

Kinetics of the oxidation of copper(I) by hydrogen peroxide in acidic chloride solutions

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The kinetics of the reaction between copper(I) and hydrogen peroxide in aqueous chloride solutions was studied by use of an electrochemical technique. Oxidation by peroxide, which is formed as an intermediate during the oxidation of copper(I) by oxygen, is a reaction in which the rate is first-order in each of the reactants and which decreases with increasing chloride concentration. This effect is shown to be due to the decreasing rates of oxidation of copper(I) with increasing extent of coordination by chloride ions. A mechanism is proposed that involves single electron-transfer reactions and that is consistent with the thermodynamic properties of the reactants. *S. Afr. J. Chem.*, 1982, 35, 77—79

Die kinetika van die reaksie tussen koper(I) en waterstofperoksied in waterige chloriedoplossings is met 'n elektrochemiese tegniek bestudeer. Oksidasie met peroksied wat as 'n tussenproduk tydens die oksidasie van koper(I) deur suurstof gevorm word, is 'n reaksie waarin die tempo in elkeen van die reaktanse van die eerste orde is, maar afneem met 'n toenemende chloriedkonsentrasie. Daar word getoon dat hierdie uitwerking toe te skryf is aan die dalende oksidasietempo van koper(I) met 'n toenemende mate van koördinasie deur chloriedione. 'n Mekanisme word voorgestel wat enkelelektronoordragreaksies behels en met die termodinamiese eienskappe van die reaktanse strook. *S.-Afr. Tydskr. Chem.*, 1982, 35, 77—79

Reactions of molecular oxygen with oxidizable metal ions in solution at normal temperatures are, with few exceptions, notably slow despite the favourable thermodynamic potential associated with the reduction of oxygen to water. Although much has been published on the kinetics of the oxidation of simple metal ions, there is still no general agreement on the laws governing the rate of oxidation or on the mechanism by which the autoxidation of iron(II) and other metal ions occurs. The role of peroxide as an intermediate in these reactions has seldom been studied quantitatively.

In the course of an investigation into the kinetics of the autoxidation of iron(II) in chloride solutions,¹ the catalysis of the reaction by copper ions was observed. This catalytic effect is conveniently interpreted as a typical 'two-stroke' mechanism in which oxidation of iron(II) by copper(II) is coupled with reoxidation of copper(I) by oxygen. It was found that the data could best be fitted to the model if it was assumed that the rate of oxidation of copper(I) by oxygen is second-order with respect to the concentration of copper(I).

The only published information on the autoxidation of copper(I) in chloride solutions is provided by Nord,² who found that the rate was first-order in each of copper(I), oxygen, and protons. He suggested a mechanism in which the rate-determining step is a reaction between a copper-oxygen complex ion, CuO_2^+ , and a proton. In view of this apparent discrepancy with our observations for the reaction order for copper(I), it was decided that a further investigation of the kinetics, under the conditions of our experiments, was justified. In the course of a study of the oxidation of copper(I) by oxygen, it was found that peroxide is a detectable intermediate in the reduction of oxygen to water by copper(I) in acidic chloride solutions. It was therefore considered desirable to establish the kinetics and mechanism of the peroxide reaction as a precursor to the interpretation of the oxygen reaction.

In a recent paper, Skinner *et al.*³ reported on an investigation into the kinetics of the oxidation of iron(II) and copper(I) by hydrogen peroxide in 2.0M-hydrochloric acid solutions. They used a ring-disc electrode, together with a digital simulation procedure for the analysis of the data. Some doubt was expressed as to the validity of the results obtained by this method, because the rate constants for the oxidation of iron(II) were three to four times greater than those found by other workers under comparable conditions. The reaction with copper(I) was found to be first-order in

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both copper(I) and peroxide, but no information was presented on the influence of acid or chloride concentrations on the rate.

Experimental

The rates of oxidation of dilute copper(I) solutions by hydrogen peroxide were measured by an amperometric technique in which the current [due to the oxidation of copper(I)] at a rotating platinum electrode, potentiostatted at 0.7 V, versus a saturated calomel reference electrode, was followed as a function of time. At potentials above about 0.4 V, the oxidation of copper(I) is mass-transport controlled, whereas oxygen and peroxide are electrochemically inactive. The typical voltammograms shown in Figure 1 illustrate these points. Reactions were begun by the injection of a small volume of copper(I) solution (0.01M-CuCl in 1M-HCl) into a thermostatted electrochemical cell containing a solution of the required composition. Oxygen-free nitrogen was used to remove oxygen from the solutions. All

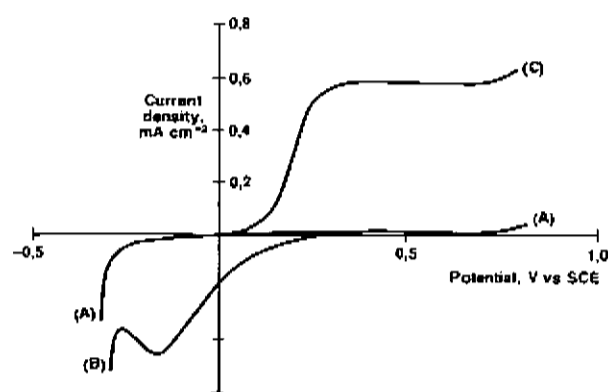


Figure 1 Linear sweep (10 mV/s) voltammograms obtained at a rotating (1000 r/min) platinum-disc electrode in a deoxygenated solution containing (A) 0.1M-HCl and 0.9M-NaCl, (B) as in (A) plus 2×10^{-3} M- H_2O_2 , and (C) as in (A) plus 10^{-3} M- Cu^I .

kinetic runs were carried out under conditions such that the concentration of the oxidant was much greater than that of the copper(I). Analytical reagent-grade chemicals were used without further purification, and all solutions were made up with high-purity water from a Millipore system. Copper(I) solutions were stored under nitrogen in the presence of a few pieces of copper wire for the prevention of oxidation. All runs were carried out at $25 \pm 0.1^\circ C$, and the ionic strength was maintained at 1.0M by the addition of sodium chloride or sodium perchlorate.

A conventional three-electrode potentiostatic system was employed with a potentiostat assembled in this laboratory. Current-time curves were obtained on a Hewlett-Packard 7046A recorder. The rotating-disc electrode was assembled and the speed controlled according to techniques described by Paul.⁴

Results and Discussion

Plots of $\ln(i_t - i_\infty)$ versus time were linear under all the reaction conditions studied. Variable i_t is the current due to the oxidation of copper(I) at time t , and i_∞ is the background current at the completion of the reaction. Since $(i_t - i_\infty)$ is proportional to the concentration of copper(I), the linearity of these plots indicates a first-order dependence of the rate on the concentration of copper(I), the concentration of hydrogen peroxide being considerably greater than the initial concentration of copper(I) in all cases. Variation of the initial concentration of peroxide showed that the pseudo-first-order rate constant (k_{obs}) is proportional to the concentration of peroxide, as evidenced by the constancy of the second-order rate constant (k). These results are given in Table 1, which also lists the results of additional experiments revealing that the rate is unaffected by the presence

Table 1 Variation of the rate of oxidation with the concentration of peroxide, copper(II), and acid ($[copper(I)] = 10^{-4}M$)

[H ⁺]	[Cl ⁻]	[H ₂ O ₂]	k_{obs}	k
M	M	mM	s ⁻¹	M ⁻¹ s ⁻¹
0.01	1.00	0.63	0.098	156
0.01	1.00	1.25	0.204	163
0.01	1.00	2.50	0.412	165
0.10	1.00	0.63	0.104	165
0.10	1.00	1.25	0.196	157
0.10	1.00	2.50	0.400	160
0.20	1.00	0.63	0.102	163
0.20	1.00	1.25	0.192	153
0.20	1.00	2.50	0.418	167
0.20 ^a	1.00	1.25	0.195	156
0.50	1.00	0.60	0.104	174
0.50	1.00	1.21	0.199	164
0.50	1.00	2.42	0.451	186
0.50	1.00	4.84	0.720	149
1.00	1.00	0.63	0.111	176
1.00	1.00	1.25	0.220	176
1.00	1.00	2.50	0.416	167
1.00	0.10	0.45	0.165	367
1.00	0.10	0.90	0.336	373
0.50	0.10	0.45	0.165	367
0.50	0.10	0.90	0.349	388
0.20	0.10	0.45	0.168	373
0.10	0.10	0.45	0.162	359
0.10	0.10	0.90	0.307	341
0.10 ^b	0.10	0.90	0.313	348

^a Solution contained $10^{-2}M$ of copper(II).

^b Run carried out with same solution as in the previous run after it had been standing for 15 minutes.

of an excess of copper(II), and also that the rate is essentially independent of the acidity at constant chloride concentrations of 1.0M and 0.1M. Decomposition (catalytic or otherwise) of the peroxide was found to be negligible in the time required to carry out a run, as shown by the last result in Table 1.

The rate was found to decrease with increasing chloride concentration at a constant acidity of 0.1M, and a plot of the second-order rate constant versus the reciprocal of the chloride concentration is shown in Figure 2. The non-zero intercept and non-linear dependence of the rate on the reciprocal of the chloride concentration implies, firstly, that the rate equation has at least two terms, and secondly, that copper(I) complexes containing more than one chloride ion are involved in the reaction. This is consistent with published information on the distribution of the various species in chloride solutions of copper(I).⁵ Thus, in the range of interest, the major contributing species is $CuCl_2^-$, with $CuCl_3^{2-}$ becoming significant at the higher chloride concentrations, while $CuCl(aq)$ does not exceed 5% of the total copper(I) even at low concentrations. The simplest possible reaction scheme that takes these facts into account is the following:



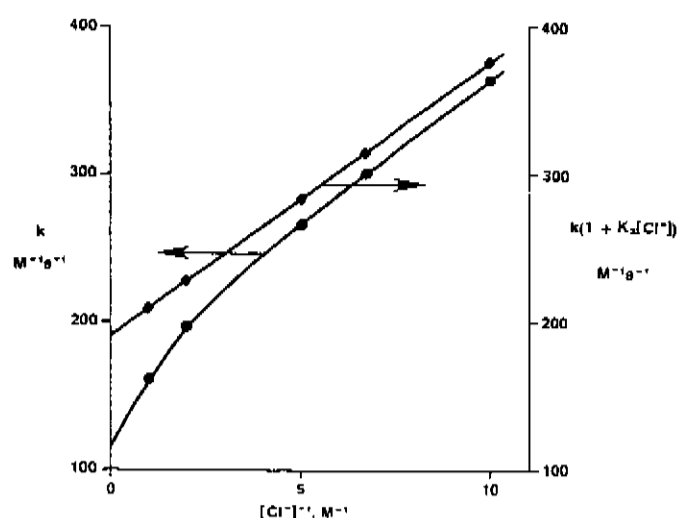
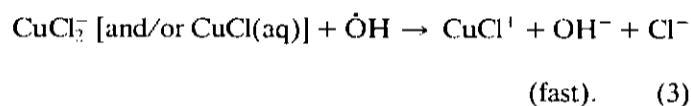
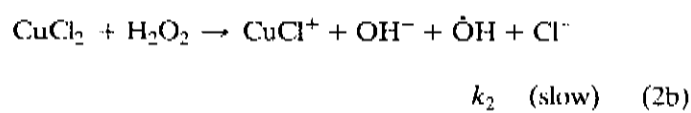
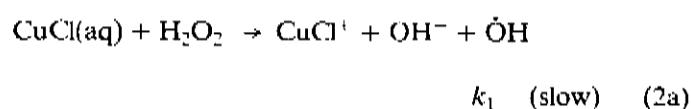


Figure 2 Variation of the second-order rate constant for the oxidation of copper(I) by hydrogen peroxide with the reciprocal of the chloride concentration.



Substitution of the equilibrium concentrations of $\text{CuCl}(\text{aq})$ and CuCl_2^- in the rate expressions for the two parallel slow reaction steps yields the rate equation

$$-\frac{d[\text{Cu}^{\text{I}}]}{dt} = k[\text{Cu}^{\text{I}}][\text{H}_2\text{O}_2],$$

in which the second-order rate constant k is a function of the chloride concentration, *i.e.*,

$$k = \frac{2}{1 + K_3[\text{Cl}^-]} \left\{ \frac{k_1}{K_3[\text{Cl}^-]} + k_2 \right\}.$$

Thus, a plot of $k(1 + K_3[\text{Cl}^-])$ versus $1/[\text{Cl}^-]$ should be linear. Such a plot is shown in Figure 2, and a 'best fit' to the data is obtained for $K_3 = 0.3$. This value compares favourably with that obtained by Fritz,⁵ approximately 0.5. By use of a value of $K_2 = 200$ as found by Fritz, values of $k_1 = 3700 \text{ M}^{-1}\text{s}^{-1}$ and $k_2 = 190 \text{ M}^{-1}\text{s}^{-1}$ can be derived from the slope and intercept of the linear plot in Figure 2.

It is interesting to compare the results of this investigation with that of Skinner *et al.*³ Extrapolation of the data in

Figure 2 to 2M-HCl yields an observed second-order rate constant of $140 \text{ M}^{-1}\text{s}^{-1}$. Comparison with the published data requires division by 2, and the resulting value of $70 \text{ M}^{-1}\text{s}^{-1}$ should be compared with that of $260 \text{ M}^{-1}\text{s}^{-1}$ obtained by Skinner at 25°C in 2M-HCl using the ring-disc technique. This difference of a factor of 3 to 4 is very similar to that observed by the same authors for their results of the oxidation of iron(II) when compared with previously published data, and suggests a consistent error of this magnitude in their method. The validity of our result was tested by a measurement of the rate by the stopped-flow method, in which the appearance of copper(II) was monitored at 800 nm in a Nortech stopped-flow apparatus at 25°C. For an initial concentration of copper(I) at 0.01M and peroxide of 0.07M, a second-order rate constant of $210 \text{ M}^{-1}\text{s}^{-1}$ was obtained at a chloride concentration of 0.25M. This compares favourably with that obtained by interpolation of the data in Figure 2.

The above mechanism, in which the transfer of the first electron is rate-determining in the reduction of peroxide, is not unexpected in the light of thermodynamic data⁶ that reveal that the one-electron reduction of peroxide to the hydroxyl-radical ($E^\circ = 0.71 \text{ V}$) is considerably less favourable than the transfer of the second electron ($E^\circ = 2.85 \text{ V}$). The relatively favourable standard free-energy change for reaction (2a) of about 26 kJ ensures that inhibition by the products [particularly copper(II)] is not observed, which is in contrast to that found for the corresponding reaction of copper(I) with oxygen.⁷

An attempt was made to determine whether the trend shown by the relative magnitudes of k_1 and k_2 also extended to the oxidation of the hexaquo ion, *i.e.*, coordination by chloride ions resulting in a decreased reactivity to oxidation. Thus, a solution containing 1M- CuSO_4 and 1M- H_2SO_4 was equilibrated with pieces of copper foil at 25°C. The small amount of copper(I) formed (roughly 10^{-4}M) was reacted with hydrogen peroxide and, as in the case of the reaction in chloride solution, the decrease in the copper(I) concentration with time was followed electrochemically. The reaction was extremely fast, and one could arrive at only a lower limit of the rate constant of $5000 \text{ M}^{-1}\text{s}^{-1}$, which does, however, confirm the trend shown by the results obtained in chloride solutions.

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References

- 1 R.P. Colborn and M.J. Nicol, *J. S. Afr. Inst. Min. Metall.*, 1973, 73, 281.
- 2 H. Nord, *Acta Chem. Scand.*, 1955, 9, 430.
- 3 J.F. Skinner, A. Glasel, Li-Chuen Hsy, and B.L. Funt, *J. Electrochem. Soc.*, 1980, 127, 315.
- 4 R.L. Paul, *Electrochim. Acta*, 1978, 23, 991.
- 5 J.J. Fritz, *J. Phys. Chem.*, 1980, 84, 2241.
- 6 G. Milazzo and S. Caroli, 'Tables of standard electrode potentials', Wiley, 1978.
- 7 M.J. Nicol, to be published.