Solvent-free selective photocatalytic oxidation of benzyl alcohol to benzaldehyde by molecular oxygen using 9-phenyl-10-methylacridinium

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9-Phenyl-10-methylacridium ion acts as an effective photocatalyst for solvent free selective photocatalytic oxidation of benzyl alcohol to benzaldehyde under visible light irradiation *via* efficient photoinduced electron transfer from benzyl alcohol to the singlet excited state of the acridinium ion.

The gas-phase catalytic oxidation of benzyl alcohol by O_2 to benzaldehyde has attracted increasing attention because of its practical importance of chlorine-free benzaldehyde, which has been difficult to obtain in the conventional method, *i.e.*, hydrolysis of benzyl chloride.[1–5] The use of clean oxidants such as O_2 is highly desired from the point of view of improving reaction atom efficiency and from the increasing need to substitute conventional stoichiometric oxidizing reagents with environmentally benign oxidants.[6] In the gas-phase oxidation process, however, it has been impossible to prevent completely the total oxidation of benzyl alcohol to CO_2. Such carbon loss can be avoided in the liquid-phase catalytic oxidation of benzyl alcohol at temperatures much lower than that employed in the gas-phase oxidation process. However, the reflux temperature is still required to oxidize benzyl alcohol using solid catalysts, resulting in the further oxidation of benzyl alcohol.[7–13] In contrast, the photocatalytic oxidation of benzyl alcohol with O_2 proceeds in solution at ambient temperature, but a large amount of solvent has been required because of the instability or insolubility of the photocatalyst in neat benzyl alcohol.[14–17]

We report herein solvent-free liquid phase photocatalytic selective oxidation of benzyl alcohol to benzaldehyde using 9-phenyl-10-methylacridinium perchlorate ($AcrPh^+ClO_4^-$) as an effective photocatalyst under visible light irradiation at ambient temperature [eqn (1)].

$$\text{PhCH}_2\text{OH} + O_2 \xrightarrow[\text{AcrPh}^+]{h\nu\,(\lambda > 310\text{ nm})} \text{PhCHO} + H_2O_2 \quad (1)$$

$AcrPh^+ClO_4^-$ is soluble in benzyl alcohol. Photoirradiation of benzyl alcohol containing $AcrPh^+ClO_4^-$ (2.0×10^{-2} mol dm^{-3}) with a mercury lamp by cutting off the light of $\lambda < 310$ nm results in formation of benzaldehyde and hydrogen peroxide. The time course of the photocatalytic reaction was monitored by ^{1}H NMR spectroscopy as shown in Fig. 1. The formation of H_2O_2 was detected by the iodometric titration.[15] During the photooxidation of benzyl alcohol, the UV-vis absorption band due to $AcrPh^+$ decreases gradually. After 15 h photoirradiation, the yield of benzaldehyde based on the initial amount of $AcrPh^+$ exceeds

800%, demonstrating an efficient recycling of $AcrPh^+$ in the photocatalytic oxidation of benzyl alcohol. When $AcrPh^+$ is replaced by 10-methylacridinium ion ($AcrH^+$), $AcrH^+$ is readily converted to 9-benzyl-10-methyl-9,10-dihydroacridine [$AcrH(CH_2Ph)$] by the radical coupling reaction under photo-irradiation even in O_2-saturated benzyl alcohol.[15,18,19] $AcrH(CH_2Ph)$ has no photocatalytic activity for the oxidation of benzyl alcohol with O_2. The much enhanced stability of $AcrPh^+$ as compared to $AcrH^+$ under the photocatalytic conditions is attributed to the steric effect of the phenyl group.[19]

The quantum yield (Φ) was determined as $35 \pm 5\%$ from an increase in absorbance due to benzaldehyde by using a ferrioxalate actinometer under irradiation of monochromatized light of $\lambda = 358$ nm, respectively[20,21] The virtually same Φ value was obtained in air-saturated benzyl alcohol.

The fluorescence of the singlet excited state $^1AcrPh^{+*}$ (* denotes the excited state) is known to be efficiently quenched by electron transfer from aromatic electron donors to $^1AcrPh^{+*}$.[21,22] In neat benzyl alcohol, the fluorescence of $^1AcrPh^{+*}$ is mostly quenched by electron transfer from benzyl alcohol. The occurrence of electron transfer from benzyl alcohol to $^1AcrPh^{+*}$ is confirmed by the laser flash photolysis experiments. Laser flash excitation (355 nm from an Nd:YAG laser, 4–6 ns fwhm) of $AcrPh^+$ (5.0×10^{-5} mol dm^{-3}) in O_2-saturated benzyl alcohol affords transient absorption bands at $\lambda_{max} = 500$ and 520 nm due to $AcrPh^{\bullet}$,[21,22] with bleaching of the absorption band due to $AcrPh^+$ as shown in Fig. 2(a). However no transient absorption band of the radical cation ($PhCH_2OH^{\bullet+}$) was observed by nanosecond laser flash measurements. This indicates that the deprotonation of
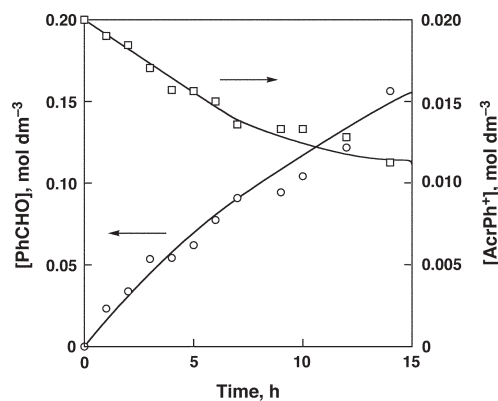

Fig. 1 Time profiles of formation of benzaldehyde ($\bigcirc$) and consumption of $AcrPh^+$ ($\square$) in the photocatalytic oxidation of benzyl alcohol in the presence of $AcrPh^+$ (2.0×10^{-2} mol dm^{-3} in O_2-saturated benzyl alcohol with a mercury lamp by cutting off the light of $\lambda < 310$ nm at 298 K.

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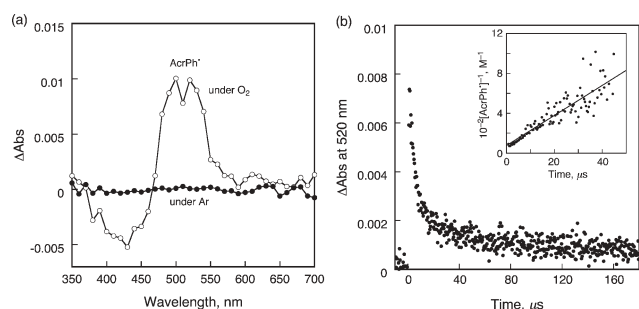
Fig. 2 (a) Transient absorption spectra observed by the photoexcitation of O$_2$-saturated (○) and deaerated (●) benzyl alcohol in the presence of AcrPh$^+$ (5.0 × 10^{-5} mol dm^{-3}) at 400 ns after laser excitation at 298 K. (b) Decay time profile of absorbance at 520 nm obtained by the photoexcitation of O$_2$-saturated benzyl alcohol solution containing AcrPh$^+$. Inset: Second-order plot.

PhCH$_2$OH$^{•+}$ has already occurred at the microsecond time scale. The decay of the absorption due to AcrPh$^•$ obeys second-order kinetics (Fig. 2(b)). From the second-order plot the second-order rate constant is determined as 1.5 × 10^{10} dm^3 mol^{-1} s^{-1}, which is close to the diffusion-limited value. In contrast, no transient absorption was observed in deaerated benzyl alcohol (Fig. 2(a)). Thus, fast back electron transfer from AcrPh$^•$ to PhCH$_2$OH$^{•+}$ and the radical coupling occur in the solvent cage.

Fig. 3(a) shows the transient absorption spectra observed by the femtosecond laser flash photolysis of O$_2$-saturated benzyl alcohol in the presence of AcrPh$^+$.[23] The singlet–singlet absorption of ^{1}AcrPh$^+$* is clearly observed at 450 and 700 nm at 4 ps after the femtosecond laser excitation.[24] The absorption band of ^{1}AcrPh$^+$* decreases (Fig. 3(b)) with a concomitant increase in the absorption band due to PhCH$_2$OH$^{•+}$ at 480 nm,[25] which then decreases at the
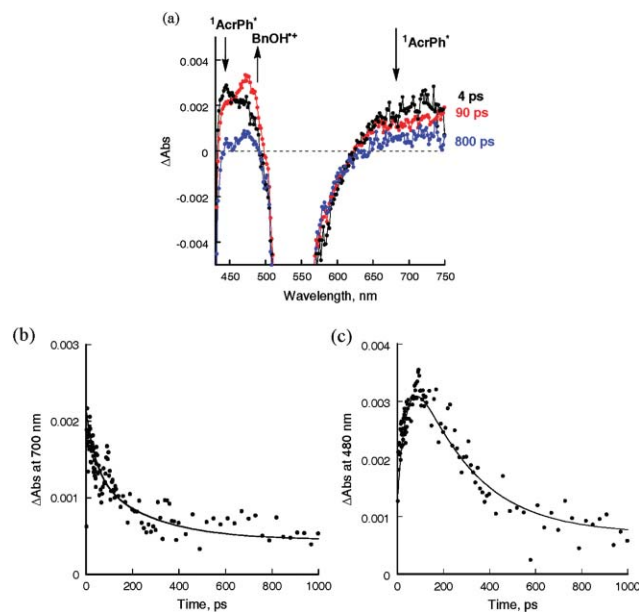

Fig. 3 (a) Transient absorption spectra observed by the femtosecond laser excitation (λ = 420 nm) of O$_2$-saturated benzyl alcohol containing AcrPh$^+$ (8.0 × 10^{-4} mol dm^{-3}) at 4.0, 90 and 800 ps after laser excitation at 298 K. Time profiles at (b) 700 nm and (c) 480 nm. The solid lines in (b) and (c) are the two-exponential fitting for the rise or decay of the absorbance.

longer time scale (Fig. 3(c)). The rate constant of formation of PhCH$_2$OH$^{•+}$ was determined as 2.4 × 10^{10} s^{-1} (Fig. 3(c)). This indicates that electron transfer from PhCH$_2$OH to AcrPh$^+$ occurs rapidly in the solvent cage. The decay rate constant of PhCH$_2$OH$^{•+}$ is determined as 4.0 × 10^9 s^{-1} from the decay of the transient absorption at 480 nm due to PhCH$_2$OH$^{•+}$ (Fig. 3(c)), which corresponds to the deprotonation process in the solvent cage.

The ESR spectrum was measured to detect radical intermediates involved in the AcrPh$^+$-catalyzed photooxidatio of benzyl alcohol with O$_2$. An O$_2$-saturated benzyl alcohol containing AcrPh$^+$ (5.0 × 10^{-2} M) was irradiated by a high-pressure mercury lamp at 298 K and observed at 123 K. The observed ESR spectrum consists of an anisotropic signal at g_{zz} = 2.0338 and a nearly isotropic signal at g = 2.0028 (Fig. 4(a)). The former signal is assigned to HO$_2$$^•$, because the g_{zz} value is diagnostic of hydrogen peroxyl radicals.[26,27] The latter nearly isotropic signal mainly corresponds to the isotropic signal of AcrPh$^{•}$[21] in addition to small contribution from the g_{xx} and g_{yy} components of HO$_2$$^•$.[28] The photoirradiation at 123 K of a glass of benzyl alcohol containing AcrPh$^+$ in the ESR cell tube results in the color change from yellow to red as shown in Fig. 4(b). The red color results from formation of AcrPh$^•$, which has the absorption at 520 nm as shown in Fig. 2(a).[21]

Based on the results described above, the photocatalytic mechanism of solvent-free oxidation of benzyl alcohol with O$_2$ is shown in Scheme 1. The photocatalytic reaction is started by fast electron transfer from PhCH$_2$OH to ^{1}AcrPh$^+$* with the rate constant of 2.4 × 10^{10} s^{-1} to produce PhCH$_2$OH$^{•+}$ and AcrPh$^•$, both of which were detected as the transient absorption spectra in Fig. 3(a). PhCH$_2$OH$^{•+}$ deprotonates rapidly with a rate constant of 4.0 × 10^9 s^{-1} (Fig. 3(c)) to produce PhCH(OH)$^•$ that reacts with O$_2$ to afford PhCHO and HO$_2$$^•$. The formation of HO$_2$$^•$ is detected by ESR in Fig. 4(a). The second-order decay of AcrPh$^•$ observed in Fig. 2(b) corresponds to the bimolecular electron transfer from AcrPh$^•$ to HO$_2$$^•$ to yield H$_2$O$_2$ after protonation, accompanied by regeneration of AcrPh$^+$.

In conclusion, solvent-free selective oxidation of benzyl alcohol to benzaldehyde proceeds efficiently using AcrPh$^+$ as an effective photocatalyst under visible light irradiation at ambient temperature.
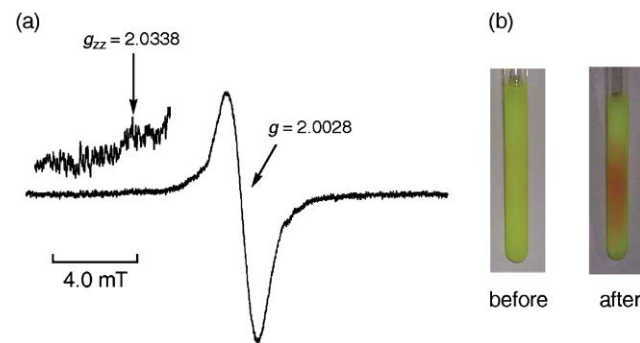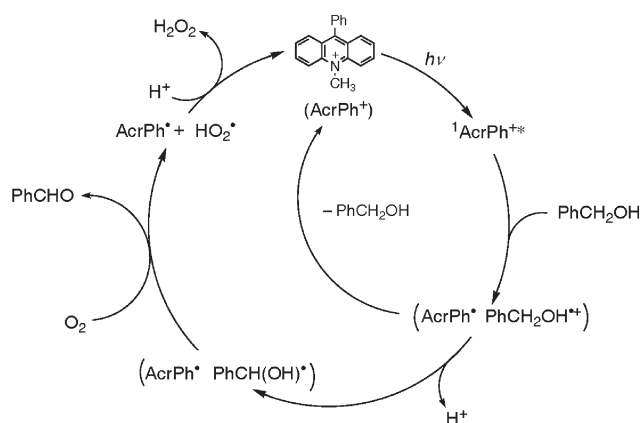

Fig. 4 (a) ESR spectrum of oxygen-saturated benzyl alcohol containing AcrPh$^+$ (5.0 × 10^{-3} mol dm^{-3}) after photoirradiation with a high-pressure mercury lamp at 298 K and recorded at 123 K. (b) Photo-images of O$_2$-saturated frozen benzyl alcohol solutions of AcrPh$^+$ before and after photoirradiation at low temperatures and taken at 143 K.

Notes and references

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