



# Decomposition pathways of glycolic acid on titanium dioxide

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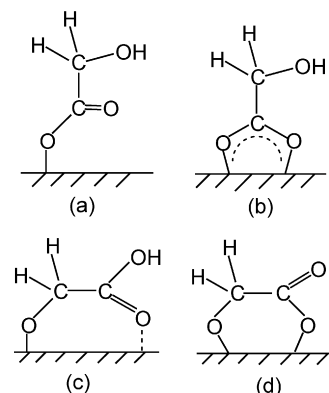
## ABSTRACT

Fourier-transformed infrared spectroscopy has been employed to study the adsorption, thermal reactions and photodegradation of glycolic acid (HOCH<sub>2</sub>COOH) on TiO<sub>2</sub> in a gas–solid system. The intriguing research focus is the reactivity and evolution of the two functional groups. Glycolic acid can exist on TiO<sub>2</sub> at 35 °C in two dissociative adsorption forms, OCH<sub>2</sub>COOH and HOCH<sub>2</sub>COO, which are derived from hydrogen loss of the COH and COOH groups, respectively. Heating the surface to a temperature higher than ~100 °C causes a largely enhanced carbonyl stretching band at ~1750 cm<sup>-1</sup>, indicative of oxidation of the OCH<sub>2</sub> groups of the surface glycolic acid molecules. This chemical process is supported by the adsorption of glyoxylic acid (HCOCOOH) on TiO<sub>2</sub>. As the surface temperature is further increased to 200 °C or higher, formate (HCOO) and methoxy (CH<sub>3</sub>O) are produced. Their formation is proposed via dioxymethylene (OCH<sub>2</sub>O) intermediate. CO and CO<sub>2</sub> are found to be the final thermal products. Photoirradiation of a TiO<sub>2</sub> surface covered with glycolic acid at ~325 nm leads to its decomposition, generating CO<sub>2</sub>, CH<sub>3</sub>O, HCOO and carbonate species. O<sub>2</sub> is found to promote the photochemical reactions of glycolic acid on TiO<sub>2</sub> to form CO<sub>2</sub>, HCOO and carbonates. O<sub>2</sub> may play a role hampering recombination of photogenerated electron–hole pairs and participating in the formation of CO<sub>2</sub> and HCOO.

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## 1. Introduction

In the atmosphere, carboxylic acid molecules account for a substantial portion of organic compounds in aerosols. It has been found that approximately 3.6% of the organic content of aerosols in a polluted troposphere is composed of glycolic acid [1]. TiO<sub>2</sub> as a photocatalyst for degradation of organic molecules has attracted much attention. Glycolic acid is the simplest  $\alpha$ -hydroxycarboxylic acid with the functional groups of OH and COOH bonded at neighboring carbon atoms. Various dissociative adsorption forms of glycolic acid on TiO<sub>2</sub>, as shown in Scheme 1, are possible to be produced, on the basis of previous studies of CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, HCOOH and CH<sub>3</sub>COOH [2–4]. The structures of Schemes 1a and 1b are due to dehydrogenation of the carboxyl group, with monodentate and bidentate (or bridging) coordinations on the surface, respectively. In the cases of HCOOH and CH<sub>3</sub>COOH, monodentate, bidentate or bridging form of the carboxylates can be differentiated by the difference of the antisymmetric and symmetric COO stretching frequencies [5]. Glycolic acid may lose the H of the alcohol's hydroxyl group, producing the structure of Scheme 1c. As both the OH groups of glycolic acid involve in the chemical interaction with TiO<sub>2</sub> surface, it is likely to generate the structure of Scheme 1d. In the previous adsorption study of glycolic acid on a TiO<sub>2</sub> film



**Scheme 1.** Structures possibly generated from dissociative adsorption of glycolic acid on TiO<sub>2</sub>.

in aqueous solutions, the Scheme 1d form has been suggested to exist on the surface in terms of the measurement of three broad peaks at 1088, 1370 and 1611 cm<sup>-1</sup> using attenuated total reflection infrared spectroscopy [6]. In fact, the stability of the various intermediates of glycolic acid (Scheme 1) on TiO<sub>2</sub> could be affected by the presence of water medium. However, in this aqueous glycolic acid report, this point was not evaluated and no thermal change was investigated. Photocatalytic reaction of aqueous glycolic acid suspended with Pt/TiO<sub>2</sub> particles, forming H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>CO and HCOCOOH as the photoproducts, has been reported [7]. Owing

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to the difficulty in applying surface analytical techniques in these suspension systems, the surface subjects of adsorption, reaction intermediates, and decomposition pathways were hardly described. Therefore, the photoreactions that occurred in the solution and on the surface could not be judged.

It is important and interesting to study the thermal and photochemical reaction pathways of glycolic acid on surfaces, but there is a dearth of surface investigations regarding this molecule. The intriguing research focus would be the reactivity and evolution of the reaction centers, such as the two functional groups (COH and COOH) and C–C bond, in the decomposition of glycolic acid, which are not expected to be the same due to different mechanisms in the thermal and photochemical reactions. In the present research, the adsorption, thermal reactions and photodegradation of glycolic acid on TiO<sub>2</sub> are investigated in a gas–solid interaction system with Fourier-transformed infrared spectroscopy.

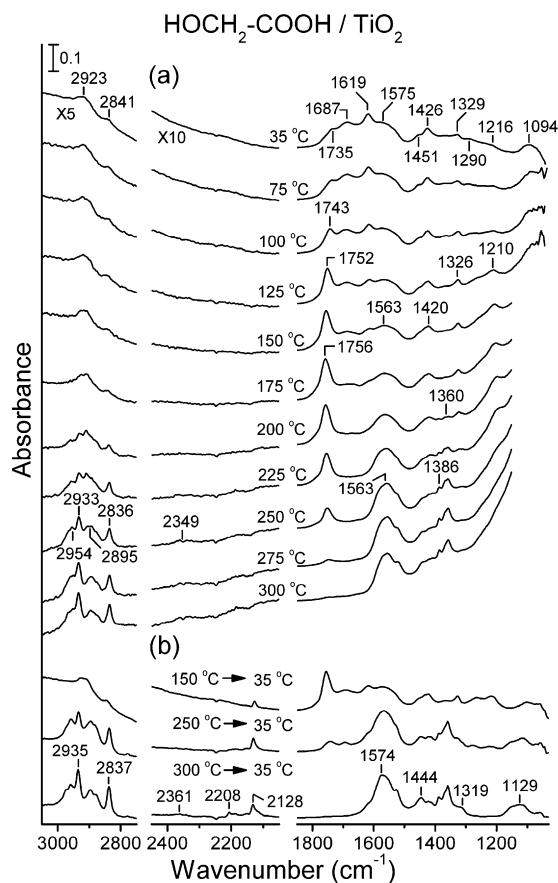
## 2. Experimental

The sample preparation of TiO<sub>2</sub> powder supported on a tungsten fine mesh (~6 cm<sup>2</sup>) has been described previously [8,9]. In brief, TiO<sub>2</sub> powder (Degussa P25, ~50 m<sup>2</sup>/g, anatase 70%, rutile 30%) was dispersed in water/acetone solution to form a uniform mixture, which was then sprayed onto a tungsten mesh. After that, the TiO<sub>2</sub> sample was mounted inside the IR cell for in situ FTIR spectroscopy. The IR cell with two CaF<sub>2</sub> windows for IR transmission down to ~1000 cm<sup>-1</sup> was connected to a gas manifold which was pumped by a turbomolecular pump with a base pressure of ~1 × 10<sup>-7</sup> Torr. The TiO<sub>2</sub> sample in the cell was heated to 450 °C under vacuum for 24 h by resistive heating. The temperature of TiO<sub>2</sub> sample was measured by a K-type thermocouple spotwelded on the tungsten mesh. Before each run of the experiment, the TiO<sub>2</sub> temperature was held at 450 °C in a vacuum for 2 h and at 350 °C for 0.5 h in the presence of 3.0 Torr O<sub>2</sub>. After the heating treatment, the cell was evacuated. 10 Torr of O<sub>2</sub> was introduced into the cell as the sample was cooled to 70 °C. When the TiO<sub>2</sub> temperature reached 35 °C, the cell was evacuated again for gas or vapor dosing and an infrared spectrum was taken as reference background. The glycolic acid (HOCH<sub>2</sub>COOH, 99%) and glyoxylic acid (HCOCOOH·H<sub>2</sub>O, 98%) used in this study were purchased from Acros and Aldrich, respectively. The dissociation constants of glycolic acid and glycol in 25 °C aqueous solution are 1.5 × 10<sup>-4</sup> and 6.0 × 10<sup>-15</sup>, respectively [10]. The vial containing glycolic acid or glyoxylic acid was evacuated for ~30 h prior to introduction of its vapor into the infrared cell. <sup>16</sup>O<sub>2</sub> (99.998%) and <sup>18</sup>O<sub>2</sub> (99 atom%) were purchased from Matheson and Isotec, respectively. The pressure was monitored with a Baratron capacitance manometer and an ion gauge. In the photochemistry study, both the UV and IR beams were 45° to the normal of the TiO<sub>2</sub> sample. The UV light source used was a combination of a 350-W Hg arc lamp (Oriel Corp), a water filter, and a band-pass filter with a bandwidth of ~100 nm centered at ~325 nm. The photon power at the position of TiO<sub>2</sub> sample was ~0.24 W/cm<sup>2</sup> measured in the air by a power meter (Moletron, PM10V1). Infrared spectra were obtained with a 4 cm<sup>-1</sup> resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with CO<sub>2</sub>-free dry air. The spectra presented here have been ratioed against the TiO<sub>2</sub> background spectrum. In the study of photooxidation, the photoirradiation time was started to count as the UV lamp was turned on. It took 40–50 s to reach the full power.

## 3. Results and discussion

### 3.1. Adsorption of glycolic acid on TiO<sub>2</sub>

The first spectrum in Fig. 1a shows the infrared absorptions measured after adsorption of glycolic acid on TiO<sub>2</sub> at 35 °C, with



**Fig. 1.** Infrared spectra taken at the indicated temperatures after glycolic acid adsorption on TiO<sub>2</sub> at 35 °C (a). Infrared spectra taken at 35 °C after the surface heating to higher temperatures (b). The regions between 2050 and 2450 cm<sup>-1</sup> and between 2750 and 3050 cm<sup>-1</sup> have been multiplied by a factor of 10 and 5, respectively.

peaks or shoulders at 1094, 1216, 1290, 1329, 1426, 1451, 1575, 1619, 1687, 1735, 2841 and 2923 cm<sup>-1</sup>. The adsorption procedure was carried out by exposing a high temperature-heated TiO<sub>2</sub> surface to the vapor of glycolic acid for 15 h at 35 °C. Then, the infrared cell was evacuated for 1 h to remove residual molecules present in the gas phase and weakly adsorbed surface species and was closed for subsequent TiO<sub>2</sub> infrared measurements and surface heating or photoirradiation. The observed infrared frequencies are compared to those of glycolic acid in Ar matrix in Table 1. The 1619 cm<sup>-1</sup> is ascribed to adsorbed water possibly from decomposition of glycolic acid and/or residual water in the hygroscopic glycolic acid used. Some of the other peaks, such as 1094, 1451 and 2923 cm<sup>-1</sup>, are close to the characteristic HOCH<sub>2</sub>COOH bands measured in argon matrix [11]. Based on the relation between the infrared frequencies and vibrational modes reported previously for glycolic acid [11], the 1094 cm<sup>-1</sup> is assigned to C–O stretching, 1451 cm<sup>-1</sup> to CH<sub>2</sub> scissoring, and 2923 cm<sup>-1</sup> to CH<sub>2</sub> stretching mode, signifying the presence of these chemical groups on the surface. The 1687 and 1731 cm<sup>-1</sup> are due to carbonyl absorptions, but they are red-shifted as compared to the 1774 cm<sup>-1</sup> observed for the isolated HOCH<sub>2</sub>COOH molecules in Ar [11]. The shift of carbonyl band toward lower frequency arises from its interaction with surface Lewis acid sites (Ti<sup>+4</sup> ions) or OH groups through the lone-pair on the oxygen atom, which has also been observed in the adsorption of formic acid and acetic acid on TiO<sub>2</sub> [3,4]. The broad 1575 cm<sup>-1</sup> shoulder cannot be assigned to any functional bands of HOCH<sub>2</sub>COOH, but is indicative of carboxylate formation. Acetate on TiO<sub>2</sub> has infrared positions at ~1440 and 1540 cm<sup>-1</sup> [4]. In fact, the 1426 and 1575 cm<sup>-1</sup> bands are

**Table 1**  
Comparison of the infrared frequencies ( $\text{cm}^{-1}$ ) of glycolic acid and glycolate.

HOCH <sub>2</sub> COOH <sup>a</sup> in Ar matrix	Approx. mode	HOCH <sub>2</sub> COO <sup>b</sup>		HOCH <sub>2</sub> COOH on TiO <sub>2</sub> (35 °C)
		on TiO <sub>2</sub>	on CdS	
3561	str-OHa			
	str-OHc			
2947	str-CH <sub>2</sub>			
2929	str-CH <sub>2</sub>			2923
				2841
1774	str-C=O			1735
				1687
		1611	1573	1575
1452	sci-CH <sub>2</sub>			1451
1439	wag-CH <sub>2</sub> + bend-OHa	1370	1413	1426
1332	bend-OHa + bend-OHc			1329
1265	wag-CH <sub>2</sub> + bend-OHa			1290
1231	tw-CH <sub>2</sub>			1216
1143	bend-OHc + str-COc			
1090	str-COa	1088	1077	1094

<sup>a</sup> Ref. [11]. str: stretching; sci: scissoring; wag: wagging; tw: twisting; bend: bending; a: alcohol; c: carboxyl.

<sup>b</sup> Ref. [6].

similar to those reported for HOCH<sub>2</sub>COO on CdS film (1413 and 1573  $\text{cm}^{-1}$  in Table 1), which are assigned to symmetric and antisymmetric COO stretching modes [6]. The difference of COO antisymmetric and symmetric stretching frequencies of carboxylates ( $\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ ) can reveal their bonding geometries on surfaces and in metal complexes. Using acetate as an example, the  $\Delta$  values for the monodentate, chelating bidentate or bridging forms are much larger than, significantly less than, and close to that of sodium acetate ( $\Delta = 164 \text{ cm}^{-1}$ ), respectively [5]. Therefore, it can be concluded that the carboxylate ( $\nu_{\text{s}}(\text{COO}) = 1426 \text{ cm}^{-1}$ ,  $\nu_{\text{as}}(\text{COO}) = 1575 \text{ cm}^{-1}$ ,  $\Delta = 149 \text{ cm}^{-1}$ ) generated from glycolic acid adsorption on 35 °C TiO<sub>2</sub> is bonded with a bridging form (Scheme 1b). Interestingly, HOCH<sub>2</sub>COO on a TiO<sub>2</sub> film in aqueous glycolic acid has been suggested to exist in Scheme 1d form with the  $\nu(\text{COO})$  at 1370 and 1611  $\text{cm}^{-1}$  (Table 1). According to the  $\Delta$  value (241  $\text{cm}^{-1}$ ), this form can be regarded as monodentate coordination for the COO group. The acetate ligand of Rh(ac)(CO)(PPh<sub>3</sub>)<sub>2</sub> complex also has a monodentate coordination with  $\nu(\text{COO})$  at 1376 and 1604  $\text{cm}^{-1}$  [5]. Since no infrared band near 1370  $\text{cm}^{-1}$  is observed in the 35 °C spectrum, it suggests that the adsorption forms of Schemes 1a and 1d are not the major species if they do exist in the present system.

In the previous studies of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH on TiO<sub>2</sub>, the two alcohols undergo dissociative adsorption at 35 °C, forming the corresponding alkoxys due to O–H bond scission [2,3]. Therefore, the possibility for the formation of the intermediate of Scheme 1c in the present glycolic acid case can not be excluded. This surface species would have carboxyl infrared absorptions due to the C=O and C–O vibrations. Note that interaction of the C=O with surface Ti<sup>4+</sup> ions or OH groups may occur and lead to the red-shifted frequencies (1687 and 1735  $\text{cm}^{-1}$ ) as observed in the 35 °C spectrum. In addition to the dissociative adsorption species of Schemes 1b and 1c, some glycolic acid molecules may remain intact on TiO<sub>2</sub> at 35 °C, because molecularly adsorbed HCOOH and CH<sub>3</sub>OH have been found upon adsorption at this temperature [2,3].

### 3.2. Thermal reaction of glycolic acid on TiO<sub>2</sub>

In order to know the thermal behavior of the glycolic acid adsorbed on TiO<sub>2</sub> at 35 °C, the surface was successively heated to the temperatures as indicated in Fig. 1a for 1 min, with a rate of  $\sim 2 \text{ }^\circ\text{C/s}$ , and then cooled back to  $\sim 35 \text{ }^\circ\text{C}$  after each surface heating. A series of infrared spectra were measured at the indicated higher temperatures and at  $\sim 35 \text{ }^\circ\text{C}$  during the cycles of temperature change. The spectra measured at temperatures larger

than  $\sim 125 \text{ }^\circ\text{C}$  and at wavenumbers smaller than  $\sim 1200 \text{ cm}^{-1}$  were significantly perturbed, with uprising baselines toward lower wavenumber and much poorer S/N ratios. Therefore, the region below  $\sim 1200 \text{ cm}^{-1}$  in the spectra obtained at 150 °C or higher temperatures are not shown in Fig. 1a. The infrared absorption feature in the 75 °C spectrum is basically same as that of 35 °C one. Heating the surface to 100 °C causes an increase in the peak intensity at 1743  $\text{cm}^{-1}$ . This peak continues to grow and shift its frequency to 1752  $\text{cm}^{-1}$ , together with slightly enhanced absorptions at 1210 and 1326  $\text{cm}^{-1}$  in response to the temperature increase to 125 °C. Desorption of water occurs, as evidenced by the reduced 1619  $\text{cm}^{-1}$  peak. The 1752  $\text{cm}^{-1}$  peak belongs to a typical carbonyl stretching mode. In the 175 °C spectrum, the carbonyl peak is located at 1756  $\text{cm}^{-1}$  and its intensity further increases as compared to that in the 125 °C spectrum. Meanwhile, the 1687  $\text{cm}^{-1}$  intensity diminishes and the peak shape for the absorption near 1425  $\text{cm}^{-1}$  also varies. These temperature-dependent results indicate that a chemical transformation of the surface glycolic acid is underway. Further heating to 200 °C gives rise to a small band at  $\sim 1360 \text{ cm}^{-1}$  and a change in the shape for the peaks located between 2800 and 3000  $\text{cm}^{-1}$ , signaling a start of new product formation, i.e. a start of another chemical transformation. The change in the infrared absorption continues with an increase of temperature. At 225 °C, there is a small gaseous CO<sub>2</sub> band at 2349  $\text{cm}^{-1}$ . In the 250 °C spectrum, the major peaks appear at 1360, 1386, 1563, 1756, 2836, 2895, 2933 and 2954  $\text{cm}^{-1}$ , but the carbonyl absorption (1756  $\text{cm}^{-1}$ ) decreases. In accordance with the dissociative adsorption of HCOOH and H<sub>2</sub>CO on TiO<sub>2</sub> [2,12], the set of the peaks at 1360, 1386, 1563, 2895 and 2954  $\text{cm}^{-1}$  reveals the formation of surface formate (HCOO). The 2836 and 2933  $\text{cm}^{-1}$  peaks with a comparable intensity are attributed to methoxy (CH<sub>3</sub>O), which is also generated in the CH<sub>3</sub>OH adsorption on TiO<sub>2</sub> [2]. At 300 °C, the surface is mainly covered with HCOO and CH<sub>3</sub>O and the carbonyl absorption at  $\sim 1750 \text{ cm}^{-1}$  almost disappears. Fig. 1b shows the infrared spectra taken at  $\sim 35 \text{ }^\circ\text{C}$  after the surface heating to the temperatures indicated, which have a better signal-to-noise ratio and spectral baselines. Furthermore, the lower-temperature spectra may exhibit the surface species from readsorption of gaseous products not detected during the heating process. In Fig. 1b, the 2128 and 2208  $\text{cm}^{-1}$  peaks are attributed to adsorbed CO. The 2128  $\text{cm}^{-1}$  absorption starts to appear at 150 °C, indicating that some of the surface glycolic acid molecules decompose and evolve CO into the gas phase. Adsorbed CO<sub>2</sub> (2361  $\text{cm}^{-1}$ ) and carbonate species (1319, 1444 and 1574  $\text{cm}^{-1}$ ) are also found. It is well known that CO and CO<sub>2</sub> can interact with TiO<sub>2</sub> at 35 °C, forming carbonate species on the surface [13,14]. Due to the improvement of the spectral baseline, the C–O stretching band of CH<sub>3</sub>O is detected at 1129  $\text{cm}^{-1}$  in addition to its CH<sub>3</sub> stretching modes of 2837 and 2935  $\text{cm}^{-1}$ .

In Fig. 1a, the enhancement of the carbonyl absorption ( $\sim 1750 \text{ cm}^{-1}$ ) at a temperature approximately larger than 100 °C demonstrates that oxidation of surface glycolic acid occurs. The most probable reaction center for this oxidation process is the HOCH<sub>2</sub> group, therefore adsorption and thermal development of glyoxylic acid (HCOCOOH) on TiO<sub>2</sub> have been investigated. Fig. 2 shows the glyoxylic acid infrared results obtained in the closed cell. The adsorption procedure was carried out by exposing a high temperature-treated TiO<sub>2</sub> surface to the vapor of glyoxylic acid for 5 h at 35 °C, followed by evacuation for several hours. The detailed analysis for the possible surface species generated after glyoxylic acid adsorption on TiO<sub>2</sub> and the infrared assignment will be presented elsewhere. However, the glycolic acid and glyoxylic acid molecules on TiO<sub>2</sub> have a strong resemblance in absorption feature between 1200 and 1800  $\text{cm}^{-1}$  at higher temperatures, for example at 150 °C, pointing out the oxidation of the surface glycolic acid to glyoxylic acid. Due to the presence of carboxylate group (1420

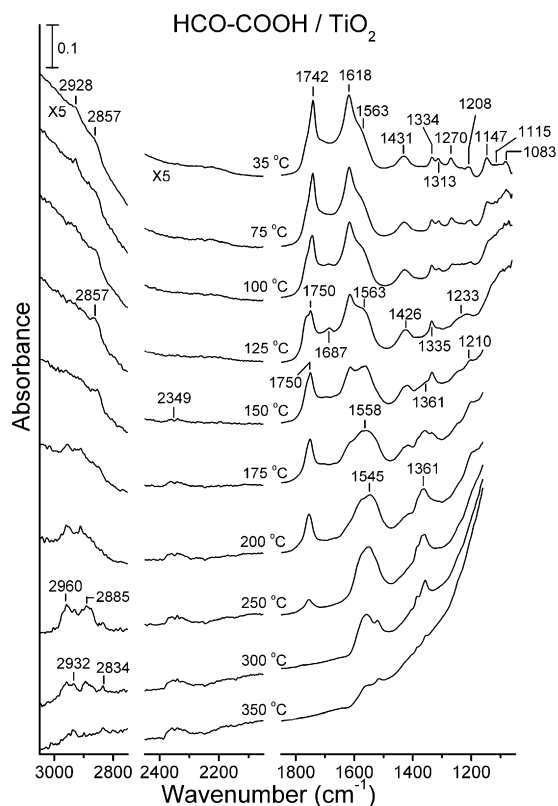


Fig. 2. Infrared spectra taken at the indicated temperatures after adsorption of glyoxylic acid on  $\text{TiO}_2$  at 35 °C.

and  $1563\text{ cm}^{-1}$ ) and carbonyl group ( $\sim 1750\text{ cm}^{-1}$ ) in the 150 °C spectrum of Fig. 1a, glycolate ( $\text{HCOCOO}$ ) can be one of the surface species at this temperature. In Fig. 1a,  $\text{CH}_3\text{O}$  and  $\text{HCOO}$  appear at 200 °C or higher temperatures.  $\text{CH}_2\text{O}$  on  $\text{TiO}_2$  has been reported to undergo the Cannizzaro reaction, via dioxymethylene ( $\text{OCH}_2\text{O}$ ) to form  $\text{CH}_3\text{O}$  and  $\text{HCOO}$  simultaneously, and oxidation to form  $\text{HCOO}$  [12]. For the surface species of glycolic acid, such as the structures of Schemes 1b and 1c, rupture of the C–C bond can generate  $\text{OCH}_2$  entity and lead to the formation of dioxymethylene on  $\text{TiO}_2$ . In Fig. 2, decomposition of glyoxylic acid on  $\text{TiO}_2$  also can produce  $\text{HCOO}$  and  $\text{CH}_3\text{O}$ , with the characteristic peaks at  $\sim 1360$ ,  $1550$ ,  $2830$  and  $2930\text{ cm}^{-1}$  in the 250 and 300 °C spectra, but the peak intensities of  $\text{CH}_3\text{O}$  relative to those of  $\text{HCOO}$  are much smaller, as compared to the case of glycolic acid. In brief summary, the spectral feature varying with temperature shown in Fig. 1a demonstrates two thermal reaction pathways for the surface species of glycolic acid on  $\text{TiO}_2$ , i.e. oxidation of the  $\text{OCH}_2$  group to carbonyl, which starts at ca. 100 °C, and C–C bond scission, which starts at ca. 200 °C.

Unimolecular decomposition of gaseous glycolic acid molecules in the temperature range 280.4–389.4 °C and pressure range 30.5–201.6 Torr has been investigated previously [15]. A cyclic transition state is proposed for the formation of the products of  $\text{CH}_2\text{O}$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  and the preexponential factor and activation energy are determined to be  $10^{14}\text{ s}^{-1}$  and  $209\text{ kJ mol}^{-1}$ , respectively [15]. However, the activation energy required for the thermal decomposition of glycolic acid in the gas phase is much larger than that on  $\text{TiO}_2$ . For example in Fig. 1, the activation energy for the formation of the carbonyl group ( $\sim 1750\text{ cm}^{-1}$ ) can be roughly estimated to be  $84\text{ kJ mol}^{-1}$  with the Redhead equation used in temperature-programmed desorption studies [16], assuming a first-order kinetics with a preexponential factor of  $10^{13}\text{ s}^{-1}$  and a maximum formation rate at 150 °C. Similarly, the formation of  $\text{CH}_3\text{O}$  and  $\text{HCOO}$  can also be determined to be  $111\text{ kJ mol}^{-1}$ , assuming a maximum

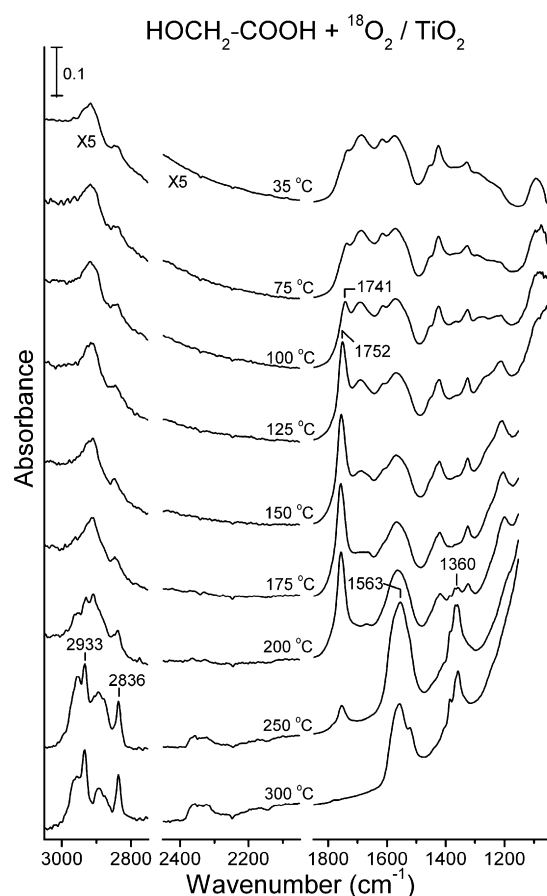


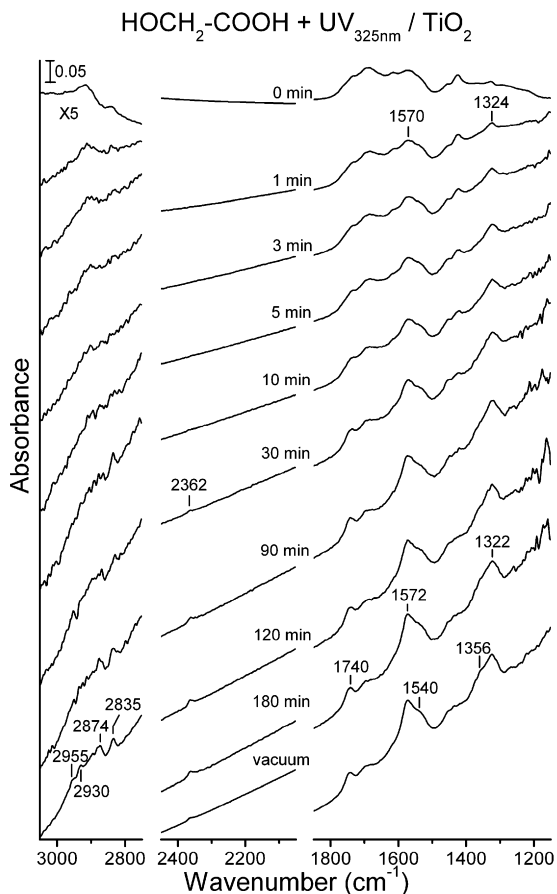
Fig. 3. Infrared spectra taken at the indicated temperatures in  $^{18}\text{O}_2$  after glycolic acid adsorption on  $\text{TiO}_2$  at 35 °C.

rate at 250 °C. The reduced activation energies show the catalytic behavior for the thermal decomposition of glycolic acid on  $\text{TiO}_2$ . To further check the reaction type for the thermal decomposition of glycolic acid on  $\text{TiO}_2$ , its spectral change with temperature has been investigated in  $^{18}\text{O}_2$  and the infrared result is displayed in Fig. 3. The preparation process for the adsorption of glycolic acid on 35 °C  $\text{TiO}_2$  was same as that for Fig. 1, but the heating was carried out in 10 Torr of  $^{18}\text{O}_2$ . The comparison between Fig. 3 and Fig. 1a reveals that the temperature-dependent spectral changes in both cases are very similar. Note the resemblance in the temperature ranges for the formation of the carbonyl group ( $\sim 1750\text{ cm}^{-1}$ ),  $\text{CH}_3\text{O}$  ( $\sim 2835$  and  $2935\text{ cm}^{-1}$ ) and  $\text{HCOO}$  ( $\sim 1360$  and  $1560\text{ cm}^{-1}$ ) in the presence and absence of  $\text{O}_2$ . No red-shift is observed for the frequencies of the carbonyl and  $\text{HCOO}$  in  $^{18}\text{O}_2$ , indicating no  $^{18}\text{O}$  atom is incorporated into these groups. This finding suggests that  $\text{O}_2$  neither changes the thermal decomposition pathways of the surface glycolic acid nor increases its reaction rate.

### 3.3. Photocatalytic degradation of glycolic acid on $\text{TiO}_2$ in the absence of $\text{O}_2$

Fig. 4 shows the infrared spectra measured before and after the indicated times during photoirradiation of glycolic acid on  $\text{TiO}_2$  at 325 nm in the closed cell. In the 1-min spectrum, the absorptions at  $1324$  and  $1570\text{ cm}^{-1}$  are enhanced, which are attributed to adsorbed  $\text{CO}_3$ . These two bands continue to grow with an increase of irradiation time. Adsorbed  $\text{CO}_2$  is produced, with the characteristic peak at  $2362\text{ cm}^{-1}$ . After the photon exposure for 180 min, adsorbed  $\text{HCOO}$  ( $1356$ ,  $1540$ ,  $2874$  and  $2955\text{ cm}^{-1}$ ) and  $\text{CH}_3\text{O}$  ( $2835$  and  $2930\text{ cm}^{-1}$ ) are also found. In the photooxidation of formic acid on  $\text{TiO}_2$ ,  $\text{CO}_2$  has been detected as the product [17]. For acetic



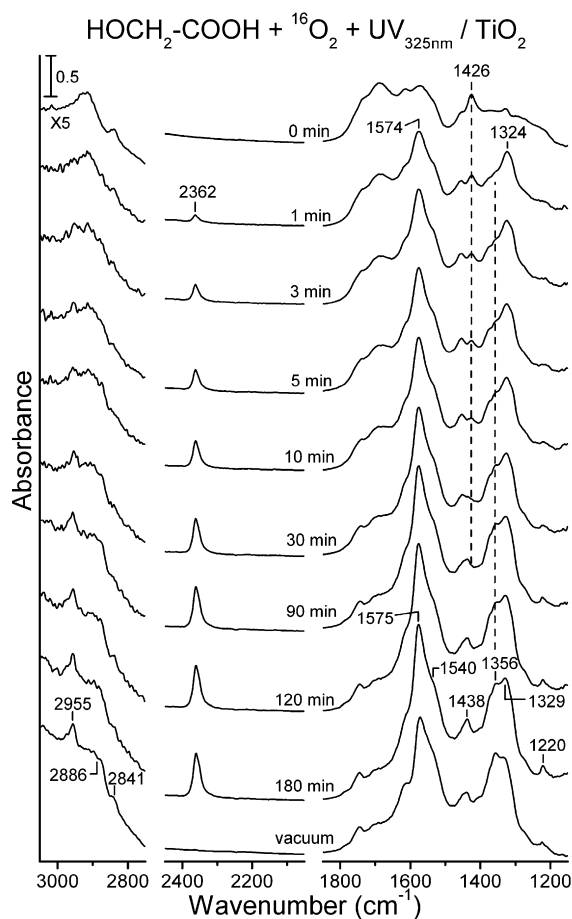


**Fig. 4.** Infrared spectra taken before and after the indicated photoirradiation times for glycolic acid adsorbed on  $\text{TiO}_2$ . The last spectrum was taken in a vacuum after the 180-min photoillumination. The region of  $2750\text{--}3050\text{ cm}^{-1}$  has been multiplied by a factor of 5.

acid on  $\text{TiO}_2$ , photoirradiation induces the formation of  $\text{CH}_4$  in addition to  $\text{CO}_2$  [4]. The photochemical processes of these two surface carboxylic acids clearly indicate the destiny of the  $\text{COOH}$  and  $\text{COO}$  groups, decomposing into  $\text{CO}_2$ . In the present case of surface glycolic acid, the photogenerated  $\text{CO}_3$  and  $\text{CO}_2$  most likely originate from the decomposition of the carboxyl and/or carboxylate groups. Furthermore, the formation of  $\text{CH}_3\text{O}$  and  $\text{HCOO}$  is due to the  $\text{OCH}_2$  entity generated after the  $\text{C}\text{--}\text{C}$  bond breakage of the surface glycolic acid subjected to the UV illumination.

### 3.4. Photocatalytic degradation of glycolic acid on $\text{TiO}_2$ in the presence of $\text{O}_2$

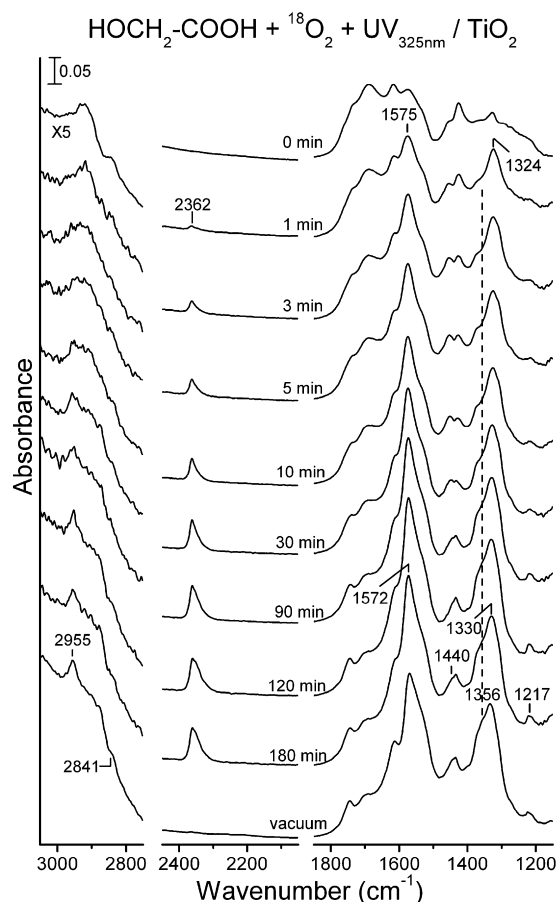
Fig. 5 shows the infrared spectra measured before and after the indicated times during photoirradiation of glycolic acid on  $\text{TiO}_2$  initially in 10 Torr of  $^{16}\text{O}_2$  in the closed cell. The effect of dioxygen can be revealed in comparison to the result of Fig. 4. To further explore the roles of dioxygen and the lattice oxygen play in the degradation of glycolic acid on  $\text{TiO}_2$ , the photoirradiation has been carried out in  $^{18}\text{O}_2$  as well and the infrared measurements are shown in Fig. 6.  $\text{CO}_3$  ( $1324$  and  $1574\text{ cm}^{-1}$  in the 1-min spectrum of Fig. 5) is rapidly generated upon photoillumination and its amount is much larger than that produced after the same time without  $\text{O}_2$ . In addition,  $\text{CO}_2$  peak at  $2362\text{ cm}^{-1}$  is detected. These two species build up, as indicated by the monotonic increase in the peak intensities, when the photoirradiation continues. Other carbonate species appear at  $1220$  and  $1438\text{ cm}^{-1}$ . Formate peaks at  $1356$ ,  $1540$ ,  $2886$  and  $2955\text{ cm}^{-1}$  are also detected and stronger than those observed in the absence of  $\text{O}_2$ . However,  $\text{CH}_3\text{O}$  forma-



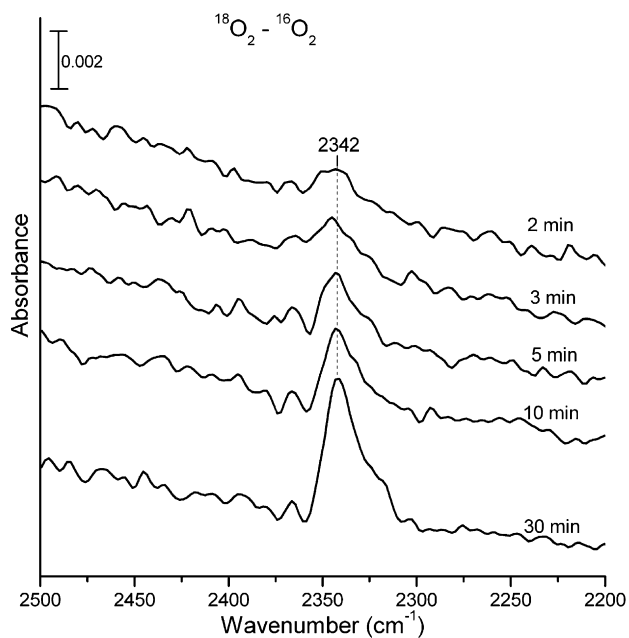
**Fig. 5.** Infrared spectra taken before and after the indicated photoirradiation times for glycolic acid adsorbed on  $\text{TiO}_2$ , initially in 10 Torr of  $^{16}\text{O}_2$  in a closed cell. The last spectrum was taken in a vacuum after the 180-min photoillumination. The region of  $2750\text{--}3050\text{ cm}^{-1}$  has been multiplied by a factor of 5.

tion is suppressed in terms of the lack of the peaks at  $\sim 2830$  and  $2930\text{ cm}^{-1}$ .  $\text{O}_2$  apparently accelerates the photooxidation of the surface glycolic acid to form  $\text{CO}_2$ , carbonate species and  $\text{HCOO}$ . In  $^{18}\text{O}_2$ , the surface glycolic acid should have the same photochemistry as in  $^{16}\text{O}_2$ , including the types of products and their formation times and amounts, but, through the comparison between Figs. 5 and 6 in terms of the peak shifts in wavenumber, the participation of dioxygen in the photoproduct formation can be examined. First of all, the intensity ratios of  $\sim 1356\text{ cm}^{-1}$  ( $\text{HCOO}$ ) to  $\sim 1325\text{ cm}^{-1}$  ( $\text{CO}_3$ ) for the spectra measured in  $^{18}\text{O}_2$  are always smaller than those measured in  $^{16}\text{O}_2$  after the same irradiation times. This result clearly indicates that  $^{18}\text{O}$  is incorporated into the  $\text{HCOO}$  formation, leading to the  $\text{COO}$  symmetric stretching vibration being shifted toward lower frequency and overlapped with the  $\text{CO}_3$  absorption. For comparison purpose, the frequencies of symmetric stretching of  $\text{C}^{16}\text{O}^{16}\text{O}$  for  $\text{H}^{13}\text{C}^{16}\text{O}^{16}\text{ONa}$ ,  $\text{C}^{16}\text{O}^{18}\text{O}$  for  $\text{HC}^{16}\text{O}^{18}\text{ONa}$ , and  $\text{C}^{18}\text{O}^{18}\text{O}$  for  $\text{HC}^{18}\text{O}^{18}\text{ONa}$  have been reported to be  $1340$ ,  $1315$ , and  $1297\text{ cm}^{-1}$ , respectively [18]. In Fig. 6, the  $\text{CO}_2$  peaks still appear at  $\sim 2360\text{ cm}^{-1}$  ( $\text{C}^{16}\text{O}^{16}\text{O}$ ), but with wider widths. Fig. 7 shows the differences between the adsorbed  $\text{CO}_2$  spectra obtained in  $^{18}\text{O}_2$  and  $^{16}\text{O}_2$  after 2, 3, 5, 10 and 30 min photoirradiation. Apparently,  $^{18}\text{O}$ -incorporated carbon dioxide is generated with the peak at  $2242\text{ cm}^{-1}$  in addition to  $\text{C}^{16}\text{O}_2$ .

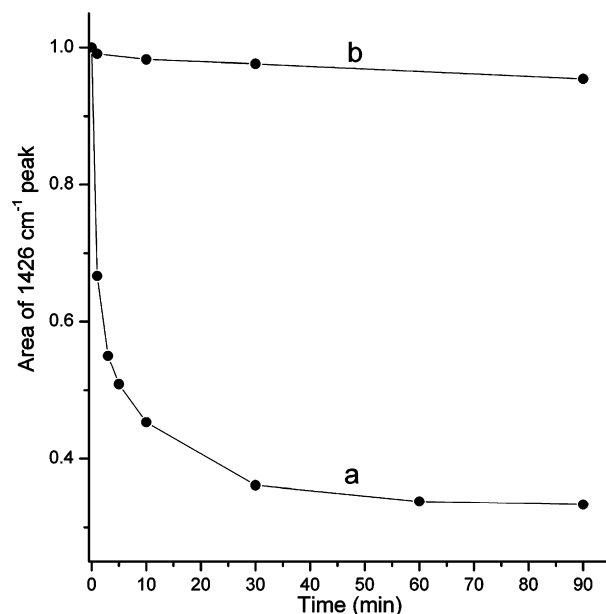
As  $\text{TiO}_2$  absorbs UV light, electron–hole pairs are generated inside the particles. The hole species can diffuse to the surfaces and initiate oxidation processes for adsorbed molecules. One of the functions of  $\text{O}_2$  reported in the previous  $\text{TiO}_2$  studies is to capture the photogenerated electrons, elongating the lifetime of the



**Fig. 6.** Infrared spectra taken before and after the indicated photoirradiation times for glycolic acid adsorbed on TiO<sub>2</sub>, initially in 10 Torr of <sup>18</sup>O<sub>2</sub> in a closed cell. The last spectrum was taken in a vacuum after the 180-min photoillumination. The region of 2750–3050 cm<sup>-1</sup> has been multiplied by a factor of 5.



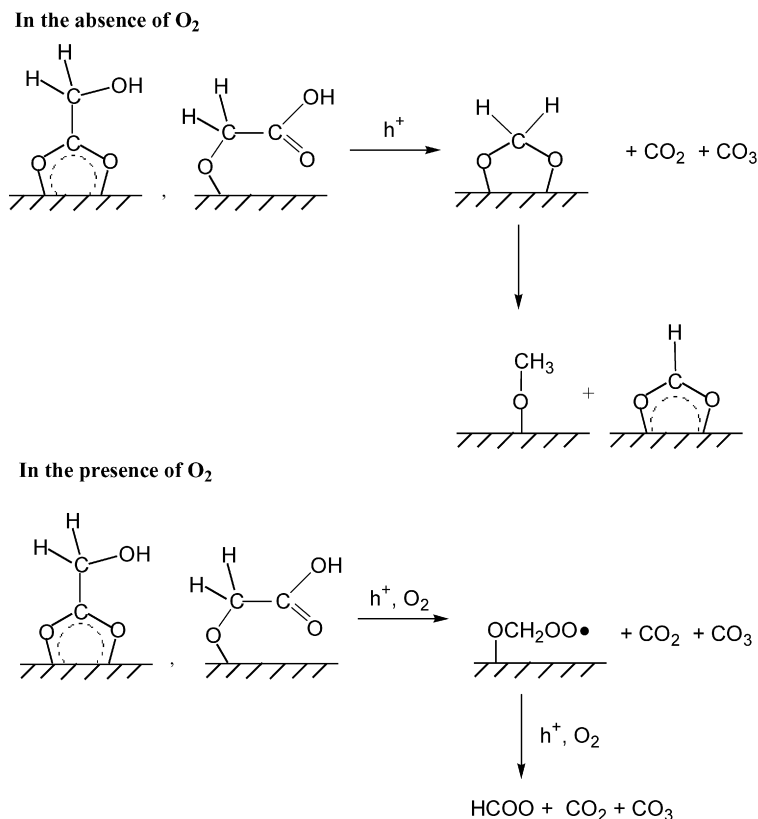
**Fig. 7.** Difference spectra of CO<sub>2</sub> measured in <sup>18</sup>O<sub>2</sub> and <sup>16</sup>O<sub>2</sub> after 2, 3, 5, 10 and 30-min photoirradiation of glycolic acid on TiO<sub>2</sub>. Since the intensities of C<sup>16</sup>O<sub>2</sub> (2262 cm<sup>-1</sup>) measured in <sup>18</sup>O<sub>2</sub> and <sup>16</sup>O<sub>2</sub> are not exactly the same, the <sup>16</sup>O<sub>2</sub> spectra of 2, 3, 5, 10 and 30 min have been multiplied by a factor of 0.52, 0.55, 0.62, 0.69 and 0.70, respectively, in the subtraction processes.



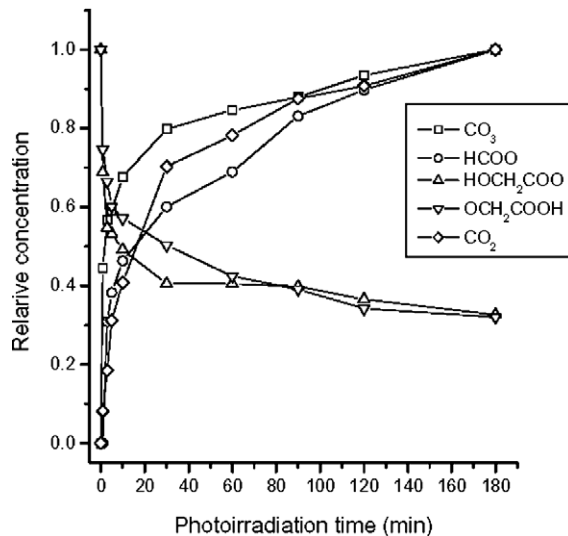
**Fig. 8.** Comparison of the time-dependent integrated intensities of the 1426 cm<sup>-1</sup> peak representing glycolic acid on TiO<sub>2</sub> subjected to UV exposure in O<sub>2</sub> (a) or thermal heating at 50 °C (b).

holes and thus increasing the photooxidation efficiency. The initial photoreaction process of the surface glycolic acid after hole capture involves C–C bond rupture that produces CO<sub>2</sub> and/or CO<sub>3</sub> from decomposition of the COOH and/or COO groups. The OCH<sub>2</sub> derived from the C–C bond scission may become a OCH<sub>2</sub>O species in the absence of O<sub>2</sub>, which undergoes the Cannizzaro reaction to form CH<sub>3</sub>O and HCOO and/or oxidation to form HCOO. In contrast, the OCH<sub>2</sub> may become a radical species (OCH<sub>2</sub>·), which can recombine with O<sub>2</sub>. The resulting OCH<sub>2</sub>OO· finally decomposes on the surface, forming CO<sub>2</sub>, CO<sub>3</sub> and HCOO that contain the O from dioxygen. The suggested mechanism for the photocatalysis of glycolic acid on TiO<sub>2</sub> is shown in Scheme 2. Since it was found that the surface temperature was increased to ~50 °C during photoirradiation of the TiO<sub>2</sub> in O<sub>2</sub>, a thermal control experiment was carried out with the same condition as that for Fig. 5, but holding the temperature at 50 °C for 180 min instead of photon exposure. Infrared measurements (supporting Fig. S1) show that, after 180-min surface heating at 50 °C, only a peak at 1743 cm<sup>-1</sup> is enhanced without the photoproducts being observed. Fig. 8 makes a comparison for the time-dependent integrated intensities of the 1426 cm<sup>-1</sup> peak used to represent glycolic acid on TiO<sub>2</sub> subjected to UV exposure in <sup>16</sup>O<sub>2</sub> (Fig. 5) or thermal heating at 50 °C without photoillumination (supporting Fig. S1), showing photocatalytic decomposition of the surface glycolic acid molecules. Note that the OH and COOH groups of glycolic acid are transparent to the light used in the present photoreaction studies [19]. It is also interesting to note that photocatalysis of glyoxylic acid, malonic acid and succinic acid over TiO<sub>2</sub> in water generates oxalate on the surface as an intermediate [20–22], but this species is not observed in our case.

Fig. 9 shows the relative amounts of the reactant (Schemes 1b and 1c), intermediate (HCOO) and products (CO<sub>2</sub> and CO<sub>3</sub>) involved in the photodecomposition of glycolic acid on TiO<sub>2</sub> in the presence of O<sub>2</sub> as a function of photoirradiation time. The relative amounts of Scheme 1b, HCOO, CO<sub>2</sub> and CO<sub>3</sub> are calculated from the areas of their characteristic peaks at ~1557, 1562, 2362 and 1578 cm<sup>-1</sup>, respectively. The sum of the peak areas of ~1680 and 1737 cm<sup>-1</sup> is used to represent the amount of Scheme 1c structure. Since the infrared absorptions of these surface species overlap considerably, a curve-fitting procedure is applied to the spectra of HCOCOOH (150 °C spectrum in Fig. 2) and HCOO and CO<sub>3</sub> (supporting Fig. S2)



**Scheme 2.** Proposed mechanism for the photodecomposition of glycolic acid on TiO<sub>2</sub> in the absence and presence of O<sub>2</sub>.



**Fig. 9.** Relative amounts as a function of photoirradiation time for the reactant, intermediate and products involved in the photodecomposition of glycolic acid in the presence of O<sub>2</sub>. The maximum amount of each species is scale to 1.

and the spectra obtained during the photoirradiation. In the fitting process, the deconvoluted peaks are made of 30% Lorentz + 70% Gauss and their positions and widths are allowed to be varied by a few wavenumbers to obtain a best fit. In Fig. 9, the surface glycolic acid is found to be decreased in concentration rapidly in the initial photoirradiation stage and then declines gradually, being consistent with the growing trend of HCOO, CO<sub>2</sub> and CO<sub>3</sub> formed from the photodecomposition of glycolic acid. Since the glycolic acid photodecomposition is initiated by holes, its rate must also be controlled by the rate with which the photogenerated charge carriers reach the TiO<sub>2</sub> surface. Photooxidation efficiency can be limited by

the increase of electron–hole recombination due to accumulation of electrons on the TiO<sub>2</sub> surface after prolonged photoillumination [23].

#### 4. Conclusions

On TiO<sub>2</sub>, glycolic acid can interact with the surface via OH or COOH group, forming two dissociative structures of OCH<sub>2</sub>COOH and HOCH<sub>2</sub>COO at 35 °C. At a temperature larger than ~100 °C, the OCH<sub>2</sub> group of the surface glycolic acid is oxidized to carbonyl. C–C bond scission of the glycolic acid occurs to form CH<sub>3</sub>O and HCOO at higher temperatures (≥200 °C). Upon UV irradiation of glycolic acid on TiO<sub>2</sub>, it decomposes into CO<sub>2</sub>, CO<sub>3</sub>, CH<sub>3</sub>O and HCOO. O<sub>2</sub> accelerates the photooxidation of glycolic acid to form CO<sub>2</sub>, CO<sub>3</sub> and HCOO and also takes part in their formation.

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#### Supplementary material

The online version of this article contains additional supplementary material.

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