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The Reaction between Copper(II) Ions and L-Ascorbic Acid in Chloride Media

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Abstract

The reaction of copper(II) with L-ascorbic acid was studied in the presence of chloride ions. The results are described in relation to previous studies and the point is made that the kinetics in a complexing medium such as chloride are fundamentally different from those in a weakly complexing medium such as perchlorate. This was reinforced by an electrochemical study of copper(II) in the presence of various concentrations of chloride ion.

Introduction

There have been a number of studies on the reaction of copper(II) with L-ascorbic acid in a variety of media [1, 2]. Some of these have been investigations of the kinetics and mechanism of the reaction [3, 4]. There have been some studies of the reaction involving L-ascorbic acid and copper(II) in chloride media with oxygen, in which copper(II) is involved in a catalytic role. However, there has been only one paper published on the kinetics of the reaction of L-ascorbic acid with copper(II) in chloride media [5]. In this last work, chloride was used to maintain the ionic strength of the reaction mixture. Great care has to be exercised in the choice of ions, particularly anions for this purpose (but also cations [6, 7]). Thus nitrate ions for example have been shown to have a considerable influence, stemming from effects other than just ionic strength, on a number of reactions involving cobalt(III) complexes [8, 9]. The well-known complexing ability of chloride ions is likely to be a factor in any reaction involving transition metal aqua ions when the metal is present in a small concentration and chloride in a high concentration. A factor 1000:1 for chloride: copper concentrations would not be uncommon when chloride is used to control the ionic strength of a reaction mixture. The complexing of chloride with copper(II) in the presence of L-ascorbic acid has indeed been frequently invoked by Jameson and Blackburn [10] in the interpretation of the mechanism of the so-called auto oxidation of L-ascorbic acid in the presence of copper(II) ions in chloride media. The purpose of this paper is to comment on and hopefully clarify one or two features of the study of the oxidation of L-ascorbic acid in acidic media by copper(II) ions published recently by Martinez *et al.* [5].

Experimental

Where available all reagents were BDH Analar grade. The L-ascorbic acid was used as received and solutions were always freshly prepared. Ionic strength was maintained using sodium perchlorate.

Kinetic runs were carried out using a High-Tech SF-10 portable stopped flow unit coupled to a Perkin-Elmer Lambda 3 UV–Vis spectrophotometer and the data were collected using an Acorn BBC Model B computer. All spectra were run on the Perkin-Elmer Lambda 3 spectrophotometer.

For the electrochemistry the working electrode was a Corning platinum disc of surface area 0.25 cm which was always pretreated before use by being immersed in concentrated sulphuric acid, anodised, then cathodised for one minute each in 0.5 M sulphuric acid at 5 mA, then washed thoroughly with deionised water. A platinum wire counter electrode and saturated calomel electrode were used in a two compartment electrochemical cell and all potentials cited are with respect to the latter. Cyclic voltammograms were obtained in duplicate at 25.0 + 0.1 °C using a PAR 264A potentiostat with a J.J. Lloyd PL 3 XY recorder and solutions preflushed with nitrogen.

Results and Discussion

It is clear to anyone who has observed the reaction of copper(II) ion with L-ascorbic acid in both chloride and other media (such as perchlorate) that the reactions are different. At a pH of about 2.5 in a perchlorate medium at room temperature, mixing equal volumes of 0.01 M copper(II) sulphate and 0.1 M L-ascorbic acid produces a characteristic green colour with an absorbance having a maximum at 410 nm. However in a chloride medium under the same conditions the reaction results in a colourless solution with no absorbance in the visible.

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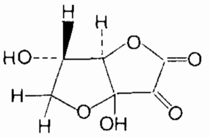
It is expected that the reactants in the two different media will not be the same. It is known that copper(II) forms chloro complexes in aqueous chloride solution [11]. Under the conditions described above (which are not too different from those described by Martinez and coworkers) a considerable amount of copper(II) will be present as $CuCl_2^-$ and other complexes. These will constitute a major part of the reacting copper(II). That is, the reaction is not expected to involve exclusively aqua copper(II) ions, but also all these other species.

Furthermore, the products will not be those assumed by these workers. In the presence of chloride ions, copper(I) readily forms insoluble copper(I) chloride, CuCl. Indeed this is how it is most easily prepared [12]. However, in a large excess of chloride ions copper(I) chloride has a substantial solubility [13]. It is then present as $CuCl_2^-$ or $CuCl_3^{2-}$. At a 1.0 M concentration of chloride, 0.005 M copper(I) would be present as these species. The solution is colourless.

Perhaps it is relevant to mention that the nature of the oxidation product of L-ascorbic acid is not simple. It has been pointed out by Creutz [14] that the ascorbate free radical is highly acidic (pK – 0.46) so that under the conditions used by Martinez and coworkers it would be present as the deprotonated moiety $A^{\dot{-}}$; neither is the two electron oxidation product that which is suggested by these workers. It has been shown [15] that although the oxidation of L-ascorbic acid is reversible for the first second or so of the reaction, the so-called dehydroascorbic acid then cyclises to form the product



which is not reversibly reconverted into L-ascorbic acid. We have examined the nature of the reaction between chloride ions on the one hand and a mixture of copper(II) ions and an excess of L-ascorbic acid on the other. The green colour of copper(II) in L-ascorbic acid is rapidly discharged on the addition of chloride. It is thus possible to carry out a titration reaction to examine how much chloride ion is required to remove the green colour of the copper(II) in L-ascorbic acid. It is difficult to see the endpoint even at a copper(II) concentration of 0.05 M and an L-ascorbic acid concentration of 0.5 M, but it is nevertheless perfectly possible to obtain a good estimate of the equivalence point. In fact the ratio of chloride to copper(II) was found to be 2:1.

It is not clear whether or how the stoichiometry of the reaction was established by them. Nevertheless in view of the difference in behaviour between chloride and perchlorate media, it is clearly of interest to examine the stoichiometry of the copper(II) and the L-ascorbic acid in the reaction. A Yoe–Jones plot [16] for this system is shown in Fig. 1. This shows that the stoichiometry for Cu(II):H_2A = 2:1, as quoted by Martinez and coworkers.

Under conditions of high acid concentration, it was observed that the green colour of the Cu(II)/H_2A mixture was discharged comparatively slowly on the addition of chloride ions and the effect of chloride ion concentration on the rate was obtained. The rate constants are shown in Table I. In the middle of the range of chloride ion concentration, the reaction gave good pseudo first order kinetics, but at both low and high chloride ion concentrations, the pseudo first order kinetics were not as good. There is however clearly a considerable dependence of the rate on chloride ion concentration. A six-fold increase in rate is observed for a three fold change in chloride ion concentration. This is unlikely to be an ionic strength effect. The dependence of the observed rate constants on chloride ion concentration appears to be second order (Fig. 2).

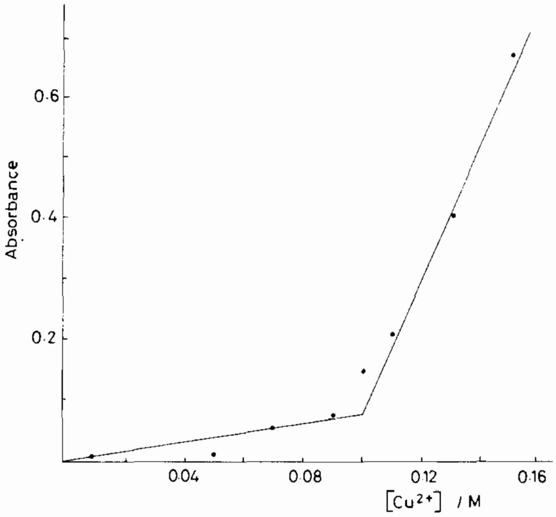


Fig. 1. Variation of absorbance at 750 nm with copper(II) ions added to 0.05 M L-ascorbic acid.

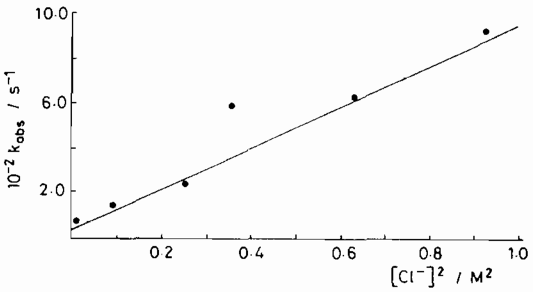


Fig. 2. Variation of observed rate constant with square of chloride ion concentration. [H_2A] = 0.05 M.

TABLE I. Effect of Chloride Ion Concentration on the Observed Rate Constant for the Reaction of Chloride with Copper(II) and Ascorbic Acid

Chloride ion concentration (M)	Observed rate constant ($s^{-1} \times 10^2$)
0.10	0.993
0.30	1.59
0.50	2.48
0.60	6.09
0.80	6.40
0.95	9.36

The stoichiometry of the reaction is

$$2Cu^{2+} + H_2A + 4Cl^- \longrightarrow 2CuCl_2^- + DHA + 2H^+$$

It is known that at pH 2.5 copper(II) forms a complex with L-ascorbate, HA^-

$$Cu^{2+} + HA^- \rightleftharpoons [CuHA]^+$$

This is believed to be responsible for the green colour of such solutions. The reaction observed here at pHs in the region of 2.5 is therefore

$$[CuHA]^+ + 2Cl^- \xrightarrow{k} CuCl_2^- + A^- + H^+$$

$$[CuHA]^+ + A^{\overset{+}{\cdot}} + 2Cl^- + H^+ \xrightarrow{\text{fast}} CuCl_2^- + A$$

At a given pH, this reaction would be expected to be second order in chloride ion concentration, as observed.

Studies of the reaction of L-ascorbic acid with copper(II) in aqueous perchlorate media suggest that there is rapid formation of an ascorbato complex and slow (on the Martinez and coworkers' timescale) reduction to copper(I). The situation is fundamentally different in chloride media in that there is rapid reduction of copper(I) at low acid concentrations (around pH 2.5). If we assume that Martinez and coworkers obtained their data at constant $[Cl^-]$ and that the reacting species is $CuCl^+$ (instead of Cu^{2+}), then their equilibria become

$$Cu^{2+} + Cl^- \rightleftharpoons [CuCl]^+$$

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

$$HA^- + [CuCl]^+ \xrightarrow{k_1} A^{\cdot} + CuCl + H^+$$

$$H_2A + [CuCl]^+ \xrightarrow{k_2} A^{\cdot} + CuCl + 2H^+$$

$$HA^{\cdot} + [CuCl]^+ \xrightarrow{k_3} A + H^+ + CuCl$$

The effects of this on their rate constants, k_1, k_2, and k_3 are complex relationships involving $[Cl^-]$, but at constant $[Cl^-]$ give identical kinetic behaviour to that observed. This means that k_1 as a function of $[Cl^-]$ cannot be related directly to the Cu^{2+}/Cu^+ redox couple. In order to confirm this we examined the redox behaviour of copper(II) in solutions of chloride ion using cyclic voltammetry.

Redox Behaviour of Copper(II) in Chloride Media

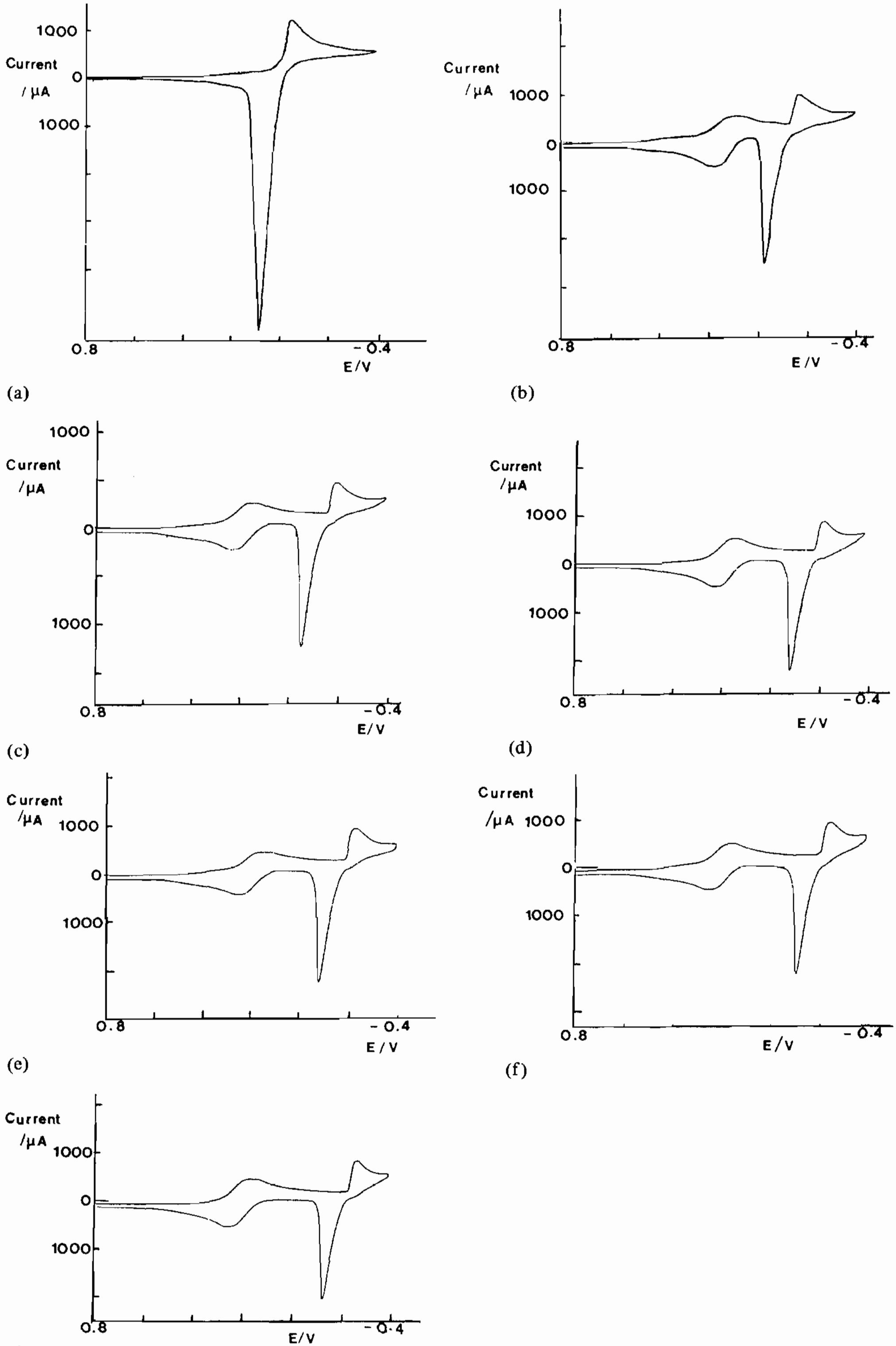
Figure 3a–g shows a series of cyclic voltammograms (CVs) for copper(II) solutions over a range of chloride ion concentrations. Table II summarises E_p data from the CVs. At 0.0 M chloride ion concentration a small adsorption wave at around 0.20 V, followed by a main redox wave due to aqua— Cu(II)/Cu(0) electrodeposition and stripping process is observed. Dramatic changes in the copper(II) redox system are produced by the introduction of chloride ions into the electrolyte solutions. A redox wave is now observed at more positive electrode potentials. This is undoubtedly a one-electron redox process with stabilisation of the copper(I) oxidation state by the presence of chloride ions [17]. (The pre-peak observed at around +0.40 V indicates that adsorption is involved. A similar observation has been made in the study of the electrochemistry of the Cu(II)/Cu(I) system in 1.0 M hydrochloric acid [18].)

A second main wave, which has approximately one half the integrated charge of Fig. 1a, is then found for the Cu(I)/Cu(0) electrodeposition and stripping redox process. Shifts in E_p values for both

TABLE II. E_p Data from the Cyclic Voltammograms[a]

NaCl	a (V)	b (V)	c (V)	d (V)
1.0	0.16(0.16)	−0.27(0.25)	−0.14(−0.12)	0.25(0.26)
0.8	0.17(0.17)	−0.24(−0.24)	−0.11(−0.11)	0.25(0.25)
0.6	0.14(0.15)	−0.23(−0.22)	−0.09(−0.07)	0.24(0.25)
0.5	0.15(0.14)	−0.22(−0.22)	−0.09(−0.09)	0.22(0.22)
0.4	0.15(0.15)	−0.18(−0.18)	−0.05(−0.05)	0.24(0.23)
0.2	0.10(0.09)	−0.16(−0.16)	−0.02(−0.02)	0.20(0.18)
0.0		−0.07(−0.04)	0.07(0.09)	

[a] a to d are E_p values from the CVs as follows: a is the first reduction peak, b is the second reduction peak, c is the first oxidation peak, d is the second oxidation peak. Values in parenthesis are duplicate runs.



(a) (b)

(c) (d)

(e) (f)

(g)

Fig. 3. CVs at 10 mV/s over the range +0.80 to −0.40 V. Negative scan initially from +0.80 V in all cases. Solution compositions were as follows: (a) 5 mM $CuSO_4$, 1.0 M $NaClO_4$; (b) 5 mM $CuSO_4$, 0.2 M NaCl, 0.8 M $NaClO_4$; (c) 5 mM $CuSO_4$, 0.4 M NaCl, 0.6 M $NaClO_4$; (d) 5 mM $CuSO_4$, 0.5 M NaCl, 0.5 M $NaClO_4$; (e) 5 mM $CuSO_4$, 0.6 M NaCl, 0.4 M $NaClO_4$; (f) 5 mM $CuSO_4$, 0.8 M NaCl, 0.2 M $NaClO_4$; (e) 5 mM $CuSO_4$, 1.0 M NaCl.

the Cu(II)/Cu(I) (positive direction) and Cu(I)/Cu(0) (negative direction) processes with increase in chloride concentration reveal the increased stability of the chloride–copper(I) complex with respect to both copper(II) and copper(0) oxidation states.

Conclusions

Both electrochemical studies of the copper(II)–chloride system and kinetic studies of the reaction of the copper(II)/L-ascorbic acid system with chloride reveal that the redox behaviour of copper(II) in chloride media is fundamentally different from that of copper(II) in perchlorate media. Chloride ions cannot be used simply to maintain ionic strength in such systems since their influence is much more extensive than ionic strength effects.

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