography (Hitachi 163; column: PEG 4000). Qualitative analyses were performed using a GC-MS (Shimazu QP-1000; column: PEG 1500) after distillations of the electrolyte in order to condense the oxidation products. The amount of oxygen in solution was controlled by bubbling nitrogen or oxygen into the solution.

Results and Discussion

The role of oxygen in the mechanism of the photocatalytic oxidation of alcohols was studied by controlling the relative amount of oxygen in solution. Two main sets of experiments were performed: 1) in the "absence" of oxygen by prior purging the solution with nitrogen and 2) in the "presence" of oxygen by bubbling of the solution with oxygen or air. The four lower alcohols were investigated in the absence of oxygen, but only ethanol was studied in the presence of oxygen.

1. Photocatalytic Oxidation of Alcohols in the Absence of O_2. A. Spin Trapping Reaction: Prior to irradiation, the intensity of the ESR spectrum was insignificant. UV irradiation to the slurry of TiO_2 containing 2-methyl-2-propanol and DMPO gave the ESR spectrum shown in Fig. 1(a). The peak-to-peak values (indicated by the arrows in the figure) were used as a measure of the relative concentration of the spin adducts. Methanol, ethanol, and 2-propanol gave similar ESR spectra, but their adduct concentrations were much smaller than that of 2-methyl-2-propanol, as shown in Table 1. Slurries of C_5 alcohols, such as 2-methyl-2-butanol and 3-methyl-2-butanol, also gave concentrations of spin adducts about equal to that of 2-methyl-2-propanol. However, in the case of these higher alcohols, the ESR spectra were more complicated, suggesting that several kinds of radicals were formed and subsequently trapped by DMPO. The hyperfine splitting constants of the spectra of the alcohol-TiO_2-DMPO slurries in the absence of oxygen (Fig. 1, curve a) indicate that the radical trapped by DMPO is a carbon-centered radical.[19] The production of carbon-centered radicals in photocatalytic reaction

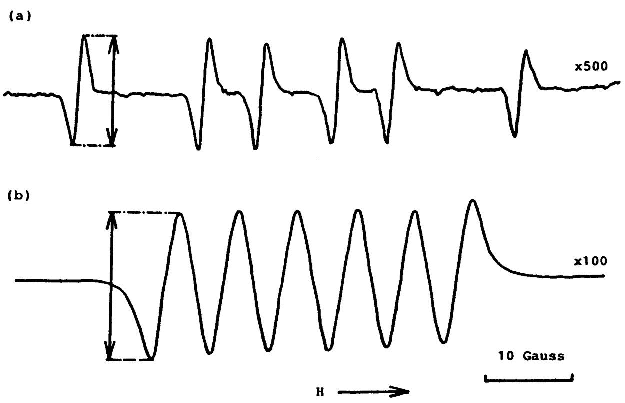

Fig. 1. ESR spectra observed after illumination of a slurry of 2-Me-2-PrOH, TiO_2, and DMPO; (a) spectrum in the absence of oxygen; (b) spectrum in the presence of oxygen.

Table 1. Comparison of Results of Spin Trapping and Current Doubling Experiments. The Relative Spin Adduct Concentrations were Determined from the Peak to Peak Values of ESR Spectra, and the Percent of the Photocurrent Increase Due to the Addition of an Alcohol was Determined from the Photocurrent Increase with Respect to Photocurrent in the Absence of Alcohol

Alcohol	Experimental method	
	Spin adduct concn. (a.u.)	Photocurrent increase (%)
MeOH	<1	25
EtOH	<1	27
2-PrOH	<1	30
2-Me-2PrOH	8	0

has also been suggested from product analyses of the slurries of 2-methyl-2-propanol and Pt-loaded TiO_2 by Nishimoto et al.[20]

Our results suggest that the radical species produced from 2-methyl-2-propanol have a sufficiently long lifetime to be trapped by DMPO, whereas those produced from methanol, ethanol, and 2-propanol had much shorter lifetimes and, hence, were not trapped. The fact that the latter three alcohols gave low concentrations of spin adducts suggests that the photocatalytically produced radicals were involved in another process whose reaction rate is faster than that of the spin-trapping reaction. The other process will be discussed in the section on current doubling. The significant difference among these alcohols is due to the fact that 2-methyl-2-propanol does not have an α-hydrogen, whereas the other three alcohols do. The results concerning the two C_5 alcohols, one of which has an α-hydrogen, can propably be explained by a rapid fragmentation of the photocatalytically produced radicals.

B. Current Doubling Reactions: We made current doubling measurements on the four lower alcohols in order to comfirm the work of Miyake et al.,[13] and also on the two higher C_5-alcohols. The results of the current-doubling experiments with the four lower alcohols in the absence of oxygen are shown in Table 1. The photocurrent was not increased by the addition of 2-methyl-2-propanol; however, upon by the addition of the other three alcohols the photocurrent increased within a range of 25 to 30%. Incidentally, the increase in current doubling was not as large with TiO_2 as with ZnO.[13–15] Our results with the six alcohols agree with the conclusions of Miyake et al.,[13] namely that an alcohol with an α-hydrogen reacts as a current-doubling reagent, but that an alcohol without α-hydrogen does not.

The results of the current-doubling experiments can be interpreted according to the band model theory, as shown in Fig. 2. This figure shows two mechanisms for oxidation, one for an alcohol with an α-hydrogen and the other for an alcohol without an α-hydrogen. The redox potentials of all alcohols are sufficiently low to be oxidized by the hole in the valence band of TiO_2. Therefore, regardless of whether the alcohols have an α-hydrogen or not, photoproduced holes oxidize the alcohols by electron transfer to the valence band of TiO_2, and an initial radical is produced. The redox potential of the produced radical determines whether the radical species can inject another electron into the conduction band of TiO_2 or not. An alcohol with α-hydrogen affords a radical which can inject another electron, while an alcohol without α-hydrogen does not.[21]

The results of spin trapping and current doubling shown in Table 1 (that is, current doubling reagents do not give a high concentration of spin adducts) suggest that the rate of second-electron injection into the conduction band is faster than that of spin trapping by DMPO under our conditions.

2. Photocatalytic Oxidation of Ethanol in the Presence of O_2. A. Spin Trapping Reactions: The introduction of oxygen into a spin-trapping slurry system containing 2-methyl-2-propanol changed both the hyperfine splitting (h.f.s.) constants and the intensities of the ESR spectra. The ESR spectrum is shown in Fig. 1 (curve b), where it is compared with the spectrum (curve a) observed when nitrogen was introduced into the slurry. In the presence of oxygen the hyperfine structures of the ESR spectra observed for all four alcohols were similar, and the h.f.s. constants indicated that oxygen-centered radicals were traped.[21] The concentrations of the spin adducts from all four alcohols could be increased by oxygen bubbling, and the intensity of the spectrum was significantly greater for 2-methyl-2-propanol than the other alcohols, as was the case in the absence of oxygen (Table 2).

There are two possible mechanisms for the formation of oxygen-centered radicals: (1) molecular oxygen reacts with the photocatalytically produced C-centered

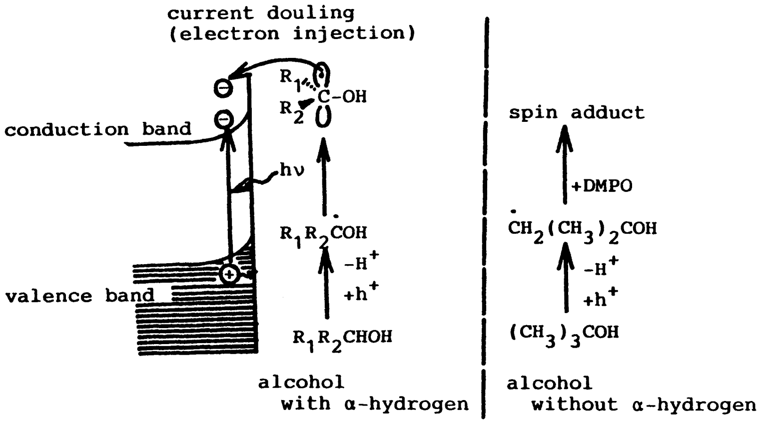

Fig. 2. Reaction mechanism of the current doubling and the spin trapping reactions of alcohols with and without α-hydrogens on TiO_2.

Table 2. Relative Spin Adduct Concentrations of Slurries of Alcohols TiO_2, and DMPO upon Irradiation in the Presence of Oxygen or Nitrogen. Spin Adduct Results under Nitrogen Were Taken from Table 1

Alcohol	Spin adduct concentration (a.u.)			
	MeOH	EtOH	2-PrOH	2-Me-2-PrOH
Under N_2	<1	<1	<1	8
Under O_2	4	4	4	56

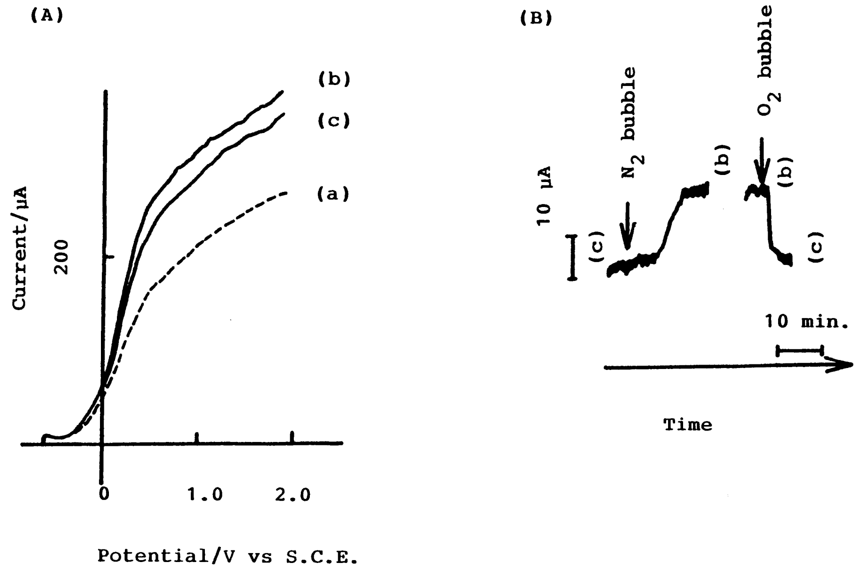

Fig. 3. Oxygen effect on the current doubling reaction of ethanol. (A) current–potential curves under illumination (a) without ethanol under nitrogen or oxygen, (b) with ethanol under nitrogen, and (c) with ethanol under oxygen; (B) time profile of photocurrent under oxygen or nitrogen in the presence of ethanol measured at 0.0 V vs S.C.E.

radicals, and (2) an oxygen anion radical, which is produced through the reduction of molecular oxygen by electrons from the conduction band, reacts with an alcohol molecule to produce a radical species. However, hydrogen atom abstraction from alcohol by a superoxide ($O_2^{\bar{\cdot}}$) is unlikely.[22] In this case a hydroperoxyl radical ($HO_2^{\cdot}$) or a hydroxyl radical ($\cdot OH$) produced by a cathodic reaction from oxygen molecule[5] may play a significant role. In both cases the formation of a C-centered radical is the first step and the reaction of this radical with oxygen molecule may give an O-centered radical.

The fact that oxygen increased the concentrations of the spin adducts for all alcohols, even for alcohols with an α-hydrogen, suggests that the rate of a second-electron injection step (i.e., current doubling) is not much faster than that of the reaction of the radicals with oxygen species. In this study we were not able to specify the reason why the concentrations of the spin adducts were increased by oxygen. However, we can propose several mechanisms, as follows, which may account for these results. First, an oxygen adsorbed on TiO_2 accepts a photoexcited electron from the conduction band and this results in a decrease of the recombination of the photoproduced hole with the electron. The resulting larger concentration of holes react with an alcohol to produce radicals more efficiently than the holes in the absence of oxygen. Secondly, an oxygen reacts with a photoproduced radical by a radical chain mechanism which is discussed later. By means of this chain mechanism the concentration of radicals increased and, hence, a higher concentration of spin adducts resulted. Thirdly, the reduction of an oxygen molecule leads to the formation of radical species which abstract a hydrogen atom from ethanol to give more radical species. Lastly, the trapping rate constant of DMPO differs according to the type of radical. For example, DMPO traps O-centered radicals more efficiently than C-centered radicals, which suggests even at the same concentration O-centered radicals give more spin adducts than C-centered radicals do.[23]

B. Current Doubling Reactions: The introduction of oxygen gas into the electrolyte containing ethanol partially reduced the current increase due to the addition of alcohol, as shown in Fig. 3 (A). The difference in the photocurrent increase under nitrogen and oxygen is small but significant. It was further substantiated by the time profile of the photocurrent with ethanol under nitrogen or oxygen bubbling into an electrolyte, as shown in Fig. 3(B). In this experiment, when oxygen gas was replaced with nitrogen, the photocurrent increased slowly. Later, when the nitrogen was replaced with oxygen, the photocurrent decreased rapidly. Both these changes were reversible. The difference in the time profile between the photocurrent increase and decrease can be attributed to the oxygen adsorbed on the TiO_2. The radical species which injects another electron is adsorbed on the TiO_2. Therefore, effective oxygen should also be found on the TiO_2. It takes more time to remove the oxygen from the surface of TiO_2 by nitrogen gas bubbling than to provide adsorbed oxygen by oxygen gas bubbling. Consequently, the photocurrent increased slowly and decreased rapidly.

The reduction of the photocurrent by introducing oxygen into the photoelectrochemical system suggests that oxygen or an oxygen radical species reacted with the initial radical species. To account for the fact that oxygen did not completely eliminate the photocurrent increase, we propose that the reaction rate of electron injection from the alcohol radical species is comparable to that of the reaction of the radicals with oxygen species. Since these results were obtained with an electrode system in which most of the electrons in the conduction band were collected by the counter electrode and consumed to produce hydrogen, we conclude that the active species at the TiO_2 surface is probably molecular oxygen and not an oxygen anion radical.

C. Photoelectrochemical Oxidation of Ethanol and Product Analysis: A photoelectrolysis of an ethanol-HCl solution under nitrogen or oxygen led to a product with the same retention time in gas chromatograms. GC-MS revealed that the only product was acetaldehyde, the amount of which was about ten-times greater in the presence of oxygen, as shown in Fig. 4. The current efficiency for the production of acetaldehyde under nitrogen is about 20%. The low efficiency may be attributed to a competitive oxidation of water.

Acetaldehyde is reported to be produced by the current-doubling reaction with ethanol.[13] Moreover, our results show that acetaldehyde formation is enhanced by the presence of oxygen. This result and the discussions in the previous section lead us to conclude that molecular oxygen is the active species for the enhanced production of acetaldehyde compared to that in the absence of oxygen. To account for the photoelectrochemical oxidation of ethanol we propose the reaction mechanism shown in Fig. 5. Molecular oxygen reacts with a C-centered radical(I), which is produced photocatalytically to give a peroxyl radical (II), which in turn decomposes by an autoxidation step to produce acetaldehyde and hydroperoxyl radical(III). This radical(III) abstracts hydrogen from ethanol and leads to the production of another C-centered radical(I). According to this reaction mechanism, one photon results in the formation of several acetaldehyde

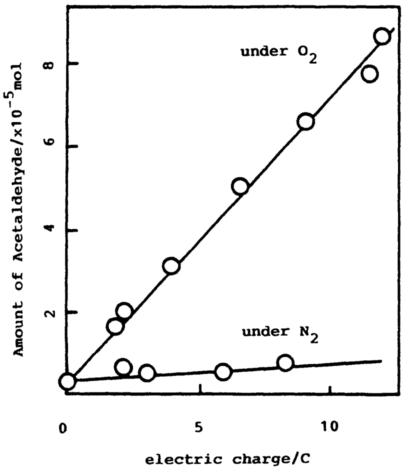

Fig. 4. The effect of oxygen on the amount of acetaldehyde produced by photoelectrolysis of ethanol in aqueous 0.1 M HCl (1:1). W.E.:TiO_2 on SnO_2 coated glass; C.E.:Pt; R.E.:S.C.E.; photoelectrolysis at 2.5 V vs. S.C.E.

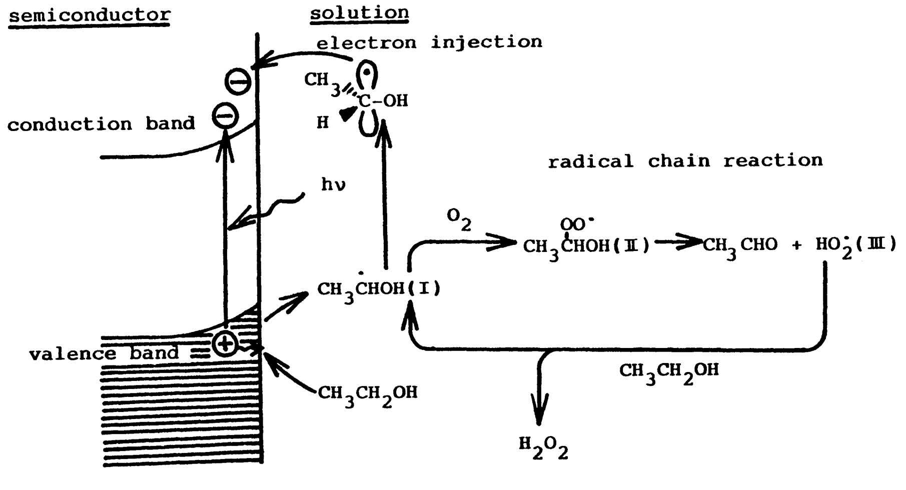

Fig. 5. Reaction mechanism of ethanol oxidation on illuminated TiO_2 in the presence of oxygen. The reduction processes are omitted.

molecules. This increase in the amount of acetaldehyde results from a free radical chain reaction mechanism involving molecular oxygen. Such a free radical chain mechanism has been suggested for photoirradiated slurries containing olefins and TiO_2 or CdS.[1] The formation of another product, H_2O_2, was also reported on photoexcited TiO_2, although it has only a transient existence in aqueous dispersion of TiO_2.[24]

Conclusion

In this article, we compared the photocatalytic reactions in slurries and on photoelectrodes and obtained a good correlation between the results from both systems. An alcohol with an α-hydorgen is oxidized to the radical species which can inject another electron into the conduction band of TiO_2. The rate of electron injection is faster than that of a spin-trapping reaction by DMPO and is comparable with that of the reaction with oxygen. The reaction process becomes a radical chain process under oxygen. An alcohol without an α-hydrogen is oxidized to the radical species which can not inject another electron. Therefore, this radical is trapped by DMPO. These results indicate a criterion for the application of photocatalytic reactions of alcohols to organic syntheses. Alcohols with α-hydrogen can be used for the in situ preparation of carbonyl compound for the *N*-alkylation of amines[6] since they are subjected to a rapid two-electron oxidation. On the other hand, alcohols without α-hydrogen can be used for the generation of radical species for the radical coupling reactions[20] because the produced radicals are relatively stable. The oxidation of 2-methyl-2-propanol on Pt electrode does not produce a new C–C bond like on photocatalyst, but gives acetone and 2-methylpropane.[25]

In our discussions of the photooxidation of alcohols we have stated that oxidation starts from direct reaction with the photoproduced holes in the valence band of TiO_2. However, it is equally possible that the oxidation occurs by an indirect process involving hydroxy radicals produced by oxidation of surface OH groups by holes, which we do not distinguish from the direct reaction with a hole.

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