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Sensitized photoreduction of silver ions in the presence of acetophenone

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Abstract

Aqueous silver perchlorate ($AgClO_4$)–acetophenone (AP)–sodium dodecylsulfate (SDS) solutions were photolyzed with near-UV light. The formation of colloidal silver and the photobleach of AP were caused by irradiation with 310 nm light, which was absorbed solely by AP (sensitized photoreduction). Gross features of the sensitized photoreduction of Ag^+ and the photobleach of AP were interpreted in terms of a simple reaction scheme entailing suitable combinations of the kinetics parameters. The kinetics parameters for the $AgClO_4$–AP–SDS solutions were compared with those for the $AgClO_4$–benzophenone–SDS solutions. It was noticed that the progress of the photoreaction was accompanied by the change in the extinction coefficient of the colloidal silver. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Sensitized photoreduction; Photochemical formation of colloidal silver; Acetophenone; Photobleach

1. Introduction

Ultrafine particles of noble metal, such as silver and gold have attracted considerable attention in the fields of photo-physicochemistry [1–4] and material science related to nonlinear optical materials [5–8]. We have proposed ‘photo-acetone method’ as a tractable method to prepare finely dispersed colloidal metals (Ag, Au, Pt, Cu) in high reproducibility [9]. When UV light ($\lambda = 253.7$ nm) is irradiated to the $AgClO_4$ solutions in the presence of acetone and protective agent, sodium dodecylsulfate (SDS), colloidal silver is formed as a result of the photoreduction of Ag^+. The agglomerated colloidal silver is subjected to the peptization by acetone ketyl radical (AK), giving rise to high quality colloidal silver particles of 10–20 nm in size.

When benzophenone (BP) was used instead of acetone, the formation of colloidal silver occurred by irradiation with $\lambda = 365$ nm, which was absorbed solely by BP (sensitized photoreduction) [10]. In this case, it is likely that the peptizing action of benzophenone ketyl radical (BPK) contributed to the formation of the ultrafine silver particles. As far as we know, no research groups have paid attention to the sensitized photoreduction of Ag^+ and the peptizing action of the colloidal silver other than our group. Acetophenone (AP) has a molecular structure similar to acetone and BP, and absorbs near-UV light. It is probable that the replacement of BP with AP could initiate similar sensitized photoreduction of Ag^+ and peptization of the colloidal silver by the actinic light absorbed by AP. In this article, we have focused on the photochemical reaction of the $AgClO_4$–AP–SDS solutions irradiated with 310 nm light which is absorbed by AP.

2. Experimental

Acetophenone (Aldrich 99.8%) and $AgClO_4$ (nacalai tesque, special grade) were used as received. Commercially available SDS (nacalai tesque, special grade) was purified by repeated recrystallization from distilled water. All of the solutions were aqueous solutions prepared with distilled water in the dark and containing SDS (35 mM).

A 500 W high-pressure mercury lamp (UI-501C; Ushio Denki) with a power supply (HB-50102AA; Ushio Denki) was used as the light source for near-UV light. A combination of the glass filter (UV-D35; Toshiba) and a water filter was adequate to select 310 nm light. A 365 nm light incident on the reaction cell simultaneously had no effect, because irradiation of an $AgClO_4$–AP–SDS solution with 365 nm light for a long time did not cause any spectral change. The reaction cell was a rectangular quartz vessel, 10 mm × 10 mm × 40 mm in size. The 3–3.5 cm^3 of solution was placed in the cell for photolysis. Irradiation of the solution was carried out in air at room temperature. The incident photon number of 310 nm light was $1.08 \times 10^{16}\ cm^{-2}\ s^{-1}$.

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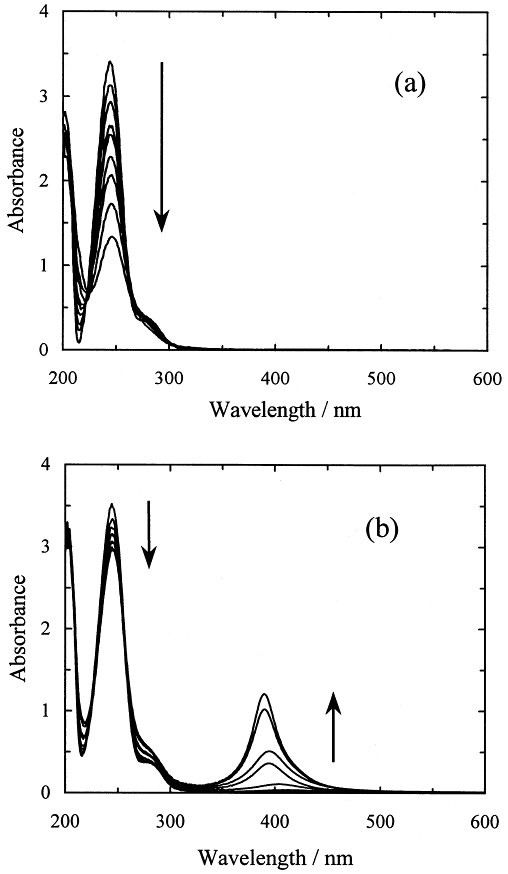

Fig. 1. Absorption spectra of the reaction mixtures before and after irradiation with 310 nm light. (A) AP(2.9 mM)–SDS solution. (B) $AgClO_4$(0.5 mM)–AP(2.8 mM)–SDS solution. The arrows show the direction of the change with the irradiation. Irradiation time; 0, 5, 10, 15, 20, 25, 30, 45 and 60 min. Light path length = 1 mm.

The absorption spectra of the solutions before and after photolysis were measured with a Shimadzu spectrophotometer (UV-260). The concentrations of AP in solutions were estimated spectrophotometrically from the absorption peak at $\lambda = 245$ nm due to a π, π^* transition of AP [11]. Here, a molar extinction coefficient (ε_{AP}) of 1.1×10^4 M^{-1} cm^{-1} was employed.

The measurements of Ag^+ concentrations in the solutions were carried out with an EA-920 ion analyzer equipped with a silver ion selective electrode 94-16 (Orion Research) and a reference electrode 90-02 (Orion Research).

3. Results and discussion

An AP(2.9 mM)–SDS solution and an $AgClO_4$(0.5 mM)–AP(2.8 mM)–SDS solution were photolyzed with 310 nm light. The variations in the absorption spectra with irradiation are shown in Fig. 1. In the absence of $AgClO_4$, a rapid decrease of the π, π^* absorption ($\lambda = 245$ nm) of AP was evident. About 71% of the AP disappeared after 60 min of irradiation. However, the rate of the photobleach slowed down in the presence of $AgClO_4$. 72% of the AP remained after 60 min of irradiation. Moreover, in the presence of $AgClO_4$, the colloidal absorption band of silver developed at $\lambda = 400$ nm. On the contrary, the irradiation of an $AgClO_4$(0.1 mM)–SDS solution with 310 nm light, which is not absorbed by Ag^+, did not cause any spectral change. In this way, the sensitized photoreduction of Ag^+ by AP was confirmed.

These observations are in close analogy with the 365 nm photolysis of the $AgClO_4$–BP–SDS solution [10]. It is reasonable to assume that the sensitized photoreduction of Ag^+ by AP would proceed as below.

$$\mathrm{AP} \underset{k_0}{\overset{\lambda=310\ \mathrm{nm},\ \alpha I}{\rightleftharpoons}} \mathrm{AP}^* \tag{1}$$

$$\mathrm{AP}^* + \mathrm{RH} \xrightarrow{K_1} \mathrm{APK} + {}^{\bullet}\mathrm{R} \tag{2}$$

$$\mathrm{APK} + (\mathrm{Ag}_m)^+ \xrightarrow{k_2} \mathrm{AP} + (\mathrm{Ag}^0)_m + \mathrm{H}^+ \tag{3}$$

$$\mathrm{APK} \xrightarrow{k_3} \mathrm{Byproducts} \tag{4}$$

The excitation of AP by 310 nm light yields an acetophenone triplet (AP*), which abstracts a H atom from SDS (RH), giving rise to an acetophenone ketyl radical (APK) and an alkyl radical (${}^{\bullet}$R). Some APK reduces silver ion clusters $(Ag_m)^+$ ($m \geq 1$) and goes back to AP. Other APK changes into certain byproducts such as the corresponding pinacol and hydrol. A subsequent agglomeration process of silver atoms and clusters produces colloidal silver. Here, reaction (1) consists of a forward reaction (the incident photon number I and absorption coefficient α) and a reverse reaction (rate constant k_0). K_1, k_2 and k_3 are the rate constants of reactions (2), (3) and (4), respectively.

Under stationary-state conditions, the rate of the photobleach of AP, V(AP) (M s^{-1}) and the rate of photoreduction of Ag^+, $V(Ag^+)$ (M s^{-1}) would be expressed by [10]

$$V(\mathrm{AP}) = \frac{k_1 k_3[\mathrm{AP}]}{k_3 + k_2[\mathrm{Ag}^+]} \tag{5}$$

$$V(\mathrm{Ag}^+) = \frac{k_1 k_2[\mathrm{Ag}^+][\mathrm{AP}]}{k_3 + k_2[\mathrm{Ag}^+]} \tag{6}$$

Here, k_1 is given by $\alpha I K_1[\mathrm{RH}]/(k_0 + K_1[\mathrm{RH}])$. The abbreviations represent the initial concentrations of the reactants. $AgClO_4$(0.2 mM)–AP(0–4.7 mM)–SDS solutions were irradiated with 310 nm light and V(AP) was evaluated from the decrease of the absorbance of π, π^* transition of AP. The V(AP) was plotted versus [AP] in Fig. 2. In accordance with Eq. (5), the dependence of V(AP) on [AP] was represented by a straight line with a positive slope of 1.3×10^{-4} s^{-1}.

Next, we examined the dependence of V(AP) on $[Ag^+]$ for $AgClO_4$(0–0.9 mM)–AP(2.8 mM)–SDS solutions. When $[Ag^+]$ increased, V(AP) was decreased as expected from Eq. (5). From the slope and abscissa of the straight line fitted for $V(\mathrm{AP})^{-1}$ versus $[Ag^+]$ plot (Fig. 2), $k_1 = 2.3 \times 10^{-4}$ s^{-1} and $k_3/k_2 = 4.7 \times 10^{-4}$ M were evaluated.

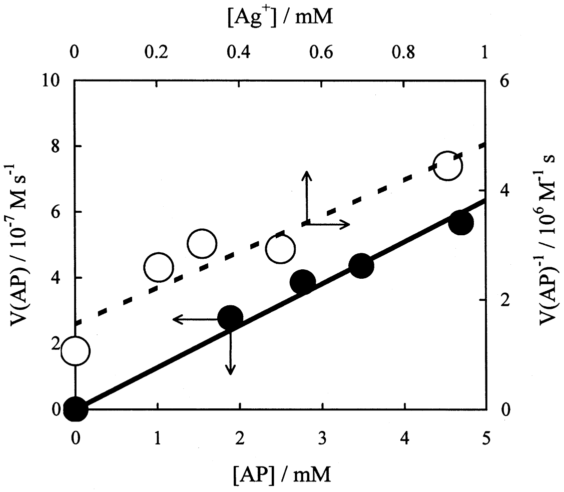

Fig. 2. The dependence of V(AP) on [AP] and [Ag^+]. (●, Solid line) V(AP) versus [AP] plot for $AgClO_4$(0.2 mM)–AP(0–4.7 mM)–SDS solutions. (○, dashed line) $V(AP)^{-1}$ versus [Ag^+] plot for $AgClO_4$(0–0.9 mM)–AP(2.8 mM)–SDS solutions. Irradiation with 310 nm light. The lines were drawn by using a least-squares method.

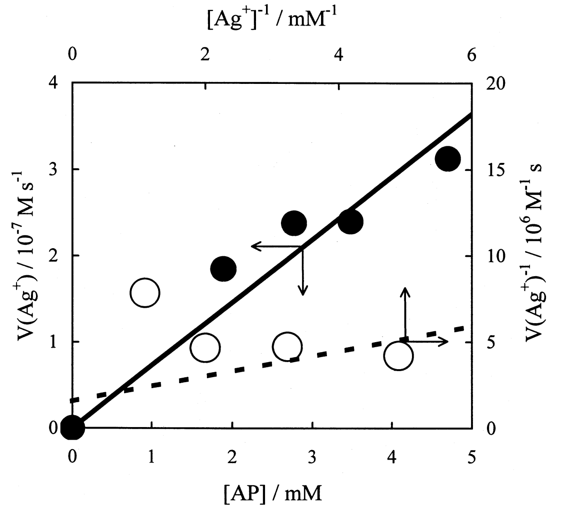

Fig. 3. The dependence of $V(Ag^+)$ on [AP] and [Ag^+]. (●, Solid line) $V(Ag^+)$ versus [AP] plot for $AgClO_4$(0.2 mM)–AP(0–4.7 mM)–SDS solutions. The solid line was drawn by using a least-squares method. (○, dashed line) $V(Ag^+)^{-1}$ versus $[Ag^+]^{-1}$ plot for $AgClO_4$(0–0.9 mM)–AP(2.8 mM)–SDS solutions. The dashed line was theoretically constructed by using the parameters $k_1 = 2.3 \times 10^{-4}\ s^{-1}$ and $k_3/k_2 = 4.7 \times 10^{-4}$ M in Eq. (6). Irradiation with 310 nm light.

According to Eq. (6), $V(Ag^+)$ is dependent on the initial concentration of AP and $AgClO_4$. $AgClO_4$(0.2 mM)–AP(0–4.7 mM)–SDS solutions were photolyzed and $V(Ag^+)$ was evaluated from the decrease of the Ag^+ concentration. The dependence of $V(Ag^+)$ on [AP] is shown in Fig. 3. In accordance with Eq. (6), the $V(Ag^+)$ versus [AP] plot yielded a straight line with a slope of $7.3 \times 10^{-5}\ s^{-1}$. From the slope and $k_1 = 2.3 \times 10^{-4}\ s^{-1}$, $k_3/k_2 = 4.2 \times 10^{-4}$ M was obtained. This value is fairly close to the k_3/k_2 value obtained from Fig. 2.

$AgClO_4$(0–0.9 mM)–AP(2.8 mM)–SDS solutions were irradiated and the dependence of $V(Ag^+)^{-1}$ on $[Ag^+]^{-1}$ was plotted in Fig. 3. The experimental points corresponding to $[Ag^+]/[AP] < 0.2$ were close to the theoretical $V(Ag^+)^{-1}$ versus $[Ag^+]^{-1}$ relation drawn by using $k_1 = 2.3 \times 10^{-4}\ s^{-1}$, $k_3/k_2 = 4.7 \times 10^{-4}$ M and Eq. (6). On the other hand, the experimental data points for $[Ag^+]/[AP] > 0.2$ did not fall on the theoretical curve. We have examined the effects of N_2 bubbling on the change of the colloidal absorption band. The $AgClO_4$(1 mM)–AP(3 mM)–SDS solution ($[Ag^+]/[AP] = 0.33$) and the $AgClO_4$(0.2 mM)–AP(3 mM)–SDS solution ($[Ag^+]/[AP] = 0.067$) were photolyzed for 15 min and the variations in the absorption spectra during dark storage were monitored. In the former solution, more than 50% of the peak absorbance (colloidal absorption band) was decreased during 10 min storage, irrespective of N_2 bubbling or not. In contrast, the decrease in the peak absorbance was less than 5% for the latter solution. Therefore, it is plausible that small silver particles formed at the early stage of the reaction in the solutions $[Ag^+]/[AP] > 0.2$ are likely to suffer from the re-oxidation during Ag^+ analysis procedure. In addition, when the $AgClO_4$ concentration was large, the presence of the induction period in the decrease of the concentration of Ag^+ was noticed. The existence of such induction period will contaminate the reaction scheme based on the stationary-state assumptions. These properties would bring about the scatter of the experimental points for the solutions $[Ag^+]/[AP] > 0.2$. On the other hand, when $[Ag^+]/[AP]$ is not so large, we can safely reproduce the $V(Ag^+)^{-1}$ versus $[Ag^+]^{-1}$ relation by using the reaction scheme (1)–(4).

As a result of the sensitized photoreduction of Ag^+, the colloidal silver was formed and the colloidal absorption band developed at $\lambda = 400$ nm. It is interesting to compare the concentration of the reduced silver, which can be estimated from the decreases of the Ag^+ concentration, with the optical density of colloidal absorption band. $AgClO_4$(0.2 mM)–AP(1.9–4.7 mM)–SDS solutions were photolyzed with 310 nm light. The optical density of colloidal absorption band was plotted versus the concentration of the reduced silver (Fig. 4). The optical density was not proportional to the concentration of the reduced silver. Furthermore, it should be noted that the optical density kept on increasing even if the photoreduction of Ag^+ almost completed. The extinction coefficient of colloidal silver (ε_{Ag}) was evaluated from each data point in Fig. 4 and was plotted versus irradiation time in Fig. 5. At the earlier stage of the photolysis, the ε_{Ag} was smaller than the usual value of 1.5×10^4 g-atom^{-1} dm^3 cm^{-1} [12]. However, at the latter stage, the ε_{Ag} upraised more than the usual value and went up to over 3.5×10^4 g-atom^{-1} dm^3 cm^{-1}. These observations indicated that the spectral shape and the magnitude of ε_{Ag} of the colloidal absorption band suffer considerable changes during the reaction. The spectral changes are caused by the variations of the size and shape of the colloidal silver [1]. If electron injection to colloidal silver from

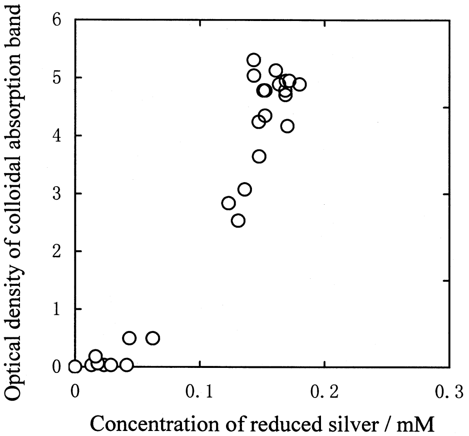

Fig. 4. Comparison between the concentration of the reduced silver and optical density of colloidal absorption band in the $AgClO_4$(0.2 mM)–AP(1.9–4.7 mM)–SDS solutions irradiated by 310 nm light. Although light path length to measure optical density was 1–10 mm, the optical density in this figure is given as if the light path length was 10 mm.

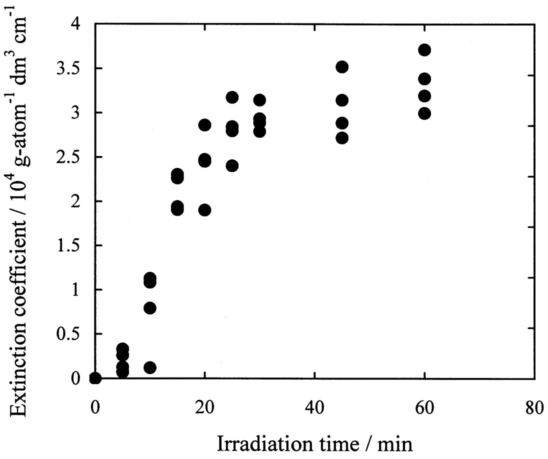

Fig. 5. Variation of the extinction coefficient of colloidal silver with irradiation time for the $AgClO_4$(0.2 mM)–AP(1.9–4.7 mM)–SDS solutions. Irradiation with 310 nm light.

APK occurs, it induces the peptization of colloidal silver agglomerates [9,10], resulting in the variations of the size and shape. In addition, it has been theoretically proposed by Henglein that the increase of the electron density in the silver particles could increase the optical density and ε_{Ag} of colloidal absorption band [3]. These two effects could bring about the spectral change and the variation of ε_{Ag}. It is interesting whether electron injection from APK really occurs after the photoreduction of Ag^+ has almost completed. To confirm those assumptions, the direct detection and kinetic studies of APK in the reaction mixture are needed. The research plan along this line is now under way.

The photolysis of $AgClO_4$–AP–SDS solutions with 310 nm light and that of $AgClO_4$–BP–SDS solutions with 365 nm light proceed in basically the same reaction mechanism. We have reported 365 nm photolysis of the $AgClO_4$–BP–SDS solution in the former paper [10]. In that article, we evaluated the rate of formation of colloidal silver, V(Ag), instead of $V(Ag^+)$. In order to interpret the reaction kinetics, ε_{Ag} of 7.5×10^3 g-atom^{-1} dm^3 cm^{-1} was suggested to be better than the usual value of 1.5×10^4 g-atom^{-1} dm^3 cm^{-1} in the initial reaction stage. To rationalize our former treatment, we have measured the decrease of Ag^+ concentration in the $AgClO_4$–BP–SDS system. It appeared that the $V(Ag^+)$ and the V(Ag), which was calculated from ε_{Ag} of 7.5×10^3 g-atom^{-1} dm^3 cm^{-1}, were roughly equal to each other at least at the initial stage of photolysis of the $AgClO_4$(0.3 mM)–BP(0.06–0.20 mM)–SDS and $AgClO_4$(0.16–0.41 mM)–BP(0.20 mM)–SDS solutions. These results would guarantee almost all treatments in the former paper.

In the former paper, we have reported $k_1 = 7.2 \times 10^{-4}$ s^{-1} and $k_3/k_2 = 1.6 \times 10^{-4}$ M for $AgClO_4$–BP–SDS system [10]. In the present study, we obtained $k_1 = 2.3 \times 10^{-4}$ s^{-1} and $k_3/k_2 = (4.7–4.2) \times 10^{-4}$ M for the $AgClO_4$–AP–SDS system. Considering the different incident photon numbers and the absorption coefficient between 310 nm light and 365 nm light[1], the efficiency of the generation of APK is not so different from that of BPK. The ratio of the efficiency of the generation of APK to that of BPK was 0.88. On the other hand, there is a significant difference between k_3/k_2 of BPK and APK, which would reflect the different reactivity of these two radicals. Because of a more negative reduction potential of APK compared with BPK [13,14], k_2 of APK should be larger than that of BPK. Therefore, it is plausible that k_3 of BPK is smaller than that of APK. In order to improve the efficiency of the sensitized photoreduction of Ag^+ by aromatic ketone, the control of the production of the ketyl radical in the micelle and its consumption by the coupling and disproportionation reactions would be important. In this way, many features of the sensitized photoreduction of Ag^+ in the presence of aromatic ketones could be interpreted, though qualitatively, in terms of the reaction scheme (Eqs. (1)–(4)).

4. Conclusions

The sensitized photoreduction of Ag^+ and photochemical formation of colloidal silver in $AgClO_4$–AP–SDS solutions were studied for the first time. Irradiation with 310 nm light absorbed solely by AP brought about the formation of colloidal silver and the photobleach of AP (sensitized photoreduction). It was adverted that the progress of the photoreaction was accompanied by the change in the extinction coefficient of colloidal silver. A qualitative interpretation of the mechanism of the sensitized photore-

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[1] The ratio of the incident photon number of 310 nm light to that of 365 nm light was 0.54. The ratio of the absorption coefficient of AP at $\lambda = 310$ nm to that of BP at $\lambda = 365$ nm was 0.67.

duction of Ag^+ and the photobleach of AP was done by using a simple reaction scheme, Eqs. (1)–(4). The rate of photoreduction of Ag^+, $V(Ag^+)$ and the rate of photobleach of AP, V(AP) were expressed in closed forms. The dependence of $V(Ag^+)$ and V(AP) on the initial reactant concentrations were examined, and combinations of some of the kinetics parameters, k_1 and k_3/k_2 were evaluated. These kinetics parameters were compared with those for the $AgClO_4$–BP–SDS solutions initiated by 365 nm light. Although the efficiency of the formation of APK and BPK is not so different from each other, a significant difference between k_3/k_2 of APK and BPK is observed which is attributable to larger rate constant k_3 of AP for the reaction (4).

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