Role of Copper Dimers and the Participation of Copper(III) in the Copper-catalysed Autoxidation of Ascorbic Acid. Part III.[1] Kinetics and Mechanism in 0.100 mol dm^{-3} Potassium Chloride

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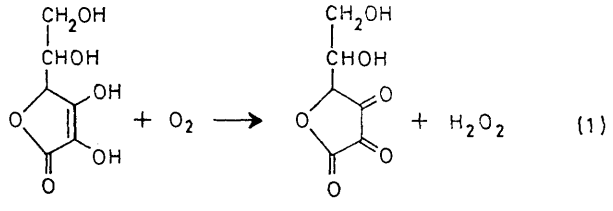
The kinetics of the copper(II)-catalysed oxidation of ascorbic acid by molecular oxygen have been investigated in the range pH 1.80—5.00 using 0.100 mol dm^{-3} KCl as background electrolyte. The reaction was followed both by continuous measurement of oxygen consumption (using a Clark-type oxygen-sensitive electrode) and by direct spectrophotometric measurement (on samples) of the unchanged ascorbic acid. At constant $[H^+]$ the rate law conforms to (i) where $[L]_T$ is the total concentration of ascorbic acid and $[Cu]_T$ is the total concentration of Cu^{II}. On the basis of this, and on thermodynamic evidence, a chain mechanism is proposed in which a copper–copper binuclear species (containing both ascorbate and chloride ligands) is the reactive species. The dependence on $[H^+]$ is too complex, however, to be fully explained. Both one- and two-electron transfer mechanisms are discussed and preference is shown for that involving an initial two-electron transfer to the dioxygen and consequently to the participation of what is formally Cu^{III}.

$$-d[L]_T/dt = -d[O_2]/dt = k[Cu]_T[L]_T^{\frac{1}{2}}[O_2]^{\frac{1}{2}} \quad (i)$$

An interesting feature of the copper(II)-catalysed oxidation of ascorbic acid by molecular oxygen is the way in which the observed kinetics, and hence the mechanism, depend on the nature and concentration of added electrolytes. In Part II of this work [1] we reported the behaviour in 0.100 mol dm^{-3} $K[NO_3]$ and present here the results of a detailed study in 0.100 mol dm^{-3} KCl. In nitrate solution the interest centred around the half-order dependence on oxygen concentration, and it is remarkable that in 0.100 mol dm^{-3} KCl solution both ligand and oxygen dependences are half order, whereas they become zero and first order in 0.100 mol dm^{-3} KBr,[2] reverting to 'nitrate' behaviour in fluoride solution.[2] The overall stoicheiometry of the autoxidation reaction



invariably follows equation (1) quite closely, only deviating significantly after *ca.* 85% completion of reaction.

[1] Part II, R. F. Jameson and N. J. Blackburn, *J.C.S. Dalton*, 1976, 534.
[2] R. F. Jameson and N. J. Blackburn, unpublished work.

RESULTS

Ascorbate Dependence.—The rate of disappearance of ascorbic acid (H_2L) was followed by direct spectrophotometric measurement of the concentration of unchanged ascorbic acid remaining in samples taken periodically from the reacting mixture. The use of a rather concentrated HCl–KCl solution (0.2 mol dm^{-3}) that is required in this method (see below) effectively 'quenched' the reaction whilst spectrophotometer readings were taken. Experiments were made at various total catalyst concentrations, $[Cu]_T$, over the range pH 1.80—5.00, the $[O_2]$ and $[H^+]$ being maintained constant throughout the run.

An induction period in the rate was observed which increased with pH but which, for a given pH, could be eliminated by increasing the total ascorbic acid concentration sufficiently; in practice this meant that, although no induction period was in fact ever observed below *ca.* pH 2.40, it is most probable that, were it possible to work with lower ascorbate concentrations, the induction period would have been seen. However, the results are presented here in two parts.

(a) *Induction period absent.* Figure 1 shows typical plots of the normalised optical density, D/D_0, as a function of time for various total catalyst concentrations, and Figure 2 con-

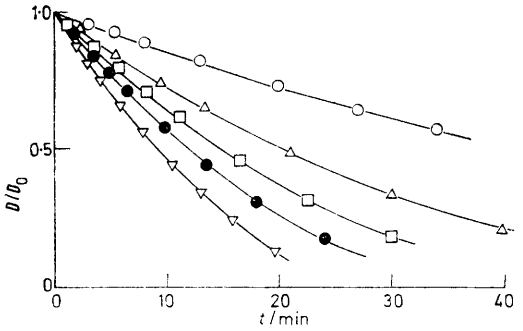


FIGURE 1 Rate of disappearance of ascorbic acid, measured spectrophotometrically, at pH 2.13. $10^5[Cu]_T$/mol dm^{-3}: (○), 2.21; (△), 4.20; (□), 6.52; (●), 8.13; (▽), 9.84

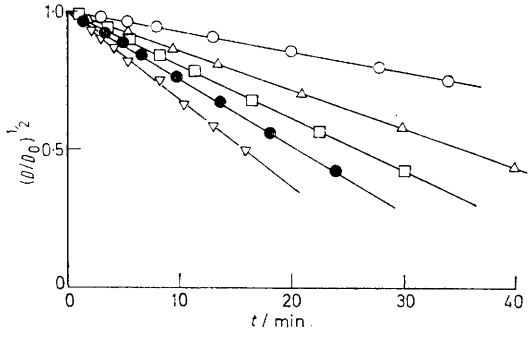


FIGURE 2 Linear dependence of $(D/D_0)^{\frac{1}{2}}$ on time for a representative pH of 2.13. Symbols as in Figure 1

firms the half-order dependence on $[L]_T$ by plotting $(D/D_0)^{\frac{1}{2}}$ against time. Thus we may write equation (2) which integrates to give (3). This enables $k_{obs.}$ to be obtained from

$$-d[L]_T/dt = k_{obs.}[L]_T^{\frac{1}{2}} \quad (2)$$

$$([L]_T/[L]_{T,0})^{\frac{1}{2}} \equiv (D/D_0)^{\frac{1}{2}} = 1 - \left\{\frac{k_{obs.}}{2[L]_{T,0}^{\frac{1}{2}}}\right\}t \quad (3)$$

the data and the linearity of $k_{obs.}$ with respect to $[Cu]_T$ establishes the kinetic behaviour, equation (4) where k' in-

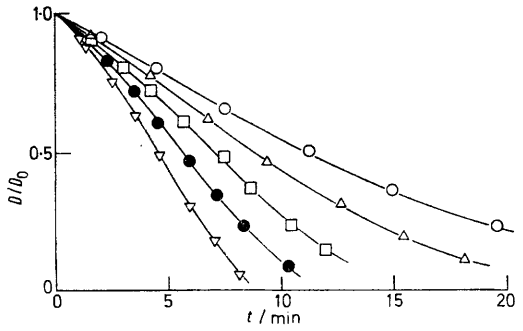


FIGURE 3 Rate of disappearance of ascorbic acid: dependence of induction period on pH. pH Values: (○), 2.42; (△), 2.80; (□), 3.85; (●), 4.50; (▽), 5.00

volves some dependence on $[O_2]$ (some representative values of k' are given in the Table).

$$-d[L]_T/dt = k'[Cu]_T[L]_T^{\frac{1}{2}} \quad (4)$$

(b) *Induction period present.* Figures 3 and 4 illustrate the behaviour when an induction period is present and show clearly (*i*) that this induction period increases with pH for a

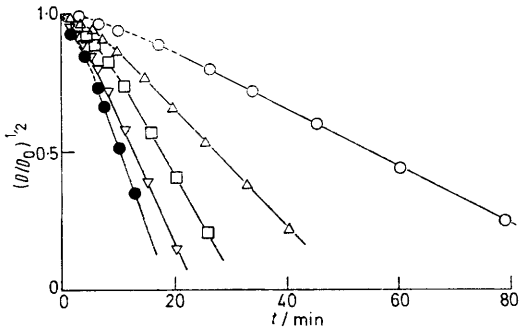


FIGURE 4 Linear variation of $(D/D_0)^{\frac{1}{2}}$ with time after the induction period (pH 3.35). $10^5[Cu]_T$/mol dm^{-3}: (○), 0.92; (△), 1.80; (□), 2.66; (▽), 3.48; (●), 4.28

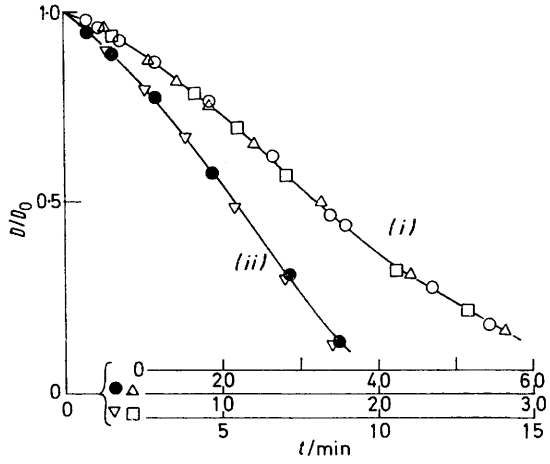


FIGURE 5 First-order dependence on $[Cu^{2+}]_T$ over the whole reaction period using normalised time scales. (*i*) pH 3.85, $10^5[Cu]_T$/mol dm^{-3} = 0.94 (○), 1.91 (△), and 3.85 (□); (*ii*) pH 5.00, $10^5[Cu]_T$/mol dm^{-3} = 1.85 (●) and 3.70 (▽)

given total ascorbic acid concentration, and (*ii*) that half-order dependence on $[L]_T$ is once again a property of the post-induction period. The Table shows that a first-order dependence on catalyst concentration is also exhibited in the post-induction period so that rate law (4) still applies. However, two points remain to be made, and these will be made diagrammatically. First in Figure 5 values of D/D_0

Pseudo-half-order rate constants for the rate of disappearance of ascorbic acid (measured spectrophotometrically); $k' = k_{obs.}/[Cu]_T$ [see equation (4)]

pH	$10^5[Cu]_T$ / mol dm^{-3}	$10^5 k_{obs.}$ / mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$ s^{-1}	k' / dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ s^{-1}
1.81[a]	4.88	0.82	0.168
	7.47	1.20	0.161
	9.76	1.49	0.153
	12.0	2.00	0.167
2.42[a]	2.19	1.92	0.877
	4.33	3.78	0.872
	6.41	5.80	0.904
	8.41	7.25	0.862
	10.5	9.28	0.883
2.80[a]	0.901	1.25	1.39
	1.79	2.47	1.38
	2.63	3.74	1.42
	3.44	4.89	1.42
3.00[b]	2.60	4.30	1.65
3.35[b]	0.919	1.84	2.00
	1.80	3.22	1.79
	2.66	5.23	1.97
	3.48	7.04	2.02
	4.28	8.36	1.95
3.85[b]	0.901	1.88	2.09
	1.91	4.11	2.15
	2.66	5.58	2.10
	3.48	7.33	2.11
	4.28	9.00	2.10

[a] No induction period present. [b] Induction period present.

for runs in which the total catalyst concentration was varied by constant multiples have been plotted against time scales that were varied inversely by the same factors and the exact normalisation exhibited shows that first-order dependence on $[Cu]_T$ is a feature of the whole reaction including the induction period. Second, Figure 6 illustrates how

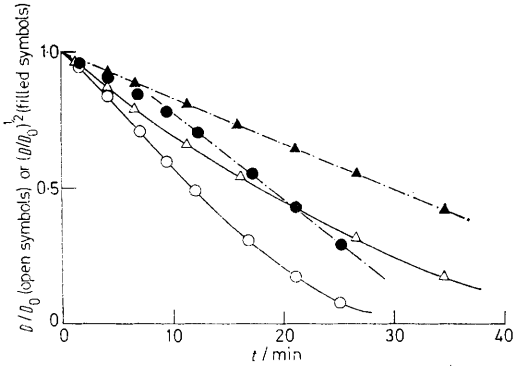


FIGURE 6 Effectiveness in removing the induction period by increasing $[L]_T$ at pH 3.00, $10^5[Cu]_T$/mol dm^{-3} = 2.50, and $10^2[L]_T$/mol dm^{-3} = 2.00 (○), 7.01 (△). Filled symbols are used to illustrate square-root dependences

effective a less than four-fold increase in $[L]_T$ is in completely removing the induction period at pH 3.00: this is important when the dependence on $[O_2]$ is considered (see below).

Oxygen Dependence.—The rate of disappearance of O_2 is shown in Figure 7 to be half order with respect to $[O_2]$ by plotting $([O_2]/[O_2]_0)^{\frac{1}{2}}$ against time for various pH. Note that there is no suggestion of an induction period even at pH 3.55, but this is only to be expected as $[L]_T \gg [O_2]$ (in order that $[O_2]$ was effectively the only variable) and this is known to eliminate the induction period in spectrophotometric (*i.e.* ascorbate-dependence) runs (see above). If it is true that $-d[O_2]/dt = -d[L]_T/dt$, then we can write

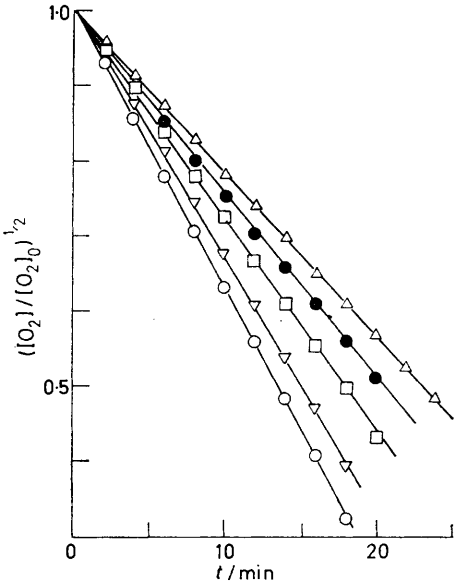


FIGURE 7 Linear variation of $([O_2]/[O_2]_0)^{\frac{1}{2}}$ with time illustrating the half-order dependence on oxygen concentration. pH = 2.20 (△), 2.60 (●), 2.80 (□), 3.05 (▽), and 3.85 (○)

equation (5) and this was readily verified in two ways, *viz.* (*i*) by calculating k from k' of equation (4) from experiments

$$-d[L]_T/dt = k[Cu]_T[L]_T^{\frac{1}{2}}[O_2]^{\frac{1}{2}} \quad (5)$$

in which air as well as pure oxygen was used to saturate the solutions, whereupon the k values were found to agree well within experimental error on the basis of a square-root relation with $[O_2]$, and (*ii*) by the fact that the k values obtained spectrophotometrically and from oxygen-electrode measurements agreed quite well at low ligand concentrations (Figure 8). It is to be noted that if $[L]_T$ is very high then variation with respect to $[Cl^-]$ dominates, and the way the rate varies with $[Cl^-]$ must be taken into account.[2,3]

Dependence on $[H^+]$.—Corresponding values of log k [equation (5)] and pH are presented in Figure 8 and it is apparent that the relation with $[H^+]$ is complicated. If anything the rate seems to exhibit two limits, namely that of independence of $[H^+]$ at high pH (which could probably be the result of complete complexation of the Cu^{2+} at higher pH values), whereas proportionality to $1/[H^+]^2$ is certainly a possibility at low pH although one must allow for the rather imprecise nature of the data (Figure 8). There is, however, good agreement between spectrophotometric and oxygen-electrode determinations.

Equilibrium Studies in the Absence of Oxygen.—The copper(II)–ascorbate system in nitrate media gives rise to the complexes $[Cu(H_2L)]^{2+}$, $[Cu(HL)]^+$, $[Cu_2(HL)_2]^{2+}$, and

[3] R. F. Jameson and N. J. Blackburn, *J. Inorg. Nuclear Chem.*, 1975, **37**, 809.

$[CuL_2]$.[1] But in chloride-containing solutions the behaviour is entirely different, which is perhaps not surprising in view of the very different kinetic behaviour. Solutions containing a ligand : metal ratio between 4 : 1 and 20 : 1 gave rise to formation curves that had a vertical section at $\bar{n} = 1$ from virtually the beginning of the titration (pH *ca.* 2.0) and are thus not very informative. Analysis of 1 : 1 and 1 : 2 mixtures yielded much more information.

The 1 : 1 formation curves retained an initial vertical $\bar{n} = 1$ section, implying formation of a relatively strong mixed ascorbate and chloride complex. At $\bar{n} = 1$ all the protons formally ascribable to the first ionisation of ascorbic acid (H_2L) have been released and thus the extra protons must arise either out of a second ionisation

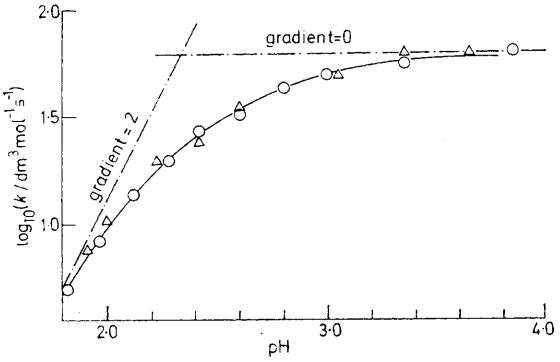


FIGURE 8 pH dependence of the rate: (○), spectrophotometric determinations of ascorbic acid; (△), oxygen-electrode determinations of oxygen. Range of concentrations covered: $[Cu]_T = 0.5 \times 10^{-5} - 12.0 \times 10^{-5}$; $[L]_T = 0.1 \times 10^{-2} - 8.0 \times 10^{-2}$ mol dm^{-3}

(the pH is far too low to consider the hydrolysis of Cu^{II} as a source) or from an internal redox reaction of the type (6)

$$2Cu^{2+} + HL^- + 2Cl^- \longrightarrow 2CuCl + L' + H^+ \quad (6)$$

where L′ is dehydroascorbic acid. The latter possibility would seem to be implausible on three grounds, however; first there is no sign of CuCl being formed, secondly the spectrum obtained at the end-point is consistent with the presence of Cu^{II}, and finally the kinetic behaviour in bromide solution [where we do postulate copper(I) intervention] is very different.[2,3]

We may express the total titratable protons, $[H^+]_T$, by (7)

$$[H^+]_T = [H^+]_A + 2[L]_T - [OH^-]_A \quad (7)$$

where $[H^+]_A$ is the concentration of added mineral acid present at the commencement and $[OH^-]_A$ is the concentration of added base during the titration. We then define $\bar{n}'$ as the average number of protons bound per copper at a given point in the titration, *i.e.* as in equation (8), and

$$\bar{n}' = ([H^+]_A - 2[L]_T - [OH^-]_A - [H^+])/[Cu]_T \quad (8)$$

present the results calculated on this basis in Figure 9. The curve clearly corresponds to the titration curve for an acid with $\log K^H = 4.05$ arising from the release of an extra 0.5 protons per copper. This is explicable on the basis of a reaction of stoicheiometry (9) since the free ascorbic acid

$$2Cu^{2+} + 2HL^- \overset{Cl^-}{\rightleftharpoons} [Cu_2L]^{2+} + H_2L \quad (9)$$

released ($\log K_2^H$ 4.045 [1,4]) would explain the observed half-equivalence point (Figure 9). {It is to be noted that the $[Cu_2L]^{2+}$ of equation (9) must contain chloride ions in order to explain the very different behaviour in nitrate.[1]}

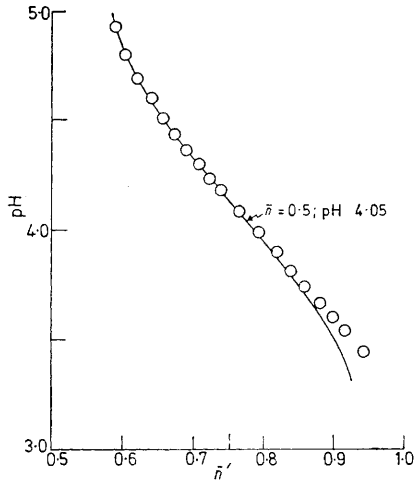


FIGURE 9 Protons bound per copper, $\bar{n}'$, for a 1 : 1 copper(II) : ascorbate titration [I = 0.100 mol dm^{-3} (KCl), 25.00 ± 0.01 °C]

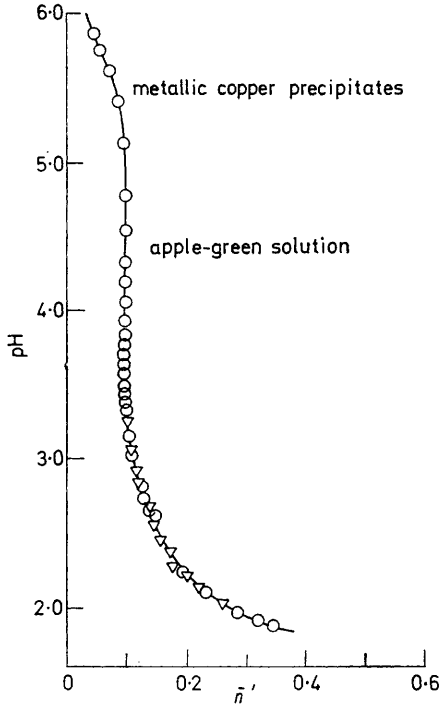


FIGURE 10 Protons bound per copper, $\bar{n}'$, for 2 : 1 copper(II) : ascorbate titrations [I = 0.100 mol dm^{-3} (KCl), 25.00 ± 0.01 °C]

Further clarification follows from 1 : 2 ligand : metal titrations illustrated in Figure 10; the 1 : 2 mixtures indeed titrated as a strong acid as required by equation (10), but

$$2Cu^{2+} + HL^- \rightleftharpoons [Cu_2L]^{2+} + H^+ \quad (10)$$

[4] M. M. Taqui Khan and A. E. Martell, *J. Amer. Chem. Soc.*, 1967, **89**, 4176.

there is also evidence for the existence of protonated complexes, *e.g.* [Cu(HL)], as shown by the rapid rise in pH at $\bar{n}' = 0.09$ rather than at $\bar{n}' = 0.0$. At higher pH values, namely *ca.* pH 5, the solutions turned apple green and copper metal was finally precipitated, behaviour analogous to that pertaining to nitrate-containing solutions.[1]

DISCUSSION

The results outlined above have established that the rate law at constant $[H^+]$ and in 0.100 mol dm^{-3} Cl^- is given by equation (11) which immediately suggests an

$$\text{Rate} = -d[L]_T/dt = -d[O_2]/dt = k[Cu]_T[L]_T^{\frac{1}{2}}[O_2]^{\frac{1}{2}} \quad (11)$$

explanation in terms of a chain reaction. Furthermore, kinetics that are half order in a reactant often imply a chain mechanism in which a free radical containing that reactant undergoes unimolecular propagation and bimolecular termination.[5] In this case there is also the added information that the order with respect to total catalyst concentration is twice that with respect to either ligand or to oxygen. Thus it is probable that such a free radical contains both ascorbate and oxygen at some stage of the redox interaction, and, what is more, it is formed or propagated in a step or steps that involve two coppers per oxygen and ascorbate. The potentiometric studies have shown the high probability of the existence of Cu_2Cl_nL and the binding and subsequent two-electron reduction of dioxygen by such a species would fulfil the kinetic requirements. Thus the following scheme is proposed in which L^{2-} is the ascorbate anion, $L^{-\bullet}$ its one-electron product (semiquinone), and L′ its two-electron oxidation product (dehydroascorbic acid). Chloride ions have been omitted since their stoicheiometry and specific role is not understood (see below).

Initiation

$$2Cu^{2+}(aq) + HL^- \xrightarrow{K_1} [Cu_2L]^{2+} + H^+ \quad (12)$$

$$[Cu_2L]^{2+} + O_2 \overset{K_2}{\rightleftharpoons} [Cu_2L(O_2)]^{2+} \quad (13)$$

$$[Cu_2L(O_2)]^{2+} \xrightarrow{k_1} [CuL(O_2)]^{-\bullet} + Cu^{3+}(aq) \quad (14)$$

$$Cu^{3+}(aq) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cu^{2+}(aq) + OH^\bullet + H^+ \quad (15)$$

$$OH^\bullet + H_2L \xrightarrow{k_3} L^{-\bullet} + H_3O^+ \quad (16)$$

(or $OH^\bullet + HL^- \longrightarrow L^{-\bullet} + H_2O$ at higher pH)

Propagation

$$L^{-\bullet} + [Cu_2L(O_2)]^{2+} \xrightarrow{k_4} [CuL(O_2)]^{-\bullet} + L' + Cu^{2+} \quad (17)$$

$$[CuL(O_2)]^{-\bullet} \xrightarrow{k_5} Cu^{2+}(aq) + L^{-\bullet} + O_2^{2-} \quad (18)$$

Termination

$$2[CuL(O_2)]^{-\bullet} \xrightarrow{k_6} 2O_2^{2-} + L^{2-} + L' + 2Cu^{2+}(aq) \quad (19)$$

Applying the steady-state hypothesis yields equations (20)—(23). Adding (20), (21), (22), and (23) leads

$$d[Cu^{III}(aq)]/dt = 0 = k_1[Cu_2L(O_2)^{2+}] - k_2[Cu^{III}(aq)] + k_{-2}[Cu^{II}(aq)][OH^\bullet][H^+] \quad (20)$$

$$d[L^{-\bullet}]/dt = 0 = k_3[OH^\bullet][H_2L] - k_4[L^{-\bullet}][Cu_2L(O_2)^{2+}] + k_5[CuL(O_2)^{-\bullet}] \quad (21)$$

$$d[CuL(O_2)^{-\bullet}]/dt = 0 = k_1[Cu_2L(O_2)^{2+}] + k_4[L^{-\bullet}][Cu_2L(O_2)^{2+}] - k_5[CuL(O_2)^{-\bullet}] - 2k_6[CuL(O_2)^{-\bullet}]^2 \quad (22)$$

$$d[OH^\bullet]/dt = 0 = k_2[Cu^{III}(aq)] - k_{-2}[Cu^{II}(aq)][OH^\bullet][H^+] - k_3[OH^\bullet][H_2L] \quad (23)$$

directly to equations (24) and (25). If it can be assumed

$$k_1[Cu_2L(O_2)^{2+}] = k_6[CuL(O_2)^{-\bullet}]^2 \quad (24)$$

$$i.e. \quad [CuL(O_2)^{-\bullet}] = (k_1/k_6)^{\frac{1}{2}}[Cu_2L(O_2)^{2+}]^{\frac{1}{2}} \quad (25)$$

that the unimolecular decomposition step (18) (k_5) is rate determining, then equation (26) is obtained. But at

$$\text{Rate} = k_5(k_1/k_6)^{\frac{1}{2}}[Cu_2L(O_2)^{2+}]^{\frac{1}{2}} \quad (26)$$

constant pH, $[HL^-]$ is proportional to $[L]_T$ and the well defined kinetic orders suggest that the extent of polymer formation is small under the conditions of the experiments so that $[Cu^{2+}(aq)]$ is likewise proportional to $[Cu]_T$. Equation (26) may thus be expressed in terms of total concentrations from the pre-equilibria (12) and (13) giving equation (27) at constant pH and $[Cl^-]$, which

$$\text{Rate} = k_5(k_1/k_6)^{\frac{1}{2}}K_1^{\frac{1}{2}}K_2^{\frac{1}{2}}[Cu]_T[L]_T^{\frac{1}{2}}[O_2]^{\frac{1}{2}} \quad (27)$$

is the observed rate law (11). Unfortunately the $[H^+]$ dependence is complex (Figure 8) and possibly related to the appearance and pH dependence of the induction period, and therefore no attempt was made to include a term in $[H^+]$ in the rate law.

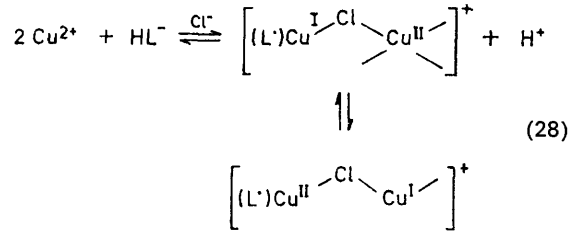
The radical $[CuL(O_2)]^{-\bullet}$ is identical to that postulated as the chain carrier in the nitrate system [1] and indeed the mechanisms are themselves identical from step k_4 onwards. The radical may be formulated as either a copper(II)–semiquinone–peroxide complex or as a copper(II)–ascorbate–peroxide species due to the 'non-innocent' behaviour of the ascorbate and, as we have pointed out previously [1] for the nitrate system, we feel that the copper(III) formulation is the more likely. The other copper fragment of the initial redox process [step k_1, equation (14)] is unambiguously Cu^{III} which has been shown by Meyerstein [6] to react reversibly with water to form hydroxyl radicals which themselves react readily with any oxidisable species present. Copper(III) appears in fact to undergo only inner-sphere reduction, and its first-order rate of reduction in aqueous solution decreases by a factor of 10 between pH 2.98 and 4.36 ($k/s^{-1} = 2.8 \times 10^3$ and 2.5×10^2 respectively [6]). This is thought to be due to the decrease in the Cu^{III}–Cu^{II} redox potential on co-ordination of OH^-. Such an

[5] K. Laidler, 'Chemical Kinetics,' 2nd edn., McGraw-Hill, 1965.

[6] D. Meyerstein, *Inorg. Chem.*, 1971, **10**, 638.

equilibrium provides a good explanation of the induction period since the rate of regeneration of catalyst will decrease as the pH increases and will therefore hinder the attainment of the steady state. The elimination of the induction period by high $[L]_T$ can also be explained if it is assumed that when ascorbic acid is in excess ($>10^{-2}$ mol dm^{-3}) Cu^{III} may also react by hydrogen-atom transfer from H_2L, as has been suggested by Anbar for the copper-catalysed oxidative deammination reactions.[7] This latter suggestion is particularly strongly supported by the fact that Margerum [8] has recently prepared stable copper(III) complexes of deprotonated amides and peptides. Also the remarkably low values of the redox potentials for the Cu^{III}–Cu^{II} couple that he reports (*e.g.* 0.631 V for the deprotonated tetraglycine complex [8]) would seem to add even greater credulity to the idea of involving Cu^{III} in the present study, and indeed to its involvement in biochemical reactions of which this is a model.[3,8]

The kinetic inertness of square-planar d^8 ions (*cf.* Pt^{2+} and Au^{3+}) may also be a factor in explaining why peroxide remains bound to the radical $[CuL(O_2)]^{-\bullet}$ (giving rise to the half-order dependence), while the peroxide may itself help to stabilise the copper(III) state through 'hard–hard' interactions. However, some degree of internal redox reaction in the absence of oxygen cannot be entirely discounted, although the complete two-electron process of the type (6) has been ruled out above. The strong acid behaviour could be the result of semiquinone formation since the ascorbate semiquinone has pK_a −0.45.[9] Furthermore, the release of protons observed when chlorides are added to copper(II)–ascorbate mixtures in nitrate solutions at low pH is by no means instantaneous [2] and thus it is more difficult to refute a one-electron internal redox process such as (28) in which



(28)

it has been supposed that at least one chloride acts as a bridge (*cf.* the classical example of the solubilisation of $CrCl_3$ by Cr^{2+}).

The partially reduced binuclear copper site could be expected to be a good oxygen-binding site, reacting as in equations (29) and (30). The species $[Cu^{II}(L^{\bullet})(O_2^{\bullet})]$ in

$$[(L^{\bullet})Cu^{II}(\mu\text{-}Cl)(\mu\text{-}O_2)Cu^{I}]^{+} \longrightarrow [Cu^{II}(L^{\bullet})(O_2^{\bullet})] + Cu^{2+} + Cl^{-} \quad (29)$$

$$[Cu^{II}(L^{\bullet})(O_2^{\bullet})] + HL^{-} \longrightarrow [Cu(L^{\bullet})(O_2)]^{-} + L^{-\bullet} + H^{+} \quad (30)$$

equation (29) is a semiquinone–copper(II)–hyperoxide bi-radical, and after reaction (30) this mechanism would proceed as before [*i.e.* from k_4, equation (17) above] and a steady-state treatment leads to the desired rate law. This process has the advantage of eliminating the need to postulate Cu^{III} but suffers from the following objections. (*i*) The radical formed in (30) must be formulated as a copper(II) complex so that its unimolecular decomposition [equation (18), step k_5] amounts to ligand dissociation from a labile d^9 metal centre which would be unlikely to be rate determining and bimolecular termination is equally improbable. (*ii*) An unfavourable one-electron transfer to dioxygen has had to be invoked and it is hard to see why monomers should not be equally reactive. This is ruled out especially by the kinetics which require two coppers per oxygen and per ascorbate. (*iii*) In 0.100 mol dm^{-3} bromide solution the oxygen dependence is first order while the ascorbate dependence is zero order,[2,3] suggesting a rate determining reoxidation of Cu^{I} by O_2 following stabilisation of Cu^{I} by Br^{-}. It might justifiably be expected therefore that very high chloride concentrations should ultimately lead to similar kinetics if Cu^{I} were involved. At high chloride concentrations the dependence on $[O_2]$ remains accurately half order, however.[2,3]

We therefore propose that, although there might well be a limited degree of charge transfer within the reactive $[Cu_2Cl_nL]^{(n-2)-}$ species in the absence of oxygen, this merely serves to encourage the binding of O_2 across the copper–copper binuclear site and is followed by the copper(III) mechanism proposed here (and similarly for the kinetics in nitrate medium [1]). The involvement of a binuclear copper site must be of considerable mechanistic importance in the field of enzyme kinetics and we have discussed this in a previous communication.[3]

EXPERIMENTAL

Ascorbic acid was Fison's AnalaR grade and was used without further purification. All copper solutions were made from accurately weighed pieces of AnalaR copper foil that were dissolved in the minimum of pure nitric acid; the nitric acid was removed with concentrated HCl and the resulting mixture was evaporated to dryness before being made up to volume with deionised water. The resulting solutions were also checked for copper content by complexiometric titration with ethylenediaminetetra-acetate (edta) and standardised potentiometrically for $[H^+]$. Analysis for ascorbic acid was performed spectrophotometrically at 243 nm according to the method of Ogata and Kosugi.[10] Samples were taken by pipette from the reacting solutions at noted intervals of time. A Radiometer E5046 oxygen-sensitive electrode was used to measure the oxygen content of solutions and to measure the rate of oxygen consumption.

In spectrophotometric runs, pure oxygen or, in some cases, air was bubbled continuously through the reaction mixture using a sintered-glass outlet. A thermostatted oil-bath was used to maintain the temperature at 25.00 ± 0.01 °C for both kinetic and e.m.f. studies. The pH was

[7] M. Anbar, *Adv. Chem. Ser.*, 1965, **49**, 126.
[8] D. W. Margerum, *Chem. Eng. News*, 1975, **53** (49), 26.
[9] G. P. Laroff, R. W. Fessenden, and R. H. Schuler, *J. Amer. Chem. Soc.*, 1972, **94**, 9062.
[10] Y. Ogata and Y. Kosugi, *Bull. Chem. Soc. Japan*, 1969, **42**, 2282.

maintained constant by use of a Radiometer pH-stat acting *via* a Russell CMAT microcombination electrode that was calibrated against 0.05 mol dm^{-3} potassium hydrogenphthalate (pH 4.008). For potentiometric titrations, a Beckman Research pH meter was used in conjunction with Beckman AS7LB glass electrodes and Radiometer K401 calomel reference electrodes. An atmosphere of pure nitrogen was maintained over all these solutions.

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