

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244992195>

Lang-12-736-FlowESR-KoenumaKira

DATASET · JULY 2013

READS

57

4 AUTHORS, INCLUDING:



Kiminori Ushida

Kitasato University

111 PUBLICATIONS **1,500** CITATIONS

SEE PROFILE



Yoshio Nosaka

Nagaoka University of Technology

228 PUBLICATIONS **5,723** CITATIONS

SEE PROFILE

Reaction Mechanism of the Decomposition of Acetic Acid on Illuminated TiO₂ Powder Studied by Means of *in Situ* Electron Spin Resonance Measurements

Yoshio Nosaka,^{*,†} Katsuchika Koenuma,[†] Kiminori Ushida,[‡] and Akira Kira[‡]

Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940-21, Japan, and Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-01, Japan

Received October 25, 1995[®]

The existence of methyl radicals in the photo-Kolbe reaction was confirmed by means of *in situ* measurements with flow electron spin resonance for deuterated acetic acid. From the dependence of the flow rate, two reaction paths were deduced for methyl radical formation. These were assigned to those caused by trapped holes and $\cdot\text{OH}$ radicals. It is suggested that the former path is dominant when platinum has not been loaded onto TiO₂ powder.

Photocatalytic reactions with semiconductor powders have been paid much interest because of their possible applications to solar energy storage and mineralization of wastewater.¹ However, the primary events and the nature of intermediates formed during photocatalyzed oxidation of organic molecules have not yet been clearly understood.² In order to investigate the mechanism of photocatalytic reactions, it is important to monitor intermediate radicals directly. While a spin-trapping technique has been used³ to detect the paramagnetic species, *in situ* observation for reacting intermediates provides essential information for understanding the reaction mechanisms. Bard and co-workers first reported photocatalytic decomposition of aqueous acetic acid in their pioneering work and named the reaction the "photo-Kolbe reaction".⁴ They suggested the formation of methyl radicals, since the triphenylmethyl radical was observed by electron spin resonance (ESR) as an intermediate in the decomposition of triphenylacetic acid in acetonitrile solution.⁵ Further studies of the reaction mechanism were reported by Yoneyama *et al.*⁶ and Sakata *et al.*,⁷ on the basis of an analysis of reaction products. Although Bard *et al.* did not detect methyl radicals in aqueous acetic acid,⁵ Kaise *et al.* have recently reported their observation of this radical by using a flow cell in ESR spectroscopy.^{8,9} In the present flow ESR experiments, we confirm the existence of the methyl radical by using a deuterated

compound and found that the dependence of radical concentrations on the flow rate is opposite to their results. From discussion of this dependence, two reaction paths are deduced for methyl radical formation and are assigned to those reacted with trapped holes and $\cdot\text{OH}$ radicals.

Experimental Section

A photocatalyst, platinized TiO₂ (Pt/TiO₂), was prepared as follows. One gram of TiO₂ (Japan Aerosil P-25 and Hombikat UV-100) and H₂PtCl₆·6H₂O up to 8 mg were mixed in 10 cm³ of 0.1 mol dm⁻³ HCl. The solution was neutralized with Na₂CO₃ and then set to pH 5 with acetic acid. The mixture was irradiated for 9 h with a 500 W high-pressure Hg lamp under deaerated conditions with N₂ bubbling. The gray powder thus obtained was washed thoroughly with distilled water and dried for 8 h at 150 °C. ESR spectra were measured with JEOL JES RE-2X and RSV-2000 spectrometers. A flat flow cell with an internal cross section of 0.3 mm × 5 mm was placed in the cavity of the spectrometer and irradiated with the Hg lamp through a B-370 (Hoya) glass filter. An aqueous solution (150 cm³) of 0.1 mol dm⁻³ acetic acid (Nacalai Tesque Co.) or deuterated acetic acid (Aldrich Chemicals Co.) was circulated with a tube pump (Tokyo Rikaki, MP-3B). The solution was deaerated by N₂ bubbling. The flow rate ranged from 0.4 to 20 cm³ min⁻¹.

Results

Figure 1 shows the ESR spectra observed during the photocatalytic reaction with Pt/TiO₂ in acetic acid and acetic acid-*d*₄ solutions. Although Kaise *et al.*^{8,9} reported the formation of both $\cdot\text{CH}_3$ and $\cdot\text{CH}_2\text{COOH}$ radicals in a photocatalytic reaction with Pt/TiO₂, the amount of the unstable intermediates largely depends on the photocatalyst. When the amount of loaded platinum is small, the $\cdot\text{CH}_3$ signal is large. Very small 1:2:1 triplet signals assigned to $\cdot\text{CH}_2\text{COOH}$ radicals are observed for the photocatalyst shown in Figure 1A. With this particular photocatalyst, the ESR spectrum for the reaction product obtained in deuterated acetic acid is shown in Figure 1B. Since the amount of $\cdot\text{CD}_2\text{COOD}$ is negligible, the observed ESR spectrum may be attributed to $\cdot\text{CD}_3$, which exhibits a hyperfine splitting pattern of 1:3:6:7:6:3:1. The observed hyperfine splitting was 0.35 ± 0.02 mT and fits with the calculated value of 0.349 mT from the result for $\cdot\text{CH}_3$ (2.274 mT)⁸ and the ratio of the proton to deutron gyromagnetic ratio (6.514). Thus, the formation and *in situ* observation of methyl radicals were confirmed at room temperature in aqueous solution.

Results obtained in the presence of another batch of Pt/TiO₂ photocatalyst showed that the magnitude of the

* E-mail: nosaka@voscc.nagaokaut.ac.jp.

[†] Nagaoka University of Technology.

[‡] Institute of Physical and Chemical Research.

[®] Abstract published in *Advance ACS Abstracts*, January 15, 1996.

(1) For example: *Photochemical Conversion and Storage of Solar Energy*; Pelizzetti, Ed., Schiavello, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.

(2) Serpone, N.; Pelizzetti, E.; Hidaka, H. *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: London, 1993, p 225.

(3) (a) Jaeger, G. D.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 3146. (b) Noda, H.; Oikawa, K.; Ohya-Nishiguchi, H.; Kamada, H. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2031.

(4) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 2239; 5985.

(5) Kraeutler, B.; Jaeger, G. D.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4903.

(6) Yoneyama, H.; Takao, Y.; Tamura, H.; Bard, A. J. *J. Phys. Chem.* **1983**, *87*, 1417.

(7) Sakata, T.; Kawai, T.; Hashimoto, K. *J. Phys. Chem.* **1984**, *88*, 2344.

(8) Kaise, M.; Kondoh, H.; Nishihara, C.; Nozoye, H.; Shindo, H.; Nimura, S.; Kikuchi, O. *J. Chem. Soc., Chem. Commun.* **1993**, 395.

(9) Kaise, M.; Nagai, H.; Tokuhashi, K.; Kondo, S.; Nimura, S.; Kikuchi, O. *Langmuir* **1994**, *10*, 1345.

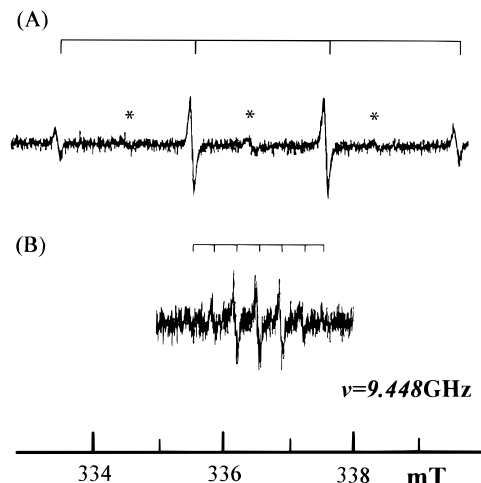


Figure 1. ESR spectra observed during photocatalytic reaction with Pt/TiO₂ powder in deaerated aqueous acetic acid (A) and acetic acid-d₄ (B) solutions. Asterisks indicate the triplet signal of $\cdot\text{CH}_2\text{COOH}$ radicals.

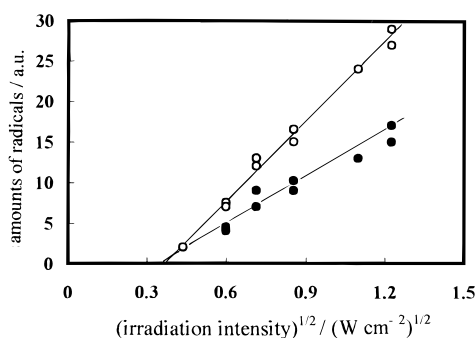


Figure 2. Relative amounts of unstable intermediates (\circ , $\cdot\text{CH}_3$; \bullet , $\cdot\text{CH}_2\text{COOH}$) observed in the photocatalytic decomposition of acetic acid plotted as a function of the square root of the incident-light intensity during the ESR measurements, at a flow rate of $0.5 \text{ cm}^3 \text{ min}^{-1}$.

1:2:1 triplet for the $\cdot\text{CH}_2\text{COOH}$ radical was compatible with that of the 1:3:3:1 quartet for $\cdot\text{CH}_3$. The spectra were measured at various light intensities and at various flow rates. The relative concentrations of the two radicals are calculated from the height and width of each signal. Namely, for the $\cdot\text{CH}_2\text{COOH}$ radical the height of the central peak of the 1:2:1 triplet was multiplied by its width and then by 4/2. Similarly, for $\cdot\text{CH}_3$ radical the height of second peak in the 1:3:3:1 quartet was multiplied by its width and by 8/3. Figure 2 shows these relative concentrations as a function of the intensity of the incident light. The ratio of the two radicals is almost unchanged in the range of light intensity studied. The amount of each radical exhibits a square-root dependence upon light intensity, indicating that the electron-hole recombination reaction reduces the yield of the redox reaction¹⁰ which is the initial step of the decomposition of acetic acid.

Figure 3 shows the relative radical concentration as a function of the flow rate. The amount of $\cdot\text{CH}_3$ radical decreased rapidly up to $5 \text{ cm}^3 \text{ min}^{-1}$, while the amount of $\cdot\text{CH}_2\text{COOH}$ radical decreased slightly over the flow rate examined. Kaise *et al.*⁸ reported that the signal intensity decreased with decreasing flow rate from 2.6 to 1.3 and to $0 \text{ cm}^3 \text{ min}^{-1}$. The discrepancy in the observed rate dependencies may originate from the different catalytic activity, because Kaise *et al.*⁸ platinumized the same P-25 TiO₂ by cation exchange. The present observation of the flow-rate dependence revealed that the $\cdot\text{CH}_3$ radical was

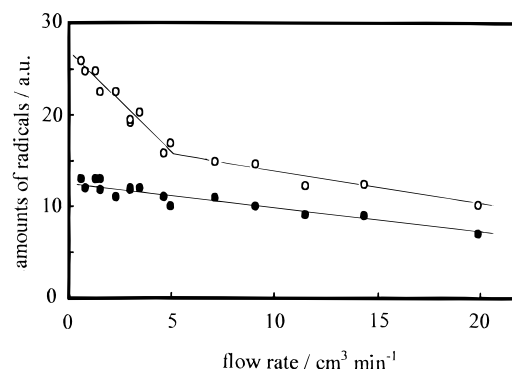


Figure 3. Relative amounts of unstable intermediates (\circ , $\cdot\text{CH}_3$; \bullet , $\cdot\text{CH}_2\text{COOH}$) observed in the photocatalytic decomposition of acetic acid plotted as a function of the flow rate in the ESR measurements at a light intensity of 1.2 W cm^{-2} .

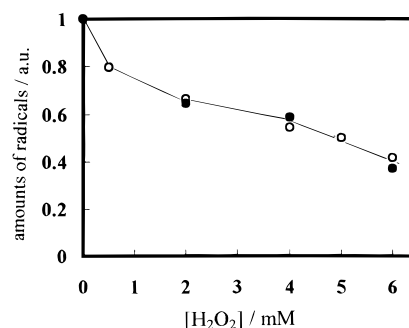


Figure 4. Relative decrease in the amount of unstable intermediates (\circ , $\cdot\text{CH}_3$; \bullet , $\cdot\text{CH}_2\text{COOH}$) plotted as a function of increasing concentration of H_2O_2 . The flow rate was $0.5 \text{ cm}^3 \text{ min}^{-1}$, and the light intensity was 1.2 W cm^{-2} .

produced by two independent reaction paths. Since the ratio $[\cdot\text{CH}_3]/[\cdot\text{CH}_2\text{COOH}]$ becomes constant at a flow rate greater than $5 \text{ cm}^3 \text{ min}^{-1}$, these two radicals are expected to be produced *via* an identical initial process in this region of the flow rate.

Since $\cdot\text{OH}$ and H_2O_2 may be involved in the reaction mechanism, the amount of radicals was measured in the presence of H_2O_2 . The decrease observed in the amount of both radicals as the concentration of H_2O_2 was increased is shown in Figure 4.

Discussion

Bard *et al.* described the photocatalytic decomposition of acetic acid referred to as the Kolbe reaction as follows:⁴



Here h^+ represents photoinduced holes at the valence band. Recently it was revealed that the holes are rapidly trapped to form $\text{Ti}-\text{O}^\cdot$ radicals at the surface.¹¹ Since a large amount of $\cdot\text{H}$ is produced on the surface of the catalyst, $\cdot\text{CH}_3$ should be consumed predominantly by forming CH_4 under the present conditions.⁷ Kaise *et al.*⁸ suggested the formation of $\cdot\text{CH}_2\text{COOH}$ from $\cdot\text{CH}_3$, eq 2



However, it was deduced⁷ from an experiment in D_2O that reaction 2 is a minor process in the absence of a strong electron acceptor such as the Ag^+ ion. Conversely, formation of $\cdot\text{CH}_2\text{COOH}$ radical *via* reaction with $\cdot\text{OH}$

(10) Nosaka, Y.; Fox, M. A. *J. Phys. Chem.* **1988**, *92*, 1893.

(11) Micic, O. I.; Zhang, Y.; Cromack, K. R.; Trifunac, A. D.; Thurnauer, M. C. *J. Phys. Chem.* **1993**, *97*, 4207.

has been investigated in a radiation chemical study.¹²



In homogeneous solution, the rate constant¹³ for reaction 3 is $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ while that¹⁴ for reaction 2 is $6 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Thus, reaction 3 should be the predominant process in the formation of $\cdot\text{CH}_2\text{COOH}$. The attack of $\cdot\text{OH}$ on the carboxyl group is reported to make only a minor contribution in the radiation chemical study.¹² However, for the photocatalytic reaction with Pt/TiO₂, Yoneyama *et al.*⁶ proposed cleavage of the C–C bond during the attack by the $\cdot\text{OH}$ radical.



They deduced the existence of this reaction from the dependence of the formation rates of methane and ethane on the concentration of acetic acid. An enthalpy change estimated¹⁵ for reaction 3 is larger than that of reaction 4 by only 23 kJ mol^{−1}. Consideration of the entropy change leads to the conclusion that reaction 4 takes place easily. Thus, both $\cdot\text{CH}_2\text{COOH}$ and $\cdot\text{CH}_3$ radicals are formed competitively *via* $\cdot\text{OH}$ radicals with a measurable ratio. This situation should be true for the results shown in Figure 3 at flow rates greater than 5 cm³ min^{−1}.

The duration of the irradiation for each particle is calculated to be about 0.2 s at a flow rate of 5 cm³ min^{−1}. Since diffusion of acetic acid to the surface takes less than 0.2 s, the rate-determining step in reaction 1 should be the diffusion process on the surface. The slower the flow rate, the faster reaction 1 becomes, because the density of photons for one particle increases and many trapped holes are formed at the surface. At the slow flow rate, direct oxidation (1) of acetic acid then contributes to the formation of the $\cdot\text{CH}_3$ radical. Competing with this

reaction, trapped holes react with H₂O to form $\cdot\text{OH}$ radicals. The rate of this reaction is independent of the flow rate because a large amount of H₂O exists at the surface. Thus, reactions 3 and 4 may be independent of the flow rate. The small decrease observed can be explained by the decrease in the period for carrier accumulation in the particles. The fact that accumulation occurs before the onset of the reaction is proved by the observation of a threshold in the light intensity dependence shown in Figure 2.

The assumption of a competitive formation of $\cdot\text{CH}_3$ and $\cdot\text{CH}_2\text{COOH}$ *via* $\cdot\text{OH}$ radicals and the observation of only a negligible amount of $\cdot\text{CH}_2\text{COOH}$ lead to the conclusion that formation of $\cdot\text{OH}$ becomes a minor process when platinum is not loaded onto TiO₂ powder. This may be true only in the absence of oxygen molecules, because O₂ is known to be reduced photocatalytically to O₂^{•−} and forms H₂O₂ and $\cdot\text{OH}$.² We observed, however, that the presence of a small amount of O₂ reduces the signal intensity. The observed radicals react with O₂ by further oxidation,¹⁶ and their concentrations decrease in the present steady-state experiment. Although the formation of $\cdot\text{OH}$ by the reduction of H₂O₂ has been expected, the observed amount of $\cdot\text{CH}_3$ and $\cdot\text{CH}_2\text{COOH}$ radicals decreases with the amount of H₂O₂ added, as shown in Figure 4. Thus, H₂O₂ may react with the observed radicals rather than by the formation of $\cdot\text{OH}$ radicals.

For further discussion on the reaction mechanism, the pH dependence of radical formation must be measured, because methane was not formed at a higher pH^{6,7} where formation of hydrogen increased.⁷ However, such experiments will not be easy to carry out, since the dispersivity of fine TiO₂ particles also changes with pH.

Acknowledgment. This study is partly supported by Grant-in-Aid for Scientific Research (No. 05237105, 06239224) from the Japanese Ministry of Science, Education and Culture.

LA9509615

(12) Neta, P.; Simic, M.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 4207.

(13) Fisher, M. M.; Hamill, W. H. *J. Phys. Chem.* **1973**, *77*, 171.

(14) Davies, M. J.; Gilbert, B. C.; Thomas, C. B.; Young, J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1199.

(15) *Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1979, p F231.

(16) Bahnemann, D. W. *Photochemical Conversion and Storage of Solar Energy*; Pelizzetti, E.; Schiavello, M. Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991, 251.