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Kinetics and Mechanism of Oxidation of Ascorbic Acid by Ruthenium(III)

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Oxidation of ascorbic acid (AH_2) by ruthenium(III) has been investigated kinetically in acidic medium, which indicated a first order dependence with respect to ascorbic acid and ruthenium(III) and an inverse order dependence with respect to hydrogen ion concentration. An insignificant effect on the reaction rate was observed with a change in ionic strength. Energy of activation and entropy of activation have been calculated and an appropriate mechanism consistent with the experimental data has also been formulated.

Key Words: Spectrophotometric, Kinetic, Mechanism, Oxidation, Ascorbic acid, Ruthenium(III)

INTRODUCTION

Ascorbic acid (AH_2) is a strong reducing agent in aqueous solutions[1] and in general has been used for the titrimetric determination of several inorganic and organic compounds[2]. It is well established that the acidic property of the ascorbic acid is due to enediol formation at the third carbon atom[3]. Thus the oxidation of ascorbic acid involves a two electron change to yield the product dehydroascorbic acid[4]. The redox potential[5] 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. The study of oxidation of ascorbic acid by different metal ions, *viz.*, osmium(VIII)[6], copper(II) and iron(III)[7], iridium(IV)[8], chromium(VI)[9], vanadium(V)[10], silver(I)[11], mercury(II)[12] and selenium(IV)[13] have already been reported. The work described here relates to the oxidation of ascorbic acid by ruthenium(III).

EXPERIMENTAL

Ruthenium(III) chloride (E. Merck) solution of non-concentration was prepared in bidistilled water containing a known amount of perchloric acid. Freshly prepared solution of ascorbic acid was exclusively used before starting any experiment. KCl (Qualigen), K_2SO_4 (Qualigen) and perchloric acid (S. Mrck) solutions of known concentration were prepared in double distilled water.

Experimental details for investigation of kinetic studies in the process of oxidation of ascorbic acid were identical to those described earlier[13]. All the absorbance measurements were undertaken in the verified Beer's law range for ruthenium(III) concentration at λ_{max} of 460 nm.

RESULTS AND DISCUSSION

Effect of Changing Ruthenium(III) Concentration: The values of rate constants (k_1) for the variation of Ru(III) concentration are reported in Table-1.

TABLE-1

VALUES OF RATE CONSTANTS (k_1) at $[AH_2] = 8.3 \times 10^{-3}$ M, $[H^+] = 5.0 \times 10^{-1}$ M and $I = 10.0 \times 10^{-2}$ M KCl

$[Ru(III)] \times 10^4$ M	$k_1 \times 10^3$ min^{-1} at different temperatures (°C)			
	15	20	25	30
4.0	7.32	12.39	19.05	32.54
6.7	7.29	12.40	19.06	32.54
8.0	7.30	12.40	19.06	32.60
10.0	7.34	12.36	19.06	32.58

A perusal of Table-1 indicates a first order dependence of the reaction with respect to ruthenium(III).

Effect of Changing Ascorbic Acid (AH_2) Concentration: The values of rate constants k_1 and k_2 for the change in ascorbic acid concentration are recorded in Table-2.

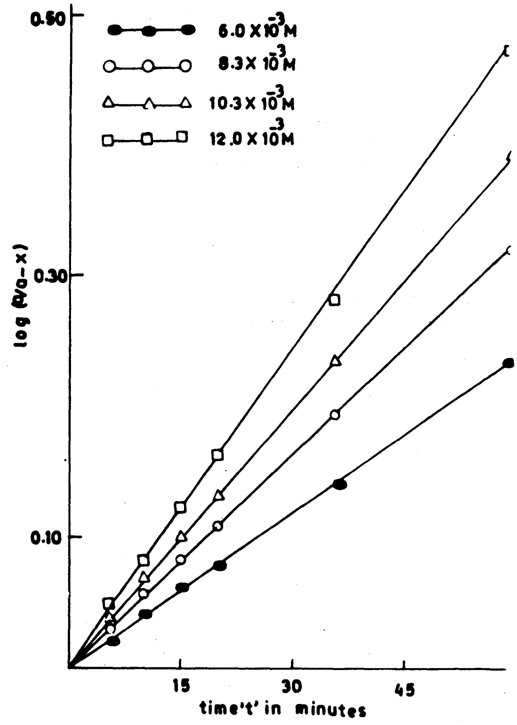

Fig. 1. Plot of log (a/a-x) vs time 't' effect of changing ascorbic acid concentration at 20°C.

TABLE-2

VALUES OF RATE CONSTANTS (k_1 AND k_2) AT [Ru(III)] = 6.7×10^{-4} M, $[H^+] = 5.0 \times 10^{-1}$ M and I = 10.0×10^{-2} M KCl

$[AH_2] \times 10^3$ M	$k_1 \times 10^3$ min^{-1} at different temp. (°C)				k_2 dm^3 mole^{-1} min^{-1} at different temp. (°C)			
	15	20	25	30	15	20	25	30
6.0	5.37	8.81	13.86	23.43	0.90	1.47	2.31	3.91
8.3	7.21	12.56	19.04	32.58	0.87	1.51	2.30	3.93
10.0	8.83	15.02	23.14	39.14	0.88	1.50	2.31	3.91
12.0	10.67	18.16	27.81	46.80	0.90	1.51	2.32	3.90

It is observed in Table-2 that the first order rate constants increase proportionately with the increase in ascorbic acid concentration, showing a first order dependence with respect to $[AH_2]$, which is further supported by the linear plots of log $[a/(a - x)]$ *vs.* time (Fig. 1). The total order of reaction is two, *i.e.*, first order in ascorbic acid as well as in ruthenium(III) which is evident from the calculated values of bimolecular constants (k_2).

Effect of Changing Hydrogen Ion Concentration: The effect of change of $[H^+]$ between $(1.0–7.0) \times 10^{-1}$ M shows the reaction is significantly influenced by 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 $[H^+]$.

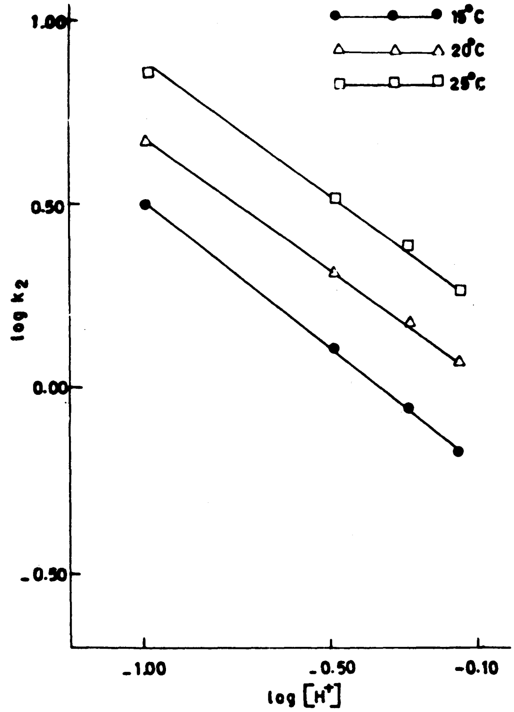

Fig. 2. Plot of log k_2 vs. log $[H^+]$ effect of changing hydrogen ion concentration

Effect of Changing Temperature: In the temperature range of 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 59.3 kJ $mole^{-1}$, 9.56×10^8 dm^3 $mole^{-1}$ sec^{-1}, –76.98 J K^{-1} $mole^{-1}$ and 56.84 kJ $mole^{-1}$, respectively.

Effect of Changing Ionic Strength: No significant effect on rate of oxidation was observed by KCl and K_2SO_4 between $(2.5\text{–}20.0) \times 10^{-2}$ M.

Stoichiometry: The stoichiometry of the oxidation reaction between ascorbic acid and ruthenium(III) chloride was experimentally obtained under the conditions $[H^+] = 5.0 \times 10^{-1}$ M, $I = 10.0 \times 10^{-2}$ M KCl at 20°C, which may be represented as follows:

$$\underset{}{C_6H_8O_6} + \underset{Ru(III)}{2RuCl_3} = C_6H_6O_6 + \underset{Ru(II)}{2RuCl_3^-} + 2H^+$$

Reaction Mechanism

The oxidation reaction shows an overall two electron transfer as ascorbic acid change to dehydroascorbic acid. In the course of oxidation reaction, the first step involves the formation of ascorbate ion (AH^-) in a reversible fast step through the enolization of ascorbic acid[3–6] which may be represented as under:

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

The second and rate determining step involves the interaction between ascorbate ion and ruthenium(III) trichloride, whereby ascorbate free radical is formed accompanied by reduction of Ru(III) to Ru(II) as follows:

$$AH^- + \underset{Ru(III)}{RuCl_3} \xrightarrow{k_2} \underset{Ru(II)}{RuCl_3^-} + AH^\bullet \qquad \text{(slow)} \tag{2}$$

$AH^\bullet$ formed in step 2 as an intermediate which further reacts with another molecule of $RuCl_3$ in a fast step to give dehydroascorbic acid and $RuCl_3^-$ in step-3:

$$AH^\bullet + \underset{Ru(III)}{RuCl_3} \xrightarrow{k_3} \underset{Ru(II)}{RuCl_3^-} + A + H^+ \qquad \text{(fast)} \tag{3}$$

The formation of free radical ($AH^\bullet$) was also confirmed by the test as reported earlier[14]. Establishing the differential equation for the consumption of ruthenium(III), the rate law may be represented as follows:

$$\frac{d[Ru(III)]}{dt} = [Ru(III)]\{k_2[AH^-] + k_3[AH^\bullet]\} \tag{4}$$

Applying the steady state treatment with respect to $[AH^-]$ and $[AH^\bullet]$, we get:

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

and

$$[AH^\bullet] = \frac{k_1k_2[AH_2]}{k_3\{k_{-1}[H^+] + k_2[Ru(III)]\}} \tag{6}$$

Now, substituting the values of $[AH^-]$ and $[AH^\bullet]$ from equation (5) and (6) in equation (4), we obtain:

$$\frac{d[Ru(III)]}{dt} = \frac{2k_1k_2[Ru(III)][AH_2]}{k_{-1}[H^+] + k_2[Ru(III)]} \tag{7}$$

In the proposed mechanism, step-2 is slow and rate determining and therefore $k_2 \ll k_{-1}$. Hence, for fairly large $[H^+]$, it may be assumed that $k_{-1}[H^+] \gg k_2[Ru(III)]$. Thus, the overall rate law equation 7 may be transformed to:

$$\frac{d[Ru(III)]}{dt} = \frac{2k_1k_2[Ru(III)][AH_2]}{k_{-1}[H^+]} \tag{8}$$

Substituting k' for $2k_1k_2$ in equation (8), the final rate law equation may be written as:

$$\frac{d[Ru(III)]}{d} = \frac{k'[Ru(III)][AH_2]}{k_{-1}[H^+]} \tag{9}$$

The above rate law equation (9) shows a first order dependence both in ascorbic acid and ruthenium(III) trichloride and inverse first order dependence in $[H^+]$, which is in close agreement with the observed experimental kinetic data. The results of the effect of the addition of neutral salts, *viz.*, potassium chloride and potassium sulphate, indicate no significant effect on the rate of reaction. The values of entropy of activation (ΔS_a) and frequency factor (A) have been calculated as -76.68 JK $mole^{-1}$ and 9.56×10^8 dm^3 $mole^{-1}$ sec^{-1}, respectively, which also indicate the involvement of a natural molecule of $RuCl_3$ and univalent negative ascorbate ion in the rate controlling step-2, as proposed in the above mechanism.

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