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KINETICS OF THE CUPRIC SALT-CATALYSED AUTOXIDATION OF L-ASCORBIC ACID IN AQUEOUS SOLUTIONS[1]

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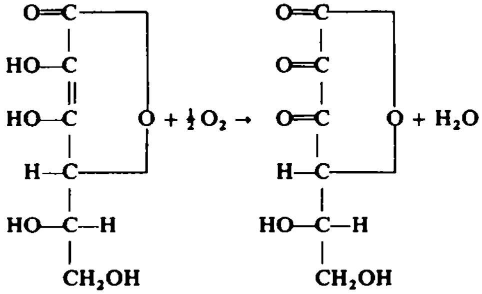
Abstract—The kinetics of the cupric salt-catalysed autoxidation of L-ascorbic acid has been studied in unbuffered aqueous solutions at ca. 35°. The catalytic ability is in the order $CuCl_2 \geq Cu(NO_3)_2 \sim CuSO_4$. The effect of ionic strength is negligible. The observed effects of pH, cupric ion concentration and partial pressure of oxygen at various temperatures on the reaction rate suggests a mechanism which may involve two courses for the formation of monodehydroascorbate radical (HA·):

$$H_2A \rightleftarrows H^+ + HA^-$$

$$\begin{cases} HA^- + Cu(II) \rightleftarrows [HACu(II)]^- \xrightarrow{slow} HA\cdot \\ HA^- + Cu(II) + O_2 \rightleftarrows [HACu(II)O_2]^- \xrightarrow{slow} HA\cdot \end{cases}$$

The final product, dehydro-ascorbic acid (DA), may be formed from both HA· and $A^{\overline{\cdot}}$ (radical anion). The resulting hydrogen peroxide reacts readily with ascorbic acid, giving also DA.

A NUMBER of workers have reported on the complexity of the metallic ion-catalysed autoxidation of L-ascorbic acid (H_2A) to dehydorascorbic acid (DA).



H₂A DA

(1)

The rate of reaction is known to depend on pH, catalyst, oxygen pressure, temperature, buffer, etc. Even in the well studied autoxidation catalysed by cupric ion at lower pH, there is a diversity of opinion among investigators. For example, the order with hydrogen-ion concentration has been reported to be −0·5,[2] −0·7,[3] −1,[4] −2[5] and a non-integral number.[6]

It has been said that the reaction is unimolecular in ascorbic acid, but Silverblatt *et al.*[3] have reported that the first-order constant varies with its initial concentration.

The present study was undertaken to obtain some information on the kinetics of this cupric ion-catalysed autoxidation in unbuffered aqueous solutions, especially as to the effect of the initial concentration of ascorbic acid, pH, temperature and also the concentration and nature of cupric ion.

RESULTS AND DISCUSSION

Effect of cupric salts. The acceleration of the autoxidation of ascorbic acid by cupric salts such as $CuCl_2$,[7] $Cu(NO_3)_2$[8] and $CuSO_4$[3] is well known.

The rates with various cupric ion concentration were measured and pseudo-first-order constants were calculated by means of an ordinary first-order equation.

$$k = \frac{2{\cdot}303}{t}\log\frac{[H_2A]_0}{[H_2A]} \tag{2}$$

where $[H_2A]_0$ and $[H_2A]$ donate the concentration of ascorbic acid at reaction time zero and t, respectively. The results are presented graphically in Fig. 1. Apparently, the rate is proportional to the concentration of cupric ion as has been reported.[7]

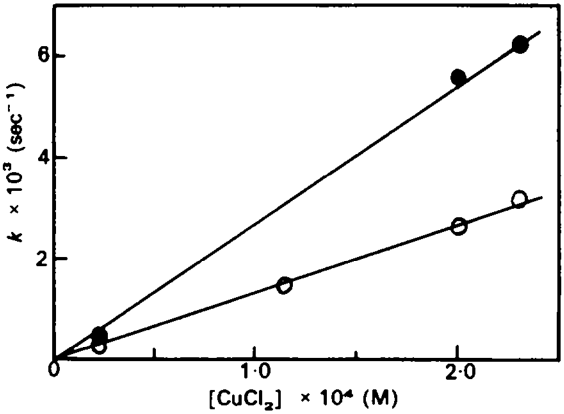


FIG. 1. Effect of cupric ion concentration of the first-order rate constant at 35° using $CuCl_2$ as catalyst. Initial concentration of ascorbic acid $[H_2A]_0$, ●, $1{\cdot}15 \times 10^{-2}$M; ○, $2{\cdot}3 \times 10^{-2}$M.

At very high concentration of $CuCl_2$, (e.g. above $2{\cdot}3 \times 10^{-3}$M with $[CuCl_2]$: $[H_2A]_0 \sim 0{\cdot}1$), an oxygen uptake increases by a factor of ca. 2 on account of the accumulation of hydrogen peroxide. The present kinetic experiments, however, were not extended to this concentration of $CuCl_2$.

The cupric ion-catalysed oxidation in hydrochloric acid is said to proceed ca. 50–100 times as fast as in nitric or perchloric acid of the same concentration,[5] but it is not certain if there is a difference in the catalytic ability between cupric salts. The catalysis was compared using some cupric salts of different anions in the absence of excess acid or anion (Table 1).

TABLE 1. EFFECT OF CATALYSTS ON RATE CONSTANTS IN AN AQUEOUS SOLUTION AT 35°

$[Cu^{2+}]$ $2{\cdot}3 \times 10^{-4}$M	$[H_2A]_0$, $2{\cdot}3 \times 10^{-2}$M	$[H_2A]_0$, $5{\cdot}0 \times 10^{-2}$M
	10^3k, sec^{-1}	10^3k, sec^{-1}
$CuCl_2$	3·22	1·36
$Cu(NO_3)_2$	2·56	1·29
$CuSO_4$	2·39	1·26

The Table shows that cupric nitrate and sulphate have virtually similar effects, but cupric chloride is a little more effective than the other two especially at the lower concentration of ascorbic acid ($2{\cdot}3 \times 10^{-2}$M). In order to obtain more accurate data at higher concentration of ascorbic acid, cupric chloride was used as a catalyst for all the experiments described.

Effect of the concentration of ascorbic acid. Most workers have reported reaction to be first-order with ascorbic acid, e.g. the pseudo-first-order constant was estimated by Dekker *et al.*[5] in $1{\cdot}06 \times 10^{-3}$M perchloric acid at 24·9° to be 31–27 × 10^{-4} min^{-1} at different initial concentrations of ascorbic acid ($1{\cdot}46 \times 10^{-4}$M and $72{\cdot}6 \times 10^{-4}$M). However, the reaction rate is controlled significantly by the stirring rate of the reaction mixture, and as pointed out by some workers[9, 10] insufficient stirring is responsible for the many contradictory results found in the literature.

According to our observation, the reaction rate is independent of the ascorbic acid concentration, when the stirring rate is low (e.g., below 300 rpm with a 35 mm Teflon magnetic stirrer in the reaction bulb of 45 mm diameter), but as the stirring becomes more vigorous (e.g. more than 500 rpm), the rate of reaction tends to depend on the ascorbic acid concentration. This means that vigorous stirring enables the dissolution of oxygen gas fast enough so that it cannot be rate-determining.

The observed first-order rate constant calculated by Eq. 2, however, tends to decrease with increasing initial concentration of ascorbic acid (Table 2).

TABLE 2. EFFECT OF INITIAL CONCENTRATION OF ASCORBIC ACID (AND pH) IN UNBUFFERED SOLUTIONS WITH [$CuCl_2$] $2{\cdot}0 \times 10^{-4}$M AT 35°

$[H_2A]_0 \times 10^2$M	pH	10^3k, sec^{-1}	$[H_2A]_0 \times 10^2$M	pH	10^3k, sec^{-1}
1·15	3·20	5·65	3·0	2·99	1·88
1·5	3·14	4·68	5·0	2·86	1·22
2·0	3·09	3·0	8·0	2·82	0·8
2·3	3·02	2·65	10·0	2·70	0·61

This decrease appears to be caused in part by an increase of the ionic strength and/or acidity of ascorbic acid itself, but even if the ionic strength and pH are changed by adding KNO_3 and HNO_3, respectively, with a constant concentration of ascorbic acid, such a sharp decrease as in Table 2 is not observed. This phenomena will be discussed later.

Effect of ionic strength. As described above, the increase of rate constant with the initial concentration of ascorbic acid may be due to the increase of ionic strength, i.e. the ions dissociated from substrate or catalyst may suppress the reaction. For the examination of the effect of ionic strength, the rates were measured in solutions with various ionic strength using KNO_3. The results are shown in Table 3.

As is obvious from the Table, the k value is not affected by the ionic strength, hence the effect of initial concentration of ascorbic acid cannot be ascribed to the ionic strength.

Effect of acidity. Table 2 lists the pH values in unbuffered aqueous solutions of ascorbic acid together with the rate constant. The relation between hydrogen-ion concentration and first-order constant can easily be obtained by plotting pH *vs* log

Table 3.
Effect of ionic strength with [$CuCl_2$] 2·0 × 10^{-4}M at 35°

KNO_3, M	[H_2A]$_0$, 2·3 × 10^{-2}M	[H_2A]$_0$, 8·0 × 10^{-2}M
	10^3k, sec^{-1}	10^3k, sec^{-1}
0	2·65	0·8
10^{-3}	2·62	0·73
10^{-2}	2·72	0·78

k as a broken line in Fig. 2, indicating a linear relation with a slope of 2 in a range of pH 2·7–3·2.

$$\log k = 2\,\mathrm{pH} - 4{\cdot}2$$

This effect of acidity can be checked by varying pH alone with constant concentration of ascorbic acid. This change of pH was done by adding nitric acid because of no appreciable influence of the nitrate ion as shown in Table 3. Plots of log k *vs* pH (real lines in Fig. 2) at higher acidity on addition of various amounts of nitric acid for the acid source gave lines having a slope of about unity at lower pH and 0·63–0·83 at higher pH.

The apparent disagreement of pH-rate profiles is observed as shown in real and broken lines in Fig. 2. This fact may be explained by assuming that the rate constant k is inversely proportional to the ascorbic acid concentration, because of (i) association of ascorbic acid (a strong Ramman line[11] near 1700 cm^{-1} and a shift of UV absorption spectra at 270 mμ[12]) or (ii) transformation into keto form and (iii) the effect of chloride ion as shown in Table 1, and/or (iv) the complex dependency of the rate equation on [H_2A] as shown in Eq. 13, if the stoichiometric concentration of total copper is taken into account.

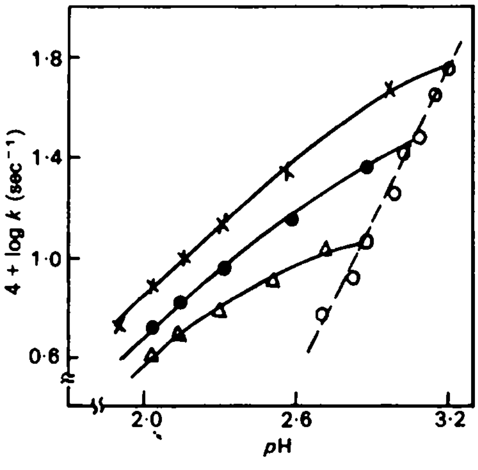


Fig. 2. Effect of pH of solution caused by the initial concentration of ascorbic acid (----○----) and added HNO_3 with initial concentration of ascorbic acid, X1·15 × 10^{-2}M, ● 2·3 × 10^{-2}M and △ 5·0 × 10^{-2}M) on the first-order rate constant at 35°.

Effect of oxygen pressure and temperature. All experiments described were conducted by supplying pure oxygen. In order to examine the effect of partial pressure of oxygen, a mixture of oxygen and nitrogen was used for the oxidation keeping the initial total pressure in the reaction vessel to be 1·0 atm, which is the sum of partial pressures of O_2, N_2 and vapourized solvent. Effect of oxygen pressure was investigated at 30°, 35°, 40° and 45°, the results are shown in Table 4 and Fig. 3.

TABLE 4. EFFECT OF OXYGEN PRESSURE, p (ATM) AND REACTION TEMPERATURE ON THE FIRST-ORDER RATE CONSTANT, k (SEC^{-1}) WITH [CuCl] $2{\cdot}0 \times 10^{-4}$M AND $[H_2A]_0$ $2{\cdot}3 \times 10^{-2}$M

30°	p	0·958	0·757	0·592	0·362	
	10^3k	1·69	1·47	1·10	0·80	
35°	p	0·945	0·822	0·592	0·362	
	10^3k	2·65	2·39	1·95	1·30	
40°	p	0·927	0·855	0·658	0·526	0·395
	10^3k	3·98	3·53	2·96	2·60	2·48
45°	p	0·905	0·822	0·592	0·29	
	10^3k	5·5	4·54	4·1	2·96	

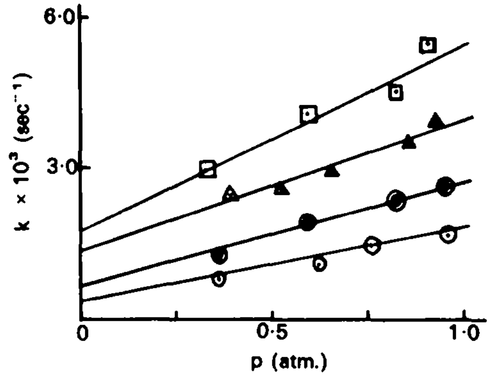


FIG. 3. Effect of partial pressure of oxygen.
Total pressure, 1·0 atm; $[H_2A]_0$ $2{\cdot}3 \times 10^{-2}$M, $[CuCl_2]$ $2{\cdot}0 \times 10^{-4}$M ○ 30°, ⊙ 35°, △ 40°, ⊡ 45°.

Weissberger *et al.*[8] have found that the oxidation rate of divalent ascorbate ion is proportional to the partial pressure of oxygen (p) but that of monovalent ascorbate ion is independent of p. A number of investigators[3, 6, 7, 13] reported that the oxygen dependency of reaction rate in an acidic solution deviates from proportionality.

As shown in Fig. 3, straight lines do not pass through the origin. This means that the reaction involves two simultaneous steps, i.e., a step dependent on p and a step independent of p. The comparison of these steps will be described later.

Mechanism. The rate data together with the other known facts suggests the following mechanism for the autoxidation at pH ca. 3, $[H_2A]_0$ of ca. $10^{-2} - 10^{-1}$M and ca. 35°.

$$H_2A \overset{K_3}{\rightleftarrows} H^+ + HA^- \tag{3}$$

$$HA^- + Cu(II) \overset{K_4}{\rightleftarrows} [HACu(II)]^- \tag{4a}$$

$$[HACu(II)]^- \xrightarrow[\text{slow}]{k_4} HA\cdot + Cu(I) \tag{4b}$$

$$[HA^-] + Cu(II) + O_2 \overset{K_5}{\rightleftarrows} [HACu(II)O_2]^- \tag{5a}$$

$$[HACu(II)O_2]^- \xrightarrow[\text{slow}]{k_5} HA\cdot + Cu(II) + \cdot O_2^- \tag{5b}$$

The monodehydroascorbate radical (HA·) formed is then transformed into dehydroascorbic acid (DA).

$$HA\cdot \overset{\text{Base}}{\leftrightarrows} A^{\dot{-}} \xrightarrow{Cu(II)} DA + Cu(I) \tag{6}$$

and/or

$$HA\cdot \rightarrow DA\,(+\,H_2A) \tag{7}$$

Ascorbic acid is stable in pure water.[14] In our experiments without copper catalyst at 35°, pseudo-first-order constant k in pure water was ca. 10^{-6} sec^{-1} or less than 1/1000 of k with a catalyst of $2{\cdot}0 \times 10^{-4}$M $CuCl_2$ under the same conditions. It is plausible that the Cu(II)-catalysed autoxidation proceeds by an electron transfer from ascorbate ion to Cu(II).

Although the electron transfer may be easier between Cu(II) and divalent ascorbate ion (A^{2-}) which is richer in electrons, the dissociation constant (first and second dissociation constants are ca. 4×10^{-5} and 10^{-12}, respectively) indicates that the concentration of A^{2-} is extremely low at pH ca. 3.

The reactive species HA^- donates an electron to Cu(II) forming probably a complex as shown in Fig. 4 or 5, where R is $CH(OH)CH_2OH$ and L_1 and L_2 are ligands which may be Cl and H_2O or O_2, respectively.

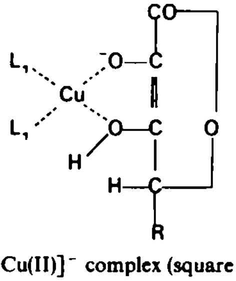


FIG. 4. $[HACu(II)]^-$ complex (square planar).

It is known that in the absence of oxygen, ascorbic acid can reduce cupric salts to give cuprous salts.[15] Hence, the complex in Fig. 4 is conceivable, at least, in an insufficient supply of oxygen in a solution. The complex in Fig. 5 is similar to that for the cupric ion-catalysed autoxidation of *o*-phenylenediamine.[16]

Both complexes are subject to rate-determining decomposition expressed as Eqs. 4b and 5b. Khan and Martell[4] proposed that the reaction proceeds by way of only

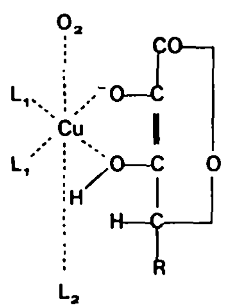


FIG. 5. $[HACu(II)O_2]^-$ complex (octahedral).

Eq. 5a based on their results at 25°. However, as was discussed in the previous section, the rate equation includes a term independent of oxygen pressure at a lower concentration of ascorbic acid.

The slightly S-shaped conversion curve of this reaction suggests the presence of a short induction period which is probably caused by the formation of hydrogen peroxide during this period according to 4b and 5b together with the steps described below.

$$Cu(I) + O_2 + H^+ \rightarrow Cu(II) + HO_2\cdot \tag{8}$$

$$O_2^{\cdot} + H^+ \rightarrow HO_2\cdot \tag{9}$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \tag{10}$$

All these steps are very fast and hydrogen peroxide reacts with ascorbic acid in the stoichiometry:

$$H_2O_2 + H_2A \rightarrow DA + 2H_2O \tag{11}$$

Eq. 11 was confirmed by the reaction of $1{\cdot}08 \times 10^{-2}$M hydrogen peroxide with ascorbic acid of various concentrations ($2{\cdot}0 \times 10^{-2}$, $4{\cdot}0 \times 10^{-2}$ and 10^{-1}M) at 35°. The reaction rate may be expressed as:

$$d[DA]/dt = \tfrac{3}{2}\{k_4[HACu(II)]^- + k_5[HACu(II)O_2]^-\} \tag{12}$$

Eq. 12 can be expressed using the total stoichiometric copper concentration $[Cu]_T$ as follows.

$$d[DA]/dt = \frac{3}{2}\,\frac{K_3[Cu]_T(k_4K_4 + k_5K_5p)}{[H^+]} \times \frac{[H_2A]}{1 + \dfrac{K_3(K_4 + K_5p)}{[H^+]}[H_2A]} \tag{13}$$

Eq. 13 seems to explain the observed facts, i.e., the deviation of kinetics for Eq. 2 at lower acidity, especially at higher concentration of ascorbic acid, and the observed constancy of k with various initial concentrations of ascorbic acid at higher acidity as obvious in Fig. 2.

Reactions 6 or 7 are considered for the formation of dehydroascorbic acid (DA) from radical HA·. Reactions between radical anion $A^{\cdot}$ and Cu(II) giving DA should be rapid, although the concentration of $A^{\cdot}$ is low at lower pH. On the other hand, the concentration of HA· should be higher, hence its reaction with oxygen molecule[17] and the disproportionation reaction[18] between two HA· to give DA and H_2A may occur.

Apparent activation energy was 14·4 kcal mole^{-}1 estimated from Fig. 6.

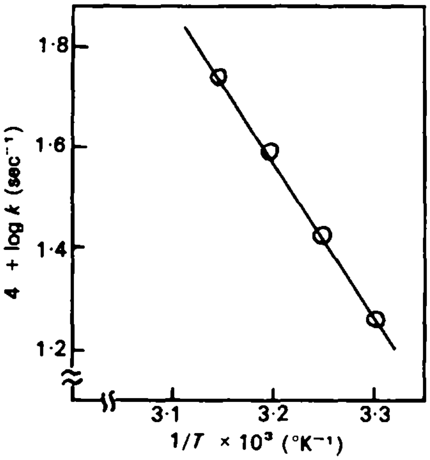


FIG. 6. Arrhenius plot for apparent activation energy.

EXPERIMENTAL

Materials. Ascorbic acid was of 99·5% pure with decomposition point of 190·9° (lit.[19] 190–192° (dec)) and optical rotation of $[\alpha]_D^{25}$ +20·94° (lit.[19] $[\alpha]_D^{25}$ 20·5–21·5°). Used water was passed through a cation exchange resin, Amberlit MB-1, followed by the distillation in a glass-joint flask. O_2 and N_2 were of over 99·7% and 99·95% pure, respectively. Cupric chloride, nitrate, sulphate, potassium nitrate and nitric acid were of guaranteed reagent grade.

Reaction products criterion. The cupric salt-catalysed autoxidation products obtained from ascorbic acid at pH ca. 3 were analysed for content by the well established methods, i.e., titration with 2,6-dichlorophenolindophenol.[15a] At an initial stage of reaction no hydrogen peroxide could be detected by iodometry with taking into account a content of ascorbic acid. Cuprous ion was virtually absent in the reaction mixture. The hydrogen sulfide reduction of reaction mixture followed by filtration and iodometry proved that dehydroascorbic acid was a main oxidation product, i.e., a total percentage of ascorbic acid and dehydroascorbic acid in the reaction mixture was 100 ± 5%. The other by-products could not be detected. These facts were also confirmed by the amount of O_2 consumed, and was in accordance with literature on the autoxidation at a lower pH, i.e., the stoichiometry is expressed as Eq. 1.

Kinetic procedure. A reaction vessel shown in Fig. 7 was used in a thermostat in which the difference of pressures in both bulbs can be read as the difference of mercury levels of both capillary tubes. An aqueous soln of cupric salt, whose copper concentration was estimated by iodometry, was introduced into the right-side bulb (B) and a soln of ascorbic acid of a measured amount in another bulb (A) which can be stirred by a Teflon stirrer. After evacuation of the vessel by an aspirator, a soln of cupric salt (10 ml) was also poured from a burette into the left-side bulb. The vessel was again evacuated, and then O_2 gas was introduced into both bulbs. The cocks A_1 and B_1 were quickly closed and the reaction was started with vigorous magnetic stirring. The difference of levels of manometer at definite intervals of time gave the estimation of O_2 press. The pH was measured by a Hitachi-Horiba Type-4 pH meter calibrated at 3 points.

The consumed molarity of O_2 (Δm) can be calculated by Eq. 14.

$$\Delta m = \frac{\Delta h\, V}{760\, RT} \tag{14}$$

where Δh is the manometric difference, V, the volume of reaction bulb (74·4 cm^3), R, the gas constant and T, the reaction temperature in Kelvin.

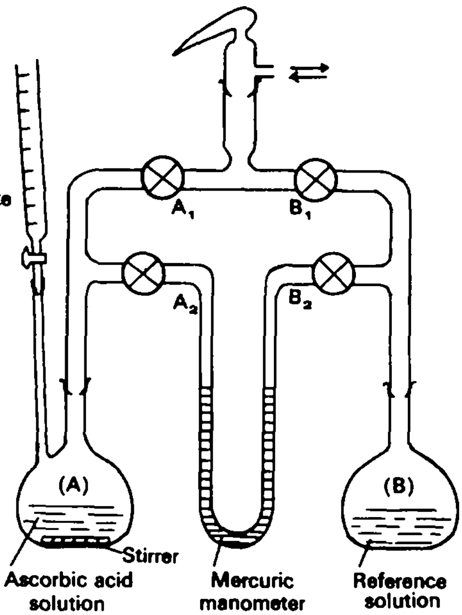


FIG. 7. Apparatus for the kinetic experiment for the autoxidation of ascorbic acid.

The stoichiometric Eq. 1 affords the amount of remaining ascorbic acid $[H_2A]$ at time t as follows:

$$[H_2A] = [H_2A]_0 - 2\,\Delta m \tag{15}$$

Here, $[H_2A]_0$ is the initial concentration of ascorbic acid. Some examples of conversion curve and plot of log $[H_2A]$ *vs* t were shown in Figs 8 and 9. The first-order kinetic law with ascorbic acid was almost satisfied at lower concentration of ascorbic acid with stirring of 800 rpm.

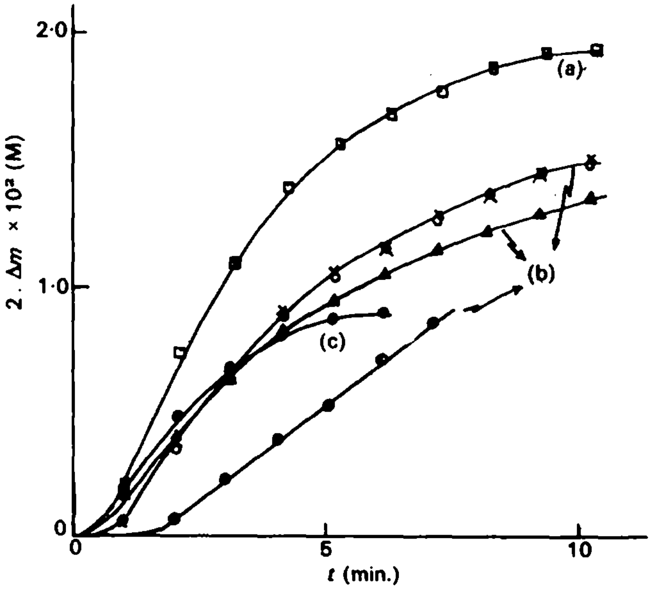


FIG. 8. Conversion curves.

Initial concentration of ascorbic acid: (a) 10^{-1}M (stirring of 800 rpm), (b) $2{\cdot}3 \times 10^{-2}$M (○ 800 rpm, X 500 rpm, △ 300 rpm, ◑ 100 rpm) and (c) $1{\cdot}15 \times 10^{-2}$M (800 rpm).

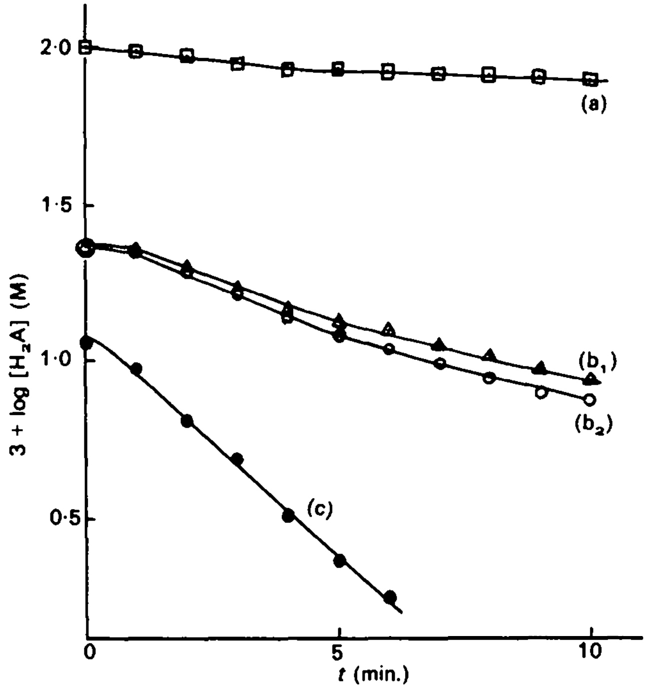


FIG. 9. Plots of log [H_2A] vs. time.
Initial concentration of ascorbic acid: (a) 10^{-1}M (stirring of 800 rpm), (b_1) 2·3 × 10^{-2}M (300 rpm), (b_2) 2·3 × 10^{-2}M (800 rpm) and (c) 1·15 × 10^{-2}M (800 rpm).

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