## FORMATION OF UNSTABILIZED OLIGOMERIC SILVER CLUSTERS DURING THE REDUCTION OF Ag<sup>+</sup> IONS IN AQUEOUS SOLUTION

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Deaerated aqueous AgClO<sub>4</sub> solutions containing also 0.2 M methanol were exposed to a high energy electron pulse which produced reducing species (hydrated electrons, H-atoms and  $CH_2OH$  radicals), and the absorption spectrum of the reduced silver species measured at various times after the pulse. The sharp 300 and 330 nm absorption bands of oligomeric silver clusters could be detected, the life time of the clusters amounting to several seconds. Both the build-up of the clusters by agglomerations of the silver atoms formed initially and the decay of the clusters are catalytically accelerated by sulfate anions,  $10^{-5}$  M concentrations of the latter already exerting a strong effect. The absorption bands of the clusters are more narrow than in solutions containing a polyanionic stabilizer. The wavelengths of the absorption maxima are the same as for polyphosphate stabilized clusters.

#### 1. Introduction

The reduction of silver ions in aqueous solution generally yields colloidal particles of metallic silver which have a plasmon excitation band in the 380 to 400 nm range. It has recently been found that under certain conditions, i.e. the presence of polyphosphate [1,2] or organic polyanions [3] during the reduction, clusters of oligomeric silver, which live for hours, are also formed. These clusters have rather strong and sharp absorption bands; in the presence of polyphosphate, these bands appear at 275 nm (Ag<sub>4</sub><sup>2+</sup>), 300 nm (trimer), 330 nm (pentamer), and 345 nm (heptamer) [4,5]. With the exception of Ag<sub>4</sub><sup>2+</sup>, these clusters are readily oxidized by oxygen and they can undergo various chemical reactions including photo-electron emission.

The question now arises whether clusters are also formed in the absence of a stabilizing polyanion. If they are formed under these conditions, their life time must be rather short as they have never been detected in conventional reduction experiments. However, the observation of short-lived species is possible using pulse radiolysis. In such an experiment,  $Ag^+$  ions are reduced by hydrated electrons to yield silver atoms which subsequently agglomerate. The final product of agglomeration are metallic particles having the plasmon absorption band as mentioned above. By taking the absorption spectrum at different times during particle growth one should be able to detect the build-up and decay of the absorption bands of intermediate clusters.

Pulse radiolysis experiments on silver ion solutions have been carried out already 9 years ago [6]. In these experiments, the deaerated solution of  $2.5 \times 10^{-4}$  M Ag<sub>2</sub>SO<sub>4</sub>, which also contained 0.1 M methanol (to scavenge the OH radicals simultaneously formed with the hydrated electrons) was pulsed to generate some 10<sup>-6</sup> M Ag atoms. The build-up of the 380 nm plasmon absorption band was recorded in the millisecond range in order to find the minimum particle size at which this metallic property first is noticeable. Similar experiments have most recently been reported by Belloni and coworkers [7] also using silver sulfate solutions. In all these studies, one did not search for absorption bands in the 300 to 345 nm range, where (as we know today) oligomeric clusters absorb. In the present paper, we wish to report on observations in this wavelength range, which reveal that short-lived clusters (life times of up to many seconds) can indeed be detected in the absence of a polyanionic stabilizer.

The pulse radiolysis equipment has been described previously [8].

#### 2. Results and discussion

#### 2.1. Experiments with AgClO<sub>4</sub> solutions

In the experiments of fig. 1, a deaerated  $5 \times 10^{-4}$ M AgClO<sub>4</sub> solution containing 0.2 M methanol was exposed to a 1.5 µs pulse of 3.6 MeV electrons and the absorption spectrum measured at various times after the pulse. The pulse produced  $1.3 \times 10^{-5}$  M hydrated electrons and  $3 \times 10^{-6}$  M H atoms; both species are known to react very rapidly with Ag<sup>+</sup> ions to form silver atoms (the rate constants being  $3.5 \times 10^{10}$  and  $3.1 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, respectively [9]). At the concentration of Ag<sup>+</sup> used, the reduction occurred practically during the pulse. After the pulse, the silver atoms agglomerate to form larger particles. 1.3×10<sup>-4</sup> M CH<sub>2</sub>OH radicals were also formed during the pulse. They do not immediately reduce free Ag<sup>+</sup> ions during the pulse but can later reduce them on the Ag<sub>n</sub> clusters which are formed during the agglomeration of silver atoms [3,4].

After 0.1 ms in fig. 1, reduced silver species are present which have absorption maxima at 275 and 310 nm and a weak shoulder is recognized at 330 nm, i.e. at wavelengths where clusters of oligomeric silver absorb. Almost no absorption is present at this time at longer wavelengths (> 380 nm) where metallic particles absorb. After 25 ms, the 330 nm band, which has been ascribed to Ag<sub>5</sub> [5], is very well developed.



Fig. 1. Irradiation of a deaerated solution of  $5 \times 10^{-4}$  M AgClO<sub>4</sub> and 0.2 M methanol by one pulse of high-energy electrons. Spectrum at various times after the pulse. The pulse produced  $1.6 \times 10^{-5}$  M silver atoms.

It still grows up to about 400 ms. At this time, the spectrum also contains a well developed 300 nm band. At very much longer times, the decay of the 330 nm band can be observed. During this decay, the absorptions in the 380 to 500 nm range increase slightly without formation of a sharp plasmon band. The decay of the 330 nm absorption is shown in fig. 2b, whereas fig. 2a shows that the build-up of the absorption occurs in two steps.

The experiments of fig. 1 already give a positive answer to the above question as to whether silver clusters can be detected in the reduction of silver ions without having a polyanionic stabilizer in the solution. In fact, the life time of several seconds of the 330 nm cluster (fig. 2b) is surprisingly long. On the other hand, it is too short a time in which to detect the clusters in conventional reduction experiments.

The cluster absorption bands at 330 and 300 nm in fig. 1 are more narrow than in the previous experiments on solutions containing polyphosphate [1,4,5]. However, the wavelengths of the maxima are the same for polyphosphate stabilized and unstabilized clusters. It thus seems that the interaction of the clusters with the polyphosphate chains is not very strong. On the other hand, stabilization of the clusters on chains of polyacrylate and polymethacrylate leads to shifts of about 10 nm of the absorption bands and to a drastic increase in the cluster life times [3], which indicates a stronger interaction.

That two processes contribute to the build-up of the 330 nm cluster absorption (fig. 2a) is under-



Fig. 2. Build-up (a) and decay (b) of the 330 nm absorption of the Ag<sub>5</sub> cluster. The half-life time of the first process of build-up was 20  $\mu$ s, that of the second process 90 ms.

stood by the mechanism recently proposed [4,5]. As mentioned above, silver atoms are formed during the pulse as hydrated electrons and H atoms attack  $Ag^+$ ions. After the pulse, small clusters are formed by agglomeration of the silver atoms and the CH<sub>2</sub>OH radicals can reduce additional silver ions on them:

$$Ag_n + Ag^+ + CH_2OH \rightarrow Ag_{n+1} + H^+ + CH_2O \qquad (1)$$

(*n* probably smaller than 3). The participation of organic radicals in the reduction of  $Ag^+$  is limited to about 100 µs, i.e. their life time (for mutual deactivation). The first step in fig. 2a occurs in this time range. However, the second step occurs at much longer times where radicals are no longer present. It must be a step in which the very small silver clusters undergo agglomerations between themselves to form the larger species absorbing at 330 nm.

The two build-up steps follow second-order rate laws. This is concluded from the observation that the reciprocal half-life times were proportional to the dose of the pulse.

### 2.2. Experiments with solutions containing sulfate

The easy detection of unstabilized silver clusters demonstrated above brings up the question of why the clusters have not been observed in the earlier pulse radiolysis studies of silver salt solutions. Besides the fact that the absorption bands are rather narrow and may readily be overlooked in experiments where a wide spectral range is recorded, there exists a second, more important reason: In the earlier investigations solutions of silver sulfate instead of perchlorate were used. As is shown below, all agglomeration processes, including the agglomeration of intermediate clusters to form colloidal metallic particles, are significantly accelerated by sulfate. The life time of the clusters is so short under these conditions that they can hardly be detected.

The spectra in fig. 3 should be compared to those in fig. 1. In the experiments of fig. 3, the absorption spectrum of a deaerated  $2.5 \times 10^{-4}$  M Ag<sub>2</sub>SO<sub>4</sub> solution containing also 0.2 M methanol is shown at various times after the pulse. The pulse was as strong as in the experiments of fig. 1. Shortly after the pulse, the 310 nm absorption peak of Ag<sub>2</sub><sup>+</sup> is seen. This species is formed by rapid complexation of Ag-atoms generated during the pulse: Ag+Ag<sup>+</sup>  $\rightarrow$  Ag<sub>2</sub><sup>+</sup>. As its



Fig. 3. Irradiation of a deaerated  $2.5 \times 10^{-4}$  M Ag<sub>2</sub>SO<sub>4</sub> solution containing 0.2 M methanol. Spectrum at various times after the pulse. The pulse produced  $1.6 \times 10^{-5}$  M silver atoms.

specific absorption is well known, one could determine from the height of the 310 nm peak the concentration of silver atoms reduced during the pulse. The  $Ag_2^+$  species disappears in the 10 µs range to yield larger silver particles [4-6]. After 8 ms in fig. 3, i.e. a time at which there is no sign of metal particles in the spectrum of fig. 1, the plasmon absorption band is fully developed. One can detect some structure in the spectrum at 0.5 ms, in which the plasmon band is partly developed and the 330 nm cluster band is very weakly present.

The half-life times of the first build-up process in fig. 2 and the decay of the 330 nm absorption band are plotted in fig. 4 as functions of the sulfate concentration. The solution was the same as in the ex-



Fig. 4. Half-life time of the first build-up process and of the decay of the 330 nm absorption band as functions of the concentration of added sodium sulfate. Solution as in fig. 1. Note that the ordinate scale is logarithmic for the decay and linear for the buildup.  $1.6 \times 10^{-5}$  M silver atoms per pulse.

periments of fig. 1 and sodium sulfate was added in different amounts. The acceleration of the decay by sulfate is more pronounced than that of the build-up. Note the logarithmic scale on the left ordinate side, and that  $10^{-5}$  M sulfate is sufficient to increase the rate of the decay by 3 orders of magnitude. In the presence of sulfate ions, the build-up and decay of the 330 nm cluster both followed second-order kinetics. The  $SO_4^{2-}$  ion must somehow complex the silver particles and in this way catalyse their mutual interaction. It should also be remembered that the solutions still contained many excess  $Ag^+$  ions. It could be that these ions decrease the rate of growth of silver clusters and that added sulfate counteracts this effect.

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