Kinetics of the Autoxidation of Cuprous Chloride in Hydrochloric Acid Solution

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It is shown that the velocity of the autoxidation of cuprous ion in hydrochloric acid solution is proportional to the concentrations of oxygen and cuprous ion. The velocity increases with increasing hydrogen ion concentration, the reciprocal velocity being a linear function of the reciprocal hydrogen ion concentration, provided $cH^+ \geq 0.1$. As the rate of reaction was high, it proved impossible to saturate the reacting solutions with oxygen, so that the oxygen concentration had to be determined by calculations assuming a steady state.

The kinetic expression found suggests the following mechanism:

followed by a sequence of fast steps in which three more cuprous ions per oxygen molecule are oxidised. The values of the rate constants for the individual steps are discussed.

It is well known that copper ions play an important part as a catalyst in many oxidations. The mechanism of this behaviour is generally associated with the ability of copper to exist in two oxidation states in solution¹. To solve the kinetic problems of such reactions adequately it is necessary to know the kinetics of the oxidation of cuprous ion. The present investigation is of preliminary character as various factors which influence the rate have been varied within rather narrow limits only. The results have been used in evaluation of the kinetics and mechanism of the copper catalysed autoxidation of ascorbic acid, which is treated in a following paper.

The autoxidation of cuprous chloride in mixed solution of sodium chloride and hydrogen chloride was investigated. The chloride concentration was kept throughout at 1.000 *M*. The hydrogen ion concentration varied from 0.400 to 0.020 *M* and the sodium ion concentration correspondingly from 0.600 to 0.980 *M*. The initial concentration of chlorocuprous ion was generally about 0.008 *M*. It has been shown in this laboratory² that cuprous ions in such solutions exist essentially as $CuCl_2^-$.

Fig. 1. Experimental set up (see text).

All reagents used were "Baker's analyzed". The cuprous chloride was washed with dilute hydrochloric acid to remove oxidised products, otherwise the chemicals were used as delivered. The solutions were made up under anaerobic conditions. 225 ml of suitable mixtures of 1.000 *M* hydrochloric acid and 1.000 *M* sodium chloride were deaerated in a two necked bottle by a stream of carbon dioxide. To this solution was added a saturated solution of cuprous chloride in 1 *M* sodium chloride, generally 25 ml.

As discussed below it was impossible to saturate the solutions with oxygen because of the high rate of the reaction. Therefore it was necessary to determine the progress of the reaction in separate runs each of which gave one interrelation between time and degree of reaction only. The reaction was carried out in a small reaction vessel (Fig. 1), a vertical glass cylinder with a sintered glass disc as a gas inlet in the bottom. The volume of the reaction vessel was about 25 ml.

In each run 15 ml of the reaction mixture was transferred from the stock solution in the two necked bottle by a pipette, the tip of which was somewhat enlarged to ensure quick delivery. The gas, a mixture of oxygen and nitrogen, generally with 4.05 % oxygen, was taken from a small steel cylinder and passed through a wash bottle with 1 *M* sodium chloride, submerged in the thermostat, to ensure proper temperature and humidity. The rate of the gas flow was carefully controlled by a flow meter. No temperature difference was detectable between the contents of the reaction vessel and the thermostat water.

At the end of the time scheduled for the individual runs the gas flow was discontinued by releasing the pressure below the glass disc. The amount of oxygen in the solution was generally so small compared with the cuprous ion concentration that no great error was introduced by further reaction. 10.00 ml of the reacted solution was transferred by means of a Krogh syringe to a sulphuric acid and ferric chloride solution, and the ferrous ion formed titrated with 0.01 *N* potassium permanganate with ferroin as an indicator. A small blank was subtracted.

Ferric salt was used as oxidant because cuprous ions do not react stoichiometrically with permanganate or with ceric sulphate³. When cuprous salt was titrated directly, *i.e.*, without addition of ferric ion, the results were found to depend on such things as acidity, rate of titration, and rate of carbon dioxide current. The method here described was tested on solid cuprous chloride purified in the following way: dissolution in concentrated hydrochloric acid, reprecipitation by dilution, washing with glacial acetic acid and drying at 130° C. The results were in agreement with stoichiometry within 0.5 %.

The first runs showed that the velocity of the reaction does not depend on illumination or on added cupric chloride. It was further shown that although hydrogen peroxide could be detected by the spot test with lead sulphide it was only formed in negligible amount and could not be determined by the usual quantitative methods. The stoichiometry of the reaction is therefore:

The reaction vessel described above ensures a very intimate contact between gas phase and solution. Even so it was impossible to approach a state of saturation with oxygen, so that the concentration of oxygen in the reacting solution had to be determined by a steady state method, *i.e.*, by calculations assuming the rate of flow of oxygen from the gas phase into the liquid to be equal to the flow of oxygen in the opposite direction plus the rate of oxygen consumption:

$$k_1 p\text{O}_2 = k_{-1}c\text{O}_2 + s \quad (\text{I})$$

Here s is the experimentally determined speed of the reaction: $\left(-\frac{d\text{Cu}^+}{dt}\right)$, and k_1 and k_{-1} the first order constants of forward and backward reaction according to the scheme

The exact values of these constants are determined by the conditions of experiment but the ratio between them is of course the solubility of oxygen in the liquid according to Henry's law. Whenever s is small compared with the two other terms the oxygen concentration of the reacting solution will approach saturation. An early attempt to determine the kinetics of the autoxidation of cuprous ion was unsuccessful because s was very nearly equal to $k_1 p\text{O}_2$, so that the oxygen transference apparently was the sole rate determining factor⁴. In the present investigation the upper limit for s was about semisaturation upwards. It is evident that a necessary condition for success was a careful control of the factors which determine the rate of diffusion of oxygen into the solution.

Fig. 2 demonstrates the proportionality between velocity and oxygen concentration in the liquid phase. We may write:

$$s = c\text{O}_2 f(c, h) \quad (\text{II})$$

where c is the cuprous ion concentration and h the hydrogen ion concentration. The elimination of $c\text{O}_2$ between I and II gives:

Fig. 2. Demonstration of the proportionality between rate and oxygen pressure in gas phase.

Ordinate: Cuprous ion concentration.

Abscissa: Time multiplied by oxygen pressure, divided by 0.0405. All times are hence referred to $p_{O_2} = 0.0405$.

Δ } denote values from experiments with $\left\{ \begin{array}{l} 0.208 \\ 0.082 \\ 0.0405 \end{array} \right.$
 $\times$ } $[H^+] = 0.100$ and with oxygen pressures

$$s = -\frac{dc}{dt} = \frac{k_1 p_{O_2} \cdot f(c, h)}{k_{-1} + f(c, h)}$$

or

$$\frac{1}{s} = -\frac{dt}{dc} = \frac{1}{k_1 \cdot p_{O_2}} + \frac{k_{-1}}{k_1 \cdot p_{O_2} \cdot f(c, h)} \quad (III)$$

The integral form is:

$$t = \frac{c_0 - c}{k_1 \cdot p_{O_2}} + \frac{k_{-1}}{k_1 \cdot p_{O_2}} \cdot \int_c^{c_0} \frac{dc}{f(c, h)} \quad (IV)$$

The first term on the right hand side of (IV) can be determined in two ways, either by direct experiments or indirectly by analysis of the experimental material from the main experiments. The accuracy of this investigation being rather low, it was considered unfavourable to use the latter method. Inspection of (I) shows that k_1 may be easily determined if it is possible to design experiments in which the steady state concentration of oxygen in the liquid phase is nearly zero. Therefore s was determined in experiments with solutions of sodium sulphite or with higher concentrations of cuprous chloride. Using sulphite it was found that the velocity of reaction was independent of sulphite

concentration and proportional to the oxygen pressure of the gas phase. For the experimental conditions used in the investigation was found:

$$s = 0.0483 \text{ pO}_2 \text{ equivalent/liter} \cdot \text{minute}$$

The initial velocity of oxidation of concentrated solutions of cuprous chloride was nearly zero order in cuprous ion and proportional to the oxygen pressure. This velocity was almost identical with the velocity from the sodium sulphite experiments, so no doubt these velocities are actually the rate at which oxygen is transferred from gas to liquid.

Knowing k_1 we can determine the first term on the right hand side of (IV) and define a new parameter:

$$t' = t - \frac{c_0 - c}{k_1 \cdot \text{pO}_2} = \frac{k_{-1}}{k_1 \cdot \text{pO}_2} \int_0^{c_0} \frac{dc}{f(c, h)} \quad (\text{V})$$

Here t' is the time the reaction from c_0 to c would have taken had the solution been saturated with oxygen. The influence of the oxygen deficiency is thus eliminated.

It was now found that $\ln c$ is nearly a linear function of t' . This indicates linearity between velocity and c . Strict linearity of the logarithmic plot cannot be expected as the velocity increases with acidity, which again falls as the reaction proceeds. The relation between reciprocal velocity and reciprocal hydrogen ion concentration is nearly linear when $h \geq 0.1$. In less acid solution the rate is higher than corresponding to this relationship. We shall confine the attention to the acidity region in which the simple relation holds.

Analysis of the available experimental material gives the expression

$$\frac{1}{s} = -\frac{dt}{dc} = \frac{20.7}{\text{pO}_2} + \frac{1.62 \cdot 10^{-2}}{\text{pO}_2 \cdot c} + \frac{1.40 \cdot 10^{-2}}{\text{pO}_2 \cdot c \cdot h} \quad (\text{VI})$$

Introducing $h = h_0 - c_0 + c$, h_0 and c_0 being initial values of h and c , the integration gives:

$$t = \frac{(c_0 - c) \cdot 20.7}{\text{pO}_2} + \frac{1.62 \cdot 10^{-2}}{\text{pO}_2} \cdot \ln \frac{c_0}{c} + \frac{1.40 \cdot 10^{-2}}{\text{pO}_2 (h_0 - c_0)} \ln \frac{(h_0 - c_0 + c) \cdot c_0}{h_0 \cdot c} \quad (\text{VII})$$

The acidity change during the experiments was so small that the following approximation is useful

$$\ln \frac{h_0 - c_0 + c}{h_0} = -\frac{c_0 - c}{h_0}$$

Therefore

$$t = \left[\frac{20.7}{\text{pO}_2} + \frac{1.40 \cdot 10^{-2}}{\text{pO}_2 \cdot (h_0 - c_0) h_0} \right] (c_0 - c) + \left[\frac{1.62 \cdot 10^{-2}}{\text{pO}_2} + \frac{1.40 \cdot 10^{-2}}{\text{pO}_2 \cdot (h_0 - c_0)} \right] \ln \frac{c_0}{c} \quad (\text{VIII})$$

Table 1. *I* and *II* mean zero- and first order terms respectively. pO_2 was 0.208, initial hydrogen ion concentration 0.100. Hence the zero order factor was 92.5 and the first order factor 0.808.

<i>t</i> obs.	<i>c</i> · 10 ³	<i>I</i>	ln <i>c</i> · 10 ³	<i>II</i>	<i>t</i> calc.
0	8.01	0	2.081	0	0
0.25	6.78	0.11	1.914	0.13	0.24
0.50	5.65	0.22	1.732	0.20	0.42
0.75	4.70	0.30	1.548	0.47	0.77
1.00	3.80	0.39	1.335	0.66	1.05
1.50	2.30	0.53	0.833	1.01	1.54
2.00	1.51	0.60	0.412	1.35	1.95
2.50	0.82	0.66	−0.128	1.96	2.62
3.00	0.43	0.71	−0.844	2.36	3.07
3.50	0.24	0.73	−1.427	2.83	3.56

Table 2. pO_2 was 0.0405, initial hydrogen ion concentration 0.400. Hence the zero order factor was 512 and the first order factor 1.28.

<i>t</i> obs.	<i>c</i> · 10 ³	<i>I</i>	ln <i>c</i> · 10 ³	<i>II</i>	<i>t</i> calc.
0	7.80	0	2.054	0	0
0.5	7.05	0.38	1.953	0.13	0.51
1.0	6.32	0.76	1.844	0.27	1.03
1.5	5.67	1.09	1.735	0.41	1.50
2.0	4.95	1.46	1.599	0.58	2.04
3.0	3.70	2.10	1.308	0.95	3.05
4.0	2.60	2.66	0.956	1.41	4.07
5.0	1.74	3.10	0.554	1.92	5.02
6.0	1.14	3.38	0.131	2.46	5.84

The agreement between (VIII) and experiment is demonstrated in the Tables 1 and 2. The coefficients of the two terms are calculated from the experimental conditions. The expression is then used to calculate *t*, and the agreement between theory and experiment is illustrated by the concordance between experimental and calculated values of *t*.

The experimental expression, *e.g.* equation (VI), suggests the following mechanism:

The corresponding expression for the reciprocal rate, as derived by a steady treatment, is ⁵:

$$\frac{1}{s} = \frac{1}{k_1 pO_2} + \frac{k_{-1}}{k_1 k_2 \cdot pO_2 \cdot c} + \frac{k_{-1} k_{-2}}{k_1 k_2 k_3 pO_2 \cdot c \cdot h} \quad (IX)$$

* Strictly speaking nothing is known about the products of reaction (+ 3).

which is identical with (VI). The third step must be irreversible, otherwise the rate would depend on the cupric ion concentration. Almost certainly three more cuprous ions are oxidised by the HO_2 radical in a sequence of fast reactions, but these steps are not kinetically perceptible as the terms after the third must be small when the rate is uninfluenced by cupric ion concentration. The only alternative to this mechanism is reformation of oxygen by reactions between the partly reduced oxygen molecules (HO_2 , H_2O_2 , HO), which is clearly improbable because such molecules would be rare.

It should now be emphasized that this expression is valid only when $c\text{H}^+ \geq 0.1$. At lower hydrogen ion concentrations the rate is somewhat higher than corresponding to the expression. The reason for this complex relationship is probably that the cuprous-oxygen complex formed in the second step may react further in two ways, one of which is reaction (+3) in the mechanism given above. It may be assumed that (+3) has a dominating probability compared with an alternative mechanism (which does not involve hydrogen ions) when hydrogen ion concentration is 0.1 or greater, but that the other mechanism gains significance when the hydrogen ion concentration is essentially lower. The deviation between (VII) and experiment is about 15 % at $c\text{H}^+ = 0.05$ and about 40 % at $c\text{H}^+ = 0.02$. Universal agreement would imply that cuprous ions are not oxidised in neutral solution.

We shall now investigate what information we can get from the absolute values of the constants. Comparison of (VI) and (IX) gives:

$$k_1 = 0.048; \quad \frac{k_1 k_2}{k_{-1}} = 62; \quad \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} = 71$$

The solubility of oxygen in water at 25°C is about 10^3 mole/atmosphere, so $k_{-1} k_{-2} = 10^{-3}$. Therefore k_2 is about $60 \cdot 10^3$ mole $^{-1}$ · minute $^{-1}$, or 10^3 mole $^{-1}$ · sec $^{-1}$. The kinetic expressions derived above do not take into account that presumably four cuprous ions are oxidised every time one passes through the rate determining steps, so k_2 is actually about 250. The Arrhenius equation

$$k = Z \cdot \exp(-E/RT) \quad (\text{X})$$

where Z is the frequency factor and E the energy of activation would with "normal" Z value, 10^{11} , suggest an energy of activation of roughly 12 000 calories per mole.

k_{-2}/k_3 is nearly one. This means that a CuO_2^+ complex when formed has about equal probability to react according to (+3) and (−2) in a solution which is 1 *M* in hydrogen ions. Christiansen⁶ has pointed out that at least one of the two reactions in an element of a sequence of reactions has zero energy of activation. As now both (+2) and (−3) are slow we would expect (−2) and (+3) to be fast reactions where the exponential factor of (X) are unity. The closeness to unity of k_{-2}/k_3 indicates that this condition is fulfilled, although the value should rather have been 10^2 , as the most probable value (according to the mechanism suggested) of the frequency factor would be 10^{13} for k_{-2} , corresponding to a monomolecular reaction, and 10^{11} for k_3 , as (+3) is bimolecular. The value 1 might suggest that (−2) actually is bimolecular, e.g. a reaction between CuO_2^+ and chloride ion, which was present at molar con-

centration in all experiments. As a matter of fact it was found that the reaction proceeds much faster when the chloride concentration was reduced.

A result of this investigation, the indication of the existence of a complex between cuprous ion and oxygen, is an extension of the analogy between cuprous ion and haemoglobine, shown by their similar behaviour towards carbon monoxide.

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