J. Phys. Chem. A **2002,** *106,* 3123−3127

Pulse Radiolysis Study of Absorption Spectra of Ag^0 and Ag_2^+ in Water from Room Temperature up to 380 °C

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Received: July 24, 2001; In Final Form: January 7, 2002

The reduction of silver ions by hydrated electrons is observed at different temperatures (from 25 to 300 °C) at 200 atm pressure in aqueous solutions and also in supercritical water (380 °C at 300 atm) using nanosecond pulse radiolysis techniques. An Arrhenius plot in the range of 25−250 °C shows that the reaction rate constant between silver ions and hydrated electrons can be considered to be controlled by diffusion. Measurements of transient absorption spectra show that, with increasing temperature, the wavelength maxima of the absorption spectra of the silver atom and the charged dimer, Ag_2^+ are shifted to the red. The shift is more pronounced for Ag_2^+ than for Ag^0.

Introduction

Pulse radiolysis of a metal ion solution offers a powerful method[1] to reduce solvated metal ions and then to study by time-resolved spectroscopy the formation of metal atoms and their coalescence. Numerous pulse-radiolysis studies have been devoted to the radiation-induced reduction of various metal ions[2] and aggregation of metal atoms.[3−6] Soon after the irradiation pulse is absorbed by a solution containing the monovalent solvated cation M^+, the population of atoms is created through the reaction 1:

$$e_{aq}^- + M^+ \rightarrow M^0 \qquad (1)$$

The formation of the atoms is correlated with the decay of solvated electrons. The binding energy between the transition metal atom and an ion is stronger than the atom−solvent bond energy. Therefore, the atoms dimerize or associate with excess ions:

$$M^0 + M^+ \rightarrow M_2^+ \qquad (2)$$

and by a multistep process these species progressively coalesce into clusters. Silver solutions constitute a model system due to the possible monoelectronic reduction of the ions to the zerovalent state, to their stability as noncomplexed cations, and their easy complexation with various ligands. In fact, the silver ion aqueous solution was the first system thoroughly studied by pulse radiolysis[7−10] and was recently revisited.[11−14]

The optical absorption spectra of transient silver atoms and charged dimers produced by reactions 1 and 2 have been observed by pulse radiolysis in various solvents.[15] An indication of the influence of the atom−solvent interaction is given by the solvent dependence of the optical absorption spectra in solution. The absorption band is blue-shifted with increasing polarity of the solvent as measured by the static dielectric constant.[16] These features are comparable to those of the solvated electron[17] and suggest a charge-transfer-to-solvent (CTTS) character of the absorption spectra. In addition, electron spin−echo modulation analysis when the ion is suddenly converted to the atom by irradiation at 4 K in ice or methanol glasses has shown[18] that the structure of the solvation shell of the precursor Ag^+ (4 D_2O molecules) is maintained. However, after a brief warming to 77 K before returning to 4 K, the analysis indicates a drastic change with one single deuteron (out of eight) moving much closer to the silver atom. The former structure of $Ag^+_{D_2O}$ is reversibly obtained by photoionization of the atom through excitation at $\lambda_{exc} = 400$ nm. Therefore, it was concluded that the solvated metal monomer may be considered as a tight cation−electron solvent complex. These results suggest that the Ag^0−solvent interaction looks rather like that of an Ag^+ core plus one negative charge mostly delocalized on the surrounding solvent molecules according to their polarity, thus supporting the CTTS structure put forward by Walker et al.[19]

Only in ammonia, the absorption spectra of silver atoms and dimers were observed at two different temperatures: −50 °C[20] and 23 °C.[15] The maximum of absorption was found at 435 and 450 nm, respectively. Recently, transient absorption spectra of reduced silver ions (Ag_2^+, Ag_3^+, and Ag_4^{2+}) in solution of supercritical C_2H_6 (100 bar, 80 °C) containing 0.8 M CH_3OH have been reported.[21] The spectra are found to be similar to those obtained at room temperature in water. However, up to now the direct observation of the absorption spectra of silver atoms, Ag^0, and those of the charged dimers, Ag_2^+, has not been done in water at different temperatures. In the present work, we report the temperature effect on the rate constant of silver atoms formation by hydrated electrons and the temperature dependence of the absorption spectra of Ag^0 and Ag_2^+ in water.

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10.1021/jp012853z CCC: $22.00

Experimental Section

The experiment was carried out at the University of Tokyo with a new high-temperature irradiation cell (Taiatsu Techno). Details of the apparatus for pulse radiolysis were described elsewhere.[22] The pulsed electron beam has an energy of 35 MeV, and its width was 50 or 10 ns with a dose of 10−70 Gy per pulse. The dose per pulse at room temperature was determined using N_2O− saturated 0.01 M KSCN solution and $G\epsilon((SCN)_2^{-\bullet})$ of 5.2×10^{-4} m^2/J at 472 nm.[23] As compared to the cell previously used,[24] the design of the new cell was very similar but improved. The size of the cell was more compact, making the setup of the optical detection system easier. The diameter of sapphire window for optical access was enlarged from 3 to 6 mm in order to obtain better signal/noise ratio. The cell can withstand temperatures up to 400 °C and pressures up to 400 atm. The optical path was 15 mm. The solution was loaded into the cell by an HPLC pump. The water temperature was monitored with a thermocouple placed inside the cell and the pressure was adjusted with a back pressure regulator. The flow rate of the solution was 2 mL/min, corresponding to a residence time of about 12 s in the cell. Fresh $AgClO_4$ solution prepared with Millipore filtered water was used and the solution was purged with argon gas. 0.1 M *tert*-butyl alcohol was added to completely scavenge $OH^\bullet$ radicals. To compensate for the loss of *tert*-butyl alcohol after long-time gas purging, an appropriate amount of *tert*-butyl alcohol was added to the bulk solution every 2−3 h. The reason for the use of *tert*-butyl alcohol instead of 2-propanol (which is usually used for silver ions reduction) is that the radicals of 2-propanol complex silver ions, and in some conditions, the hydroxyalkyl radical can reduce the silver ion.[8] To avoid that reaction we used *tert*-butyl alcohol as the $OH^\bullet$ scavenger. In that case, the reduction yield is two times less but the radical of *tert*-butyl alcohol is not reactive with silver ions, and the analysis of the signals is easier.

For the pressure of 200 atm, the water density at 25, 100, 200, and 300 °C is around 1, 0.95, 0.86, and 0.73 g/cm^3, respectively, and for 300 atm and 380 °C the water density is around 0.5 g/cm^3. We note that all concentrations, those of hydrated electron, silver ion, silver atom, and the charged dimer, are changed by changing the temperatures. In the present work, we did not normalize the absorption spectra obtained at different temperature. But to calculate the rate constant of hydrated electron with silver ion we take into account the water density change with the temperature.

Results and Discussion

Figure 1 presents the decays of the hydrated electron in three different solutions at different temperatures observed at 700 nm, except in supercritical water (at 380 °C and 300 atm) for which the absorbance is recorded at 800 nm. All the solutions contain 0.1 M *tert*-butyl alcohol as the $OH^\bullet$ scavenger and are free from oxygen. Solution a is without silver ions but the solutions b and c contain 10 μM and 25 μM silver ions, respectively. In the absence of silver ions and oxygen (solution a), as $OH^\bullet$ radicals are scavenged by the alcohol, the decay of the hydrated electron is mostly due to the following reactions:

$$e_{aq}^{-} + H_3O^{+} \rightarrow H \tag{3}$$

$$e_{aq}^{-} + e_{aq}^{-} \rightarrow H_2 + 2OH^{-} \tag{4}$$

For the three solutions, the decay of hydrated electrons observed at 700 nm (or at 800 nm) becomes faster with increasing temperature and the initial optical density decreases with increasing temperature. At a given temperature, the decay of hydrated electrons becomes faster by increasing the silver ion concentration. For example, at 100 °C, the reaction half-life of the hydrated electron in solutions a, b, and c are 700, 300, and 90 ns, respectively. For the solution containing 25 μM silver ions, the decay of hydrated electron is so fast that we could not observed it at temperatures higher than 250 °C. At all temperatures the observed decay of the hydrated electron in solution c follows pseudo-first-order kinetics. We also did the experiment at a higher concentration of silver ions (50 μM), but the decay of hydrated electron is too fast and difficult to observe within our time resolution (10 ns) at temperatures higher than 100 °C. To estimate the rate constant at different temperatures, the values of the concentration of silver ions in water are corrected according to the change of water density at high temperatures. Figure 2 presents the Arrhenius plot of the rate constant of the reaction between hydrated electrons and silver ions (reaction 1). According to the plot in Figure 2, the rate constant of the reaction 1 is best fitted to the Arrhenius relationship and the apparent activation energy was found to be 17.8 kJ mol^{-1}. We note that the apparent activation energy over 0−300 °C for self-diffusion in water is 15.5 kJ mol^{-1} [25−27] and it is also reported that the diffusion of the hydrated electron over the temperature range 4−90 °C could be described by an Arrhenius plot with an activation energy of 20.75 kJ mol^{-1}.[28] Although the temperature dependence of the rate constants of

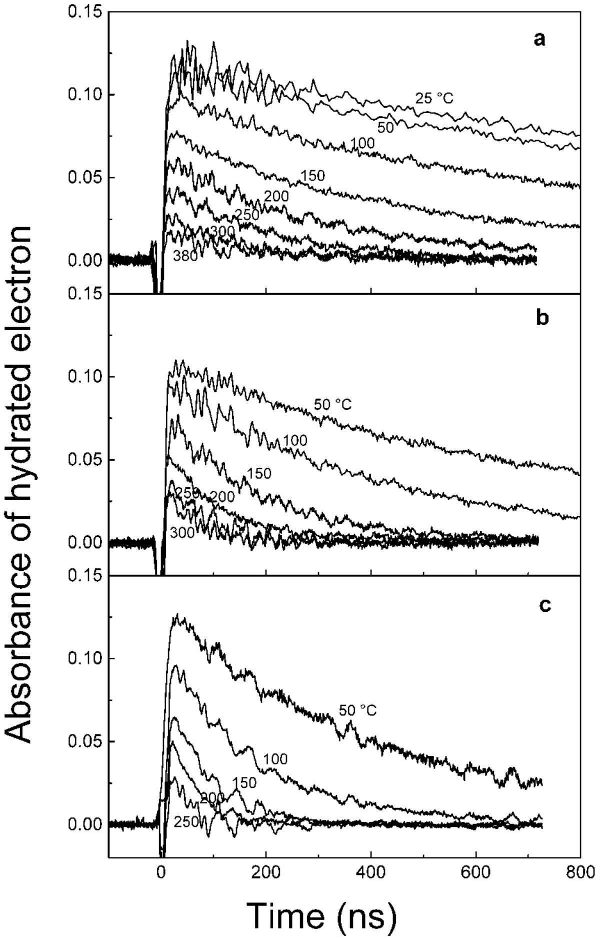

Figure 1. Decay of hydrated electron in various aqueous solutions containing 0.1 M *tert*-butyl alcohol at different temperatures (a) Water, (b) 10 μM $AgClO_4$, (c) 25 μM $AgClO_4$. The dose was 17 Gy/pulse and the optical path was 15 mm. At 380 °C, the pressure was 300 atm and the wavelength was 800 nm while at the other temperatures, 200 atm and 700 nm, respectively.

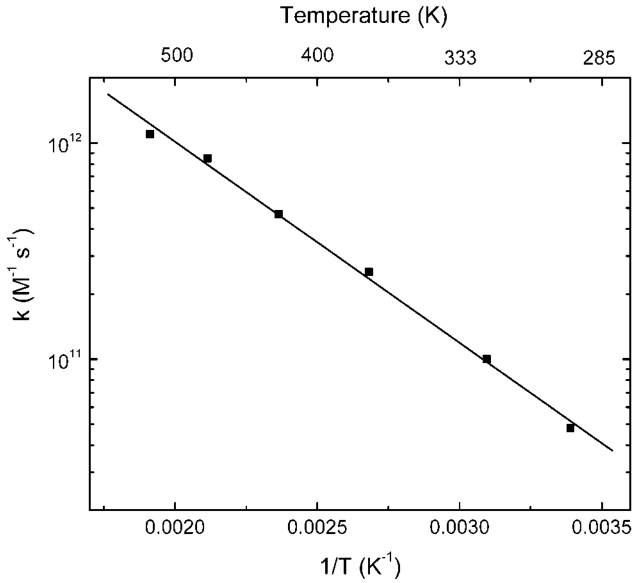

Figure 2. Arrhenius plot of the rate constant of the reaction between hydrated electrons and silver ions, obtained by pulse radiolysis of a solution containing 25 μM $AgClO_4$ and 0.1 M *tert*-butyl alcohol.

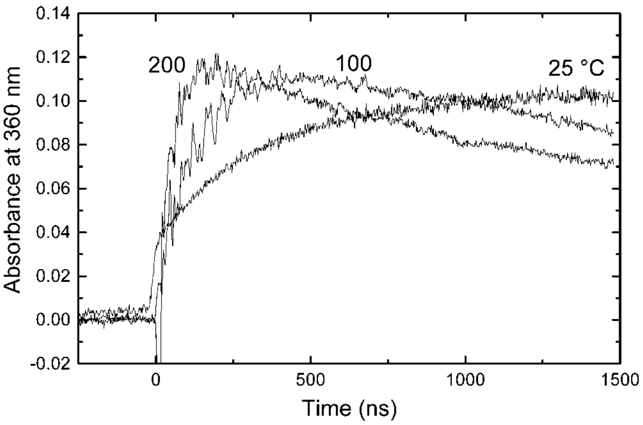

Figure 3. Time profiles of absorbance at 360 nm obtained at different temperatures for the same dose (35 Gy). The solutions contain 20 μM silver ions and 0.1 M *tert*-butyl alcohol.

hydrated electron is strongly dependent on the kinds of reactants, as pointed by Buxton et al.,[29] we can assume that the reaction between hydrated electrons and the silver ions is diffusion controlled.

Figure 3 shows the kinetics at different temperatures observed at 360 nm in solutions containing 25 μM silver ions and 0.1 M *tert*-butyl alcohol. The kinetics observed at 360 nm corresponds to the formation of silver atoms and is correlated with the decay of hydrated electrons. As is shown (Figure 3), for identical dose and silver ion concentration the maxima of the atom formations at 25, 100, and 200 °C are reached at 1500, 450, and 150 ns after the pulse, respectively. The maximum time for silver atom formation at different temperatures is related to the temperature-dependent rate constants of reaction 1 and reaction 2. Figure 4 shows the spectra of the silver atom obtained at the above temperatures. The absorption spectrum at 200 °C is weaker than those obtained at room temperature (25 °C) and at 100 °C. It is well-known that the water density decreases by increasing the temperature but the change of density is not very strong and cannot explain the lowering of the obtained spectrum intensity at 200 °C. That can be explained by the fact that the concentration of silver ions used for the experiments 200 °C is 2.5 times lower than that used at room temperature and at 100 °C. Then, at low concentrations of silver ions and at high temperatures reaction 4 becomes very efficient and the yield of atoms formed is decreased. We found the maximum of the absorption band at 355 ± 2 nm at room temperature in water, which is in agreement with the results reported in the literature. We observed that the maximum of the absorption band is shifted to the red by increasing the temperature. At 100 °C the maximum of absorption band is located at 365 ± 2 nm, and at 200 °C it is shifted to 368 ± 2 nm. In our conditions, we could not observe the silver atoms above 200 °C. It is well-known that the decay of silver atoms in water leads to the formation of the charged dimers (reaction 2). For a given dose and a given silver ion concentration, at 25 °C the decay of atoms is slow but at 100 and 200 °C the decays are much faster. We note that the rate constant of reaction 2 at room temperature is 8.0×10^9 L mol^{-1} s^{-1}.[11] The rate constant of reaction 2 is also increased with increasing temperature and at temperatures higher than 200 °C the atoms are formed within the pulse and only Ag_2^+ can be observed at the end of the pulse. Moreover, it was shown that the Ag_2^+ species, can undergo a dimerization into Ag_4^{2+} (at room temperature $2k = 4 \times 10^9$ L mol^{-1} s^{-1}), or react with another cation to yield Ag_3^{2+} (at room-temperature $k = 2.0 \times 10^9$ L mol^{-1} s^{-1}).

$$Ag_2^+ + Ag_2^+ \rightarrow Ag_4^{2+} \tag{5}$$

$$Ag_2^+ + Ag^+ \rightarrow Ag_3^{2+} \tag{6}$$

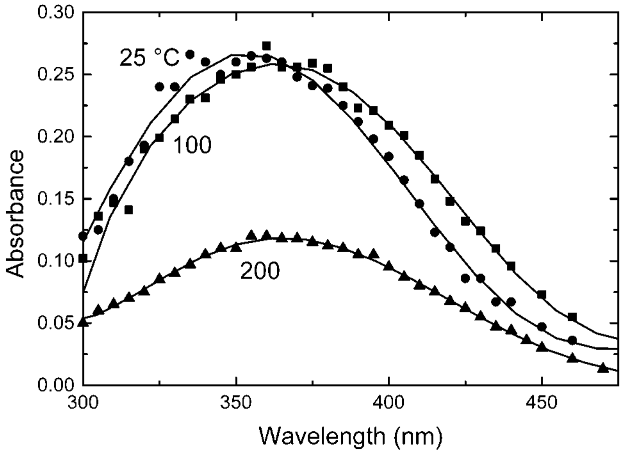

Figure 4. Absorption spectra of Ag^0 at different temperatures. For 25 and 100 °C the solution contained 0.1 M *tert*-butyl alcohol and 50 μM $AgClO_4$ and the dose per pulse was 62 Gy. The absorption spectra are recorded at 700 and 250 ns after the pulse at 25 and 100 °C, respectively. At 200 °C the solution initially contained 0.1 M *tert*-butyl alcohol and 20 μM $AgClO_4$ and the dose per pulse was 35 Gy and the spectra is recorded 200 ns after the pulse. Optical path of the cell was 15 mm.

It is reported that at room temperature the transient Ag_3^{2+} exhibits an intense absorption spectrum with two maxima, at 310 and 265 nm whereas Ag_4^{2+} absorbs at 270 nm.[12,13] Therefore, to observe Ag_2^+ at different temperatures we performed the experiments under different conditions of the dose and silver ion concentration for which Ag_2^+ is the most abundant species in the solution at a given time after the pulse. The analysis of the kinetics observed at different wavelengths and at different temperatures and the kinetics simulations (with the software Facsimile from AEA Technology plc) helped us to find the conditions where the observed spectra at a given time is mostly due to Ag_2^+. For the simulation we took into account the reactions 1−4, the *G* value of the hydrated electron, the

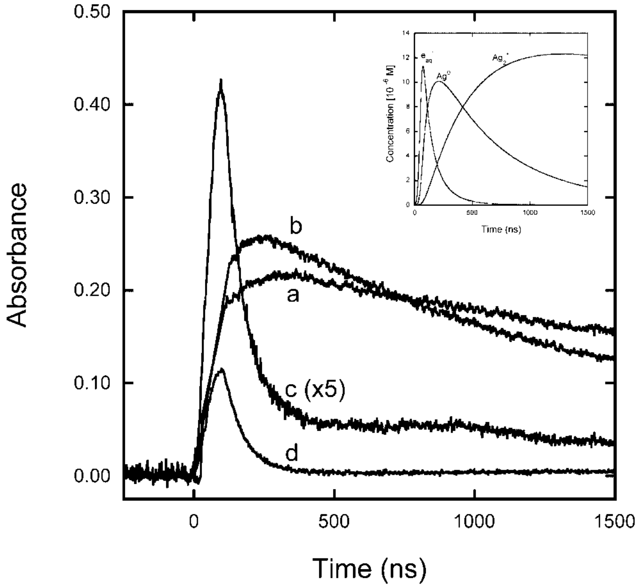

Figure 5. Time profiles of absorbance at (a) 325, (b) 360, (c) 500, and (d) 550 nm obtained at 100 °C for solution containing 50 μM silver ions and 0.1 M *tert*-butyl alcohol. Inset: Simulation of the kinetic behaviors of hydrated electron, Ag^0 and Ag_2^+. Conditions: Pulse width = 100 ns (fwhm), dose/pulse = 64 Gy, temperature = 100 °C, G value for e^-_{hyd}, is 2.90, $pK_w = 12.3$, density of H_2O: 0.956 g/cm^3. $k_1 = 2.8 \times 10^{11}$ M^{-1} s^{-1}; $k_2 = 8 \times 10^{10}$ M^{-1} s^{-1}; $k_3 = 3.35 \times 10^{10}$ M^{-1} s^{-1}; $k_5 = 10^{10}$ M^{-1} s^{-1}.

density of water, and the pK_w at different temperatures.[28] The rate constants of the reactions 1−3 are experimentally known (The value for the rate constant of the reaction 1 is from the present work.), and for the reaction 4 we performed a crude approximation according to the change of the diffusion with increasing the temperature. An example of the simulations and the experimental kinetics at 100 °C is given (Figure 5, inset). The decay of hydrated electron (observed at 550 nm) is correlated with the formation of silver atoms and the decay of the silver atoms is correlated to the formation of Ag_2^+. At 200 ns, we observed that the maximum of the absorption band is around 360 nm (Figure 4). Above 200 ns the signal at 360 nm decreases showing the decay of silver atoms. The signal recorded at 325 nm where both silver atom and charged dimer absorb reaches a maximum around 350 ns indicating the formation of Ag_2^+ following the decay of silver atoms (Figure 5). At 700 ns the maximum of the recorded spectra is changed and it is located around 340 nm (Figure 6). At 500 nm we can observe more clearly the kinetics of Ag_2^+. After the decay of hydrated electron at 500 nm, an absorbance lasting up to 900 ns is observed; above 900 ns it decreases. As silver atom does not absorb at 500 nm, hence the weak signal at 500 nm due to Ag_2^+ confirms that at 700 ns Ag_2^+ is the most abundant species. Therefore, we can attribute that the change between the spectra at 200 and 700 ns is due to the reaction 2 and the absorption band observed at 700 ns is mostly due to Ag_2^+. Moreover, as the rate constant increases with increasing the temperature, for the same conditions of the dose and the silver ion concentration as those at 100 °C, it is expected that at 200 and 300 °C the Ag_2^+ is observed at a time shorter than 700 ns. Indeed, for the same solution (containing 50 μM silver ions), at 200 and 300 °C the hydrated electrons is almost vanished within the pulse and the lifetime of silver atoms is less than that reported at 100 °C. Therefore, at 200 and 300 °C, the recorded spectra at 250 and 150 ns after the pulse are mostly due to Ag_2^+.

The absorption spectra reported in Figure 6 are not normalized. Although the absorption of silver atoms and Ag_4^{2+} (or Ag_3^{2+}) has slight contribution to the recorded spectra in Figure 6, the major contribution is from the absorption band of Ag_2^+.

It is reported that the absorption spectra of Ag_2^+ depend on the solvent.[16,17] At room temperature, the maximum of the absorption spectra of Ag_2^+ in NH_3, ethylediamine, and HF was found at 390, 345, and 300 nm, respectively, showing a CTTS character for the absorption band of Ag_2^+. According to the recorded transient spectra, the maximum of the absorption band of Ag_2^+ is shifted from 315 to 380 nm by increasing the temperature from 25 to 300 °C. At 380 °C the shift is less than that at 300 °C and the intensity of the absorption spectrum is very weak (Figure 6). Due to the absence of information concerning the rate constant of reactions, as well as due to the absence of exact yields of hydrated electron formation at high temperatures, we cannot be sure that the spectrum obtained at 380 °C corresponds to Ag_2^+. It could be due to Ag_4^{2+} or the resultant spectrum can be from the overlap of the absorption spectra of Ag_2^+ and Ag_4^{2+}. It is also important to note that the

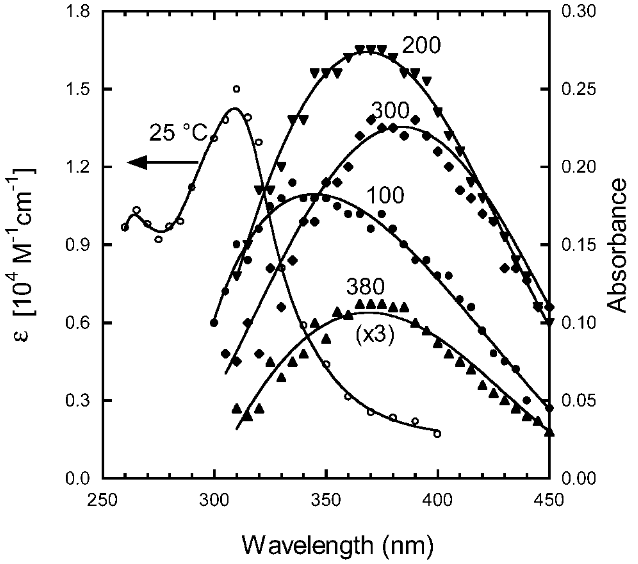

Figure 6. Absorption spectra of Ag_2^+ at different temperatures. The absorption spectrum at 25 °C is taken from ref 11. At 100, 200, and 300 °C the concentration of silver ions was 50 μM and the absorption spectra are recorded at 700, 250 and 150 ns after the pulse, respectively, and the dose per pulse was 62 Gy. At 380 °C, the solution contained 20 μM silver ions and the spectrum (enlarged 3 times) was recorded 120 ns after the pulse. Optical path of the cell was 15 mm.

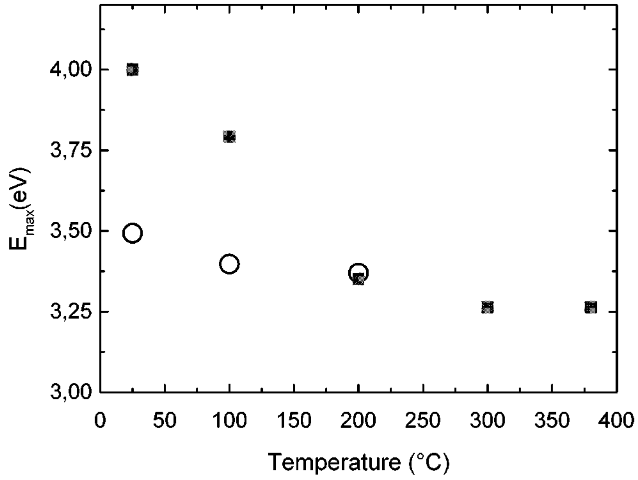

Figure 7. Temperature dependence of the absorption maximum energy of Ag^0 (○) and Ag_2^+ (■) in water. Conditions are the same as those in Figures 4 and 5.

density of supercritical water at 380 °C (and 300 atm) is almost half of that for water at room temperature. Therefore the reported absorption spectra should be corrected taking into account the change of water density.

Figure 7 shows the change of the maximum of absorption band for the silver atom and the charged dimer in water versus the temperature from 25 to 300 °C. The shift of the absorption spectra of Ag_2^+ is very clear and it is more pronounced than that of silver atoms. This result is in agreement with the fact that the solvation energy of neutral silver atom is much less (less than 0.1 eV) than that of the charged dimers (around 3.5 eV). Therefore, the solvent molecules around Ag_2^+ are more organized and the temperature effect on the solvation shell is expected to be much pronounced.

Conclusion

The rate constant for the reduction of silver ions by hydrated electrons is fitted to the Arrhenius relationship (from 25 to 300 °C at 200 atm) and the apparent activation energy is found to be 17.8 kJ mol^{-1}. The measurements of transient absorption spectrum show that the maximum of the absorption spectra of silver atom is shifted from 355 to 370 nm when the temperature is increased from 25 to 200 °C. The shift of the absorption maximum is more pronounced for the charged dimer, Ag_2^+. The maximum of the absorption band located at 315 nm at room temperature is shifted to 380 nm at 300 °C in water. We note that the shift of the maximum of the absorption band of hydrated electron for which the hydration free energy is 1.6 eV is also very significant.[22,30]

Our observations over a wide range of temperature confirm clearly that the absorption spectra of Ag_2^+ presents CTTS characteristics but that of silver atom does not depend so significantly to the temperature.[31] A molecular dynamics simulation is in progress to help in understanding of the orientation of water molecules around the atom and the charged dimer with increasing temperatures.

Acknowledgment. This work was supported by Japan Society for the Promotion of Science under the contract JSPS-RFTF 98P00901. The authors warmly thank Tomomi Morioka, graduate student, for the help in several experiments. The authors also thank Dr. Kenji Takahashi, Hokkaido University, for the design of the new cell. This work was also partly supported by the innovative basic research program in the field of high temperature engineering using the HTTR conducted by Japan Atomic Energy Research Institute.

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(31) According to a personal communication made by our colleague Dr. P. Archirel, the recent SCF calculations shows that the solvation of the external electron of silver atom is very improbable then the silver atom spectra in water does not present a real CTTS character. That could explain why we find that the shift of the absorption spectra versus temperature is not very important.