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Copper(II)-catalyzed Oxidation of Iron(II) by Molecular Oxygen in Tripolyphosphate Solution

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In a previous work on the oxygen oxidation of Fe(II) in tripolyphosphate solutions,[1] the anomalous results first obtained led us to suspect the presence of Cu(II) as an impurity. Actually the oxidation rate was subsequently proved to be markedly increased by the addition of small amounts of Cu(II). The effect of Cu(II) as a catalyst has been reported in the Fe^{2+}–O_2,[2–4] Mo(V)–O_2,[5] V(III)–Fe(III),[6] V(III)–O_2[7] and ascorbic acid-O_2[8–10] reactions. In connection with these studies,

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the effect of Cu(II) on the oxidation reaction of Fe(II) in an excess of the triphosphate solution was studied spectrophotometrically, and the results thus obtained discussed, with a view to getting some information concerning the role of Cu(II) as a reaction accelerator.

Experimental

The Cu(II) solution was prepared from reagent-grade cupric sulfate. The sodium triphosphate ($Na_5P_3O_{10}\cdot 6H_2O$) was recrystallized five times from 25% aqueous ethanol solutions. Redistilled wster was used for the preparation of all the solutions. The hydrogen ion concentration of the triphosphate solution, in which certain amounts of Cu(II) were dissolved if necessary, was adjusted by adding dilute perchloric acid or dilute sodium hydroxide. Just before each run, the Fe(II) solution was prepared by the use of reagent-grade ferrous ammonium sulfate. By mixing 20 m*l* of the triphosphate and 1 m*l* of the Fe(II) solution, the reaction was initiated. The ionic strength of each reaction mixture was kept at 0.10 M $NaClO_4$. The oxidation reaction was followed spectrophotometrically at 20°C by determining the concentrations of the Fe(III), whose molar extinction coefficient at 260 mμ is 4620 $M^{-1}\,cm^{-1}$ in the pH range employed in excesses of triphosphate solutions. The method of kinetic measurement used here was virtually identical with that described before.[1] All the oxidation rates used here were obtained from the slopes of the corresponding concentration-time curves, which are essentially linear in the first stage of the reactions.

Results and Discussion

The rate laws for the oxidation reaction of the Fe(II) in excesses of triphosphate solutions at particular pH values were obtained from the results of several series of runs; in each run one of the solute concentration was varied, while all the other concentrations remained constant. The rate laws thus obtained are defined by the following expressions, from (1) to (4). At a given concentration of the Cu(II) and at pH=3.0 under 1 atm of air ($p_{O_2}=0.21$ atm), a plot of the oxidation rate against the concentration of the Fe(II), [Fe(II)], gives a straight line with a zero intercept, which accounts for the rate expression:

$$\frac{d[\mathrm{Fe(III)}]}{dt} = k_1[\mathrm{Fe(II)}] \quad (1)$$

From the solpe of this particular line the pseudo-first-order rate constant, k_1, is calculated. Linear variations of the rate with the Fe(II) concentration were also obtained at other pH values studied. In the 2.0—3.0 pH range, the linear dependence of the rate on the Cu(II) concentration holds well; this indicates the catalytic behavior of the Cu(II). The rate equation obtained is:

$$\frac{d[\mathrm{Fe(III)}]}{dt} = k_2+k_2'[\mathrm{Cu(II)}] \quad (2)$$

At pH values lower than 2, however, the rate hardly increases at all with an increase in the Cu(II) concentration, showing the saturation of the catalytic effect of the Cu(II). At pH values higher than 2, the values of the rate constants of k_2 and k_2' are calculated from the intercept and from the slope of the straight line of the rate-[Cu(II)] curve respectively. The dependence of the rate on the partial pressure of oxygen shows that the rate increases slightly with an increase in the pressure, and the relationship between these gives a straight line. The rate law at given concentrations of the Fe(II) and the Cu(II) at pH=3.0 is of the form:

$$\frac{d[\mathrm{Fe(III)}]}{dt} = k_3+k_3'p_{O_2} \quad (3)$$

A simillar rate dependence was also obtained at other pH values studied.

The oxidation reaction of Fe(II) in excesses of triphosphate solutions in the absence of Cu(II) has been studied previously.[1] In this case the rate law at a particular pH is expressed by:

$$\frac{d[\mathrm{Fe(III)}]}{dt} = k_a[\mathrm{Fe(II)}]p_{O_2} \quad (4)$$

This rate expression was also confirmed in the present study in the 1.5—3.0 pH range. The values of all the apparent rate constants in the four equations, (1) to (4), at pH=3.0 are summarized in Table 1. The results obtained are consistent with the following rate equation at a particular pH (pH =2.0—3.0):

$$\frac{d[\mathrm{Fe(III)}]}{dt} = k_a[\mathrm{Fe(II)}]p_{O_2}+k_b[\mathrm{Fe(II)}][\mathrm{Cu(II)}] \quad (5)$$

where k_a is the apparent rate constant of the uncatalyzed reaction path and, k_b, that of the catalyzed path. The correlation between the appatent rate constants in Eqs. (1)—(5), which were obtained separately from several series of runs, has been established within the range of experimental error. The rate profiles for the catalyzed and uncatalyzed reaction paths are shown in Fig. 1. A reaction mechanism which accounts for Eq. (5) can be expressed by following reactions in these equations the charges of all the complex species are neglected for the sake of simplification:

$$\mathrm{Fe(II)} + O_2 \rightarrow \mathrm{Fe(III)} + O_2^- \quad (6)$$

$$\mathrm{Fe(II)} + \mathrm{Cu(II)} \rightleftarrows \mathrm{Fe(III)} + \mathrm{Cu(I)} \quad (7)$$

$$\mathrm{Cu(I)} + O_2\ (\text{or } O_2 + H^+) \rightleftarrows \mathrm{Cu(II)} + O_2^-\ (\text{or } HO_2) \quad (8)$$

$$O_2^- + H^+ \rightleftarrows HO_2\ (pK_{HO_2} = 3.3\text{—}4.7^{11)}) \quad (9)$$

The rate-determining step of the uncatalyzed path may be (6), while that of catalyzed path may be (7). Reaction (7) indicates the initiation of

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TABLE 1. APPARENT RATE CONSTANTS FOR THE OXIDATION REACTION OF Fe(II) IN EXCESS OF TRIPHOSPHATE SOLUTIONS AT 20°C
$\mu=0.10$ ($NaClO_4$), pH=3.0

k_1[a)]	k_2[b)]	k_2'[b)]	k_3[c)]	k_3'[c)]	k_a[d)]
0.52 (min^{-1})	2.0×10^{-6} (M min^{-1})	6.0 (min^{-1})	3.2×10^{-5} (M min^{-1})	2.0×10^{-5} (M min^{-1}atm^{-1})	4.0×10^{-2} (min^{-1}atm^{-1})

a) $[Cu(II)]=1.9\times10^{-5}M$, $[TPP]=10^{-3}M$, $p_{O_2}=0.21$ atm.
b) $[Fe(II)]=2.4\times10^{-4}M$, $[TPP]=10^{-3}M$, $p_{O_2}=0.21$ atm.
c) $[Cu(II)]=4.8\times10^{-6}M$, $[Fe(II)]=2.4\times10^{-4}M$, $[TPP]=10^{-3}M$.
d) $[TPP]=10^{-3}M$, in the absence of Cu(II).

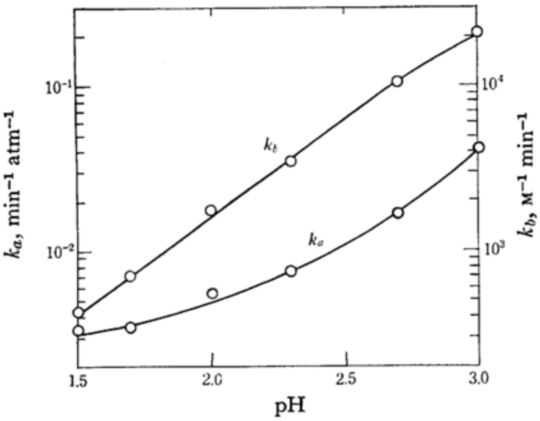

Fig. 1. Rate profile for the Cu(II) catalyzed oxidation of Fe(II) in excess of triphosphate solution at 20°C.
$10^{-3}M$ triphosphate, $\mu=0.10M$ ($NaClO_4$)

the catalytic cycle; the resulting Cu(I) reacts rapidly with oxygen in (8).[2)] The rapid back reaction in (7) was confirmed in the Cu(II)-catalyzed Fe^{2+}–O_2[2,3)] and V(III)–Fe(III)[6)] reactions, but this may be ignored in the initial stage of the reaction discussed here. The HO_2 and O_2^- radicals can either oxidize successively the Fe(II), as in the Weiss mechanism,[12)] or react with the Cu(II) in (8).[2)] The back reaction in (8) may account for the saturation of the oxidation rate as the Cu(II) concentration increases at pH values lower than 2.[2)] The increase in the k_a value with an increase in the pH seems to be due to an increase in the concentration of such Fe(II)-triphosphate complexes as $Fe^{II}HL$,[1)] where HL is the monoprotonated triphosphate anion ($HP_3O_{10}^{4-}$), which is oxidized more rapidly than the aquo ferrous ion by molecular oxygen. Under the present experimental conditions, the $Fe^{II}(HL)_2$ may be neglected.[1)] Therefore, the main species susceptible to oxidation in (6) and (7) under the present experimental conditions may be Fe^{2+} and $Fe^{II}HL$. Though the stability constants of $Fe^{II}HL$ and $Fe^{II}(HL)_2$ have not yet been reported, this estimate also be supported by the consideration that the stability constant of $Fe^{II}HL$ may well be smaller than 10^5 since: i) the stability constant of $Cu^{II}HL$ reported[13)] is $10^{5.2}$ ($\mu=0.1$) and ii) the stability of a Fe(II) complex is generally lower than that of the corresponding Cu(II) complex (Irving-Williams order[14)]).[*1] The real features of the (6) reaction in the 1.5—3.0 pH range seem to be indicated by (6′) and (6″), and that of (7), by (7′), since the normal Cu(II) complex, Cu(II)L, is negligible in the pH region ($K_{Cu(II)L}=10^{7.3}$, $\mu=0.1$[13)]).[*1]

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \qquad (6')$$

$$Fe^{II}HL + O_2 \rightarrow Fe^{III}HL + O_2^- \qquad (6'')$$

$$\left\{\begin{array}{c} Fe^{2+} \\ \upharpoonleft\downharpoonright \\ Fe^{II}HL \end{array}\right\} + \left\{\begin{array}{c} Cu^{2+} \\ \upharpoonleft\downharpoonright \\ Cu^{II}HL \end{array}\right\} \rightleftarrows Fe(III) + Cu(I) \qquad (7')$$

As the rate of (6′) may be influenced by the anions present,[2,3)] and as the stability constant of $Fe^{II}HL$ is unknown, a precise analysis of the rate profiles of k_a and k_b was not undertaken at present. However, it may be suggested that the rate constant of (6″) is appreciably greater than that of (6′) since the k_a value increases markedly with an increase in the pH value. An increase in the k_b value with an increase in the pH may be attributed to the fact that the redox reaction between the Fe(II) and the Cu(II) is accelerated by the formation of the Fe(II) and Cu(II) complexes with triphosphate anions.

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