

# Parallel Pathways for Photocatalytic Decomposition of Acetic Acid on TiO<sub>2</sub>

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Acetic acid decomposes photocatalytically on TiO<sub>2</sub> at room temperature in an inert atmosphere through two parallel pathways. In one pathway, acetic acid decomposes to gas-phase CO<sub>2</sub> and apparently forms hydrogen and methyl groups, which combine on the surface to form CH<sub>4</sub>. In the other pathway, acetic acid extracts oxygen from the TiO<sub>2</sub> lattice to form adsorbed H<sub>2</sub>O and gas-phase CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>. The extracted oxygen is replenished by diffusion from the bulk in an inert atmosphere or by gas-phase O<sub>2</sub>. The formation of CH<sub>4</sub> and CO<sub>2</sub> in the first pathway does not consume lattice oxygen. The first step in photocatalytic decomposition (PCD) of acetic acid appears to be dissociation of the O–H bond, producing surface acetates. However, molecularly adsorbed acetic acid reacts at the same rate and with the same selectivity as surface acetates. Only the  $\alpha$ -carbon forms CO<sub>2</sub> during PCD. When gas-phase O<sub>2</sub> is present, adsorbed methyl groups oxidize before they are hydrogenated to CH<sub>4</sub>. The oxidizing agent during photocatalytic oxidation (PCO) is different from that during PCD and is most likely adsorbed oxygen. Adsorbed oxygen reacts with acetic acid in a different pathway from the two reactions observed for PCD, so a Mars Van Krevelen mechanism for PCO appears unlikely. The TiO<sub>2</sub> surface is not homogeneous and some surface sites are more active during both PCD and PCO. Co-adsorbed water increases the rate of CH<sub>4</sub> formation, apparently by reacting with CH<sub>3(ads)</sub> to form CH<sub>4</sub>, but in contrast to adsorbed O<sub>2</sub>, water does not react with acetic acid in a separate pathway that is different from those observed for PCD without water. © 1999 Academic Press

## INTRODUCTION

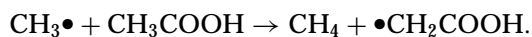
Heterogeneous photocatalytic oxidation (PCO) has potential applications for complete oxidation of organic pollutants in dilute systems. A wide range of organics can be oxidized to CO<sub>2</sub> and H<sub>2</sub>O at room temperature on TiO<sub>2</sub> catalysts in the presence of UV or near-UV illumination. The UV light excites electrons from the valence to the conduction band of the semiconductor catalyst, leaving holes behind. The electron–hole pairs can initiate redox reactions with surface species.

To clarify the relative importance of adsorbed and lattice oxygen during PCO, photocatalytic reaction of acetic

acid was studied in the absence of gas-phase O<sub>2</sub>. This reaction will be referred to as photocatalytic decomposition (PCD) to distinguish it from PCO, which takes place when gas-phase O<sub>2</sub> is present. Acetic acid was used as a model reactant because it readily undergoes both PCD and PCO and it is a volatile organic compound (VOC) that is formed during PCO of other organics, such as ethanol (1–3). Transient reaction was used to obtain a better understanding of the surface processes.

Kraeutler and Bard (4) studied liquid-phase PCD of acetic acid and sodium acetate solutions on TiO<sub>2</sub> and platinumized TiO<sub>2</sub> in a batch reactor at 328 K. In the absence of molecular oxygen, acetic acid decomposed mainly to CH<sub>4</sub> and CO<sub>2</sub> with small amounts of C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub> also forming. The ratio of CH<sub>4</sub> to C<sub>2</sub>H<sub>6</sub> was approximately 19 on TiO<sub>2</sub> and 11 on platinumized TiO<sub>2</sub>. When deuterated acetic acid (CH<sub>3</sub>COOD, 98% atom enrichment) reacted on platinumized TiO<sub>2</sub>, 80% of the CH<sub>4</sub> product was monodeuterated, but C<sub>2</sub>H<sub>6</sub> was not deuterated. The CH<sub>3</sub>COOD decomposed about half as fast as CH<sub>3</sub>COOH. Furthermore, addition of O<sub>2</sub> largely suppressed both CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> formation. They proposed a mechanism in which acetic acid decomposes to CO<sub>2</sub>, CH<sub>3(ads)</sub>, and H<sub>(ads)</sub>. Methane forms by combining H<sub>(ads)</sub> and CH<sub>3(ads)</sub>, and C<sub>2</sub>H<sub>6</sub> forms by recombination of two methyl radicals. They also discussed the possibility that CH<sub>3(ads)</sub> reacts with H<sub>2O(ads)</sub> to produce CH<sub>4</sub>.

Yoneyama *et al.* (5) also detected CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and H<sub>2</sub> as the major products from aqueous solutions of acetic acid and sodium acetate during illumination of Pt/TiO<sub>2</sub> in a batch reactor. Similarly, Chemseddine and Boehm (6) observed CO<sub>2</sub> formation during PCD of aqueous acetic acid and chloroacetic acids on TiO<sub>2</sub>. Yoneyama *et al.* proposed a similar mechanism to that of Kraeutler and Bard (4), with the addition of another pathway,



For anatase TiO<sub>2</sub>, the CO<sub>2</sub>/CH<sub>3</sub>• mole ratio varied from 1.3 to 33; the CH<sub>3</sub>• amount was determined by adding the amounts of C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub>. The authors attributed the greater than stoichiometric amounts of CO<sub>2</sub> produced to oxidation of ethanol and acetaldehyde intermediates.

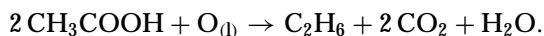
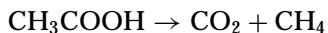
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Their results for PCD at various pH values showed that the ratio of C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> formation rates increased with reaction rate and decreased with reaction time. However, when the pH was fixed at 3.1 and the concentration of acetic acid increased, the ratio of C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> decreased as the reaction rate increased. Finally, when the sodium acetate concentration was fixed, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> rates and the C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> ratio increased with increasing acetic acid concentration. Increasing the UV intensity also increased the C<sub>2</sub>H<sub>6</sub> formation rate more than the CH<sub>4</sub> rate. The authors reasoned that the concentration of surface methyl groups increased when the rates increased, and thus second-order reactions should be favored. The C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> ratio then increased if CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were produced via first- and second-order reactions of methyl groups, respectively.

Nosaka *et al.* (7) used ESR to detect methyl radicals during PCD of acetic acid in water on TiO<sub>2</sub>. The authors proposed that a photo-induced hole reacts with acetic acid to produce CO<sub>2</sub>, CH<sub>3</sub>, and H<sup>+</sup>. They reasoned that the methyl radicals should predominantly form CH<sub>4</sub>.

Sclafani *et al.* (8) observed that *gas-phase* acetic acid decomposed photocatalytically to CH<sub>4</sub>, CO<sub>2</sub>, and small amounts of C<sub>2</sub>H<sub>6</sub>. For the two types of TiO<sub>2</sub> catalysts studied, the *steady-state* ratios of CO<sub>2</sub> to CH<sub>4</sub> were 1.7 and 20.6, and the rate of C<sub>2</sub>H<sub>6</sub> formation was less than 0.3% of the CH<sub>4</sub> rate. Since the CO<sub>2</sub>:CH<sub>4</sub> ratios were not one, as expected from stoichiometry, water must have also formed, but it could not be detected by their analysis. Moreover, since their product distributions were measured after long reaction times (40–70 h) that corresponded to steady state, some O<sub>2</sub> may have been present in their feed. They reported similar results for the other oxides studied; the CO<sub>2</sub>/CH<sub>4</sub> ratio was greater than one, and the C<sub>2</sub>H<sub>6</sub> rates were small. In contrast to the previous studies, they concluded that PCD occurred by excitation of an adsorbed species rather than by generation of electron/hole pairs in TiO<sub>2</sub>. Also, in contrast to previous PCO studies (1, 2), Sclafani *et al.* observed that CH<sub>4</sub> still formed when O<sub>2</sub> was added to the feed and concluded that TiO<sub>2</sub> is less active in air than in He because the CH<sub>4</sub> production rate decreased by 25% in air. However, CO<sub>2</sub> could not be detected during their PCO experiments, and adsorbed CH<sub>3</sub> species produced during PCO probably oxidized to CO<sub>2</sub>.

In a preliminary study (9), we showed that in the absence of gas-phase O<sub>2</sub>, acetic acid decomposes at room temperature by parallel pathways during transient experiments to form CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, and H<sub>2</sub>O:



Isotope labeling showed that the  $\alpha$ -carbon reacts exclusively to CO<sub>2</sub> whereas the  $\beta$ -carbon forms CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. Mass balances verified the indicated stoichiometries.

The objective of the current study is to understand the surface processes involved in PCD and how they relate to PCO, and to measure their rates. A monolayer of acetic acid was adsorbed on oxidized TiO<sub>2</sub>, and any excess organic was flushed from the gas phase. The surface coverage of acetic acid was known at all times since no other carbon-containing species were detected on the surface when acetic acid decomposed. The TiO<sub>2</sub> surface with adsorbed acetic acid was exposed to UV illumination in the absence of gas-phase O<sub>2</sub>, and the reaction products were detected by a mass spectrometer. Transient experiments are preferred over steady state experiments for reactions where the catalyst surface changes as lattice oxygen is removed. Since gas-phase O<sub>2</sub> did not replenish the surface during PCD, lattice oxygen extraction and diffusion of bulk oxygen to the surface could be observed. In contrast to batch reactor studies where product gases were collected and analyzed after several minutes of reaction (4, 5), a mass spectrometer immediately detects gas-phase products and the instantaneous reaction rate and selectivity are measured. Interrupted PCDs for various dark times provided insight into the role of lattice oxygen and acetic acid coverage during PCD and PCO. In some experiments, oxygen, water, or acetic acid were also injected during UV illumination or in the dark after PCD to provide information on the roles of lattice oxygen, adsorbed water, and surface diffusion of acetic acid during PCD. In some experiments, <sup>13</sup>C-labeled acetic acid (CH<sub>3</sub><sup>13</sup>COOH) was used to track the reactivity of the  $\alpha$  and  $\beta$  carbons separately. The reaction mechanism was investigated by studying PCD and PCO of methyl acetate (CH<sub>3</sub>COOCH<sub>3</sub>), which has a methyl group in place of the acid hydrogen of acetic acid. Formic acid PCO was also used to provide insight into the reactivity of different surface sites. After PCD or PCO, species that remained on the surface were characterized by temperature-programmed desorption (TPD) or oxidation (TPO).

## EXPERIMENTAL METHODS

The apparatus used for PCD, PCO, TPD, and TPO was described previously (10). Approximately 30 mg Degussa P-25 TiO<sub>2</sub> catalyst was coated as a thin layer (average thickness <0.5  $\mu\text{m}$ ) on the inside of an annular Pyrex reactor so that all the TiO<sub>2</sub> was exposed to UV light for photocatalytic oxidation. The annular reactor had a 1-mm annular spacing so that high gas flow rates could be maintained across the catalyst to minimize mass transfer effects and rapidly flush gas-phase products from the reactor. The outside diameter of the reactor was 2 cm and the reactor was 13 cm high so that sufficient catalyst mass was present to allow detection of reaction products by the mass spectrometer. Six UV lamps (GE, 4 W) surrounded the photocatalytic reactor, and the light intensity at the catalyst surface, measured with a radiometer, was typically 0.3 mW/cm<sup>2</sup>, but varying

UV intensity was used for some experiments. The radiometer only measured light from one direction, but the light that penetrated through the thin catalyst layer would strike the layer on the other side of the reactor, and thus, the intensity was greater than  $0.3 \text{ mW/cm}^2$ . This decreased intensity variations at different locations around the reactor, but the light was more intense at the midpoint of the reactor than at the ends. The maximum light intensity was near 360 nm (2).

Before each experiment the reactor was held at 723 K for 30 min in approximately 20%  $\text{O}_2$  in He and then cooled to room temperature to create a reproducible surface. Two  $1\text{-}\mu\text{L}$  pulses of acetic acid (Aldrich, 99.99+%),  $^{13}\text{C}$ -acetic acid ( $\text{CH}_3^{13}\text{COOH}$ , Isotec, 99+% atom enrichment), methyl acetate (Aldrich, 99.5%), or formic acid (Sigma, 99%) saturated the catalyst in the dark at 300 K prior to PCD or PCO, and all experiments started with the surface saturated unless otherwise indicated. After exposure to an organic, the reactor was flushed for 2 h to remove gas-phase organic, so that only reaction of the adsorbed monolayer was studied. Photocatalytic decomposition was studied by illuminating the  $\text{TiO}_2$  in  $100 \text{ cm}^3/\text{min}$  STP of He flow, and PCO was carried out in 3%  $\text{O}_2$  flow. For PCD, the He stream was purified and the flow system was designed and checked so that the  $\text{O}_2$  concentration was below the mass spectrometer detection limits. The  $\text{O}_2$  concentration during PCD is estimated to be less than 0.3 ppm (11). Metal shields were placed between the reactor and the UV lights, and after the lights attained a steady state output, the shields were removed to illuminate the catalyst and initiate transient reaction at room temperature. The gas-phase products were detected by a mass spectrometer as a function of time.

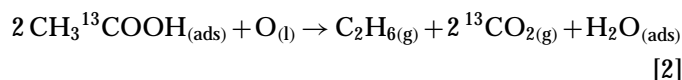
To understand the roles of lattice oxygen and surface diffusion of acetic acid, the lights were turned off periodically for varying lengths of time during both PCD and PCO, and the effect of dark time on the subsequent rates of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{CO}_2$  formation was measured. In addition, for some experiments, pulses of  $\text{O}_2$  ( $110 \mu\text{mol/g}$  catalyst), acetic acid ( $110 \mu\text{mol/g}$  catalyst), formic acid ( $160 \mu\text{mol/g}$  catalyst), or  $\text{H}_2\text{O}$  ( $180 \mu\text{mol/g}$  catalyst) were exposed to the catalyst in the dark or during UV illumination after PCD for several min.

A Balzers QMA 125 quadrupole mass spectrometer monitored the reactor effluent immediately downstream of the reactor. The mass spectrometer was interfaced to a computer to record multiple mass peaks simultaneously. The mass spectrometer signals were calibrated by injecting known volumes of gases into the flow stream downstream of the reactor, and signals were corrected for cracking in the mass spectrometer. After PCO or PCD, TPD or TPO was performed by heating the catalyst at 1 K/s to 723 K and holding at this temperature until no desorption products were detected. An He flow gas was used for TPD whereas a 20%  $\text{O}_2$  in He gas mixture was used for TPO.

## RESULTS AND DISCUSSION

As we previously reported (9), a monolayer of acetic acid decomposes on  $\text{TiO}_2$  to form gas-phase  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_6$  during UV illumination in an inert gas stream. Figure 1 shows the rate of formation of products as a function of time during acetic acid PCD. Upon UV illumination, the rate of  $\text{CO}_2$  production immediately reaches a maximum, quickly decreases to  $0.08 \mu\text{mol/g}$  catalyst/s, and then decreases more slowly. The rate of  $\text{C}_2\text{H}_6$  formation also decreases quickly after reaching its initial maximum, and then decreases much more slowly. In contrast, the  $\text{CH}_4$  formation rate does not exhibit a sharp maximum and decreases slowly throughout the PCD. All signals drop to zero when the lights are turned off. When UV illumination resumes after 420 s in the dark, the  $\text{CO}_2$  rate is 1.5 times and the  $\text{C}_2\text{H}_6$  rate is 4.5 times the rates measured before the lights were turned off. In contrast, the  $\text{CH}_4$  rate production is the same as that before the dark time.

During PCD of  $\text{CH}_3^{13}\text{COOH}$ , only  $^{13}\text{CO}_2$ ,  $^{12}\text{C}_2\text{H}_6$ , and  $^{12}\text{CH}_4$  are detected. That is, the  $\alpha$ -carbon is oxidized exclusively to  $\text{CO}_2$ , and  $\beta$ -carbon only forms  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . These results suggest two parallel pathways for acetic acid decomposition during PCD:



Note that the acid hydrogens form  $\text{H}_2\text{O}$  in reaction [2], but the H atoms may also be present on the surface as  $\text{OH}_{(\text{ads})}$  groups. As reported previously (9) for these reactions, the rate of  $\text{CO}_2$  formation equals the sum of the  $\text{CH}_4$  rate plus twice the  $\text{C}_2\text{H}_6$  rate for the entire time of the experiment. These signals are coincident when plotted this way.

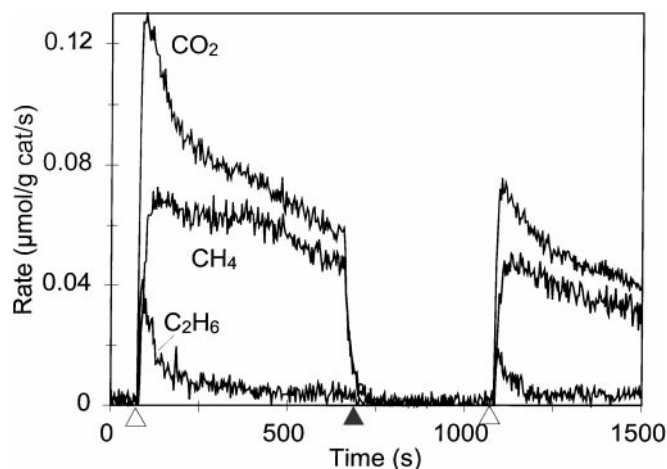


FIG. 1. Product formation rates during photocatalytic decomposition in He flow of a monolayer of acetic acid on  $\text{TiO}_2$ . The UV lights were turned on (open triangles) and off (solid triangles) as indicated.

Reaction [1] does not require oxygen whereas reaction [2] does. Presumably lattice oxygen is extracted in reaction [2] since no gas-phase oxygen was present during PCD. Thus, the rates of C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> formation are greater after the dark time because lattice oxygen diffuses from the TiO<sub>2</sub> bulk to replenish the surface oxygen vacancies in the dark, as was seen for PCD of formic acid (11). The higher concentration of surface oxygen after the dark time increases the rate of reaction [2]. Indeed, the rate increase for CO<sub>2</sub> in Fig. 1 after the dark time is approximately twice that for C<sub>2</sub>H<sub>6</sub>, as expected for reaction [2] stoichiometry. Also, the rates of C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> formation drop rapidly from their initial rates as lattice oxygen is removed from the surface. In contrast, the CH<sub>4</sub> rate after a dark time is the *same* as before the lights were turned off since reaction [1] does not require lattice oxygen. For the same reason, the CH<sub>4</sub> rate drops more slowly with time than the C<sub>2</sub>H<sub>6</sub> rate. Presumably, acid hydrogens combine with CH<sub>3</sub> groups to form CH<sub>4</sub> during acetic acid PCD. However, during formic acid PCD, acid hydrogens do *not* combine with each other or with the hydrogen originally bound to the carbon (11). Similarly, no H<sub>2</sub> forms during PCD of acetic acid by recombination of two acid hydrogens. Thus, adsorbed methyl groups may react with H<sub>2</sub>O to produce CH<sub>4</sub>, as proposed by Kraeutler and Bard (4).

During TPD after PCD, only acetic acid and the products of its bimolecular ketonization (acetone, CO<sub>2</sub>, and H<sub>2</sub>O) desorb from the TiO<sub>2</sub> surface. The TPD spectra are similar to those previously reported for TPD of acetic acid without reaction [1]. That is, only acetic acid and H<sub>2</sub>O are on the surface after PCD; if methyl groups formed during PCD, they quickly reacted to form CH<sub>4</sub>. The H<sub>2</sub>O seen during TPD can be from both the ketonization reaction and reaction [2], since H<sub>2</sub>O that forms during PCD adsorbs strongly on TiO<sub>2</sub>. The appearance of gas-phase products (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CO<sub>2</sub>) during PCD is reaction limited since these species are too weakly adsorbed on TiO<sub>2</sub> to have a significant coverage at room temperature. No desorption products were detected during TPD after exposing TiO<sub>2</sub> to CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub>, and only a small amount of CO<sub>2</sub> adsorbed on TiO<sub>2</sub> (12). During PCO of a monolayer of acetic acid, both formaldehyde and formate reaction intermediates are on the surface [1], but neither was detected during TPD after PCD. Thus it appears that lattice oxygen does not oxidize the CH<sub>3</sub> groups. This is confirmed since <sup>12</sup>CO<sub>2</sub> does not form during PCD of CH<sub>3</sub><sup>13</sup>COOH. This indicates that adsorbed oxygen is necessary for some oxidation steps during PCO, whereas lattice oxygen may be used in others. Although gas-phase O<sub>2</sub> is not needed to oxidize the α carbon in acetic acid to CO<sub>2</sub>, it is required to oxidize the β carbon.

#### Photocatalytic Decomposition with O<sub>2</sub> Injections

As described above, oxygen from the TiO<sub>2</sub> bulk diffuses to replenish the surface vacancies when the lights are turned

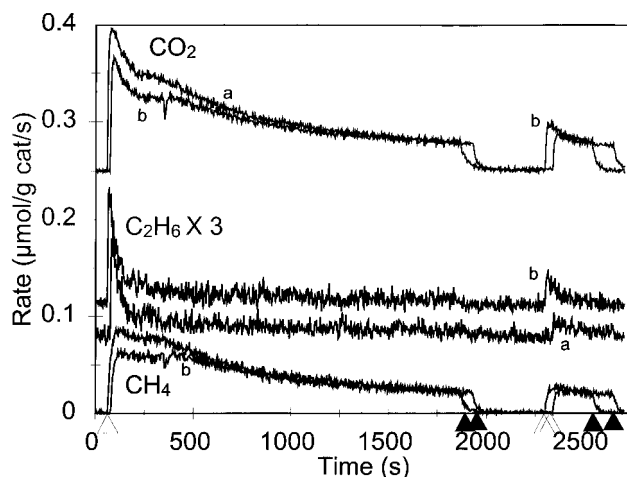


FIG. 2. Product formation rates during photocatalytic decomposition of a monolayer of acetic acid on TiO<sub>2</sub>. After approximately 1900 s, the lights were turned off for 420 s and during the dark time (a) no change was made in the system or (b) a pulse of O<sub>2</sub> was injected over the TiO<sub>2</sub>. The UV lights were turned on (open triangles) and off (solid triangles) as indicated.

off following PCD. Figure 2 shows results from two PCDs of acetic acid. Both PCDs have a 420-s dark time. The second PCD is at a UV intensity that is 83% of that in the first experiment, and a 110 μmol/g catalyst pulse of O<sub>2</sub> is injected during the dark time. Initially, the CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> rates are 1.4 and 1.2 times greater, respectively, at the higher light intensity. After the initial maxima, the C<sub>2</sub>H<sub>6</sub> rates essentially coincide until after the 420-s dark time. The difference in the rates of CH<sub>4</sub> production decreases until eventually the two rates are almost the same after 1700 s. The rates are expected to cross eventually since the greater rate at the higher UV intensity consumes acetic acid faster.

After the dark time, the rates of CH<sub>4</sub> formation are essentially the same for both experiments and equal to the rates before the dark time. This indicates that lattice oxygen is not required for CH<sub>4</sub> formation (reaction [1]) since the O<sub>2</sub> pulse in the dark replenishes lattice oxygen that was extracted during PCD. It also indicates that the adsorbed oxygen coverage is low after the O<sub>2</sub> pulse since adsorbed oxygen would be expected to photocatalytically oxidize adsorbed CH<sub>3</sub>; the CH<sub>4</sub> formation rate did not decrease after the dark time. The C<sub>2</sub>H<sub>6</sub> rate after the O<sub>2</sub> pulse in the dark is twice the C<sub>2</sub>H<sub>6</sub> rate without the O<sub>2</sub> injection, even though the UV intensity is lower for the O<sub>2</sub> pulse experiment. Since the O<sub>2</sub> replenished the lattice oxygen, reaction [2] for C<sub>2</sub>H<sub>6</sub> is expected to be faster. These experiments were repeated using the same UV intensity for each with similar results; the O<sub>2</sub> pulse during the dark time increased the C<sub>2</sub>H<sub>6</sub> rate, but not the CH<sub>4</sub> rate.

Figure 3 shows the effect of an O<sub>2</sub> pulse injected *with the UV lights on during PCD* of CH<sub>3</sub><sup>13</sup>COOH. After 1000 s, an O<sub>2</sub> pulse (560 μmol O<sub>2</sub>/g catalyst) quadruples the rate of

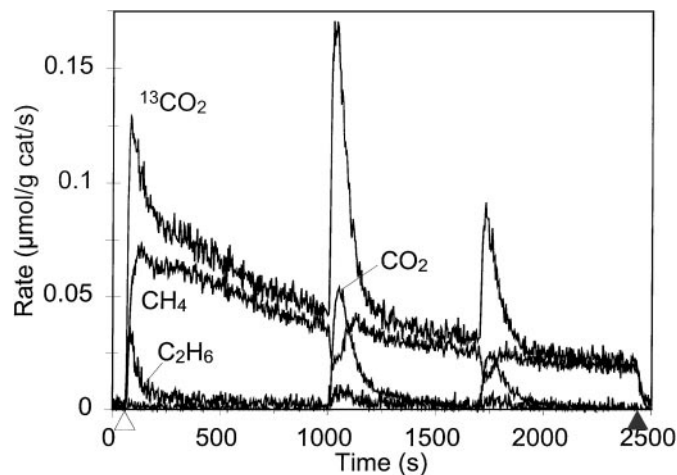


FIG. 3. Product formation rates during photocatalytic decomposition of a monolayer of acetic acid on  $\text{TiO}_2$ . Pulses of  $\text{O}_2$  were injected over the  $\text{TiO}_2$  at 1000 and 1700 s with the UV lights on.

$^{13}\text{CO}_2$  formation, decreases the rate of  $\text{CH}_4$  production by 40%, and increases the  $\text{C}_2\text{H}_6$  formation rate a factor of 3.5. In addition,  $^{12}\text{CO}_2$  forms as  $\text{O}_2$  oxidizes the  $\beta$ -carbon; the  $^{12}\text{CO}_2$  rate is 27% of the  $^{13}\text{CO}_2$  rate. As shown in Fig. 2,  $\text{O}_2$  readily oxidizes reduced  $\text{TiO}_2$  in the dark and produces an increase in the rate of  $\text{C}_2\text{H}_6$  formation. The dramatic decrease in the  $\text{CH}_4$  rate in Fig. 3, combined with the appearance of  $^{12}\text{CO}_2$ , indicates that surface methyl groups, if produced during PCD, react quickly with oxygen to form  $\text{CO}_2$  before they are hydrogenated to  $\text{CH}_4$ . The decrease in the  $\text{CH}_4$  rate upon  $\text{O}_2$  injection cannot be attributed to subsequent oxidation of gas-phase  $\text{CH}_4$  to  $\text{CO}_2$  since less than 1% of an injected  $\text{CH}_4$  pulse oxidizes to  $\text{CO}_2$  over fresh, illuminated  $\text{TiO}_2$  in flowing 20%  $\text{O}_2$ . After 1700 s of PCD, a 220  $\mu\text{mol/g}$  catalyst pulse of  $\text{O}_2$  produces similar results as the larger pulse.

Gas-phase  $\text{O}_2$  decreases the rate of  $\text{CH}_4$  production, presumably because  $\text{CH}_3$  groups are oxidized faster than they are hydrogenated, or because adsorbed and lattice oxygen oxidize H atoms before they can react with the  $\text{CH}_3$  groups. This implies that injecting  $\text{O}_2$  during PCD decreases either the coverage of adsorbed methyl groups or the coverage of surface H atoms. The  $\text{C}_2\text{H}_6$  rate increased during the  $\text{O}_2$  injection, which suggests that either the  $\text{CH}_3$  surface concentration increased because the H atoms were removed or  $\text{C}_2\text{H}_6$  does not form by recombination of surface methyl groups. Part or all of this rate increase is due to the increase in lattice oxygen. If  $\text{CH}_3$  groups do not recombine to make  $\text{C}_2\text{H}_6$ , some other bimolecular reaction may produce  $\text{C}_2\text{H}_6$  during PCD.

Note in Fig. 3 that the  $^{13}\text{CO}_2$  rate increased to approximately 0.17  $\mu\text{mol/g cat/s}$  after the first  $\text{O}_2$  injection whereas the rate of  $^{13}\text{CO}_2$  formation expected from reactions [1] and [2] (the sum of the  $\text{CH}_4$ ,  $^{12}\text{CO}_2$ , and twice the  $\text{C}_2\text{H}_6$  rates)

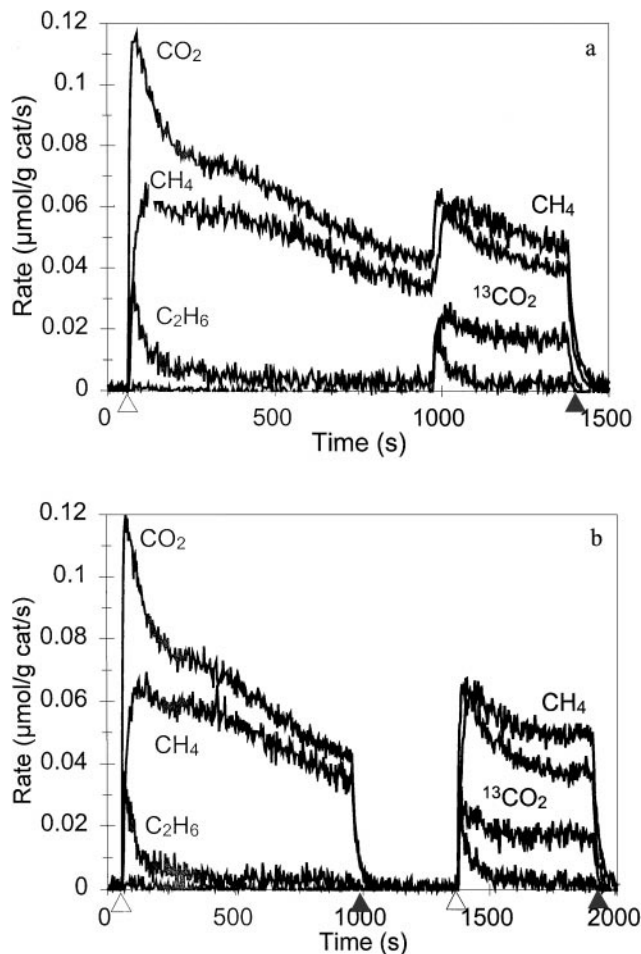
is only 0.09  $\mu\text{mol/g cat/s}$ . Furthermore, the amount  $^{12}\text{CO}_2$  produced during the first  $\text{O}_2$  pulse was 7.5 times the uptake of  $\text{CH}_4$ . Since TPD after PCD showed no long-lived intermediates during PCD, the excess  $^{12}\text{CO}_2$  must have been produced by acetic acid reacting with adsorbed oxygen. The second  $\text{O}_2$  pulse produced similar results. These observations indicate that adsorbed oxygen, which is present during PCO but not PCD, reacts with acetic acid in a different pathway than either reaction [1] or [2]. Therefore, the mechanism for PCO is expected to be different than that of PCD. Furthermore, PCO and PCD studies of formic acid (11) indicate that the  $\text{TiO}_2$  surface is not oxygen deficient during PCO in 3%  $\text{O}_2$  flow. This means that either lattice oxygen does not participate in PCO or any oxygen extracted from the surface is quickly replenished by the gas phase. Figures 2 and 3 show that adsorbed oxygen replenishes reduced  $\text{TiO}_2$  at room temperature in the dark and during UV illumination, as seen during formic acid PCD (11).

#### Acetic Acid injection

Figure 4a shows PCD of a monolayer of acetic acid with a 110  $\mu\text{mol/g}$  catalyst pulse of  $\text{CH}_3^{13}\text{COOH}$  injected during UV illumination at 950 s. After the  $^{13}\text{C}$ -acetic acid injection,  $^{13}\text{CO}_2$  forms and the  $^{12}\text{CO}_2$  and  $\text{CH}_4$  rates are 1.4 and 1.7 times their respective rates before the injection. The  $^{12}\text{CO}_2$  rate increases even though the  $^{12}\text{C}$ -acetic acid coverage did not increase. If reaction [2] is second-order in acetic acid concentration, the  $^{12}\text{CO}_2$  rate should increase with the addition of  $\text{CH}_3^{13}\text{COOH}$  to the surface. The  $^{13}\text{CO}_2$  rate after the injection was approximately one-third of the total  $\text{CO}_2$  rate, even though  $^{13}\text{C}$ -acetic acid comprised only 20% of the total acetic acid coverage. This indicates a possible heterogeneity of UV intensity, or some sites are more active for PCD since the  $^{13}\text{C}$ -acetic acid injection might preferentially adsorb on the more active sites. The rate of  $\text{CH}_4$  formation after  $^{13}\text{C}$ -acetic acid injection was nearly equal to its initial rate, indicating that the total acetic acid coverage after the  $^{13}\text{C}$ -acetic acid injection was near saturation. The  $\text{CH}_4$  rate after injection equaled the initial rate even though lattice oxygen was removed during PCD, because the pathway to form  $\text{CH}_4$  does not require lattice oxygen.

The  $\text{C}_2\text{H}_6$  rate after the injection was only 60% of the initial rate, even though the acetic acid coverage was nearly a monolayer. A lower rate is expected since PCD extracts lattice oxygen, and  $\text{C}_2\text{H}_6$  formation requires lattice oxygen. The rate of  $\text{C}_2\text{H}_6$  production after the injection is eight times the rate before the injection, however. The dramatic increase in the rate of  $\text{C}_2\text{H}_6$  formation is partly because  $\text{C}_2\text{H}_6$  forms in a bimolecular reaction. However second-order kinetics would predict a doubling of the rate, based on the increase in acetic acid coverage, suggesting that some  $\text{TiO}_2$  sites are more active for  $\text{C}_2\text{H}_6$  formation.

Figure 4b shows PCD of a monolayer of acetic acid with a 110  $\mu\text{mol/g}$  catalyst pulse of  $\text{CH}_3^{13}\text{COOH}$  injected in the



**FIG. 4.** Product formation rates during photocatalytic decomposition of a monolayer of acetic acid on TiO<sub>2</sub>. (a) A pulse of CH<sub>3</sub><sup>13</sup>COOH was injected at 900 s with the UV lights on. (b) A pulse of CH<sub>3</sub><sup>13</sup>COOH was injected at 900 s during the 420 s dark time. The UV lights were turned on (open triangles) and off (solid triangles) as indicated.

dark at 950 s. When UV illumination resumes, <sup>13</sup>CO<sub>2</sub> forms at essentially the same rate as in Figure 4a, and the <sup>12</sup>CO<sub>2</sub> and CH<sub>4</sub> rates are 1.6 and 1.7 times their respective rates before the dark time. The C<sub>2</sub>H<sub>6</sub> rate after the dark time is approximately 90% of the initial rate, but does not equal the initial rate, presumably because diffusion of bulk oxygen to the surface was not complete after 420 s in the dark. The C<sub>2</sub>H<sub>6</sub> rate increases more when <sup>13</sup>C-acetic acid is injected during the dark than when <sup>13</sup>C-acetic acid was injected during UV illumination since C<sub>2</sub>H<sub>6</sub> formation requires lattice oxygen and oxygen from the bulk replenished the surface during the dark time. Similar to in Fig. 4a, the rate of CH<sub>4</sub> formation after the dark time is equal to the initial rate, indicating the coverage after injection equals the initial coverage.

#### Heterogeneity of Surface Sites

A similar experiment to that in Fig. 4b was done with formic acid to determine whether the changes in the rates

are because most reaction takes place on a small number of highly active sites. We have seen that formic acid also undergoes PCD on TiO<sub>2</sub> (11). After 1200 s of PCD of a monolayer of formic acid, 90 μmol HCOOH/g catalyst was injected with the lights on. This pulse increased the HCOOH coverage from 0.9 to 1 mL and the subsequent rate of CO<sub>2</sub> production was 2.5 times the rate before the pulse. The injected formic acid is expected to adsorb on active sites that were empty after 1200 s of PCD. Since the rate after the formic acid injection was about 25% of the initial CO<sub>2</sub> production rate but the surface was saturated, PCD is not limited by surface diffusion of formic acid to active sites but instead is limited by the availability of surface lattice oxygen. That the CO<sub>2</sub> rate increased a factor of 2.5 after only 10% of a monolayer was added suggests that some sites are more active for PCD of formic acid, and the rate increase is not caused by nonuniform UV illumination.

#### Role of Weakly Bound Acetic Acid

Titania covered with a monolayer of acetic acid was heated to 450 K to desorb weakly bound acetic acid. Kim and Barteau (13) concluded that reversibly adsorbed acetic acid is not dissociated on anatase TiO<sub>2</sub>, and more strongly adsorbed acetic acid dissociates to form acetate. Heating to 445 K desorbs weakly bound acetic acid so that 85% of a monolayer is left on the surface. During the subsequent PCD, the initial rates of C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub> formation are approximately 75 and 81%, respectively, of those for PCD of a monolayer of acetic acid. Since the PCD rate is approximately proportional to coverage, undissociated acetic acid apparently reacts the same as surface acetate or it reacts to first form surface acetate. For PCD in the liquid phase, Yoneyama *et al.* (5) observed that when sodium acetate concentration was fixed and acetic acid concentration increased, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> rates and the C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> ratio increased after 15.5 h in a batch reactor. From this they suggested that undissociated acetic acid participates in the reaction. However, the increase in the C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> ratio with increasing acetic acid concentration does not necessarily indicate that molecularly adsorbed acetic acid reacts differently from surface acetate. It could be attributed to higher acetic acid concentrations, which should increase the rate of the bimolecular reaction to form C<sub>2</sub>H<sub>6</sub> more than the CH<sub>4</sub> rate.

#### UV Intensity

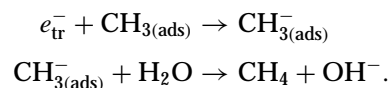
Decreasing the light intensity by 88% after several minutes of PCD decreases the overall reaction rate by an order of magnitude, but the selectivity is the same. The UV intensity was then set to its original value for several minutes. A subsequent increase to approximately 1.4 times the original UV intensity increases the rate of CH<sub>4</sub> production by 40%, whereas the C<sub>2</sub>H<sub>6</sub> formation rate increases by only 20%. The C<sub>2</sub>H<sub>6</sub> formation rate increases less than the CH<sub>4</sub> since

it is limited at the higher intensities by availability of lattice oxygen and coverage of acetic acid. Note in Fig. 2 that the higher UV intensity increases the initial rate of CH<sub>4</sub> formation more than the initial C<sub>2</sub>H<sub>6</sub> rate. Furthermore, the C<sub>2</sub>H<sub>6</sub> formation rates for the two UV light intensities coincide after 30 s of UV illumination whereas the higher UV intensity produces a significantly greater CH<sub>4</sub> rate for 600 s and a slightly greater rate throughout PCD. This is consistent with other results that show surface concentration of acetic acid and availability of lattice oxygen limit the rate of C<sub>2</sub>H<sub>6</sub> formation.

#### Co-adsorbed Water

Water did not change the rate of formic acid PCD when it was injected either in the dark or during UV illumination, indicating that water at room temperature does not oxidize the reduced TiO<sub>2</sub> (11). In contrast, Fig. 5 shows PCD of an acetic acid monolayer when pulses of H<sub>2</sub>O are injected during UV illumination and in the dark. Water injection at 800 s more than doubles the CO<sub>2</sub> and CH<sub>4</sub> rates, whereas the C<sub>2</sub>H<sub>6</sub> rate is 4.8 times the rate before the injection. A portion of the rate increase could be because water displaces acetic acid to more active sites that are vacant because acetic acid on these sites reacted first. The increase in the rate of reaction [2] could be completely due to acetic acid displacement to more active sites, since the C<sub>2</sub>H<sub>6</sub> rate after injection is only about half the initial rate. However, note that the CH<sub>4</sub> rate during the water pulse is *greater than the initial rate*, indicating that water increases the rate of reaction [1]. This rate may increase because methyl groups abstract hydrogen from water to form CH<sub>4</sub>. Kraeutler and Bard (4) suggested the possibility of methyl radicals reacting with a trapped electron to form a methyl anion. This

anion could react with water to form CH<sub>4</sub>:



A pulse of water during the 120-s dark period nearly doubles the CH<sub>4</sub> rate and triples the C<sub>2</sub>H<sub>6</sub> rate. The rate increases for both CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are not as large as the previous pulse in the light, most likely because less acetic acid was on the surface. The amount of CO<sub>2</sub> produced during the water injections is equal to the amount of CH<sub>4</sub> plus twice the amount of C<sub>2</sub>H<sub>6</sub>. This indicates that water does not react with acetic acid by another pathway, in contrast to adsorbed O<sub>2</sub>. Water could increase the rate by displacing acetic acid to more active sites and acting as a hydrogen source for reaction [1].

#### Initial Steps of Photocatalytic Decomposition

When a monolayer of methyl acetate is exposed to UV light in He flow, *no reaction takes place*. Subsequent TPO confirmed that methyl acetate coverage was similar to that of acetic acid. The lack of reaction indicates that the first step in acetic acid PCD is abstraction of acid hydrogen to form adsorbed acetate. This result agrees with the observation by Kraeutler and Bard (4) that during PCD in the liquid phase, CH<sub>3</sub>COOH decomposed almost twice as fast as CH<sub>3</sub>COOD.

Although methyl acetate does not react during PCD, it readily oxidizes to CO<sub>2</sub> and H<sub>2</sub>O in the presence of gas-phase O<sub>2</sub>. This suggests that the oxidizing agent for PCO is different from that for PCD. Apparently adsorbed oxygen oxidizes organics during PCO, whereas lattice oxygen only oxidizes some species, such as the acid hydrogen in acetic acid. This suggests that a Mars Van Krevlen mechanism for PCO is not likely, since the oxidizing species would then be the same for PCD and PCO. Since the only difference between PCD and PCO is gas-phase O<sub>2</sub>, the oxidizing agent for PCO is most likely an adsorbed oxygen species.

Gravelle *et al.* (14) observed that gas-phase O<sub>2</sub> produced O<sub>2</sub><sup>-</sup> on illuminated TiO<sub>2</sub>. The O<sub>2</sub><sup>-</sup> surface concentration decreased when the catalyst was exposed to isobutane and UV illumination, but no reaction took place between isobutane and O<sub>2</sub><sup>-</sup> in the dark. Similarly, Linsebigler *et al.* (15) concluded that an excited O<sub>2</sub> species oxidized CO to CO<sub>2</sub> on illuminated TiO<sub>2</sub>(110) and this species was most likely either O<sub>2</sub><sup>-</sup> or O<sub>2</sub><sup>2-</sup>. Lu *et al.* (16) showed that CH<sub>3</sub>Cl did not react on TiO<sub>2</sub>(110) except in the presence of O<sub>2</sub>.

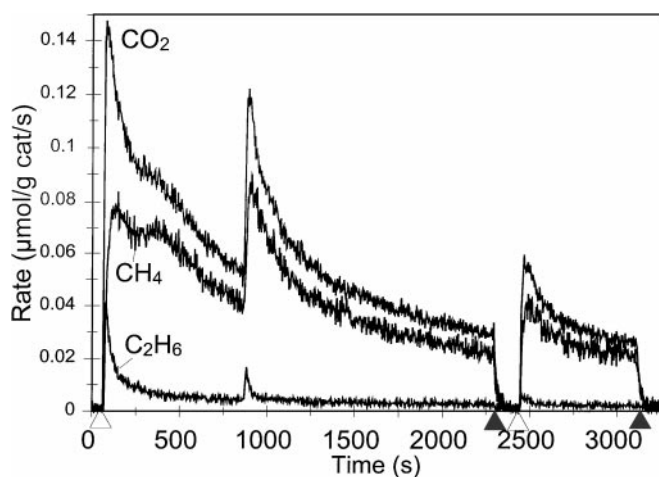


FIG. 5. Product formation rates during photocatalytic decomposition of a monolayer of acetic acid on TiO<sub>2</sub>. The lights were turned on and off as indicated by the open and solid triangles, respectively. Water was injected after 800 s (with the UV lights on) and 2300 s (in the dark).

#### CONCLUSIONS

In an inert atmosphere, acetic acid photocatalytically decomposes on TiO<sub>2</sub> at room temperature through parallel pathways to form CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, but methyl acetate does not decompose under the same conditions. Acetic

acid extracts lattice oxygen during C<sub>2</sub>H<sub>6</sub> formation. Oxygen extracted during acetic acid photocatalytic decomposition (PCD) is replenished by diffusion from the bulk or from gas-phase O<sub>2</sub> when present. Lattice oxygen is not consumed to produce CH<sub>4</sub> during PCD, and adsorbed O<sub>2</sub> quickly oxidizes either CH<sub>3</sub>(<sub>ads</sub>) or H(<sub>ads</sub>) before they recombine with H to produce CH<sub>4</sub>. Some sites have higher activity during both PCD and PCO. Dissociation of the O–H bond appears to be the first step in PCD and subsequent reaction occurs via the resulting acetate species. The oxidizing agent during photocatalytic oxidation (PCO) is different from that during PCD and is most likely adsorbed oxygen. Adsorbed oxygen reacts with acetic acid in a different pathway from the two reactions observed for PCD, so a Mars Van Krevlen mechanism for PCO is unlikely. Water increases the rate of CH<sub>4</sub> formation, apparently by reacting with methyl groups, but in contrast to adsorbed O<sub>2</sub>, it does not react with acetic acid in a separate pathway from PCD.

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