December, 1994] © *1994 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *67*, *3165—3171(1994)* 3165

Photochemical Formation of Colloidal Silver in the Presence of Benzophenone

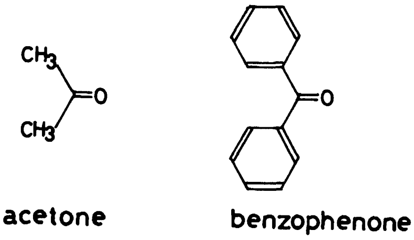
Tomoo SATO, Naohide MAEDA, Hideo OHKOSHI, and Yoshiro YONEZAWA*
Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606

(Received May 23, 1994)

An aqueous silver perchlorate–sodium dodecylsulfate (SDS)–benzophenone (BP) solution was photolyzed with either UV or near-UV light. Irradiation with 253.7 nm light, which was absorbed by both BP and silver ions, brought about the formation of collidal silver and the photobleach of BP. Peptization of colloidal silver agglomerates after prolonged irradiation was ascribed to electron injection from the benzophenone ketyl radical (BPK). The formation of colloidal silver and the photobleach of BP were also caused by irradiation with 365 nm light, which was absorbed solely by BP (sensitized reaction). A simple reaction scheme was introduced and the initial rates for the sensitized photoreduction of silver ions and the photobleach of BP were expressed in closed forms. Suitable combinations of the kinetics parameters and the extinction coefficient of colloidal silver were proposed in order to interpret the dependences of the initial rates on the reactant concentrations.

We have studied the photochemical formation of colloidal metal particles in solutions by using sodium dodecylsulfate (SDS) as a protective agent.[1,2] When a silver perchlorate ($AgClO_4$)–SDS–acetone [$(CH_3)_2CO$] solution was irradiated with 253.7 nm light, a sharp and intense absorption band of colloidal silver (λ=397 nm) appeared within an irradiation time of less than 10 min. In this reaction, both silver ions (Ag^+) and $(CH_3)_2CO$ absorbed 253.7 nm light independently, and any excess acetone ketyl radical [$(CH_3)_2\dot{C}OH$, AK] could inject electrons into colloidal silver particles and agglomerates, giving rise to fine silver particles (peptizing action). Colloidal silver particles are stabilized by SDS micelles. We have thus proposed a novel "photo-acetone method", available for the preparation of fine metal particles.[2]

The photochemistry of aliphatic ketones and aromatic ketones in the excited state has been one of the most fundamental and important subjects in organic photochemistry.[3—5] Substitution of $(CH_3)_2CO$ for benzophenone [$(C_6H_5)_2CO$, BP] seems to be interesting, because BP has two absorption bands in the UV—near-UV region, due to a π, π^* transition (252 nm) and an n, π^* transition (325 nm), respectively (Scheme 1).[5] The structure and reactions of the benzophenone ketyl radical [$(C_6H_5)_2\dot{C}OH$, BPK] have been extensively studied for a long time.[6—8] Although 365 nm light from a high-pressure mercury lamp is not absorbed by Ag^+, it could initiate photochemical reactions by an n, π^* transition of BP. A detailed study concerning the sensitized photoreduction of Ag^+ would offer useful information on the photochemistry of $AgClO_4$–SDS–ketone systems, e.g., the photoreactivity of BPK in the presence of colloidal metal particles. In this study, we focused on photochemical reactions in an $AgClO_4$–SDS–BP solution, and proposed a simple reaction scheme involving the sensitized photoreduction of Ag^+ and the photobleach of BP.



Scheme 1.

Experimental

BP (Wako Chemicals Co.) and benzhydrol, $AgClO_4$, isopropyl alcohol (Pr^iOH), and HNO_3 (Nacalai Tesque Co.) were used as received. Commercially available SDS (Nacalai Tesque Co.) was purified by repeated recrystallization from water. All of the solutions were aqueous solutions prepared with distilled water in the dark.

A 200-W low-pressure mercury lamp (UL-2-2Q) with a power supply (UL2-2EBH; Ushio Denki Co.) was used as the light source for 253.7 nm light. A filtered solution of cobalt(II) sulfate was adequate to cut off $\lambda<253.7$ nm. A 500-W high-pressure mercury lamp (UI-501C) with a power supply (HB-50102 AA; Ushio Denki Co.) was used as the light source for near-UV light. A combination of glass filters (UV-D35 and UV-35; Toshiba Co.) and a copper(II) sulfate filtered solution was useful for selecting 365 nm light. The reaction cell was a rectangular quartz vessel, $10\times10\times40$ mm^3 in size. The cell was set up in a dark box, and a 3—3.5 cm^3 solution was placed in it for photolysis. The incident photon numbers of 253.7 and 365 nm light (determined by a tris(oxalato)ferrate(III) actinometer[9]) were 1.2×10^{16} $cm^{-2}s^{-1}$ and 2.0×10^{16} $cm^{-2}s^{-1}$, respectively. Irradiation of the solution was carried out in air at room temperature.

The absorption spectra of the solutions before and after irradiation were measured with a Shimadzu spectrophotometer (UV-260). The light path-length of the cell used for spectroscopic measurements was usually 0.5—2 mm, according to the absorbance of the solutions. The absorption spectra in the figures and the absorbance in the text have been given as if the cell length for every solution were 10 mm.

Results

253.7 nm Photolysis of $AgClO_4$–SDS–BP Solutions. An $AgClO_4$ (10^{-3} M)–SDS (0.035 M)–

BP (1.9×10^{-4} M) (1 M=1 mol dm^{-3}) solution and an $AgClO_4$ (10^{-3} M)–SDS (0.035 M)–benzhydrol (2×10^{-4} M) solution were irradiated with 253.7 nm light. The variations in the absorption spectra with irradiation are shown in Fig. 1. A sharp colloidal absorption (λ=391 nm) developed in the presence of BP. The absorbance was about 4.3 (90 min of irradiation) and 16 (210 min of irradiation). On the other hand, the absorbance of the colloidal absorption in the $AgClO_4$–SDS–benzhydrol solution was only about 2.9 (λ=400 nm) after 120 min of irradiation. When 10 : 1 (v : v) H_2O–Pr^{i}OH was used as a solvent to increase the solubility of BP, the absorbance of the sharp colloidal absorption (λ=402 nm) amounted to about 20 after 120 min of irradiation of the $AgClO_4$ (10^{-3} M)–SDS (0.035 M)–BP (3×10^{-3} M) solution. As a reference, an aqueous $AgClO_4$ (10^{-3} M)–SDS (0.035 M) solution was photolyzed under the same conditions. However, the colloidal absorption band was not evident, even after 120 min of irradiation. The amount of reduced silver in the reaction mixture ($\Delta N_{\rm Ag}$) was analyzed as before, by means of a combination of dialysis, dissolution in HNO_3 and atomic absorption spectrometry.[2)] In the $AgClO_4$ (10^{-3} M)–SDS (0.035 M)–BP (1.7×10^{-4} M) solution, $\Delta N_{\rm Ag}$ were 0.31 µmol (irradiation time 20 min), 0.59 µmol (40 min), 0.89 µmol (60 min), 1.5 µmol (120 min), 1.9 µmol (150 min) and 2.2 µmol (210 min), respectively.

The photochemical formation of colloidal silver was accompanied by the photobleach of BP. We examined the photobleach of BP more precisely in an SDS–BP solution and in an $AgClO_4$–SDS–BP solution. Although the photobleach of BP proceeded only slightly in an aqueous solution of BP (1.5×10^{-4} M), it was almost completed within 1 min in an SDS (0.035 M)–BP (1.5×10^{-4} M) solution. The amount of BP remaining in the solution was estimated spectrophotometrically from the absorption peak at λ=250—260 nm of the π, π^* transition of BP. Hereafter, a molar extinction coefficient ($\varepsilon_{\rm BP}$) of 1.4×10^4 mol^{-1} dm^3 cm^{-1} is employed. The amounts of BP in an SDS (0.035 M)–BP (1.3×10^{-4} M) solution and in an $AgClO_4$ (10^{-3} M)–SDS (0.035 M)–BP (1.4×10^{-4} M) solution are plotted versus the irradiation time in Fig. 2. About 92% of the BP disappeared after 1 min of irradiation in the absence of $AgClO_4$. On the other hand, $AgClO_4$ slowed down the photobleach of BP. It took about 12 min for a 92% decrease of BP in the $AgClO_4$–SDS–BP solution.

365 nm Photolysis of $AgClO_4$–SDS–BP Solutions. An $AgClO_4$ (10^{-4} M)–SDS (0.035 M)–BP (1.7×10^{-4} M) solution was photolyzed with either 253.7 or 365 nm light; the variations in the absorption spectra with the irradiation are shown in Fig. 3. During the early stage, the growth of a colloidal absorption band by 253.7 nm light and by 365 nm light was not so different from one another. In fact, the absorbance after 30 min of irradiation with 253.7 nm light was about 0.8 (λ=391 nm), and the corresponding one with 365 nm light was about 0. 8 (λ=402 nm). The irradiation of an $AgClO_4$ (10^{-4} M)–SDS (0.035 M) solution with 365 nm light for a long time did not cause any spectral change. In this way, BP caused a photochemical formation of colloidal silver by 365 nm light (sensitized photoreduction of Ag^+). The photobleach of BP in an SDS (0.035 M)–BP (2.7×10^{-4} M) solution was almost completed after 60 min of irradiation with 365 nm light. The amounts of BP left in an SDS (0.035 M)–BP (1.5×10^{-4} M) solution and in an $AgClO_4$ (8×10^{-4} M)–SDS (0.035 M)–

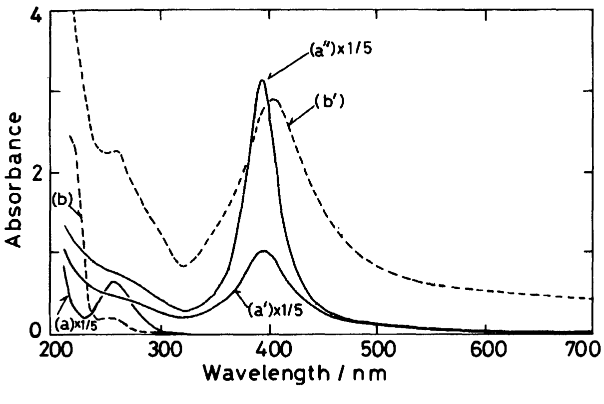


Fig. 1. Absorption spectra of the reaction mixtures before and after irradiation with 253.7 nm light. The aqueous solutions contain 10^{-3} M $AgClO_4$, 0.035 M SDS and BP or not. —: 1.9×10^{-4} M BP, (a) 0 min, (a′) 120 min, (a″) 210 min, ---: 2×10^{-4} M benzhydrol, (b) 0 min, (b′) 120 min, Note that the absorbances of (a), (a′), (a″), are reduced by 1/5.

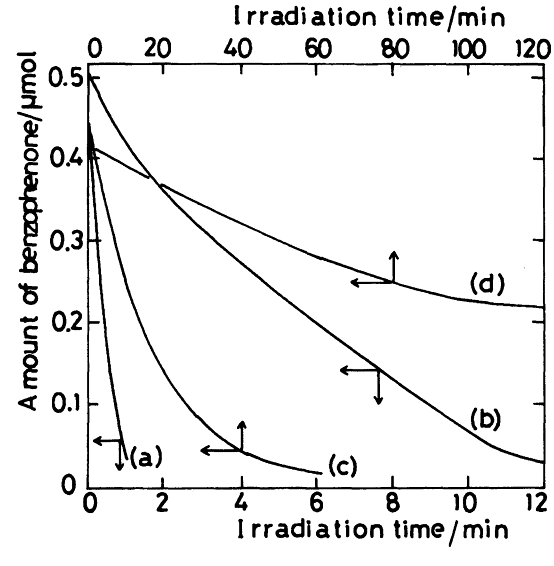


Fig. 2. Decrease of the amount of benzophenone with irradiation time of (a), (b) 253.7 nm light, or (c), (d) 365 nm light. The reaction mixtures contain; (a) 0.035 M SDS and 1.3×10^{-4} M BP, (b) 10^{-3} M $AgClO_4$, 0.035 M SDS, and 1.4×10^{-4} M BP, (c) 0.035 M SDS and 1.5×10^{-4} M BP, (d) 8×10^{-4} M $AgClO_4$, 0.035 M SDS, and 1.4×10^{-4} M BP.

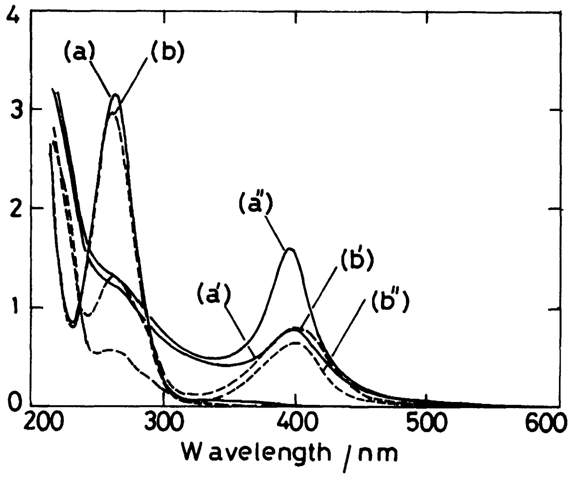


Fig. 3. Absorption spectra of the reaction mixtures before and after irradiation. The aqueous solutions contain 10^{-4} M $AgClO_4$, 0.035 M SDS, and 1.7×10^{-4} M BP. —: Irradiation with 253.7 nm light for (a) 0 min, (a′) 30 min, (a″) 60 min, ---: Irradiation with 365 nm light for (b) 0 min, (b′) 30 min, (b″) 60 min.

BP (1.4×10^{-4} M) solution are included in Fig. 2. The rate of the photobleach was decreased in the presence of $AgClO_4$. It took about 45 min (without $AgClO_4$) and more than 120 min (with $AgClO_4$) for a 92% decrease of BP.

The variations in the absorption spectra of $AgClO_4$ (3×10^{-4} M)-SDS (0.035 M)-BP (0.9×10^{-4} M, 2.5×10^{-4} M) solutions with irradiation are shown in Fig. 4. In a solution containing BP with an initial concentration ([BP]) of 0.9×10^{-4} M, the absorbance at the colloidal absorption band was about 0.82 (irradiation time 60 min) and 0.79 (120 min). It was about 1.9 (60 min) and 2.3 (120 min) in a solution with [BP]= 2.5×10^{-4} M. The decrease of BP in SDS (0.035 M)-BP (0.5×10^{-4}—2.7×10^{-4} M) solutions with the irradiation time is shown in Fig. 5. The concentration of BP was estimated spectrophotometically by using $\varepsilon_{BP}=1.4\times10^4$ mol^{-1} dm^3 cm^{-1}. The rate of the photobleach (V°_{BP} M s^{-1}) was evaluated from the initial slope of the disappearance. It has been found that V°_{BP} is roughly proportional to [BP] with a proportionality constant of about 9.8×10^{-4} s^{-1}. The absorbance at the colloidal absorption band versus the irradiation time curves in $AgClO_4$ (3×10^{-4} M)-SDS (0.035 M)-BP (0.5×10^{-4}—2.5×10^{-4} M) solutions are shown in Fig. 6. The absorbance continued increasing with the irradiation for [BP]=2.5×10^{-4} M, while it attained some maximum value and then tended to decrease after prolonged irradiation for [BP] less than 1.7×10^{-4} M. Such a result, together with the observation that the yellow color of the reaction mixture responsible for colloidal silver was somewhat faded after prolonged irradiation with 365 nm light or after long dark storage, would indicate that the higher is the initial concentration of BP, the greater is the photochemical formation of colloidal silver.

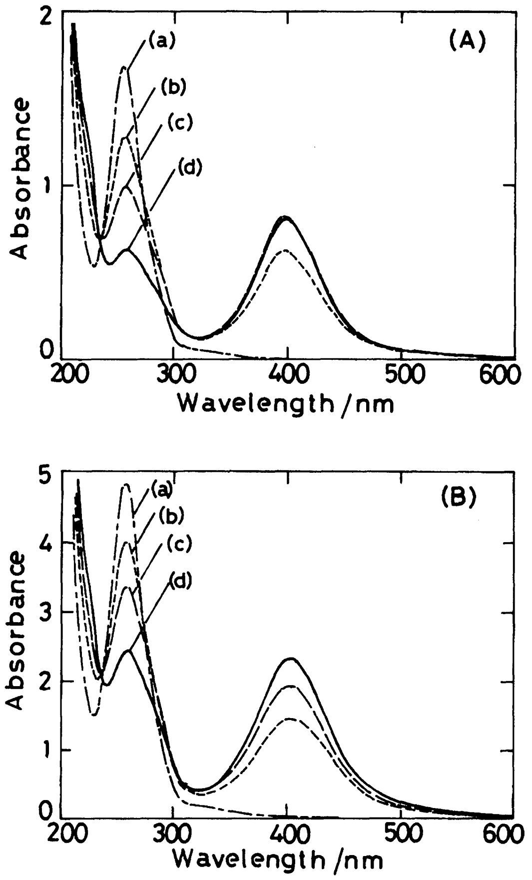


Fig. 4. Absorption spectra of the reaction mixtures before and after irradiation with 365 nm light. The aqueous solutions contain 3×10^{-4} M $AgClO_4$, 0.035 M SDS and (A) 0.9×10^{-4} M BP or (B) 2.5×10^{-4} M BP. Irradiation time; (a) 0 min, (b) 30 min, (c) 60 min, (d) 120 min.

Discussion

Sensitized Photoreduction of Ag^+ Ions. 365 nm light causes the photochemical formation of colloidal silver and the photobleach of BP in the presence of SDS. The excitation of BP by 365 nm light yields a benzophenone triplet, $(C_6H_5)_2CO^*$, which abstracts an H atom from SDS, giving rise to a benzophenone ketyl radical (BPK):[10)]

$$(C_6H_5)_2CO \underset{k_0}{\overset{365\ \mathrm{nm}, \alpha I}{\rightleftarrows}} (C_6H_5)_2CO^* \qquad (1)$$

$$(C_6H_5)_2CO^* + RH \xrightarrow{k_1} (C_6H_5)_2\dot{C}OH + \dot{R}, \qquad (2)$$

where RH and $\dot{R}$ denote and SDS molecule and an alkyl radical formed from SDS, respectively. It is reasonable to assume that BPK could reduce certain silver ion clusters, $(Ag_m)^+$, $(m\geqq1)$, to form silver atoms, Ag^0, and clusters, $(Ag^0)_m$:

$$(C_6H_5)_2\dot{C}OH + (Ag_m)^+ \xrightarrow{k_2} (C_6H_5)_2CO + (Ag^0)_m + H^+ \qquad (3)$$

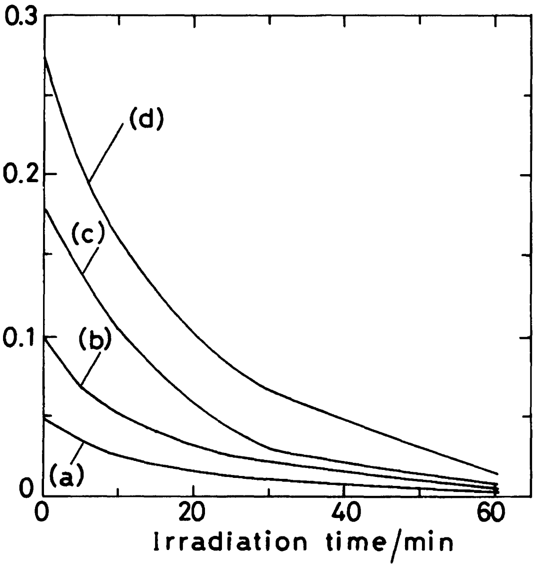


Fig. 5. Photobleach of benzophenone by irradiation with 365 nm light. The aqueous solutions contain 0.035 M SDS and BP. (a) 0.5×10^{-4} M BP, (b) 1.0×10^{-4} M BP, (c) 1.7×10^{-4} M BP, (d) 2.7×10^{-4} M BP. $\overline{\mathrm{BP}}$ is the concentration of BP in the solutions.

A subsequent agglomeration process of silver atoms and clusters produces colloidal silver, $(\mathrm{Ag}^0)_n$, as described in a previous paper.[2] SDS micelles could prevent the colloidal silver particles from coalescing with each other. BPK also undergoes a coupling reaction and a disproportionation reaction:[6,7,11]

$$\begin{aligned}2(\mathrm{C_6H_5})_2\dot{\mathrm{C}}\mathrm{OH} &\xrightarrow{k_3} (\mathrm{C_6H_5})_2\mathrm{C(OH)\text{-}C(OH)}(\mathrm{C_6H_5})_2\\ &\searrow (\mathrm{C_6H_5})_2\mathrm{CO} + (\mathrm{C_6H_5})_2\mathrm{CHOH} \qquad (4)\end{aligned}$$

Since 365 nm light is solely absorbed by BP, the reduction of Ag^+ is limited by the amount of BPK formed by reaction (2). We have focussed on the sensitized photoreduction of Ag^+ by BP, which seems to be a dominant reaction, at least during the early stage. We have introduced a simple reaction scheme for a qualitative interpretation of the mechanism of a sensitized reaction. For the sake of simplicity, the following approximations in Eqs. 1, 2, 3, and 4 have been made: reaction (1) consists of a forward reaction (the incident photon number I and a fraction α) and a reverse reaction (rate constant k_0). $(\mathrm{Ag}_m)^+$ in reaction (3) is replaced by Ag^+. The disproportionation reaction in reaction (4) is neglected. Reaction (4) is regarded as being a unimolecular reaction. k_1, k_2, and k_3 are the rate constants of reactions (2), (3), and (4), respectively. Under stationary-state conditions, the concentrations of $(\mathrm{C_6H_5})_2\mathrm{CO}^*$ and BPK are given by

$$[(\mathrm{C_6H_5})_2\mathrm{CO}^*] = \frac{I\alpha[\mathrm{BP}]}{k_0 + k_1[\mathrm{RH}]} \qquad (5)$$

and

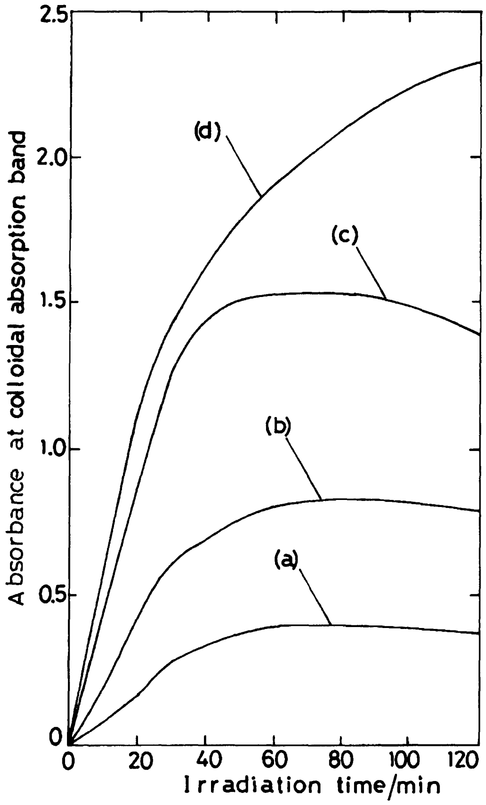


Fig. 6. Variations of absorbance at the colloidal absorption band of silver with irradiation time of 365 nm light. The aqueous solutions contain 3×10^{-4} AgClO$_4$, 0.035 M SDS, and BP. (a) 0.5×10^{-4} M BP, (b) 0.9×10^{-4} M BP, (c) 1.7×10^{-4} M BP, (d) 2.5×10^{-4} M BP.

$$[\mathrm{BPK}] = \frac{k_1[\mathrm{RH}]}{k_3 + k_2[\mathrm{Ag}^+]}\frac{I\alpha[\mathrm{BP}]}{k_0 + k_1[\mathrm{RH}]}. \qquad (6)$$

Here, abbreviations representing the initial concentrations of the reactants (AgClO$_4$, [Ag$^+$]; SDS, [RH]; and BP, [BP]) have been used. It is likely that they do not change very much, at least during the early stage of the reaction. The rate of formation of Ag^0 (V_{Ag}) and the rate of the photobleach of BP (V_{BP}) are then expressed by

$$V_{\mathrm{Ag}} = \frac{\theta I k_1 k_2[\mathrm{RH}][\mathrm{BP}][\mathrm{Ag}^+]}{k_3 + k_2[\mathrm{Ag}^+]} \qquad (7)$$

and

$$V_{\mathrm{BP}} = \frac{\theta I k_1 k_3[\mathrm{RH}][\mathrm{BP}]}{k_3 + k_2[\mathrm{Ag}^+]}, \qquad (8)$$

with

$$\theta = \frac{\alpha}{k_0 + k_1[\mathrm{RH}]}. \qquad (9)$$

In a similar manner, the rate of the photobleach in the absence of AgClO$_4$ is expressed by

$$V^{\circ}{}_{\mathrm{BP}} = \theta I k_1[\mathrm{RH}][\mathrm{BP}]. \qquad (10)$$

As mentioned in the previous section, the proportionality constant of $V^{\circ}{}_{\mathrm{BP}}$ versus [BP] in Fig. 5 is 9.8×10^{-4} s^{-1}, which, in turn, is equal to $\theta I k_1[\mathrm{RH}]$ in Eq. 10.

Equation 7 presumes a linear relation between V_{Ag} and [BP] for a constant $[Ag^+]$. Since the amount of reduced silver is rather small during the early stage, the quantitative analysis as cited in the previous section[2) would be accompanied by relatively large errors. We have therefore tried to estimate the amount of reduced silver from the colloidal absorption band. According to Henglein,[12) we first made use of an extinction coefficient (ε_{Ag}) of 1.5×10^4 g-atom^{-1} dm^3 cm^{-1} at the colloidal absorption peak (λ=390—410 nm). V_{Ag} was evaluated from the initial slope of the absorbance-versus-irradiation time curve in Fig. 6; the results are given in Fig. 7. It has been observed that the dependence of V_{Ag} on [BP] is really represented by a straight line with a slope of 2.6×10^{-4} s^{-1}. By using $\theta I k_1$[RH]$=9.8\times10^{-4}$ s^{-1} and $[Ag^+]=3\times10^{-4}$ M, the ratio of k_3 to k_2 in Eq. 7 amounts to $(k_3/k_2)=8.1\times10^{-4}$ M.

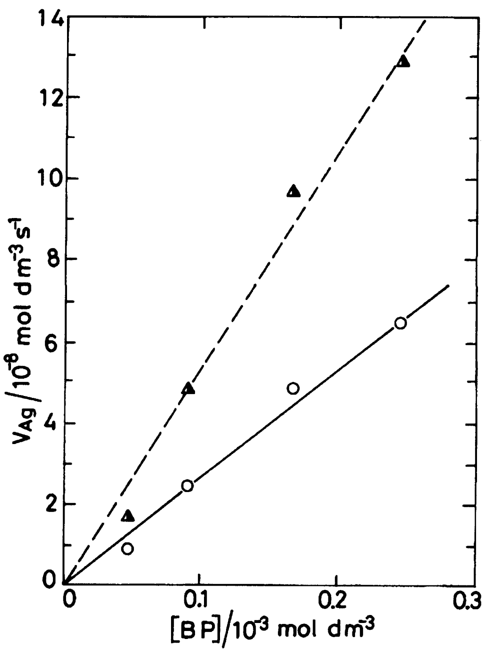


Fig. 7. The rate of formation of Ag^0, V_{Ag}, in the 3×10^{-4} M $AgClO_4$–0.035 M SDS–BP solutions. Initial concentrations of benzophenone, [BP]$=0.5\times10^{-4}$—2.5×10^{-4} M. Irradiation with 365 light. The concentration of colloidal silver has been estimated from the colloidal absorption band with the extinction coefficient $\varepsilon_{Ag}=1.5\times10^4$ g-atom^{-1} dm^3 cm^{-1} (○—○) or $\varepsilon_{Ag}=7.5\times10^3$ g-atom^{-1} dm^3 cm^{-1} (▲- - -▲).

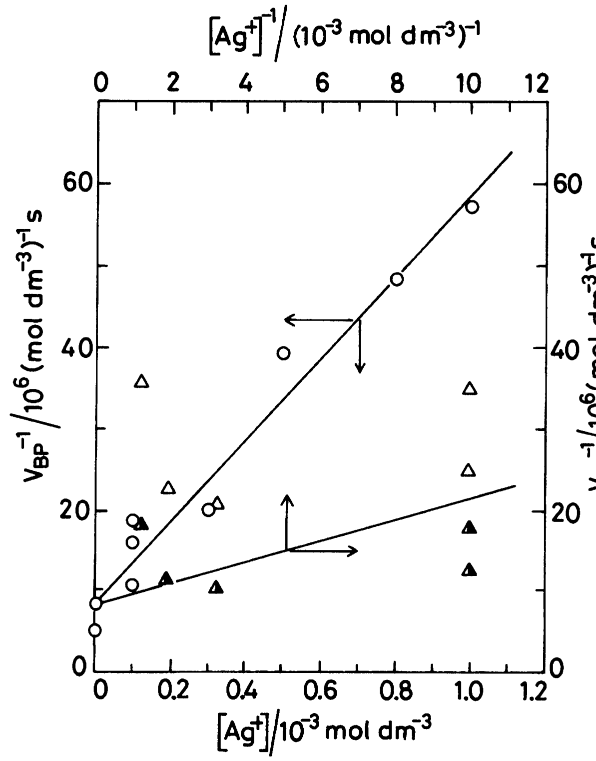


Fig. 8. The rate of formation of Ag^0, V_{Ag} (△,▲), and the rate of photobleach, V_{BP} (○), in the $AgClO_4$–0.035 M SDS–1.7×10^{-4} M BP solutions. Initial concentrations of Ag^+, $[Ag^+]=0$—10^{-3} M. Irradiation with 365 nm light. The concentration of colloidal silver was estimated from the colloidal absorption band with the extinction coefficient $\varepsilon_{Ag}=1.5\times10^4$ g-atom^{-1} dm^3 cm^{-1} (△) or $\varepsilon_{Ag}=7.5\times10^3$ g-atom^{-1} dm^3 cm^{-1} (▲). An experimental $V_{BP}{}^{-1}$ versus $[Ag^+]$ line has been drawn by using a method of least squares. A theoretical $(V_{Ag})^{-1}$ versus $[Ag^+]^{-1}$ line has been constructed by using the parameters $\theta I k_1$[RH][BP]$=1.2\times10^{-7}$ M s^{-1} and $(k_3/k_2)=1.6\times10^{-4}$ M in Eq. 7.

To obtain further insight into Eqs. 7 and 8, we examined V_{Ag} and V_{BP} in $AgClO_4$ (0—10^{-3} M)-SDS (0.035 M)—BP (1.7×10^{-4} M) solutions. The dependences of V_{Ag} and V_{BP} on $[Ag^+]$ are shown in Fig. 8. V_{BP} was evaluated from the initial slope of the disappearance of BP. V_{Ag} was evaluated from the initial slope of the absorbance of the colloidal silver versus irradiation time curve, together with $\varepsilon_{Ag}=1.5\times10^4$ g-atom^{-1} dm^3 cm^{-1}. In accordance with Eq. 8, the $(V_{BP})^{-1}$ versus $[Ag^+]$ plot yielded a straight line. According to a method of least squares, the slope and abscissa are 5.1×10^{10} M^2 s and 8.2×10^6 M^{-1} s, respectively, from which $\theta I k_1$[RH][BP]$=1.2\times10^{-7}$ M s^{-1} and $(k_3/k_2)=1.6\times10^{-4}$ M are obtained. A substitution of [BP]$=1.7\times10^{-4}$ M resulted in $\theta I k_1$[RH]$=7.2\times10^{-4}$ s^{-1}. In spite of the relatively large experimental errors, an agreement of $\theta I k_1$[RH], as estimated from Figs. 5 and 8, seems to be satisfactory. On the other hand, the disagreement of (k_3/k_2) from Figs. 7 and 8 is a remaining question. Moreover, a reciprocal relation between V_{Ag} and $[Ag^+]$, as expected from Eq. 7, does not fit to a theoretical line drawn by using $\theta I k_1$[RH][BP]$=1.2\times10^{-7}$ M s^{-1} and $(k_3/k_2)=1.6\times10^{-4}$ M (Fig. 8).

Considering the size-dependent optical constants of small metal particles,[13,14) it is probable that the extinction coefficient of colloidal silver is smaller than 1.5×10^4 g-atom^{-1} dm^3 cm^{-1} during the early stage. We tentatively chose $\varepsilon_{Ag}=7.5\times10^3$ g-atom^{-1} dm^3 cm^{-1} and recalculated V_{Ag}. A new V_{Ag} is plotted versus [BP] in Fig. 7, and the ratio (k_3/k_2) of 2.6×10^{-4} M has been evaluated. This value seems to be slightly closer to 1.6×10^{-4} M than the previous (k_3/k_2). Renewed data points of the reciprocal plot between V_{Ag} and $[Ag^+]$ have approached the theoretical line (Fig. 8).

Indeed, many crude approximations have been included. The reaction scheme (Eqs. 1, 2, 3, and 4) with suitable parameters (θIk_1[RH], (k_3/k_2) and ε_{Ag}) could elucidate, at least qualitatively, many features of the sensitized photoreduction of Ag^+ and the photobleach of BP in a micellar solution. It is not so unreasonable to assume that the extinction coefficient of colloidal silver formed during the early stage is smaller than the usual value of 1.5×10^4 g-atom^{-1} dm^3 cm^{-1}.

Peptizing Action of Benzophenone Ketyl Redical. When the $AgClO_4$–SDS–BP solution is irradiated, 253.7 nm light is absorbed by both Ag^+ and BP. Excited Ag^+ induces the photooxidation of H_2O, resulting in the formation of Ag^0, H^+ and the OH radical.[1,15] The excitation of BP could cause the same reactions as Eqs. 2, 3, and 4, irrespective of the wavelength of the incident light, 253.7 nm or 365 nm. Such an assumption has been confirmed by an observation that the photobleach of BP was considerablly suppressed in the presence of Ag^+ ions. The development of a sharp colloidal absorption band in the $AgClO_4$–SDS–BP solution irradiated with 253.7 nm light bears resemblance to the remarkable effect of $(CH_3)_2CO$ in an $AgClO_4$ (10^{-3} M)–SDS (0.035 M)–$(CH_3)_2CO$ (0.1 M) solution.[2] In this context, BPK is capable of peptizing colloidal silver particles and agglomerates by electron injection.

$$(C_6H_5)_2\dot{C}OH + (Ag^0)_n \longrightarrow (C_6H_5)_2CO + (Ag^0)_n{}^- + H^+ \tag{11}$$

It is likely that the peptizing action of AK is larger than that of BPK because of the higher concentration of $(CH_3)_2CO$ and the reducing ability of AK.[11,16—18]

We have so far disregarded the peptizing action of BPK under irradiation with 365 nm light. In this case, the reaction conditions appear to be less favourable to peptization than irradiation with 253.7 nm, because excess BPK is not formed in high concentrations. In fact, we have reported that even in an $AgClO_4$ (10^{-3} M)–SDS (0.035 M)–$(CH_3)_2CO$ solution, a sharp colloidal absorption band did not appear upon irradiation with 253.7 nm light, when $[(CH_3)_2CO]$ was less than 5×10^{-4} M.[2] A fading of the yellow colour of the reaction mixture and a decrease of the absorbance at the colloidal absorption band in the $AgClO_4$–SDS–BP solution (mentioned in the Results section) would be due to unoptimized reaction conditions. However, peptization would be possible if a fresh BP solution is added to the reaction mixture, and the mixture is then subjected to further irradiation with 365 nm light. To examine different reducing and peptizing abilities, the detection and direct characterization of ketyl radicals from $(CH_3)_2CO$ and BP in the presence of Ag^+ are desirable. A research plan along this line is now in progress.

Conclusions

The photochemical formation of colloidal silver in an $AgClO_4$–SDS–BP solution was studied for the first time. Irradiation with 253.7 nm light absorbed by both Ag^+ and BP brought about the formation of colloidal silver and the photobleach of BP. Similar reactions were caused by 365 nm light, which was absorbed solely by BP (sensitized reaction). A simple reaction scheme, Eqs. 1, 2, 3, and 4 was introduced for a qualitative interpretation of the mechanism of a sensitized reaction during the early stage; the rate of formation of colloidal silver (V_{Ag}) and the rate of photobleach of BP (V_{BP}) were expressed in closed forms. The dependences of V_{Ag} and V_{BP} on the initial reactant concentrations were examined, and combinations of some of the kinetics parameters, θIk_1[RH] and (k_3/k_2), were evaluated. It was suggested that an extinction coefficient of colloidal silver formed during the early stage is smaller than the usual value of 1.5×10^4 g-atom^{-1} dm^3 cm^{-1}. With reference to our previous work on the peptizing action of the acetone ketyl radical, it was proposed that BPK is capable of peptizing colloidal silver particles and agglomerates by electron injection.

References

1) Y. Yonezawa, T. Sato, M. Ohno, and H. Hada, *J. Chem. Soc., Faraday Trans. 1*, **83**, 1559 (1987).

2) Y. Yonezawa, T. Sato, S. Kuroda, and K. Kuge, *J. Chem. Soc., Faraday Trans.*, **87**, 1905 (1991).

3) J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, **21**, 499 (1970).

4) J. C. Scaiano, *J. Photochem.*, **2**, 81 (1973/1974).

5) N. J. Turro, in "Modern Molecular Photochemistry," Benjamin/Cummings, Menlo Park (1978), Chaps. 3 and 5.

6) a) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961); b) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

7) a) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); b) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

8) E. Hayon, T. Ibata, N. N. Lichtin, and M. Simic, *J. Phys. Chem.*, **76**, 2072 (1972).

9) a) C. A. Parker, *Proc. R. Soc. London, Ser. A*, **A220**, 104 (1953); b) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **A235**, 518 (1956).

10) a) Y. Sakaguchi, S. Nagakura, and H. Hayashi, *Chem. Phys. Lett.*, **72**, 420 (1980); b) Y. Sakaguchi, H. Hayashi, and S. Nagakura, *J. Phys. Chem.*, **86**, 3177 (1982).

11) T. Shiragami, H. Ankyu, S. Fukami, C. Pac, S. Yanagida, H. Mori, and H. Fujita, *J. Chem. Soc., Faraday Trans.*, **88**, 1055 (1992).

12) A. Henglein, *J. Phys. Chem.*, **83**, 2209 (1979).

13) A. Henglein and R. Tausch-Treml, *J. Colloid Inter-*

face Sci., **80**, 84 (1981).

14) a) U. Kreibig, *J. Phys. F*, **F4**, 999 (1974); b) L. Grenzel, T. P. Martin, and U. Kreibig, *Z. Phys. B*, **B21**, 339 (1975).

15) H. Hada, Y. Yonezawa, A. Yoshida, and A. Kurakake, *J. Phys. Chem.*, **80**, 2728 (1976).

16) M. Breitenkamp, A. Henglein, and J. Lilie, *Ber. Bunsenges. Phys. Chem.*, **80**, 973 (1976).

17) Y. Yonezawa, K. Kawai, M. Okai, K. Nakagawa, and H. Hada, *J. Imaging Sci.*, **30**, 114 (1986).

18) D. R. Boate, L. J. Johnston, and J. C. Scaiano, *Can. J. Chem.*, **67**, 927 (1989).