Photocatalytic Reactions of Acetic Acid on Platinum-loaded TiO_2: ESR Evidence of Radical Intermediates in the Photo-Kolbe Reaction

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Two elusive radical intermediates; a methyl radical ($^{\cdot}CH_3$) and a carboxymethyl radical ($^{\cdot}CH_2CO_2H$), have been confirmed for the first time by direct observation of their ESR absorptions at room temperature on the photocatalytic reactions of acetic acid and metal (platinum)-loaded titanium dioxide (Pt/TiO_2) in aqueous solution.

The photocatalytic reactions of organic molecules occurring at semiconducting TiO_2 powders have been the subject of numerous studies, owing to their importance in solar energy conversion and the degradation of toxic chemical compounds.[1]

In studies of photochemical reactions of acetate ions at an illuminated TiO_2 electrode, Bard and coworkers demonstrated[2,3] that a carboxylate anion (RCO_2^-) is photocatalytically decarboxylated to give hydrocarbons due to the combination of intermediate radicals: the photo-Kolbe reaction. The ESR spectrum of a less reactive triphenylmethyl radical ($Ph_3C^{\cdot}$) was directly observed with triphenylacetic acid and Pt/TiO_2 in their detection of an intermediate hydrocarbon radical ($R^{\cdot}$). Detection of the reactive radical **1**$^{\cdot}$ was performed in neat glacial acetic acid by the spin trapping technique. The importance of the technique as an analytical tool for detection and identification of short-lived radicals has been recognized and successfully applied to ESR detection of organic and inorganic free radicals by Janzen[4] and Rehorek,[5] respectively. However, there have been many indecisive factors over the identification of intermediate radicals, since the fingerprints are indirectly observed. No direct detection of radical intermediates including **1**$^{\cdot}$ has been successful so far although radical involvement in the mechanism of the photo-Kolbe reaction of acetic acid has been considered in many studies.[1-3]

Here we report the photocatalytic reactions of acetic acid and metal (platinum)-loaded titanium dioxides (Pt/TiO_2) in aqueous solution. The existence of two elusive radical intermediates; a methyl radical ($^{\cdot}CH_3$; **1**) and a carboxymethyl radical ($^{\cdot}CH_2CO_2H$: **2**$^{\cdot}$), were directly confirmed for the first time at room temperature by the use of electron spin resonance (ESR) spectroscopy.

In our experiment, particulate photocatalysts, Pt/TiO_2, were prepared by cation exchange[6-8] from a solution of $H_2PtCl_6{\cdot}6H_2O$ and a nonporous TiO_2 (anatase: Nippon Aerosil P25). Steady-state ESR measurements under photoirradiation with a flow system were carried out at room temperature using a 500 W high-pressure Hg lamp. Dissolved oxygen in the solution was excluded by continuous Ar bubbling throughout ESR measurement. A glass filter (300 to 400 nm transmission) was used in all photolyses of sample solutions because the band gap of TiO_2 (anatase) semiconductor was reported to be 3.23 eV,[9] which corresponds to a photon with λ 383 nm.

Fig. 1 shows ESR spectra varying the amount of Pt loaded on TiO_2 in the 0.1 mol dm^{-3} acetic acid solution. Spectra (*a*)–(*c*) are obtained with 0.9, 0.3 and 0.0 wt% Pt/TiO_2, respectively. The spectra in Fig. 1(*a*) and (*b*) are superpositions of spectra due to two different intermediate radicals. One of them (△) is identified as the methyl radical (**1**$^{\cdot}$)[10-12] with $g = 2.00252$ and three equivalent protons with $a_H = 22.74$ G (1 G = 10^{-4} T). The other one (○) is the neutral carboxymethyl radical[11,13] (**2**$^{\cdot}$) with $g = 2.00323$, and two equivalent protons with $a_H = 21.35$ G. The ESR parameters of both radicals agree well with that of Fessenden and coworkers.[10,13] No trace of ESR absorption is observed in spectrum (*c*). The Pt loading on TiO_2 is indispensable for the efficient photocatalytic reaction in this system. However, the radical intermediates did not increase with the amount of Pt on TiO_2 [compare Fig. 1(*a*) and (*b*)]. This implies that greater Pt loading does not facilitate photocatalytic decomposition of acetic acid.

Flow rate dependence of ESR spectra (**1**$^{\cdot}$ and **2**$^{\cdot}$) was examined with 0.1 wt.% Pt/TiO_2 (flow rates; 2.6, 1.3 and 0.0 ml min^{-1}). A decrease in ESR intensity with lower flow rate was observed for both radicals possibly due to depletion of the reacting acetic acid. However, the signals of **1**$^{\cdot}$

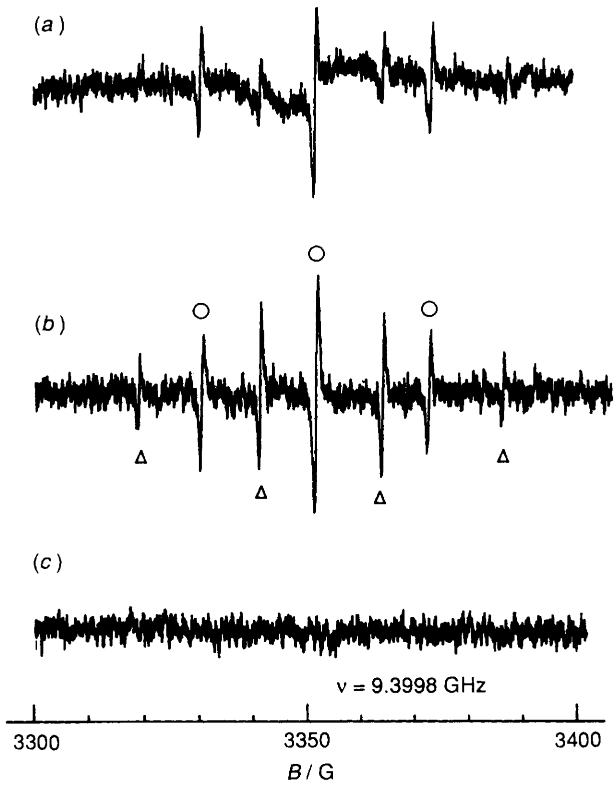


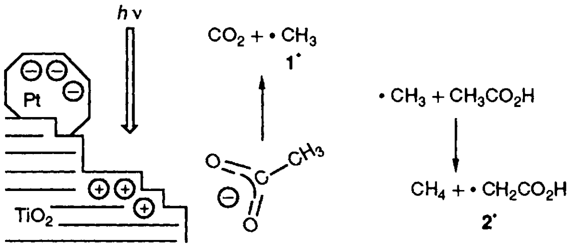
Fig. 1 ESR spectra observed at room temperature during UV irradiation of a solution containing 0.1 mol dm^{-3} acetic acid in Pt/TiO$_2$ photocatalyst (4 g l^{-1}) suspended water; flow rate 2.6 ml min^{-1}, (*a*) 0.9 wt.% Pt loaded TiO$_2$, (*b*) 0.3 wt.% Pt loaded TiO$_2$, (*c*) 0.0 wt.% Pt loaded TiO$_2$. The methyl radical (△; $\mathbf{1}^\bullet$) and the carboxymethyl radical (○; $\mathbf{2}^\bullet$) are superposed.

remained even at flowless condition although that of $\mathbf{2}^\bullet$ disappeared completely. This can probably be ascribed to the diffusional supply of the reactant from bulk solution to the reaction surface of the catalysts and prolonged lifetime of $\mathbf{1}^\bullet$ without reacting acetic acid.

Characteristics of all the ESR spectra show that the motion of these two radicals is unrestrained and isotropic like in homogeneous liquids, and indicate that reaction between $\mathbf{1}^\bullet$ and acetic acid is considerably slower than the diffusion-controlled case in aqueous solution although the methyl radical is known to be very reactive and abstracts hydrogen from many organic molecules.[14,15] Consequently our ESR evidence shows that $\mathbf{1}^\bullet$ is not anchored to the surface of the photocatalyst but exists in the bulk solution phase or the radicals are teritorially bound[16] in the two-dimensional solution area surrounding the surface of the photocatalyst.

Thus, experimental results strongly support that the intermediate $\mathbf{1}^\bullet$ was produced by a photocatalytic decarboxylation of acetate anion on the TiO$_2$ surface[17] of Pt/TiO$_2$. Photocreated electron-hole pairs on the surface of TiO$_2$ were effectively separated with platinum deposition. Thus, the metal on the TiO$_2$ particles could promote the photocatalytic activity of the catalyst compared with TiO$_2$ alone. Another observed intermediate radical $\mathbf{2}^\bullet$ is presumably created by abstraction of a hydrogen atom from a methyl group of acetic acid by $\mathbf{1}^\bullet$,[15,18] as shown in Scheme 1. As one of the plausible precursors, an acetoxyl radical (MeCO$_2^\bullet$) is considered by one electron transfer from an acetate anion to be the photocatalyst. We have not depicted the radical in Scheme 1 because no ESR absorption for the radical has been observed so far.

Although there was no direct evidence, a hydroxyl radical ($^\bullet$**OH**; $\mathbf{3}^\bullet$) has been presumed as a possible intermediate in the photocatalytic reaction of Pt/TiO$_2$ in aqueous solutions.[18,19] Moreover, there is a pioneering ESR work by Dixon and Norman,[11] of free radical $\mathbf{3}^\bullet$ reactions with various organic molecules. They obtained ESR spectra of a radical $\mathbf{1}^\bullet$ and a radical $\mathbf{2}^\bullet$ in the reaction of $\mathbf{3}^\bullet$ with acetic acid using a mixed flow system. In our photocatalytic experiments, however, the possible existence of free radical $\mathbf{3}^\bullet$ in a bulk aqueous phase is not considered, because we could not observe ESR absorption of this radical[12,20] at all in the absence of acetic acid. Moreover, no radical adducts of $\mathbf{3}^\bullet$ were detected in the presence of a maleic acid or a furmaric acid, although these radical adducts were observed by Dixon[11] and Fisher.[21]



Scheme 1

In relation to the photo-Kolbe reaction, our results suggest that in addition to the creation of methyl radicals and their dimerization to ethane there is another radical-invovled reaction in this photocatalytic system: methane formation by a hydrogen abstraction of the methyl radical[15,16,21] in acetic acid.

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