Kinetics of reduction of silver (I)-gelatin complex in aqueous alkaline solution

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The kinetics of reduction of silver (I)-gelatin complex by ascorbic acid and hydrazine has been studied spectrophotometrically with trace concentration of reducing agents in alkaline medium with low ionic strength (<0.1 M) in the temperature range 15°C-41°C. The reduction is first order in both the reactants with an inverse first order dependence on [H+] for ascorbic acid oxidation and shows an almost zero order dependence on [H+] for hydrazine oxidation. The activation parameters are found to be ΔH° = 20.67 ± 2.5 kJ mol⁻¹, and ΔS° = -24.1 ± 4.5 J K⁻¹ mol⁻¹ for the reduction of the complex by ascorbic acid while those for the reduction of silver (I)-gelatin complex by hydrazine were found to be 23.72 ± 2.05 kJ mol⁻¹ and 12.3 ± 2.5 JK⁻¹ mol⁻¹, respectively. A tentative mechanism consistent with the kinetics is discussed.

Aqueous solution of gelatin forms a colourless, 1:1 weak complex with silver (I) ion in alkaline medium which have been found to be very important, but inexpensive analytical reagent in recent years. The interaction of silver (I) ion with gelatin is greatly influenced by pH. The binding of silver ions with −NH₂ group of gelatin may be as follows:

\[ \text{Ag}^+ + \text{H}_2\text{N} \cdots \text{COOH} + \text{OH}^- \rightarrow \text{H}_2\text{N} \cdots \text{COO}^+ \text{Ag} + \text{H}_2\text{O} \cdots (1) \]

and

\[ \text{H}_2\text{N} \cdots \text{COO}^+ \text{Ag} + \text{OH}^- \rightarrow \text{AgH} \cdots \text{COO}^- + \text{H}_2\text{O} \cdots (2) \]

Alternatively,

\[ \text{AgH} \cdots \text{COO}^- + \text{OH}^- \rightarrow [\text{AgN} \cdots \text{COO}]^2^- + \text{H}_2\text{O} \cdots (3) \]

and

\[ [\text{AgN} \cdots \text{COO}]^2^- + \text{H}_2\text{O} \rightarrow \text{Ag}^+ + \text{OH}^- + \text{HN} \cdots \text{COO}^- \cdots (4) \]

where the gelatin skeleton is represented by dotted lines. It is probable that the free silver ions are reduced to silver metal. At about pH 8, 1 ml of 0.5% gelatin solution effectively binds 453 μg of silver (I) ion, verified by the expulsion of free silver by dialysis at 30°C (ref. 4). Mild reducing agents such as ascorbic acid, hydrazine, formaldehyde, carbon monoxide, and hydrogen sulphide reduce the complex to gelatin stabilized silver sol (of reproducible particle size) with an absorption maximum at 415 nm yielding a good number of analytical methods particularly useful for monitoring environmental pollutants. Very recently, silver (I)-gelatin complex has regained the interest of organic chemists mainly for phenol coupling reactions. Though the reduction of silver (I) by ascorbic acid or hydrazine is well known, spectrophotometric studies of the reduction process by trace amounts of reducing agents are not fully explored. This is the first report of its kind exploring feasibility of complexing properties as well as the sol stabilizing properties of gelatin. The aqueous solution of stabilized silver sol system has been found to be very helpful to obtain well defined surface enhanced Raman spectra (SERS) for widely different analytes. So it is interesting to investigate the kinetic behaviour of silver (I)-gelatin complex with reducing systems supporting the two electron transfer mechanism.

Experimental

All absorbance measurements were made with a Shimadzu UV-160 digital spectrophotometer with 1-cm quartz cells. A digital pH meter (ECIL, Govt. of India enterprise, Hyderabad) was used for pH measurements.

All materials were of AnalR quality. Doubly distilled water was used in all preparations. The temperature was controlled within ±0.1°C using laboratory designed thermostatic bath. A stock solution of silver nitrate (10⁻² M) was prepared by dissolving silver nitrate in distilled water. Fresh stock solutions (~10⁻³ M) of ascorbic acid (AH₂) and hydrazine were prepared in distilled water and were standardized by classical methods. Gelatin solution (1%) was prepared by dissolving 1 g of powdered gelatin in 100 ml of warm distilled water. Buffer solutions with pH range from 9-11 were prepared from Na₂CO₃ and NaHCO₃ solutions and the pH was adjusted using a pH
The stoichiometries of the overall reactions of silver (I)-gelatin complex with different reducing agents were investigated spectrophotometrically at a constant pH of 10.0, and at an ionic strength of 0.1 M. The Ag(I) complex concentration [Ag(I)-gelatin] was always greater than the concentrations of reducing agents, [Red], used so the reducing agents were oxidised completely at the final stage. The concentration of the Ag(I)-complex consumed for the formation of silver sol was calculated with the value of spectral characteristic (ε) of silver sol as reported. The absorbance values of the sol solutions bear a linear relationship with the concentration of the reducing agent, [Red]. Ratios of [Ag⁺ consumed]/[Red] for several different initial concentrations of Ag⁺ indicate that the stoichiometries of the overall reaction conform to the following equations.

\[
2Ag^+ + AH_2 \rightarrow A + 2Ag^0 + 2H^+ \quad \ldots (5)
\]

\[
4Ag^+ + N_2H_4 \rightarrow N_2 + 4Ag^0 + 4H^+ \quad \ldots (6)
\]

Plots of \(\log (A_a - A_i)\) versus time, \(t\), where \(A_a\) and \(A_i\) represent the absorbances at time \(t\) and infinite time, were linear indicating that the reaction is first order in [Ag⁺].

Pseudo-first order rate constants, \(k_{obs}\), derived from the gradients of these plots, were obtained using various concentrations of reductants. The overall second order rate constants, \(k\), were obtained by dividing the approximate values of \(k_{obs}\) by [Red], as shown in Table 1. The constancy of the values so obtained indicates that the reaction is also first order in [Red]. The excellent linearity of the first order plots and the constancy of second order rate constants confirm that the reaction is overall second order.

Gelatin concentration does not affect the rate of reduction. It only serves the purpose of complexation of silver (I) and stabilization of sol.

Dependence of the rate of reaction on the hydrogen ion concentration could not be tested over a wide range of pH. The silver (I)-gelatin complex is susceptible to reduction in alkaline medium only. In spite of the extremely low solubility of silver carbonate, the carbonate-bicarbonate buffer was used to adjust the pH of the medium as the weak Ag(I)-gelatin complex is as strong as to reach the solubility product of silver carbonate and the reaction is carried out in the presence of a large excess of complexing agent i.e. gelatin. The constancy of rate constants of the reduction of the complex at different buffer concentrations also authenticates the merits of carbonate-bicarbonate buffer. Moreover, gelatin in alkaline medium can bind freshly precipitated silver carbonate from aqueous solution which justifies the use of the carbonate buffer. An inverse first order dependence on [H⁺] was obvious from the linear plots of \(\log k\) against \(\log [H^+]\) for ascorbic acid oxidation in the pH range of 8-11 which had negative gradient of -1 whereas for the reduction of the complex by hydrazine there was zero order dependence on [H⁺]. Higher pH above 11.0 should be avoided due to the possible hydrolysis of gelatin and decomposition of reducing substances.

The temperature dependence study was made at four different temperatures ranging from 15°C to 41°C. The activation parameters were calculated using the least squares method to be \(\Delta H^* = 20.67 \pm 2.5 \text{ kJ mol}^{-1}\), \(\Delta S^* = -24.1 \pm 4.5 \text{ JK}^{-1} \text{ mol}^{-1}\) for the oxidation of ascorbic acid and \(\Delta H^* = 23.72 \pm 2.05 \text{ kJ mol}^{-1}\) and

<table>
<thead>
<tr>
<th>Reductant</th>
<th>([5 \times 10^{-3}] \text{ mol dm}^{-3})</th>
<th>([5 \times 10^{-4}] \text{ mol dm}^{-3})</th>
<th>(10^2 k_{obs}) (s⁻¹)</th>
<th>(10^{-2} k/\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1})</th>
</tr>
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<tbody>
<tr>
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<td>0.181</td>
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<td></td>
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<td>1.40</td>
<td>1.40</td>
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</tbody>
</table>

NOTES
\[ \Delta S^* = -12.3 \pm 2.5 \text{ JK}^{-1} \text{ mol}^{-1} \], for hydrazine oxidation.

The effect of large amount of electrolyte on the reaction rate cannot be studied due to the aggregation of sol particles. Ionic strength of less than 0.1 M does not influence the rate of reduction of complex, nor does it influence sol aggregation process through which sol may be precipitated.

The low entropy of activation for each of the reactions confirms the result of stoichiometric analysis; i.e., the processes under investigation are nothing but oxidations of ascorbic acid or hydrazine to dehydroascorbic acid or nitrogen respectively.

**Reaction with ascorbic acid**

The reduction of silver (I)-gelatin complex by ascorbic acid involves a transfer of two electrons giving dehydroascorbic acid. Reduction by ascorbic acid has been shown to take place through intermediate formation of the free radical AH, well studied by Mushran et al.\(^\text{11,12}\). The presence of free radicals in the oxidation of ascorbic acid was confirmed by the ESR method by Lagercrasutz\(^\text{13}\).

The mechanism in Scheme 1 is proposed in accordance with experimental findings.

\[ \begin{align*}
AH_2 & \overset{k_1}{\rightarrow} AH^- + H^+ \quad \text{(fast)} \quad \ldots (7) \\
AH^- + Ag^+ & \underset{k_2}{\rightarrow} AH^+ + Ag^0 \quad \text{(slow)} \quad \ldots (8) \\
AH^+ + Ag^+ & \rightarrow A + Ag^0 + H^+ \quad \text{(slow)} \quad \ldots (9)
\end{align*} \]

The above mechanism leads to the rate law

\[ -d[Ag^+] / dt = k'[N_2H_4][Ag^+] / [H^+] \]

where \( k'' = 2k_1k_2 / k_1 + k_3 \)

**Reactions with hydrazine**

The reduction of silver (I)-gelatin complex by hydrazine proceeds through the formation of the intermediate \( N_2H_3^+ \) radical. The formation of \( N_2H_3 \) radical and various short-lived hydronitrogens, (either free radicals or molecules), during the oxidation reactions of hydrazine has been well documented\(^\text{14}\). Here, the first stage involves the formation of \( AgN_2H_4^+ \) in the primary fast reversible step which is followed by the slow and rate-determining step, involving the formation of \( N_2H_4 \) radical. The \( N_2H_3 \) radical is subsequently attacked by another silver (I) ion to give diimide. This diimide then undergoes either a single step, or a series of fast steps (by successive removal of protons), leading to the formation of nitrogen (Scheme 2).

\[ \begin{align*}
Ag^+ + N_2H_4 & \rightarrow AgN_2H_4^+ \rightarrow Ag^0 + N_2H_3 + H^+ \quad \ldots (11) \\
Ag^+ + N_2H_4 & \rightarrow Ag^0 + N_2H_2 + H^+ \quad \ldots (12) \\
2N_2H_2 & \rightarrow N_2 + N_2H_4 \quad \ldots (13)
\end{align*} \]

**Scheme 2**

Rate law (14) can be derived from Scheme 2

\[ -d[Ag^+] / dt = k'[N_2H_4][Ag^+] \]

where \( k'' = 2k_1k_2 / k_1 + k_3 \).

Gelatin itself neither takes part in reduction nor hampers the path of the reaction. As soon as reduction of the silver (I)-gelatin complex starts, bonded gelatin will just enhance the concentration of free gelatin in solution and also stabilize silver sol. Thus gelatin helps to evaluate the mechanisms of reactions of those systems which are readily bonded to gelatin, and easily reduced to their sols.

The reactions involving ascorbic acid have been monitored spectrophotometrically from 700s and the \( N_2H_4 \) reduction from 300s. The absorbance values were insignificant and could not be followed before those prescribed time schedule.

**References**