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Formation of Peroxodiphosphate by the Copper(II)-Catalyzed Oxidation Reaction of the Phosphinate Ion by the Molecular Oxygen. Kinetics and Mechanisms in Aqueous Solutions

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It was found that peroxodiphosphate ions (denoted by PDP and meaning all forms of $P_2O_8{}^{4-}$, $HP_2O_8{}^{3-}$, $H_2P_2O_8{}^{2-}$, etc.) were formed by the oxidation of the phosphinate ion ($PH_2O_2{}^-$) by molecular oxygen (O_2) using trace amounts of the copper(II) ion as a catalyst in aqueous solutions. The formation rate was dependent on the acidity being maximum at around pH 3.5, and was inhibited by the presence of radical scavengers or a complex-forming substance of ethylenediaminetetraacetic acid (EDTA). The formation of PDP was not observed when ions such as Ir^{IV} and Ce^{IV} were used in place of the copper(II) ion. Thus, this reaction is specific only for the copper(II) ion, which can be easily reduced to Cu^+ by the phosphinate ion, where the reduced species are capable of reacting with molecular oxygen to efficiently produce the superoxide of $O_2^{-\bullet}$ or $HO_2^{\bullet}$. After some PDP had been formed in the presence of air or oxygen, if the reacting solution was changed to be anaerobic by bubbling nitrogen through the solution, the PDP began to decompose according to the first-order rate law with respect to the concentrations of PDP. The kinetics and mechanisms for not only the formation, but also the decomposition of PDP, are presented.

The present authors[1—5] have investigated the peroxodisulfate ion ($S_2O_8{}^{2-}$) reduction (or decomposition) reaction kinetics by measuring the polarographic diffusion current of $S_2O_8{}^{2-}$. When an experiment concerning the reduction of peroxodisulfate by the phosphinate ion ($PH_2O_2{}^-$) was carried out using copper(II) ion as a catalyst, we discovered that the polarographic diffusion current unexpectedly increased in the presence of oxygen.[6] Such a current increase was observed even without adding the peroxodisulfate ion. This stimulated us to carry out the present study.

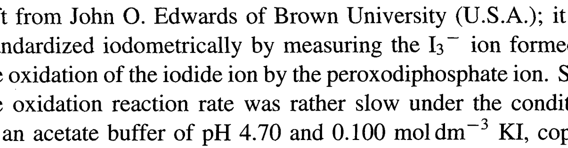
The peroxodiphosphate ion ($P_2O_8{}^{4-}$ or PDP) is comparable to the peroxodisulfate ion ($S_2O_8{}^{2-}$), having an analogous structure.[7] In view of the structural analogy between the two ions, similar reactions are not surprising. Actually, our observation concerning the polarographic diffusion current mentioned above was similar in both polarograms of peroxodiphosphate and peroxodisulfate. Several similarities and differences between peroxodiphosphate and peroxodisulfate have been documented by Crutchfield[7] and Edwards.[8] The synthesis method due to the electrolytic oxidation of the phosphate or sulfate ion is also similar in each case: $PO_4^{3-} \rightarrow PO_4^{2-\bullet} + e^-$; $2PO_4^{2-\bullet} \rightarrow P_2O_8{}^{4-}$ or $SO_4{}^{2-} \rightarrow SO_4^{-\bullet} + e^-$; $2SO_4^{-\bullet} \rightarrow S_2O_8{}^{2-}$.

It is of interest that the oxidation number of unity (P^I) in the phosphinate ion can be easily oxidized to that of five (P^V) in the peroxodiphosphate ion by molecular oxygen (see the mechanisms assumed in the present paper). This may be specific in phosphorous compounds for O_2 oxidation. We believe that the kinetic investigation of the title's formation reaction is novel, as yet unreported.

The visualized structures for peroxodiphosphoric acid and phosphinic acid are as follows (Chart 1): The acid-dissociation constants of peroxodiphosphoric acid are 2.0, 0.30, $(6.6\pm0.3)\times10^{-6}$, and $(2.1\pm0.1)\times10^{-8}$ $dm^3\ mol^{-1}$ for K_{a1}, K_{a2}, K_{a3}, and K_{a4}, respectively.[8] The acid-dissociation constant of phosphinic acid is 4.0×10^{-2} $dm^3\ mol^{-1}$ for K_{a1}.[9] Therefore, the predominant species in the present study of the pH range 2—5 were $H_2P_2O_8{}^{2-}$ and $PH_2O_2^-$.

Experimental

Chemicals. Potassium peroxodiphosphate ($K_4P_2O_8$) was a gift from John O. Edwards of Brown University (U.S.A.); it was standardized iodometrically by measuring the $I_3{}^-$ ion formed by the oxidation of the iodide ion by the peroxodiphosphate ion. Since the oxidation reaction rate was rather slow under the conditions of an acetate buffer of pH 4.70 and 0.100 $mol\,dm^{-3}$ KI, copper(II) sulfate of 2.00×10^{-6} $mol\,dm^{-3}$ was added as a catalyst; the concentrations of $I_3{}^-$ formed were measured using a Shimadzu UV-150-02 spectrophotometer with an absorption coefficient of 2.50×10^4 $dm^3\ mol^{-1}\ cm^{-1}$ at 350 nm. The sodium phosphinate ($Na_2PH_2O_2$) and other chemicals were of guaranteed grade from Wako Pure Chemical Industries, Ltd. Deionized water was further distilled in a glass still.



Peroxodiphosphoric acid

Phosphinic acid

Chart 1.

Procedure. The reaction was started by mixing a sodium phosphinate solution with a copper(II) sulfate solution containing sulfuric acid. Each solution containing $PH_2O_2^-$ or Cu^{2+} was separately saturated with the given gas by bubbling oxygen, air, or nitrogen through the solution before mixing the solutions. The gas was then continuously bubbled through the reacting solution. The temperature of the reaction solution was controlled to within 0.1 °C. Aliquot solutions were taken out at appropriate time intervals in order to measure the concentrations of the formed peroxodiphosphate. Preliminary experiments showed that the potassium peroxodiphosphate ($K_4P_2O_8$) in 1.00×10^{-2} mol dm^{-3} $HClO_4$ with 0.010% gelatin gave a polarographic reduction current at 0.40 V vs. a saturated calomel electrode (SCE), and that the limiting-diffusion current was proportional to the concentrations of $K_4P_2O_8$. Thus, measurements of the concentrations of formed PDP were made in a solution of 1.00×10^{-2} mol dm^{-3} $HClO_4$ and 0.010% gelatin, where 0.40% acrylamide was added in order to slow down the reaction. The characteristics of the dropping mercury electrode (DME) used were $m=1.39\times10^{-3}$ g s^{-1} and $t_d=5.18$ s drop^{-1} under conditions of 5.00×10^{-2} mol dm^{-3} KNO_3 at 25 °C, 0.20 V vs. SCE, and the mercury pressure (or height) of 50.0 cm.

Results and Discussion

After the given times for standing the $PH_2O_2^-$ solution containing trace amounts of the copper(II) ion under saturation with a gas of nitrogen, air, or oxygen, an aliquot solution was removed at an appropriate time to measure the polarogram. The results are shown in Fig. 1. The polarographic reduction wave at 0.40 V vs. SCE, which was obtained from the reaction solution saturated with air or oxygen, was found to be same as that of PDP.

Figure 2 shows plots of the concentrations of PDP formed against the reaction time for a solution saturated with oxygen at different concentrations of $PH_2O_2^-$. The concentrations of $PH_2O_2^-$ strongly influence the formation rate of PDP. In the case of the copper(II) dependence on PDP formation, it was found to be proportional to the concentrations of added copper(II) (see Fig. 3).

pH Effect. The concentrations of the formed PDP were plotted against pH of the reacting solution (Fig. 4). PDP formation was maximum at pH≈3.5.

Effect of Radical Scavengers and Chelate Reagents. The addition of 0.80% (w/v) acrylamide or 0.50% (v/v) acrylonitrile into the reacting solution 65 min after initiating the reaction under the conditions given in Fig. 1 at O_2-sat. completely retarded the formation of PDP; thereafter, PDP did not decompose (see the inset in Fig. 2). Ethylenediaminetetraacetic acid (EDTA), which is capable of forming a complex with the copper(II) ion, retarded the reaction as well.

Copper(II)-Catalyzed Decomposition of PDP. When the reacting solution, once saturated with oxygen or air for a certain time, was changed to a nitrogen-saturated solution, the formed PDP began to decrease according to the first-order dependence with respect to the PDP concentration (see Fig. 5). Plots of ln [PDP] vs. time were rectilinear for at least 90% of the reaction, and the first-order rate constant was obtained from the slope of this line. Thus, the rate law for the PDP decomposition is described by

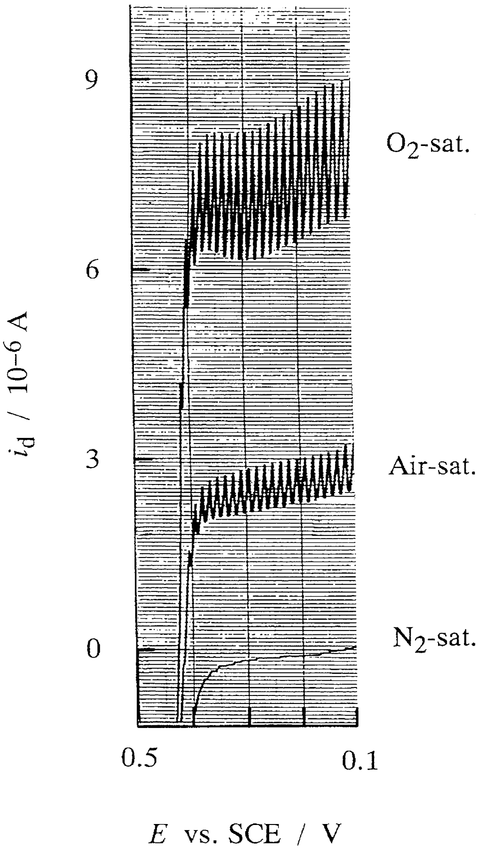


Fig. 1. Polarogram of the product PDP. Reaction solution of 0.400 mol dm^{-3} $NaPH_2O_2$, 1.00×10^{-3} mol dm^{-3} H_2SO_4, 1.00×10^{-5} mol dm^{-3} $CuSO_4$, and 9.00×10^{-3} mol dm^{-3} Na_2SO_4 at 25 °C and pH 3.56 was saturated with nitrogen, air, or oxygen for 40 min, and then the aliquot (20 ml) was mixed with solution (30 ml) containing 0.017% gelatin, 1.70×10^{-2} mol dm^{-3} $HClO_4$, and 0.67% acrylamide in order to measure the polarogram at pH 2.0.

$$-d[PDP]/dt = k_{obsd}[PDP]. \qquad (1)$$

As can be seen in Figs. 6 and 7, the observed rate constants (k_{obsd}) were proportional to the concentrations of copper(II), and increased with increasing the $PH_2O_2^-$ concentration. The temperature dependence of the rate was examined under the conditions given in Fig. 5. The values of $10^4\ k_{obsd}$ were 1.93, 4.75, 7.10, and 11.4 s^{-1} at 20.0, 25.0, 30.0, and 35.0 °C, respectively. Plots of $\log k_{obsd}$ vs. T^{-1} are rectilinear with 88±5 kJ mol^{-1} as the activation energy. The ionic-strength dependence of the rate was also examined at 25.0 °C. The values of $10^4\ k_{obsd}$ are 4.75, 4.16, 4.00, and 3.56 s^{-1} at ionic strengths (I) of 0.43, 0.53, 0.63, and 0.73 mol dm^{-3}, respectively, where the ionic strengths were adjusted with sodium perchlorate. Plots of $\log k_{obsd}$ vs. $I^{1/2}/(1+I^{1/2})$ are rectilinear with a slope of −1.8. As can be seen in Fig. 8, the pH effect was large and had a resemblance to that on the formation shown in Fig. 4.

Mechanism of Reaction. Considering the following redox potentials,[10)]

$$Cu^{2+} + 2e^- \rightleftarrows Cu \qquad E^0 = 0.337\ V \qquad (2)$$

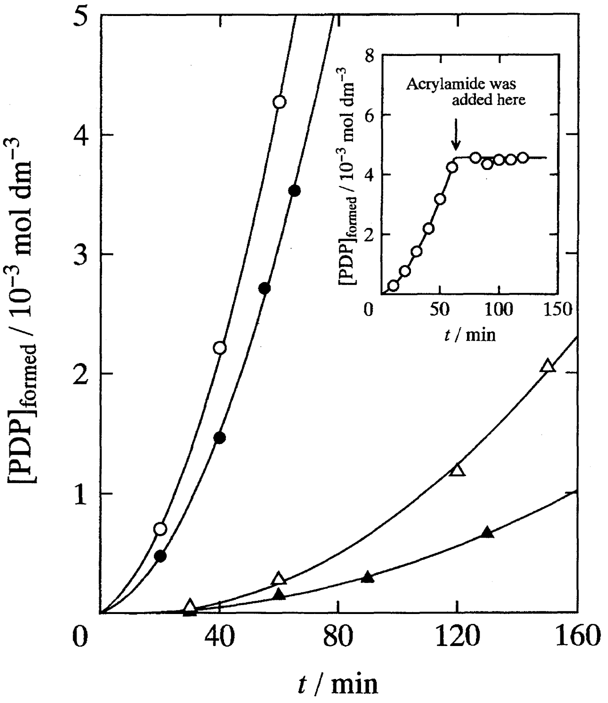


Fig. 2. Plots of $[PDP]_{formed}$ vs. t in the solution saturated with O_2. Conditions are the same as in Fig. 1 except for the various concentrations of $NaPH_2O_2$ of 0.100 (▲), 0.200 (△), 0.300 (●), and 0.400 mol dm^{-3} (○). The inset indicates the effect of the radical scavenger of acrylamide: acrylamide (0.80% (w/v)) was added into the reacting solution at $t = 65$ min after initiating the reaction under the same conditions as in Fig. 1 of O_2-sat.

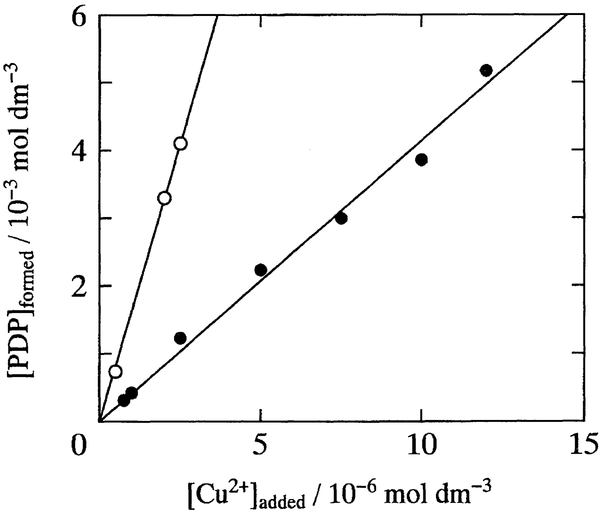


Fig. 3. Plots of $[PDP]_{formed}$ vs. $[Cu^{2+}]_{added}$. Plots ● and ○ indicate the PDP formation at 50 and 120 min, respectively. The solid lines are the least-square's fits. Conditions are the same as in Fig. 1 of O_2-sat.

$$Cu^{2+} + e^- \rightleftarrows Cu^+ \qquad E^0 = 0.135\ \text{V} \qquad (3)$$

$$H_3PO_3 + 2H^+ + 2e^- \rightleftarrows HPH_2O_2 + H_2O \qquad E^0 = -0.50\ \text{V} \qquad (4)$$

$$O_2 + e^- \rightleftarrows O_2^{-\bullet} \qquad E^0 = -0.56\ \text{V} \qquad (5)$$

$$O_2 + H^+ + e^- \rightleftarrows HO_2\cdot \qquad E^0 = -0.13\ \text{V} \qquad (6)$$

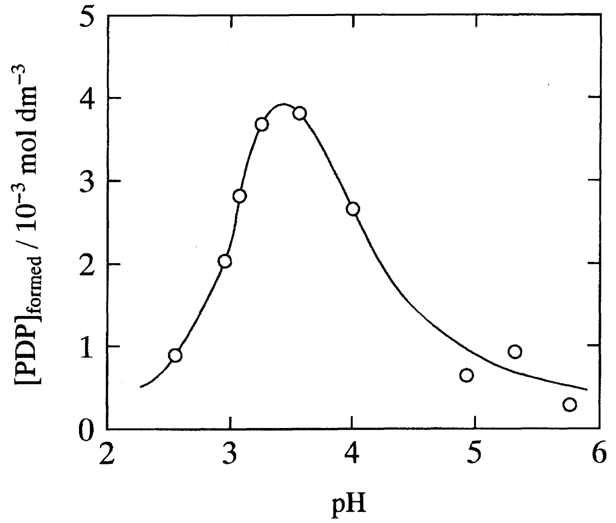


Fig. 4. pH Effect on the PDP formation. Conditions are the same as in Fig. 1 of O_2-sat. at $t = 50$ min. Values of pH are changed by changing the contents of sulfuric acid, keeping the relationship of $[H_2SO_4] + [Na_2SO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}.

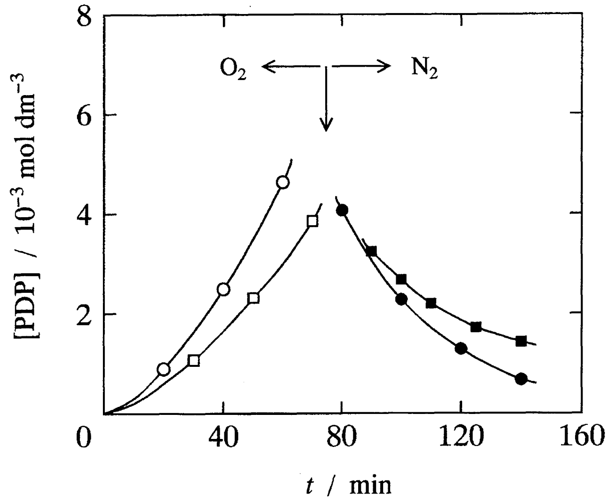


Fig. 5. Profile for the formation and decomposition of PDP under the same conditions as in Fig. 1. Plots ○ and ● indicate those in 1.00×10^{-5} mol dm^{-3} $CuSO_4$, and □ and ■, 5.00×10^{-6} mol dm^{-3} $CuSO_4$. The reaction solution was saturated with O_2 for some times, and was then saturated with N_2 (i.e., plots of ● and ■).

the reduction of Cu^{2+} to Cu or Cu^+ by HPH_2O_2 can easily occur, and the oxidation of Cu and Cu^+ to Cu^{2+} by O_2 can not easily occur. On the other hand, Cu(II)-catalysis is evident from Fig. 3, and seems to be due to the redox cycle of Cu^{2+}/Cu^+. The following equilibrium constants can be obtained from the above potentials:

$$2Cu^+ \rightleftarrows Cu + Cu^{2+} \qquad K = 1.6 \times 10^6 \qquad (7)^{10)}$$

$$Cu^+ + O_2 + H^+ \rightleftarrows Cu^{2+} + HO_2\cdot \qquad K = 0.654\ \text{dm}^3\,\text{mol}^{-1} \qquad (8)$$

When $HO_2\cdot$ or $O_2^{-\bullet}$ could be consumed by the other reaction (Eq. 12), Cu^+ might be oxidized to Cu^{2+} by O_2. Pre-

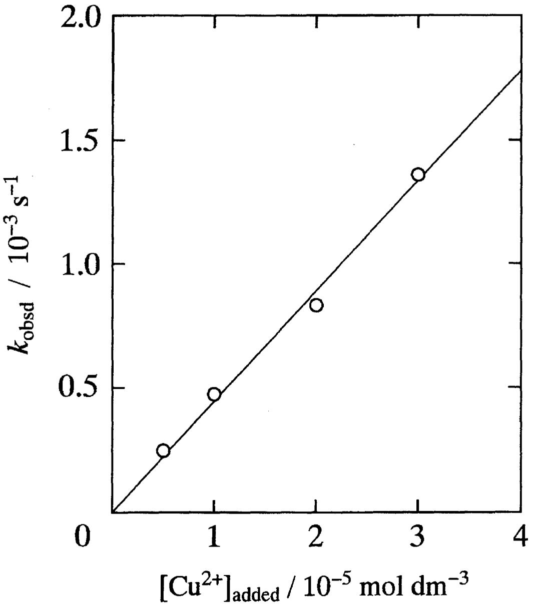


Fig. 6. Plots of k_{obsd} vs. $[Cu^{2+}]_{added}$ for the decomposition of PDP under the same conditions as in Fig. 5. The solid line is the least-square's fit.

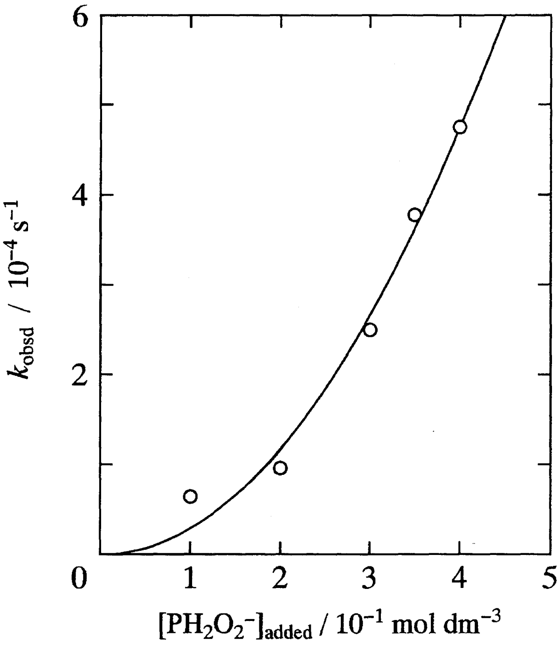


Fig. 7. Plots of k_{obsd} vs. $[PH_2O_2^-]_{added}$ for the decomposition of PDP under the same conditions as in Fig. 5.

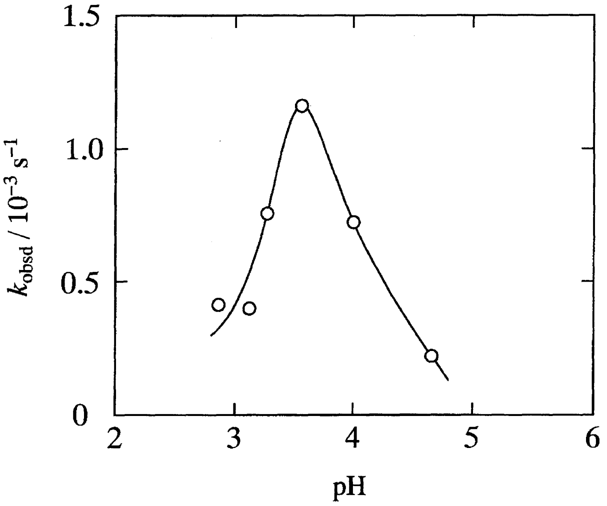


Fig. 8. pH Effect on k_{obsd} for the decomposition of PDP under the same conditions as in Fig. 5.

liminary experiments showed that the oxidizing ion, such as Ce(IV) or Ir(IV), could not act as a catalyst for this reaction. Thus, this reaction is specific only for the copper(II) ion, which can be easily reduced to Cu^+ by $PH_2O_2^-$, where the reduced species are capable of reacting with O_2 to efficiently produce $HO_2\cdot$ or $O_2^{-\bullet}$. This fact indicates that $PH_2O_2\cdot$, which is produced by the one-electron oxidation of $PH_2O_2^-$, is not an initiator for this reaction. Namely, the reaction of $PH_2O_2\cdot + O_2 \rightarrow H_2PO_4\cdot$ or $PH_2O_2\cdot + O_2 \rightarrow \{PH_2O_2^+ + O_2^{-\bullet}\} \rightarrow H_2PO_4\cdot$ can not be assumed in the mechanism. Consequently, the following mechanism is presented to account for the results obtained in the presence of O_2:[11]

$$PH_2O_2^- + Cu^{2+} \rightleftarrows PH_2O_2\cdot + Cu^+ \quad (9)$$

$$2Cu^+ \rightleftarrows Cu + Cu^{2+} \quad (7)$$

$$2PH_2O_2\cdot \rightleftarrows PH_2O_2^- + PH_2O_2^+ \quad (10)$$

$$Cu^+ + O_2 + H^+ \rightleftarrows Cu^{2+} + HO_2\cdot \quad (8)$$

$$HO_2\cdot \rightleftarrows O_2^{-\bullet} + H^+ \quad (11)$$

$$PH_2O_2^+ + O_2^{-\bullet} \rightarrow H_2PO_4\cdot \quad (12)$$

$$2H_2PO_4\cdot \rightarrow H_4P_2O_8 \quad (13)$$

Assuming the steady states' conditions, the following equations were obtained:

$$\begin{aligned} d[H_4P_2O_8]/dt &= k_{13}[H_2PO_4\cdot]^2 \\ &= k_{12}[PH_2O_2^+][O_2^{-\bullet}] \\ &= k_{12}(K_8K_9K_{10}K_{11})[PH_2O_2\cdot][O_2] \\ &= k_{12}\{K_8(K_9)^2K_{10}K_{11}\}[PH_2O_2^-][O_2][Cu^{2+}]/[Cu^+] \end{aligned} \quad (14)$$

All of the above reactions are thought to be fast. The k_{13} value is reported to be 5.0×10^8 dm^3 mol^{-1} s^{-1} at pH 3.5.[12] When $HO_2\cdot$ and $O_2^{-\bullet}$ could be rapidly consumed by reactions 11 and 12, it is possible for the oxidation of Cu^+ to Cu^{2+} by O_2 to occur rapidly according to Eq. 8. The backward-reaction rate of Eq. 9 competes with the forward-reaction rates in Eqs. 7, 8, and 10. Rate equation 14 explains most of the characteristics concerning the PDP formation reaction: the PDP formation rate was proportional to the concentrations of the copper(II) ion added (Fig. 3), and was extremely retarded by EDTA. These facts indicate that reaction 9 acts as the initiating reaction. The complete retardation effect by the radical scavengers (see the inset in Fig. 2) indicates that PDP formation in the presence of O_2 should contain radical species in the mechanisms of the reaction. The rate constants for the reactions of $H_2PO_4\cdot$ /$HPO_4^{-\cdot}$ with acrylonitrile and acrylamide are 5.9×10^7 and 2.2×10^8 $dm^3\,mol^{-1}\,s^{-1}$ at pH≈4, respectively.[13]

In the case of the PDP decomposition reaction in the absence of O_2, both the radical scavengers and the complex-forming substance EDTA completely retarded the reaction, and, therefore, the mechanism is assumed to be as follows:

$$PH_2O_2^- + Cu^{2+} \rightleftarrows PH_2O_2\cdot + Cu^+ \tag{9}$$

$$2Cu^+ \rightleftarrows Cu + Cu^{2+} \tag{7}$$

$$H_4P_2O_8 + Cu^+ \rightleftarrows H_2PO_4^- + H_2PO_4\cdot + Cu^{2+} \tag{15}$$

$$PH_2O_2^- + H_2PO_4\cdot \rightleftarrows PH_2O_2\cdot + H_2PO_4^- \tag{16}$$

$$2PH_2O_2\cdot \rightleftarrows PH_2O_2^- + PH_2O_2^+ \tag{10}$$

$$PH_2O_2^+ + H_2O \rightarrow H_2PO_3^- + 2H^+ \tag{17}$$

Reaction 17 might be much slower than reaction 12 in the presence of O_2. All of the reactions, except for Eq. 15, are fast, and the rate-determining step for the PDP decomposition is thought to be reaction 15. The rate law can be written as follows, assuming that the concentrations of Cu^+ and $PH_2O_2\cdot$ are constant during the reactions:

$$\begin{aligned} -d[H_4P_2O_8]/dt &= k_{15}[H_4P_2O_8][Cu^+] \\ &= k_{15}[H_4P_2O_8][Cu^{2+}][PH_2O_2^-]/[PH_2O_2\cdot] \\ &= k_{obsd}[H_4P_2O_8] \\ (\text{or } d[PDP]/dt &= k_{obsd}[PDP]) \qquad (18) \text{ or } (1) \end{aligned}$$

The predominant species of PDP at the pH range of 2—4 is $H_2P_2O_8^{2-}$.[7] The slope of −1.8 in the plots of $\log k_{obsd}$ vs. $I^{1/2}/(1+I^{1/2})$ may indicate that the ionic-strength dependence is mainly due to reaction 15. The rate of reaction 15 can compete with that of reaction 8 in the presence of O_2. If the rate constant for Eq. 15 is not greatly different from that for Eq. 8, the PDP formation rate should decrease with increasing the concentrations of PDP in a constant concentration of O_2. Nevertheless, the PDP formation rate increases with forming PDP (refer to the PDP formation curves in Fig. 2). Therefore, the forward rate-constant for Eq. 8 is thought to be much larger than that for Eq. 15.

The large pH dependence on both cases (Figs. 4 and 8) is thought to be caused by the change in the redox capabilities of anions involved in each reaction mechanism. The pH dependence in both cases of the formation and decomposition of PDP was similar. This fact indicates that both cases in the presence and absence of O_2 are greatly controlled by the common Cu^+ formation reaction 9, the disproportionation of Cu^+ (Eq. 7), and/or reaction 10. However, the pH dependence seems to be very complex, because not only Eq. 9, but also reactions 8 and 11—13 in the presence of O_2, and reactions 15—17 in the absence of O_2, are more or less influenced by the pH in solutions. The oxidation capabilities in the phosphate radicals decrease in the order $H_2PO_4\cdot > HPO_4^{-\cdot} \geq PO_4^{2-\cdot}$, and the rate constant for Eq. 16 involving $H_2PO_4\cdot$ is 3.9×10^8 $dm^3\,mol^{-1}\,s^{-1}$ at pH 4.[14]

The dissociation of $H_4P_2O_8$ to $H_2PO_4\cdot$ is very slow, and Cu^+ catalyzes the dissociation reaction (Eq. 15) as well as peroxodisulfate ions (Eq. 19).[1] Although the $SO_4^{-\cdot}$ radical anion oxidizes Cu(I) in reaction 20, the $PH_2O_2\cdot$ radical does not oxidize Cu^+ and the disproportionation of $PH_2O_2\cdot$ (Eq. 10) predominantly contributes to the decomposition of peroxodiphosphate ions.

$$S_2O_8^{2-} + Cu^+ \rightarrow SO_4^{2-} + SO_4^{-\cdot} + Cu^{2+} \tag{19}$$

$$SO_4^{-\cdot} + Cu^+ \rightarrow SO_4^{2-} + Cu^{2+} \tag{20}$$

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11) It is noted that 2(9)+(7)+(10) is $PH_2O_2^- + Cu^{2+} \rightleftarrows PH_2O_2^+ + Cu$.

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