Formation of the Silver Hydride Ion AgH⁺ upon the Reduction of Silver Ions by H• in Aqueous Solution. A Pulse Radiolysis Study

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Dedicated to Prof. Dr. Arnim Henglein on the occasion of his 80th birthday

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The reaction of hydrogen atoms and of alcohol radicals with monovalent silver ions is studied in aqueous solution by means of pulse radiolysis. In acidic aqueous solutions containing silver ions and an alcohol, hydrogen atoms react with silver ions to form AgH⁺ with a rate constant of $k = 1.5 \times 10^{10} \,\mathrm{dm^3 \, mol^{-1} \, s^{-1}}$. This complex dissociates into free silver atoms and hydrogen ions with a first order rate constant of $2 \times 10^7 \,\mathrm{s^{-1}}$. A reaction of alcohol radicals with silver ions could not be observed in aqueous solutions containing either methanol, ethanol or 2-propanol during times of up to 15 ms; the rate constant would therefore have to be smaller than $1 \times 10^4 \,\mathrm{dm^3 \, mol^{-1} \, s^{-1}}$.

1. Introduction

The comprehension of fundamental reactions in the reduction of metal ions is essential for the understanding of subsequent colloid formation. In this paper we address the reduction of silver ions by hydrogen atoms in aqueous solution, and, because it could serve as an additional source of reduced silver, the reaction of silver ions with alcohol radicals, as well. There are three

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reports [1, 2] available which deal with the reduction of silver ions by hydrogen atoms and in which rate constants of $1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [3], $2.8 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [4] or $1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [5] were given. The reduction of silver ions by alcohol radicals has led to contradictory results in the past. For pulse radiolysis experiments, some reports state that this reaction does not occur at all [6, 7], while others include this reaction in their reaction mechanisms [8, 9]. For gamma irradiation, this reduction has obviously been observed [10, 11]. But no value for the rate constant is given.

In order to gain more insight into the reduction of silver ions by hydrogen atoms in aqueous solutions we have re-investigated this reaction, in the course of which a short-lived complex of silver hydride ions is evidently being formed. The reduction of silver ions by alcohol radicals was also investigated with great care. No trace of such a reaction was found in pulse radiolysis experiments during the period the alcohol radicals are present in solution before they dimerize to dihydroxy alcohols.

2. Experimental

The pulse radiolysis apparatus [12, 13] and the computer software [14, 15] of the 4 MeV van de Graff accelerator facility ELBENA at the Hahn-Meitner-Institut were described earlier. The optical detection system in the UV range consists of an intensified XBO 450 lamp [16], several lenses and mirrors, a UV band-pass filter in front of the monochromator (Bausch&Lomb, 33-86-75) [17] and an R7400U photomultiplier tube (Hamamatsu) in a nine-stage configuration [18]. The high transmission UV band-pass filters (UV-R types, Schott) are centered every 30 nm from 220 nm to 340 nm. They are inserted in order to avoid stray-light effects. The photo detector was connected to the digital recorder (Tektronix TDS7104) *via* a baseline compensation circuit [19] employing a special adapter [20] in order to keep the time constant of the detection electronics as small as possible. The charge per pulse was measured by integrating Cherenkov emission in a "foil" of fibers [21]. Further details of the pulse radiolysis apparatus can be found elsewhere [22].

Nitrous oxide and argon were of ultra high purity. Solutions were prepared daily using HQ-water (Millipore). After purging two liters of this water with argon for two hours, the reactants were added. After that, the solution was purged further either with argon or nitrous oxide for another hour. The pH of the HQ-water was measured to be 6.2 before bubbling and 6.8 after bubbling and pH will be referenced here as "natural". HClO₄ was used to adjust pH. Experiments were carried out at 23 °C.

Some of the experiments were carried out at low pH. At this pH the kinetic salt effect need to be considered. The rate constants given here were those for natural pH.



Fig. 1. Kinetic curves at 360 nm. Solutions: $1 \times 10^{-4} \text{ mol dm}^{-3} \text{ AgClO}_4$, 0.01 mol dm⁻³ HClO₄, purged with Ar and containing 0.1 mol dm⁻³ MeOH (curve a), 0.01 mol dm⁻³ EtOH (curve b), or 0.01 mol dm⁻³ 2-PrOH (curve c). Irradiation dose corresponds to $2.5 \times 10^{-6} \text{ mol dm}^{-3}$ of e_{aq}^{-1} (*G* = 2.6), pulse duration 15 ns (curve a) or 100 ns (curves b and c). Each curve represents the average of 50 experiments. Curve for reaction (0) is also added (dashed line).

3. Results and discussion

The reduction of silver ions by hydrogen atoms is generally assumed to occur according to

$$\mathbf{H}^{\bullet} + \mathbf{A}\mathbf{g}^{+} \to \mathbf{A}\mathbf{g}^{0} + \mathbf{H}^{+} \,. \tag{0}$$

This reaction is studied here in acidic solutions where hydrated electrons of the water radiolysis are converted into hydrogen atoms. The solutions also contain an aliphatic alcohol for scavenging hydroxyl radicals. Figure 1 shows the increase in absorption *vs.* time after irradiation with a short electron pulse, the irradiated solution contains silver ions and either methanol, ethanol or 2-propanol. On a shorter time scale, the build-up in absorption is also shown in Fig. 2 for the same silver ion concentration (curve b) and for a concentration five times higher (curve a). Clearly, a delay in absorption build-up can be seen in both figures, the calculated absorption as predicted by reaction (0) is included as the dashed lines for the sake of comparison. As shown in Fig. 1, the initial increase in absorption is the same, for all three alcohols. Also, the initial increase does not change on this time scale when the hydrogen ion concentration is varied from 0.01 to 0.05 mol dm⁻³. In Fig. 3 the absorption *vs.* time curves are shown for a silver solution con-



Fig. 2. Kinetic curves at 360 nm and analysis of curve b. Solutions: 5×10^{-4} mol dm⁻³ (curve a) or 1×10^{-4} mol dm⁻³ (curve b) of AgClO₄, 0.05 mol dm⁻³ HClO₄, 0.01 mol dm⁻³ 2-PrOH, purged with Ar. Dose corresponds to 5×10^{-6} mol dm⁻³ of e_{aq}^- (G = 2.6), pulse duration 5 ns. Each curve represents the average of 50 experiments. Calculated contributions of Ag⁰ (dotted line), AgH⁺ (dash-dotted line) and Ag₂⁺ (dash-dotted-dotted line), and their sum (solid line). Curve for reaction (0) is also added (dashed line).

taining alcohol and purged with N₂O and for various hydrogen ion concentrations between natural pH and pH 2. At natural pH, all hydrated electrons are scavenged by nitrous oxide so that only the hydrogen atoms generated during water radiolysis react with silver. At lower pH, however, more and more hydrated electrons escape scavenging and react with hydrogen ions to form additional hydrogen atoms, *i.e.*, the amplitude of absorption increases with lower pH. As can be seen from Fig. 3, the shape of all curves is independent of pH, i.e., the absorption maximum occurs at about one microsecond, followed by a decay. In all cases, a certain amount of hydrogen atoms are lost for the reaction with silver because they react also with the alcohol. The alcohol radicals which were generated either by the reaction of hydrogen atoms or by hydroxyl radicals with the alcohol contribute to the absorption as well, see Fig. 3. The shape of the spectrum obtained at about one microsecond after irradiation (not shown) measured in solutions of Figs. 1 or 2 resembles strongly to that of free silver atoms [23], although slightly lower in amplitude. Moreover, the subsequent formation of the dimer and trimer silver clusters is observed as the absorption at 360 nm fades away. In order to explain the induction period, we propose here that the reaction of hydrogen atoms with silver ions occurs via the formation of an intermediate complex of silver hydride ions



Fig. 3. Absorption vs. time curves at 360 nm at various pH for a solution containing 1×10^{-4} mol dm⁻³ AgClO₄, 0.01 mol dm⁻³ 2-PrOH and purged with N₂O. Irradiation dose corresponds to 2.5×10^{-6} mol dm⁻³ of e_{aq}^{-} . Each curve represents the average of 50 experiments.

according to

$$\mathbf{H}^{\bullet} + \mathbf{A}\mathbf{g}^{+} \to \mathbf{A}\mathbf{g}\mathbf{H}^{+} \,. \tag{1}$$

Because the decay of the 360 nm absorption at times longer than one microsecond as well as the simultaneous formation of the silver dimer and trimer clusters follow a pseudo first-order law, it is further suggested that the silver hydride ions subsequently dissociate yielding free silver atoms and hydrogen ions

$$AgH^+ \to Ag^0 + H^+ \,. \tag{2}$$

In acidic solution, hydrated electrons generated in water radiolysis are converted into hydrogen atoms *via*

$$\mathbf{e}_{\mathrm{aq}}^{-} + \mathbf{H}^{+} \to \mathbf{H}^{\bullet} \tag{3}$$

thus enhancing the amount of hydrogen atoms in these experiments. Hydrated electrons can also react directly with silver ions

$$e_{aq}^{-} + Ag^{+} \to Ag^{0} . \tag{4}$$

While the reaction of hydrogen atoms with alcohol

$$\mathbf{H}^{\bullet} + \mathbf{R}\mathbf{H} \to \mathbf{R}^{\bullet} + \mathbf{H}_2 \tag{5}$$

competes with reaction (1), scavenging of hydroxyl radicals by the alcohol

$$^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \tag{6}$$

prevents oxidation of silver ions via

$$^{\circ}OH + Ag^{+} \rightarrow AgOH^{+}$$
. (7)

Silver atoms created according to reactions (1) and (2) react with silver ions in solution as reported earlier [23]

$$Ag^0 + Ag^+ \to Ag_2^+ \tag{8}$$

$$\operatorname{Ag}_{2}^{+} + \operatorname{Ag}^{+} \to \operatorname{Ag}_{3}^{2+}.$$
(9)

A reaction of alkyl radicals with silver ions according to

$$\mathbf{R}^{\bullet} + \mathbf{A}\mathbf{g}^{+} \to \mathbf{A}\mathbf{g}^{0} + \mathbf{R}^{+} \tag{10}$$

would create additional silver atoms. Such a reaction was, however, not observed as discussed below in detail.

A direct dissociation of silver hydride ions according to reaction (2) is assumed here, although, if this species exhibits hydride characteristics, one would expect an additional reaction with hydrogen ions to yield Ag^{2+} and H_2 . This assumption is made because in the experiments described above, i) no influence of the hydrogen ion concentration on the initial build-up of absorption can be seen, ii) the spectrum observed at about one microsecond can clearly be assigned to that of the free silver atom, and, iii) the formation of the silver dimer and trimer colloids can be observed and identified by their sequential build-up at 310 nm and 260 nm.

Silver hydride ions as the intermediates in the reaction of hydrogen atoms with silver ions were postulated several years ago [24–26, 32].

The experiments of Figs. 1 and 2 are carried out in acidic silver solution in which the hydrogen ion concentration is large enough so that hydrated electrons react predominantly with hydrogen ions to form hydrogen atoms. Their formation time is short compared to the time scale of the experiments. Adding various aliphatic alcohols, such as methanol, ethanol or 2-propanol to the solution shows practically no influence on the initial increase in absorption of free silver atoms, as shown in Figs. 1 and 2. Their concentration is, however, critical because they should ideally scavenge all hydroxyl radicals without reacting with the hydrogen atoms. Tert.-butyl alcohol was not used because of its instability in acidic solutions [27].

reactio	on					rate constant k	ref.	
Н•	+	Ag^+	\rightarrow	AgH ⁺		$1.5 imes 10^{10} dm^3 mol^{-1} s^{-1}$	Х	(1)
AgH ⁺			\rightarrow	Ag^0	$+ H^+$	$2 \times 10^7 \text{ s}^{-1}$	Х	(2)
e_{aq}^{-}	+	H^+	\rightarrow	H•		$2.3\times 10^{10}dm^3mol^{-1}s^{-1}$	[1]	(3)
e_{aq}^{-}	+	Ag^+	\rightarrow	Ag^0		$4.8 imes 10^{10} dm^3 mol^{-1} s^{-1}$	[23]	(4)
Н•	+	RH	\rightarrow	R•	$+ H_2$			(5)
•OH	+	RH	\rightarrow	R•	+ H ₂ O			(6)
•OH	+	Ag^+	\rightarrow	$AgOH^+$		$1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[31]	(7)
Ag^0	+	Ag^+	\rightarrow	Ag_2^+		$8.5 imes 10^9 dm^3 mol^{-1} s^{-1}$	[23]	(8)
Ag_2^+	+	Ag^+	\rightarrow	Ag_{3}^{2+}		$2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[23]	(9)
R•	+	Ag^+	\rightarrow	Ag^0	$+ R^+$	$< 1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Х	(10)
H•	+	H•	\rightarrow	H_2		$7.75 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[1]	(11)
•OH	+	•OH	\rightarrow	H_2O_2		$5.5 imes 10^9 \ dm^3 \ mol^{-1} \ s^{-1}$	[1]	(12)
e_{aq}^{-}	+	e_{aq}^{-}	\rightarrow	H_2	$+ 2OH^{-}$	$5.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	[1]	(13)
R•	+	R•	\rightarrow	product				(14)
(X): this work Rate constants for reaction (5) [28,29] $k_5 = 1.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for methanol $k_5 = 1.8 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for ethanol $k_5 = 5.3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 2-propanol								
Rate constants for reaction (6) [28,30] $k_6 = 9 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for methanol $k_6 = 2.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for ethanol $k_6 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 2-propanol								
Rate constants for reaction (14) [28,29] $2k_{13} = 2.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for methanol $2k_{13} = 1.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for ethanol $2k_{13} = 1.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 2-propanol								

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Scheme 1. Reaction mechanism used in the computer simulation.

The kinetic curves for the formation of silver hydride ions and free silver atoms could easily be fitted by computer simulation using the reaction mechanism of Scheme 1. Computer simulation could be carried out unambiguously because the molar absorbtivities for the silver components [23], alcohol radicals [28] and radiolysis products as well as the rate constants, except for those of reactions (1) and (2), are well known. Also, the shape and the amplitude of the calculated absorption curves depend sensitively on the rate constants for reactions (1) and (2) thus allowing their accurate determination. From fitting all kinetic curves, *i.e.*, the experimental data of Figs. 1, 2 and 3 as well as those used for obtaining the spectrum of Fig. 4, the values for the rate constants for reactions (1) and (2) were determined to be $k_1 = 1.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_2 = 2 \times 10^7 \text{ s}^{-1}$.



Fig. 4. Calculated concentration *vs.* time curves for curve b of Fig. 2: H[•] (thick dotted line), AgH⁺ (thick solid line), Ag⁰ (thick dashed line), Ag₂⁺ (thick dash-dotted line), e_{aq}^{-} (thin solid line), •OH (thin dotted line), R[•] (thin dashed line).

The calculated contributions of silver hydride ions, of silver atoms and of dimer silver clusters are added to the experimental curve of the lower silver concentration (curve b) in Fig. 2. The corresponding concentration *vs*. time curves for various transient species are depicted in Fig. 4. As time elapses, a little less than half of the hydrogen atoms are already consumed by reacting with silver ions and the alcohol; the latter reaction accounts for 30% of the total hydrogen atom consumption. The silver dimer cluster is formed only to a few percent under these experimental conditions. The amplitude in absorption at longer times in Fig. 1 depends on the amount of hydrogen atoms being scavenged by the various alcohols. The maximum absorption of silver hydride ions occurs at 125 ns with low amplitude because these species vanish quickly according to reaction (2). The spectrum of silver hydride ions, as a result of computer simulation is shown in Fig. 5. The data scatters considerably due to their low contribution in absorption. Nevertheless, the curve shows a maximum at around 350 nm and increases at shorter wavelengths.

The reaction of alcohol radicals with silver ions according to reaction (10) is also studied with great care because this reaction would severely influence the results obtained above by serving as an additional source of reduced silver. An aqueous solution containing silver ions, alcohol and purged with nitrous oxide at natural pH, was irradiated. On the microsecond time scale, a small absorption with a maximum at 360 nm is observed immediately after irradiation (not shown). This absorption is due to the formation of free silver atoms because a fraction of hydrated electrons escapes scavenging by nitrous oxide and reacts directly with silver ions according to reaction (4). After this absorption



Fig. 5. Spectrum of AgH^+ from computer analysis (marker) and fit (solid line). Experimental conditions as for curve b in Fig. 2.



Fig. 6. Kinetic curve at 360 nm and analysis thereof. Solution: $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ AgClO}_4$, 2 mol dm⁻³ 2-PrOH at natural pH and N₂O saturated. Dose corresponds to 6.8×10^{-6} mol dm⁻³ of •OH (G = 5.3). Curve represents the average of 800 experiments. Calculated contributions of R• (dashed line) and the dihydroxy alcohol (dotted line).

disappears, another small absorption remains as shown in Fig. 6. This absorption decays during 15 ms to a small constant value; this decay clearly follows a second order reaction law when varying irradiation intensity. The absorption on the millisecond time scale is identified as that of the respective alcohol radical by its molar absorbtivity and rate of decay [28–30] as it dimerize to dihydroxy alcohol. On this time scale no further absorption due to the initial formation of silver compounds can be observed, *i.e.*, no clue for the reduction of silver ions by alcohol radicals generated from methanol, ethanol, or 2-propanol can be found. Computer simulation reveals that the rate constant, if this reaction occurs at all, must be smaller than 1×10^4 dm³ mol⁻¹ s⁻¹. This value is clearly too low for the reduction of silver ions by these alcohol radicals in pulse radiolysis experiments, but the value might be large enough to make this reaction possible in gamma radiolysis experiments where dose rate is extremely low. Unfortunately, measurements of the transient conductance were not possible at our laboratory due to the high intrinsic conductance of the solutions.

4. Conclusions

The reaction of hydrogen atoms with silver ions in aqueous solution was studied in great detail. The product of this reaction is assigned to a short-lived complex of silver hydride ions, which dissociates subsequently into free silver atoms and hydrogen ions. The rate constants for the formation and disappearance of silver hydride ions have been determined as well as its spectrum. Any absorption due to the reaction of some alcohol radicals with silver ions was not detected by the pulse radiolysis experiments described above, which means that the rate constant of this reaction would have to be very small.

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