FTIR study of adsorption and photoreactions of acetic acid on TiO₂

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Fourier-transformed infrared spectroscopy has been employed to study the adsorption and photoreactions of acetic acid on powdered TiO₂. Molecular acetic acid and acetate groups are present on TiO₂ following acetic acid adsorption at 35 °C. Acetic acid is adsorbed via hydrogen bonding or Lewis acid–base interaction and is removed at 170 °C, leaving acetate on the surface. The adsorbed acetate groups adopt a bidentate coordination. CO₂(g) is detected as a photoproduct in the UV irradiation of surface acetate. In the presence of water, some surface acetate is converted into acetic acid, and, in this case, both CO₂(g) and CH₃(g) are observed in the photoillumination. However, effect of water on the reaction rate for CO₂(g) and CH₃(g) formation is not significant. O₂ can increase the photodecomposition rate of acetic acid on TiO₂, and in addition to CH₄(g) and CO₂(g), oxygenated compounds such as CH₃OH(g), CH₂O(g) and HCOOCH₃(g) are detected. It is likely that these species are generated due to photoreactions involving photoelectrons and O₂, attacking adsorbed acetic acid molecules instead of attacking acetate groups.

Introduction

TiO₂ is a wide band gap semiconductor with band edge positions suitable for photocatalytic reactions of a large number of organic molecules. Photons with energy larger than the band gap can excite the electrons from the valence band to the conduction band, forming electron–hole pairs as photoreaction initiators.¹⁻² Photoreactions of acetic acid induced by TiO₂ or platinumized TiO₂ have been studied previously using EPR,³⁻⁴ gas–liquid chromatography,⁵⁻⁹ and mass spectrometry.¹⁰ These investigations were carried out with the catalysts either in aqueous solutions of CH₃COOH or CH₃COO⁻/CH₃COO⁻ mixtures or in contact with acetic acid vapor.⁹,¹⁰ It was found by Bard et al.⁷,⁸ that, in aqueous reaction systems of acetic acid or acetic acid/acetate with TiO₂ or Pt/TiO₂, in the absence of O₂, CO₂(g) and CH₃(g) were the major products with minor amounts of C₂H₄(g) and H₂(g). When CH₃COOD (98 atom%) was used to react with Pt/TiO₂, the generated methane was composed of 80% CH₃D(g) and 20% CH₄(g). Meanwhile, CH₃COOH photodecomposed ~1.9 times as fast as CH₃COOD, showing an isotope effect on the reaction rate. In addition to the gaseous products of CO₂(g), CH₄(g), CH₃(g) and H₂(g), photodecomposition of acetic acid also generated insignificant amounts of oxygenated compounds in aqueous medium.⁷⁻⁸ Bard et al. proposed a mechanism for the observed gaseous products of acetic acid photodecomposition:⁷,⁸

\[
\begin{align*}
\text{h}^+ + \text{CH₃OO}^- &\rightarrow \text{CH₃}^- + \text{CO}_2 \quad (1) \\
e^- + \text{CH₃COOH} &\rightarrow \text{H(ads)} + \text{CH₃COO}^- \quad (2) \\
e^- + \text{CH₃}^- + \text{CH₃COOH} &\rightarrow \text{CH₄} + \text{CH₃COO}^- \quad (3) \\
2\text{CH₃}^- &\rightarrow \text{C₂H₆} \quad (4) \\
2\text{H(ads)} &\rightarrow \text{H₂} \quad (5) \\
\text{CH₃}^- + \text{H(ads)} &\rightarrow \text{CH₄} \quad (6)
\end{align*}
\]

An alternative possible pathway for the formation of CH₄ was also proposed, i.e.,

\[
e^- + (\text{CH₃})^-\text{(ads)} \rightarrow (\text{CH₃})^-\text{(ads)} \quad (7)
\]

In the in situ EPR study of Pt/TiO₂ suspended in acetic acid aqueous solution, Nosaka et al. observed the formation of CH₃ and CH₃COOH radicals and proposed the following mechanism for their formation:⁵

\[
\begin{align*}
\text{h}^+ + \text{CH₃COOH} &\rightarrow \text{CH₃}^- + \text{CO}_2 + \text{H}^+ \quad (9) \\
\text{OH}^- + \text{CH₃COOH} &\rightarrow \text{CH₃}^- + \text{CO}_2 + \text{H}_2\text{O} \quad (10) \\
\text{h}^+ + \text{H}_2\text{O} &\rightarrow \text{OH}^- + \text{H}^+ \quad (11) \\
\text{OH}^- + \text{CH₃COOH} &\rightarrow \text{CH₃COOH} + \text{H}_2\text{O} \quad (12)
\end{align*}
\]

Sclafani et al. investigated the photodecomposition of flowing acetic acid vapor over a series of pure insulators and semiconductor oxides.⁹ The main products detected by gas chromatography were CO₂(g) and CH₄(g), with a trace of C₂H₄(g). CO₂(g) formation was much faster than CH₄(g). Muggli et al. studied photocatalytic decomposition of a monolayer of acetic acid on TiO₂ in He flow using mass spectrometry.¹⁰ They also observed the formation of CO₂(g), CH₄(g) and C₂H₆(g) and suggested the following two parallel pathways during transient experiments for acetic acid photodecomposition:

\[
\begin{align*}
\text{CH₃COOH(ads)} &\rightarrow \text{CO}_2 + \text{CH₄} \quad (13) \\
2\text{CH₃COOH(ads)} + \text{O(l)} &\rightarrow \text{C₂H₆} + 2\text{CO}_2 + \text{H}_2\text{O(ads)} \quad (14)
\end{align*}
\]

Eqn. (14) involves TiO₂ lattice oxygen O(l). Unfortunately, in these previous reports the subject of surface adsorption of acetic acid and its relation to photoreactivity were hardly discussed. Without knowing the surface adsorption, the adsorbates involved in photoreactions may not be exactly assigned. For example, Bard et al. proposed the acetate ion as hole acceptor in eqn. (1), while Nosaka et al. proposed acetic acid as hole acceptor in eqn. (9). In the present paper, we first studied the adsorption of acetic acid on TiO₂ using Fourier-transformed infrared spectroscopy. It was found that acetic acid was adsorbed both molecularly and dissociately on TiO₂ at 35 °C. Adsorbed acetic acid was removed from surface by briefly annealing the TiO₂ at 170 °C, leaving...
the surface covered with acetate groups. We then studied the photoreaction of surface acetate and the effect of H₂O addition to the reaction system to mimic the reaction in the solution phase. The investigation was further extended to TiO₂ surface covered with both acetic acid and acetate groups to differentiate their contributions to the reaction products. Finally, we investigated the effect of the addition of O₂.

Experimental

The sample preparation of TiO₂ powder supported on a tungsten fine mesh (~6 cm²) has been described previously. In brief, TiO₂ powder (Degussa P25, ~50 m² g⁻¹, anatase 70%, rutile 30%) was dispersed in a water/acetone solution to form a uniform mixture which was then sprayed onto a tungsten mesh. After that, the TiO₂ sample was mounted inside the IR cell for simultaneous photochemistry and FTIR spectroscopy. The IR cell, with two CaF₂ windows for IR transmission down to 1000 cm⁻¹, was connected to a gas manifold which was pumped by a 60 L s⁻¹ turbomolecular pump with a base pressure of ~1 x 10⁻⁷ Torr. The TiO₂ sample in the cell was heated to 450 °C under vacuum for 24 h by resistive heating. The temperature of the TiO₂ sample was measured by a K-type thermocouple spotwelded on the tungsten mesh. Before each run of the experiment, the TiO₂ sample was heated to 450 °C in vacuum for 2 h. After the heating, 10 Torr O₂ was introduced into the cell as the sample was cooled to 70 °C. When the TiO₂ temperature reached 35 °C the cell was evacuated for gas dosing. The TiO₂ surface after the above treatment still possessed residual isolated hydroxy groups. The O₂ (99.98%, Matheson) was used as received in a compressed state. CH₃COOH (99.9%, Fisher) was purified by several cycles of freeze-pump-thaw prior to introduction into the infrared cell. The pressure was monitored with a Baratron capacitance manometer and an ion gauge. In the photochemistry study, both the UV and IR beams were set 45° to the normal of the TiO₂ sample. The UV light source used was a combination of a Hg arc lamp (Oriel Corp) operated at 350 W, a water filter, and a band pass filter with a band width of ~100 nm centered at ~320 nm (Oriel 51650). The UV absorption of CH₃COOH for the wavelength used in the present study was negligible. IR spectra were obtained with a 4 cm⁻¹ resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with CO₂-free dry air. The spectra presented here have been ratioed against a clean surface providing the metal-oxide CH₃COOH characteristic bands at 1027, 1049, 1324, 1338, 1454, 1535 and 2935 cm⁻¹. The peaks of 1675 and 1736 cm⁻¹ are characteristic absorptions of carbonyl stretching. In addition, the peaks at 1296 and 1415 cm⁻¹ are close to the acetic acid absorptions in the gas phase. These observations indicate that acetic acid is molecularly adsorbed on the surface at temperatures less than 170 °C. The weak band at 1736 cm⁻¹ reveals that some of the surface acetic acid is adsorbed with hydrogen bonding, as suggested by the similar carbonyl stretching frequency of dimetric acid in the gas phase. This hydrogen bonding may come from the interaction of a adsorbed acetic acid with surface OH groups or with another acetic acid molecule. The other carbonyl peak, at 1675 cm⁻¹, is ~60 cm⁻¹ lower than that of the adsorbed acetic acid with hydrogen bonding and is attributed to acetic acid bonded at Lewis acid sites (Ti⁴⁺) through the oxygen lone-pair electrons of the carbonyl group. The same carbonyl stretching frequency has been reported for methyl formate adsorbed on TiO₂. After removal of the surface acetic acid, the 170 °C spectrum in Fig. 1(a) shows infrared bands at 1027, 1049, 1324, 1338, 1454, 1535 and 2935 cm⁻¹. These are assigned to adsorbed acetate groups, as supported by the similar formic acid decomposition process on TiO₂. The peaks at 1027 and 1049 cm⁻¹ are related to CH₃ rocking and C=C stretching, 1324 and 1338 cm⁻¹ to CH₂ bending, 1454 and 1535 cm⁻¹ to –COO– stretching, and 2935 cm⁻¹ to CH₂ stretching. In particular, the 81 cm⁻¹ difference between the –COO– antisymmetric and symmetric stretching frequencies of 1535 and 1454 cm⁻¹ reveals that the acetate group is bonded by a chelating bidentate configuration, as

Results and discussion

Fig. 1(a) shows the IR spectra of a clean TiO₂ surface in contact with ~2 Torr of CH₃COOH at 35 °C, followed by evacuation and brief annealing at the indicated temperatures. As marked in the spectrum of in contact with ~2 Torr CH₃COOH, absorption bands appear at 1027, 1047, 1184, 1293, 1340, 1423, 1452, 1535, 1674, 1732, 1779, 1798, 2569, 2636, 2698, 2939, 3025, 3074, 3128 and 3578 cm⁻¹. Since the gas phase CH₃COOH is present in the infrared cell, to find its contribution to the spectrum in Fig. 1(a), infrared absorptions of gaseous acetic acid, taken under the same optical conditions, are shown in Fig. 1(b). Acetic acid molecules present in the gas phase show the monomeric form with characteristic bands at 1176, 1780, 1795 and 3581 cm⁻¹ as well as the dimeric form with characteristic bands at 1294, 1426 and 1733 cm⁻¹. The monomer/dimer ratio is concentration dependent. The dimer is held together by hydrogen bonding between two monomers, resulting in a lower carbonyl stretching frequency (1733 cm⁻¹) than those of monomer (1780, 1795 cm⁻¹). In Fig. 1(a), the gaseous acetic acid is removed from the infrared cell by evacuation. The remaining peaks at 1027, 1049, 1296, 1341, 1415, 1453, 1535, 1675, 1736 and 2936 cm⁻¹ are due to adsorbed surface species. The peaks at 1296, 1415, 1675 and 1736 cm⁻¹ decrease in intensity with increasing surface temperature under vacuum and disappear at 170 °C, suggesting that they originate from the same adsorbed compound. The peaks of 1675 and 1736 cm⁻¹ are characteristic absorptions of carbonyl stretching. In addition, the peaks at 1296 and 1415 cm⁻¹ are close to the acetic acid absorptions in the gas phase. These observations indicate that acetic acid is molecularly adsorbed on the surface at temperatures less than 170 °C. The weak band at 1736 cm⁻¹ reveals that some of the surface acetic acid is adsorbed with hydrogen bonding, as suggested by the similar carbonyl stretching frequency of dimetric acid in the gas phase. This hydrogen bonding may come from the interaction of a adsorbed acetic acid with surface OH groups or with another acetic acid molecule. The other carbonyl peak, at 1675 cm⁻¹, is ~60 cm⁻¹ lower than that of the adsorbed acetic acid with hydrogen bonding and is attributed to acetic acid bonded at Lewis acid sites (Ti⁴⁺) through the oxygen lone-pair electrons of the carbonyl group. The same carbonyl stretching frequency has been reported for methyl formate adsorbed on TiO₂. After removal of the surface acetic acid, the 170 °C spectrum in Fig. 1(a) shows infrared bands at 1027, 1049, 1324, 1338, 1454, 1535 and 2935 cm⁻¹. These are assigned to adsorbed acetate groups, as supported by the similar formic acid decomposition process on TiO₂. The peaks at 1027 and 1049 cm⁻¹ are related to CH₃ rocking and C=C stretching, 1324 and 1338 cm⁻¹ to CH₂ bending, 1454 and 1535 cm⁻¹ to –COO– stretching, and 2935 cm⁻¹ to CH₂ stretching. In particular, the 81 cm⁻¹ difference between the –COO– antisymmetric and symmetric stretching frequencies of 1535 and 1454 cm⁻¹ reveals that the acetate group is bonded by a chelating bidentate configuration, as
shown in Scheme 1. CH$_3$COO(a) is used to represent the surface acetate, showing only its adsorbed state and chemical formula, but not its electric charge.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{O} \quad \text{C} \quad \text{O} \\
\text{O} \quad \text{Ti} \quad \text{O} \\
\end{array}
\]

Scheme 1

**Photochemistry of CH$_3$COO(a)**

Fig. 2 shows the IR spectra taken both before and after the indicated times during photoirradiation of CH$_3$COO(a) in a closed cell. The only product detected by our spectrometer is CO$_2$(g) at 2349 cm$^{-1}$. The solid curve with data points in Fig. 3 shows the relative CO$_2$(g) concentration as a function of UV irradiation time. From the slope of the curve in Fig. 3, the photoreaction rate is higher in the initial stages and becomes smaller for longer illumination times. The two dashed curves in Fig. 3 are simulated CO$_2$ production curves with first-order kinetics, but different rate constants. As expected, the experimental data do not follow first-order reaction kinetics, since the surface is inhomogeneous. The slower reaction rate for elongated UV irradiation in the experimental curve partially results from the decrease of CH$_3$COO(a) concentration with light exposure. Most importantly, it reflects retarded efficiency of photogenerated holes to initiate the surface reaction with photoirradiation time. The decrease of reaction rate with illumination is likely to be due to electron accumulation on the surface, which increases the recombination of electron-hole pairs.

Photoreaction of CH$_3$COO(a) in 10 Torr of O$_2$ was also investigated. It is found that the observed CO$_2$(g) formation after 180 min irradiation is ~3 times that without O$_2$. No other products were detected.

**Photochemistry of CH$_3$COO(a) in the presence of water**

The effect of water on the CH$_3$COO(a) photoreaction was studied by preparing the acetate-adsorbed TiO$_2$ surface followed by introduction of H$_2$O into the cell, to give a ~0.1 Torr equilibrium vapor pressure, and UV illumination on the surface. It is found that after exposure of H$_2$O vapor to CH$_3$COO(a), acetic acid is formed on the surface as indicated by its characteristic peaks at 1291 and 1671 cm$^{-1}$ in the 0 min spectrum in Fig. 4, accompanying a ~15% decrease of acetate. A surface reaction of CH$_3$COO(a) + H$_2$O(a) → CH$_3$COOH(a) must take place on TiO$_2$. Fig. 4 shows that, in the presence of H$_2$O, the infrared absorption at 3017 cm$^{-1}$ is enhanced under UV irradiation. To easily see the band, an IR spectrum was taken after the 180 min irradiation, followed by evacuation to remove gaseous products from the cell, and then subtracted from the 180 min spectrum in Fig. 4. The inset in Fig. 4 is the difference spectrum, clearly showing a sharp peak at 3017 cm$^{-1}$ which is attributed to CH$_3$(g). Fig. 5 shows the relative concentration of CO$_2$(g) and CH$_4$(g) as a function of UV irradiation time. Because of the noise in the baseline of the spectra, an absorption band for CH$_4$(g) is not discernible when its peak intensity is less than ~10% of that after the 180 min UV irradiation in Fig. 4. Therefore, in this case, the relative CH$_4$(g) concentration is set to zero in the initial photooxidation stage in Fig. 5. To obtain absolute amounts of CO$_2$(g) and CH$_4$(g) formed, two calibration curves of peak area vs. pressure for CO$_2$(g) at 2349 cm$^{-1}$ and CH$_4$(g) at 3017 cm$^{-1}$ have been established. It is found that the absolute ratio CO$_2$(g)/CH$_4$(g) is ~1.71 after 180 min photoillumination in Fig. 4. This reveals that, in the photodecomposition of CH$_3$COO(a) or CH$_3$COOH(a), some of the intermediates or products in the gas phase or on the surface derived from the CH$_3$ moiety of the two adsorbed forms were not detected by our infrared spectrometer. The nonstoichiometric ratio of CO$_2$(g)/CH$_4$(g) may also explain the very low CH$_4$(g) signal during the initial stage of the photo-oxidation process as shown in Figs. 4 and 5.

Fig. 4 IR spectra taken before and after the indicated times during photoirradiation of CH$_3$COO(a) in ~0.1 Torr water vapor. Each spectrum was recorded with five scans. All the traces in the region 1000–1900 cm$^{-1}$ have been multiplied by a factor of 0.1. To clearly show the CO$_2$(g) absorption, the three curves in 2250–2450 cm$^{-1}$ region of the 10, 90 and 180 min spectra are obtained after the background spectrum prior to UV irradiation is subtracted, and then multiplied by a factor of 10. The inset shows that CH$_4$(g) (3017 cm$^{-1}$) is formed. The weight of the TiO$_2$ powder used was 88 mg.

Fig. 5 Relative concentrations of CO$_2$(g) and CH$_4$(g) formed in the photoreaction of adsorbed acetate with water over TiO$_2$ as a function of UV irradiation time. The maximum amount for each species is scaled to 1.

Fig. 6 IR spectra taken before and after the indicated times during photoirradiation of a TiO$_2$ surface initially in contact with 2 Torr of acetic acid followed by evacuation at 35°C. The spectra are presented in the same way as those in Fig. 4. The weight of the TiO$_2$ sample used was 88 mg.

Fig. 7 Relative concentrations of CO$_2$(g) and CH$_4$(g) formed in the photoreaction of adsorbed acetic acid and acetate as a function of UV irradiation time. The maximum amount for each species is scaled to 1.

factor ~2.3 after 180 min light exposure, as compared to that in Fig. 3 without water. Because both CH$_3$COO(a) and CH$_3$COOH(a) were present on the surface in the photodecomposition study of CH$_3$COO(a) in the presence of H$_2$O, photoreactions catalyzed by a TiO$_2$ surface covered with CH$_3$COOH(a) and CH$_3$COO(a) from acetic acid adsorption were investigated. The results are shown in Fig. 6. Fig. 7 shows the relative concentrations of the CH$_4$(g) and CO$_2$(g) photoproducts as a function of UV irradiation time. Compared to the case of Fig. 4 with CH$_3$COO(a), CH$_3$COOH(a) and H$_2$O in the reaction system, the amount of CO$_2$(g) formed in Fig. 6 after 180 min irradiation is ~95% of that in Fig. 4, but the CH$_4$(g) is ~80%. It is found that the absolute ratio of CO$_2$(g)/CH$_4$(g) is ~1.84 after 180 min photoirradiation in Fig. 6 and that a similar amount of CH$_3$COOH(a) is consumed (Figs. 4 and 6). From these comparative studies, it is concluded that CH$_3$COOH(a) contributes significantly to the formation of CO$_2$(g) and CH$_4$(g) shown in Fig. 4. Water may enhance the formation of CO$_2$(g) and CH$_4$(g), but seems not
to be very significant. The major role of H₂O is to transform surface acetate groups to acetic acid which also takes part in photodecomposition.

**O₂ effect on acetic acid photoreaction**

Figs. 8 and 9 show spectra for the photoreaction of a TiO₂ surface initially in contact with ~4 Torr of CH₃COOH and a mixture of ~4.5 Torr CH₃COOH and ~10 Torr O₂ in a closed cell, respectively, to show the O₂ effect. In Fig. 8, CO₂(g) and CH₃(g) are the only photoproducts detected in the absence of O₂, but with acetic acid present in the gas phase to replenish the adsorbate consumed in the photoreaction, the amounts of CO₂(g) and CH₃(g) formed after 180 min irradiation are ~1.7 times of that in Fig. 6. A considerable amount of gaseous acetic acid is still present in the cell at the end of the photoillumination. In contrast to the case without O₂, oxygen-containing species such as CH₃OH(g) at 1034 cm⁻¹, CH₃O(g) at 1745 cm⁻¹, H₂O(g) at 1653, 1683 cm⁻¹ and HCOOCH₃(g) at 1208, 1755 and 1767 cm⁻¹ are generated in the presence of O₂ as shown in Fig. 9. In addition, the gaseous acetic acid is almost depleted after 180 min irradiation with a concomitant significant increase of CO₂(g) and CH₃(g). The CO₂(g) and CH₃(g) formed after 180 min in Fig. 9 are ~10 and ~2.5 times of those in Fig. 8, respectively. The presence of O₂ largely increases the photoreaction rate. Since, in Fig. 9, the TiO₂ is covered with both CH₃COOH(a) and CH₃COO(a), it is interesting to further explore which species is responsible for the significantly increased CO₂(g) amount in the presence of O₂. In the discussion of Fig. 2 for CH₃COO(a) photoreaction it has been stated that O₂ can only increase the CO₂(g) amount by a factor of ~3 compared to the case without O₂. Taking this and the similar amount of CH₃COO(a) in Figs. 2 and 9 together into consideration, CO₂(g) formation from CH₃COO(a) photoreaction only contributes ~6% of the CO₂(g) found in Fig. 9. Therefore it is concluded that CH₃COOH(a) is the major precursor in the photodecomposition to CO₂(g) in the presence of O₂. Adsorbed O₂ can capture photogenerated electrons to form anionic oxygen species that may act as oxidants. Scavenging of photogenerated electrons by O₂ increases the lifetime of holes and therefore speeds up the photoreactions they induced. The enhanced formation of CH₃(g) in Fig. 9 as compared to the case without O₂ is attributed to the enhanced formation of CH₃, that contributes to CH₃ formation according to Bard et al.’s eqns. (3), (6) and (8), because the presence of O₂ extends the lifetime of holes. In addition, the formation of H₂O or other oxygenated species also can increase the yield of CH₃(g) from reactions with CH₃⁻. Fig. 10 shows the relative concentrations of the gaseous reactants and products as a function of photolrradiation time for Fig. 9. The gaseous acetic acid decreases with photolllumination in contrast to the case without CO2(g). CH₃(g), H₂O(g) and HCOOCH₃(g) are the only photoproducts detected, and HCOOCH₃(g) is a minor product.

![Fig. 8 IR spectra taken before and after the indicated times during photolrradiation of a TiO₂ surface initially in contact with ~4 Torr of acetic acid. Each spectrum was recorded with five scans. The weight of the TiO₂ sample used was 67 mg. All spectra in the region 1000–1900 cm⁻¹ have been multiplied by a factor of 0.2. To clearly show the CO₂(g) absorption, the four curves in the 2250–2450 cm⁻¹ region of the 2, 10, 60 and 180 min spectra are obtained after the spectrum prior to UV irradiation is subtracted, and then multiplied by a factor of 5.](image)

![Fig. 9 IR spectra taken before and after the indicated times during photolrradiation of a TiO₂ surface initially in contact with a mixture of ~4.5 Torr of acetic acid and ~10 Torr O₂. Each spectrum was recorded with five scans. The weight of the TiO₂ sample used was 67 mg. To clearly show the CO₂(g) absorption, the four curves in the 2250–2450 cm⁻¹ region of the 2, 10, 60 and 180 min spectra are obtained after the spectrum prior to UV irradiation is subtracted.](image)

When the surface is covered with both TiO₂, increases the possibility for electron exposure through TiO₂ excitation; however, its photodecomposition rate decreases with UV illumination time, probably due to electron accumulation on the surface that increases the possibility for electron-hole recombination. When the TiO₂ surface is covered with both CH₃COOH(a) and CH₃COO(a), CH₃(g) is also observed in addition to CO₂(g). Eqns. (1), (3) and (6) proposed by Bard et al. may explain the formation of CH₃(g) and CO₂(g), but CH₃COO⁻ and CH₃COOH should be replaced by CH₃COO(a) and CH₃COOH(a) in the present study, i.e., absorbed acetate and acetic acid are involved in the photoreaction. In eqns. (2) and (3), CH₃COOH(a) acts as a photoelectron scavenger, allowing the rate of CH₃COOH(a) photodecomposition by hole capture to be increased and therefore enhancing CO₂(g) formation. Although our results can be explained by Bard et al.‘s mechanism, the possibility of hole capture of CH₃COOH(a) to form CH₃(g) and CO₂(g) cannot be completely ruled out. In the photodecomposition of CH₃COOH(a) in the absence of CH₃COOH(a), the CH₃ formed from a hole + CH₃COOH(a) may be adsorbed on the surface, ejected into the gas phase or may react with H(a) as shown in eqn. (6) to form CH₄(g). Ejection of CH₃ radicals has been observed in the thermal dissociation of CH₃I on copper single crystal surfaces,11,12 Al(CH₃)₃ on Al,13 Ga(CH₃)₃ on GaAs(100),14 CH₃Br on K/Ag(111)15 and methoxy groups on O/Mo(110).16 The latter case demonstrates that methyl radicals can also be ejected from oxidized metal surfaces, not just from bare metal ones. Additionally, CH₃ radical has been detected by EPR in the photoreaction of aqueous acetic acid on Pt/TiO₂ at 77 K.3,4 Since CH₃ radicals are reactive species, if the ejection process is important, CH₄(g) formation would be reduced according to Bard et al.‘s mechanism. Based on the bidentate bonding configuration of CH₃COO(a), CH₃⁺ ejection is likely to occur since the CH₃ group in CH₃COO(a) points away from the surface. The methyl radicals thus formed may either stick on or react with adsorbates on the cell surface. Since our cell is only ~10 cm long, low concentration of gaseous species may not be observable. This may explain why CH₄(g) is not detected in the spectra shown in Fig. 2. Fig. 4 shows that CH₃COO(a) can react with H₂O to form CH₃COOH. The presence of H₂O may enhance the formation of CH₃(g) and CO₂(g) in the photodecomposition of CH₃COO(a), but the effect is not significant. Addition of O₂ to the photoreaction system of acetic acid over TiO₂ considerably increases its reaction rate and produces the oxygen-containing products methanol, formaldehyde and methyl formate. The major species reacting with oxygen is CH₃COOH(a) instead of CH₃COO(a). Schwitzgebel et al. have investigated the photodecomposition of aqueous n-octanoic acid catalyzed by TiO₂-coated glass microbubbles and observed the formation of n-heptanol, n-heptanal, n-heptanoic acid and CO₂.27 They proposed a reaction mechanism involving organoperoxy and tetroxide intermediaes in order to balance the equations of the photocatalytic reactions. Here a similar mechanism is proposed to account for the formation of methanol and formaldehyde in the photoreaction of CH₃COOH in the presence of O₂:

\[
\text{CH₃COOH} + h^+ \rightarrow \text{CH}_3^+ + \text{CO}_2 + \text{H}^+ \\
\text{H}^+ + \text{O}_2 \rightarrow \cdot\text{OOH} \\
\text{CH}_3^+ + \text{O}_2 \rightarrow \text{CH}_3\text{OO}^- \\
\text{CH}_3\text{OO}^- + \cdot\text{OOH} \rightarrow \text{CH}_3\text{OOOCH}
\]

CH₃OOOCH + CH₃COOH → CH₃OH + CH₂O

+ O₂ + CO₂

The O₂⁻ is due to photoelectron capture by O₂.

Finally, in our present study of the photocatalytic degradation of acetic acid, no C₃H₆(g) is observed, because the process for C₃H₆(g) is a minor process. Although a small amount of C₃H₆(g) may be formed in the cell, its signal must be below the detection limit of our infrared spectrometer.

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References


