Factors Influencing Product Distribution in Photocatalytic Decomposition of Aqueous Acetic Acid on Platinized TiO_2

Hiroshi Yoneyama, Yoshiyuki Takao, Hideo Tamura,

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka, Japan

and Allen J. Bard*

Department of Chemistry, University of Texas, Austin, Texas 78712 *(Received: September 9, 1982)*

Reaction products of the photocatalytic decomposition of acetic acid/acetate mixtures at Pt/TiO_2 were determined quantitatively for the gas phase and qualitatively for species in solution under a variety of experimental conditions. The relative yield of ethane to methane produced was high when the decomposition rate was high, and the amount of CO_2 produced usually exceeded that of methyl radical consumed in the formation of methane and ethane. Analysis of the solutions revealed that ethanol and acetyldehyde were produced, and further oxidation of these substances seems likely to be at least partly responsible for the excess production of CO_2. The production of methane occurred even under conditions where the formation of adsorbed hydrogen was made insignificant by the preferential reduction reaction (Pd deposition) during the photodecomposition of acetic acid/acetate mixtures. Electrolysis experiments at a single-crystal TiO_2 anode also showed that, even under very high anodic bias, where any cathodic reaction is completely suppressed, methane was produced with higher yields than ethane. The processes to account for these phenomena are discussed.

Introduction

Light-induced decarboxylation of acetic acid on platinized TiO_2 powder in aqueous solutions (the photo-Kolbe reaction) was reported by Kraeutler and Bard in 1978,[1] who showed that the major reaction products in deaerated solutions were carbon dioxide and methane with minor production of ethane and hydrogen. They investigated effects of a variety of experimental conditions on the rate of the decarboxylation reaction mainly by collecting carbon dioxide and explained the reaction in terms of semiconductor photoelectrochemical behavior. The purpose of the present paper is to give more insight into the reaction mechanisms by quantitative determination of the products under a variety of experimental conditions similar to those chosen in the previous study.

Heterogenous reactions on semiconductors are governed in many cases by electrochemistry.[2-5] This is also true for the decomposition of acetic acid on TiO_2 powder, because partial platinization of the catalyst surface enhances the rate of reaction,[1] as also has been reported for other kinds of heterogeneous reactions such as the decomposition of water,[6] hydrogen evolution with consumption of sacrificial organic substances,[7] and amino acid photosynthesis.[8] As a useful model, a grain of platinized TiO_2 can be considered to be a microphotoelectrochemical cell.[9] One route to the production of methane is then the photooxidation of acetate on platinum-free surfaces to give methyl radical, which then combines with adsorbed hydrogen formed cathodically on platinum sites.[1] Alternative pathways to methane are also possible. These can be probed by experiments with oxidizing agents that are reduced in preference to water or protons, thus minimizing adsorbed hydrogen formation. The factors which influence the relative yields of methane to ethane produced also provide information about the reaction mechanism. These are discussed here, and a mechanism is proposed based on this work and previous investigations by electrochemical and electron spin resonance spin trapping techniques.[10-15]

Experimental Section

Catalyst Preparation. Rutile and anatase powder (Fuji Titanium Co.) were reduced in a stream of hydrogen at 650 °C for 1 h and then platinized photochemically.[15] The specific surface area of the rutile was 2.6 $m^2\ g^{-1}$, while the anatase powder was 4.7 $m^2\ g^{-1}$ as determined by a Shimazu-Micrometrics surface area analyzer (Model 2205). The platinum loading was 3% by weight. Because of the difference in surface area between the rutile and anatase powders, another rutile powder, prepared by hydrolyzing titanium tetrachloride, was used to observe the effects of surface area. The pretreatment procedures described above were applied to this powder, which had a specific surface area of 5.0 $m^2\ g^{-1}$.

The TiO_2 electrode (single crystal, 10 mm diameter × 1 mm thick) was reduced under the same conditions as the powder catalyst. One end face of (001) orientation was polished successively with 0.3- and 0.05-μm alumina to give a mirrorlike surface. After being washed in an ultrasonic bath, it was treated with a mixture of sulfuric acid and

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TABLE I: Rate of Formation of Methyl Radical (as Methane and Ethane) and Relative Mole Ratio of Gas Components Produced[a]

	rutile				anatase			
	rate of $\cdot CH_3$ formation, $\mu mol\ h^{-1}$	mole ratio			rate of $\cdot CH_3$ formation, $\mu mol\ h^{-1}$	mole ratio		
pH		CH_4/C_2H_6	$CO_2/\cdot CH_3$	H_2/C_2H_6		CH_4/C_2H_6	$CO_2/\cdot CH_3$	H_2/C_2H_6
7.5	0.24	85	50	100	1.3	67	7.7	55
6.0	0.97	58	3.4	22	3.5	28	1.8	14.5
5.1	2.6	29	2.1	11	9.7	16	1.3	8.7
3.9	3.4	16	1.0	15	15	12	1.3	6.8
3.1[b]	4.2	19	1.1	5.8	13	11	1.7	5.0
2.0[b]	3.4	30	1.9	27	3.5	17	2.0	5.5
0.9[b]	0.98	14	5.0	27	3.7	19	1.3	7.4
0.1[b]	0.94	41	2.9	29	3.0	32	33	14.3

[a] Experiments were carried out at a 4.6 M total concentration of acetic acid/acetate by using 20 mL of solution and 0.3 g of catalyst. Illumination time: 2 h. [b] Sulfate ions are included depending upon pH values.

ammonium sulfate (1:1) at 200 °C for 1 h.[16] The crystal was then mounted in a glass tube with silicone rubber adhesive (Shin-Etsu Chemical, KE 42 RTV) after making ohmic contacts to the back face with InGa alloy.

Reaction Cell. Photocatalytic experiments were carried out in a tubular one-compartment cell (30-mm diameter, ca. 95-mm height). A gas inlet for flushing nitrogen to purge the solution of dissolved oxygen was attached to the cell top via a glass joint, with an oulet in the upper portion of the side wall. In addition, a port for sampling gases was also contained in the side wall; this was a silicone fitting such as that used as the injection port of a gas chromatograph. In cases where electrolysis experiments were carried out, another one-compartment cell was employed in which a test electrode of TiO_2 and a platinum counterelectrode were set in the cell and connected to lead wires sealed in ground joints.

Gas Analysis. Determination of gases evolved in the photocatalytic reaction was carried out by gas chromatography with a Yanaco Model G 180 gas chromatograph. Hydrocarbon gases such as methane and ethane, simple aliphatic alcohols, and aldehydes were analyzed with a Porapak Q column at an oven temperature of 120 °C and a flame ionization detector. Carbon dioxide was determined with a thermal conductivity detector and a Porapak Q column at 90 °C and hydrogen with molecular sieve 5A at 90 °C.

Photocatalytic and Photoelectrolytic Experiments. A 500-W super-high-pressure mercury arc lamp (Ushio Electric Co., USH-500) served as a light source. A quartz lens was used to concentrate the light beam to about a 20-mm diameter; the total light intensity at the cell was ~3.6 W, as determined by a laser power meter (Coherent Radiation, Model 201). Except where noted, experiments were carried out under essentially these illumination conditions. Usually, 0.3 g of catalyst was used. This was suspended in 20 mL of solution, and nitrogen was bubbled into the suspension for 30 min under agitation with a magnetic stirrer. Stopcocks of the gas inlet and outlet were then closed and the suspension was irradiated.

In the photoelectrolysis product yield experiments at a rutile electrode, no reference electrode was employed, and a constant current was applied between the photoanode and the counterelectrode. In cases where current–potential curves were measured, an aqueous saturated calomel electrode (SCE) served as the reference electrode.

Solution Preparation. All chemicals were of reagent grade (Wako Pure Chemical Co.). Sodium acetate/acetic acid mixed solutions were prepared with doubly distilled water. Except where noted, the total concentration of acetic acid/acetate was 4.6 M, and a stock solution of this concentration was prepared by mixing acetic acid and sodium acetate at 4 and 0.6 M, respectively. This stock solution had a pH of 3.9 and solutions of different pH were prepared by adding the appropriate amount of sulfuric acid or sodium hydroxide to the solution.

Results

Photocatalytic Decomposition in the Absence of Competitive Oxidizing Agents. The photocatalytic decomposition of acetic acid/acetate deaerated solutions yielded stable gaseous products such as methane, ethane, hydrogen, and carbon dioxide. Besides these gaseous products, ethanol and acetaldehyde were found in the liquid phase. Since these aquated substances can be oxidized photochemically on platinized TiO_2 to give CO_2 as the final product,[17] the total yield of these substances depends upon the total irradiation time and solution conditions. Quantitative analyses of these substances were not undertaken. Table I gives analytical results on the stable gaseous products.

As shown in Table I, the amount of CO_2 exceeded that expected from the sum of methane and ethane produced according to the following equation:

$$CH_3COO^- + h^+ \rightarrow \cdot CH_3 + CO_2 \qquad (1)$$

i.e., taking $(CH_4) = (\cdot CH_3)$ and $(C_2H_6) = 2(\cdot CH_3)$, $CO_2/\cdot CH_3$ should equal 1. The discrepancies observed would be brought about at least in part by further decomposition of the organic compounds produced, such as via the above-mentioned photocatalytic decomposition of ethanol and acetaldehyde. The maximum rate of $CH_4 + C_2H_6$ formation occurred at pH 3–4, which is in rough accord with the results obtained by Kraeutler and Bard from the rate of carbon dioxide production.[2] The ratio of methane to ethane produced depends upon the photodecomposition rate (Figure 1). The relative ratio of the ethane to methane increased with an increase in the decomposition rate. Comparison of the maximum rate given in Table I between the rutile and anatase catalyst confirms the results already reported that anatase is more active than rutile. This was also true of the rutile catalyst with the same specific surface area as the anatase (5.0 $m^2\ g^{-1}$).

The results mentioned above concern those obtained in solutions containing a total concentration of 4.6 M acetic acid/acetate at different pH. When the solution pH was

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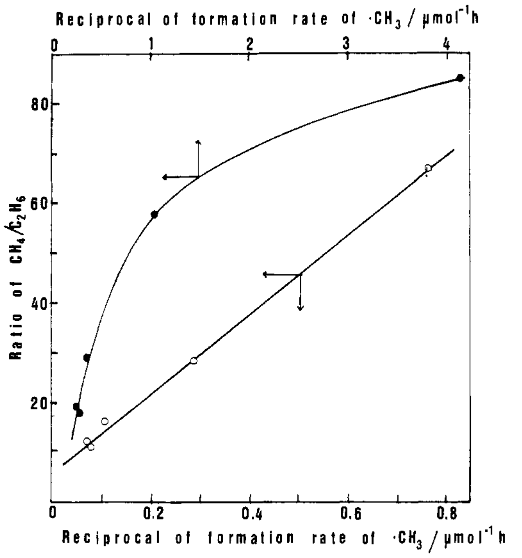

Figure 1. Ratio of methane to ethane vs. reciprocal of the formation rate of methyl radical in the production of these substances. Constant illumination intensity and different pH. Open symbol: anatase catalyst. Filled symbol: rutile catalyst. (Data taken from Table I, for pH >2.5.)

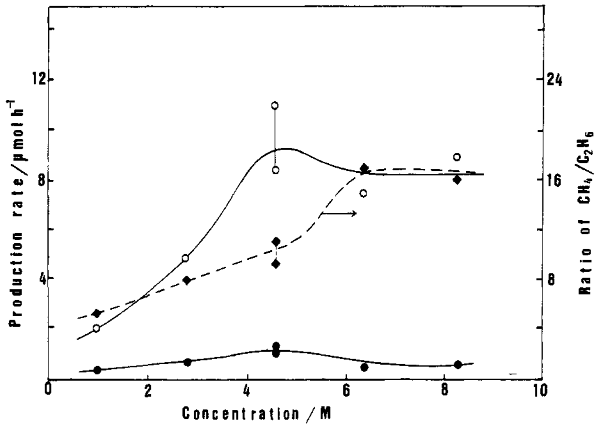

Figure 2. Production rate of methane and ethane, and ratio of methane to ethane as a function of the total concentration of acetic acid/acetate at pH 3.1. Experiments were carried out with 0.3 g of platinized anatase powder in 20 mL of solution for 2 h: (○) CH_4, (●) C_2H_6.

fixed at 3.1 and the total concentration of acetic acid/acetate was varied, the production rate of both methane and ethane increased with an increase in the total concentration up to $\sim$5 M (Figure 2) but remained essentially constant or dropped beyond this concentration. This also was true for the production of hydrogen and carbon dioxide. A total concentration of 4.6 M at pH 3.1 was chosen for studies on the effect of illumination intensity, described below. If the concentration of acetic acid was varied with the concentration of sodium acetate fixed at 0.1 M, the rate of production of both methane and ethane increased with an increase in the acetic acid concentration (Figure 3). This suggests participation of the acetic acid molecule itself in the decomposition reaction.

The rate of the decomposition reaction increased almost linearly with increasing illumination intensity; an increase in intensity also favored ethane formation (Figure 4).

Effects of Pd^{2+} as an Oxidizing Agent on Ethane Yield. Methane formation should be suppressed and ethane formation proportionally enhanced by adding an appropriate oxidant which (1) is easily reduced, (2) shows no appreciable reactivity for reoxidation when reduced, and (3) is not attacked by methyl radicals. Pd^{2+} was chosen as a chemical species having these properties. The photodeposition of palladium occurs as the cathodic process with simultaneous evolution of oxygen at TiO_2.[3,18] Since the redox potential of Pd^{2+}/Pd is more positive than that of H^+/H_2, Pd^{2+} should compete effectively with H^+ for photogenerated electrons. This is the basis for the photodeposition of palladium and also was found to be valid in acetic acid/acetate solutions by measuring current–potential curves of the TiO_2 electrode in the presence and absence of Pd^{2+}.

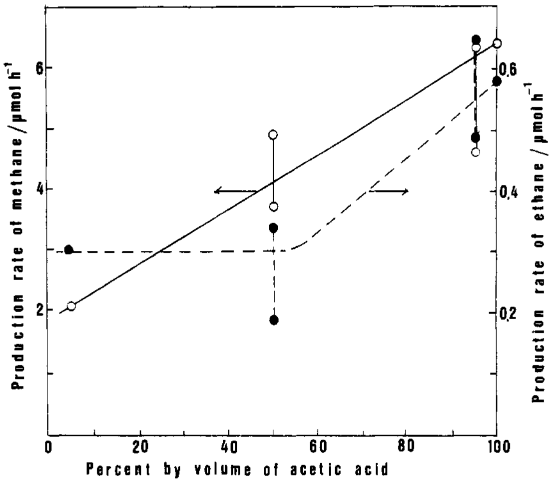

Figure 3. Production rate of methane and ethane as a function of the concentration of acetic acid. Solution: 0.1 M sodium acetate (*x* vol % acetic acid + (100 − *x*) vol % H_2O). Catalyst: Pt/rutile (0.5 g). Solution volume: 20 mL. Illumination time: 15.5 h.

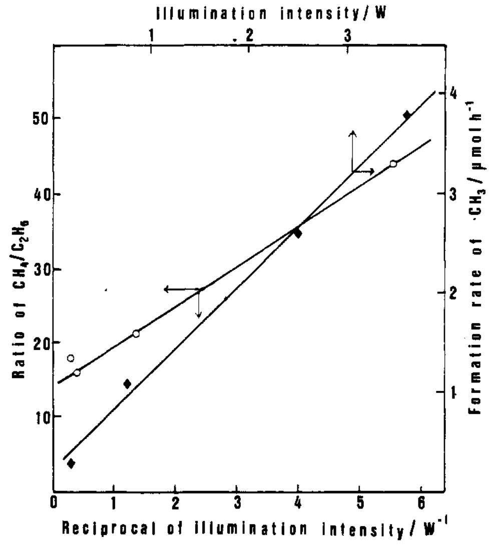

Figure 4. Dependence of the ratio of methane to ethane on the reciprocal of illumination intensity and that of the formation rate of methyl radical on the illumination intensity. Solution: 20 mL of 4.6 M acetic acid/acetate at pH 3.1. Catalyst: 0.3 g of platinized anatase powder.

The amounts of methane, ethane, hydrogen, and carbon dioxide produced were determined intermittently as a function of illumination time. For comparative purposes, similar experiments were carried out in the absence of Pd^{2+}. The results showing the time course of the production of these substances are given in Figures 5 and 6 for the presence and absence of Pd^{2+}, respectively. In the absence of Pd^{2+}, the production rate of methane, ethane,

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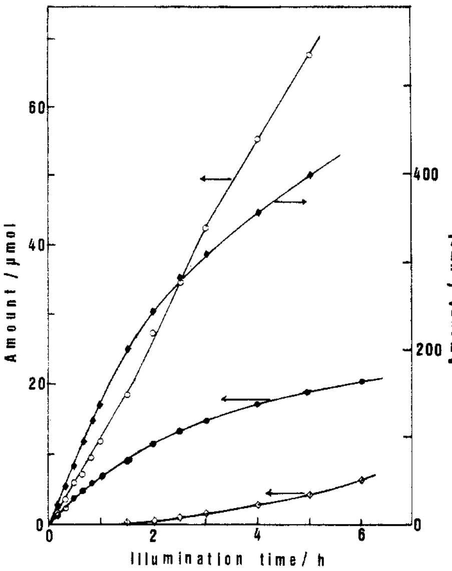

Figure 5. Production of methane, ethane, hydrogen, and carbon dioxide as a function of illumination time. Experiments were carried out with 0.3 g of platinized anatase catalyst in 20 mL of 4.6 M acetic acid/acetate containing 10 mM $PdCl_2$ at pH 3.1: (○) CH_4, (●) C_2H_6, (♦) CO_2, (◇) H_2.

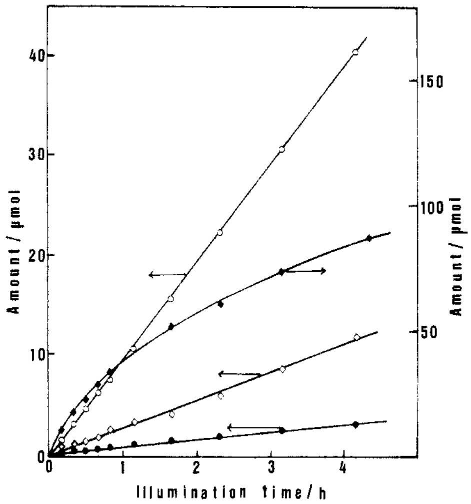

Figure 6. Production of methane, ethane, hydrogen, and carbon dioxide as a function of illumination time. Experiments were carried out with 0.3 g of platinized anatase catalyst in 20 mL of 4.6 M acetic acid/acetate ($PdCl_2$ free) at pH 3.1: (○) CH_4, (●) C_2H_6, (♦) CO_2, (◇) H_2.

and hydrogen was invariant with illumination time, but not so for carbon dioxide, which results not only from the decarboxylation to yield methane and ethane but also from the decomposition of side-reaction products such as ethanol and acetaldehyde. Illumination of solutions containing Pd^{2+} without platinized TiO_2 caused some decomposition of acetic acid, but this rate was negligible compared with that obtained in the presence of the photocatalyst. In the presence of the photocatalyst, the concentration of Pd^{2+} decreased from 10 to 3.7 mM for the first hour of illumination and to 0.42 mM after another hour.

The time courses of the ratio of methane to ethane, determined on the basis of these figures, are shown in Figure 7. The results in Figures 5–7 lead to the following conclusions: (1) The production rate of methane, ethane, and carbon dioxide is higher in the presence of Pd^{2+} than in its absence; (2) hydrogen evolution is completely suppressed by the introduction of Pd^{2+} into the solution for the first hour of illumination; (3) the ratio of methane to ethane is much smaller in the presence of Pd^{2+}. These observations are related to the expected role of Pd^{2+} in the photocatalytic decomposition of acetic acid, where it enhances the reaction rate by being selectively reduced. Note, however, that even when bulk hydrogen evolution is completely suppressed, methane is still produced. This suggests that methane is formed by reactions other than the reaction of methyl radical with adsorbed hydrogen.

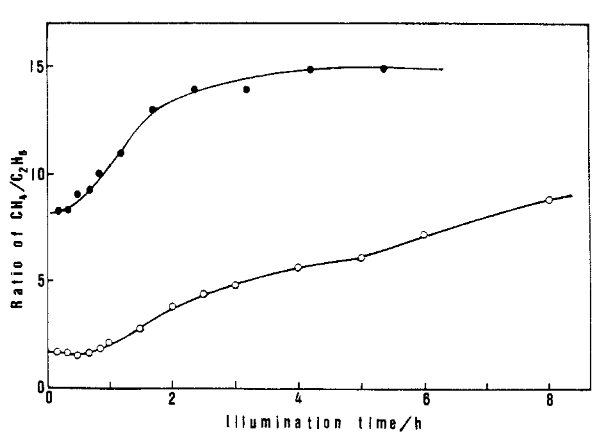

Figure 7. Ratio of methane to ethane produced vs. illumination time. Data from Figures 5 and 6: (○) in the presence of 10 mM $PdCl_2$; (●) $PdCl_2$ free.

As palladium deposition progresses, the photocatalytic activity of platinized TiO_2 powder must be modified by the deposited palladium, so that the relatively high ratio of ethane to methane produced, observed in the presence of Pd^{2+}, could in part reflect the modified catalytic activity. To clarify this point, we carried out photocatalytic experiments with palladium-loaded platinized TiO_2 powder prepared by the same photocatalytic process as described above. The amount of palladium loaded was ca. 6% by weight, and the photocatalytic experiments were performed in 20 mL of 4.6 M acetic acid/acetate at pH 3.1 in the presence of 0.3 g of catalyst. The rates obtained (in μmol h^{-1}) are as follows: methane, 15; ethane, 0.48; hydrogen, 0.62; carbon dioxide, 17. On the other hand, results obtained by using the palladium-free platinized TiO_2 catalyst under the same experimental conditions are as follows: methane, 11; ethane, 1.0; hydrogen, 5.1; carbon dioxide, 22. These results suggest that palladium-loaded TiO_2 enhances the production of methane but retards that of ethane in solutions where proton reduction can occur, in accord with the well-known fact that palladium works effectively as a hydrogeneration catalyst. The results obtained in the presence of Pd^{2+} in solution are not, therefore, those expected on the basis of the catalytic activity of the deposited palladium. Rather, the results can reasonably be interpreted by assuming suppression of the formation of hydrogen atoms in the cathodic process by competitive reduction of Pd^{2+} over H^+.

Anodic Oxidation at a TiO_2 Electrode. Analysis of the gas phase of the electrolytic cell was performed after constant-current electrolysis carried out at a single-crystal TiO_2 electrode under several different conditions. The results obtained are shown in Table II, in which the current efficiency for the formation of methyl radical, measured as the total of methane and ethane, is given. The current efficiency (η) for methyl formation is defined by eq 2

$$\eta = 100\{(CH_4) + 2(C_2H_6)\}/\{Q/96487\} \qquad (2)$$

where (CH_4) and (C_2H_6) are the moles of methane and ethane produced by the electrolysis and Q is the charge (coulombs) consumed in the electrolysis.

The current efficiency depended upon the current density employed and was low for high current density.

TABLE II: Time-Averaged Amount of Methane, Ethane, Carbon Dioxide, and Methyl Radical Consumed in the Production of Methane and Ethane, and Current Efficiency for the Formation of Methyl Radical[a]

current density, μA cm^{-2}	pH	electrolysis time, h	av rate of production, μmol h^{-1} CH_4	C_2H_6	CO_2	$\cdot CH_3$	current efficiency for $\cdot CH_3$,[b] %
50	0.03	15.5	0.43	0.018	1.5	0.47	63
50	7.5	15.5	0.30	0.0023	7.2	0.30	40
52.6	3.1	15.5	0.59	0.026	1.1	0.64	86
526	3.1	13.5	0.27	0.079	1.3	0.43	5.8
5260	3.1	2.0	0.18	0.09	24	0.36	0.5

[a] Electrolysis was carried out in 4.6 M acetic acid/acetate mixture under a nitrogen atmosphere. Current density was varied by changing illumination intensity. [b] The current efficiency for the production of methyl radicals was calculated on the basis of eq 2 in the text.

This suggests that side reactions such as the formation of acetaldehyde and ethanol and other intermediates occur and that oxidation of these to produce CO_2 increases with increasing current density. The effect of solution pH on the ratio of methane to ethane, obtained by comparing the results given in this table at the same current density (50 μA cm^{-2}), suggests that methane production is favored by solutions of high pH. This is in qualitative agreement with the results obtained in the photocatalytic experiments at particles (Table I). Phenomenologically, such results seem to be reasonable, since the rate of production of methyl radical is relatively low in solutions of high pH.

Discussion

Basic Process. The light-induced decarboxylation of acetate on TiO_2 powder is believed to occur via an electrochemical mechanism, as described in the Introduction. Anodic oxidation of acetate produces methyl radical in its initial step as shown in eq 1. The acetic acid molecule itself may be oxidized, too, but this is energetically more difficult and less likely to occur. Note that acetate can be oxidized at illuminated TiO_2 electrodes in acetonitrile, as well as in aqueous solutions.[10]

The cathodic process is the formation of adsorbed hydrogen on Pt sites:[22]

$$H^+ + e^- \rightarrow \cdot H_{ad} \qquad (3)$$

Methane can be produced by coupling of methyl radical with a hydrogen atom:

$$\cdot CH_3 + \cdot H_{ad} \rightarrow CH_4 \qquad (4)$$

Ethane can form by dimerization of methyl radicals as in the Kolbe electrosynthesis:

$$\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6 \qquad (5)$$

The photocatalytic decomposition of acetic acid/acetate, however, does not proceed solely by this route. If eq 1, 4, and 5 described the overall reaction, the amount of ethane produced should be equal to that of hydrogen, and carbon dioxide to the sum of the amount of produced methane and twice that of ethane. However, as shown in Figure 5 and Table I, for example, hydrogen and carbon dioxide are produced in greater amounts than expected from the above-mentioned chemical stoichiometry. These results show that other organic intermediates, e.g., ethanol and acetaldehyde, are produced and that these are decomposed to CO_2 and H_2.

Oxidation Processes. Anodic oxidation of acetate competes with that of water depending upon its concentration. Studies[13] with ring-disk electrodes at 310 μA cm^{-2} showed that oxygen evolution is completely suppressed if the total concentration of equimolar mixtures of acetate/acetic acid exceeds 0.35 M. Thus, the remarkable dependence of the current efficiency for methane and ethane production on the current density, shown in Table II, cannot be explained by the occurrence of competing bulk oxygen evolution. However, it is probable that hydroxyl radicals are formed in competition with the methyl radical formation and the extent to which this occurs depends on the magnitude of the current density. The hydroxyl radicals produced are then involved in the subsequent chemical and/or electrochemical reactions to yield finally CO_2 as the main product.

Involvement of hydroxyl radicals has already been postulated in light-induced heterogeneous reactions such as photocatalytic oxidation of hydrocarbons[14] and amino acid photosynthesis,[8] based on the finding that illumination of platinized TiO_2 powder suspended in aqueous solutions causes the production of hydroxyl radicals on the powder surface.[14] Hydroxyl radicals may also be involved in the photocatalytic decomposition of acetic acid, because the rate of production of methane and ethane decreases with increasing pH beyond 3.9, as shown in Table I. This correlates with the concentration of acetic acid in solution which is estimated on the basis of the dissociation constant (pK_a 4.78):

$$CH_3COOH + \cdot OH \rightarrow \cdot CH_3 + CO_2 + H_2O \qquad (6)$$

Thus, methyl radicals can be produced by direct reaction of acetate with holes (eq 1) and by hydroxyl radical attack of acetic acid (eq 6). Further support to eq 6 is given by the results in Figure 3, where the amount of methyl radical consumed in methane and ethane formation increases with an increase in the concentration of acetic acid.

Cathodic Processes. Important observations on the cathodic processes are the fact that the hydrogen evolution is dramatically suppressed in the presence of Pd^{2+} as a competing oxidant. In its absence the main cathodic process is therefore the hydrogen atom formation. As already stated, the amount of hydrogen produced was larger than expected based on the chemical stoichiometry of eq 1 and 3–5. Such discrepancies must be brought about mainly by the photocatalytic decomposition of alcohol and aldehyde produced[17] as already discussed.

Methane Formation. One principal process for methane formation is given in eq 3. However, another route to methane formation is suggested by the following: (1) even when hydrogen evolution is completely suppressed by the preferential reduction of Pd^{2+}, methane is produced; (2) methane is produced at a TiO_2 photoelectrode under a high anodic bias, where saturated photocurrents occur and adsorbed hydrogen cannot exist in the vicinity of the electrode. These results strongly suggest that methyl radicals can abstract hydrogen from acetic acid:

$$\cdot CH_3 + CH_3COOH \rightarrow CH_4 + \cdot CH_2COOH \qquad (7)$$

Support to this process is given by the results already reported on the electrolysis at TiO_2 electrodes in aceto-

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nitrile solutions, where mass spectra of the gas produced suggested the formation of methane,[15] though the main signals were due to those of ethane. Concerning the process given by eq 7, however, Kraeutler and Bard thought that such a process is less likely to occur because in their experiments with water-free monodeuterated acetic acid, CH_3COOD, monodeuterated methane, CH_3D, was produced with high yields. However, Kawai et al.[20] have shown recently that photolysis of anhydrous CH_3COOH in D_2O on platinized TiO_2 powder produces both CH_3D and CH_4, suggesting that reaction 7 is significant, as observed in electrosynthesis at a metal electrode.[21] They have also suggested that the morphology of Pt deposited on the powder surface plays an important role in determining the ratio of CH_4 to CH_3D produced. TiO_2 powder with finely dispersed Pt on the surface gave mainly CH_3D, while those with larger patches of Pt gave mainly CH_4. In the case of the former, reactions 3 and 4 are important, while in the latter these are less important and reaction 7 is significant, since the anodic sites of the photocatalysis are not well mixed with Pt as are the cathodic sites, so that there is less chance for reaction 4 to occur.

Ratio of Methane to Ethane. Ethane production production becomes favored as the rate of the decomposition of acetic acid increases. Illumination intensity and solution pH are important variables. As shown in Figure 5, the reciprocal of the formation rate of methyl radicals varies linearly with the ratio of methane to ethane. The production rate of methane, v_{CH_4}, should be proportional to the surface concentration of methyl radicals, while that of ethane, $v_{C_2H_6}$, to the square root of surface concentration:

$$v_{CH_4} \sim k_1[\cdot CH_3] \qquad (8)$$

$$v_{C_2H_6} \sim k_2[\cdot CH_3]^2 \qquad (9)$$

The CH_4/C_2H_6 ratio is then governed by the following rate law:

$$CH_4/C_2H_6 \simeq [\cdot CH_3]^{-1} \sim I^{-1} \qquad (10)$$

Since the rate of formation of methyl radical is proportional to the illumination intensity, I, by either process (eq 1 or 7), a linear relation should be established between the CH_4/C_2H_6 ratio and the reciprocal of the illumination intensity.

The total rates of the methane and ethane production are also changed by changing the solution pH. Since the total rates must be proportional to the production rate of methyl radical, the above-described relation should also be observed when the solution pH is changed, as observed for the anatase catalyst (Figure 1). The nonlinear relation between these two quantities observed for the rutile catalyst suggests that either eq 8 or 9, or both, does not take place with this catalyst. Although the reason for this is presently unclear, the pursuit of these differences in relation to surface chemistry will be important to understand semiconductor photocatalysis in more detail.

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Registry No. Acetic acid, 64-19-7; acetate, 71-50-1; Pt, 7440-06-4; TiO_2, 13463-67-7; Pd^{2+}, 7440-05-3.