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The Copper(II) Catalyzed Reaction of L-Ascorbic Acid with Tris(oxalato)cobaltate(III) Ion in Aqueous Solution

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The kinetics of the reaction between tris(oxalato)cobaltate(III) ion and L-ascorbic acid were studied in aqueous solution over a range of copper(II) ion concentrations, ascorbic acid concentrations, pH values and temperatures. A rate law of the type rate = $k[HA^-][Cu^{2+}][Co^{3+}]$*, where* HA^- *= ascorbate, is suggested by the experimental results. A mechanism involving a copper-ascorbate complex is proposed.*

Introduction

The intervention of copper(II) as a catalyst is very common in redox reactions occurring in living systems [1]. Thus, the catalysis of the hydroxylation of dopamine by dopamine hydroxylase is thought to involve a reaction in which ascorbate reduces a copper(II) protein species to the corresponding copper(I) protein [2]. Similarly ascorbic acid oxidase is a protein which contains six atoms of copper per mole of protein. It is clear then, that an understanding of the role of copper(II) as a catalyst in redox systems, particularly involving ascorbic acid should provide information relevant to these important biological systems.

Ascorbic acid has been used directly as the reducing agent for the cobalt(III) ion [3] and also for cobalt(III) complexes [4–6]. The kinetics of the reduction of copper(II) by ascorbic acid have been studied [7].

The oxidation of ascorbic acid by dioxygen is catalysed by copper(II) and this important reaction has been the subject of a number of kinetic studies which have examined the catalysis by copper(II) ion and copper(II)-containing ions [8].

Direct reduction of a number of cobalt(III) complexes by the metastable hydrated copper(I) ion in acid aqueous solution was studied from a kinetic standpoint by Parker and Espenson [9]. These workers also studied [10] the copper(II) catalysis of the reduction of cobalt(III) complexes by vanadium(III), while Higginson and Sykes [11] had previously examined the related reaction of copper(II) catalysis of the reduction of iron(III) by vanadium(III).

The recent study of the reduction of tris(oxalato)cobaltate(III) ion by ascorbic acid by Kimura, Yamamoto and Yanabe [6] demonstrated that this redox reaction is also strongly catalysed by copper(II). This paper is a study of this reaction under conditions of fairly high copper(II) concentrations and in a pH range where we can expect both ascorbic acid and the hydrogen ascorbate ion to be present in equilibrium.

Experimental

Reagents

Reagents where available BDH Analar grade reagents were used. Analar L-ascorbic acid was used and solutions were always used freshly prepared. The copper(II) was in the form of Analar copper(II) sulphate. Ionic strength was maintained using sodium perchlorate.

Potassium tris(oxalato)cobaltate(III) was prepared by a literature method [12].

Kinetic Measurements

All kinetic runs were carried out using a Hi Tech SF-10 portable stopped flow device. This is a stopped flow unit which incorporates the reactant syringes, mixing cell and stop syringe in a flexible system in which the solutions are thermostatted using pumped water and the mixing cell fits into a normal spectrophotometer cell holder. This work was carried out using a Perkin Elmer Lambda 3UV/Vis spectrophotometer. This has the advantage that it operates satisfactorily with the cell compartment open. This allows the use of the SF-10 system without modification of the cell compartment cover. For the rates of reaction studied here the spectrophotometer was fast enough to follow even the most rapid reactions. The 1 volt full scale output from the spectrophotometer was taken directly into an Acorn BBC Model B computer, which incorporates its own 12-bit analogue-digital convertor. The signal was handled by the computer

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*Throughout this paper oxalate = ethanedioate.

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using a program the details of which have been discussed elsewhere [13].

The solution of the cobalt(III) complex was made up in a solution of copper(II) sulphate of the appropriate concentration. The ionic strength was adjusted (usually to 1.0 *M*) using sodium perchlorate. Ascorbic acid, always freshly prepared, was made up in the appropriate sodium perchlorate solution. The pH was adjusted using sodium hydroxide or perchloric acid solution as appropriate. Preliminary runs showed that outgassing the solutions using argon did not affect the values of the rate constants obtained.

Results and Discussion

Preliminary experiments confirmed the observation of Kumura, Yamamoto and Yanabe [6], that the cobalt(III) complex is reduced by ascorbic acid and that the reduction is considerably accelerated by the presence of copper(II) sulphate. Furthermore it was soon recognized that the slowing-down of the reaction produced by oxalate ion as described by these workers affected the nature of the absorbance–time plots as the oxalate released in the reaction diminished the catalytic effect of the copper(II). It was found essential, therefore, that in order to obtain good first order plots, the excess of copper(II) over cobalt(III) complex had to be at least tenfold. Good first-order plots were also not obtained with small concentrations (less than $\sim 10^{-3}$ *M*) of the cobalt(III) complex. An at least thirtyfold excess of ascorbic acid over cobalt(III) complex was maintained in all experiments. Under these conditions excellent first order plots for the disappearance of the cobalt(III) complex were obtained for at least two half lives. When a solution of ascorbic acid is mixed with a green solution of tris(oxalato)cobaltate(III) ion containing copper(II) sulphate there is a rapid change in colour from green to almost colourless (a faint residual colour remains from the copper species present). The spectrum of this solution showed a progressive diminution of λ_{max} with time. These were recorded using the Perkin Elmer Lambda 3 spectrophotometer using its fastest scan capability. The product spectrum is that expected for a cobalt(II) salt in the presence of copper(II) and ascorbic acid. Rate constants were measured at 400 nm. The diminution of absorbance at this wavelength represents the disappearance of tris(oxalato)cobalt(III) ion. Some rate constants were measured at 600 nm and found to be identical with those obtained under the same conditions at 400 nm within experimental error. At least three and often five or six runs were used to determine the rate constant under each set of conditions. Rate constants were measured with the variation of ascorbic acid concentration, copper(II) ion concentration, pH and temperature, with other parameters remaining constant. The effect of ionic strength was determined by measuring the rate of reaction in the presence of sodium perchlorate at an ionic strength of 1.0 *M* and also in the absence of sodium perchlorate with all other parameters identical. The variations of various parameters with the exception of the ionic strength effect were carried out at three temperatures. These results are given in Table I.

Variation of k_{obs} with pH

Over the pH range 2.01 to 3.40, there was a rapid and considerable variation in the observed first order rate constant, similar to that observed in virtually all the studies of the kinetics of ascorbic acid reduction of cobalt(III) complexes [5–7]. The first pK_a of ascorbic acid at 25 °C is 3.95 [6], thus this pH range represents a significant amount of change from ascorbic acid to hydrogen-ascorbate ion. In fact a series of plots of k_{obs}^{-1} against $[H^+]$ gives straight lines at each of the three temperatures studied here, Fig. 1.

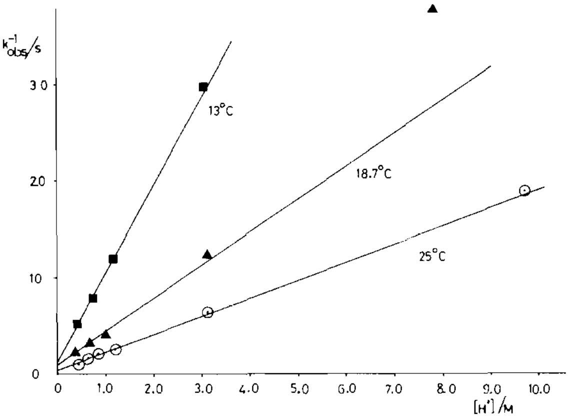


Fig. 1. Effect of variation of $[H^+]$ on the observed rate constant with 1.5×10^{-3} *M* $[Co(C_2O_4)_3]^{3-}$, 0.005 *M* Cu^{2+}, 0.05 *M* ascorbic acid.

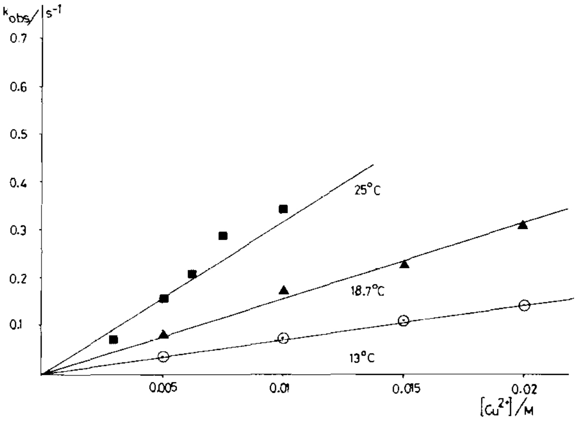


Fig. 2. Effect of variation of $[Cu^{2+}]$ on the observed rate constant with 1.5×10^{-3} *M* $[Co(C_2O_4)_3]^{3-}$, 0.05 *M* ascorbic acid and pH = 2.5.

TABLE I. Effect of Various Parameters on the Observed Rate Constant. Concentration of tris(oxalato)cobaltate(III) ion is 1.5×10^{-3} *M* in all cases. Ionic strength is 1.0 *M* with sodium perchlorate.

Temperature/K	pH	concentration of copper/*M*	concentration of ascorbic acid/*M*	observed rate constant/s^{-1}
298	2.01	0.005	0.05	0.053
	2.50	0.005	0.05	0.159
	2.92	0.005	0.05	0.394
	3.08	0.005	0.05	0.484
	3.21	0.005	0.05	0.610
	3.40	0.005	0.05	0.864
	2.50	0.005	0.10	0.246
	2.50	0.005	0.15	0.313
	2.50	0.005	0.20	0.377
	2.50	0.005	0.25	0.412
	2.50	0.0025	0.05	0.083
	2.50	0.0062	0.05	0.207
	2.50	0.0075	0.05	0.290
	2.50	0.010	0.05	0.347
291.7	2.10	0.005	0.05	0.0266
	2.50	0.005	0.05	0.082
	3.00	0.005	0.05	0.251
	3.15	0.005	0.05	0.328
	3.40	0.005	0.05	0.467
	2.50	0.005	0.075	0.104
	2.50	0.005	0.10	0.102
	2.50	0.005	0.12	0.153
	2.50	0.005	0.15	0.129
	2.50	0.005	0.20	0.160
	2.50	0.010	0.05	0.169
	2.50	0.015	0.05	0.225
	2.50	0.020	0.05	0.311
289.0	2.50	0.005	0.05	0.0334
	2.92	0.005	0.05	0.146
	3.08	0.005	0.05	0.194
	3.27	0.005	0.05	0.285
	2.50	0.005	0.10	0.0452
	2.50	0.005	0.15	0.0567
	2.50	0.005	0.20	0.0745
	2.50	0.005	0.25	0.0742
	2.50	0.010	0.05	0.0731
	2.50	0.015	0.05	0.114
	2.50	0.020	0.05	0.144
	2.50	0.005	0.05	0.063[a]

[a] Ionic strength = 0.01 *M*.

Variation of k_{obs} with Copper(II) Concentration

This is shown for the three temperatures in Fig. 2. It can be seen that over the range 0.005 *M* to 0.025 *M* at the three temperatures, there is a linear variation of k_{obs} against copper(II) ion concentration.

Variation of k_{obs} with Total Ascorbic Acid Concentration

Unlike the reaction which occurs in the absence of copper(II) ion [6], the reaction studied here does not appear to be first order in ascorbic acid, but shows a curvature in the plot of k_{obs} against total ascorbic acid concentration (Fig. 3) which indicates that there is a levelling off of the rate at higher ascorbic acid concentrations. The effect of ionic strength variation when all other parameters were held constant, was also studied and it can be seen from Table I that the effect of reducing the ionic strength is to increase the rate of reaction.

It has been suggested on many occasions [1, 6] that the catalytic activity of copper(II) in redox reactions of the type studied here is due to the reduction to copper(I) which then reduces the substrate, being itself oxidised back to copper(II) and

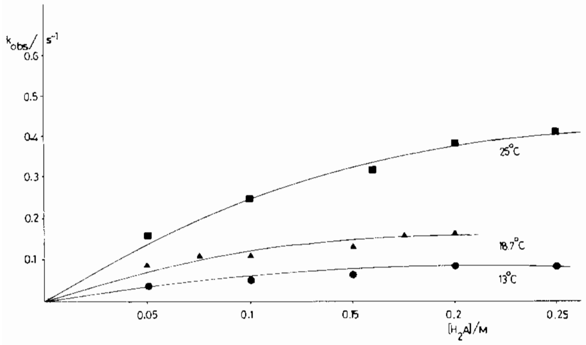


Fig. 3. Effect of variation of total ascorbic acid concentration on the observed rate constant with 1.5 × 10^{-3} *M* [$Co(C_2O_4)_3^{2-}$], 0.005 *M* Cu^{2+} and pH = 2.5.

then again reduced to copper(I) *etc.* The intervention of other oxidation states of copper such as copper(III) has been suggested in the complex redox reactions involving the oxidation of ascorbic acid by dissolved dioxygen in the presence of copper(II). In the reaction studied here, a cycle of reactions involving the copper(II)/copper(I) oxidation states would seem to offer a reasonable explanation for the observed behaviour. It is known [7] that copper(II) is readily reduced in the pH range 2 to 4 by ascorbic acid to copper(I) at a rate which is fast compared with the reactions studied here. The overall effect would be:

$$H_2A + 2Cu(II) \longrightarrow A + 2Cu(I)$$

where H_2A = ascorbic acid
A = dehydroascorbic acid.

However, it is also known that a solution containing copper(II) and ascorbic acid contains complexes formed between the ascorbic acid and the copper(II) [15] in the pH range studied here:

$$Cu^{2+} + HA^- \rightleftharpoons Cu(HA)^+ \qquad K_M$$

and

$$H^+ + Cu^{2+} + HA^- \rightleftharpoons Cu(H_2A)^{2+} \qquad K_{MH}$$

where

$$K_M = \frac{[CuHA^+]}{[Cu^{2+}][HA^-]} \qquad (1)$$

and

$$K_{MH} = \frac{[Cu(H_2A)^{2+}]}{[H^+][Cu^{2+}][HA^-]} \qquad (2)$$

$$\text{Also } K_a = \frac{[H^+][HA^-]}{[H_2A]} \qquad (3)$$

If the rate of reaction is first order in [Cu^{2+}], [HA^-] and [complex], then

$$\text{Rate} = k[Cu^{2+}][HA^-][Co(C_2O_4)_3{}^{3-}] \qquad (4)$$

$$\therefore k_{obs} = k[Cu^{2+}][HA^-] \qquad (5)$$

The total copper(II) is therefore represented by:

$$[Cu]_T = [Cu^{2+}] + [CuHA^+] + [CuH_2A^{2+}] \qquad (6)$$

and the total ascorbic acid present is given by:

$$[H_2A]_T = [HA^-] + [H_2A] \qquad (7)$$

Thus, we may write the concentration of [HA^-] as:

$$[HA^-] = \frac{K_a}{(K_a + [H^+])}[H_2A]_T \qquad (8)$$

Combining eqns. (1), (2), (6) and (8), we obtain

$$[Cu^{2+}] = \frac{(K_a + [H^+])[Cu]_T}{(K_a + [H^+] + K_M K_a [H_2A]_T + K_{MH} K_a [H^+][H_2A]_T)}, \qquad (9)$$

combining eqns. (5), (8) and (9), we get:

$$k_{obs} = \frac{K_a k [Cu]_T [H_2A]}{(K_a + [H^+] + K_M K_a [H_2A]_T + K_{MH} K_a [H^+][H_2A]_T)} \qquad (10)$$

This can be arranged to give:

$$\frac{1}{k_{obs}} = \left\{\frac{(K_a + [H^+])}{K_a k [Cu]_T}\right\}\frac{1}{[H_2A]_T} + \left\{\frac{K_M + K_{MH}[H^+]}{k[Cu]_T}\right\} \qquad (11)$$

Thus at any given temperature at constant pH and constant copper concentration, this is expected to give a straight line for a plot of $k_{obs}{}^{-1}$ against $[H_2A]^{-1}$. Such a plot for this system is shown in Fig. 4. Equation (10) may be further arranged to give:

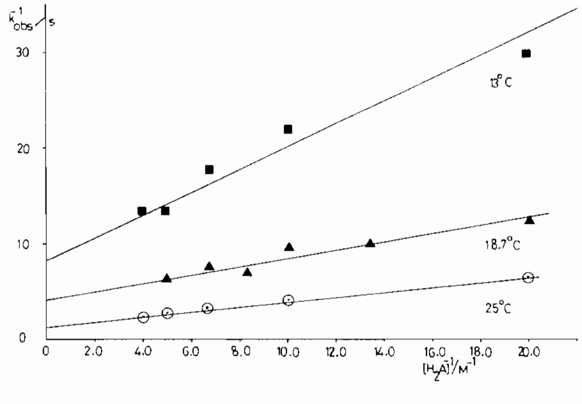


Fig. 4. Plot of reciprocal of observed rate constant against reciprocal of total ascorbic acid concentration with 1.5 × 10^{-3} *M* [$Co(C_2O_4)_3^{2-}$], 0.005 *M* Cu^{2+} and pH = 2.5.

$$\frac{1}{k_{obs}} = \left\{\frac{(1 + K_{MH}K_a[H_2A]_T)}{K_a k[Cu]_T[H_2A]_T}\right\}[H^+] + \frac{(1 + K_M[H_2A]_T)}{k[Cu]_T[H_2A]_T} \qquad (12)$$

A plot of k_{obs}^{-1} against $[H^+]$ when $[Cu]_T$ and $[H_2A]_T$ are constant, is thus expected to give a straight line at any given temperature, Fig. 1.

Equation (11) shows that from a plot of k_{obs}^{-1} against $[H_2A]_T^{-1}$, the gradient is:

$$\text{gradient} = \frac{(K_a + [H^+])}{K_a k[Cu]_T}$$

From which k may be calculated, since K_a is known (8).

Also, from eqn. (12), whose gradient is given by:

$$\text{gradient} = \frac{(1 + K_{MH}K_a[H_2A]_T)}{K_a k[Cu]_T[H_2A]_T}$$

and whose intercept is given by

$$\text{Intercept} = \frac{(1 + K_M[H_2A]_T)}{k[Cu]_T[H_2A]_T}$$

Therefore, using the value of k obtained from eqn. (12), the value of K_{MH} may be calculated from the gradient and K_M may be calculated from the intercept of a plot of k_{obs}^{-1} against $[H^+]$. Values calculated by this method are given in Table II. It can be seen that the values at 25 °C are in fair agreement with those obtained by Jameson and Blackburn [15] under similar conditions considering the large number of parameters involved in the analysis and the consequent large errors. By far the largest difference is in K_M. The conditions used in the two studies were somewhat different in that Jameson and Blackburn used an ionic strength of 0.1 *M* which was maintained using potassium nitrate. In fact the value of K_M as determined in the system described here is closer to the value of 40 M^{-1} which was obtained by Khan and Martell [16].

The linear dependence of the observed rate constant on the copper concentration passing through the origin is also in keeping with the above reaction scheme. A comparison of the observed and calculated slopes is given in Table III (calculated from eqn. (10)). The effect of ionic strength variation on the rate is in the opposite direction to that observed for the direct reaction of ascorbic acid with tris(oxalato)-cobaltate(III) ion [6]. Kimura, Yamamoto and Yanabe [6] drew attention to the fact that for the direct reaction, the direction of variation of rate with ionic strength was in keeping with the reaction of the negatively charged complex with the negatively charged HA^- ion. In the same way, in the presence of copper(II) under the conditions described here, the direction of variation of rate with ionic strength is in keeping with the reaction of the negatively charged complex with a positively charged species such as $[CuHA]^+$.

Recently proposed mechanisms for the reduction of molecular dioxygen have involved a rate law having a half order dependence on the concentration of molecular dioxygen [8] and the intervention of a dimeric copper/ascorbate species. It seems more likely in the reaction studied here that a simpler mechanism involving the formation of an ascorbate–copper–cobalt(III) complex bridge obtains. This is similar to the mechanism originally proposed by Taqui Khan and Martell [16] for the copper(II) catalysed reduction of molecular dioxygen.

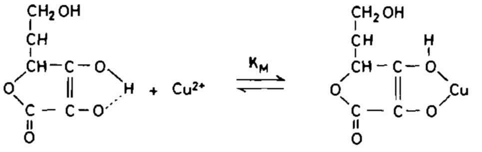
TABLE II. Values of k, K_{MH} and K_M Calculated from Eqns. (11) and (12).

Temperature/°C	$k/M^{-2}\ s^{-1}$	K_{MH}/M^{-2}		K_M/M^{-1}		
		This work	Ref. 15	This work	Ref. 15	Ref. 16
25.0	2.43×10^4	5.11×10^4	1.58×10^4	41	251	37
18.7	1.69×10^4	11.2×10^4		20.5		
13.0	0.66×10^4	8.1×10^4		6.6		

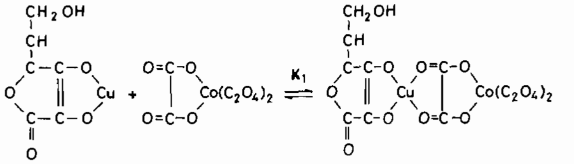
TABLE III. A Comparison of the Slopes Calculated from eqn. (10) Using Data from Table II with the Experimental Values Calculated from Fig. 3.

Temperature/°C	calcd slope/$M^{-1}\ s^{-1}$	expl slope/$M^{-1}\ s^{-1}$
25.0	30.9	36.9
18.7	16.5	14.9
13.0	6.7	7.4

The process envisaged is the initial formation of the copper(II) ascorbate complex $[CuHA]^+$:



This is then followed by a further equilibrium step in which an inner sphere ascorbate–copper(II)–cobalt(III) complex system is the result:



The electron is then transferred *via* the copper(II) ion from the ascorbate to the metal:

$$HACuC_2O_4Co^{III}(C_2O_4)_2 \xrightarrow{k_1} HA^{\bullet}CuC_2O_4Co^{II}(C_2O_4)_2$$

This is then followed by the fast reactions:

$$HA^{\bullet}CuC_2O_4Co^{II}(C_2O_4)_2 \xrightarrow{\text{fast}} HA^{\bullet} + Cu^{2+} + Co^{2+} + 3C_2O_4{}^{2-}$$

and

$$HA^{\bullet} + HA^{\bullet} \xrightarrow{\text{fast}} HA^- + A + H^+$$

where A is dehydroascorbic acid.

The rate law which applies to this series of reactions is:

$$\frac{-d[Co^{3+}]}{dt} = k_1K_MK_1[HA^-][Cu^{2+}][Co^{3+}]$$

This corresponds to the observed rate law (eqn. (4)) where $k = k_1K_MK_1$.

We can only speculate about the nature and structure of the copper-bridge, but similar bridged intermediates have been proposed to be involved in the reduction of oxalato cobalt(III) complexes by other reductants. Thus, the reduction of tris(oxalato)cobaltate(III) by iron(II) has been described in terms of a transition complex containing a Co–iron–oxalate bridge [17], though whether this is bidentate is left to debate. The fast reactions of two ascorbate radicals to form hydrogenascorbate and dehydroascorbate has previously been proposed as the final step in the direct reduction of cobalt(III) complexes by ascorbic acid [4].

Acknowledgements

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