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# Reduction of $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ to $\text{Ag}^0(\text{NH}_3)_2$ in Solution. Redox Potential and Spectral Study

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Pulse radiolysis is used to determine the absorption spectra of the transient species formed during the decay of the hydrated electron in an aqueous solution of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ . The absorption spectrum attributed to  $\text{Ag}^0(\text{NH}_3)_2$  presents three peaks at 345, 385, and 435 nm. A theoretical estimation of the redox potential of the couple  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0(\text{NH}_3)_2$  yields the value  $-2.4 \text{ V}_{\text{NHE}}$ . This value is consistent with the fact that  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  is not directly reduced by  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  and shows that the redox potential of the silver monomer couple is lowered by ammonia ligands.

## Introduction

The study of the size-dependent ionization potential of metal aggregates in solution started in the 1970s.<sup>1–4</sup> Most of the experiments were carried out on short-lived silver cluster systems.<sup>5–9</sup> These few results showed the drastic influence of the nuclearity  $n$  on the ionization potential (IP) of the smallest clusters. The role of the hydration energy is so important, mostly at low  $n$ , that the general trend is an increase of the IP with  $n$  relative to vacuum.<sup>10</sup> In particular, the IP of metal atoms in solution is very low, and the reduction of isolated metal cations in solution as silver ions requires very strong reducing species. As the metal cations  $\text{M}^+$  are often complexed by ligands (L), it is interesting to understand the influence of ligands on the redox potential of the monomer couple  $\text{M}^{\text{I}}\text{L}/\text{M}^0\text{L}$  which concerns the first step of the nucleation. The first estimation of such a redox potential has been carried out recently in the case of silver monomer couple complexed by two cyanides.<sup>11</sup> The redox potential of the  $\text{Ag}^+/\text{Ag}^0$  couple in aqueous solution ( $-1.74 \text{ V}_{\text{NHE}}$ ) is significantly decreased by the cyanide ligands down to  $-2.6 \text{ V}_{\text{NHE}}$ .<sup>11</sup> This estimation has also been confirmed by the experiment.<sup>12</sup> On the other hand, spectra composed of two or three bands have already been observed in the case of the transient  $\text{Ag}^0$  complexed by ligands such as EDTA and cyanide.<sup>13</sup> The presence of additional absorption bands bears witness to the interaction between the silver atom and these ligands.

In the present work, we study the effect of the ligand ammonia. First of all, we observe the product of the reaction of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  with the hydrated electron by pulse radiolysis. Then we evaluate the redox potential of the couple  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0(\text{NH}_3)_2$  and eventually we experimentally check the reactivity of 2-propanol radical as reducing agent toward  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ .

## Experimental Section

All the reagents were pure chemicals:  $\text{AgClO}_4$  from Aldrich, 2-propanol, ammonia, and acetone from Prolabo. The aqueous solutions of silver ions were prepared in the dark with an excess of  $\text{NH}_3$  for complexing all silver ions at pH 11. The solutions were also degassed in vacuum. The irradiation source was a  $^{137}\text{Cs}$   $\gamma$  facility of  $10^{14} \text{ Bq}$  with a dose rate of  $1 \text{ kGy h}^{-1}$ .

Electron pulses (3 ns duration) were delivered by a Febetron 706 accelerator (600 keV electron energy) to samples contained in a quartz Suprasil cell with a thin entrance window (0.2 mm)

for the beam and an optical path length of 1 cm. The cell was degassed by a nitrogen flow. The solution was changed after each pulse.

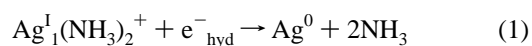
$\text{OH}^\bullet$  and  $\text{H}^\bullet$  radicals produced during radiation are scavenged by 2-propanol ( $0.2 \text{ mol L}^{-1}$ ) to form  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  radicals. Concentrations of hydrated electrons and alcohol radicals which form during pulse amount to  $5 \times 10^{-5}$  and  $6 \times 10^{-5} \text{ mol L}^{-1}$ , respectively. In the presence of acetone and 2-propanol all radicals produced under irradiation are scavenged to form  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  or  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  depending on the pH.

Absorption of transient species was analyzed by means of a classical xenon lamp, monochromator, and photomultiplier setup connected with a transient digitizer. Splitting of the beam makes it possible to record the signals simultaneously at two different wavelengths.<sup>14</sup>

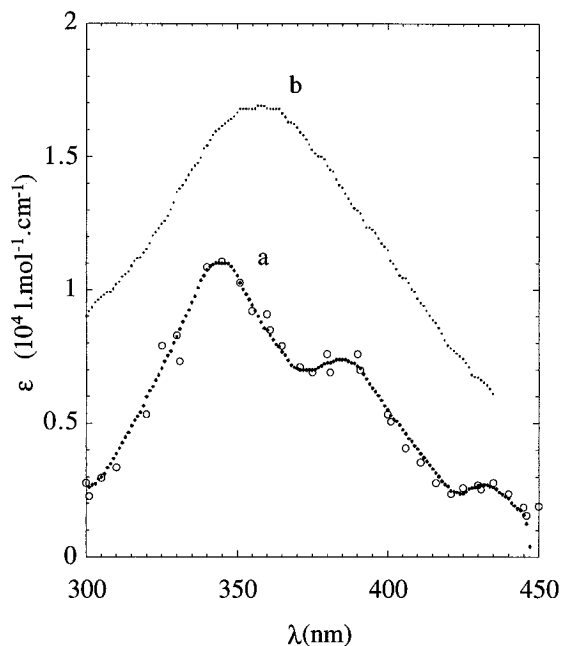
## Results

**1. Spectral Study.** Pulse radiolysis of an aqueous solution of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  is used to determine the absorption spectrum of the transient species formed during the decay of the hydrated electron. The absorption spectrum obtained 125 ns after the pulse (Figure 1a) presents three peaks at 345, 385, and 435 nm, the later being the least intense. Figure 2 shows the kinetic evolution of the optical density (OD) at these three wavelengths and at 600 nm where the hydrated electron absorbs. The absorbance at 345, 385, and 435 nm is due partly to the hydrated electron and partly to the product of the reduction of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  by  $\text{e}^-_{\text{hyd}}$ . As the absorbance increases after the pulse, the extinction coefficient of the product is larger than that of the hydrated electron.

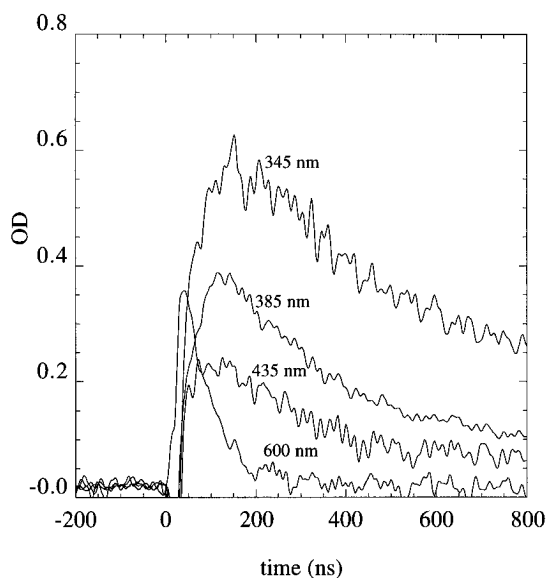
The hydrated electron decays quickly in an aqueous solution of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ , with a constant  $k(\text{Ag}^{\text{I}}(\text{NH}_3)_2^+ + \text{e}^-_{\text{hyd}}) = 3.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>15</sup> This decay is correlated with the increase of the optical densities at 345, 385, and 435 nm. The kinetic evolution is similar at these three wavelengths, and the maximum absorption is reached 125 ns after the pulse. Therefore, we ascribe these three absorption peaks to the same transient species formed during the decay of the hydrated electron. The spectrum shown in Figure 1a is quite different from that reported by Pukies et al.<sup>15</sup> which displays a very flat band in the range 250–400 nm and which has been attributed to the silver atom without ammonia, produced by the following reaction:



<sup>®</sup> Abstract published in *Advance ACS Abstracts*, June 15, 1996.



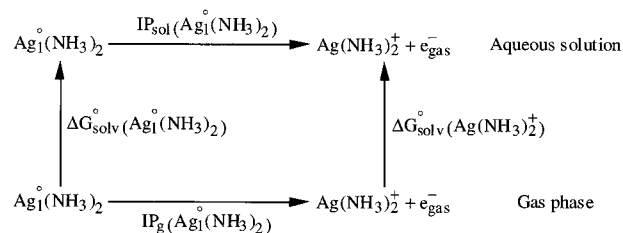
**Figure 1.** (a) Spectrum obtained by pulse radiolysis of a solution containing  $5 \times 10^{-4} \text{ mol L}^{-1}$  of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  ( $5 \times 10^{-4} \text{ mol L}^{-1}$  of  $\text{AgClO}_4$ ,  $10^{-2} \text{ mol L}^{-1}$  of  $\text{NH}_3$ ) and  $0.2 \text{ mol L}^{-1}$  of 2-propanol at  $\text{pH} = 11$ , 120 ns after the pulse (O, experimental points; ..., fit) (b) Spectrum of the free silver atom in aqueous solution determined by Janata et al.<sup>16</sup>



**Figure 2.** Time profile of the absorbencies at various wavelengths: decay of the hydrated electron at 600 nm and formation of the silver atom complexed by ammonia observed at 345, 385, and 435 nm. Conditions of Figure 1.

However, the absorption spectrum of  $\text{Ag}^0$  in a free aqueous medium, as determined by Janata et al.<sup>16</sup> (Figure 1b) consists of only one single absorption band centered at 360 nm and is obviously different from that we observed 125 ns after the pulse in the presence of ammonia. We therefore conclude that the reduction of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  by the hydrated electron does not directly lead to the products ( $\text{Ag}^0 + 2\text{NH}_3$ ), as suggested by Pukies et al.,<sup>15</sup> but leads to the complexed silver atom. Since no species is formed with only one absorption band centered at 360 nm, reaction 1 may not occur.

However, considering the redox potential values, reaction 1 is thermodynamically possible. Indeed, the redox potential  $E^\circ_1$  of the couple  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0 + 2\text{NH}_3$  is easy to calculate



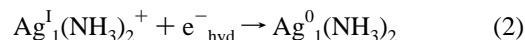
**Figure 3.** Thermodynamical cycle used for the evaluation of the ionization potential in solution of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2$ .

from that of the couple  $\text{Ag}^+/\text{Ag}^0$ , taking into account the complexation constant ( $K = 10^{7.2}$ ) of  $\text{Ag}^+$  by two ammonia molecules. At 298 K, we obtain

$$E^\circ_1(\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0 + 2\text{NH}_3) = E^\circ(\text{Ag}^+/\text{Ag}^0) - 0.059 \log K = -2.2 \text{ V}_{\text{NHE}} \quad [1]$$

Since the redox potential of the couple  $n\text{H}_2\text{O}/e^-_{\text{hyd}}$  amounts to  $-2.9 \text{ V}_{\text{NHE}}$ , reaction 1 could occur, contrary to the case of cyanide.<sup>11</sup>

As we attribute the absorption spectrum of Figure 1a to  $\text{Ag}^0(\text{NH}_3)_2$ , the reduction of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  by the hydrated electron must be written as follows:



The product of this reaction readily reacts with  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  giving a dimer silver cluster complexed with ammonia: this is proved by the absorption spectrum obtained during the decay of  $\text{Ag}^0(\text{NH}_3)_2$ , clearly displaying the characteristic band of the dimer silver cluster at 310 nm. This dimerization has always been observed, as well in the free medium, as in the presence of ligands.<sup>13</sup> We therefore undertake the theoretical estimation of the redox potential of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0(\text{NH}_3)_2$ . We use the simple method which we successfully used for the couple  $\text{Ag}^{\text{I}}(\text{CN})_2^-/\text{Ag}^0(\text{CN})_2^{2-}$ .<sup>11</sup>

**2. Redox Potential Evaluation.** The ionization potential of a species in solution  $\text{IP}_{\text{sol}}$  is related to the redox potential  $E^\circ$  according to

$$\text{IP}_{\text{sol}}(\text{Red}) (\text{eV}) = |e|E^\circ(\text{Ox/Red})(\text{V}_{\text{NHE}}) + 4.5 \quad [2]$$

where  $|e|$  is the elementary charge in absolute value and where 4.5 eV is the Fermi potential of the Normal Hydrogen Electrode (NHE), with respect to the vacuum.<sup>17</sup> The  $\text{IP}_{\text{sol}}$  of  $\text{Ag}^0(\text{NH}_3)_2$  is evaluated through the determination of the ionization potential of  $\text{Ag}^0(\text{NH}_3)_2$  in the gas-phase  $\text{IP}_{\text{g}}$  and the calculation of the free enthalpies of solvation of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  and  $\text{Ag}^0(\text{NH}_3)_2$  (respectively  $\Delta G^\circ_{\text{sol}}(\text{Ag}^{\text{I}}(\text{NH}_3)_2^+)$  and  $\Delta G^\circ_{\text{sol}}(\text{Ag}^0(\text{NH}_3)_2)$ ). According to the thermodynamical cycle including gas-phase and solvated species (Figure 3), we have

$$\text{IP}_{\text{sol}}(\text{Ag}^0(\text{NH}_3)_2) = \text{IP}_{\text{g}}(\text{Ag}^0(\text{NH}_3)_2) + [\Delta G^\circ_{\text{sol}}(\text{Ag}^{\text{I}}(\text{NH}_3)_2^+) - \Delta G^\circ_{\text{sol}}(\text{Ag}^0(\text{NH}_3)_2)] \quad [3]$$

In eq 3, the entropy of the gas-phase ionization has been neglected.

The ionization potential of  $\text{Ag}^0(\text{NH}_3)_2$  in the gas phase has been evaluated from the values of the ionization potential of free  $\text{Ag}^0$  and of the binding energies  $D^+$  of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  and  $D^0$  of  $\text{Ag}^0(\text{NH}_3)_2$  according to eq 4, where we assume that the

$$\text{IP}_{\text{g}}(\text{Ag}^0(\text{NH}_3)_2) = \text{IP}_{\text{g}}(\text{Ag}^0) + D^+ - D^0 \quad [4]$$

geometry is that of the ionized species. We have evaluated

$D^+$  and  $D^0$  with the SCF method and used the experimental value (7.6 eV) of the ionization potential of the free silver atom.<sup>18</sup>

The SCF calculations have been made with the help of core pseudopotentials<sup>19</sup> for simulating the inner shells of the Ag and N atoms, and with the following (contracted) Gaussian basis sets: (3s, 2p, 3d) for Ag, (4s, 3p, 2d) for N, (3s, 1p) for H.

We have assumed the  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  complex to be linear: this geometry is the most probable because it minimizes the repulsion of the two ammonia dipole moments. The geometrical parameters  $R_{\text{AgN}}$ ,  $r_{\text{NH}}$ , and  $\theta_{\text{HNN}}$  have been optimized by SCF calculations of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ . The optimized values are  $R_{\text{eq}} = 4.350 \pm 0.005$  au,  $r_{\text{eq}} = 1.900 \pm 0.005$  au, and  $\theta_{\text{eq}} = 106.7 \pm 0.5^\circ$ . These last two values are identical with the values optimized by SCF calculations of the free ammonia molecule, and close to the experimental values  $r_{\text{exp}} = 1.913$  au and  $\theta_{\text{exp}} = 106.7^\circ$  in the same molecule.

The values of the binding energies are  $D^+ = -2.68$  eV and  $D^0 = +0.38$  eV, which means that at the equilibrium distance of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ ,  $\text{Ag}^0(\text{NH}_3)_2$  is a repulsive system. The ionization potential of  $\text{Ag}^0(\text{NH}_3)_2$  is calculated using eq 4: we get 4.51 eV.

Note that the present result may not be directly compared to the experimental value obtained very recently by Freudenberger et al. (5.2 eV).<sup>20</sup> Since we use for both species the equilibrium geometry of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ , our  $\text{IP}_g$  value should be called the vertical electron affinity of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ . Since the authors of ref 20 measure the true vertical  $\text{IP}_g$  of  $\text{Ag}^0(\text{NH}_3)_2$ , the geometry of both species in their experiment is the most stable geometry of the neutral complex, namely, a  $(\text{NH}_3)_2$  cluster with a silver atom located at its surface. This explains that our  $\text{IP}_g$  value is smaller.

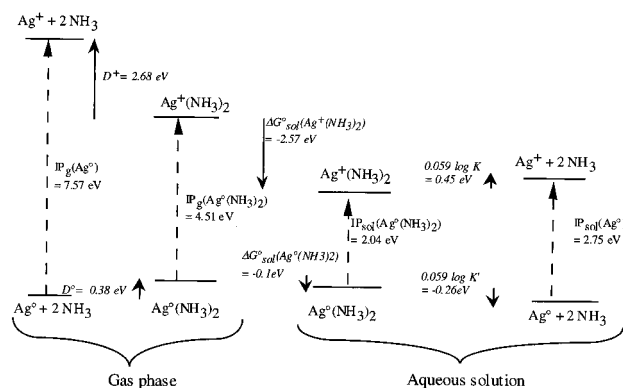
The free enthalpies of solvation are determined with the help of the cavity model developed by Rinaldi et al.<sup>21,22</sup> This method has been described in the case of cyanide:<sup>11</sup> the solvent is considered to be an infinite continuum medium in which an elliptic cavity contains the solute. The shape of the cavity is derived from the location of the atoms and their van der Waals and covalent radii. Since our thermodynamical cycle includes species with the same geometry, the same cavity is used for  $\text{Ag}^0(\text{NH}_3)_2$  and  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$ . The complexes are modeled by a linear distribution of charges. Silver is represented by a point charge  $q$  ( $q = 0$  for  $\text{Ag}^0$ ,  $q = 1$  for  $\text{Ag}^+$ ) and each ammonia molecule by two charges  $\delta$ , distant by  $r$  with  $r\delta = 1.47$  D, which is the experimental gas-phase value of the dipole of the ammonia molecule. We have checked that the results hardly depend on the values of  $r$  and  $\delta$ . We get

$$\Delta G_{\text{solv}}^{\circ}(\text{Ag}^{\text{I}}(\text{NH}_3)_2^+) = -2.57 \text{ eV} \quad [5]$$

$$\Delta G_{\text{solv}}^{\circ}(\text{Ag}^0(\text{NH}_3)_2) = -0.10 \text{ eV} \quad [6]$$

The free enthalpy of solvation of  $\text{Ag}^0(\text{NH}_3)_2$  is very small, which is normal for a neutral species. Besides, the value obtained for  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  ( $-2.6$  eV) is less negative than the experimental value for  $\text{Ag}^+$  ( $-4.4$  eV<sup>23</sup>): this is because the size of the first species is much larger than the size of the second one. The size and the global charge of the complexes are thus the main factors ruling the free enthalpies of solvation as in the Born model.

Using eq 3, we finally obtain for the ionization potential in solution of  $\text{Ag}^0(\text{NH}_3)_2$  the value 2.04 eV, which corresponds to a redox potential of  $-2.41$  V<sub>NHE</sub> for the couple  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0(\text{NH}_3)_2$  (eq 2). The results are summed up in Figure 4,



**Figure 4.** Ionization potential of silver, in the gas phase and in aqueous solution, in the absence and in the presence of ammonia molecules.

**TABLE 1: Different Values Used for the Calculation of the Redox Potentials of the Couples  $\text{Ag}(\text{CN})_2^-/\text{Ag}^0(\text{CN})_2^{2-}$ <sup>11</sup> and  $\text{Ag}^+(\text{NH}_3)_2/\text{Ag}^0(\text{NH}_3)_2$**

	$\text{Ag}^{\text{I}}(\text{CN})_2^-/\text{Ag}^0(\text{CN})_2^{2-}$	$\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0(\text{NH}_3)_2$
$\text{IP}_g(\text{Ag}^0\text{L}_2)$ (eV)	-5.39	4.51
$\Delta G_{\text{solv}}^{\circ}(\text{Ag}^+\text{L}_2)$ (eV)	-3.34	-2.57
$\Delta G_{\text{solv}}^{\circ}(\text{Ag}^0\text{L}_2)$ (eV)	-10.62	-0.10
$E^{\circ}(\text{Ag}^+\text{L}_2/\text{Ag}^0\text{L}_2)$ (V)	-2.61	-2.41

where the solvation and complexation effects are stressed. These effects induce a drop of the ionization potential in comparison with the value obtained in the gas phase in the absence of ammonia. We have deduced the value of the complexation constant  $K'$  of  $\text{Ag}^0$  by two  $\text{NH}_3$  and found  $8.6 \times 10^{-5}$ , which indicates that the transient species  $\text{Ag}^0(\text{NH}_3)_2$  could dissociate in aqueous solution at the thermodynamical equilibrium. However, this dissociation is never observed because of the faster dimerization. We now recall the two main shortcomings of our theoretical method, discussed in ref 11:

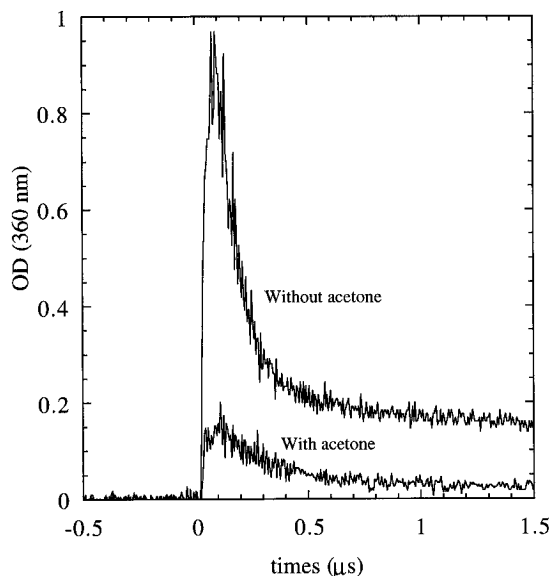
First, we use a thermodynamical cycle, which implies the calculation of intermediate quantities (solvation energies and gas phase IP). This would be simplified by the inclusion of the reaction field potential of the solvent in the SCF potential.

Second, the application of the cavity method to ionic species is disputable, because the solute-solvent interaction is strong. A more correct treatment would imply that we explicitly consider a few water molecules in the SCF calculations.

We shall see that this simple method makes it possible to explain the reactivity of silver complexes toward reduction.

We now compare the present results with those obtained in the case of cyanide ligands.<sup>11</sup> Table 1 shows the different values used for the calculation of  $E^{\circ}(\text{Ag}^{\text{I}}\text{L}_2/\text{Ag}^0\text{L}_2)$ , and the complexing constants  $K$  and  $K'$  of  $\text{Ag}^+$  and  $\text{Ag}^0$  by 2 L, where L is  $\text{CN}^-$ <sup>11</sup> and  $\text{NH}_3$ . Note that the values of the two redox potentials are close to one another, despite very different values of the ingredients (ionization potentials in the gas phase and solvation energies). These differences are obviously due to the different charges of the ligands. Because of the negative charge of cyanide,  $\text{Ag}^0(\text{CN})_2^{2-}$  is autoionizing in the gas phase (its ionization potential is negative) and its solvation energy is large. Conversely  $\text{NH}_3$  has no charge, consequently the IP of  $\text{Ag}^0(\text{NH}_3)_2$  is positive and its solvation energy is small.

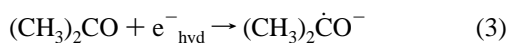
**3. Reduction of  $\text{Ag}^+$  and  $\text{Ag}(\text{NH}_3)_2^+$  by the 2-Propanol Radical: Pulse Radiolytic Study.** To check the theoretical value obtained for  $E^{\circ}(\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0(\text{NH}_3)_2)$ , and the lowering of the redox potential of the silver monomer couple in the presence of ammonia, radiolysis experiments are undertaken. The aim is to situate the redox potential of the couple  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0(\text{NH}_3)_2$  by testing the reactivity of



**Figure 5.** Time profile of the absorption at 360 nm of a solution containing  $\text{AgClO}_4$  ( $5 \times 10^{-4} \text{ mol L}^{-1}$ ), 2-propanol ( $0.2 \text{ mol L}^{-1}$ ) in the absence and in the presence of acetone ( $0.2 \text{ mol L}^{-1}$ ) at pH = 5.

$\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  toward a transient reducing agent (the 2-propanol radical, the redox potential of which is well-known ( $-2.1 \text{ V}_{\text{NHE}}$  at pH = 11 and  $-1.7 \text{ V}_{\text{NHE}}$  at pH = 5<sup>24</sup>). The alcohol radical is produced in all our experiments during the reduction of  $\text{OH}^\bullet$  by 2-propanol. 2-Propanol radical is chosen because of its low redox potential in comparison with the other commonly used alcohols.

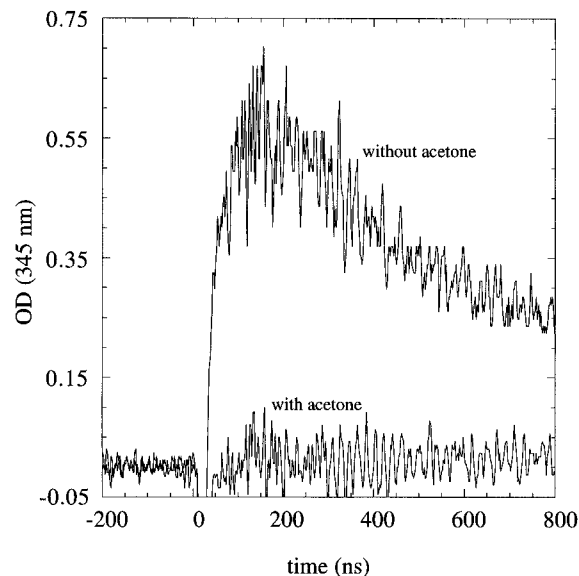
When the reactivity of the 2-propanol radical toward  $\text{Ag}^+$  and  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  is to be tested, acetone is added to the solution. Acetone reacts with the hydrated electron according to



with a rate constant  $k = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>25</sup> At pH = 5, the acidic form of the radical,  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ , is formed. Hence, in the presence of acetone, the only reducing agent present in solution after the pulse is the alcohol radical.

**3.a. Reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  with  $\text{Ag}^+$ .** First, we check the reaction of silver ions in the absence of ligand with the radical  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ . Figure 5 presents, for the same dose, the absorption at 360 nm (the absorption maximum of free silver atom in solution) as a function of time in the presence and in the absence of acetone, the pH after the pulse being 5. In both cases, silver atoms are formed after the pulse, but the yield of the silver atom formation is 5 times lower in the presence of acetone. The reduction of  $\text{Ag}^+$  by  $e^-_{\text{hyd}}$  is thus more efficient. The low yield obtained when the only reducing agent is the radical of 2-propanol can be explained by two reasons: first, the dimerization reaction of radicals of alcohol is very fast,  $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and therefore a part of these radicals cannot react with silver ions; second, since the redox potentials of the both systems  $\text{Ag}^+/\text{Ag}^0$  and  $(\text{CH}_3)_2\text{CO}/(\text{CH}_3)_2\dot{\text{C}}\text{OH}$  are very close, the electron transfer from the radical to the silver ions is not efficient.

By using a thermodynamical cycle involving the electrochemical potential of the silver bulk electrode and the sublimation energy of metallic silver (the solvation energy of one single  $\text{Ag}^0$  atom was neglected), Henglein estimated the redox potential of the  $\text{Ag}^+/\text{Ag}^0$  couple to be  $-1.80 \text{ V}$ .<sup>5</sup> However, we have adjusted this value to  $-1.74 \text{ V}$ . This value corresponds to the adjusted free energy of sublimation of metallic silver at room temperature ( $2.54 \text{ eV}$ <sup>18</sup>). This estimated redox potential of silver monomer couple ( $-1.74 \text{ V}_{\text{NHE}}$ ) could be improved by consider-

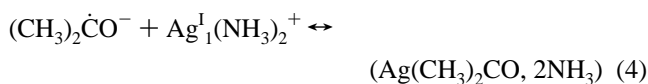


**Figure 6.** Time profile of the absorption at 345 nm of a solution containing  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  ( $5 \times 10^{-4} \text{ mol L}^{-1}$ ) and 2-propanol ( $0.2 \text{ mol L}^{-1}$ ) in the absence and in the presence of acetone ( $0.2 \text{ mol L}^{-1}$ ) at pH = 11.

ing the unknown free energy of solvation of  $\text{Ag}^0$  (in the case of  $\text{Hg}^0$  the value is estimated to be close to  $0.078 \text{ eV}$ ). Taking the solvation energy of silver atom into account would make the redox potential of  $\text{Ag}^+/\text{Ag}^0$  higher than  $-1.74 \text{ V}$ . We therefore conclude that the reaction between the radical of 2-propanol and the silver ion can take place whatever the pH (between 5 and 11). This result is different from that of Henglein et al.,<sup>6</sup> who reported that the radical of 2-propanol does not transfer its electron to  $\text{Ag}^+$  and assumed that this nonreactivity was due to unfavorable redox potentials.<sup>5</sup>

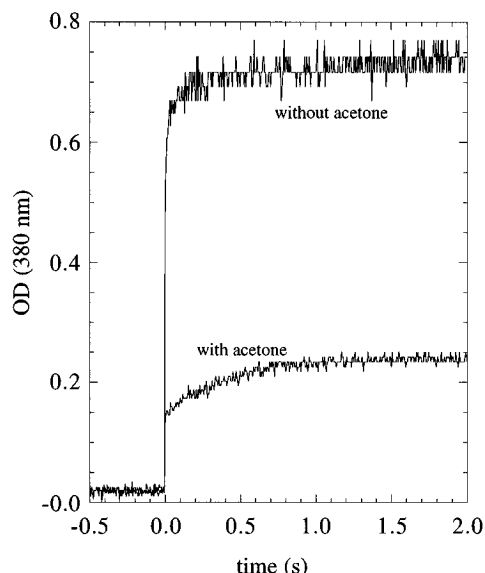
**3.b. Reaction of  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  with  $\text{Ag}(\text{NH}_3)_2^+$ .** The short time evolution of the OD at 345 nm (maximum of the absorption spectrum of  $\text{Ag}^0(\text{NH}_3)_2$ ) is represented in Figure 6, in the absence of acetone ( $e^-_{\text{hyd}}$  and  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  as reducing agents) and in the presence of acetone ( $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  as the single reducing agent). It appears that  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  is reduced to  $\text{Ag}^0(\text{NH}_3)_2$  by the hydrated electron but not by the  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  radical. Hence we conclude that the redox potential of the couple  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+/\text{Ag}^0(\text{NH}_3)_2$  is situated between  $-2.9 \text{ V}_{\text{NHE}}$  (redox potential of  $n\text{H}_2\text{O}/e^-_{\text{hyd}}$ ) and  $-2.1 \text{ V}_{\text{NHE}}$  (redox potential of  $(\text{CH}_3)_2\text{CO}/(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ ) at pH = 11. Such a value is consistent with the theoretical one ( $-2.4 \text{ V}_{\text{NHE}}$ ) which we have determined.

At longer times, an increase of the optical density at 380 nm, indicating the formation of large clusters, is observed, both in the presence and in the absence of acetone (Figure 7). However, when the  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  radical is the only reducing agent present in solution, the maximum of the OD is lower than in the presence of the hydrated electron. We propose the following mechanism:



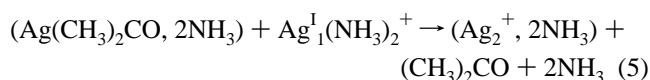
similar to that postulated by Henglein in the case of the reduction of  $\text{Ag}^+$  by  $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ .<sup>6</sup> The first step would imply the complexation equilibrium between  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  and the alcohol radical, according to reaction 4.

The complexation of metallic cations by radical of alcohol has already been observed in aqueous free medium.<sup>26</sup> The complexed form could then react with the  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  cation

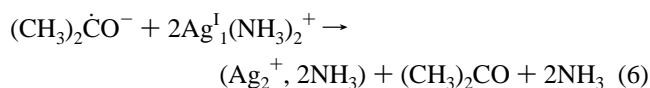


**Figure 7.** Time profile of the absorption at 380 nm (where large silver clusters absorb) of a solution containing  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  ( $5 \times 10^{-4} \text{ mol L}^{-1}$ ) and 2-propanol ( $0.2 \text{ mol L}^{-1}$ ) in the absence and in the presence of acetone ( $0.2 \text{ mol L}^{-1}$ ) at pH = 11.

to form the  $(\text{Ag}_2^+, \text{NH}_3)$  complex, as follows:



The balance of reactions 4 and 5 can be written



The redox couples involved in this mechanism (reactions 4 and 5) are thus  $(2\text{Ag}^{\text{I}}(\text{NH}_3)_2^+ / (\text{Ag}_2^+, 2\text{NH}_3) + 2\text{NH}_3)$  and  $((\text{CH}_3)_2\text{CO} / (\text{CH}_3)_2\dot{\text{C}}\text{O}^-)$ , instead of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+ / \text{Ag}^0(\text{NH}_3)_2$  and  $((\text{CH}_3)_2\text{CO} / (\text{CH}_3)_2\dot{\text{C}}\text{O}^-)$ . Using a simple thermodynamical cycle, we can show that the couple  $(2\text{Ag}^{\text{I}}(\text{NH}_3)_2^+) / (\text{Ag}_2^+, 2\text{NH}_3) + 2\text{NH}_3$  has a redox potential higher than that of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+ / \text{Ag}^0(\text{NH}_3)_2$ . Therefore, the reduction of  $(2\text{Ag}^{\text{I}}(\text{NH}_3)_2^+)$  into  $(\text{Ag}_2^+, \text{NH}_3)$  by  $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$  should be possible, even if the alcohol radical cannot reduce directly  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  to  $\text{Ag}^0(\text{NH}_3)_2$ .

Nanometric silver clusters display an absorption band around 400 nm. By  $\gamma$  irradiation of an aqueous solution of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  in the presence or in the absence of acetone, silver aggregates, observed at this wavelength, are formed and the yield of reduction of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  is the same in both cases. However, in pulse radiolytic experiments, the reduction yield is lower in the presence of acetone. This phenomenon can be explained by the very fast reaction of recombination between two radicals of alcohol which is negligible in  $\gamma$ -radiolysis experiments.

## Conclusion

We have determined the absorption spectrum of  $\text{Ag}^0(\text{NH}_3)_2$ , which displays three peaks at 345, 385, and 435 nm. This spectrum is very different from that of free silver atom in solution and the additional bands must be attributed to the interaction between the ammonia ligands and the silver atom. We have evaluated the redox potential of the  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+ / \text{Ag}^0(\text{NH}_3)_2$  couple with the help of a thermodynamical cycle. We have used the SCF method for the electronic structure of the different gas-phase species and the cavity model for the solvation effects. The value of this redox potential is found to

be  $-2.4 \text{ V}_{\text{NHE}}$ . To check this theoretical value and to confirm the lowering of the redox potential of silver monomer couple in the presence of ammonia, radiolysis experiments have been undertaken. The reactivity of  $\text{Ag}^+$  and  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  toward 2-propanol radical (the redox potential of which is  $-1.7 \text{ V}_{\text{NHE}}$  at pH = 5 and  $-2.1 \text{ V}_{\text{NHE}}$  at pH = 11) is tested. The electron transfer from the radical of 2-propanol to free silver ion takes place but the electron transfer from this radical to  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+$  does not occur at pH = 11. This means that the redox potential of  $\text{Ag}^{\text{I}}(\text{NH}_3)_2^+ / \text{Ag}^0(\text{NH}_3)_2$  is lower than  $-2.1 \text{ V}_{\text{NHE}}$ . This result is compatible with the estimated theoretical value.

The main qualitative result of the present work is the lowering of the redox potential of the silver monomer couple by ligands. The two present ligands ( $\text{CN}^-$ ,  $\text{NH}_3$ ) have very different natures and charges. This seems to show that this ligand effect is general.

The redox potentials studied here are very important for the understanding of metal aggregation in solution because they rule the first step: the reduction of the metal cation. The improvement of the theoretical and experimental evaluation methods of metal monomer redox potential is therefore desirable. In particular, the inclusion of the reaction field of the solvent in the SCF method and the refinement of the experimental test should be undertaken.

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