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The Influence of Transition Metal Ions on the Kinetics of Ascorbic Acid Oxidation by Methylene Blue in Strongly Acidic Media

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The kinetics of the oxidation of L-ascorbic acid (H_2 A) by methylene blue was investigated in strongly acidic media over the temperature range 22-40°C. The kinetic studies were carried out as a function of different variables like concentration, pH, ionic strength and temperature. The rate was found to be a linear relation with [H_2 A], [M.B.] and [H^+]. Ionic strength dependence formation indicated complex formation by monocationic and anionic species in solution. The reaction rate was greatly catalyzed by the presence of trace amounts of copper (II) ion. Possible mechanisms for the catalyzed and uncatalyzed reactions are proposed. Kinetic evidence for a specific catalytic effect by binding of alkali metal ions to oxidant is also reported. The derived rate equations are in good agreement with the experimental observations.

Introduction

The oxidation of ascorbic acid (Vitamin C) is a very important redox reaction, as it has interesting biological properties and is also a powerful reductant. Ascorbic acid is a lactone with a 2,3-endiol group. The enolic group imparts acidity to the molecule; the enol group at position 3 has a pK_a of 4.1 and the enol at position 2 has a pK_a of 11.6. It is very effective as a reducing agent and is quantitatively reversibly oxidized in aqueous solution by different oxidizing agents. Ascorbic acid is susceptible to oxidation in both acidic and basic media. The products of the oxidation depend largely on the pH of the reaction; however, its oxidation by various oxidizing agents in acid solution produces dehydroascorbic acid, a lactone whose ring can be easily hydrolyzed to give the free carboxylic group[1].

A number of papers have been devoted to the oxidation of ascorbic acid in acidic and basic media with various inorganic[2−7] and organic substrates[8,9]. However, the reduction of organic dyestuff with ascorbic acid is very seldom reported[10]. Recently, Strizhak studied the kinetics of the catalytic and uncatalytic oxidation of ascorbic acid by methylene blue, a cationic organic dyestuff, and reported the effects of the concentration of the reactants and pH of the medium on the reaction[11,12]. However, his reports were somewhat limited in kinetic and mechanistic details. We have therefore extended the study to involve a new pH range, ascorbic acid concentration, salt effects, ionic strength and temperature. Most interesting,

however, is our observation that number of transition metals catalyzed the same reaction with variable capability.

The present investigation describes the results of a comprehensive comparative study of the different catalyzed oxidation reactions of ascorbic acid by methylene blue and proposes a new reaction mechanism based partially on experimental results and partially on previously published results[11,12].

Reagents and Equipment

A.R. grade ascorbic acid, methylene blue, potassium chloride, lithium chloride, sodium chloride, citric acid and disodium hydrogen phosphate were used without further purification. All solutions were freshly prepared in double distilled water and kept in darkness. A stock solution of H_2A and methylene blue were prepared by dissolving appropriate amounts of these compounds in citric acid-disodium hydrogen phosphate buffer system at pH = 2.20. pH measurements were performed with a digital pH meter (± 0.01 pH) equipped with combined glass and calomel electrodes. The desired temperature (± 0.1°C) was maintained in the reaction cell of the spectrophotometer by water circulating thermostatic bath.

Experimental

An excess of ascorbic acid was used in all cases in order to achieve pseudo-first order kinetic conditions. The corresponding rate constants were evaluated from the plots of ln (A_t-A_∞) vs. time.

Results and Discussion

[H_2A] Dependence

Initial concentrations of the reductant in the range $0.5x10^{-2}$ to $3x10^{-2}$ mol. L^{-1} were used to study the influence of [H_2A] with fixed 1.0 x 10^{-5} mol. L^{-1}methylene blue at 32°C. The pH of the solution was 2.20. The pseudo-first order rate constant increasesd with increasing ascorbate concentration. The plot of k_{obs} vs. $[H_2A]_t$ was linear with a small intercept (Fig. 1). This result implies that the reaction is first order with respect to ascorbate concentration. The rate-determining step of the reaction can therefore be of the form of eq. (1):

$$H_2A + [M.B.] \leftrightarrow \text{Products} \quad (1)$$

The product of this reaction is M.B.-Ascorbate intermediate.

Effect of Methylene Blue

The effect of methylene blue concentration, shown in Fig. 2. The plots of k_{obs} vs. methylene blue concentration ranging from (0.5-2.0) × 10^{-5} mol. L^{-1} show a linear relationship between k_{obs} and [M.B.]. This fact reveals also a first order dependence in the oxidant.

An overall second order rate equation will be expressed in the form

$$-d[M.B.]/dt = k_{obs}[M.B.] = k_2[H_2A]_t[M.B.]$$

where k_2 is the 2^{nd} order rate constant, and $[H_2A]_t$ indicates total concentration of all the forms of L-Ascorbic acid and can be set as $[H_2A] + [HA^-]$ in the working pH.

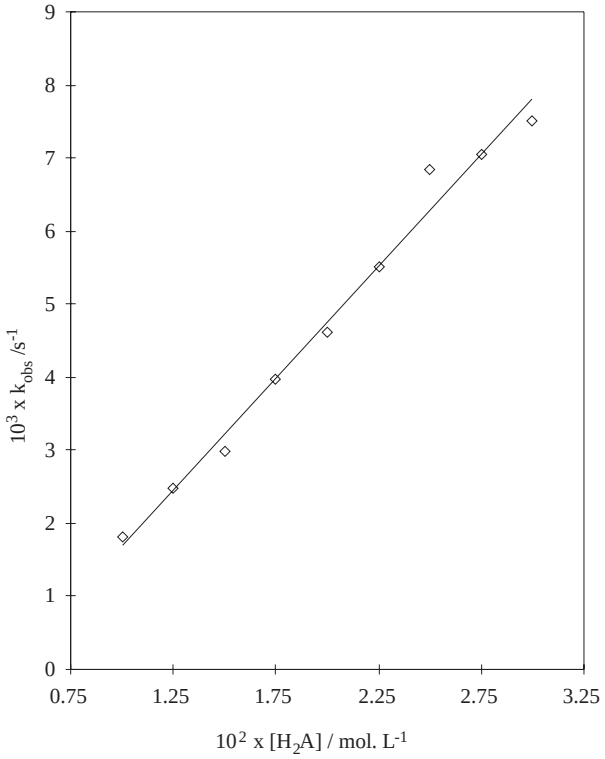

Figure 1. Plot of k_{obs} vs. [H_2A] showing the pseudo-first-order dependence on the reductant. [M.B]=1×10^{-5} mol. L^{-1}; pH=2.20; T=32°C

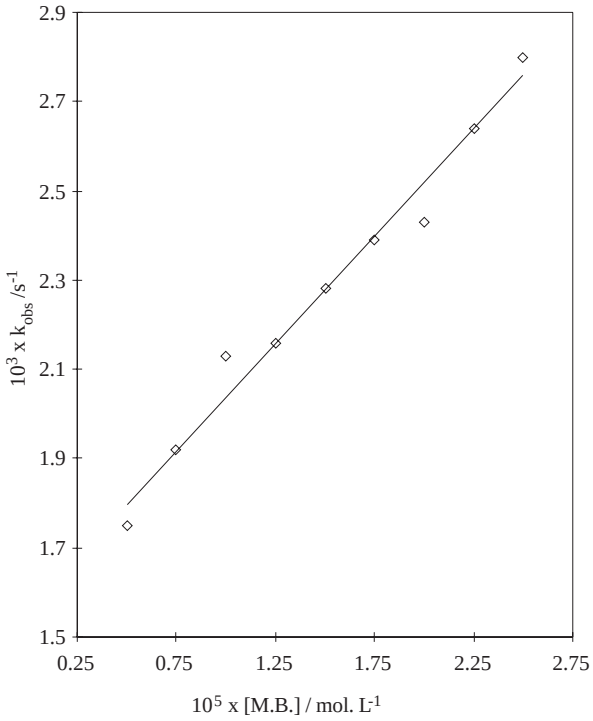

Figure 2. Plot of k_{obs} vs. [M.B] showing the pseudo-first-order dependence on the oxidant. [H_2A]=1.5×10^{-5} mol. L^{-1}; pH=2.20; T=32°C

Effects of Ionic Strength

The effect of ionic strength on the reaction kinetics was investigated using varying concentrations of added neutral salts of the type YCl (where Y = Li^+, Na^+, K^+) at pH 2.20 and 32°C. Figure 3 shows that [K^+] had no effect on k_{obs} while the plots of k_{obs} vs. [Li^+] and [Na^+] gave straight lines and slopes declined from 7.06 to 2.23 s^{-1}

Scheme 1 at pH = 2.20

$$H_2A \underset{k_a}{\overset{k_a}{\rightleftharpoons}} AH^- + H^+ \qquad \text{(I)}$$

$$H_2A + M.B^+ \xrightarrow{k_1} HA^\bullet + M.B^\bullet + H^+ \qquad \text{(II)}$$

$$AH^- + M.B^+ \xrightarrow{k_2} C \qquad \text{(III)}$$

$$C \xrightarrow[fast]{k_3} M.B^+ + HA^- \qquad \text{(IV)}$$

$$[Y^+] + [M.B^+] \underset{k_{YMB}}{\overset{k_{YMB}}{\rightleftharpoons}} Y[M.B]^+ \qquad \text{(V)}$$

$$M.B^\bullet + HA^\bullet \xrightarrow[fast]{k_4} MBH + A \qquad \text{(VI)}$$

$$AH^- + Y[M.B]^+ \xrightarrow{k_5} AH^\bullet + Y[M.B] \qquad \text{(VII)}$$

$$AH^\bullet + Y[M.B] \xrightarrow[fast]{k_6} MBH + A + Y^+ \qquad \text{(VIII)}$$

$$-d[M.B^+]/dt = [M.B^+]\{k_1[H_2A] + k_2[AH] + k_{YMB}[Y^+](k'_{YMB}k_{YMB}[Y^+] / k'_{YMB} + k_5[AH^-])\}$$

where $k_1[H_2A] + k_2[AH^-] = k_{nc}$

and $k_5 k_{YMB}[AH^-][Y^+] / (k'_{YMB} + k_5[AH^-]) = k_c$

so $k_{obs} = k_{nc} + k_c [Y^+]$ (2)

Steps (I-V) have already been suggested [11] but they did not take into account all the experimental observations related to salt effect in the reported work.

For the specific catalysis by two alkali metal ions steps (VI-VIII) must also be taken.

According to equation 2, the plots of the k_{obs} values vs. $[Y^+]$ give the values of slope (k_c) and intercept (k_{nc}). The value of k_{nc} remains the same for all the metal ions utilized, but the slope k_c decreases from Li^+ to K^+, which supports the suggestion of a specific catalytic effect by ion pair formation. The values for the association constant k_{YMB} of equilibrium step (V) corresponding to that of $[Li^+]$ are calculated and reported in Table 1.

Table 1. Ordinates k_{nc} and k_c of the linear regression eq. (2) according to the data of Fig. 3.

Y^+	k_{nc}/s^{-1}	k_c/s^{-1}	K_{YMB}/s^{-1}	Polarizability $a^+_M/10^{24}C\ m^3$
Li^+	1.52	7.06	1.0	0
Na^+	1.51	2.23	0.32	0.17
K^+	1.50	0	-	0.82

Catalysis by ion pairing of alkali metal ions is a general feature common to many chemical reactions between two charged species or an uncharged and a charged species [13–15]. In our studies, results show that catalysis by ion pair formation increased the electronic repulsion between the reactants, since the ion association constant k_{YMB} became smaller with increasing cation size.

According the Debye-Huckel equation, the ionic strength dependence plot of $\log k_1$ vs. $\mu^{1/2} / (1+ \mu^{1/2})$ gave a negative slope, confirming that complex formation takes place through the interaction of monocationic species and an anionic species, (eq. 3) [16].

pH Effect

Kinetic runs were carried out at 32°C in citric acid/disodium hydrogen phosphate buffer systems with the fixed ascorbic acid concentration over the pH range 2.00-3.00 at a constant ionic strength of 0.1 M KCl. The rate of complex formation was found to have linear dependence on $[H^+]$. This dependence is explained in terms of eq. (3) and (4).

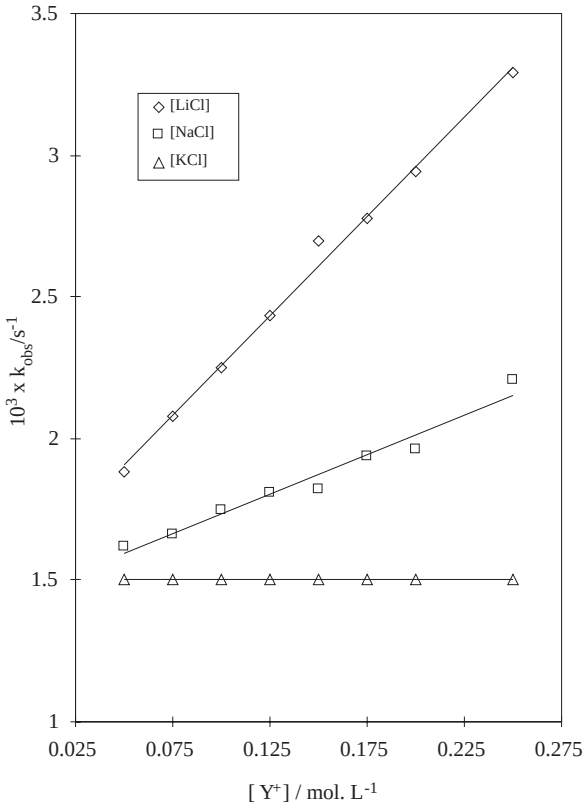

Figure 3. Plot of k_{obs} vs. alkali-metal ion concentration showing a special effect. [M.B.]=1 × 10^{-5} mol. L^{-1} [H_2A]=1.5 × 10^{-2} mol. L^{-1}; pH=2.20; T=32°C

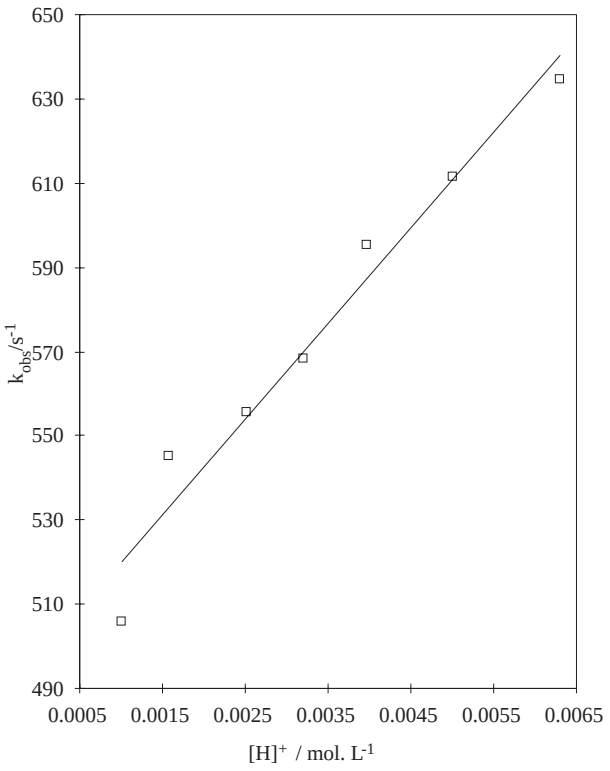

Figure 4. Effect of [H^+] on pseudo-first-order rate constant. Other conditions as in Fig. 3.

$$H_2A \leftrightarrow HA^- + H^+ \quad (3)$$

$$[M.B]^+ + HA^- \rightarrow \text{Complex} \quad (4)$$

The rate expression for the reaction in terms of k_{obs} is written as

$$k_{obs} = k_1 k_a [H_2A]_T (K_a + H^+) \quad (5)$$

$$\text{where } [H_2A]_T = [H_2A] + [HA^-] \quad (6)$$

Inversing equation (5) we obtain

$$k_{obs}^{-1} = 1/ k_1 [H_2A]_T + [H^+] 1/k_1 K_a [H_2A]_T \quad (7)$$

Substituting the values of the dissociation constant K_a obtained by potentiometric titration at different temperatures[17] by the slope of the plot of k_{obs}^{-1} vs. [H^+] in accordance with eq. (7), the rate constant k_1 at 32°C is 24.90 s^{-1}. The average value of rate constant k_1 calculated by using eq. (5) is equal to 24.66 s^{-1}. These results indicate that there is no significant reaction of [$M.B^+$] with undissociated H_2A under the present experimental conditions.

Catalyst Dependence

Different transition elements, Cu (II), Fe (II), V (V), Cr (VI), Mn (II), Co (II), Pb (II), Zn (II), Ni (II), Tl (I) and Hg (II), were tested as a catalyst for this reaction. The results show that Co (II), Pb (II), Zn (II), Ni (II), Tl (I) and Hg (II) have no catalytic effect on the rate of reaction while Cu (II), Fe (II), V (V), Cr

(VI) and Mn (II) accelerate the reaction rate with varying catalytic activity (Fig. 5).

Variation of concentration of the catalyst in the range 0.1 ppm to 0.5 ppm was done at 32°C with fixed 1.5 x 10^{-2} M [H_2A] and 1 × 10^{-5} M [M.B] at pH 2.20. It was observed that the rate of reaction between L-ascorbic acid and methylene blue was greatly accelerated by the presence of trace amounts of copper (II) ions.

A plot of rate versus [Cu (II)], [Fe (III)], [V (V)], [Cr (VI)], [Mn (II)] gives a straight line with the same values of intercept of about 12.40 s^{-1}, which is equal to the rate of the uncatalyzed reaction. The values of slopes are quite different: 26.15, 16.86, 12.53, 4.43 and 1.65 s^{-1} for Cu (II), Fe (II), V (V), Cr (VI) and Mn (II) respectively. Table 2 shows the comparison between the catalytic efficiency of Cu (II) with other transition metals. Here χ indicate the ratio of rate constants of Cu (II) with other transition metals. This observation infers that Cu (II) has the maximum catalytic efficiency among all the metals used.

Table 2. χ indicates the catalytic efficiency of Cu(II) compound with other suggested ions.

Transition metal ions	χ
Fe (III)	1.55
V (V)	2.08
Cr (VI)	5.90
Mn (II)	15.86

Plots of k_{cat} vs. [Cu (II)] showed a straight line with an intercept. The reaction was described by the following equations:

$$-d[M.B^+]/dt = k_{cat}\ [\ M.B]$$

$$k_{cat} = K_a[Cu\ (II)] + (k_b + k_c\ [Cu\ (II)][H_2A]_t\ )$$

$$k_{cat.} = k_b\ [H_2A]_i + (K_a + k_c\ [H_2A])[Cu\ (II)]$$

where $[H_2A]_i$ indicates the concentration of ascorbic acid at the initial stage of the said reaction [18].

Preliminary experiments with 1.5 x 10^{-2} mol. L^{-1} [H_2A], 1x10^{-5} mol. L^{-1} [M.B], 0.1 ppm to 0.5 ppm [Cu (II)] at pH 2.20 and 32°C indicate that the rapid formation of an intermediate ascorbate complex, which subsequently decomposed to the products dehydroascorbic acid and intermediate. It was possible to record the spectrum of intermediate species during the formation and decomposition process. Fig. 6 also shows that by increasing the concentration of Cu (II) from 5.0 ppm, to 20.0 ppm the stability time of the intermediate complex decreases.

Temperature Effect

Kinetic runs were performed over the temperature range 22-40°C. The thermodynamic parameters at 25°C given in Table 3 show that the reaction is endothermic with positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$.

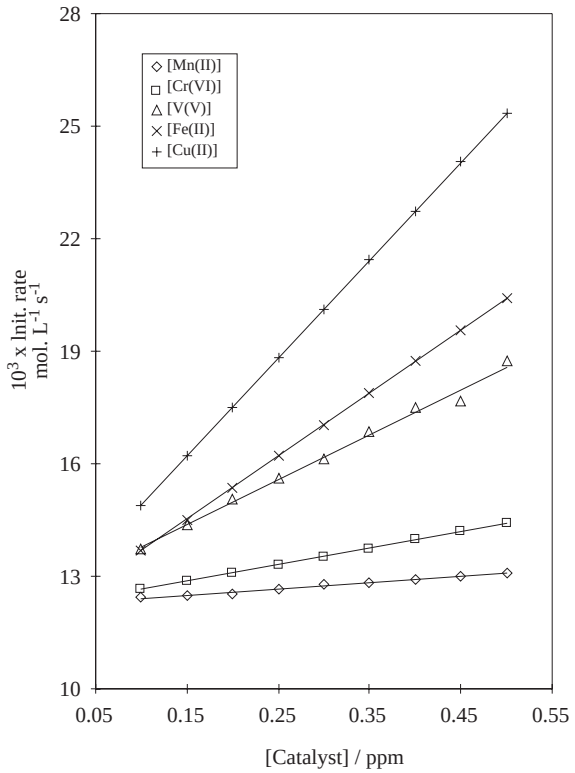

Figure 5. Decolorization rate curves of the catalytic reactions. Other conditions as in Fig. 3.

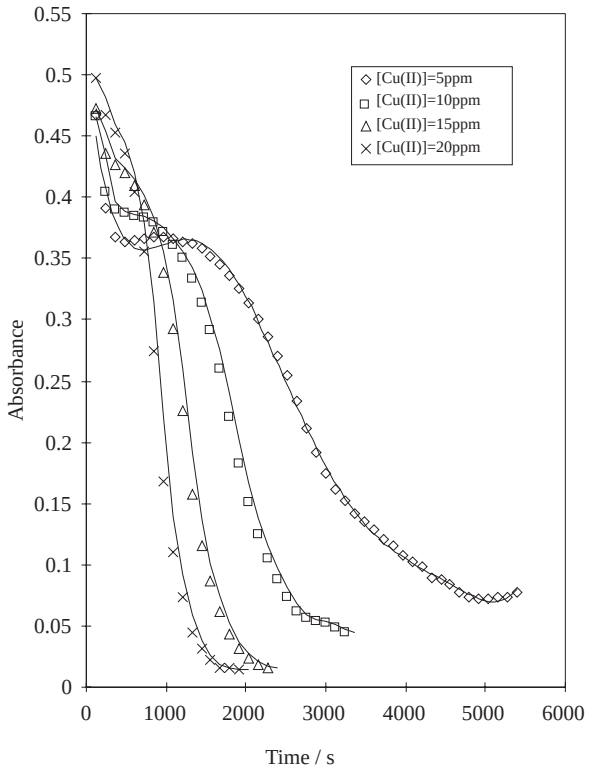

Figure 6. Plot of Time vs. Abs. for different $[Cu^{2+}]$ showing stability time of the intermediate complex.

Table 3. Thermodynamic parameters for the reaction between methylene blue and abcorbic acid.

Transition metal ions	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/kJ mol^{-1} K^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}
Absent	62.29	-92.17	89.76
V^{+5}	62.13	-92.34	89.65
Fe^{+2}	50.87	-127.84	88.96
Cu^{+2}	44.24	-138.90	85.63

Table 4. Thermodynamic and activation parameters for interaction of $M.B^+$ and HA^-

Catalyst	Ea/kJ mol^{-1}
Blank	64.77
V^{+5}	64.61
Fe^{+2}	53.35
Cu^{+2}	46.72

Activation parameters for uncatalyzed reaction.
$\Delta H_1 = 438.147$ kJ mol^{-1}
$\Delta H_2 = 457.851$ kJ mol^{-1}
$\Delta S_1 = 1.214$ kJ $mol^{-1}K^{-1}$
$\Delta S_2 = 1.137$ kJ $mol^{-1}K^{-1}$

Table 4 shows that the activation energy of catalyzed reaction increases with the size of transition metals. The specific rate constants k_1 and k_2 for the uncatalyzed reaction indicate that the k_1 values (0.0015,

0.0125 s^{-1}) are much smaller than k_2 values (0.0064, 0.0587 s^{-1}) at 32 and 36°C. This observation is very close to the reported work [15−17].

A comparison of activation parameters (Table 4) corresponding to the specific rate constants k_1 and k_2 shows that the activation process is enthalpy controlled, since enthalpy is higher for slower reactions, so the ΔH_2 values larger than ΔH_1 values indicate stronger hydration for HA^- than that for H_2A.

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