Introduction

Important advances in the thermodynamics of metal clusters in solution have been achieved through pulse radiolysis techniques. They allow the time-resolved observation of, first, the reduction of the ionic precursors into atoms, then of the progressive atomic coalescence and of the cluster reactivity dependence on their nuclearity. The most detailed mechanisms have been established for monovalent metal cations that are reducible by radiolytic species into atoms by a single electron transfer from the atoms of the less noble metal to the ions of the more noble metal. If the electron transfer is quite slow, the rate constants of the mechanism. The presence of CN− causes a swelling of both the coalescence and electron transfer from MV+ toward clusters above a critical size, and corrosion of subcritical clusters by MV+•+. We conclude that ncr = 5−6 and hence that the reference redox potential in the presence of cyanide ligands corresponds to the couple E°(Ag6−7+CN/Ag6−7-CN) ≈ −0.4 V NHE.

Pulse radiolysis was used to investigate the growth and reactivity dynamics of silver clusters in the presence of cyanide ligands, Ag6−7-CN−, and of an electron acceptor/donor, the methyl viologen redox couple whose potential is E°(MV2+/MV+) = −0.41 V NHE. The absorbance of the MV+•+ radical, produced by the same pulse as the silver atoms, is constant during an induction time delay, and then decays due to a catalytic electron transfer toward supercritical silver clusters. Correlated growth of the Ag6−7-CN− absorbance is also observed. Another process of reverse electron transfer from subcritical clusters to MV2+, concomitant with the transfer from MV+ toward clusters above a critical size, and corrosion of subcritical clusters by MV2+•+, we derive the critical number ncr and the rate constants of the mechanism. The presence of CN− causes a slowing of both the coalescence and electron transfer from MV+ toward clusters above a critical size, and corrosion of subcritical clusters by MV2+•+. We conclude that ncr = 5−6 and hence that the reference redox potential in the presence of cyanide ligands corresponds to the couple E°(Ag6−7+CN/Ag6−7-CN) ≈ −0.4 V NHE.

Experimental Section

All reagents were pure chemicals: silver salt KAg(CN)2 was from Comptoir Lyon Alemant Louyot, 2-propanol and acetone were from Prolabo, and methyl viologen chloride MVCl2 was from Aldrich.

The pulse radiolysis facility (3 ns and 600 keV electron energy) and time-resolved optical detection have been described elsewhere. The irradiation cell in Suprasil quartz allows optical absorption analysis (optical path 1 cm), penetration of the electron beam through a thin window, and circulation of the solution, which is removed after each pulse. However, due to side diffusion, the observation time range is limited to 40 s. Thus a Linac accelerator (1.5 μs pulse), delivering 4 MeV electrons, was also used in order to obtain the final absorption spectra, at longer times after the pulse, by conventional spectrophotometry in optical cells sealed under vacuum.

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Figure 1. (a) Optical absorption spectrum of a \(10^{-4} \text{ mol L}^{-1}\) solution of \(\text{Ag(CN)}_2^-\) partially reduced by \(\gamma\)-irradiation. 2-Propanol: 0.2 mol L\(^{-1}\). Optical length 1 cm. Dose = 0.160 kGy. (b) Optical absorption spectrum of a partially reduced solution of \(5 \times 10^{-4} \text{ mol L}^{-1}\) \(\text{Ag(CN)}_2^-\) in the presence of \(5 \times 10^{-3} \text{ mol L}^{-1}\) MV\(^{2+}\) taken 5 min after the irradiation pulse. 2-Propanol: 0.2 mol L\(^{-1}\). Optical length: 1 cm. Dose: 0.200 kGy.

Under irradiation aqueous solutions in the presence of 2-propanol are strong reducing media, due to the formation of hydrated electrons and of (CH\(_3\))\(_2\)C•OH radicals by alcohol scavenging of OH• and H• radicals. Due to the high sensitivity of the clusters to oxidation, all experiments were carried out in the strict absence of oxygen, removed by bubbling the solutions with an inert gas or under vacuum.

Results and Discussion

Silver Cyanide Solutions. The absorption spectrum of a \(\gamma\)-irradiated KAg(CN)\(_2\) \((10^{-3} \text{ mol L}^{-1})\) solution under vacuum does not change for doses higher than 400 Gy, which indicates total reduction. Then the spectrum remains unchanged despite the absence of any stabilizing agent in the solution (Figure 1a). The CN\(^-\) ligand of complexed ions adsorbed on clusters are efficient stabilizers of the colloid through electrostatic repulsion. The spectrum presents the characteristic plasmon band of silver clusters with a maximum at 395 nm. The extinction coefficient at 395 nm is \(\varepsilon_{395} = 21000 \text{ L mol}^{-1} \text{ cm}^{-1}\), somewhat higher than in sulfate solutions \((\varepsilon_{395} = 15000 \text{ L mol}^{-1} \text{ cm}^{-1})\).\(^{21}\) This band is also narrower. Below 400 Gy, the increase of the absorbance is proportional to the dose. From the slope and from \(\varepsilon_{395}\) of the transient Ag\(^0\)\((\text{CN})_2^-\) formed in the next step have been recently published.\(^8\)

![Figure 2](image2.png)

Figure 2. Comparison of the pulse radiolysis signals of the growth kinetics of silver clusters observed by their absorbance at 400 nm in the presence of (a) cyanide \((2 \times 10^{-3} \text{ mol L}^{-1}\) Ag(CN)\(_2^-\)) or (b) sulfate \((5 \times 10^{-3} \text{ mol L}^{-1}\) AgSO\(_4\)). Deaerated solutions, pH 6, 0.2 mol L\(^{-1}\) 2-propanol.

The kinetics at 400 nm obtained in the present system (Figure 2a) is much slower than in the well-known Ag\(_2\)SO\(_4\) system,\(^{21}\) all other conditions being identical (Figure 2b). The plateau absorbance is also lower with cyanide, due to a smaller yield, and therefore the noise is more pronounced. According to the model\(^{24}\) and assuming the same variation of the normalized value \(\epsilon(n)/\epsilon(n \to \infty)\) in both media, the superimposition of the results means that (CH\(_3\))\(_2\)C•OH is unable to reduce any Ag(CN)\(_2^-\) silver complex, and hence only hydrated electrons are involved in the primary reduction mechanism,\(^9\) as for Au(CN)\(_2^-\).\(^{12}\) The G value found for the reduction yield without acetone under these pH conditions is the same as in \(\gamma\)-radiolysis and is slightly lower than the hydrated electron yield. The spectra of Ag\(_0^+\)(CN)\(_2^-\) and of the transient Ag\(_0^+\)(CN)\(_2^-\) obtained in the experiment have been recently published.\(^8\)

In the time range of our measurements (up to 40 s), the 400 nm absorbance first increases, then tends to an asymptotic value (Figure 2a). The reducing species are readily exhausted during the first microsecond (reaction 1), and the radicals are no longer present in the medium over the millisecond range. The total amount of silver atoms therefore remains constant. Thus the absorbance increase at 400 nm in Figure 2a must be assigned to an increase in the extinction coefficient per silver atom in the clusters, induced by the coalescence as was already found for the system without CN\(^-\) ligands.\(^{21}\) Also, as in the latter case, the coalescence rate constant \(k_d\) between two clusters may be supposed independent of the nuclearity \(n\). Thus, the \(k_d\) value can be derived from results on the growth process kinetics. In fact, from the general model of growth kinetics\(^{1,24}\) resulting from all coalescence reactions between two clusters of any size, it was stated that the kinetics should be superimposed, provided the total cluster concentration \(\Sigma_0\) is normalized relative to the initial concentration of atoms \(x_0 = [\text{Ag}]=0\) as \(\Sigma_0/k_0\) and the time is expressed as \(t/r\) with \(r = 1/k_0k_0\).

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of the concentrations of all cluster nuclearities is derived.

Mixed Silver Cyanide and MV2+ Solutions. The redox potential of metal clusters in solution is known to increase with their nuclearity.1,5,6,16 Therefore, in the presence of a redox probe S/S– two cases are possible. First the aggregates may behave as an electron donor, for small n and E°(Ag(CN)2+–/Ag(CN)2–) < E°(S/S–) (the positive charge of the clusters will symbolize its oxidized form although excess CN– are adsorbed):

Agn(CN)– + S → Ag+ n(CN)– + S– (3)

Second, the aggregates may behave as an electron acceptor for supercritical values of n and E°(Ag+ n(CN)–/Agn(CN)–) > E°(S/S–):

Ag+ n(CN)– + S– → Agn(CN)– + S (4)

Successively, both processes have to compete with the concomitant evolution of silver cluster coalescence. The critical aggregate Agn(CN)– corresponds to the thermodynamic threshold beyond which the electron transfer is reversed from reaction 3 to reaction 4. It corresponds to a critical size to which a redox potential E°(Ag+ n(CN)–/Agn(CN)–) close to E°(S/S–) may therefore be assigned. The monoatomic redox couple MV2+/MV+ was chosen because of the intense optical absorption band around 600 nm of MV+ which behaves as the reference donor. In mixed solutions the hydrated electrons are scavenged partly by MV2+ and partly by Ag(CN)2– in the range of 500 ns (Figure 3). The 2-propanol radicals are all scavenged by MV2+. The evolution of silver cluster and electron donor signals is observed on different time scales, which correspond to successive steps of the process.

Figure 4. Dependence of the critical reciprocal time (t–)–1 on the initial absorbance at λ = 700 nm for variable doses per pulse. Same conditions as in Figure 3.

Time Range: 0.015 s < t < 0.15 s. Figure 3 presents the typical profiles of the time evolution of the absorbance at two wavelengths, λ = 700 nm and λ = 430 nm, obtained after the same pulse. MV+ is observed at 700 nm where the spectrum is quite intense (ελ/700(MV+) = 3460 L mol–1 cm–1). In this time range the silver aggregates are small and hence do not exhibit any absorbance at this wavelength. At 430 nm, the MV+ extinction coefficient is much smaller (ελ/430(MV+) ≈ 1000 L mol–1 cm–1) than that of Agn. It appears that MV+ (signal at 700 nm) is stable for ~15 ms under the conditions of Figure 3 before starting to decay. Correlatively, the 430 nm absorbance is first constant during the same period but then increases. As expected, the delay is induced by the time required for the clusters to grow enough such that their redox potential becomes higher than that of the reference donor, which imposes a threshold. The time delay tc is much longer than the value measured when the reference is the radical of reduced sulfonato propyl viologen SPV– in the Ag2SO4/SPV system (~100 µs), although other concentration conditions were identical and the reference couple potentials are very close: E°(SPV/SPV–) = E°(MV2+/MV+) = –0.41 V NHE.

The critical induction time, tc, depends strongly on the initial atom concentration, fixed by the dose per pulse, on the coalescence rate constant and on the critical nuclearity selected by the donor potential. At variable doses and at a given ratio [Ag(CN)]2–/[MV2+]= 1, yielding a constant initial ratio of silver atoms and donor molecules according to the scavenging competition for eaq and radicals, it is observed (Figure 4) that tc–1 depends linearly in the range of uncertainty of measurements on the initial total absorbance at 700 nm (which is proportional to the dose), as has already been found in the kinetics model1,24 and experimentally in the silver sulfate1 or polycrylate4 systems.

Time Range: 0.15 s < t < 2 s. After the induction time, the MV+ decay lasts for 1.5 s under the conditions of Figure 5, and in this interval the signal presents two successive steps, with a marked change in the slope at 0.2 and 1.5 s. The decay does not fit with a pseudo-first-order law except up to 0.15 s (Figure 5). The absorbance component after 1.5 s is due to large aggregates that are absent at shorter times. Their absorption spectrum, shifted toward higher wavelengths than for small clusters, is increasing, particularly beyond 10 s.

The slower decay after 0.2 s, which appears as a shoulder in the signal of Figure 5a did not exist in the Ag2SO4/SPV system. A possible reason could lie in the different charge of SPV/SPV– and MV2+/MV+ couples. Moreover, the perturbation of Agn(CN)– clusters by MV2+ must be very weak, as the ligand bound with CN– is quite strong. This difference between both systems Ag+ and Ag(CN)2– is rather an indirect consequence of the slower coalescence process due to CN–. Therefore, the
shoulder is assigned to supplementary formation of MV\(^{+}\)
through the reversible reduction reaction of MV\(^{2+}\) by the
subcritical silver clusters still present, which are thus corroded
(reaction 7). This corrosion process is favored by the very slow
coalescence, which during a longer time enhances the probability
of encounters with MV\(^{2+}\). A similar effect was found for the
silver coalescence in Nafion membranes controlled by a very
slow diffusion of atoms, thus favoring their oxidation by H\(_2\)O\(^{+}\).\(^{25}\)
It is therefore necessary to include in the general mechanism
the oxidation of these small aggregates (subcritical size \(n < n_c\))
with the rate constant \(k_{\text{corr}}\).

\[
\text{coalescence: } \text{Ag}_{m,\text{CN}}^{-} + \text{Ag}_{m,\text{CN}}^{-} \rightarrow \text{Ag}_{m+n,\text{CN}}^{-} \quad k_d \quad (5)
\]

\[
\text{electron transfer: } \text{Ag}^{+}_{n \geq n_c,\text{CN}} + \text{MV}^{+} \rightarrow \text{Ag}_{n,\text{CN}}^{-} + \text{MV}^{2+} \quad k_t \quad (6)
\]

\[
\text{corrosion: } \text{Ag}_{n < n_c,\text{CN}}^{-} + \text{MV}^{2+} \rightarrow \text{Ag}^{+}_{n,\text{CN}}^{-} + \text{MV}^{+} \quad k_{\text{corr}} \quad (7)
\]

Above \(n_c\), reaction 6 is repeated as soon as a new silver ion
adsorbs onto the supercritical cluster because the cluster redox
potential is increasing, so that the cluster catalyzes its growth
in an autocatalytic process.\(^1\) Symmetrically, the reverse electron
transfer from subcritical clusters to MV\(^{2+}\) (reaction 7) is even
more favored when the redox potential decreases after the loss
of an atom and is repeatedly autocatalyzed up to the complete
dissolution of the cluster.\(^{25}\) Reactions 6 and 7 do not represent
an equilibrium because the nuclearities involved are not the same
but are discriminated by \(n_c\). In this mechanism the MV\(^{2+}\)/MV\(^{+}\)
couple indeed plays the role of an electron relay from the
subcritical to the supercritical clusters. It is noteworthy that,
although both electron transfers could be \(a \ priori\) expected
(reactions 3, 4), they were not observed together until the present
work, the required conditions being that the coalescence rate of
(5) is slow enough and the corrosion rate of (7) is fast enough
to affect reaction 6. The efficient oxidation of small clusters
by MV\(^{2+}\) is also coherent with the high instability of these silver
sols to oxygen in the presence of the CN\(^{-}\) ligand.

To determine the values of \(n_c\), \(k_{\text{corr}}\), and \(k_t\), a numerical
simulation model taking into account the value of \(k_d\) determined
above and the cascades of successive coalescence (5), electron
transfer (6), and corrosion reactions (7) was carried out. The
experimental signal of the absorbance at 700 nm is compared
in Figure 6 with the kinetics calculated using the adjusted values
\(n_c = 5\), \(k_t = 5.3 \times 10^6\) L mol\(^{-1}\) s\(^{-1}\), and three different values
of \(k_{\text{corr}}\). If \(k_{\text{corr}} = 0\), the deviation is important at \(t > 0.2\) s. No
adjustment of \(n_c\) and \(k_t\) alone could account for the observed
features of the signals, particularly for the shoulder described
above. In this example the best fit is obtained for \(k_{\text{corr}} = 1.1 \times 10^2\) L mol\(^{-1}\) s\(^{-1}\).

The adjusted parameters are valid for the experimental signals
obtained under different dose-per-pulse conditions with the following uncertainties:

\[
n_c = 5 \text{ or } 6; \quad k_t = (6 \pm 2) \times 10^6\ L\ mol^{-1}\ s^{-1};
\]

\[
(5.3 \pm 0.1) \times 10^3\ L\ mol^{-1}\ s^{-1}; \quad k_{\text{corr}} = (1.0 \pm 0.2) \times 10^2\ L\ mol^{-1}\ s^{-1} \quad (8)
\]

It has been noted above that the expected linear variation of \(t_c^{-1}\) is
the initial atom concentration was indeed observed (Figure 4). In fact, at low atom concentration the observed \(t_c\) is somewhat longer than the linear variation precisely because the
coalescence of subcritical clusters is comparatively more
important.

The value of the critical size \(n_c = 5\) \(\text{to} \ 6\) corresponds to the
redox potential of the cluster containing one more silver cation
\(i.e.\) of the couple \(E^\circ(\text{Ag}_{6,7,\text{CN}}^+ / \text{Ag}_{6,7}^- / \text{CN}^-) \approx -0.4\ \text{V NHE}\). This
value compared with \(E^\circ(\text{Ag}^{+} / \text{SO}_4^{2-}) \approx -0.4\ \text{V NHE}\)
obtained in the sulfate environment means that at the same
nuclearity the small cluster redox potential in the presence of the
cyanide ligand is lower than for clusters without a ligand.
This result differs from the effect of the polyacrylate surfactant,
which also slowed down the coalescence rate constant but had
no effect on the critical size.\(^5\) Note that the presence of the
cyanide ligand induces also a decrease compared to the sulfate
medium on the electrochemical potential of the bulk silver
electrode \(E^\circ(\text{Ag}(\text{CN})\text{CN}) / \text{Ag}_{\text{metal}}^+\) \(\approx -0.395\ \text{V NHE}\) \(^{26}\) and on the
redox potential of the single silver atom \(E^\circ(\text{Ag}_{\text{CN}}^+ / \text{CN}) / \text{Ag}_{\text{CN}}^+\)
\(\approx -2.6\ \text{V NHE}\).\(^7\) The lengthening of the critical time in the
presence of CN\(^{-}\) compared to SO\(_4\)^{2-}\ results mostly from a
slower coalescence process and to a lesser extent from a higher
critical nuclearity required to reach the potential threshold
imposed by the donor.

**Time Range:** \(2\ \text{s} < t < 40\ \text{s}\). Beyond \(2\ \text{s}\) the decay at 700
nm is followed by a strong increase correlated with a decay at
430 nm (Figure 5). The new absorbance component at 700
nm is specific to large silver aggregates absent at short time.
They are more and more abundant in the distribution, partly
because of the increasing coalescence in the absence of any
phenomenon is followed at 430 nm, where Ag(CN)₂⁻ plasmon band, characteristic of small aggregates, decreases: this (increase at 430 nm in Figure 3). Simultaneously, the silver the catalytic growth through electron transfer from MV characteristic of large developed silver aggregates, resulting from different from that obtained without the viologen and is indeed another less intense around 600 nm (Figure 1b). This shape is in the Ag₂SO₄/SPV system and well identified by electron clusters with an absorbance in the red were already observed in the Ag₂SO₄/SPV system and well identified by electron microscopy.¹

Conclusion

The pulse radiolysis method has allowed the kinetics study of the ion reduction and the cluster growth in silver cyanide solutions as a preliminary study to the investigation of mixed Ag(CN)₂⁻/Au(CN)₂⁻ solutions.¹¹ From the time-resolved observation of the reaction of an electron donor acting as a developer of supercritical silver aggregates and of the catalytic growth of these centers, it appears that reduction by an electron in the presence of cyanide occurs at larger critical size of the aggregate than with sulfate for a similar redox probe.

The CN⁻ environment slows down the kinetics of both the coalescence and the electron transfer and lowers the cluster redox potential scale. Both phenomena decrease the stability of nascent metal clusters toward oxidation. This study provides the first observation of the growth of supercritical clusters together with the corrosion of the subcritical ones by the oxidized form of the donor, the latter process being indeed favored by the slow coalescence. The numerical simulation of the donor decay also allows the evaluation of the oxidation rate constant of the subcritical clusters. These results are of high interest for yielding a quantitative evaluation of the role of ligands on the cluster thermodynamics.

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References and Notes

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