Photocatalytic Decomposition of 2-Ethoxyethanol on Titanium Dioxide

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The reaction mechanism of the photocatalytic oxidation of 2-ethoxyethanol (Ethyl Cellosolve, $EtOCH_2CH_2OH$) on TiO_2 powder was investigated by gas chromatography-mass spectrometry (GC-MS), infrared (IR) spectroscopy, and electron spin resonance (ESR) with spin trapping technique. Irradiation of TiO_2 powder with UV light in the presence of $EtOCH_2CH_2OH$ under air led to the formation of ethyl formate, ethanol, acetaldehyde and carbon dioxide. The main product, ethyl formate was different from the product through the reaction pathway proposed before for primary alcohols. It was also different from the product of electrolysis on Pt. Reaction mechanism is proposed based on IR and ESR studies.

There have been many studies on the photocatalytic reactions of organic substances on illuminated semiconductor powders.[1] However, detailed mechanisms of the reactions have not been well understood so far. Therefore, this work was undertaken to investigate the reaction mechanism of photocatalytic oxidation of an organic substance on TiO_2 powder, using mainly IR spectroscopy. There have been many studies on the IR spectra of surface species on TiO_2[2-5] but studies on the photocatalytic reactions of organic substances on TiO_2 powder by IR spectroscopy are relatively few. Filimonov reported the IR spectra of the adsorbed species produced by the photocatalytic reaction of some alcohols and alkanes on TiO_2.[6] Kawai et al. studied the photocatalytic hydrogen evolution from various alcohols and water adsorbed on Pt/TiO_2 and proposed that two processes are involved in the reaction based on an IR study.[7] One was a direct reaction of alcohols with the photoproduced hole in the valence band and the other was the $\cdot OH$ formation from the reaction of the hole with an adsorbed H_2O on the photocatalyst.

The organic substance we employed was 2-ethoxyethanol ($EtOCH_2CH_2OH$) which is widely used as an organic solvent. In order to keep the environment clean and safe it is usually necessary to remove from the air the volatile organic solvents such as $EtOCH_2CH_2OH$ exhausted from manufacturing plants. A photocatalytic reaction is in principle available to treat poisonous chemical species such as CN^- in an aqueous solution[8] or stinking molecules in the air, though the reaction mechanism is not clear yet. From a practical point of view it is quite promising to employ photocatalysis for the treatment of $EtOCH_2CH_2OH$.

Furthermore, we are interested in the oxidative reaction of alkoxyethanols such as $EtOCH_2CH_2OH$ because they have two functional groups, i.e. alcoholic hydroxyl (-OH) and etheric oxy (-O-) groups. It is quite interesting from the viewpoint of organic chemistry to get information as to which group is oxidized first by the photocatalyst. For example, Nishimoto et al. investigated the photocatalytic degradation and polymerization of poly(oxyethylene) on TiO_2 powder in aqueous solution and concluded that both functional groups, alcoholic hydroxyl and etheric oxy, were oxidizable depending on the surface condition of TiO_2.[9] Ross et al. reported that 2-methoxyethanol, a homologous compound of $EtOCH_2CH_2OH$, was oxidized on a platinum and a carbon electrode through the electron transfer at the etheric oxy group rather than the hydroxyl group.[10] Sugawara studied the oxidation of a series of alkoxyethanols on a Pt electrode.[11] The oxidations of alkoxyethanol by pyrolysis[12] and permanganate[13] have also been studied. These investigations on the decomposition of alkoxyethanols showed that the reaction products were different depending on the oxidation processes. The photocatalytic reaction of 1,1-diphenylethylene on the illuminated TiO_2 powder was reported to give products different from those of the electrolysis on Pt.[14] Taking these into consideration the photocatalytic oxidation of $EtOCH_2CH_2OH$ on semiconductor powders seems quite interesting in terms of its reaction pathway and products.

In this study the photocatalytic oxidation of $EtOCH_2CH_2OH$ on TiO_2 powder was investigated, using GC-MS, IR spectroscopy, and ESR with a spin trapping method.

Experimental

Materials. TiO_2 (Nippon Aerosil, P-25) was used as a photocatalyst without pretreatments. Photoirradiation on CdS (Wako Chemicals), ZnS (Wako Chemicals), Al_2O_3 (Wako Chemicals), SnO_2 (Furuuchi Chemicals), and MnO_2 (Kanto Chemicals) powders were carried out for references. All organic reactants in the present experiments were reagent grade (Tokyo Kasei).

Products Analysis. Reaction products in the gas/solid reaction were sampled from a circulating system (volume 800 ml). This system had a fan to vaporize the organic liquid and to circulate the sample gas. It was also equipped with a Pyrex glass reactor with a flat bottom (area 50 cm^2) to support the photocatalyst. The catalyst powder (0.5 g) was evenly spread over the transparent bottom of the reactor and was irradiated from beneath with a 500 W high-pressure mercury lamp. The concentration of the organic substance in the gas phase was about 3000 ppm. Reaction products in the gas phase were analyzed periodically by the gas chroma-

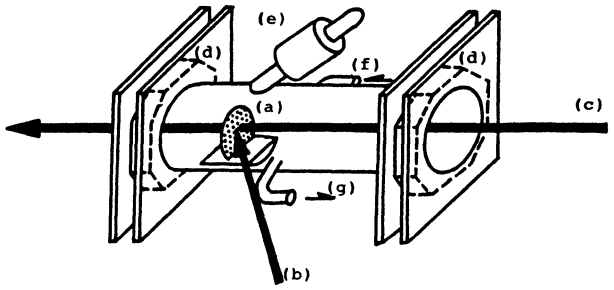


Fig. 1. The IR cell used for the simultaneous IR measurement and GC analysis; (a): TiO_2 pellet; (b): UV light for excitation; (c): IR for monitor; (d): NaCl plate; (e): tube for gas sampling; (f): gas inlet; (g): gas outlet.

tography (Hitachi 163; column: PEG 4000 for organic gases and silica gel for CO_2).

In order to identify the products by GC-MS, photocatalytic reaction of TiO_2 slurry in liquid $EtOCH_2CH_2OH$ was carried out because a gas/solid reaction in the present system did not supply a sufficient amount of the products for a qualitative analysis by GC-MS. The TiO_2 powder (500 mg) dispersed in a given 2-alkoxyethanol (5 ml) saturated with air was irradiated for 5 h in a flask which was installed with an internal high-pressure Hg lamp. The products in liquid phase were collected by distillation and then analyzed by GC-MS (Shimadzu QP1000 with a 30 m OV101 column).

IR Studies. The measurement of IR transmittance of the adsorbed species on the photocatalyst was performed with self-supporting TiO_2 disks. The TiO_2 powder was exposed overnight to the air which was saturated with the organic compound in the dark at room temperature and then the powder (50 mg) was pressed into a disk of 20 mm in diameter and about 0.1 mm in thickness. The IR spectrum was recorded after periodic UV-irradiation with a 500 W Xe-lamp through a water filter to reduce the heating effect. The IR spectrum of liquid $EtOCH_2CH_2OH$ was also recorded by a liquid film method using NaCl plates. A cell was used to analyze the gas phase which is shown in Fig. 1. The cell was first evacuated slowly after the TiO_2 disk which was adsorbed with $EtOCH_2CH_2OH$ was placed inside, and then an air saturated with $EtOCH_2CH_2OH$ was introduced into the cell. An inlet and an outlet of the cell were closed with screw cocks and then the IR measurement and the gas phase analysis were carried out after periodical UV-irradiation under the atmospheric pressure.

ESR Studies. Spin trapping method for an ESR measurement was applied to the present system. The experimental procedure was previously mentioned.[15] 5,5-Dimethyl-4,5-dihydro-3*H*-pyrrole *N*-oxide (DMPO) was used as a spin trapping reagent.

Results

Products Analysis. The gas chromatography analysis of the products in gas/solid reaction showed four peaks, three of which had the same retention times with those of acetaldehyde, ethyl formate, and ethanol, respectively, but the fourth peak which had a longer retention time than $EtOCH_2CH_2OH$ has not been identified yet. This substance was different from ethyl-

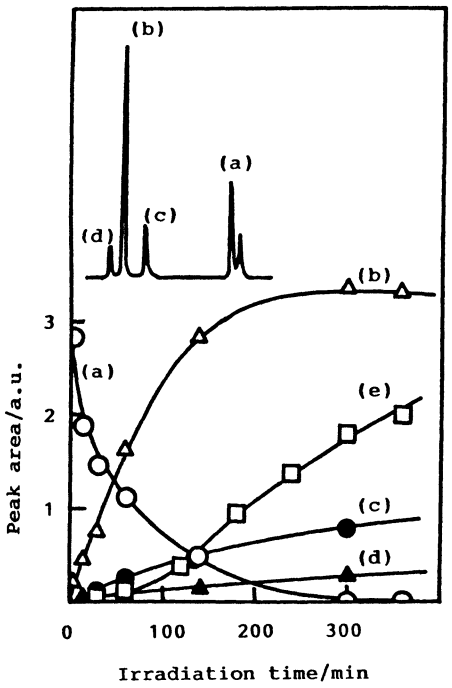


Fig. 2. Gas chromatogram of the reaction products and the time profile of each product in gas/solid reaction of $EtOCH_2CH_2OH$ on the TiO_2 powder. (a): $EtOCH_2CH_2OH$; (b): ethyl formate; (c): ethanol; (d): acetaldehyde; (e): carbon dioxide.

ene glycol and was supposed to be such an ether as produced from $EtOCH_2CH_2OH$ by photoreaction in the presence of $TiCl_4$.[16] Carbon dioxide was also detected in a separate experiment. Figure 2 shows the gas chromatogram of the products and the time profile of each product.

CdS and ZnS also gave the same products upon irradiation but were found to be less active than TiO_2. SnO_2, and Al_2O_3 powders did not photocatalyze the decomposition of $EtOCH_2CH_2OH$ because of their large bandgap energies compared with the UV light employed.

Decomposition of $EtOCH_2CH_2OH$ did not occur either when the catalyst was illuminated with a light of a longer wavelength than the bandgap of TiO_2 or when the system temperature was raised up to 353 K in the dark. In the absence of molecular oxygen, photoirradiation caused the reduction of TiO_2 and turned its color blue, and the amount of detected products was insignificant. When the sample gas was flowed over an oxidizing agent, e.g. MnO_2 powder, in the dark, the same gaschromatogram was obtained as when the UV-irradiated photocatalysts were employed. These results suggest that the reaction on the illuminated TiO_2 proceeded through a photocatalytic oxidation involving molecular oxygen in gas phase upon the bandgap illumination of the TiO_2.

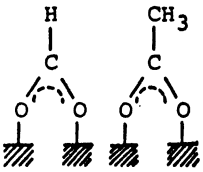
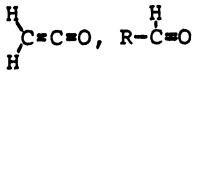
A qualitative analysis of the products in liquid/solid reaction by GC-MS showed only one peak, mass spectrum of which agreed well with that of ethyl for-

mate,[17] in addition to the out-of-scale $EtOCH_2CH_2OH$ peak which was in contrast to the results in the gas/solid experiment. There have been some reports mentioning that chemisorbed species react at low pressure gas/solid reactions while physisorbed species become important at high pressure of gas/solid and liquid/solid reactions.[18,19] In our conditions the pressure of $EtOCH_2CH_2OH$ is high enough and the physisorbed molecules react as in the case of liquid/solid phase. Therefore, the difference in the products was ascribed to the surface concentration of $EtOCH_2CH_2OH$ on TiO_2. $EtOCH_2CH_2OH$ is oxidized much easier than ethyl formate in the present conditions, which leads to the production of only ethyl formate under high concentration of $EtOCH_2CH_2OH$.

Alkyl formate is produced from alkoxyethanol by the dissociation of the C-C bond between the two oxygen atoms followed by the subsequent oxidation of one of these carbon atoms. Indeed, when 2-methoxyethanol, 2-isopropoxyethanol, or 2-butoxyethanol was used as a reactant, it was found by GC-MS that the corresponding formate was produced in each case. This result suggests that the C-C bond between the two oxygen atoms of alkoxyethanol is photocatalytically dissociated on the illuminated TiO_2 surface.

IR Studies. Adsorption of $EtOCH_2CH_2OH$ on TiO_2 in the Dark: Infrared spectra of bare TiO_2 (a), liquid $EtOCH_2CH_2OH$ (b), $EtOCH_2CH_2OH$ adsorbed on TiO_2 (c), and ethyl formate adsorbed on TiO_2 (d) are shown in Fig. 3. Bare TiO_2 has broad bands at 650—1100, 1500—1700, and 3000—3600 cm^{-1}, which are assigned to H_2O and OH groups on TiO_2. A comparison of the IR spectrum of $EtOCH_2CH_2OH$ in liquid phase with that of adsorbed $EtOCH_2CH_2OH$ on TiO_2 powder shows that the absorption band of $EtOCH_2CH_2OH$ at 1380 cm^{-1} decreased in intensity more than the bands at 1360 and 1450 cm^{-1} after the adsorption of $EtOCH_2CH_2OH$ onto TiO_2. The decrease of the band at 1380 cm^{-1} indicates that this

Table 1. IR Bands Assignment of Adsorbate on the TiO_2 Surface

IR bands/cm^{-1}	1570, 1360	1440	1730	
Surface species				
	formate	acetate	ketene	aldehyde
References	20	20	21	25

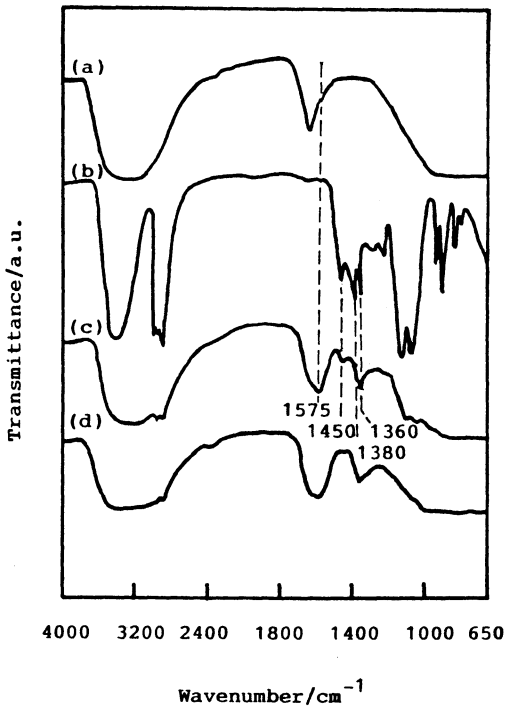


Fig. 3. Infrared spectra of bare TiO_2 (a), liquid phase $EtOCH_2CH_2OH$ (b), $EtOCH_2CH_2OH$ adsorbed on TiO_2 (c), and ethyl formate adsorbed on TiO_2 (d).

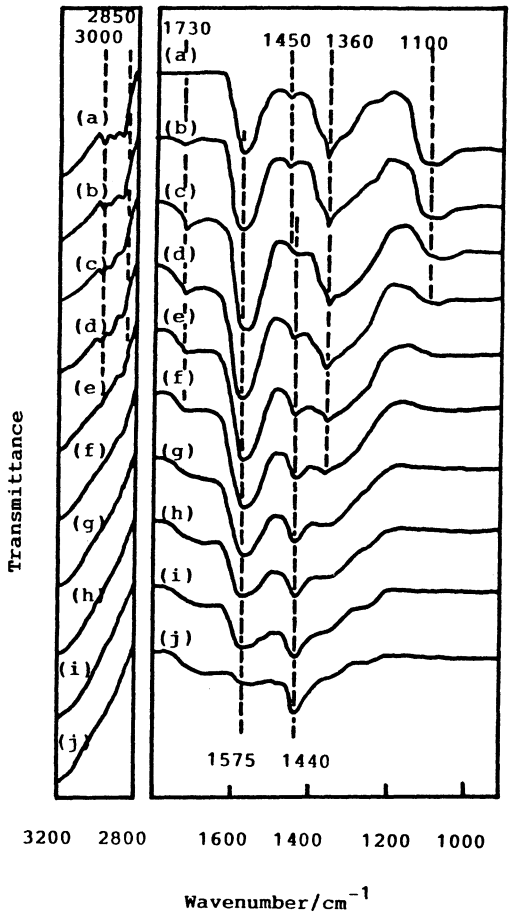


Fig. 4. The time profile of the IR spectrum of adsorbed species upon UV irradiation. Each curve shows the spectrum after the following minutes of UV irradiation (a) 0; (b) 5; (c) 10; (d) 20; (e) 40; (f) 60; (g) 90; (h) 120; (i) 150; (j) 240. The spectra were recorded with the reference of untreated TiO_2 for the wavenumbers from 650—1800 cm^{-1}.

band is due to -OH in $EtOCH_2CH_2OH$, because alcohols are reported to be adsorbed onto TiO_2 forming alkoxides, i.e. losing their -OH groups.[20] It is worth noting that the new band appearing at 1575 cm^{-1} is different from that of the surface formate species reported by Nakajima et al.[20] (Table 1). This band was ascribed to the surface complex produced from the adsorbed $EtOCH_2CH_2OH$ and oxygen species (Fig. 7 (**VI**)), which will be discussed later.

Time Dependence of IR Spectrum of the Adsorbed Species on TiO_2 Powder upon UV Irradiation: The IR spectrum of $EtOCH_2CH_2OH$ adsorbed on the TiO_2 disk showed a time dependence upon UV-irradiation as shown in Fig. 4. That is, the irradiation of the disk with UV light for the first 20 minutes caused an increase in the band intensity at 1575 and 1360 cm^{-1} and a decrease in the band intensity at 1100, 1450, and 2850—3000 cm^{-1}. In addition, new bands appeared, which are at 1440 and 1730 cm^{-1}. A prolonged UV-irradiation caused the band at 1440 cm^{-1} to increase, and the bands, at 1730, 1575, and 1360 cm^{-1} to decrease.

The band at 1440 cm^{-1} was assigned to the surface acetate species[20] (Table 1). The other band at 1530 cm^{-1} due to the surface acetate species reported by Nakajima et al. was obscured by a strong band at around 1575 cm^{-1}. The stable adsorption of the acetate species was reported[20,21] and was also evidenced in the present study by the existence of the band at 1440 cm^{-1} even after 240 minutes of UV-irradiation.

The band at around 1730 cm^{-1} is assigned to the physisorbed ethyl formate (Fig. 7 (**VII**)) which will be further photocatalytically oxidized to ethanol, acetaldehyde, and acetate as will be discussed below.

Simultaneous Measurement of an Adsorbed Species and a Gas-Phase Product: The time profiles of the intensity of the IR band at 1575 cm^{-1} and that of the amount of ethyl formate in gas phase analyzed by GC during UV-irradiation are shown in Fig. 5. The maxima occurred at 40 minutes and 25 minutes of UV-irradiation for the IR absorbance at 1575 cm^{-1} and for the amount of produced ethyl formate in the gas phase, respectively. This result suggests that the surface species which has IR band at 1575 cm^{-1} may be different from ethyl formate because the maxima are different.

Radical Detection by Spin Trapping Method: Figure 6 shows the ESR spectrum observed after 20 seconds of UV-irradiation of the TiO_2 slurry in $EtOCH_2CH_2OH$ with DMPO. The hyperfine splitting constants (a_N=14.6 G and a_H=20.6 G; 1 G=10^{-4} T) indicate that a carbon-centered radical[22] was produced by the photocatalytic reaction of $EtOCH_2CH_2OH$ on TiO_2.

Discussion

Based on the experimental results we propose a reaction mechanism of the photocatalytic decomposition of $EtOCH_2CH_2OH$ on TiO_2 as shown in Fig. 7 and the details of it will be discussed in this section.

Reaction Products. The formation of ethyl formate from $EtOCH_2CH_2OH$ on the photoexcited TiO_2 powder is interpreted through the dehydration and the subsequent oxidation of the double bond according to the oxidation mechanism proposed by Djeghri and Teichner.[23] They have studied the photocatalytic oxidation of primary, secondary, and tertiary alcohols on TiO_2 and concluded that there are two oxidation pathways; one is a direct oxidation which produces aldehydes and ketones from primary and secondary alcohols, respectively. The other is dehydration of alcohols into alkenes which are oxidized at the double bond, forming carbon dioxide and aldehydes or ketones with less carbon atoms than the original alcohols. Applying their reaction mechanisms to the photocatalytic oxidation of $EtOCH_2CH_2OH$ on the illuminated TiO_2 powder, ethoxyacetaldehyde (through direct oxidation) and ethyl formate (through dehydra-

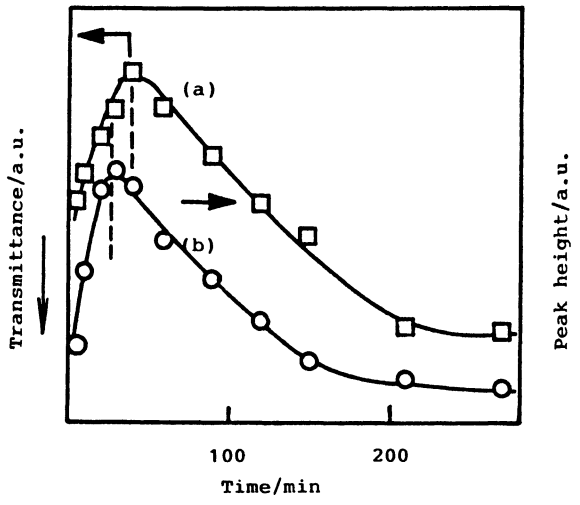


Fig. 5. The time profiles of the IR transmittance at 1575 cm^{-1} (a) and the peak height of ethyl formate in gas chromatogram (b).

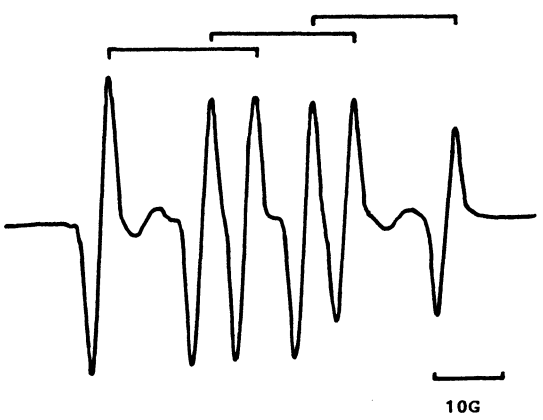


Fig. 6. ESR spectrum of the spin adduct obtained after 20 second UV irradiation of TiO_2 slurry in $EtOCH_2CH_2OH$ with DMPO.

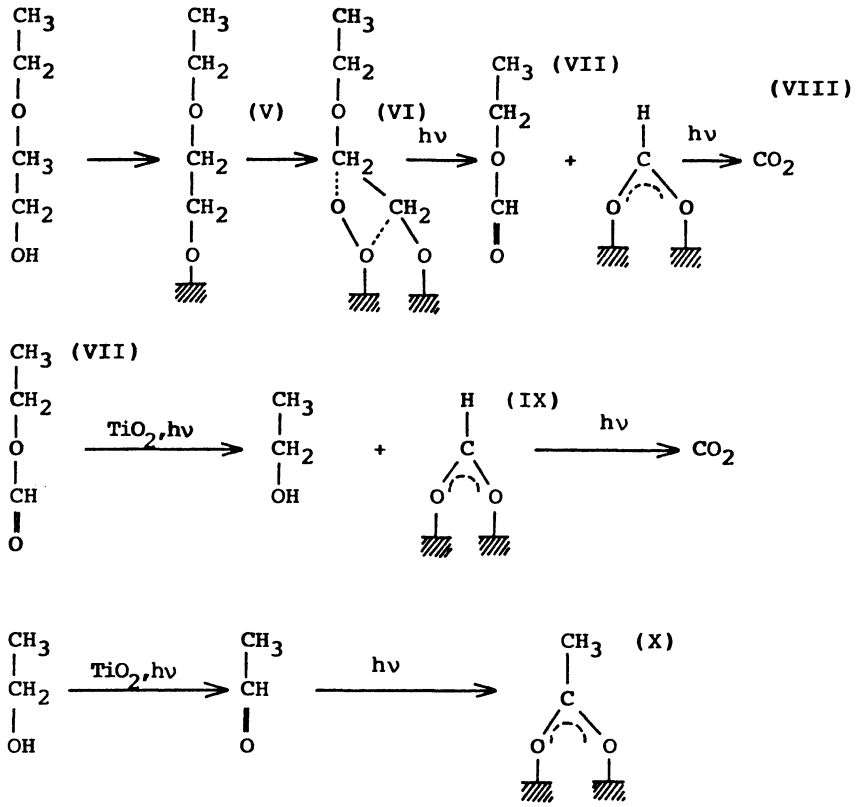


Fig. 7. The reaction scheme of the photocatalytic oxidation of $EtOCH_2CH_2OH$ on TiO_2.

tion-oxidation) are expected to be reaction products. However, only ethyl formate was detected in the present experiment, even though $EtOCH_2CH_2OH$, a primary alcohol, might tend to be oxdized directly into ethoxyacetaldehyde.

No production of ethoxyacetaldehyde may be ascribed to the molecular structure of $EtOCH_2CH_2OH$, i.e., the configuration of the oxygen atom at the β-position of the carbon atom which has the alcoholic -OH. Indeed, the indirect oxidation of alkoxyethanol was previously reported by Sugawara on a Pt electrode.[11] He investigated the electrochemical oxidation of a series of alkoxyethanols and proposed the following mechanism: Discharge occurs at an alcoholic oxygen which is followed by the fission of the C-C bond between the two oxygen atoms, producing a cation **I** and a formaldehyde **II**. This path corresponds to the step between **VI** and **VII** in Fig. 7. The cation **I** is then subjected to the C-O bond fission, producing an alcohol **III** and a formaldehyde **IV**.

$$ROCH_2CH_2OH \xrightarrow{-e,\,-H^+} ROCH_2CH_2O\cdot \xrightarrow{-e} \overset{+}{R}OCH_2\ (\mathbf{I}) \xrightarrow{+H_2O,\,-H^+} ROH\ (\mathbf{III}) + H_2CO\ (\mathbf{II}) \qquad + H_2CO\ (\mathbf{IV})$$

Scheme 1.

Our experimental results indicate that the first two steps of Scheme 1 occurred on the irradiated TiO_2 surface. The subsequent C-O bond fission, however, did not occur. Instead, oxidation of the carbon atom of **I** took place, yielding ethyl formate.

Adsorption of $EtOCH_2CH_2OH$ on TiO_2 in the Dark. We assigned the IR bands at 1575 and 1360 cm^{-1} which appeared after the adsorption of $EtOCH_2CH_2OH$ on TiO_2, to the surface species produced from adsorbed $EtOCH_2CH_2OH$ and oxygen species on TiO_2 (Fig. 7 (**VI**)). Although these bands are in good accordance with those at 1560 and 1360 cm^{-1} of the formate species on TiO_2 prepared from 2-propanol and oxygen at 523 K,[20] it is concluded that the adsorption of $EtOCH_2CH_2OH$ onto TiO_2 surface at room temperature in the dark did not produce the surface formate species. This is because raising the temperature of the TiO_2 powder with $EtOCH_2CH_2OH$ up to 353 K did not release any decomposed products which would be formed along with the surface formate species. In our experimental conditions molecular oxygen was adsorbed on the TiO_2 surface before the introduction of $EtOCH_2CH_2OH$. Molecular oxygen is reported to accept an electron from TiO_2, producing surface O_2^- which is stable at room temperature and can react with organic substances when they are introduced at higher temperatures.[24] Taking this into consideration we propose that the preadsorbed oxygen molecule accepts an electron from TiO_2 and reacts with $EtOCH_2$-

CH_2OH to form a surface formate-like species (Fig. 7 (**VI**)) which has IR bands at 1575 and 1360 cm^{-1}.

Surface Species on TiO_2 during the UV-Irradiation. The UV-irradiation caused an increase in intensity of the band at 1575 cm^{-1} (Figs. 4, 5). We assigned this band to the surface formate species (Fig. 7 (**VIII**)) for the following two reasons: (1) the bands at around 2850—3000 cm^{-1} due to $-CH_3$, and $-CH_2-$ disappeared while the band at 1575 cm^{-1} increased upon irradiation (Fig. 4). This result indicates that the species which has band at 1575 cm^{-1} produced upon UV-irradiation is neither adsorbed $EtOCH_2CH_2OH$ nor ethyl formate on TiO_2 because both of them have the IR bands at 2850—3000 cm^{-1} (Fig. 3 (c),(d)), (2) the simultaneous measurement of the intensity of the IR transmittance at 1575 cm^{-1} and the amount ot ethyl formate in gas phase (Fig. 5) showed that the production of ethyl formate precedes the surface species. This result can be interpreted as follows; surface formate species is produced from the C_1-species which is formed concomitantly with ethyl formate through the C-C cleavage.

Gonzalez et al. assigned the IR band at 1730 cm^{-1} to a surface ketene species (Table 1), which was produced by the thermal reaction of acetic acid on TiO_2.[21] This surface ketene species was produced by the dehydrogenation of a surface acetate species, which indicated that the ketene species was in a more oxidized state than the acetate species. In our experiment the band at 1730 cm^{-1} appeared only in the early stage of the illumination and it did not increase in intensity upon the prolonged UV-irradiation, which was in contrast to the progressive increase of the band at 1440 cm^{-1} with irradiation time. From this result, it is reasonable to assign the band at 1730 cm^{-1} not to the ketene species but to a precursor of an acetate species. Since free aldehyde has an IR band at around 1730—1740 cm^{-1} due to C=O stretching,[25] the formation of physisorbed aldehyde may be responsible for the IR band at 1730 cm^{-1}. When ethyl formate (Fig. 3 (d)) or acetaldehyde was adsorbed on TiO_2 in the dark, the band due to C=O was shifted to lower wavenumbers because aldehyde was chemisorbed on TiO_2. But carboxylate species such as formates and acetates were reported by Gonzalez et al. to have a dislodging effect on oxygen species bound to Ti^{4+},[21] which allowed aldehyde to physisorb onto the TiO_2 surface. Hence, we concluded that the band at 1730 cm^{-1} was due to the physisorbed ethyl formate (Fig. 7 (**VII**)) which has a formyl group in it.

Based on the results from the IR studies and products analysis we propose a reaction pathway for the photocatalytic oxidation of $EtOCH_2CH_2OH$ on TiO_2 surface, as shown in Fig. 7; $EtOCH_2CH_2OH$ is adsorbed on TiO_2 to yield surface alkoxide **V** and then reacts with the adsorbed O_2^- to produce formate-like species **VI** which has a strong IR band at 1575 and 1360 cm^{-1}. This surface species decomposes upon UV irradiation into ethyl formate **VII** in gas phase and the surface formate species on TiO_2 **VIII**. The surface formate species is oxidized further to CO_2. Further, the ethyl formate is oxidized photocatalyticaly to ethanol, acetaldehyde, and acetate species when the surface concentration of $EtOCH_2CH_2OH$ is low.

Intermediate Radical Species. The ESR experiment revealed that carbon-centered radical was produced from $EtOCH_2CH_2OH$ on TiO_2 upon UV-irradiation. Assuming that the electron transfer from the alcoholic OH of the adsorbed $EtOCH_2CH_2OH$ takes place in the primary step of the reaction, analogous to the case of Pt electrode, the photocatalytically produced radical **XI** will be converted to 2-ethoxy-1-hydroxyethyl radical **XII** or ethoxymethyl radical (**XIII**) by the subsequent β fragmentation, as shown in Scheme 2. This process corresponds to the step between **VI** and **VII** in Fig. 7.

$$EtOCH_2CH_2\dot{O}\overset{+}{H}\ (\mathbf{XI}) \begin{cases} \nearrow\ EtOCH_2\dot{C}HOH\ (\mathbf{XII}) + H^+ \\ \searrow\ EtOCH_2\dot{C}\ (\mathbf{XII}) + H_2CO + H^+ \end{cases}$$

Scheme 2.

Both of the radicals (**XII** and **XIII**) are carbon-centered. The former corresponds to the intermediate in the direct oxidation and the latter corresponds to the intermediate in the indirect oxidation.[23] From the reaction product, ethyl formate, a radical species **XIII** is supposed to be produced in the present experiment. We have already reported that alcohols with an α-hydrogen does not give a high concentration of spin adducts with DMPO in the irradiated TiO_2 suspension of alcohol. This is because the intermediate radicals immediately inject another electron into the conduction band of TiO_2, inducing a current doubling phenomenon.[15] Although $EtOCH_2CH_2OH$ is an alcohol with α-hydrogens and hence can bring about a current doubling,[26] $EtOCH_2CH_2OH$ gave experimentally a rather high concentration of a spin adduct in comparison with methanol or ethanol. The radical species **XIII** is more stable than those produced from methanol , ethanol, and 2-propanol.

Conclusion

The photocatalytic reaction of $EtOCH_2CH_2OH$ on TiO_2 powder gives ethyl formate as the primary product. The reaction product is different from the one expected from the reaction mechanism proposed for primary alcohol before. Base on our experimental results, we conclude that $EtOCH_2CH_2OH$ adsorbs on TiO_2 and reacts with the adsorbed O_2^- on the TiO_2 surface to produce a surface formate-like species . This surface species is photocatalytically oxidized to give ethyl formate and surface formate species. The former is further oxidized to ethanol, acetaldehyde, and acetate species by prolonged UV-irradiation. The photocatalytic oxidation of $EtOCH_2CH_2OH$ on TiO_2 is another example in which the products are different

from those from the electrolysis on a Pt electrode.[14)]

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