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Mechanisms of Oxidation Reactions of Iodide and Hexacyanoferrate(II) Ions, Induced by the Reaction between Phosphinate Ion and Molecular Oxygen in an Aqueous Solution

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When an I^- solution was mixed with a $PH_2O_2^-$ solution which had been kept standing for given times of 5–40 min in the presence of molecular oxygen (O_2), the I_2 (or I_3^-) was rapidly formed and then gradually reduced. The maximum amounts of the formed I_2 (or I_3^-) increased with increasing standing times of the $PH_2O_2^-$ solution, and with increasing concentrations of $PH_2O_2^-$ and H^+ in the solution. When the $[Fe(CN)_6]^{4-}$ solution was mixed with the $PH_2O_2^-$ solution, $[Fe(CN)_6]^{3-}$ was formed quantitatively, but an induction period appeared under the conditions of low concentrations of $PH_2O_2^-$ and high pH's. The induction period was shortened at higher concentrations of $PH_2O_2^-$, O_2, and/or H^+. Both oxidation reactions of I^- and $[Fe(CN)_6]^{4-}$ were extremely accelerated by the addition of small amounts of the peroxodiphosphate salt ($K_4P_2O_8$) into the solution, both were inhibited by the presence of radical scavengers, and never occurred in the N_2-saturated solution. The mechanisms for such O_2-induced/radical reactions, which are regarded as a new type of Fenton-like reagent, are discussed.

Phosphinic acid ($pK_{a1} = 1.1$) is in tautomeric equilibrium (chart 1) with phosphonous acid, but the equilibrium lies on the left.[1]

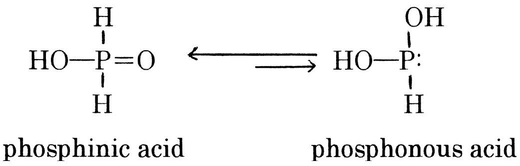
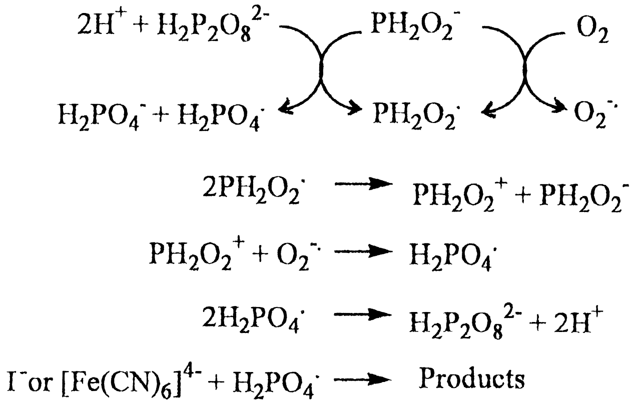


Chart 1.

For the sake of brevity, we use the name of phosphinate ion or phosphinate to represent all forms of phosphinate ion and phosphinic acid and their isomers, where the predominant species in the present study of the pH range 2–4 is the phosphinate ion $PH_2O_2^-$.

Phosphinic acid is known as a reductant with $E° = -0.5$ V vs NHE for $H_3PO_3 + 2H^+ + 2e^- \rightleftarrows HPH_2O_2 + H_2O$,[2] and its' reduction reactions by several oxidants (e.g., I_2, I_3^-, Br_2, Br_3^-, IO_3^-, Cl_2, $CuCl_2$, and $HgCl_2$) have been reported.[3] We have also studied the reactions of phosphinic acid with O_2 catalyzed by Cu(II)[4] and photo-catalyzed[5] by $[Ru(bpy)_3]^{2+}$, and with $HCrO_4^-$ induced[6] by O_2. Phosphinic acid and/or phosphinate ion has never been known as an oxidant. In this study we found that an aqueous solution of phosphinic acid and/or phosphinate in the presence of oxygen was so oxidative as to oxidize I^- and $[Fe(CN)_6]^{4-}$ to I_2 (or I_3^-) and $[Fe(CN)_6]^{3-}$, respectively. So, the present results are very exceptional and are thought to be a new type of Fenton-like reagent, because the oxidizing mixture is composed of the oxidative radical species which are produced by the reaction between an oxidant O_2 and a reductant $PH_2O_2^-$. Namely, O_2 and $PH_2O_2^-$ in this work are comparable to hydorogen peroxide and the iron(II) ion in a Fenton-reagent,[7] respectively. Although Fenton-like reagents, e.g., Ti^{3+}/H_2O_2, $Ti^{3+}/S_2O_8^{2-}$, Ti^{3+}/NH_2OH. V^{4+}/H_2O_2, Ce^{3+}/H_2O_2, and so forth, have been known,[8] the $PH_2O_2^-/O_2$ mentioned in this article is not yet known. We believe that the present work represents the first discovery of the phosphinate ion as an electron-transfer mediator in the radical-chain reaction in the presence of the molecular oxygen, where the mechanisms proposed in this article (i.e., Eqs. 1 to 8) are comparable to the Haber–Weiss mechanism[9] for the Fe^{2+}/H_2O_2 mixture. Overall reactions examined in this study are shown in Scheme 1.



Scheme 1.

Experimental

Chemicals. Potassium peroxodiphosphate ($K_4P_2O_8$) was the

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same as used in our previous studies,[4,5,6] and was a gift from John O. Edwards of Brown University (U.S.A.). Sodium phosphinate monohydrate ($NaPH_2O_2 \cdot H_2O$), potassium iodide (KI), potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6] \cdot 3H_2O$), and other chemicals used were of guaranteed grade from Wako Pure Chemical Industries. Deionized water was further distilled in a glass still.

Procedures. (1) Reaction of $PH_2O_2^-$ with I^- : A given amount of $NaPH_2O_2 \cdot H_2O$ was dissolved into a solution (90 ml, 25 °C, and given pH) which had been saturated with a given gas by bubbling air, oxygen, or nitrogen and kept standing for given times of 5–40 min. The solution was, then mixed with the KI solution (10 mL, 25 °C and 1.0 M, where M = mol dm^{-3} hereafter) which was also saturated with the given gas. Soon after the mixing, aliquot solutions were taken out into a beaker and a photo-cell separately in order to measure pH and the concentrations of iodine formed: the iodine (I_2) produced during the reactions was rapidly converted to the triiodide ion (I_3^-) in the presence of the iodide ion:

$$I_2 + I^- \rightleftarrows I_3^- \qquad \text{(A)}$$

where $k_f = 5.6 \times 10^9\ M^{-1}\ s^{-1}$ and k_f/k_b (or K_{eq}) = 710 M^{-1}.[10,11]

The concentrations of I_3^- were actually equivalent to those of I_2 since it is quantitatively converted to I_3^- in the presence of excessive I^-. The triiodide ion has large molar absorption coefficients of 3.82×10^4 and $2.5 \times 10^4\ M^{-1}\ cm^{-1}$ at 288 and 350 nm, respectively.[12] Thus, the absorbance of I_3^- could be used as a monitor for the kinetic measurements. All kinetic runs were carried out under conditions where the iodide ion was in at least 10^3-fold excess over the I_2 formed by the reaction. The temperature of the reaction solution during all the procedures was controlled to (25 ± 0.1) °C. The pH of the reaction solution was adjusted by adding sulfuric acid, acetic acid, and/or sodium acetate.

(2) Reaction with $[Fe(CN)_6]^{4-}$: A given amount of $NaPH_2O_2 \cdot H_2O$ was dissolved into a $K_4[Fe(CN)_6]$ solution (100 mL, 25 °C, and the given pH of 2.90–4.05 was adjusted by adding sulfuric acid, acetic acid and/or sodium acetate) which had been saturated with a given gas by bubbling air, oxygen, or nitrogen. The gas was then continuously bubbled through the reacting solution after starting the reaction. The temperature of the reaction solutions was controlled to (25 ± 0.1) °C. Aliquot solutions were taken out at appropriate time intervals in order to measure concentrations of the formed $[Fe(CN)_6]^{3-}$ and pH. The concentrations of $[Fe(CN)_6]^{3-}$ were determined by using a Shimadzu UV-150-2 spectrophotometer at 420 nm, where the molar absorption coefficient is $1.0 \times 10^3\ M^{-1}\ cm^{-1}$. The absorption at 420 nm for $[Fe(CN)_6]^{4-}$ was negligible.

Results

(1) Oxidation Reaction of I^-. When the iodide solution was mixed with the phosphinate solution which had been kept standing for given times of 5–40 min under conditions of the air- or O_2- saturation, the triiodide ion (I_3^-) was formed rapidly for $t \leqq 1.5$ min and then slowly disappeared rectilinearly with time (see Fig. 1, (1)). Since the similar plots of $[I_3^-]$ vs t as those in Fig. 1 were obtained under the other conditions which are different from Fig. 1, the concentrations of the initially formed triiodide ion $[I_3^-]_{t=0}$ were obtained by extrapolation to $t = 0$ in the plots of $[I_3^-]$ vs t under the varied conditions (see Table 1 and Fig. 2).

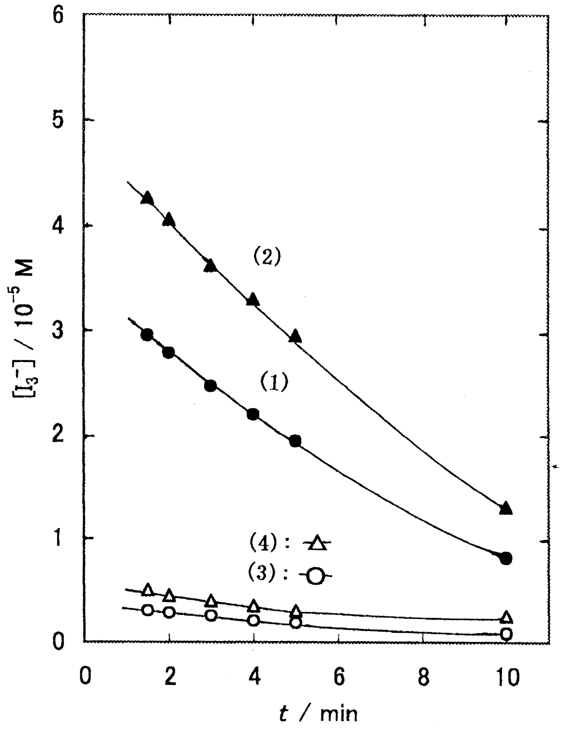

Fig. 1. Plots of $[I_3^-]$ vs t.
Conditions: 0.40 M $NaPH_2O_2$, 0.10 M KI, 25 °C, and pH 2.67.
(1) KI was mixed with the $NaPH_2O_2$ solution which had been kept standing for 40 min.
(2) KI was mixed with the $NaPH_2O_2$ solution without taking the standing time, in which 5.0×10^{-4} M $K_4P_2O_8$ was added to the $NaPH_2O_2$ solution.
(3) 1.0 (v/v)% acrylonitrile was added to the $NaPH_2O_2$ solution under the same conditions as those in (1).
(4) 1.0(v/v)% acrylonitrile was added to the $NaPH_2O_2$ solution under the same conditions as those in (2).

Dependence on Standing Time of Phosphinate Solution: The concentrations of the initially formed triiodide ion were plotted against the standing time of the $PH_2O_2^-$ solution before mixing with I^- (see Fig. 2). As can be seen in Fig. 2, concentrations of the initially formed triiodide ion increased significantly with increasing the standing time.

Effect of Peroxodiphosphate Ion: When the peroxodiphosphate salt $K_4P_2O_8$ (hereafter written as PDP to represent all forms of $H_nP_2O_8^{(4-n)-}$ (n = 0−4), where the $H_2P_2O_8^{2-}$ is a predominant species under the conditions of pH 2.0 to 4.0[13]) was initially added into the freshly prepared phosphinate solution and was mixed with the iodide solution without any standing time, the triiodide formation could be observed in the similar way, as the plot (1) in Fig. 1 showed (compare Fig. 1, (2) with Fig. 1, (1)).

Effect of Radical Scavengers: When 1.0 (v/v)% acrylonitrile was initially added into the phosphinate solution and then mixed with the iodide solution, $[I_3^-]_{t=0}$ was very small (see Fig. 1, (3)). The same effect of the acrylonitrile addition was also found in the presence of PDP (see Fig. 1, (4)).

Effect of pH: As can be seen in Table 1, $[I_3^-]_{t=0}$ decreased with increasing pH of the reacting solution under vari-

Table 1. Various Effects on Triiodide Formation

pH	$[I_3^-]_{t=0}$ / 10^{-5} M	
	Without PDP$^{a)}$	With addition of PDP$^{b),c)}$
2.67	3.5 5.5$^{d)}$ 0.00$^{e)}$	4.9$^{b)}$ 0 .00$^{b),e)}$
2.92	2.5$^{d)}$	
3.04	1.8	2.0$^{b)}$
3.16	1.2	
3.28	1.3$^{d)}$	
3.35		0.81$^{c)}$
3.41	1.1	
3.45	0.72	0.80$^{b)}$
4.14		0.53$^{b)}$ 0.52$^{c)}$
5.02	0.20	0.40$^{b)}$

Common conditions: 0.40 M $NaPH_2O_2$, 0.10 M KI, 25 °C, and air-saturation.

a) KI was mixed with $NaPH_2O_2$ which had been kept standing for 40 min.

b) KI with 5.0×10^{-4} M PDP was mixed with the $NaPH_2O_2$ solution without taking the standing time.

c) KI with 5.0×10^{-5} M PDP was mixed with the $NaPH_2O_2$ solution without taking the standing time.

d) Solution was saturated with O_2; the other conditions are the same as those of a).

e) Solution was saturated with N_2; the other conditions are the same as those of a) or b).

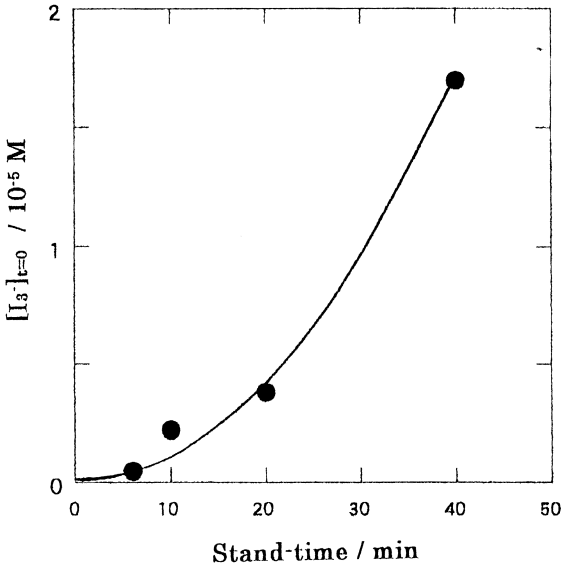

Fig. 2. Dependence of the standing time (stand-time) for the phosphinate solution on the formation of I_3^-.
$NaPH_2O_2$ solutions of pH 3.04 were kept standing for given times, and then, mixed with the KI solution. The other conditions are the same as those in Fig. 1, (1).

ous conditions.

(2) Oxidation Reaction of $[Fe(CN)_6]^{4-}$. A given amount of $NaPH_2O_2{\cdot}H_2O$ was dissolved into a $K_4[Fe(CN)_6]$ solution which had been saturated with a given gas by bubbling air, oxygen, or nitrogen under the given conditions. The formation of the hexacyanoferrate(III) ion was not found in the nitrogen saturated solution, but was found quantitatively in the air or oxygen saturated solutions. All the initial $[Fe(CN)_6]^{4-}$ was finally oxidized to $[Fe(CN)_6]^{3-}$ and there was an induction period which was much shorter at the O_2-saturated case than the air-saturated one (see Fig. 3). Such an induction period was only found under conditions of the relatively low concentrations of the phosphinate ion less than 0.10 M, and/or the pH's larger than 3.27 (see Fig. 4 and Fig. 7).

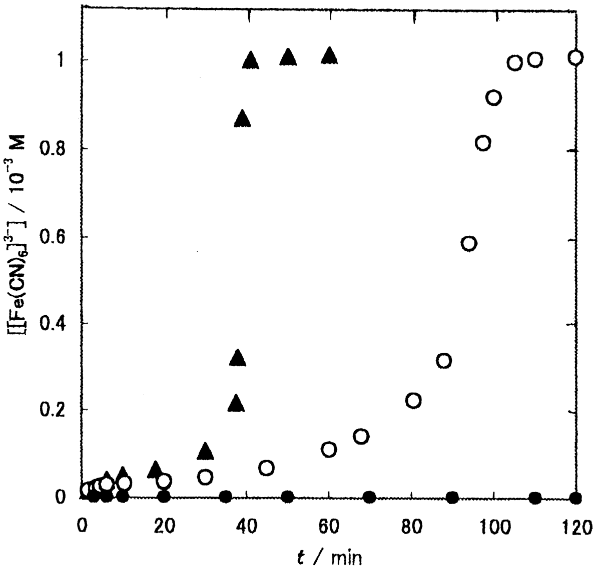

Fig. 3. Effect of the oxygen concentration.
Conditions: 1.0×10^{-3} M $K_4[Fe(CN)_6]$, 0.090 M $NaPH_2O_2$, pH 3.00, 25 °C, N_2-sat. (●), air-sat. (○), and O_2-sat. (▲).

Effect of PDP: As can be seen in Fig. 5, the induction period was shortened by adding small amounts of PDP. The PDP effect was remarkably great even when the added PDP concentrations were so negligible as to be much lower than those of the initially added $[Fe(CN)_6]^{4-}$ or those of the formed $[Fe(CN)_6]^{3-}$. This indicates that PDP is acting as a catalyst to the $[Fe(CN)_6]^{4-}$ oxidation reaction.

Effect of Radical Scavengers: When 1.0 (w/w)% acrylamide was added into the reaction solutions of either plots of open square in Fig. 4B, or plots of open triangle in Fig. 5, the formation of $[Fe(CN)_6]^{3-}$ for $t \leqq 60$ min was not appreciable, indicating the complete retardation effect on the reaction. Further, when 1.0 (w/w)% acrylamide was added into the solution corresponding to closed circle points in Fig. 5, or when the experiment corresponding to closed circle points in Fig. 5 was carried out under the conditions of N_2-saturation (see Fig. 5, inset), the plots of $[Fe(CN)_6]^{3-}$ vs t were almost the same as those in Fig. 6, (1), indicating the significant inhibiting-effect on the radical/chain reaction given by Eqs. 1 to 8 (*v.i.*).

Effect of Phosphinate Concentration: As can be seen in Fig. 7 as well as in Fig. 4B, the induction periods were extremely dependent on the phosphinate concentrations, and were shorter at the larger concentrations of the phosphinate ion. However, the oxidation rates of $[Fe(CN)_6]^{4-}$ after the induction periods did not change despite varied concentrations of $PH_2O_2^-$, but were almost constant at the concentration range of $[PH_2O_2^-] \leqq 0.10$ M. Moreover, the rates became obviously slower at 0.20 and 0.40 M $PH_2O_2^-$. The same phe-

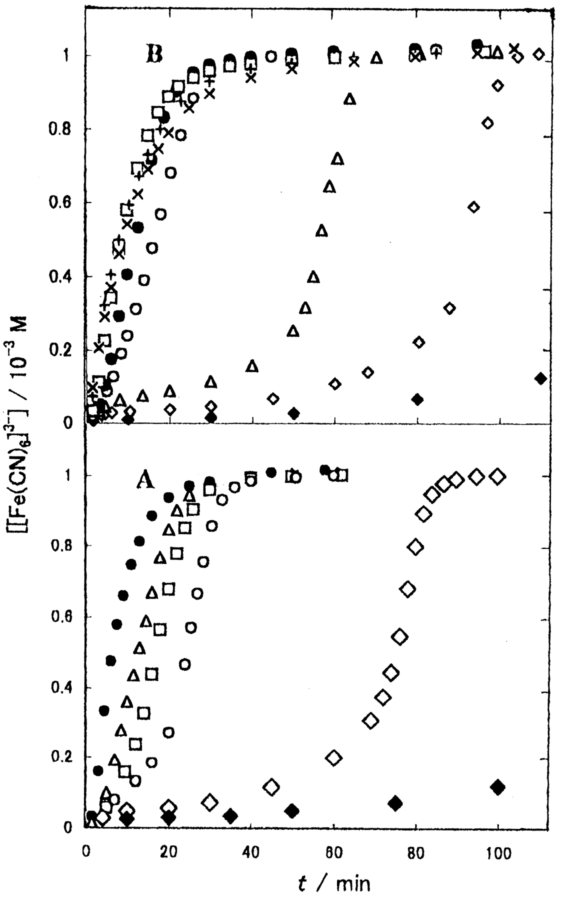

Fig. 4. Plots of $[[Fe(CN)_6]^{3-}]$ vs *t*.
Conditions: 1.0×10^{-3} M $K_4[Fe(CN)_6]$, air-sat., 25 °C, in the case of A; pH = 2.90 (●), 3.13 (△), 3.27 (□), 3.34 (○), 3.54 (◇), 4.05 (◆) in 0.10 M $NaPH_2O_2$; where the induction period at pH 4.05 was so long as to be 165 min, and in the case of B; $[NaPH_2O_2]$ / M = 0.20 (×), 0.15 (+), 0.12 (□), 0.11 (●), 0.10 (○), 0.095 (△), 0.090 (◇), 0.070 (◆) at pH 3.00 ± 0.05, where the induction period in 0.070 M $NaPH_2O_2$ was so long as to be 210 min.

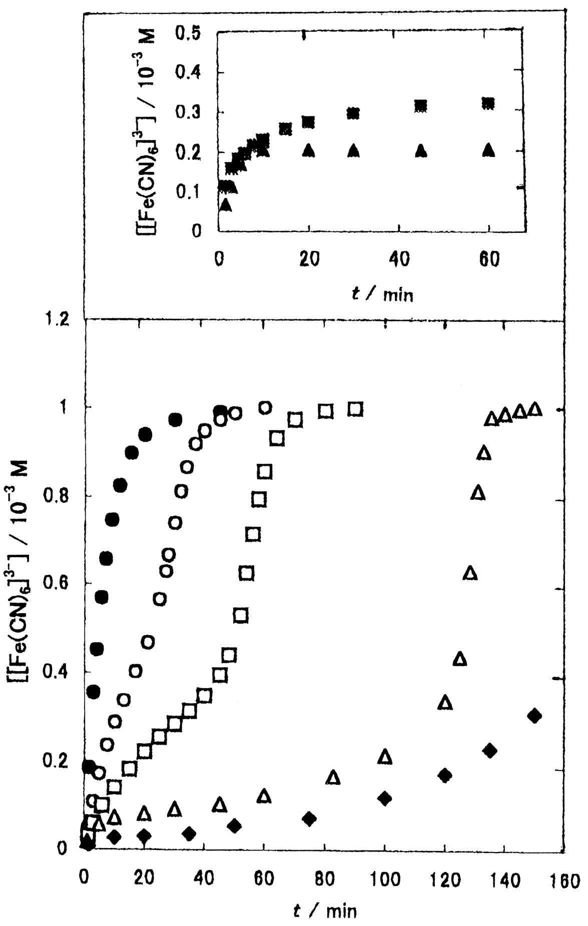

Fig. 5. Effect of PDP.
Conditions: 1.0×10^{-3} M $K_4[Fe(CN)_6]$, 0.10 M $NaPH_2O_2$, air-sat., pH 4.05, 25 °C, and $[PDP]_{added}$ / M = 0 (◆), 1.0×10^{-6} (△), 5.0×10^{-6} (□), 1.0×10^{-5} (○), 1.0×10^{-4} (●). The plots ▲ and ■ in inset indicate that the experiment corresponding to plots ● was carried out under the conditions of N_2-saturation, and that 1.0 (w/w)% acrylamide was added into the solution corresponding to plots ●, respectively.

nomena are also found in Fig. 4B, though the effect was not so obvious as in Fig. 7.

Discussion

Chain Mechanism Involving Radicals: The results in the case of the I^- oxidation reaction (i.e., Figs. 1 and 2, and Table 1) indicate that not only the oxidative radicals but also PDP was formed simultaneously during the standing time of the phosphinate solution in the presence of O_2, and that even a small amount of PDP could make the formation of iodine and/or triiodide without taking any standing time. Therefore, PDP accelerates catalytically the formation of the radical species which can oxidize the iodide ion to iodine and/or triiodide. If we consider our previous studies (refer to Fig. 1, inset in Ref. 5), we see that such a PDP formation in 10^{-5}–10^{-4} M range during the standing times in Fig. 2 would indeed be possible.

The preliminary experiments showed that the oxidation of the iodide ion to iodine and/or triiodide by PDP itself was so slow as to be negligible, comparing to the rapid formation of I_3^- in Fig. 1.[16] Accordingly, it is thought that the oxidative species for the iodide ion was not PDP itself, but was the formed radicals such as $H_2PO_4^\bullet$.

In the case of the $[Fe(CN)_6]^{4-}$ oxidation, the induction periods became shorter with increasing concentrations of oxygen or phosphinate ion or hydrogen ion, and by the addition of the small amounts of PDP (see Figs. 3, 4, 5, and 7); the reactions were extremely retarded by the radical scavengers (see Fig. 5, inset). These as well as the cases in the I^- oxidation indicate that the formation of the radical species is absolutely necessary in order to oxidize either $[Fe(CN)_6]^{4-}$ or I^-. Consequently, the following reaction mechanisms are assumed to account for the radical formations together with PDP (see also Scheme 1). For the sake of brevity, the superoxide ion $O_2^{-\bullet}$ represents all species of $O_2^{-\bullet}$ and $HO_2^\bullet$ in the equilibrium of $HO_2^\bullet \rightleftarrows O_2^{-\bullet} + H^+$ with $pK_a = 4.8$,[14] and $H_2P_2O_8^{2-}$ is representative of PDP.

$$PH_2O_2^- + O_2 \rightleftarrows PH_2O_2^\bullet + O_2^{-\bullet} \quad (1)$$

$$2PH_2O_2^\bullet \rightleftarrows PH_2O_2^- + PH_2O_2^+ \quad (2)$$

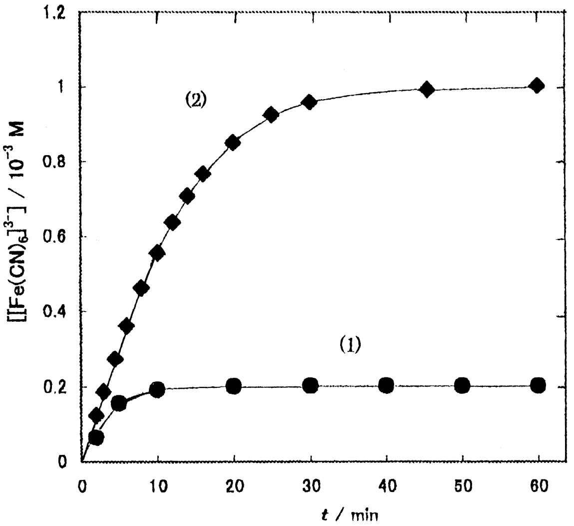

Fig. 6. Oxidation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ by PDP. Solution of 1.0×10^{-3} M $K_4[Fe(CN)_6]$ was mixed with PDP of 1.0×10^{-4} M and 1.0×10^{-3} M in curves (1) and (2) under conditions of pH 4.05 and 25 °C, respectively.

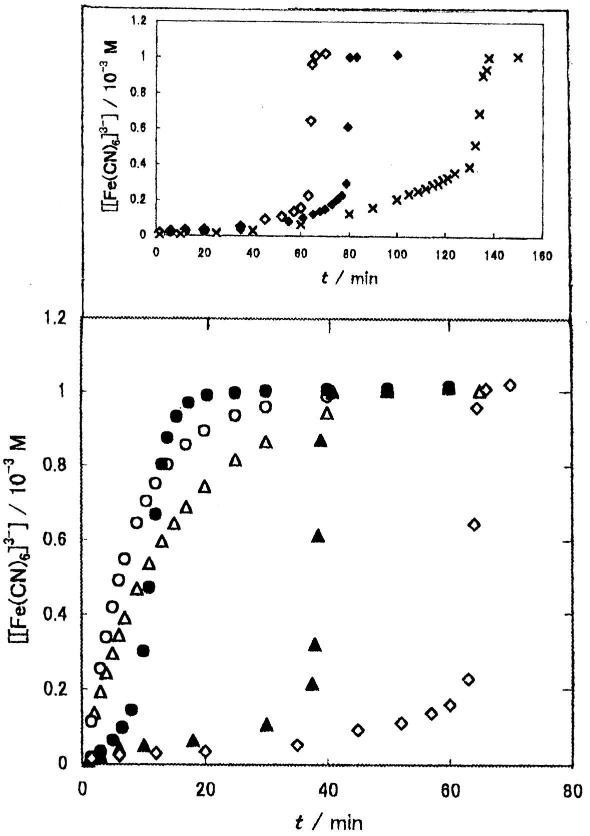

Fig. 7. Effect of phosphinate concentrations.
Conditions are the same as those of the plots ▲ in Fig. 3, but varied concentrations of $NaPH_2O_2$, that is, $[NaPH_2O_2]$ / M = 0.40 (△), 0.20 (○), 0.10 (●), 0.090 (▲), and 0.080 (◇ and ◇ in inset), 0.070 (◆ in inset), and 0.050 (× in inset).

$$PH_2O_2^{\bullet} + O_2 \rightleftarrows PH_2O_2^{+} + O_2^{-\bullet} \qquad (3)$$

$$PH_2O_2^{+} + O_2^{-\bullet} \rightarrow H_2PO_4^{\bullet} \qquad (4)$$

$$2H_2PO_4^{\bullet} \rightarrow H_2P_2O_8^{2-} + 2H^{+} \qquad (5)$$

$$PH_2O_2^{-} + H_2P_2O_8^{2-} + 2H^{+} \rightarrow PH_2O_2^{\bullet} + H_2PO_4^{-} + H_2PO_4^{\bullet} \qquad (6)$$

$$PH_2O_2^{-} + H_2PO_4^{\bullet} \rightarrow PH_2O_2^{\bullet} + H_2PO_4^{-} \qquad (7)$$

$$PH_2O_2^{\bullet} + H_2PO_4^{\bullet} \rightarrow PH_2O_2^{+} + H_2PO_4^{-} \qquad (8)$$

Hereon there are the relations of (3) = (1) + (2) and (7) = (5) + (6).

When $NaPH_2O_2$ was dissolved into water in the presence of O_2, the radicals $PH_2O_2^{\bullet}$ and $O_2^{-\bullet}$ were initially produced by the forward reaction in Eq. 1; then $H_2P_2O_8^{2-}$ (i.e., PDP) was formed through reactions (1) to (5), which occurred during the standing times of the range 5–40 min in Fig. 1, (1) and Fig. 2, and during the induction periods in Figs. 3, 4, and 7. After the PDP formation, the reaction (6) started to occur together with reactions (7) and (8), which were combined with a chain reaction to comprise Eqs. 1 to 8. Thus, we can get an overall reaction of $PH_2O_2^{-} + O_2 \rightarrow H_2PO_4^{-}$ by (3) + (4) + (7) or (1) + (3) + 2(4) + (7) + (8), indicating the occurrence of equivalent formation and decomposition of PDP as an overall reaction. Accordingly, the rate of reaction (6) increases gradually and becomes equal to that of reaction (5) (i.e., this will correspond to the termination of the induction periods in Figs. 3, 4, 5. and 7), to satisfy the steady-state conditions. It is here noted that such a steady-state concentration of PDP could be actually observed in our previous study (see plots of open square in Fig. 6A of Ref. 5), and that the amount of PDP increased gradually and reached a constant value with increasing the reaction time (see Fig. 2, inset in Ref. 5)

Oxidation of Iodide Ion: The rapid formation of I_3^{-} for $t \leqq 1.5$ min in Fig. 1 is thought to be due to the reaction by the oxidative radical $H_2PO_4^{\bullet}$ which formed by reactions (1) to (8) during the standing times of the phosphinate solution in the presence of oxygen:

$$I^{-} + H_2PO_4^{\bullet} \rightarrow I^{\bullet} + H_2PO_4^{-} \qquad (9)$$

$$I^{\bullet} + I^{-} \rightarrow I_2^{-\bullet} \qquad (10)$$

$$2I_2^{-\bullet} \rightarrow I_3^{-} + I^{-} \qquad (11)$$

The reduction rate of I_3^{-} at $t > 1.5$ min in Fig. 1 decreased with increasing pH, and is due to the reducing reaction of I_3^{-} by $PH_2O_2^{-}$. Such a reaction between I_3^{-} and $PH_2O_2^{-}$ has been known already.[3]

Oxidation of Hexacyanoferrate(II) Ion: As can be seen from Fig. 3, not only the induction period in the case of O_2-saturated solution was much shorter than that in the air-saturated one, but also the formation reaction of $[Fe(CN)_6]^{3-}$ in the O_2-saturated case was faster than that in the air-saturated case. Especially, the rate near the final stages in the plots of $[Fe(CN)_6]^{3-}$ vs t was obviously higher in the O_2-saturated case (compare Fig. 7 in the O_2-saturated case with Fig. 4B in the air-saturated case). These results can be accounted for by the increase of the concentrations of the radicals which is due to the much greater progress of reactions (1), (2), (3), and (4) in the O_2-saturated conditions. The formation reactions of $[Fe(CN)_6]^{3-}$ became faster when it reached $(3 \pm 1) \times 10^{-4}$ M $[Fe(CN)_6]^{3-}$ as shown in any of Figs. 3, 4, 5, and 7, and then stayed almost constant in all cases. Such facts indicate that the induction periods could terminate at the time when the radical concentrations reached a certain amount, and when the chain reaction could operate to maintain the steady-state conditions.

Since the oxidation reaction of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ by PDP itself was rather fast (see Fig. 6), it is thought that the $[Fe(CN)_6]^{3-}$ formation proceeded from the following reactions together with reactions (1) to (8):

$$[Fe(CN)_6]^{4-} + H_2P_2O_8^{2-} + 2H^+ \rightarrow [Fe(CN)_6]^{3-} + H_2PO_4^{\bullet} + H_2PO_4^- \quad (12)$$

$$[Fe(CN)_6]^{4-} + H_2PO_4^{\bullet} \rightarrow [Fe(CN)_6]^{3-} + H_2PO_4^- \quad (13)$$

Reactions (12) and (13) compete with reactions (6) and (7), respectively. The observed rate-constant k_6 in the rate law of $-d[PDP]/dt = k_6[PH_2O_2^-][PDP]$ was estimated to be 4.2×10^{-4}, 1.3×10^{-4}, 8.0×10^{-5} and 5.0×10^{-5} $M^{-1}\ s^{-1}$ at pH 1.97,[6] 2.12,[5] 2.52,[5] and 3.17,[5] respectively, and k_{12} in the rate law of $-d[[Fe(CN)_6]^{4-}]/dt = k_{12}[[Fe(CN)_6]^{4-}][PDP]$ was obtained to be 5.0×10^{-1} $M^{-1}\ s^{-1}$ at pH 4.0 from plots (2) in Fig. 6, assuming that the rate of reaction (13) is much faster than that of reaction (12). If one compares these rate constants with the initial concentrations of $[Fe(CN)_6]^{4-}$ and $PH_2O_2^-$, the rate of reaction (12) is much faster than that of reaction (6). Both the radical reactions (7) and (13) would be so fast as to be almost equivalent values in the rate constants, and the rate of reaction (7) would be much faster than that of reaction (13) under the conditions of $[PH_2O_2^-] \gg [[Fe(CN)_6]^{4-}]$. Therefore, the addition of PDP could propagate the chain reaction in Eqs. 1 to 8. It is to be noted that the induction periods shown in Fig. 5 were finished at around 4×10^{-4} M $[Fe(CN)_6]^{3-}$, regardless of the added concentrations of PDP. This would indicate that the radical of $H_2PO_4^{\bullet}$ reached the concentration of the steady-state conditions at the stages of the $[Fe(CN)_6]^{3-}$ formation. The addition of PDP could produce rapidly the phosphate radicals by reactions (6) and (12) which propagate the chain reaction in Eqs. 1 to 8, and thus could shorten the induction period. This was actually confirmed by comparing Fig. 5, inset to Fig. 6, (1). Namely, the radical/chain reactions (1) to (8) could not occur in the absence of O_2 and were greatly retarded by the radical scavengers, and the oxidation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ under such conditions occurred predominantly by reactions (12) and (13) (see Fig. 5, inset, and compare it with Fig. 6, (1)).

Reactions after Induction Period: Next, we consider the rates after the induction periods. They did not change with varied concentrations of $PH_2O_2^-$, but were almost constant at the concentration range of $[PH_2O_2^-] \leqq 0.10$ M as shown in both Fig. 4B and Fig. 7. This was due to a counterbalancing effect of the competing and compensating reactions between the increase or decrease in $H_2PO_4^{\bullet}$ and $PH_2O_2^{\bullet}$ by reaction (6) and the decrease or increase of $PH_2O_2^+$ by the equilibrium reactions (2) and (3), together with the competition among reactions (12), (13), (14), and (15). If one considers reactions (1) to (8), the $H_2PO_4^{\bullet}$ concentrations should increase with increasing concentrations of $PH_2O_2^-$, and lead to acceleration of the oxidation reaction of $[Fe(CN)_6]^{4-}$. On the contrary, if reactions (14) and (15) occurred together with reactions (12) and (13), the oxidation rate of $[Fe(CN)_6]^{4-}$ becomes slowed down with increasing concentrations of $PH_2O_2^-$, because the concentration of $PH_2O_2^+$ decreases and that of $PH_2O_2^{\bullet}$ increases in accordance with the equilibrium reaction (2), and the backward reaction in Eq. 14 occurs favorably under such conditions.

$$[Fe(CN)_6]^{4-} + PH_2O_2^+ \rightleftarrows [Fe(CN)_6]^{3-} + PH_2O_2^{\bullet} \quad (14)$$

$$[Fe(CN)_6]^{4-} + PH_2O_2^{\bullet} \rightarrow [Fe(CN)_6]^{3-} + PH_2O_2^- \quad (15)$$

Since the $[Fe(CN)_6]^{4-}$ concentration becomes lower on approaching the final stages of reaction, the rate of reaction (12) to form $H_2PO_4^{\bullet}$ must become slower with the progress of reaction time. On the other hand, the radical formations due to reactions (1) to (8) can occur regardless of such times. Accordingly, the oxidation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ would occur by reaction (12) soon after terminating the induction period, and would occur dominantly by reactions (13), (14) and (15) near the final stages of reaction.

On the Termination Reaction: When reaction (15) was much faster than the backward reaction in Eq. 14, i.e., when the conditions of $k_{15}[[Fe(CN)_6]^{4-}] \gg k_{-14}[[Fe(CN)_6]^{3-}]$ were satisfied, the following reaction is obtained by (14) + (15) = (16).

$$2[Fe(CN)_6]^{4-} + PH_2O_2^+ \rightarrow 2[Fe(CN)_6]^{3-} + PH_2O_2^- \quad (16)$$

Reaction (16) is analogous to and competes with the two-electron-transfer reaction (17), which is known as a termination reaction in the oxidation reaction of the phosphinate ion.[3]

$$H_2O + PH_2O_2^+ \rightarrow H_2PO_3^- + 2H^+ \quad (17)$$

If the oxidation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ proceeded via reaction (16) instead of via reactions (12) and (13), we can get the overall reaction of $2PH_2O_2^- + 2O_2 + H_2P_2O_8^{2-} + 2[Fe(CN)_6]^{4-} + 2H^+ \rightarrow 4H_2PO_4^- + 2[Fe(CN)_6]^{3-}$ by 2(3) + 2(4) + (6) + 2(7) + (8) + (16). This means that the oxidation reaction of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ occurs by the phosphinate ion together with O_2 and PDP, which is again in accordance with the results obtained in Figs. 3, 4, 5, and 7.

Under the conditions of the relatively high concentrations of $PH_2O_2^+$, reaction (17) will also participate in the terminating reaction, giving an overall reaction of $3PH_2O_2^- + 2O_2 + H_2P_2O_8^{2-} + H_2O \rightarrow H_2PO_3^- + 4H_2PO_4^-$ by 2(3) + 2(4) + (6) + 2(7) + (8) + (17).

Under such cases of the high concentrations of $PH_2O_2^-$, in which the $[Fe(CN)_6]^{4-}$ oxidation was so fast that the induction periods could disappear, the concentrations of $PH_2O_2^+$ as well as the other radicals are rather high, and the termination reactions (16) and (17) can occur favorably. The reaction (16) becomes slower with the progress of reaction times, because the $[Fe(CN)_6]^{4-}$ concentration decreases in accordance with reaction times; the rate of reaction (17) is not connected to such reaction times. Consequently, reaction (17) in the terminating reaction could have participated to a larger extent, and led to the slowdown of the oxidation reaction of $[Fe(CN)_6]^{4-}$ by increasing concentrations of $PH_2O_2^-$ in the cases of $[PH_2O_2^-] >$ 0.12 M in Fig. 4B and $[PH_2O_2^-] >$ 0.10 M in Fig. 7.

Effect of pH: In the cases of the pH's larger than 4.0, the triiodide ion scarcely formed (see Table 1), and the induction periods became extremely long (see Fig. 4A). These phenomena are similar to pH dependence of the PDP formation, which was hardly appreciable at pH $\geqq$ 3.4 (see Fig. 4, closed triangle points in Ref. 5). It is to be noted that the pH dependences on the present reactions seem to be very complex, because the redox capabilities of not only the species, such as $PH_2O_2^-$, $H_2P_2O_8^{2-}$ etc, but also the radical species, such as $PH_2O_2^\bullet$, $H_2PO_4^\bullet$, $O_2^{-\bullet}$ etc., are dependent on the acidities in the reacting solution. For example, the rates corresponding to reaction (6) decreased with increasing pH,[5] the rate constants corresponding to reaction (7) were 3.9×10^8, 5.7×10^7, and 7.9×10^7 M^{-1} s^{-1} for $H_2PO_4^\bullet$, $HPO_4^{-\bullet}$, and $PO_4^{2-\bullet}$, respectively,[15] and the PDP formation due to reactions (1), (2), (3), (4), and (5) showed a maximum around pH 2.5 and hardly occurred at pH's larger than 3.4 and at pH's less than 2.0.[5]

Conclusion Remarks: In conclusion, the phosphinate ion is a very exceptional reagent, and the phosphinate solution in the presence of oxygen (i.e., the $PH_2O_2^-/O_2$ mixture) is comparable with the Fenton-reagent.[7] It is of a new type of the Fenton-like reagents[8] and can be used as an oxidant containing the oxidative radical species of the phosphinate and phosphate ions which can be constantly present in solution, being controlled by concentrations of O_2, H^+, PDP, and/or $PH_2O_2^-$.

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16 When 5.0×10^{-4} M PDP was added into 0.10 M KI solution under the same conditions as in Fig. 1, (2) (i.e., at 25 °C and pH 2.67), the formation of I_3^- was 6.7×10^{-7}, 1.1×10^{-6}, 3.6×10^{-6}, 4.7×10^{-6}, and 7.0×10^{-6} M for 2, 5, 10, 20, and 30 minutes, respectively. These values are less than tenth concentrations of the formed I_3^- in Fig. 1, (2). The formation rate of I_3^- decreased linearly with increasing pH.