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# The Promoting Effect of Cupric Ions on the Ferric Ion Catalyzed Decomposition of Hydrogen Peroxide

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The effect of $Cu^{2+}$ ions on the $Fe^{3+}$ ion catalyzed decomposition of $H_2O_2$ was reinvestigated. Deviations from steady state, first order kinetics were observed at a higher $[H_2O_2]$ in the presence of $Cu^{2+}$ ions. The results are discussed in terms of the mechanism suggested by Kremer and Stein for the catalytic decomposition of $H_2O_2$. The promoting action of $Cu^{2+}$ is due to its acceleration of the conversion of the primary to the secondary iron (III)-$H_2O_2$ complex.

## INTRODUCTION

The promoting influence of $Cu^{2+}$ ions on the catalytic decomposition of $H_2O_2$ by $Fe^{3+}$ ions was described by Bohnson and Robertson (*1*) and investigated in detail by Andersen (*2*). The effect was discussed by various authors on the basis of different mechanisms for the unpromoted decomposition (*1–5*). However, since conflicting views regarding the mechanism of the unpromoted reaction existed (*5*), the resulting schemes were also basically different.

By performing simultaneous titrimetric and spectrophotometric measurements on the system $Fe^{3+}$–$H_2O_2$, it was found that two intermediate complexes govern the kinetics of the decomposition (*6*). It is the purpose of this work to elucidate the mode of action of added $Cu^{2+}$ ions by investigating their effect on the concentrations of these two intermediates.

## EXPERIMENTAL

Perchlorate salts of metals were used throughout. Neutral $Cu(ClO_4)_2$ was prepared by heating CuO with less than the equivalent amount of $HClO_4$. The excess CuO was filtered off and the solution was crystallized. The preparation of other materials and the methods of measurements have been described earlier (*6*).

## LOCALIZATION OF THE POINT OF INTERACTION

Four reactions were necessary for the description of the decomposition of $H_2O_2$ (*6, 7*):

$$Fe^{3+} + HO_2^- \underset{2}{\overset{1}{\rightleftharpoons}} Fe^{3+}HO_2^-$$

$$Fe^{3+}HO_2^- \xrightarrow{3} FeO^{3+} + OH^-$$

$$FeO^{3+} + H_2O_2 \xrightarrow{4} Fe^{3+} + H_2O + O_2$$

The pH dependence of the last reaction has not yet been investigated and therefore the above formulation is not meant to indicate the actual form of $H_2O_2$ reacting with $FeO^{3+}$. This point is, however, of no importance for the following discussion.

The promoting action of $Cu^{2+}$ ions may be brought about by providing an alternative path for that one of the three forward reactions which is the rate-determining step. Of these a competition with $Fe^{3+}$ ions in the decomposition of $H_2O_2$ in step 1 can be excluded since $Cu^{2+}$ ions alone only decompose $H_2O_2$ slowly. The acceleration of reaction *3* can be distinguished from that of *4* on the basis of the following consideration: It is known that the $Fe^{3+}$ ion catalyzed decomposition of $H_2O_2$ is a first order reaction in $[H_2O_2]$ at high $[H_2O_2]/$

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* This work was carried out in the Sterling Chemistry Laboratory, Yale University.

$[Fe^{3+}]$ ratios ($R > 10$), while at low $R$ the rate falls below its (extrapolated) "first order value." An analysis of the titrimetric and spectrophotometric data, obtained at low $R$, indicated that under these circumstances an accumulation of the second reaction intermediate occurred. The rate of decomposition was a function not only of $[Fe^{3+}]$ and $[H_2O_2]$, but also of $d[FeO^{3+}]/dt$; the kinetics of the decomposition was nonstationary.* The addition of $Cu^{2+}$ will shift the value of $R$ at which the transition from stationary first order to nonstationary kinetics occurs.

(*a*) Non-stationary kinetics will be observed at higher $R$ if it provides a more effective path for the conversion of $Fe^{3+}HO_2^-$ to $FeO^{3+}$. (It will increase $[FeO^{3+}]$.)

(*b*) The decomposition will become nonstationary at lower $R$ if $Cu^{2+}$ ions facilitate the decomposition of $FeO^{3+}$.

(*c*) There exists the third possibility that $Cu^{2+}$ will react with $Fe^{3+}HO_2^-$ without producing $FeO^{3+}$. Then oxygen will be evolved through a side reaction involving copper–peroxo complexes. It will be seen that in this case nonstationary kinetics will begin at lower $R$ since the rate of formation of $FeO^{3+}$ will be decreased. The side reaction will necessarily be stationary as long as $H_2O_2$ is present in a large excess over $Cu^{2+}$.

In order to test whether the kinetics of the decomposition are stationary or not, the reactants were mixed and the decrease of the total $[H_2O_2]$ hence ($[H_2O_2]_0 - 1/2[O_2]$), was followed in a definite concentration interval by titrating it with permanganate. The reaction was repeated

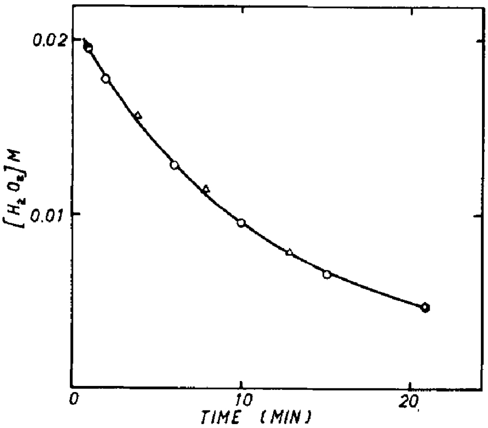

FIG. 1a. The decomposition of $H_2O_2$ by $Fe^{3+}$ ions alone. $[Fe^{3+}]_0 = 7.24 \times 10^{-3} M$; pH = 2.12; $t = 27.0°C$; ionic strength = 0.250 *M*. ○ indicates $[H_2O_2]_0 = 3.92 \times 10^{-2} M$; △ indicates $[H_2O_2]_0 = 1.96 \times 10^{-2} M$.

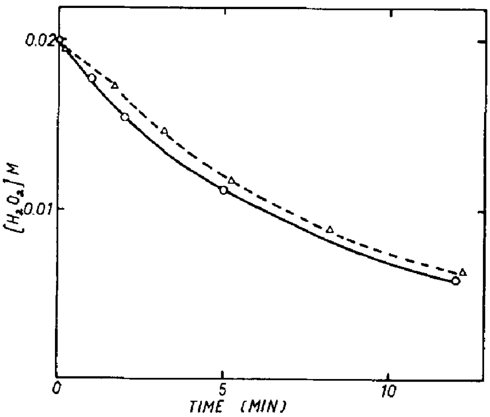

FIG. 1b. The decomposition of $H_2O_2$ by a mixture of $Fe^{3+}$ and $Cu^{2+}$ ions. $[Fe^{3+}]_0 = 7.24 \times 10^{-3} M$; $[Cu^{2+}]_0 = 9.96 \times 10^{-5} M$; pH = 2.12; $t = 27.0°C$; ionic strength = 0.250 *M*. ○ indicates $[H_2O_2]_0 = 3.90 \times 10^{-2} M$; △ indicates $[H_2O_2]_0 = 1.96 \times 10^{-2} M$.

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* If the reaction $A + B \rightarrow C$ proceeds through $n$ intermediates (X), then the general rate of formation of C is given by

$$\frac{d[C]}{dt} = k[A][B] - \frac{d[X_1]}{dt} - \frac{d[X_2]}{dt} - \cdots - \frac{d[X_n]}{dt}$$

If all the time derivatives $d[X_i]/dt$ vanish, i.e., they are much smaller than either $d[C]/dt$ or $-d[A]/dt$, then $d[C]/dt$ depends only on [A] and [B] (stationary kinetics). If, on the other hand, any of the $d[X_i]/dt$'s do not vanish, then the rate will depend also on its magnitude, which will change as the reaction proceeds (nonstationary kinetics). It follows from this difference between the two kinds of kinetics that if the initial [A] and [B] are varied, but kept in a suitable ratio so that (after an elapse of different times) the same values of [A] and [B], respectively, are obtained in every case, then from that point on the [C] vs. time curves can be superimposed only if the kinetics is stationary. The same is true for the $[A]_0 - [C]$ vs. time curves used in the above analysis.

with half of the initial concentration of $H_2O_2$ and the change of the total $[H_2O_2]$ was again measured in the same concentration range as before. The two curves were examined as to whether they can be superimposed. Figures 1a and 1b show a comparison of two pairs of curves. The pair in Fig. 1a was obtained in the presence of $Fe^{3+}$ ions alone; that in Fig. 1b with the addition of a small amount of $Cu^{2+}$. It is seen that while the decomposition is stationary with $Fe^{3+}$ ions alone, it becomes nonstationary if $Cu^{2+}$ ions are added. We have thus case (*a*) before us. The observed differences between the two curves in Fig. 1b ($3\text{–}12 \times 10^{-4}\,M$) are beyond experimental error ($\pm 1 \times 10^{-4}\,M$).

It is of interest to note that a similar feature can be discerned in the results of Andersen (*2*). He found that in the mixed inverse first and second order expression for the reciprocal decomposition velocity

$$-\frac{dt}{d[H_2O_2]} = A\,\frac{1}{[H_2O_2]} + B\,\frac{1}{[H_2O_2]^2}$$

*A* decreased, while *B* increased upon the addition of $Cu^{2+}$. The inverse square member in Andersen's treatment corresponds to the deviation from steady state, first order kinetics.

## Results at High $[H_2O_2]$

The velocity of decomposition has been investigated as a function of $[H_2O_2]$, $[Fe^{3+}]$, and $[Cu^{2+}]$ at a constant pH and ionic strength. The variation of $[Cu^{2+}]$ was extended over the range $5 \times 10^{-4}$ to $5 \times 10^{-3}\,M$, that of $[Fe^{3+}]$ from $2.5 \times 10^{-4}$ to $1.0 \times 10^{-3}\,M$. The decomposition of $H_2O_2$ was followed from 0.6 to $0.2\,M$. It was always present in a large excess over the catalyst, thereby assuring the observation of steady state kinetics.* In Fig. 2 the dependence of $-\Delta t/\Delta[H_2O_2]$ on $\Delta\ln[H_2O_2]/\Delta[H_2O_2]$ is shown at a constant $[Fe^{3+}]_0$ and different $[Cu^{2+}]_0$. The small subscript $_0$ indicates total concentrations. This method of plotting of the results gives a straight line when the order of the reaction with respect to a reactant increases from zero to one, while the concentration of the reactant decreases. This behavior is frequently encountered in enzyme kinetics and the plot is entirely analogous to that of Lineweaver and Burk, only the measuring of the slopes of experimental curves being eliminated (*8*). The slopes of the straight lines were functions of both $[Cu^{2+}]_0$ and $[Fe^{3+}]_0$. We define as Δ the difference between the inverse slopes in the presence and absence of $Cu^{2+}$. Figure 3 shows the dependence of $1/\Delta$ on $1/[Cu^{2+}]_0$ at different $[Fe^{3+}]_0$.

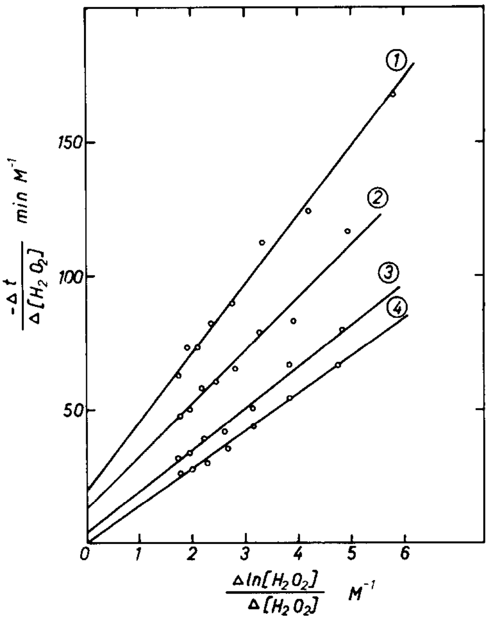

FIG. 2. $-\Delta t/\Delta[H_2O_2]$ as a function of $\Delta\ln[H_2O_2]/\Delta[H_2O_2]$. $[Fe^{3+}]_0 = 5.00 \times 10^{-4}\,M$; pH = 2.13; $t = 27.0°C$; ionic strength = $0.250\,M$. (1) $[Cu^{2+}]_0 = 4.98 \times 10^{-4}\,M$; (2) $[Cu^{2+}]_0 = 9.96 \times 10^{-4}\,M$; (3) $[Cu^{2+}]_0 = 24.9 \times 10^{-4}\,M$; (4) $[Cu^{2+}]_0 = 49.8 \times 10^{-4}\,M$.

## Discussion

The promoting effect of $Cu^{2+}$ can be accounted for by assuming three reactions in addition to the original scheme:

$$Fe^{3+}HO_2^- + Cu^{2+} \underset{6}{\overset{5}{\rightleftharpoons}} \{Fe^{3+}HO_2^-Cu^{2+}\}$$

$$\{Fe^{3+}HO_2^-Cu^{2+}\} \xrightarrow{7} FeO^{3+} + CuOH^+$$

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* At the highest $[Cu^{2+}]$ a slow decomposition by $Cu^{2+}$ ions alone occurred. The results are corrected for this effect. It resulted in a change of about 5% in the rate constant.

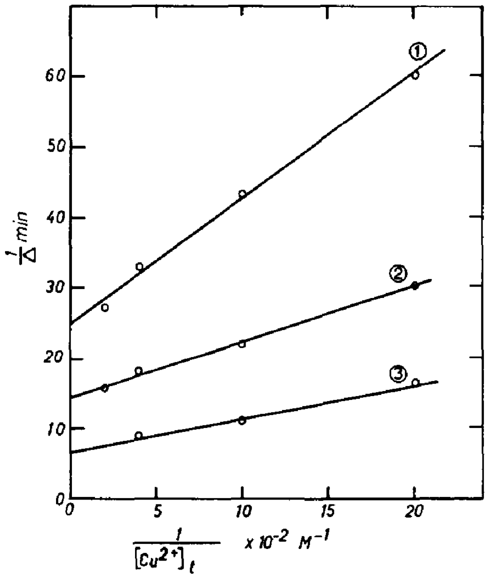


FIG. 3. $1/\Delta$ as a function of $1/[Cu^{2+}]_0$. pH = 2.13; $t = 27.0$°C; ionic strength = 0.250 $M$. (1) $[Fe^{3+}]_0 = 2.50 \times 10^{-4}\,M$; (2) $[Fe^{3+}]_0 = 5.00 \times 10^{-4}\,M$; (3) $[Fe^{3+}]_0 = 10.00 \times 10^{-4}\,M$.

Introducing the condition of stationary state for the reaction intermediates we obtain:

$$\begin{aligned} d[C_I]/dt &= k_1\{[Fe^{3+}]_0 - [C_I] - [C_{II}] - [C_{III}]\}[H_2O_2] \\ &\quad - \{k_2 + k_3 + k_5([Cu^{2+}]_0 - [C_{III}])\}[C_I] \\ &\quad + k_6[C_{III}] = 0 \end{aligned} \tag{1}$$

$$d[C_{II}]/dt = k_3[C_I] + k_7[C_{III}] - k_4[C_{II}][H_2O_2] = 0 \tag{2}$$

$$\begin{aligned} d[C_{III}]/dt &= k_5[C_I]\{[Cu^{2+}]_0 - [C_{III}]\} \\ &\quad - (k_6 + k_7)[C_{III}] = 0 \end{aligned} \tag{3}$$

$C_I$, $C_{II}$, and $C_{III}$ stand for $Fe^{3+}HO_2^-$, $FeO^{3+}$, and $Fe^{3+}HO_2^-Cu^{2+}$. These equations can be solved for the concentrations of the intermediates:

$$[C_I] = \frac{[Fe^{3+}]_0[H_2O_2]}{[H_2O_2] + K'_M + \{[Cu^{2+}]_0/([C_I] + R)\}\{[H_2O_2] + (k_7/k'_1) + (k_7/k_4)\}} \tag{4}$$

$$[C_{III}] = \frac{[C_I][Cu^{2+}]_0}{[C_I] + R} \tag{5}$$

$$K'_M = \frac{k_2 + k_3}{k'_1} + \frac{k_3}{k_4} \qquad k'_1 = \frac{k_1 K_{H_2O_2}}{[H^+]}$$

$$R = \frac{k_6 + k_7}{k_5}$$

The rate equation has a simple solution for $[C_I] \ll R$. This condition is realized when the concentration of $Cu^{2+}$ is high enough to convert a large fraction of $C_I$ to $C_{III}$.

The rate of the over-all decomposition of $H_2O_2$ is the sum of the rates through the separate paths:

$$-\frac{d[H_2O_2]}{dt} = 2(k_3[C_I] + k_7[C_{III}]) \tag{6}$$

Introducing the expressions for $[C_I]$ and $[C_{III}]$ we obtain:

$$\begin{aligned} -\frac{dt}{d[H_2O_2]} &= \frac{1}{2[Fe^{3+}]_0} \cdot \frac{R + [Cu^{2+}]_0}{Rk_3 + k_7[Cu^{2+}]_0} + \frac{1}{2[Fe^{3+}]_0} \\ &\quad \cdot \frac{RK'_M + k_7\{(1/k'_1) + (1/k_4)\}[Cu^{2+}]_0}{Rk_3 + k_7[Cu^{2+}]_0} \cdot \frac{1}{[H_2O_2]} \end{aligned} \tag{7}$$

or in integrated form

$$\begin{aligned} \frac{t_2 - t_1}{H_2O_2]_1 - [H_2O_2]_2} &= \frac{1}{2[Fe^{3+}]_0} \cdot \frac{R + [Cu^{2+}]_0}{Rk_3 + k_7[Cu^{2+}]_0} \\ &\quad + \frac{1}{2[Fe^{3+}]_0} \cdot \frac{RK'_M + k_7\{(1/k'_1) + (1/k_4)\}[Cu^{2+}]_0}{Rk_3 + k_7[Cu^{2+}]_0} \\ &\quad \cdot \frac{\ln [H_2O_2]_1 - \ln [H_2O_2]_2}{[H_2O_2]_1 - [H_2O_2]_2} \end{aligned} \tag{8}$$

The data of Fig. 2 are seen to conform with Eq. 8 at a constant $[Fe^{3+}]_0$ and $[Cu^{2+}]_0$. Denoting the slope of the straight lines as $T$ and its value at $[Cu^{2+}]_0 = 0$ as $T_0$, we obtain for $\Delta = (1/T) - (1/T_0)$

$$\begin{aligned} \frac{1}{\Delta} &= \frac{1}{2[Fe^{3+}]_0} \cdot \frac{k'_1 K'_M}{k_2} \left(\frac{1}{k'_1} + \frac{1}{k_4}\right) \\ &\quad + \frac{1}{2[Fe^{3+}]_0} \cdot \frac{K'^2_M k'_1 R}{k_2 k_7} \cdot \frac{1}{[Cu^{2+}]_0} \end{aligned} \tag{9}$$

This dependence is shown in Fig. 3. From the slopes and intercepts we obtain

$$\frac{k'_1 K'_M}{k_2}\left(\frac{1}{k'_1} + \frac{1}{k_4}\right) = (1.3 \pm 0.1) \times 10^{-2} \text{ min } M$$

$$\frac{k' K'^2_M R}{k_2 k_7} = (8.8 \pm 0.9) \times 10^{-6} \text{ min } M^2$$

at $t = 27.0$°C, pH = 2.13, ionic strength = 0.250 $M$. From these values and from $K_M'/k_3 = 0.174$ min $M$ we calculate that $k_7/Rk_3 = 2.1 \times 10^4\,M^{-1}$. Inspection of Eqs. 5 and 6 reveals that this quantity determines the relative rates of the promoted and unpromoted paths:

$$\frac{v_{Cu}}{v_{Fe}} = \frac{k_7[C_{III}]}{k_3[C_I]} = \frac{k_7}{k_3 R}[Cu^{2+}]_0$$

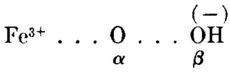
Taking $10^{-3}\,M$ $[Cu^{2+}]_0$, 95% of the decomposition proceeds through the promoted path and only 5% through spontaneous decomposition of $Fe^{3+}HO_2^-$.

With the aid of $(k'_1K'_M/k_2)/\{(1/k'_1) + (1/k_4)\}$ we can split $K'_M/k_3$ into $k_2/k'_1k_3$ and $\{(1/k'_1) + (1/k_4)\}$. We obtain $k_2/k'_1k_3 = 0.162 \pm 0.005$ min $M$ and $\{(1/k'_1) + (1/k_4)\} = (1.2 \pm 0.1) \times 10^{-2}$ min $M$. From previous results (*6*): $(k_2/k'_1k_3) + (1/k'_1) = 0.147 \pm 0.005$ min $M$, and $1/k_4 = (2.8 \pm 0.4) \times 10^{-2}$ min $M$. The value of $1/k'_1$ is probably very small since in step *1* two oppositely charged ions are associated.

The straight lines in Fig. 2 show a positive intercept as required by Eq. 8. Its value should change from $1/k_3$ at $[Cu^{2+}]_0 = 0$ to $1/k_7$ at high $[Cu^{2+}]_0$. Since $k_7 > k_3$, the intercept should decrease with increasing $[Cu^{2+}]_0$. This behavior can be seen in Fig. 2.

On lowering the concentration of $Cu^{2+}$ the condition $[C_I] \ll R$ no longer applies and the reaction becomes more complex. The increase of the reaction velocity upon the addition of $Cu^{2+}$ becomes more dependent on $[Cu^{2+}]_0$, approaching proportionality at very low $[Cu^{2+}]_0$. At the same time it becomes less dependent on $[H_2O_2]$ and $[Fe^{3+}]_0$. This behavior is expected to occur upon approaching $[C_I] \gg R$. A quantitative treatment of the data at very low $[Cu^{2+}]_0$ was not possible because of the experimental errors involved.

The promoting action of $Cu^{2+}$ ions has been considered to be due to their ready reducibility to $Cu^+$ ions (*3, 4*). However, it is seen that they catalyze the conversion of $Fe^{3+}HO_2^-$ to $FeO^{3+}$. Since both of these intermediates are in the same state of oxidation, it is evident that $Cu^{2+}$ cannot act as a redox catalyst. The promoting action can be understood on the basis of a linear transition complex in reaction *3*:



$$Fe^{3+} \, . \, . \, . \underset{\alpha}{O} \, . \, . \, . \underset{\beta}{\overset{(-)}{OH}}$$

The $HO_2$ anion is broken up as a consequence of a transfer of the negative charge from the $\alpha$ to the $\beta$ oxygen atom. (In order to accommodate an extra electron in a low lying $2p$ orbital, the O–O bond, the weakest in the molecule, must be broken. $Cu^{2+}$ ions, by coordinating $O_\beta$, facilitate the charge transfer thus causing the breakup of the molecule.

The kinetic conclusions reached in this work parallel generally those of Andersen (*2*), if allowance is made for differences in the underlying mechanisms for the unpromoted decomposition. Especially the location of the point of interaction in step 3 is common in both cases. Unfortunately, Andersen's results were obtained at such low concentrations of $H_2O_2$ that a steady state analysis could not be made rigorously. It seems that the complication of his final scheme originates from this fact.

## ACKNOWLEDGMENTS

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