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Kinetics and Mechanism of Oxidation of Ascorbic Acid by Selenium(IV)

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Kinetic studies on the oxidation of ascorbic acid (AH_2) by selenium(IV) have been made in acidic medium. The reaction showed first order dependence with respect to ascorbic acid and selenium(IV) while an inverse first order dependence was noticed with respect to hydrogen ion concentration. The change in ionic strength showed no significant effect on the reaction rate. The relevant thermodynamic parameters have been computed and a plausible mechanism consistent with the experimental results has been proposed.

Key Words: Spectrophotometric, Kinetic, Mechanism, Oxidation, Ascorbic Acid, Selenium.

INTRODUCTION

The study of oxidation of ascorbic acid by different metal ions, *viz.*, osmium (VIII)[1], copper(II) and iron(III)[2], iridium(III)[3], chromium(VI)[4], vanadium(V)[5], silver(I)[6] and mercury(II)[7] has been reported earlier. Ascorbic acid is a weak acid ($k_{a1} = 6{\cdot}2 \times 10^{-5}$) and its acidic properties are due to enediol formation at third carbon atom[8]. The oxidation of ascorbic acid (AH_2) involves a two electron change to yield the product, dehydroascorbic acid[9]. The redox potential[10] of ascorbic acid-dehydroascorbic acid system was found to be +0.185 V against a normal hydrogen electrode at 21°C and at pH 7.0.

EXPERIMENTAL

Aqueous solution of selenium(IV) tetrachloride (E. Merck) of a known concentration was prepared in double distilled water containing a known amount of perchloric acid, which was stored in borosil glass flask, darkened black from outside to avoid photochemical effects, if any. Fresh solution of ascorbic acid of known concentration was prepared before starting a particular experiment. The solutions of known concentration of potassium chloride and potassium sulphate were prepared in double distilled water. The kinetics of the oxidation of ascorbic acid was studied under the verified Beer's law range for selenium(IV) concentration at λ_{max} 415 nm. The total volume of the reaction mixture was kept 50 mL. An aliquot of 5 mL of the reaction mixture was withdrawn at known time intervals to measure the optical density in order to follow the progress of the reaction spectrophotometrically using an ELICO-Digital spectrophotometer model no.

CL-27. The studies were made at $[Se(IV)] = 12{\cdot}0 \times 10^{-4}$ M, $[AH_2] = 14{\cdot}4 \times 10^{-3}$ M, $[H^+] = 6{\cdot}0 \times 10^{-3}$ M and $I = 5{\cdot}0 \times 10^{-2}$ M KCl in the temperature range 15–25°C. The variations in concentration are mentioned in Tables 1 and 2.

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometry of the reaction between ascorbic acid and selenium(IV) tetrachloride was experimentally obtained under the conditions $[H^+] = 6{\cdot}0 \times 10^{-3}$ M, $I = 5{\cdot}0 \times 10^{-2}$ M KCl at 20°C, which may be represented as follows:

$$C_6H_8O_6 + \underset{\text{Se(IV)}}{SeCl_4} = C_6H_8O_6 + \underset{\text{Se(II)}}{SeCl_4^{2-}} + 2H^+$$

Effect of Changing Selenium (IV) Concentration

The experiments were performed with the variation of [Se(IV)] between $(5.0–15.0) \times 10^{-4}$ M and the values of rate constants (k_1) are represented in Table-1

TABLE-1

VALUES OF RATE CONSTANTS AT $[AH_2] = 14{\cdot}4 \times 10^{-3}$ M, $[H^+] = 6{\cdot}0 \times 10^{-3}$ M and $I = 5{\cdot}0 \times 10^{-2}$ M KCl

$[Se(IV)] \times 10^{-4}$ M	$k_1 \times 10^2$ min^{-1}		
	15°C	20°C	25°C
5.0	5.62	9.09	11.96
10.0	5.61	9.10	11.96
12.0	5.61	9.09	11.99
15.0	5.62	9.11	11.99

The above data indicate that the reaction follows a first order dependence with respect to the oxidant selenium(IV).

Effect of Changing Ascorbic Acid (AH_2) Concentration

The experiments were performed with the variation of $[AH_2]$ between $(10.0–25.0) \times 10^{-3}$ M. The values of rate constants k_1 and k_2 obtained are reported in Table-2.

TABLE-2

VALUES OF RATE CONSTANTS AT $[Se(IV)] = 12.0 \times 10^{-4}$, $[H^+] = 6{\cdot}0 \times 10^{-3}$ M and $I = 5{\cdot}0 \times 10^{-2}$ M KCl

$[AH_2] \times 10^{-3}$ M	$k_1 \times 10^{-2}$ min^{-1}			k_2 dm^{-3} mole^{-1} min^{-1}		
	15°C	20ÉC	25°C	15°C	20°C	25°C
10.0	3.95	6.11	7.96	3.95	6.11	7.96
14.4	5.74	9.10	11.95	3.99	6.32	8.30
20.0	7.71	12.07	15.79	3.86	6.04	7.90
25.0	9.53	14.48	19.54	3.82	5.80	7.82

The above data show that the first order rate constants increase proportionately with the increase in ascorbic acid concentration. The linear plots of log [a/((a–x)] *vs.* time (Fig. 1), also indicate that the reaction is of first order with respect to ascorbic acid concentration. The bimolecular rate constant (k_2) has also been calculated and the values obtained show that the total order of reaction is two, being first order both in ascorbic acid and selenium(IV).

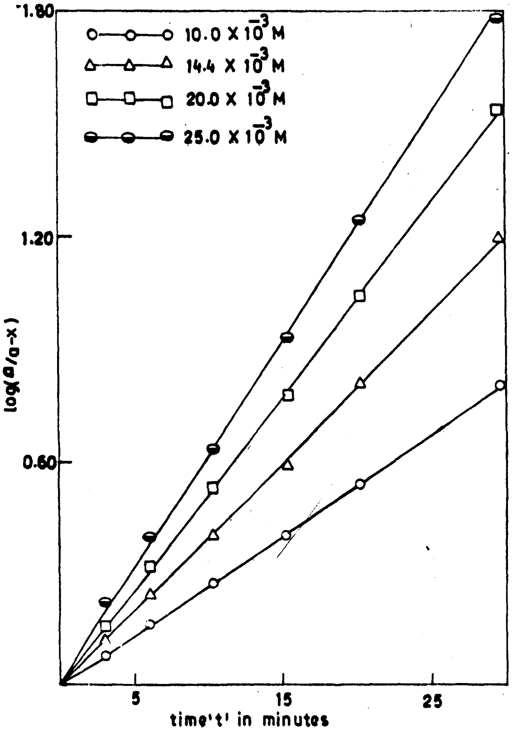

Fig. 1. Effect of changing ascorbic acid concentration at 20°C

Effect of Changing Hydrogen Ion Concentration

The effect of hydrogen ion concentration has been examined at the variation of [H^+] between (4·0–10·0) × 10^{-3} M. The rate of the oxidative process was observed highly susceptible to the change in [H^+]. The plots of log k_2 *vs.* log [H^+] (Fig. 2) are linear with a negative slope of approximately 1, indicating that the reaction has an inverse first order dependence with respect to the hydrogen ion concentration.

Effect of Changing Ionic Strength

The change in ionic strength by KCl and K_2SO_4 between (2·5–10·0) × 10^{-2} M showed no significant effect on the rate of oxidation.

Effect of Changing Temperature

The effect of changing temperature was examined in the range 15–30°C. The values of the various activation parameters, *viz.*, energy of activation (E_a), frequency factor (A), entropy of activation (ΔS_a) and enthalpy of activation (ΔH_a) were computed as 67.4 kJ $mole^{-1}$, $9{\cdot}05 \times 10^{10}$ $dm^3\, mole^{-1}\, sec^{-1}$, -39.22 J K^{-1} $mole^{-1}$ and 64.94 kJ $mole^{-1}$, respectively.

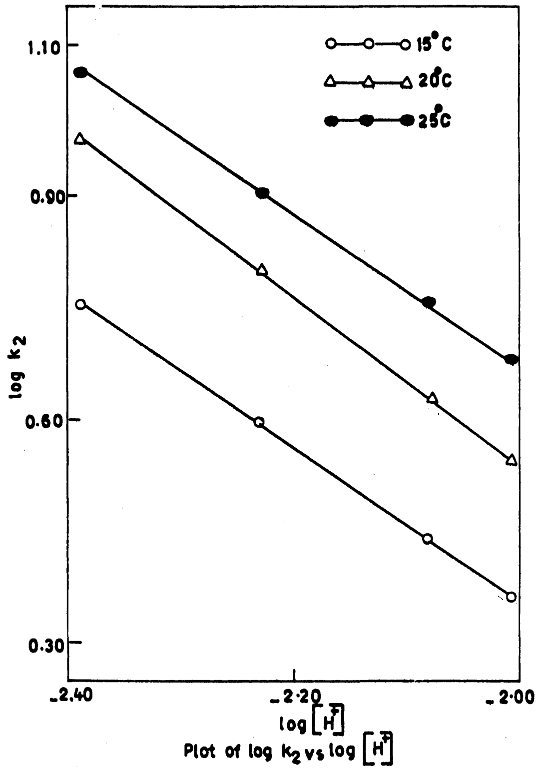

Fig. 2. Effect of changing hydrogen ion concentration

Reaction Mechanism: The oxidation of ascorbic acid (AH_2) by selenium (IV) involves an overall two-electron transfer, in which selenium(IV) is reduced to selenium(II), while ascorbic acid changes to dehydroascorbic acid (A). In general, oxidation of ascorbic acid takes place *via* the formation of ascorbate ion (AH^-)[9-12], which is undoubtedly formed in a reversible fast step through the enolisation of ascorbic acid[8] as follows:

$$AH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AH^- + H^+ \text{ (fast)} \tag{1}$$

The ascorbate ion thus formed in reaction (1) is attacked by selenium(IV) in slow process, resulting in the formation of selenium(III) and ascorbate free radical ($AH^{\bullet}$). This rate detemining step may be expressed as:

$$AH^- + SeCl_4 \xrightarrow{k_2} AH^{\bullet} + SeCl_4^- \text{ (slow)} \tag{2}$$

The reaction (2) is eventually followed by the fast step in which ascorbate free radical reacts with selenium(III) to form dehydroascorbic acid (A) and selenium (II) as the product of the reaction as under:

$$AH^{-} + SeCl_4^{-} \xrightarrow{k_3} SeCl_4^{2-} + A + H^{+} \text{ (fast)} \tag{3}$$

The formation of free radical ($AH^{\bullet}$) was confirmed by the test as reported earlier[13]

The proposed mechanism for the reduction of selenium(IV) to selenium(II) shows clearly an overall two-electron transfer through successive one-electron changes in a stepwise manner[14] as:

$$Se(IV) \rightarrow Se(III) \rightarrow Se(II)$$

The differential equation for the consumption of Se(IV) may be expressed as follows:

$$\frac{d[Se(IV)]}{dt} = k_2[Se(IV)][AH^{-}] \tag{4}$$

Applying steady state treatment with respect to AH^{-}, we get

$$[AH^{-}] = \frac{k_1[AH_2]}{k_{-1}[H^{+}] + k_2[Se(IV)]} \tag{5}$$

Now, substituting the value of $[AH^{-}]$ from equation (5) in equation (4), we get

$$\frac{d[Se(IV)]}{dt} = \frac{k_1k_2[AH_2][Se(IV)]}{k_{-1}[H^{+}] + k_2[Se(IV)]} \tag{6}$$

Since reaction (2) is slow and rate determining, hence $k_2 < k_1$ and thus for a *fairly* large concentration of hydrogen ions, the approximation $k_{-1}[H^{+}] \gg k_2[Se(IV)]$ is valid. Therefore the rate law equation (6) gets reduced to:

$$\frac{d[Se(IV)]}{dt} = \frac{k_1k_2[AH_2][Se(IV)]}{k_{-1}[H^{+}]} \tag{7}$$

The above rate law equation obtained for the reaction studied indicates a first order dependence both in ascorbic acid and selenium(IV) and an inverse first order dependence in hydrogen ions. These facts are supported by the experimental kinetic data obtained.

The involvement of a univalent negative ascorbate ion and a neutral molecule in the rate controlling reaction(2) is in accordance with the observed insignificant effect of change in ionic strength on the reaction rates. The mechanism suggested is further supported by the value of frequency factor ($9{\cdot}05 \times 10^{-10}$) dm^3 $mole^{-1}$ sec^{-1}, as well as by the negative value of entropy of activation (-39.22 J K^{-1} $mole^{-1}$).

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