Kinetics and Mechanism of Reduction of Silver(I) by Ascorbic Acid

By **Sukhdeo Prasad Mushran,*** **M. C. Agrawal, R. M. Mehrotra,** and **R. Sanehi,** Chemical Laboratories, University of Allahabad, Allahabad, India

The kinetics of reduction of silver(I) have been studied in perchloric acid solution using ascorbic acid (AH_2) as the reducing agent. First-order dependences on ascorbic acid and silver(I) concentrations are exhibited, together with an inverse first-order dependence on [H+]. The influence of ionic strength ($I < 0.08$M) is negligible. The activation energy is 10·6 ± 0·2 kcal mol^{-1}. A mechanism for the reduction process is proposed which involves bimolecular rate-determining reaction between ascorbate ion and silver(I).

ASCORBIC ACID is a very potent reducing agent. Its use as an analytical reagent has been reviewed by Erdey and Svehla.[1] Mild oxidising agents oxidise ascorbic acid (AH_2) to dehydroascorbic acid[2] (A). Ag^I may be titrated directly with ascorbic acid using Variamine Blue as indicator.[3,4] The kinetics of reduction of silver(I) by ascorbic acid are now reported and a mechanism governing the reduction process is formulated.

EXPERIMENTAL

Aqueous solutions of silver(I) nitrate and potassium thiocyanate were prepared from AnalaR grade materials (B.D.H.). Potassium thiocyanate solutions were standardised by Volhard's method[5] employing ammonium iron(III) bis(sulphate) as indicator. Ascorbic acid (AH_2) solution was always prepared fresh from a G.P.R. sample (E. Merck) of the reagent and its strength was checked by titration against standard iodine solution using starch as indicator. Perchloric acid (Riedel, AnalaR) was used to maintain hydrogen-ion concentrations. All other reagents used were of analytical grade. Twice-distilled water was used for preparation and dilution of the solutions. Reactions were carried out in dark Jena-glass vessels to avoid photochemical effects.

The progress of the reaction between ascorbic acid and silver(I) was monitored by estimating the residual silver(I) by Volhard's method using aluminium iron(III) bis(sulphate) as indicator. Aliquot portions (5 cm^3) of the reaction mixtures were withdrawn at given intervals of time using pipettes fitted with glass-wool plugs. The stoicheiometry of the reaction was determined as follows. Reaction mixtures containing 1.2×10^{-2}M-ascorbic acid, $[H^+] = 4.0 \times 10^{-2}$M, and 0·50, 1·0, 1·5, 2·0, and 3.0×10^{-2}M-Ag^I were kept at 45 °C for 5 h. The amounts of residual silver(I), estimated by Volhard's method, showed that one mole of ascorbic acid reduces two moles of silver(I) and thus the stoicheiometric equation is as in (1) (A = dehydroascorbic acid), in accord with earlier work.[3,4]

$$2Ag^+ + AH_2 \longrightarrow A + 2Ag^0 + 2H^+ \qquad (1)$$

RESULTS

The reduction of silver(I) by ascorbic acid was investigated at different initial concentrations of the reactants, ascorbic acid being in excess. Pseudo-first-order rate constants (k_1) were calculated from gradients of linear plots of log $[a/(a - x)]$ against time [a and $(a - x)$ are initial and residual silver(I) concentrations]. The gradients showed a uniform increase with increase in ascorbic acid concentration (Table 1 and Figure 1). Values of the rate constants lie within the error range ±2·5%. The reaction, therefore, exhibits a first-order dependence on ascorbic acid concentration and the average second-order rate constant, k_2, was $(4.25 \pm 0.2) \times 10^{-2}$ l mol^{-1} s^{-1} under the conditions of Table 1.

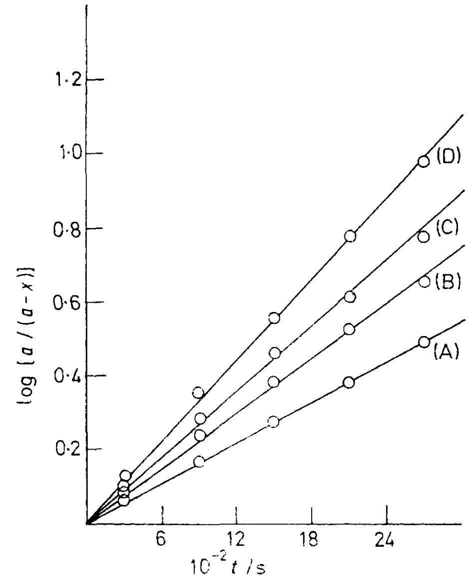

FIGURE 1 First-order rate plots at 35 °C and $[H^+] = 0.1$M for reduction of Ag^I by ascorbic acid: $[Ag^+] = 1.0 \times 10^{-3}$M and $[AH_2]$ = 10 (A), 12 (B), 16 (C), and 20×10^{-3}M (D)

TABLE 1

Effect of reactant concentration at 35 °C [a]

Expt. no.	$10^4[Ag^I]$/M	$10^3[AH_2]$/M	$10^4k_1/s^{-1}$	10^2k_2 [b]/ l mol^{-1} s^{-1}
(1)	10	10	4·2	4·2
(2)	10	12	5·5	4·6
(3)	10	16	6·7	4·2
(4)	10	20	8·3	4·2
(5)	8	10	4·4	4·4
(6)	12	10	4·2	4·2
(7)	16	10	4·0	4·0
(8)	20	10	4·2	4·2

[a] In the presence of 0·1M-H^+. [b] $k_2 = k_1/[AH_2]$.

The effect of hydrogen-ion concentration on the rate of reduction of Ag^I by ascorbic acid was studied at constant ionic strength, $[NaClO_4] = 0.5$M (Table 2). An inverse first-order dependence on $[H^+]$ was established from linear

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plots of log k_2 against log [H^+] which had gradients of −1 (Figure 2).

TABLE 2

Dependence of rate of reaction on hydrogen-ion concentration [a]

Expt. no.	$10^2[H^+]/M$	10^2k_2/l mol^{-1} s^{-1} at 30 °C	35 °C
(1)	4·0	4·3	5·5
(2)	6·0	3·2	4·2
(3)	8·0	2·5	3·3
(4)	10·0	1·9	2·5
(5)	12·0	1·5	1·9

[a] [AH_2] = 1·0 × 10^{-2}, [Ag^+] = 1·0 × 10^{-3}, and I = 0·5M.

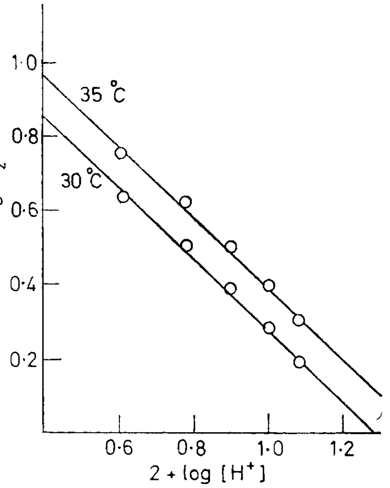

FIGURE 2 Plots of log k_2 against log [H^+] at [AH_2] = 1·0 × 10^{-2}, [Ag^+] = 1·0 × 10^{-3}, and I = 0·5M

The influence of addition of 0—0·04M-$NaClO_4$ to the initial reactant solutions at ionic strength 0·04M was negligible (Table 3). However, at higher concentrations of $NaClO_4$ (I > 0·11M) a retardation in the rate of reaction was observed. The effect of temperature on the rate of reaction was fairly marked (Table 4); the energy of activation (E_a) was 10·6 ± 0·2 kcal mol^{-1}.*

TABLE 3

Influence of ionic strength at 25 °C

Total ionic strength I/M	10^2k_2 [a]/l mol^{-1} s^{-1}
0·04	3·9
0·05	3·9
0·06	3·8
0·07	3·8
0·08	3·8

[a] [H^+] = 0·04M.

TABLE 4

Temperature dependence

T/K	10^4k_1
303	3·1
308	4·2
313	5·4
318	6·9

DISCUSSION

The reduction of silver(I) by ascorbic acid involves transfer of two electrons giving dehydroascorbic acid as product. Reductions by ascorbic acid have been shown to take place through intermediate formation of the free radical $AH^{\bullet}$ and show an inverse first-order dependence on hydrogen-ion concentration.[6-9] The formation of this radical has also been postulated by Yamazaki [10] and Grinstead.[11] Silver(I) is generally reduced to silver metal,[12,13] and, according to McAndrew *et al.*,[14] reduction of Ag^I by carbon monoxide exhibits first-order dependences on [Ag^+] and [CO] and an inverse first-order dependence on [H^+]. Similar results have been reported for the reduction of Ag^I by *p*-hydroxyphenylglycine.[15]

For the reduction of silver(I) by ascorbic acid in an acidic medium, a mechanism is proposed which involves formation of an intermediate ascorbate anion (AH^-) from AH_2 in a primary fast reversible step, (2). The intermediate ion then interacts with Ag^I in a slow and rate-determining step, (3). Step (3) is followed by a

$$AH_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} AH^- + H^+ \quad \text{fast} \qquad (2)$$

$$AH^- + Ag^+ \xrightarrow{k_4} AH^{\bullet} + Ag^0 \quad \text{slow} \qquad (3)$$

fast step, (4), in which the free radical ($AH^{\bullet}$) is attacked by a second silver(I) ion to give the product dehydroascorbic acid. After applying the steady-state treatment

$$AH^{\bullet} + Ag^+ \xrightarrow{k_5} A + Ag^0 + H^+ \qquad (4)$$

to $AH^{\bullet}$ and making the approximation $k_{-3}[H^+] \gg k_4[Ag^+]$, rate law (5) is obtained. This rate law predicts

$$-d[Ag^+]/dt = k'[AH_2][Ag^+]/[H^+] \qquad (5)$$
$$\text{where} \quad k' = 2k_3k_4/k_{-3}$$

first-order dependences on both ascorbic acid and Ag^I concentrations and an inverse first-order dependence on [H^+], in agreement with experimental results.

In the proposed mechanism, the rate-controlling step involves interaction between oppositely charged ions and thus should correspond to a negative primary-salt effect. However, addition of salt will involve an increase in concentration of ascorbate ion and consequently a positive secondary-salt effect. If both

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* 1 cal = 4·184 J.

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primary- and secondary-salt effects are determined by charge alone (at low *I*) there should be no net salt effect. The salt-effect data (Table 3) at low ionic strength are consistent with this interpretation. Further, the observed retardation by salt at higher ionic strengths ($I > 0{\cdot}11\text{M}$) seems reasonable for, in these cases, a charge-independent term involving direct proportionality to ionic strength would be more significant.

We thank the Indian National Science Academy and University Grants Commission, New Delhi, for Research Fellowships (to R. M. M. and R. S.).

[3/1434 *Received*, 9*th July*, 1973]