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Conversion of Ag^0 into Ag_2^+ in γ-Irradiated Organic Solid Solutions at 77 K as Studied by ESR

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Ethanol and 2-methyltetrahydrofuran (MTHF) solutions of silver perchlorate were irradiated with γ-rays at 77 K. Two kinds of silver atoms (Ag^0) and a small amount of dimer cations (Ag_2^+) were formed in both solids immediately after irradiation. On storing at 77 K, both Ag^0 species reacted with Ag^+ to form Ag_2^+ in ethanol, while in MTHF only the minor Ag^0 species reacted, resulting in less growth of Ag_2^+ yield than in ethanol. The mechanism for the formation of Ag_2^+ has been discussed in terms of thermal diffusion and quantum tunneling.

Silver atoms (Ag^0) and silver clusters have been produced in various liquid or solid solutions by radiolysis and in rare gas matrices by cocondensation of metal vapors and solvent gases on cold surfaces at low temperatures. These have been extensively studied by ESR and optical spectroscopies to elucidate the interaction between solute and solvent molecules.[1—10] Early ESR studies revealed that Ag^0 could be formed by radiolytical reduction of Ag^+ in an aqueous solution at 77 K[2] and that it was trapped in a variety of trapping sites.[3] Hase et al. measured absorption, emission, and excitation spectra of Ag^0 formed by radiolysis of aqueous, ethanol and 2-methyltetrahydrofuran (MTHF) solutions containing Ag^+ at 4 and 77 K. Its optical properties have been discussed in relation with its trapping sites and its ionization potential in these solids.[4]

The reaction $Ag^0+Ag^+ \rightarrow Ag_2^+$ is of particular importance because this is the first step of silver cluster formations. Pulse radiolysis studies have reported that silver ions were radiolytically reduced and then agglomerated to form oligomeric clusters and finally colloidal metal particles in an aqueous solution at room temperature.[5,6] It has been shown that Ag_2^+ was formed in γ-irradiated frozen solutions containing Ag^+ salt at 77 K[2] and that Ag^0 gave way to the molecular cluster cations Ag_2^+, Ag_3^{2+}, Ag_4^{3+}, and Ag_5^{4+} after annealing at ca. 120 K.[3a,7] Ozin and his co-workers found the occurrence of photoinduced diffusion and aggregation of the silver atoms isolated in rare gas matrices.[8]

Here we produced Ag^0 and Ag_2^+ by gamma radiolysis of ethanol and MTHF solid solutions containing Ag^+ ions at 77 K and obtained the ESR evidence that the reaction $Ag^0+Ag^+ \rightarrow Ag_2^+$ takes place during storage of the irradiated samples at 77 K. To the best of our knowledge, this is the first observation that Ag_2^+ could be formed after γ-irradiation at a low temperature such as 77 K in the dark. It has been also found that the reaction largely depends on the solvents.

Experimental

All chemicals were of reagent grade and were purchased from Nacalai Tesque Co. 2-Methyltetrahydrofuran (MTHF) was first fractionally distilled and then dried over a Na and K alloy. Other chemicals were used without further purification.

$AgClO_4$ was first dissolved in ethanol or MTHF at a concentration of 1.5×10^{-1} M (1 M = 1 mol dm^{-3}) at room temperature. Samples were prepared by dropping 15 spheres of ca. 1 mm in diameter directly in liquid nitrogen. The sample spheres were gathered into a vial and were γ-irradiated to 33 kGy at 77 K in the vial. After irradiation, the sample was poured together with liquid nitrogen into small Sprasil quartz cylindrical tubes of 5 mm in o.d. Although the concentration used is normally high enough to scavenge electrons, we observed the singlet ESR absorption with $g\approx 2.001$ due to trapped electrons (e_t^-) in the solvents. Therefore, trapped electrons were photobleached at 77 K for 1 min with light of wavelength longer than 540 nm. ESR measurements were carried out at 73 K with a JEOL JES-TE200 spectrometer. Bubbling of liquid nitrogen in the Dewar was prevented by cooling the nitrogen with a helium gas stream. Thus the temperature of ESR measurements was 73 K.

Results and Discussion

An ethanol solution of $AgClO_4$ was irradiated with γ-rays at 77 K. The ESR spectrum was measured at 73 K after photobleaching e_t^- and is shown in Fig. 1a. The groups of strong doublets split by approximately 50 mT have been assigned to Ag^0.[1] Since naturally occurring silver has two isotopes, ^{109}Ag (48.1%) and ^{107}Ag (51.9%), both of which have a nuclear spin $I = 1/2$ with slightly different nuclear moments ($g_I(109)/g_I(107)\approx 1.15$), each species gives rise to high- and low-field doublets. The weak shoulders are observed in each line and attributed to Ag^0 trapped in different

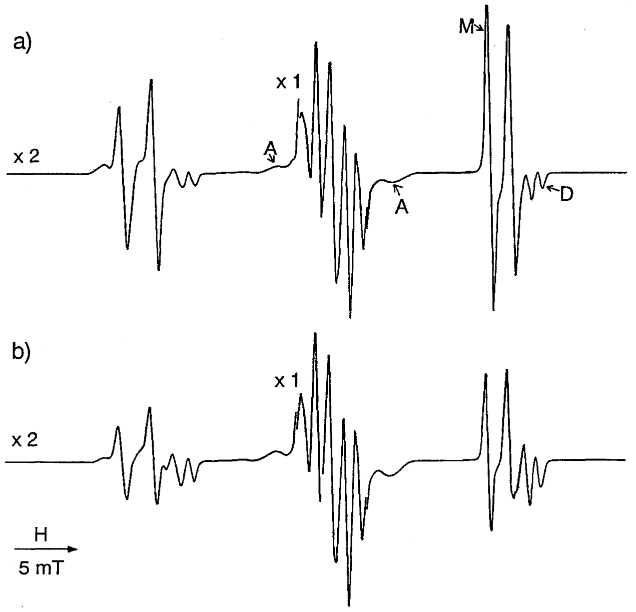

Fig. 1. (a) First derivative ESR spectrum observed at 73 K for an ethanol solution of $AgClO_4$ after γ-irradiation to 33 kGy at 77 K and subsequent photobleaching e_t^- with light ($\lambda > 540$ nm). The concentration was 1.5×10^{-1} M. (b) The spectrum measured at 73 K after storing at 77 K for 12 d. The whole spectrum is normalized so that the signal intensity due to matrix radicals at the center part fits to that in (a). The gain settings between (a) and (b) are the same each other. The relative receiver gains of the spectrometer are indicated by the numbers at the low and the center field regions. See text for the explanation of the ESR lines labeled by A, D, and M.

sites.[7a] At the high field side of each doublet, a set of lines is observed; these are attributed to a part of the triplet perpendicular components of three species, $(^{109}Ag_2)^+$, $(^{107}Ag_2)^+$, and $(^{109}Ag^{107}Ag)^+$.[2] The broad weak absorptions labeled by A can be assigned to the adduct $[AgCH(CH_3)OH]^+$ with $-a(^{109}Ag) = 13.2$ mT and $a(1H) = 4$ mT,[7b] although only the two outermost absorption lines are observed. Symons et al. observed the adduct in an ethanol solution at an elevated temperature.[7b] There is the possibility that the absorptions are due to larger cluster cations than Ag_2^+ such as Ag_4^{3+} and Ag_5^{4+}. Both of them have very small $g_{iso} \approx 1.96$.[7b] However, the species giving rise to the broad absorptions has $g_{iso} \approx 2.00$ so that this possibility can be excluded. We infer that none of the cluster cations are observed at 77 K except for Ag_2^+. The intense signal at the center part of the spectra is due to matrix radicals.

The sample was stored at 77 K in the dark for 12 d after irradiation and the ESR spectrum was recorded. This is shown in Fig. 1b. The peak-to-peak heights due to both kinds of Ag^0 decrease, while those due to Ag_2^+ concomitantly increase, indicating the conversion of Ag^0 into Ag_2^+. The yield of the adduct $[AgCH(CH_3)OH]^+$ also increases slightly. It is noted that the spectrometer gains in Fig. 1b are the same as those in Fig. 1a and that the whole spectrum is normalized so that the ESR signal intensity due to matrix radicals at the center part fits to that in Fig. 1a. Therefore the changes in the yields of Ag^0, Ag_2^+ and the adduct can be directly estimated from the changes in their ESR intensities. The same experiment was carried out for an ethanol solution containing lower concentration (1.5×10^{-2} M) of Ag^+ ions. Only a trace of Ag_2^+ was observed after irradiation at 77 K and the Ag_2^+ yield increased slightly as time elapses.

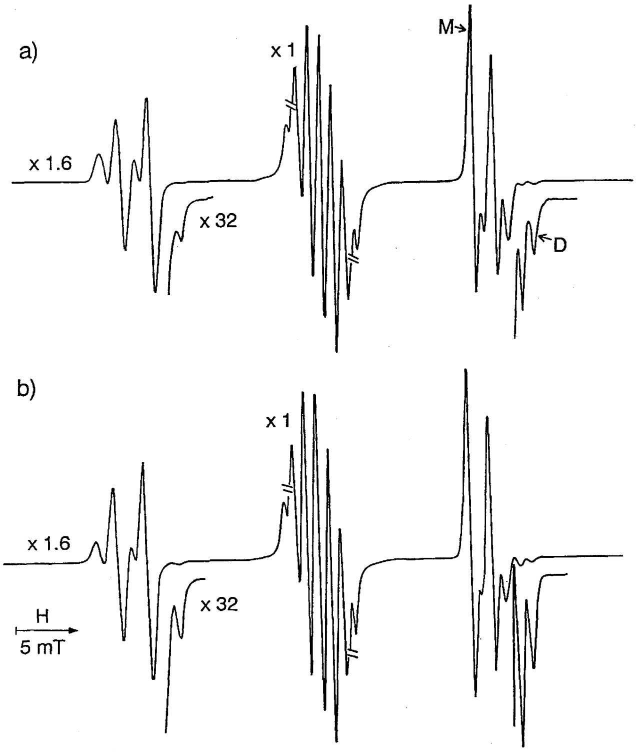

Fig. 2. (a) First derivative ESR spectrum observed at 73 K for an MTHF solution of $AgClO_4$ after γ-irradiation to 33 kGy at 77 K and subsequent photobleaching e_t^- with light ($\lambda > 540$ nm). The concentration was 1.5×10^{-1} M. (b) The spectrum measured at 73 K after storing at 77 K for 12 d. The whole spectrum is normalized so that the signal intensity due to matrix radicals at the central part fits to that in (a). The gain settings between (a) and (b) are the same each other. The relative receiver gains of the spectrometer are indicated by the numbers at the low and the center field regions. See text for the explanation of the ESR lines labeled by D and M.

An MTHF solution of $AgClO_4$ was γ-irradiated at 77 K. The spectrum was measured at 73 K after photobleaching e_t^- and is shown in Fig. 2a. Essential features of the spectrum are the same as those obtained for an ethanol solution (Fig. 1a). Two kinds of Ag^0 and Ag_2^+ were formed by irradiation. The absorptions due to a minor Ag^0 species are also observed in each satellite. The relative yield of the minor Ag^0 to the major Ag^0 is larger in MTHF than in ethanol. In MTHF, the relative yield of Ag_2^+ to the main Ag^0 is smaller than that in ethanol. Figure 2b shows the ESR spectrum measured at 77 K for the above sample after it was stored at 77 K for 12 d. The whole spectrum is normalized in the same way as that in ethanol. The peak-to-peak heights due to the main Ag^0 species remain unchanged, while the ESR intensities due to

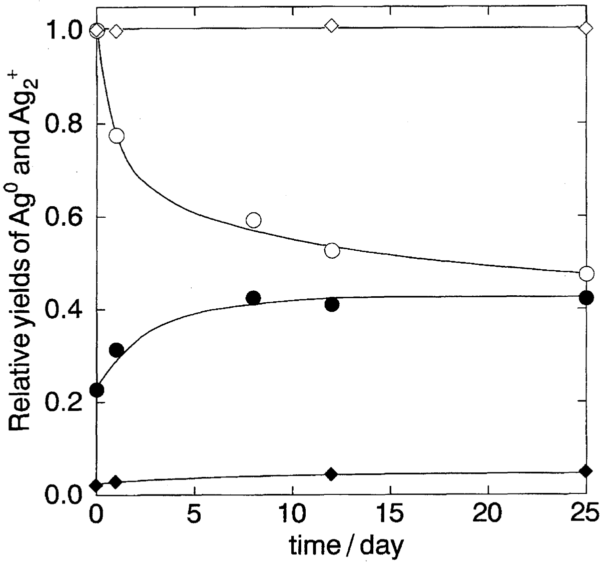

Fig. 3. Dependencies of the relative yields of Ag^0 and $Ag_2{}^+$ on time. ○, the Ag^0 yield in ethanol; ●, the $Ag_2{}^+$ yield in ethanol; ◇, the Ag^0 yield in MTHF; and ◆, the $Ag_2{}^+$ yield in MTHF. In each solution, they are normalized to the Ag^0 yield immediately after irradiation. The values for $Ag_2{}^+$ are multiplied by a factor of 3.7 to obtain the relative yield of $Ag_2{}^+$ to Ag^0 (see text). The storage temperature was 77 K.

the minor Ag^0 species decrease. The yield of $Ag_2{}^+$ slightly increases.

Figure 3 shows a plot of the relative yields of Ag^0 and $Ag_2{}^+$ as a function of storage time. Measurements of Ag^0 concentration require double integration of the first derivative spectra rather than peak-to-peak line intensity measurements. However, as the ESR signals due to Ag^0 and $Ag_2{}^+$ are overlapped, their yields are estimated from their signal intensities. To reduce errors in estimation of their yields, the high-field line due to $^{107}Ag^0$ labeled by M in Figs. 1 and 2 is used for Ag^0, and the highest field line due to $m_I = +1$ labeled by D in Figs. 1 and 2 for $Ag_2{}^+$. Only the major Ag^0 species is considered to estimate the relative yields of Ag^0 in Fig. 3. In each solvent, the yields of Ag^0 are normalized to that immediately after γ-irradiation. If we assume that the ESR spectra of Ag^0 and $Ag_2{}^+$ are isotropic and that both concentrations are the same, the intensity ratio of M to D can be roughly estimated as $4\times(48.1/51.9):1 = 3.7:1$,[2b] because the linewidths of Ag^0 and $Ag_2{}^+$ are almost the same. Therefore the values of the $Ag_2{}^+$ yield in Fig. 3 are given by multiplying the row values by a factor of 3.7 to obtain the relative yield of $Ag_2{}^+$ to Ag^0. As described before, the yield of the major Ag^0 species decreases and the $Ag_2{}^+$ yield concomitantly increases in ethanol as time elapses, while in MTHF the Ag^0 yield does not change and the $Ag_2{}^+$ yield increases slightly. Recall that the minor Ag^0 species decreases in both ethanol and MTHF as time elapses. Thus the large solvent effect was observed for the reaction $Ag^0+Ag^+ \rightarrow Ag_2{}^+$.

There are two possible mechanisms to explain this reaction: the classical diffusion mechanism and the quantum tunneling mechanism. We estimate the possibility of the former mechanism under the assumption that the reaction would take place under diffusion control. Since Ag^0 has the neutral charge, the potential energy between Ag^0 and Ag^+ is zero. Therefore, in the reaction $Ag^0+Ag^+ \rightarrow Ag_2{}^+$, the rate constant of diffusion can be expressed as[11]

$$k_D = 2\varkappa_B T(r_{Ag0}+r_{Ag+})^2/3\eta(T)r_{Ag0}r_{Ag+}, \qquad (1)$$

where k_B is the Boltzmann constant, r_{Ag0} and r_{Ag+} are the radii of Ag^0 and Ag^+, respectively, and $\eta(T)$ is the viscosity of the solvent. Taking $r_{Ag0} = 0.085$ nm, $r_{Ag+} = 0.055$ nm, and $\eta = 1\times10^{13}$ P for ethanol at 78 K,[12] we obtain $k_D = 1.8\times10^{-6}\ dm^3\ mol^{-1}\ s^{-1}$. From a simple calculation of the rate constant in the second order reaction, we can write

$$(c_{Ag0}-c_{Ag+})^{-1}\ln(c_{Ag0}-x)c_{Ag+}/\{(c_{Ag+}-x)c_{Ag0}\} = k_D t, \qquad (2)$$

where c_{Ag0} and c_{Ag+} are the initial concentrations of Ag^0 and Ag^+, respectively, and x is the decrease of the concentration of Ag^0 at time t. If we assume $G(e_t^-) = 2.6$[13] and that all the electrons can be scavenged by Ag^+ ions, the concentrations of Ag^0 and Ag^+ immediately after irradiation can be estimated as $c_{Ag0} = 1.0\times10^{-2}$ M and $c_{Ag+} = 1.4\times10^{-1}$ M, respectively, where we neglect the initial concentration of $Ag_2{}^+$. From Eq. 2, we can obtain, for example, $x = 1\times10^{-3}$ M at $t = 5$ d, which is about 10% of c_{Ag0}. Since this value is not negligible, the classical diffusion mechanism cannot be completely excluded. However, the large decrease in c_{Ag0} at $t = 5$ d by some 40% presently observed in ethanol solutions during storage at 77 K after irradiation can not be explained only by the classical diffusion model. Moreover, since the diffusion control model gives us the upper limit of the rate constant in the reaction, the effective decrease predicted from the diffusion model would be much less than the calculated value of 10%. Also, since Ag^+ interacts with polar solvent such as ethanol more than neutral molecules do and this solvent effect is not involved in Eq. 1 explicitly, the real k_D in ethanol would be smaller than $1.8\times10^{-6}\ dm^3\ mol^{-1}\ s^{-1}$.

Therefore a tunneling mechanism might play a more important role in the reaction $Ag^0+Ag^+ \rightarrow Ag_2{}^+$ taken during storage at 77 K. Kapphan et al. reported that the relaxation transition of [110] off-center states formed by the Ag^+ ions in KCl and KBr crystals occur by a phonon-assisted tunneling mechanism.[14] In this case, a mass as heavy as Ag^+ can tunnel by 0.09 nm at 1.3 K because of a low barrier (ca. 0.17 $kcal\ mol^{-1}$). The tunneling transfer of heavy Ag^0 atoms is only possible if the barrier is sufficiently low and narrow. The average distance between Ag^+ ions is about 2 nm at the Ag^+ concentration of 1.5×10^{-1} M. The distance seems too large for Ag^0 to tunnel if these Ag^+ ions are distributed in a spatially uniform way.

Recently, Hase et al. measured absorption, emission, and excitation spectra of Ag^0 formed by γ-irradiation of ethanol and MTHF solutions containing Ag^+ ions at 77 K.[4] Two emission bands have been observed at ca. 500 nm (E_1 band) and at ca. 580 nm (E_2 band) in both solutions on excitation with the light at 337 nm. From the concentration dependence of the emission intensities, E_1 band has been attributed to

$(Ag^0{\cdot}Ag^+)^*$ exciplex and E_2 band to $(Ag^0{\cdot}L_n)^*$ exciplex, where L_n represents ligand molecules. The observation of the emission from $(Ag^0{\cdot}Ag^+)^*$ exciplex indicates close locations of two Ag^+ ions in spite of Coulombic repulsion. It is possible that an Ag^+ ion is located in the vicinity of another Ag^+ ion if counter ClO_4^- anions bridge two Ag^+ ions. Indeed, pulse radiolysis studies have reported that the presence of $NaClO_4$ accelerates the formation of the silver cluster.[5] When the same experiment was carried out using $AgNO_3$ instead of $AgClO_4$, the conversion of Ag^0 to Ag_2^+ was observed to the same extent, indicating that NO_3^- anions also contribute to bridging two Ag^+ ions. Solvent molecules also contribute to closer location of two Ag^+ ions. Since Ag^+ ions are coordinated with several oxygen atoms of solvent molecules more strongly in polar solvents such as ethanol than in MTHF, the positive charge of Ag^+ ions is canceled more in ethanol than in MTHF. As the result, in some part of the ethanol matrix, two Ag^+ ions are probably located closely. Also, as the solvent molecules form a network by hydrogen bonding in hydroxylic solvents such as ethanol, the two Ag^+ ions may share some oxygen molecules in their first solvation shells, if the Ag^+ concentration is sufficiently high. In this context, Ag_2^+ formations due to tunneling, if any, occur more among Ag^0 and Ag^+ which are located in more close distances than among those in uniform distribution. This idea can also well explain the present experimental result that the Ag_2^+ yield is higher in ethanol than in MTHF. The same solvent effect has been observed for Ag(I)-β-diketone complexes.[4d] For γ-irradiated ethanol and MTHF solutions containing Ag(I)-β-diketone complexes at 77 K, the dimer cation has been observed and its yield is larger in ethanol than in MTHF.

In conclusion, the conversion of Ag^0 into Ag_2^+ has been observed in γ-irradiated ethanol and in MTHF solutions containing Ag^+ during storage at 77 K. The growth of Ag_2^+ has been found to be larger in ethanol than in MTHF. We suggest that the reaction $Ag^0+Ag^+ \rightarrow Ag_2^+$ takes place via a tunneling mechanism and that the initial solvation properties of Ag^+ in hydrophobic and hydrophilic solvents affect the tunneling efficiency.

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