# Reduction of $Ag^I$ complexes with malonate ions in aqueous solution studied by pulse radiolysis

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The formation of clusters $CH_2(COO^-)(COOAg_3^+)$ (absorption bands at 280 and 460 nm) by the reduction of silver ions in the presence of malonate ions in an aqueous solution was studied by pulse radiolysis. The disappearance of the clusters affords colloidal silver. The mechanism of silver nucleation was discussed, and the rate constants of some reactions were determined.

**Key words:** colloids, nanoparticles, silver, reduction, optical absorption, pulse radiolysis, kinetics, reaction rate constants.

The mechanism of metal ion reduction in aqueous solutions up to the formation of nanoparticles was studied in rather detail by the pulse radiolysis method using optical and conductometric detection (see review[1]). The reduction of silver ions in the $Ag^+$ aqua complexes was studied most comprehensively.[2—4] The reaction mechanism includes the formation of an $Ag^0$ atom ($\lambda_{max}$ = 360 nm) in the first step due to the reduction of an $Ag^+$ ion with a hydrated electron and then a successive chain of reactions of formation and enlargement of short-lived silver clusters

$$Ag_2^+ (\lambda_{max} = 310 \text{ nm}) \rightarrow Ag_3^{2+} (\lambda_{max} = 310 \text{ and } 265 \text{ nm}) \rightarrow$$
$$\rightarrow Ag_4^{2+} (\lambda_{max} = 270 \text{ nm}) \rightarrow Ag_8^{2+} (\lambda_{max} = 295 \text{ and } 325 \text{ nm}).$$

The $Ag_8^{2+}$ cluster is fairly stable, and its lifetime is tens of minutes. Its decay is accompanied by the appearance of a broad band at 370 nm belonging to quasi-metallic particles, and then an absorption band with a maximum at 390 nm appears. This band corresponds to a silver sol and is caused by light absorption with conductivity electrons (surface plasmons). Due to the high density of electron shells, the properties of the quasi-metallic particles are similar to those of nanosized metallic particles in which the electron levels are degenerate and valence electrons are shared and exist as conductivity electrons.

It seems substantial to assume that the complex state of metal ions in an aqueous solution should affect the nature of formed short-lived clusters and the mechanism of subsequent nucleation. The reduction of the silver complexes with ligands $CN^-$, EDTA (disodium ethylenediaminetetraacetate), and $NH_3$ was studied by pulse radiolysis.[5—7] The absorption bands of the complexed silver clusters were found to shift. In addition, additional bands appear compared to the spectra of the "free" clusters. They are caused by the metal-to-ligand charge transfer. The influence of the complex state of the clusters on the mechanism of metal nucleation was not considered.

In this work, the reduction of silver ions in aqueous solutions in the presence of malonate ions $CH_2(COO^-)_2$ was studied by pulse radiolysis. This object of the study was chosen because silver ions form rather stable complexes with such a bidentate ligand as the malonate anion. Therefore, it can be assumed that silver reduction is characterized by specific features.

## Experimental

The pulse radiolysis technique[8] and the computer program for calculations[9] have been described elsewhere. The energy of electrons generated on the van de Graf accelerator was 3.8 MeV. The pulse duration was 0.1 μs. Optical signals were obtained by the averaging of data of ~10 pulses. The average dose per pulse usually was ~4 Gy. The radiation chemical yield of hydrated electrons after the end of spur reactions was taken as 2.6 particles per 100 eV of the absorbed energy.[10]

The nature and properties of intermediate silver clusters formed due to the radiolytic reduction of the silver ions in a complex with the malonate anion were studied by the pulse radiolysis method. The radiolysis of water and aqueous solutions produces $^{\bullet}OH$ radical, which is an efficient oxidizing agent, along with hydrated electrons and hydrogen atoms, which are efficient reducing agents. Isopropyl alcohol, which is an efficient acceptor of $^{\bullet}OH$ radicals, was added to the solution to remove these radicals. As a result, short-lived particles of only

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reductive nature were generated in solution by a pulse of accelerated electrons. Reagents were available from Aldrich. Solutions were prepared with triply distilled water and saturated with argon.

## Results and Discussion

In the presence of malonate ions, silver(I) in an aqueous solution is equilibrated with the corresponding complex

$$Ag^+ + CH_2(COO^-)_2 \rightleftarrows AgOOCCH_2COO^-. \quad (1)$$

According to our measurements, the equilibrium rate constant $K_e = [Ag^+][CH_2(COO^-)_2]/[AgOOCCH_2COO^-]$ is $(8\pm2)\cdot10^{-3}$ L mol$^{-1}$.

In aqueous solutions of $AgClO_4$ at pH 7.5 in the presence of isopropyl alcohol, hydroxyl radicals ($^{\bullet}OH$) and hydrogen atoms ($H^{\bullet}$), which are formed by water radiolysis, disappear in the reaction

$$Pr^iOH + {}^{\bullet}OH\ (H^{\bullet}) \rightarrow (CH_3)_2C^{\bullet}OH + H_2O\ (H_2). \quad (2)$$

Since the redox potentials of a hydrated electron ($e_{aq}^-$) and an isopropyl radical $(CH_3)_2C^{\bullet}OH$ are −2.9 and −1.4 V, respectively, and $E^0(Ag^+/Ag^0) = -1.8$ V,[11] only electrons $e_{aq}^-$ participate in the reduction of the $Ag^+$ ions.

An $1\cdot10^{-4}$ $M$ solution of $AgClO_4$ containing 0.01 $M$ $CH_2(COO^-)_2$ and 0.5 $M$ $Pr^iOH$ exhibits an intense absorption spectrum of $e_{aq}^-$ with a maximum at 700 nm (Fig. 1) immediately after a pulse of accelerated electrons with a duration of 0.1 μs. Further the disappearance of the absorption band of $e_{aq}^-$ is accompanied by the appearance of and an increase in the intensity of the band with a maximum at 360 nm belonging to the silver atoms. A decrease in the absorption of $e_{aq}^-$ and an increase in that of $Ag^0$ are described by the same pseudo-first-order kinetic equation with respect to the concentration of the $Ag^+$ ions. The rate constant of the reaction of $e_{aq}^-$ with the $Ag^+$ ion is[3] $4.8\cdot10^{10}$ L mol$^{-1}$ s$^{-1}$. It was found that this rate constant decreases with an increase in the concentration of the malonate ions in the solution and reaches a value of $2.5\cdot10^{10}$ L mol$^{-1}$ s$^{-1}$ in the presence of 0.01 $M$ $CH_2(COO^-)_2$. According to reaction (1), this concentration corresponds to the occurrence of 45% silver as $Ag^+$ and 55% silver as a complex $AgOOCCH_2COO^-$. The observed dependence of the rate constant of the reaction of $e_{aq}^-$ with silver on the concentration of the malonate ions is due to the participation of $e_{aq}^-$ in the following reactions:

$$Ag^+ + e_{aq}^- \rightarrow Ag^0, \quad (3)$$

$$AgOOCCH_2COO^- + e_{aq}^- \rightarrow Ag^0 + CH_2(COO^-)_2. \quad (4)$$

The rate constant of reaction (4) is much lower than that of reaction (3), which is likely caused by the participation of likely charged particles. Analysis of the kinetic data shows that $k_4 = (7\pm2)\cdot10^9$ L mol$^{-1}$ s$^{-1}$.

The disappearance of the $Ag^0$ atoms is accompanied by the appearance of an absorption band with a maximum at 310 nm caused by the formation of clusters $Ag_2^+$.[2–4] The rate constant of the reaction

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ \quad (5)$$

is[3] $6\cdot10^9$ L mol$^{-1}$ s$^{-1}$. Most likely, $Ag_2^+$ are formed by the interaction of $Ag^0$ with the $Ag^+$ ions even in solutions containing 0.01 $M$ $CH_2(COO^-)_2$. The decay of $Ag_2^+$ is accompanied by the appearance of a new band at λ = 280 nm and a low-intensity band at λ = 460 nm. The kinetics of an increase in the intensity of these bands also obeys the first-order equation, and the rate is proportional to the concentration of the silver ions in solution. It can be assumed that a complex of the $Ag_3^{2+}$ trimer with the malonate ions is formed. The kinetics of a change in the absorption at λ = 460 nm is shown in Fig. 2. When malonic acid is absent, the addition of an additional $Ag^+$ ion to $Ag_2^+$ in the reaction

$$Ag^+ + Ag_2^+ \rightarrow Ag_3^{2+} \quad (6)$$

results in the $Ag_3^{2+}$ trimer, whose absorption spectrum includes bands at λ = 310 and 265 nm.[4] The rate constant of this reaction is equal to $2\cdot10^9$ L mol$^{-1}$ s$^{-1}$. In the presence of malonic acid, the reaction of the following type occurs:

$$CH_2(COO^-)(COOAg) + Ag_2^+ \rightarrow Ag_3^+OOCCH_2COO^-. \quad (7)$$

With allowance for the concentration of the silver ions bound in the complex $AgOOCCH_2COO^-$, the rate constant of reaction (7) turned out to be $(3.6\pm0.5)\cdot10^9$ L mol$^{-1}$ s$^{-1}$. This value is approximately twice as large

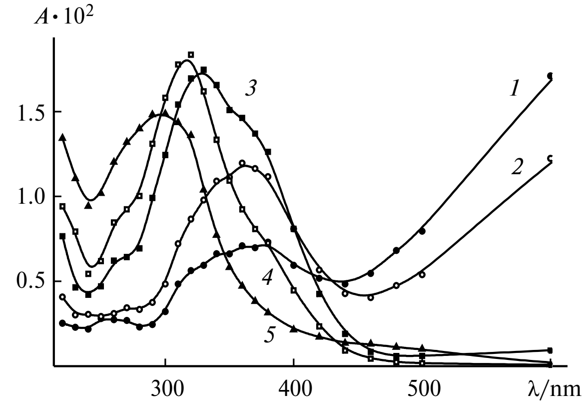


**Fig. 1.** Absorption spectra of a $1\cdot10^{-4}$ $M$ solution of $AgClO_4$ containing 0.01 $M$ $CH_2(COO^-)_2$ and 0.5 $M$ $Pr^iOH$ saturated with argon (pH 7.5) 0.3 (*1*), 0.5 (*2*), 1.6 (*3*), 3.0 (*4*) and 12.5 μs (*5*) after electron pulse. The pulse duration is 0.1 μs, and the absorbed dose is 4.3 Gy, which corresponds to the formation of $1.2\cdot10^{-6}$ $M$ hydrated electrons.

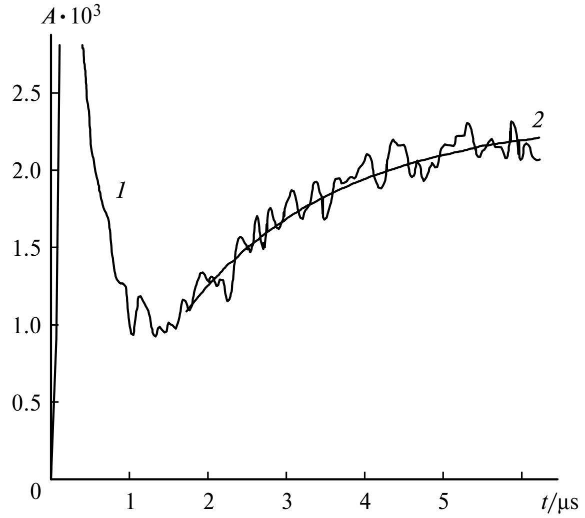


**Fig. 2.** Kinetics of a change in the absorption at $\lambda = 460$ nm of a solution containing $3 \cdot 10^{-4}$ *M* $AgClO_4$, 0.01 *M* $CH_2(COO^-)_2$, and 0.5 *M* $Pr^iOH$ (*1*) and the results of calculation at $k_7 = 3.6 \cdot 10^9$ L mol$^{-1}$ s$^{-1}$ and $\varepsilon_{460} = 2.3 \cdot 10^3$ L mol$^{-1}$ cm$^{-1}$ (*2*). The irradiation conditions are given in Fig. 1.

as $k_6$. A possible reason is the interaction *via* Eq. (7) of oppositely charged particles rather than *via* Eq. (6). Most likely, the $Ag_3^{2+}$ trimers formed in reaction (6) are also further bound to form complexes with the malonate ions. This is indicated by the fact that, after the absorption of $Ag_2^+$ has disappeared, the absorption spectra of solutions containing $5 \cdot 10^{-3}$—$5 \cdot 10^{-2}$ *M* $CH_2(COO^-)_2$ exhibit the same absorption including bands with maxima at $\lambda = 280$ and 460 nm.

The particles absorbing at $\lambda = 280$ nm begin to disappear in several tens of microseconds, and the faster decay occurs in the millisecond time scale (Fig. 3). This is accompanied by the formation of a broad optical absorption with a maximum at ~380 nm, which is caused by the absorption of surface plasmons in the colloidal metal. When the concentration of the malonate ions in solution increases, metal coagulation is accelerated similarly to the coagulation of silver in the presence of $HCOO^-$, $CH_3COO^-$, and other anions.**[12—14]** The broad optical absorption of the colloidal metal is detected on a standard spectrophotometer 5—10 min after a pulse experiment was ceased. A yellow solution of colloidal silver is unstable, and a black precipitate of the dispersed metal is formed in 1—2 h.

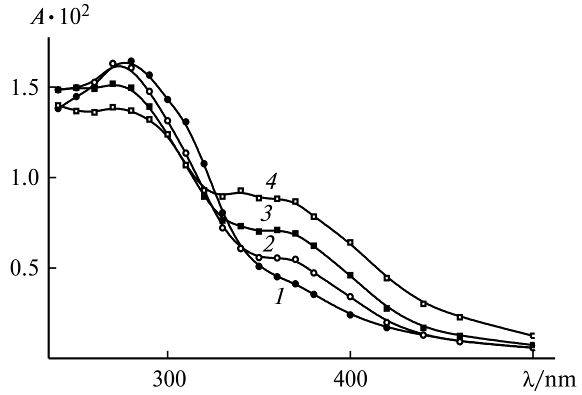


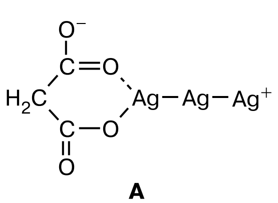
**Fig. 3.** Absorption spectra 80 (*1*), 160 (*2*), 300 (*3*), and 600 μs (*4*) after electron pulse. The solution and irradiation conditions are given in Fig. 1.

Thus, the complex state of silver in an aqueous solution exerts a substantial effect on the nature of the forming intermediate clusters and the mechanism of metal nucleation. The successive formation of molecular clusters**[1,3,4]** is observed upon the reduction of the hydrated $Ag^+$ ions by pulse radiolysis. The changes in the electronic state in the series cluster—quasi-metallic particle—nanoparticle are pronounced in the optical spectra: the individual narrow optical bands inherent in different clusters

$$Ag_2^+\ (\lambda_{max} = 310\text{ nm}) \rightarrow Ag_2^{2+}\ (\lambda_{max} = 310\text{ and }265\text{ nm}) \rightarrow$$
$$\rightarrow Ag_4^{2+}\ (\lambda_{max} = 270\text{ nm}) \rightarrow Ag_8^{2+}\ (\lambda_{max} = 295\text{ and }325\text{ nm})$$

are transformed during increasing the cluster size into broad optical bands intrinsic in quasi-metallic particles (360—380 nm) and further into an absorption band of plasmons (390 nm) corresponding to the metallic state. This pattern shows the transition of the atomic-molecular properties of a particle consisting of *n* metal atoms to the properties of the compact metal with an increase in the *n* value.

No pronounced cluster formation is observed for the reduction of the silver complex with the malonate ions. The $Ag^0$ atom is formed in the initial step of reduction, and then the $Ag_2^+$ dimer is formed. The reaction of the dimer with the complex ($k = 3.6 \cdot 10^9$ L mol$^{-1}$ s$^{-1}$) affords a silver cluster bonded to malonic acid, whose optical spectrum is characterized by absorption bands with $\lambda = 280$ and 460 nm. No similar complexes were found for the reduction of silver ions in the presence of monobasic organic acids: formic and acetic.**[2,13]** Therefore, we attribute the formation of this complex to the capability of malonic acid of acting as a bidentate ligand to form a cyclic complex with a silver ion. Possibly, the cluster has structure **A**.



**A**

However, this or another structure of the short-lived intermediate cannot be confirmed. A strong bond between the ligand and silver in this complex is unfavorable for the formation of more complicated silver clusters, as it is observed in the absence of malonic acid. Silver nucleation is directly caused by the coagulation of the

$Ag_3{}^{+}OOCCH_2COO^{-}$ clusters and is accompanied by a successive increase in the size of the metal particles.

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