Role of Trace Metal Ions. Kinetics and Mechanism of the Copper(II)-catalysed Oxidation of Ascorbic Acid with Peroxodiphosphate in Acetate Buffers

Dileep K. Mishra, T. Peter Amala Dhas, Prem D. Sharma, Anand P. Bhargava, and Yugul K. Gupta
Department of Chemistry, University of Rajasthan, Jaipur, India

The reaction between peroxodiphosphate and ascorbic acid (H_2A) in acetate buffers is essentially catalysed by trace metal-ion impurities of Cu^{II} and Fe^{III} present in the reagents. Copper(II) has an about ten times larger catalytic activity than Fe^{III}, and the activity is so specific and precise that one can calculate the amount of Cu^{II} present in a system as an impurity, from the initial rates of 'uncatalysed' reactions. The reactions in the absence and presence of copper(II) have the same characteristics. The rate law (i) is obeyed for the catalysed reaction, where K_d^1 and K_d^2 are

$$\frac{-d[H_2A]}{dt} = \frac{[H_2A]_T[Cu^{II}](k_1[H^+] + k_2K_d^1 + k_3K_d^2/[H^+])}{(K_d^1 + [H^+])} \qquad (i)$$

the acid dissociation constants of ascorbic acid, and k_1, k_2, and k_3 are the rate constants for the reactions $Cu^{II} + H_2A$, $Cu^{II} + HA^-$, and Cu^{II} and A^{2-} respectively. The values of k_1, k_2, and k_3 were found to be 27 ± 2, $(1.24 \pm 0.10) \times 10^3$, and $(1.1 \pm 0.08) \times 10^{10}$ mol^{-1} dm^3 s^{-1} at 35° and $I = 1.0$ mol dm^{-3}.

Several workers[1-8] have studied the copper(II)-catalysed oxidation of ascorbic acid where the oxidant is dissolved oxygen or air in the reaction systems, and most reported the so-called uncatalysed reaction ascribing it to the trace metal ions like copper(II) and iron(III) present in the reagents. However, probably none elaborated this uncatalysed path further and recognised it as truly catalytic. The real uncatalysed path is not significant or probably does not exist. In addition to molecular oxygen, hydrogen peroxide[9,10] has also been extensively employed for the oxidation of ascorbic acid. Another similar oxidant used is peroxodisulphate.[11] In all cases the Cu^{II}–Cu^{I} redox couple is said to operate. It is therefore appropriate to study the system peroxodiphosphate–ascorbic acid (H_2A) in order to highlight the uncatalysed path. Although silver(I) catalysis[12] in peroxodiphosphate oxidations has been reported and subsequently several catalytic studies[13] have been made, there seems to be only one study[14] (oxidation of iodide) with copper(II) wherein a complex $[Cu_2(HP_2O_8)]^+$ is said to be formed. Thus the reaction of ascorbic acid with peroxodiphosphate seemed worthy of investigation also from the viewpoint of copper(II) catalysis in peroxodiphosphate oxidations.

Peroxodiphosphate chemistry seems to be well established[15] and the compound is fairly stable in solution. However it readily undergoes hydrolysis[16] in acidic solutions yielding peroxomonophosphate. Hydrolysis can be avoided by working in buffered systems of pH > 2. The most important feature of redox reactions of peroxodiphosphate in acidic perchlorate solutions is that the rate is independent of the concentration of the reducing substance and the hydrolytic path is rate controlling.[17] Ascorbic acid is an important biochemical compound and widely used as a reducing agent.[18] It is finding increasing application as a reductant in photoconversion schemes.[19] Thus a mechanistic study of this system seemed interesting. This system has been studied previously,[20] but the unusual complex between H_2A and peroxodiphosphate reported seems unlikely. The present communication is part of a broad investigation of the role of trace metal ions as catalysts and inhibitors in inorganic redox systems.

Experimental

Materials and Solutions.—Tetrapotassium peroxodiphosphate was a gift from FMC Corporation USA. Its solutions were prepared by dissolving a known quantity of the salt in water whenever required. It was standardised iodometrically.[21,22] L-Ascorbic acid was BDH AnalaR and its solutions were always freshly prepared and kept in a refrigerator to minimise deterioration or oxidation. Its strength was determined iodimetrically.[23] All other reagents were of E. Merck analytical grade.

All kinetics studies were made in a thermostatic bath at 35 ± 0.1 °C unless stated otherwise. The reaction was initiated by temperature-equilibrated ascorbic acid. Aliquots (5 or 10 cm^3) were withdrawn at different times and added to an iodine solution of known concentration and volume, rendering the pH between 3 and 4 by adding a previously calculated amount of sodium acetate. Unreacted ascorbic acid reacted with iodine and the excess of the latter was titrated against a known thiosulphate. The pH was always >3 in order to eliminate a reaction[24] between peroxodiphosphate and iodide (present in the iodine solution).

Initial rates were calculated from plots of the concentration of H_2A *versus* time by the plane-mirror method.[25] Pseudo-first-order plots were also constructed wherever conditions permitted. The results were reproducible to ±5%. Spectrophotometric measurements were made on a Cecil CE599 automatic scanning spectrophotometer against a buffer blank using a 1-cm cell. Different reagents and the reaction mixture were subjected to atomic absorption analysis to estimate the amounts of copper(II) and iron(III) present. All solutions were prepared in twice distilled water, the second distillation being from alkaline permanganate.

Results

Stoicheiometry.—Different sets of concentrations of peroxodiphosphate and H_2A in the range 1.0×10^{-3}—1.0×10^{-2} mol dm^{-3} at pH 3.9 and 35 °C were allowed to react for about 16 h.

Table 1. Stoicheiometry of peroxodiphosphate (pdp) and ascorbic acid (H_2A) reaction in the presence and absence of methyl methacrylate (mma), pH 3.9 and 35 °C

$10^3[H_2A]$/mol dm^{-3}	10^3[pdp]/mol dm^{-3}	$\Delta[H_2A]/\Delta$[pdp]
4.0	1.0	1.02
5.0	2.0	1.03
8.0	2.0	1.00
8.0	3.0	1.03
2.0	4.0	1.02
2.0	3.0	0.98
4.0	5.0	1.04
1.0	2.0	0.96
		Average 1.00 $\pm$ 0.03
4.0	1.0	1.09*
6.0	1.0	1.3*
8.0	1.0	2.2*
4.0	2.0	0.85*
4.0	3.0	0.77*
2.0	1.0	0.98*

* In the presence of 2% mma

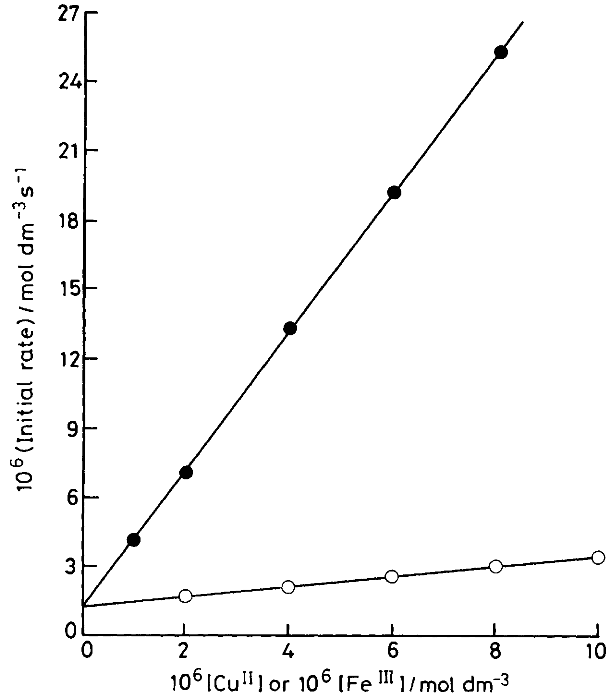

Figure 1. Plot of initial rate *versus* [Cu^{II}] (●) and [Fe^{III}] (○) at $[H_2A] = 3.0 \times 10^{-3}$ [pdp] $= 5.0 \times 10^{-3}$ mol dm^{-3}, pH 3.9, $I = 1.0$ mol dm^{-3} and 35 °C

Excess of H_2A was determined iodimetrically and excess of peroxodiphosphate was determined iodometrically. One mole of H_2A reacts with 1.0 $\pm$ 0.03 mol of peroxodiphosphate (pdp). The stoicheiometry was also determined in the presence of methyl methacrylate (mma) and all these results are given in Table 1. The stoicheiometry ($\Delta[H_2A]/\Delta$[pdp]) becomes greater or less than 1 depending on the concentrations of the two reactants. A copious flaky white precipitate is obtained which indicates polymerisation of mma.

Peroxodiphosphate Dependence.—The peroxodiphosphate concentration was varied from 1.0×10^{-3} to 2.0×10^{-2} mol dm^{-3} at two different concentrations of copper(II), 1.0×10^{-6} and 2.0×10^{-6} mol dm^{-3}, with fixed $[H_2A] = 3.0 \times 10^{-3}$ mol dm^{-3} at $I = 1.0$ mol dm^{-3}, pH 3.9, and 35 °C. The rate was independent of [pdp]. The average rates were 3.3×10^{-6} and 6.7×10^{-6} mol dm^{-3} s^{-1} at [Cu^{II}] $= 1.0 \times 10^{-6}$ and 2.0×10^{-6} mol dm^{-3} respectively. Variation of [pdp] in the same concentration range was also studied but without adding copper(II) and the rate once again was independent of [pdp]. The average rate was 1.2×10^{-6} mol dm^{-3} s^{-1}.

Ascorbic Acid Dependence.—The ascorbic acid concentration was varied from 2.0×10^{-4} to 1.0×10^{-2} mol dm^{-3} at 2.0×10^{-6} mol dm^{-3} Cu^{II} and at two temperatures and also without the addition of Cu^{II}. The rate has a first-order dependence on $[H_2A]$ and the pseudo-first order rate constant (k_0'/s^{-1}) is $(2.1 \pm 0.07) \times 10^{-3}$ and $(0.56 \pm 0.03) \times 10^{-3}$ at 35 and 25 °C respectively. The same rate constant for the uncatalysed reaction was found to be $(0.38 \pm 0.01) \times 10^{-3}$ s^{-1} at 35 °C.

Copper(II) *and Iron*(III) *Dependences.*—Variation of [Cu^{II}] in the range (1—8) $\times 10^{-6}$ mol dm^{-3} was done at 30 and 35 °C with fixed $[H_2A] = 3.0 \times 10^{-3}$ mol dm^{-3} at pH 3.9. Similarly, [Fe^{III}] was varied in the range (2—10) $\times 10^{-6}$ mol dm^{-3} at 35 °C at the same pH and $[H_2A]$. All these results are shown in Figure 1. A plot of rate *versus* [Cu^{II}] or [Fe^{III}] gives a straight line with the same intercept of 1.2×10^{-6} mol dm^{-3} s^{-1} at 35 °C, equal to the rate of the so-called uncatalysed reaction, but the slopes are quite different, being 3.0 and 0.27 s^{-1} for copper(II) and iron(III) respectively. This shows that copper(II) is about ten times more effective than Fe^{III} as a catalyst in the oxidation of ascorbic acid.

Hydrogen-ion Dependence.—The pH of the system was varied in the range 3.05—4.94 with acetate buffers for the copper(II)- and iron(III)-catalysed and uncatalysed reactions at 35 °C and $I = 1.0$ mol dm^{-3} adjusted with $NaNO_3$. The results are given in Table 2. In the case of Cu^{II} the rates decrease considerably with increasing [H$^+$], but this decrease is small in the case of the uncatalysed reaction and the rate does not change in the case of the iron(III)-catalysed reaction in the pH range employed.

Variation of Ionic Strength.—Ionic strength was varied with different concentrations of $NaNO_3$ in the range 0.2—2.0 mol dm^{-3}, but the rate did not change at all for both the catalysed and uncatalysed reactions. The values of the pseudo-first order rate constants were 2.2×10^{-3} and 0.4×10^{-3} s^{-1} for the 2.0×10^{-6} mol dm^{-3} copper(II)-catalysed and uncatalysed reactions respectively.

Reaction in the Presence of Methyl Methacrylate (*mma*).—The rates in presence of 1, 2, and 5% mma for several different sets of concentrations of reactants are given in Table 3. The rate (*i.e.* the decrease in $[H_2A]$ with time) in general increases in the presence of mma. This is particularly true when $[H_2A] >$ [pdp]. In one case when [pdp] $> [H_2A]$, the rate is almost independent of mma. The increase in rate can be explained by the larger stoicheiometry ($\Delta[H_2A]/\Delta$[pdp]) under this condition.

Effect of Ethylenediaminetetra-acetate (*edta*).—The rate decreases considerably in the presence of edta and becomes limiting when its concentration is varied from 1.0×10^{-6} to 2×10^{-2} mol dm^{-3}. Table 4 shows the results. It appears that edta complexes of Cu^{II} and Fe^{III} are much less reactive than the acetate complexes. If the limiting rates are divided by the corresponding metal-ion concentration, one obtains 9×10^{-2} s^{-1} for Cu^{II} and 2.5×10^{-2} s^{-1} for Fe^{III}. These must represent the rate constants of oxidation of H_2A in the presence of edta complexes. The corresponding rate constants for the acetate complexes are 3.0 and 0.27 s^{-1} respectively.

Table 2. Initial rates at different H^+ in the copper(II)-catalysed, uncatalysed, and iron(III)-catalysed reactions. [pdp] = 5.0×10^{-3}, $[H_2A] = 3.0 \times 10^{-3}$, $I = 1.0$, $[Cu^{II}] = 2.0 \times 10^{-6}$ in the copper(II)-catalysed reaction, and $[Fe^{III}] = 1.0 \times 10^{-5}$ mol dm^{-3} in the iron(III)-catalysed reaction; 35 °C

pH	$10^4[H^+]$/mol dm^{-3}	10^6 Initial rate/mol dm^{-3} s^{-1}		
		Copper(II)-catalysed reaction	Uncatalysed reaction	Iron(III)-catalysed reaction
5.11	0.078	—	—	4.7
4.94	0.115	59	—	—
4.50	0.316	22.5	1.5	—
4.48	0.331	—	—	5.2
4.20	0.63	11.5	1.3	5.0
3.90	1.25	6.2	1.2	4.0
3.70	1.99	—	—	5.0
3.65	2.23	3.6	1.2	—
3.55	2.8	—	1.2	—
3.40	3.94	2.15	1.2	5.1
3.05	8.91	1.2	1.1	—
2.80	15.8	0.75	1.1	—
2.55	28.2	0.55	—	—
2.35	44.6	—	0.83	—

Table 3. Initial rates in the presence of methyl methacrylate (mma); $[Cu^{II}] = 2.0 \times 10^{-6}$ and $[NaNO_3] = 1.0$ mol dm^{-3}, pH 3.9, 35 °C

10^3[pdp]/ mol dm^{-3}	$10^3[H_2A]$/ mol dm^{-3}	10^6 Initial rate/mol dm^{-3} s^{-1}			
		0	1	2	5% mma
1.0	4.0	8.8	22.5	27	27
1.0	3.0	6.6	18.5	22	22
1.0	1.0	2.2	3.5	4.2	4.2
2.0	1.0	2.2	3.5	4.2	4.2
3.0	1.0	2.2	3.3	3.75	4.2
5.0	3.0	6.6	5.8	5.6	—

Discussion

The so-called uncatalysed and copper(II)-catalysed reactions have many common characteristics and the nature of the two reactions is essentially the same. A plot of rate *versus* $[Cu^{II}]$ or $[Fe^{III}]$ (Figure 1) yields the same intercept (1.2×10^{-6} mol dm^{-3} s^{-1}) and this is equal to the experimental value of the rate constant for the uncatalysed reaction. From atomic absorption spectroscopy of the reaction mixture containing [pdp] = 5.0×10^{-3}, $[H_2A] = 3.0 \times 10^{-3}$, $[NaNO_3] = 1.0$ mol dm^{-3}, and acetate buffer of pH 3.9, the approximate concentrations of Cu^{II} and Fe^{III} were estimated to be 4.0×10^{-7} and 1.0×10^{-6} mol dm^{-3}. If one takes into account the slopes of the straight lines of Figure 1 (*i.e.* 3 and 0.27 s^{-1} for Cu^{II} and Fe^{III} respectively) and calculates the contributions to the rate by the metal ions present as impurities, one obtains the value of $(4.0 \times 10^{-7} \times 3) + (1.0 \times 10^{-6} \times 0.27) \approx 1.4 \times 10^{-6}$ mol dm^{-3} s^{-1} which is similar to 1.2×10^{-6} mol dm^{-3} s^{-1} (the intercept of Figure 1 or the rate of the uncatalysed reaction). If one adds the $[Cu^{II}]$ present in the reaction mixture as an impurity to the deliberately added $[Cu^{II}]$ and then plots the rate *versus* total $[Cu^{II}]$ one obtains an intercept of 0.3×10^{-6} mol dm^{-3} s^{-1} which is the contribution to the rate from Fe^{III} alone present as a trace impurity in the reagents, for $[H_2A] = 3.0 \times 10^{-3}$ mol dm^{-3} at 35 °C. If the same procedure is adopted for Fe^{III} to calculate the contribution of Cu^{II} present as an impurity, one obtains an intercept of 1.2×10^{-6} mol dm^{-3} s^{-1} which is the contribution to the rate from trace amounts of Cu^{II} present as impurity. Another indirect proof for trace metal-ion catalysis is the masking of the effect by edta. The results in the presence of edta given in Table 4 show that the rate is extremely slow in the presence of 1.0×10^{-4} mol dm^{-3} edta where the latter chelates the metal ions and free metal ion or its acetate complexes are not available for catalysis. The trace amounts of ($Cu^{II} + Fe^{III}$) present as impurity were calculated for other systems and these values (Table 5) are of the same order of magnitude. These results show that the uncatalysed path is essentially catalysed and that direct reaction between ascorbic acid and pdp does not occur.

Kinetic and spectroscopic evidence for a complex of Cu^{II} and pdp have been provided in the oxidation of iodide[14] and we expected this investigation to throw some more light on this point, but the rate is independent of [pdp] and the required information could not be obtained. This character of pdp was unexpected in view of the first-order dependence on $[S_2O_8^{2-}]$,[11] and half-order dependences on $[H_2O_2]$[10] and $[O_2]$[8] in the copper(II)-catalysed oxidations of H_2A by these oxidants. A few qualitative experiments have shown that the oxidation of Cu^I (which is likely to be formed in the reaction of Cu^{II} and H_2A) with pdp is very rapid and operation of the redox couple Cu^{II}–Cu^I may be responsible in making the rate independent of [pdp]. Nevertheless our spectrophotometric results qualitatively show that a complex of Cu^{II} with pdp is formed. So far as complex formation between Cu^{II} and H_2A is concerned, this has been assumed by earlier workers[1,3,4] and has also been determined[5] independently. Its stability constant is 42 ± 6 dm^3 mol^{-1}. Our spectrophotometric results also show that a complex of Cu^{II} and H_2A is formed.

Ascorbic acid is a disbasic acid and dissociates as in equations (1) and (2) with pK_a^1 and pK_a^2 approximately equal to 4 and 12

Table 4. Effect of edta on the initial rates of the pdp–H_2A reaction; [pdp] = 5.0×10^{-3}, $[H_2A] = 3.0 \times 10^{-3}$, $[NaNO_3] = 1.0$ mol dm^{-3}, pH 3.9, 35 °C

(*a*) $[Cu^{II}] = 2.0 \times 10^{-6}$ mol dm^{-3}

[edta]/mol dm^{-3}	1.0×10^{-6}	2.0×10^{-6}	5.0×10^{-6}	1.0×10^{-5}	5.0×10^{-5}	1.0×10^{-4}	2.0×10^{-2}
10^6 Initial rate/mol dm^{-3} s^{-1}	4.5	2.2	0.78	0.28	0.24	0.18	0.18

(*b*) $[Fe^{III}] = 1.0 \times 10^{-5}$ mol dm^{-3}

[edta]/mol dm^{-3}	5.0×10^{-6}	1.0×10^{-5}	2.0×10^{-5}	5.0×10^{-5}	1.0×10^{-4}	5.0×10^{-4}	1.0×10^{-3}	5.0×10^{-3}	1.0×10^{-2}
10^6 Initial rate/mol dm^{-3} s^{-1}	3.3	2.3	1.9	1.6	1.05	0.50	0.37	0.25	0.25

Table 5. Estimates of Cu^{II} + Fe^{III} present as impurities in different systems from the rates of the uncatalysed path

System	Catalyst	$10^7([Cu^{II}] + [Fe^{III}])$/mol dm^{-3} (calc.)	Source	Calculations made at pH	Calculations made at T/°C
H_2A–O_2	Cu^{II}	5.0	Ref. 1, Table 2 and Figure 4	3.45	25
H_2A–O_2	VO_2^{2+}	2.7	Ref. 26, Table 2 and Figure 3	2.85	25
H_2A–O_2	UO_2^{2+}	3.0	Ref. 27, Table 1 and Figure 1	1.02	25
H_2A–$S_2O_8^{2-}$	Cu^{II}	7.5	Ref. 11, Table 2 and Figure 2	3.43	30
H_2A–Air	Cu^{II}	3.7	Ref. 4, Table 1	4.96	30
H_2A–pdp	Cu^{II}	4.0*	This work	3.9	35

* This figure represents only Cu^{II}. If $[Fe^{III}]$ is also included the result is approximately 4.9.

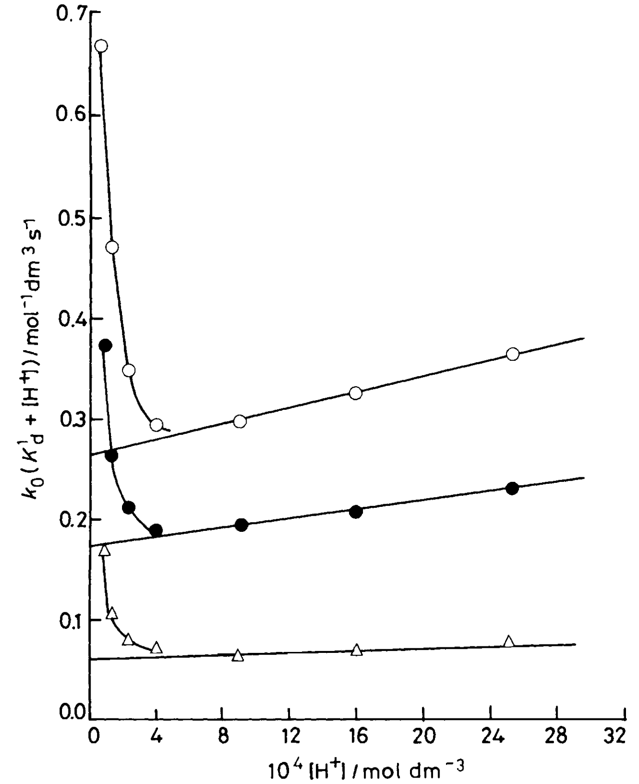

Figure 2. Plot of $k_0(K_d^1 + [H^+])$ *versus* $[H^+]$ for $[H_2A] = 3.0 \times 10^{-3}$, $[pdp] = 5.0 \times 10^{-3}$, $[Cu^{II}] = 2.0 \times 10^{-6}$, and $I = 1.0$ mol dm^{-3}. Temperature = 30 (△), 35 (●), or 40 °C (○)

$$H_2A \underset{}{\overset{K_d^1}{\rightleftharpoons}} HA^- + H^+ \qquad (1)$$

$$HA^- \underset{}{\overset{K_d^2}{\rightleftharpoons}} A^{2-} + H^+ \qquad (2)$$

respectively at 25 °C. Since the pH range employed for this study is 3—5 only the first dissociation will be of significance. Although the dianion will be present in insignificant amounts, it could contribute to the rate if it were highly reactive. The exact values of pK_d^1 at 30, 35, 40, and 45 °C were calculated as 1.17, 1.30, 1.38, and 1.48 respectively from the work of Kimura *et al.*[11a] Both forms of H_2A will be present in the pH range investigated and if both are reactive one can plot the hydrogen-ion dependence as given by Kimura *et al.*[11a] for reactions (3) and (4). Such a plot (Figure 2) of our results, instead of being linear, shows a decrease and then an increase in $k_0(K_d^1 + [H^+])$ with increasing $[H^+]$. From the nature of this curve, it appears that all three species of ascorbic acid, H_2A, HA^-, and A^{2-}, are reactive and that the much higher reactivity of the dianion more than compensates for its low concentration as compared to those of H_2A and HA^-. Considering H_2A and HA^- to be present in significant concentrations and all three species to be reactive, with the additional step (5) one obtains rate law (6).

$$H_2A + Cu^{II} \xrightarrow{k_1} \text{products} \qquad (3)$$

$$HA^- + Cu^{II} \xrightarrow{k_2} \text{products} \qquad (4)$$

$$A^{2-} + Cu^{II} \xrightarrow{k_3} \text{products} \qquad (5)$$

$$-d[H_2A]_T/dt = \frac{[H_2A]_T[Cu^{II}](k_1[H^+] + k_2K_d^1 + k_3K_d^1K_d^2/[H^+])}{(K_d^1 + [H^+])}$$

$$k_0 = \frac{k_1[H^+] + k_2K_d^1 + k_3K_d^1K_d^2/[H^+]}{(K_d^1 + [H^+])} \qquad (6)$$

This equation is likely to give a plot of such as that in Figure 2 provided $k_3 \ggg k_2 \gg k_1$. Under this situation equation (6) can be reduced to (7) and (8) at low and high $[H^+]$ respectively.

$$k_0(K_d^1 + [H^+]) = k_2K_d^1 + k_3K_d^1K_d^2/[H^+] \qquad (7)$$

$$k_0(K_d^1 + [H^+]) = k_1[H^+] + k_2K_d^1 \qquad (8)$$

The plots of Figures 2 and 3 separately conform to these two relationships. The values of k_1, k_2, and k_3 (dm^3 mol^{-1} s^{-1}) at 35 °C have been calculated and found to be 27 ± 2, $(1.24 \pm 0.1) \times 10^3$, and $(1.1 \pm 0.08) \times 10^{10}$ respectively. It has invariably been found that k_1 is smaller than k_2 not only in the copper(II)-catalysed oxidations of H_2A, but also in other bimolecular reactions[28,29] involving H_2A, and Akhtar and Haim[30] have interpreted it in terms of reversal of affinities for protons.

Alternatively if all the forms of H_2A are considered to be equally reactive and the hydrogen-ion dependence is explained by the two forms of Cu^{II}, rate law (12) will be obeyed. If Cu^{II} is present as $[Cu(O_2CMe)]^+$ and is supposed to undergo hydrolysis as in (9), the hydrolysed form of Cu^{II} may be $[Cu(OH)(O_2CMe)]$. The hydrolysis constant[31] for Cu^{2+} is $\approx 10^{-7}$ and it is likely to be small also for $[Cu(O_2CMe)]^+$. The two reactions (10) and (11) would give the rate law (12). The

$$[Cu(O_2CMe)]^+ + H_2O \overset{K_H}{\rightleftharpoons} [Cu(OH)(O_2CMe)] + H^+ \qquad (9)$$

$$[Cu(O_2CMe)]^+ + H_2A \xrightarrow{k_1'} \text{products} \qquad (10)$$

$$[Cu(OH)(O_2CMe)] + H_2A \xrightarrow{k_2'} \text{products} \qquad (11)$$

$$-d[H_2A]/dt = [H_2A][Cu^{II}](k_1' + k_2'K_H/[H^+]) \qquad (12)$$

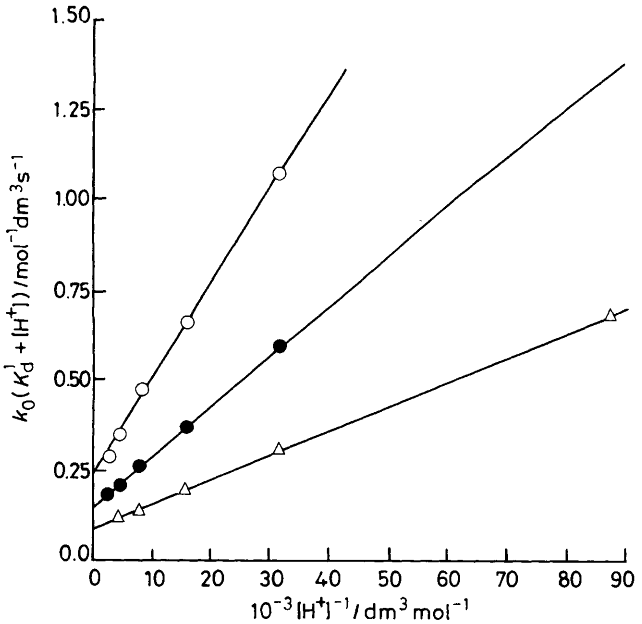

Figure 3. Plot of $k_0(K_d^1 + [H^+])$ *versus* $[H^+]^{-1}$. Conditions and symbols as in Figure 2

values of k'_1 and K_Hk_2 (mol^{-1} dm^3 s^{-1}) were found to be 120 and 0.21 at 40 °C, 67 and 0.12 at 35 °C, and 25 and 0.048 at 30 °C respectively.

The $[H^+]$ dependence of the iron(III)-catalysed reaction (Table 2) looks a little abnormal, but can be explained on lines similar to those above. Iron(III) is likely to be present mostly as $[Fe_3(OH)_2(O_2CMe)_6]^+$ (formation constant[32] $\approx 10^{22}$) and if all the ascorbic acid species are considered equally reactive there would be no change in the rate with variation of $[H^+]$ in the presence of Fe^{III}. The results for the uncatalysed reaction must be examined in the light that it is catalysed by both the metal ions, but the contribution of Cu^{II} dominates. Hence the rate constants decrease by a factor of two only on increasing $[H^+]$ a hundred-fold.

Formation of reactive free-radical intermediates[29,33] from ascorbic acid in the present system is now beyond doubt. Indirect evidence for free radicals formed from both the main reactants is provided by the stoicheiometry and rates in the presence of mma in Tables 1 and 3 respectively. The rate is larger when $[H_2A]_0 > [pdp]_0$ and under the same condition $\Delta[H_2A]/\Delta[pdp]$ is greater than 1. Thus more free radicals from H_2A are produced and consumed by mma when $[H_2A]_0 > [pdp]_0$. The results obtained under the condition $[pdp]_0 > [H_2A]_0$ show that the stoicheiometry ($\Delta[H_2A]/\Delta[pdp]$) is less than 1, but the rates are not different from those in the absence of mma. This indicates that the pdp radicals are definitely produced and consumed in polymerisation rather than in redox reaction. The plots of $[H_2A]$ *versus* time in the presence of mma when $[pdp]_0 > [H_2A]_0$ show that H_2A is not completely used up, which is unexpected. It appears that pdp is consumed elsewhere too without reacting with H_2A, thus increasing the value of $\Delta[pdp]$ and decreasing the value of $\Delta[H_2A]/\Delta[pdp]$.

Khan and Martell[1,34] have reported catalysis by iron(III) and copper(II) chelates of aminopolycarboxylic acids, though the catalysis is poor compared to that by free metal ion or by metal acetate complexes. They specifically relate the catalysis to the chelates rather than the free metal ions. In the iron(III) edta complex-catalysed oxidation of ascorbic acid by H_2O_2, Grinsted[35] found that the rate is essentially negligible in the presence of excess of edta. In the present case free metal ions may be the active species and it is doubtful whether metal chelates are reactive. It may also be mentioned in this connection that in the oxidation[36] of $[Fe(CN)_6]^{4-}$ by pdp where $[Cu^{II}(edta)]^{2-}$ acts as a catalyst, Cu^{2+}(aq) is an inhibitor. Similarly in the reduction[37] of $[Fe(CN)_6]^{3-}$ by hydroxylamine, iron(III) edta chelate acts as a catalyst, but Fe^{3+}(aq) inhibits the reaction.[38] Thus the role of free trace metal ions and their chelates is quite complex and any generalisation would not cover all cases. However, metal-ion inhibition is not common, but a knowledge of its mechanism would be useful for the understanding of biochemical reactions.

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