Catalysis Letters 55 (1998) 129–132


# Photocatalytic decomposition of acetic acid on $TiO_2$

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Received 8 August 1998; accepted 25 September 1998

During room-temperature transient experiments, acetic acid decomposes photocatalytically on $TiO_2$ in an inert atmosphere by two parallel pathways. One pathway forms $CO_2$ and $C_2H_6$ in a 2 : 1 ratio, and $H_2O$ forms with lattice oxygen that was extracted from the surface. The other pathway forms $CO_2$ and $CH_4$ in a 1 : 1 ratio.

**Keywords:** photocatalytic decomposition, $TiO_2$, acetic acid

## 1. Introduction

Heterogeneous photocatalytic oxidation (PCO) has potential applications for the complete oxidation of organic pollutants in dilute systems. A wide range of organics can be oxidized to $CO_2$ and $H_2O$ *at room temperature* on $TiO_2$ 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 then initiate redox reactions with surface species.

Recently, we used transient reaction at room temperature to study the photocatalytic reaction of formic acid in the absence of gas-phase $O_2$ in order to clarify the relative importance of adsorbed and lattice oxygen during PCO [1]. Even without $O_2$ in the gas phase, a monolayer of formic acid readily decomposed photocatalytically to form $CO_2$ and $H_2O$. This reaction was referred to as photocatalytic decomposition (PCD) to distinguish it from PCO, which takes place when gas-phase $O_2$ is present. During PCD, the $CO_2$ contained the oxygen that was originally in the formic acid, but the $H_2O$ product formed with lattice oxygen that was extracted from the $TiO_2$ surface. At longer reaction times, diffusion of bulk oxygen to the surface limited the reaction, and thus the reaction rate decreased rapidly with time. However, the PCD rate increased dramatically after the $TiO_2$ was held in the dark, because oxygen diffused to the surface during the dark time and was available for reaction when the UV lights were turned on.

In the current study, the products that form during transient PCD of acetic acid on $TiO_2$ at room temperature are determined, and PCD and PCO are compared. Acetic acid is of interest for comparison to formic acid PCD. Of particular interest is the fate of the $CH_3$ group in acetic acid since no $H_2$ was detected during PCD of formic acid, and neither $CH_4$ nor $C_2H_6$ are detected during PCO of acetic acid. In addition, PCD of acetic acid is of interest because both acetic and formic acids are surface intermediates during PCO of ethanol and acetaldehyde, and the $CH_3$ group in acetic acid is oxidized through a formate intermediate [1]. Transient experiments are preferred over steady-state experiments for reactions where the catalyst surface changes as lattice oxygen is removed. Similar to the formic acid PCD experiments [1], the $TiO_2$ surface was saturated with acetic acid, and neither $O_2$ nor acetic acid were in the gas phase. The products were detected by mass spectrometer. Because $CO_2$, $CH_4$, and $C_2H_6$ are weakly adsorbed on $TiO_2$, their appearance in the gas phase during transient reaction is limited by the surface reaction rate.

Another reason that PCD of acetic acid is of interest is because of the interesting results reported by Sclafani et al. [2]. They observed that acetic acid decomposed photocatalytically to $CH_4$, $CO_2$, and small amounts of $C_2H_6$. For the two types of $TiO_2$ catalysts studied, the *steady-state* ratios of $CO_2$ to $CH_4$ were 1.7 and 20.6, and the rate of $C_2H_6$ formation was less than 0.3% of the $CH_4$ rate. Since the $CO_2 : CH_4$ ratios were not one, as expected for the stoichiometry, water must have also formed during their reaction 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 $O_2$ may have been present in their feed. They reported similar results for the other oxides studied; the $CO_2/CH_4$ ratio was greater than one, and the $C_2H_6$ rates were small. They concluded that their PCD occurred by excitation of an adsorbed species rather than by generation of electron/hole pairs in $TiO_2$. Also, in contrast to previous PCO studies [3–5], Sclafani et al. observed that $CH_4$ still formed when $O_2$ was added to the feed. Thus, both PCO and PCD of acetic acid are presented in the current study for comparison to the results by Sclafani et al.

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## 2. Experimental methods

The apparatus used for PCD, PCO, and temperature-programmed desorption (TPD) was described previously [6]. Approximately 30 mg of Degussa P-25 $TiO_2$ catalyst were coated as a thin layer (average thickness $<0.5$ $\mu$m) on the inside of an annular Pyrex reactor so that all the $TiO_2$ was exposed to UV light for PCO. 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 approximately 0.3 mW/cm$^2$. The maximum light intensity was near 360 nm [4].

Before each experiment, the reactor was held at 723 K for 30 min in approximately 20% $O_2$ in He and then cooled to room temperature to create a reproducible surface. Two 1 $\mu$l pulses of acetic acid (Sigma, 99.99%) saturated the catalyst in the dark at 300 K prior to PCD or PCO, and all experiments started with the surface saturated. After exposure to acetic acid, the reactor was flushed for 2 h to remove all gas-phase acetic acid, so that only reaction of the adsorbed monolayer was studied. Photocatalytic decomposition was studied by illuminating the $TiO_2$ in 100 cm$^3$ (STP) of He flow per min, and PCO was carried out in 0.2% $O_2$ flow. The He stream did not have a detectable $O_2$ impurity. A small $m/e$ 32 signal was detected by the mass spectrometer, but this signal did not change when the lights were turned on. Since low concentrations of $O_2$ are readily detected when the lights are turned on [3], the small $m/e$ 32 signal was due to a background signal in the mass spectrometer vacuum chamber. We estimate the $O_2$ concentration in the He stream to be less than 0.3 ppm. Metal shields were placed between the reactor and the UV lights, and the shields were removed after the lights attained a steady-state output to illuminate the catalyst and initiate transient reaction at room temperature. To understand the role of lattice oxygen, the lights were turned off during PCD, and the effect of dark time on the subsequent rates of product formation were measured. After PCO or PCD, TPD was performed by heating the catalyst at 1 K/s to 723 K in He flow and holding at this temperature until no desorption products were detected.

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 downstream of the reactor, and signals were corrected for cracking in the mass spectrometer.

## 3. Results and discussion

During PCO, acetic acid oxidizes on $TiO_2$ to form gas-phase $CO_2$ and $H_2O$, and formic acid and formaldehyde intermediates remain on the surface [3]. In contrast, during UV illumination in an inert gas stream, a monolayer of adsorbed acetic acid photocatalytically decomposes on $TiO_2$ to form $CO_2$, $CH_4$, and $C_2H_6$ in the gas phase. Figure 1 shows the rates of formation of products as a function of time when a monolayer of acetic acid was exposed to UV irradiation in the absence of gas-phase $O_2$. Upon UV illumination, the rate of $CO_2$ production quickly reached a maximum of 0.11 $\mu$mol/g-cat s, quickly decreased to 0.06 $\mu$mol/g-cat s, and then decreased more slowly. The rate of $C_2H_6$ formation also decreased quickly after reaching its initial maximum of 0.04 $\mu$mol/g-cat s, but then decreased more slowly. The $CH_4$ formation rate did not exhibit a sharp maximum and decreased slowly throughout the PCD. All signals dropped to zero when the lights were turned off. When UV illumination resumed after 3600 s in the dark, the $CO_2$ rate was twice and the $C_2H_6$ rate was 4.3 times that measured before the lights were turned off. The increase in the $CO_2$ rate was approximately twice the increase in the $C_2H_6$ rate. In contrast, the rate of $CH_4$ production was the same as that before the dark time.

During PCD of $CH_3{}^{13}COOH$, only $^{13}CO_2$, $^{12}C_2H_6$, and $^{12}CH_4$ were detected. That is, $\alpha$-carbons were exclusively oxidized to $CO_2$ and $\beta$-carbons formed $CH_4$ and $C_2H_6$. These results suggest two parallel pathways for acetic acid decomposition during PCD:

$$CH_3COOH \rightarrow CO_2 + CH_4 \quad (1)$$

$$2CH_3COOH + O_{(l)} \rightarrow C_2H_6 + 2CO_2 + H_2O \quad (2)$$

Note that $H_2O$ is written as one of the products of reaction (2), but the H atoms may be present on the surface as OH groups. For these reactions, the rate of $CO_2$ formation should equal the sum of the $CH_4$ rate plus twice the $C_2H_6$ rate, and that is what was observed for the entire time interval. These signals are coincident when plotted this way. The differences between the $CO_2$ rate and the sum of ($CH_4 + 2C_2H_6$) rates were centered around zero, and the average difference was 6% of the signal.

Note that 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 $C_2H_6$ and $CO_2$ formation are greater after the dark time, because lattice oxygen diffuses from the bulk to replenish the surface oxygen vacancies in the dark, as was seen for PCD of formic acid [1]. The greater concentration of surface oxygen after the dark time increases the rate of reaction (2). Indeed, the rate increase for $CO_2$ after the dark time in figure 1 was approximately twice that for $C_2H_6$, as expected for reaction (2). Also, the rates of $C_2H_6$ and $CO_2$ formation drop rapidly from their initial rates as the lattice oxygen is removed from the

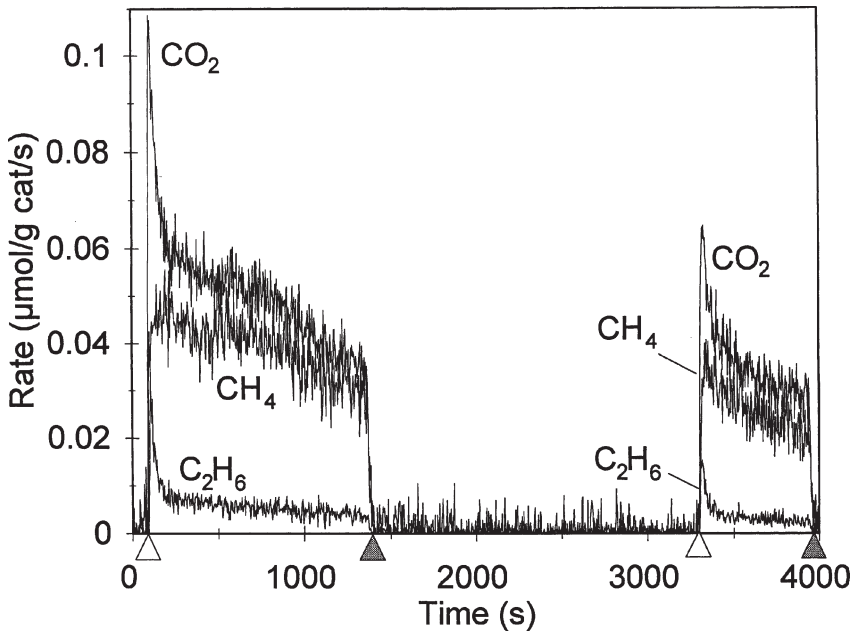


Figure 1. Formation rates of $CO_2$, $CH_4$, and $C_2H_6$ during photocatalytic decomposition of a monolayer of acetic acid on $TiO_2$ in He flow at room temperature. The UV lights were turned on (open triangles) and off (solid triangles) as indicated.

surface. In contrast, the $CH_4$ rate after a dark time was the same as the rate before the lights were turned off since reaction (1) does not require lattice oxygen. For the same reason, the $CH_4$ rate drops slower with time than the $C_2H_6$ rate. During acetic acid PCD, acid hydrogens combine with $CH_3$ groups to form $CH_4$, whereas for formic acid PCD, acid hydrogens do not combine with each other nor with the hydrogen originally bound to the carbon. Similarly, no $H_2$ forms during PCD of acetic acid by combining two acid hydrogens.

A TPD performed after PCD detected acetic acid and acetone, $CO_2$, and $H_2O$, which are products of bimolecular ketonization of acetic acid, indicating that acetic acid was on the surface when PCD was stopped. This suggests that methyl groups formed during PCD do not remain on the surface, but quickly react to form $CH_4$ and $C_2H_6$. These alkane products do not remain on the surface because they are too weakly adsorbed on $TiO_2$ to have significant coverages at room temperature. The $H_2O$ seen during TPD can be from both the ketonization reaction and reaction (2), since $H_2O$ that forms during PCD adsorbs strongly on $TiO_2$. During PCO of a monolayer of acetic acid, both formaldehyde and formate are on the surface [3], but neither was detected during a TPD after PCD. That is, the lattice oxygen does not oxidize the $CH_3$ groups. Thus, during PCO adsorbed oxygen may be necessary for some oxidation steps, whereas lattice oxygen is used in others.

During PCO of a monolayer of $CH_3{}^{13}COOH$, $^{13}CO_2$ formation rapidly reaches a maximum rate after the catalyst is exposed to UV irradiation, whereas the rate of $^{12}CO_2$ formation increases slowly to a maximum after 1050 s of illumination, as shown in figure 2. The $\alpha$-carbon in acetic acid preferentially oxidizes to $^{13}CO_2$, and only at long times are the rates of $^{12}CO_2$ and $^{13}CO_2$ comparable, and eventually the $^{12}CO_2$ rate is higher. For the time interval in figure 2, the rate of $CO_2$ formation is greater during PCO than during PCD. The initial rate of $CO_2$ formation during PCO was twice that during PCD. The rate of $CO_2$ formation decreased more rapidly after initial illumination during PCD. After 250 s, the PCD rate was 58% of the initial rate, whereas the PCO rate was 83% of the initial rate. As shown in figure 2, $^{12}$C-formaldehyde is also seen during PCO, but because of calibration difficulties, the scale for formaldehyde is arbitrary. Neither $C_2H_6$ nor $CH_4$ are observed during PCO. This suggests that during PCO, methyl groups may form on the surface but they react preferentially with oxygen before they react with either H to form $CH_4$ or another $CH_3$ to form $C_2H_6$.

Both our PCD and PCO transient results are in sharp contrast to the steady-state results of Sclafani et al. [2]. They saw $CO_2$ and $CH_4$ as the main products during PCD; their $C_2H_6$ rates were less than 0.3% of their $CH_4$ rates. In contrast, our $C_2H_6$ and $CH_4$ rates are similar at short times, and the $C_2H_6$ rate is approximately 10% of the $CH_4$ rate at longer times. Since they ran for 40–70 h, they may have depleted the lattice oxygen sufficiently that reaction (2) was slower than in our experiments. We cannot explain why their $CO_2 : CH_4$ ratios are so much greater than one, however, unless they had an $O_2$ impurity or an $O_2$ leak, but such a leak would have replenished the lattice oxygen and should have caused $C_2H_6$ to form. They did not obtain mass balances for their experiments, whereas our results are consistent with the stoichiometry of reactions (1) and (2). Similarly, during PCO they saw $CH_4$, whereas neither our transient experiments nor other previous studies have seen $CH_4$ formation during PCO.

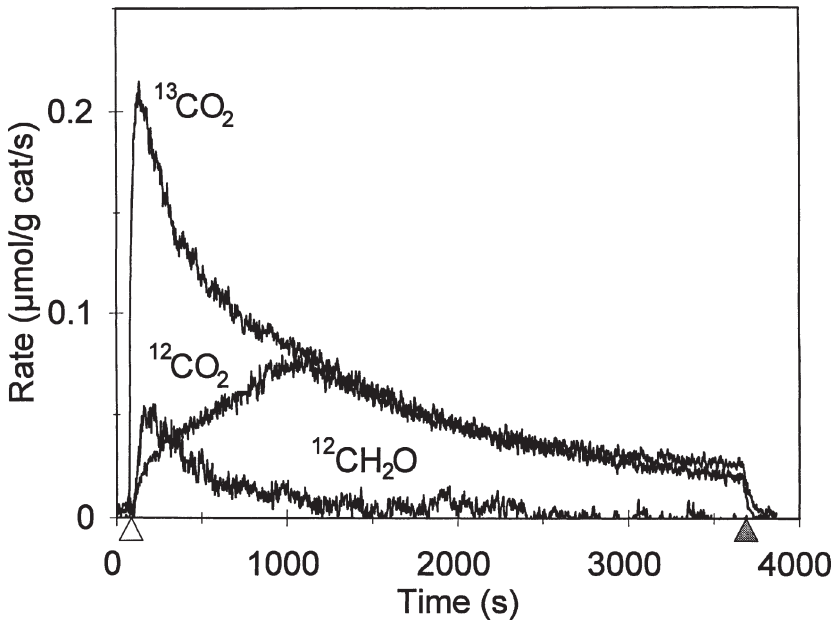


Figure 2. Product formation rates during photocatalytic oxidation of a monolayer of $CH_3{}^{13}COOH$ on $TiO_2$ in 0.2% $O_2$ at room temperature. The UV lights were turned on (open triangles) and off (solid triangles) as indicated.

## 4. Conclusions

Acetic acid decomposes photocatalytically to $CO_2$, $CH_4$, and $C_2H_6$ on $TiO_2$ by two pathways. The first pathway does not require lattice oxygen ($CH_3COOH \rightarrow CH_{4(g)} + CO_{2(g)}$), but the second pathway does ($2CH_3COOH + O_{(l)} \rightarrow C_2H_6 + 2CO_2 + H_2O$). Lattice oxygen diffuses from the bulk during dark times to replenish reduced $TiO_2$ surfaces. The $\alpha$-carbon forms $CO_2$ whereas the $\beta$-carbon forms $CH_4$ and $C_2H_6$. No long-lived intermediates are produced during PCD. During PCO, $CH_4$ and $C_2H_6$ are not produced because methyl groups react preferentially with oxygen to form formaldehyde, which then oxidizes to formate and eventually $CO_2$.

## Acknowledgement

We gratefully acknowledge support by the National Science Foundation, Grant #CTS-9714403, and SAK gratefully acknowledges support from NSF-REU Grant EEC-9531361.

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