A Novel Reaction of $HCrO_4^-$ with $PH_2O_2^-$, Induced by Molecular Oxygen, Forming Peroxodiphosphate Ions in an Aqueous Solution

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(Received May 19, 1997)

The chromate (VI) ion $HCrO_4^-$ at pH 2—4 was not appreciablly reduced by the phosphinate ion $PH_2O_2^-$ in the absence of molecular oxygen (O_2), but was reduced in the presence of O_2, forming peroxodiphosphate ions (denoted by PDP and meaning all forms of $P_2O_8^{4-}$, $HP_2O_8^{3-}$ etc.) in much higher concentrations than those of the added chromate(VI). Both the rates of the chromate decay and the PDP formation increased with decreasing pH. When the chromate(VI) ion disappeared completely, PDP formation stopped and its concentration remained constant. However, such PDP once formed in the presence of O_2 began to decompose after the solution was saturated with N_2 gas; its decomposition ceased again when the solution was again saturated with air. Such behaviors are discussed while presenting the reaction mechanisms.

Haight et al.[1] studied reactions of the chromate(VI) ion with the phosphinate ion in a strong acid solution of 1 mol dm^{-3} $HClO_4$, and reported that no reactions occur at pH 4—5 in aqueous media. This time, we found that the reaction between $HCrO_4^-$ and $PH_2O_2^-$ was largely dependent on not only the acidity, but also the molecular oxygen in the reaction solutions, and that the reaction could be induced by molecular oxygen in a solution of pH 2—4, forming large amounts of the peroxodiphosphate ion (PDP). Interestingly, the concentrations of the formed PDP were much higher than those of the added chromate(VI), and the chromate became a catalyst for PDP formation. The acid-dissociation constants of $HCrO_4^-$ and HPH_2O_2 are 3.2×10^{-7} [2] and 4.0×10^{-2} dm^3 mol^{-1},[3] respectively, and those of peroxodiphosphoric acid[4] are 2.0, 0.31, $(6.6\pm0.3)\times10^{-6}$, and $(2.1\pm0.1)\times10^{-8}$ dm^3 mol^{-1} for K_{a1}, K_{a2}, K_{a3}, and K_{a4}, respectively. The formation constant of $Cr_2O_7^{2-}$ is 98 dm^3 mol^{-1} for $[Cr_2O_7^{2-}]/[HCrO_4^-]^2$,[5] and the dichromate species remains negligible under the conditions of the present study. Therefore, the predominant species in the present study of the pH range 2—4 are thought to be $HCrO_4^-$, $PH_2O_2^-$, and $H_2P_2O_8^{2-}$.

Experimental

Chemicals. Potassium chromate (K_2CrO_4), sodium phosphinate ($NaPH_2O_2$), and other chemicals used were of guaranteed grade of Wako Pure Chemical Industries, Ltd. Deionized water was further distilled in a glass still.

Procedures. The reaction was started by mixing a sodium phosphinate solution with a potassium chromate(VI) solution containing sulfuric acid. Each solution containing $HCrO_4^-$ or $PH_2O_2^-$ was separately saturated with gas by bubbling O_2, air, or N_2 through the solution before mixing the solutions. The gas was then continuously bubbled through the reacting solution. The temperature of the reaction solutions was controlled to within 0.1 °C. Aliquot solutions were taken out at appropriate time intervals in order to measure the concentrations of the $HCrO_4^-$ and the formed PDP. The concentrations of $HCrO_4^-$ were determined spectrophotometrically using the maximum molar absorption coefficient of 1.6×10^3 dm^3 mol^{-1} cm^{-1} at 350 nm. The concentrations of the formed PDP were determined polarographically by using a polarographic reduction current at 0.25 V vs. SCE. The procedure for the polarographic measurements is the same as that reported in a previous study.[6]

Results and Discussion

Effect of Oxygen. Figure 1 shows plots of the concentrations of $HCrO_4^-$ against the reaction time for a solution in both the absence and presence of O_2. The results indicate that the reaction between $HCrO_4^-$ and $PH_2O_2^-$ was extremely slow, or did not occur, in the absence of O_2, but did occur remarkably in the presence of O_2. Since the reaction was very sensitive to O_2, slight decrease of $HCrO_4^-$ in a N_2-saturated solution in Fig. 1 might have been caused by a trace of O_2 in the N_2 gas used. On the other hand, as can be seen in Fig. 1, inset, no appreciable formation of PDP was found in the absence of O_2, but was found in the presence of O_2. The PDP formation increased with a sigmoid shape against the reaction times. As can be seen in Fig. 1, the induction period in the O_2-saturated solution was slightly shorter than that in the air-saturated solution, though the rates of PDP formation as well as chromate(VI) decay after the induction periods were almost the same in both cases. These facts indicate that the reaction paths involving O_2 do not control the whole rate of the catalyzed-chain reactions occurring after the induction periods, though the O_2 is absolutely necessary to initiate the whole reaction. In the case of an air-saturated solution, the concentrations of PDP formed at $t=50$ min, 25 °C, and pH 2.53 were 1.1×10^{-3}, 2.0×10^{-2}, 2.8×10^{-3}, 3.8×10^{-3}, and 4.0×10^{-3} mol dm^{-3} for the chromate(VI) concentrations of 1.0×10^{-6}, 3.0×10^{-6}, 5.0×10^{-6}, 8.0×10^{-6}, and 1.0×10^{-5} mol dm^{-3}, respectively, indicating the turnover number to be 10^2 to 10^3. Under the same conditions, the concentrations

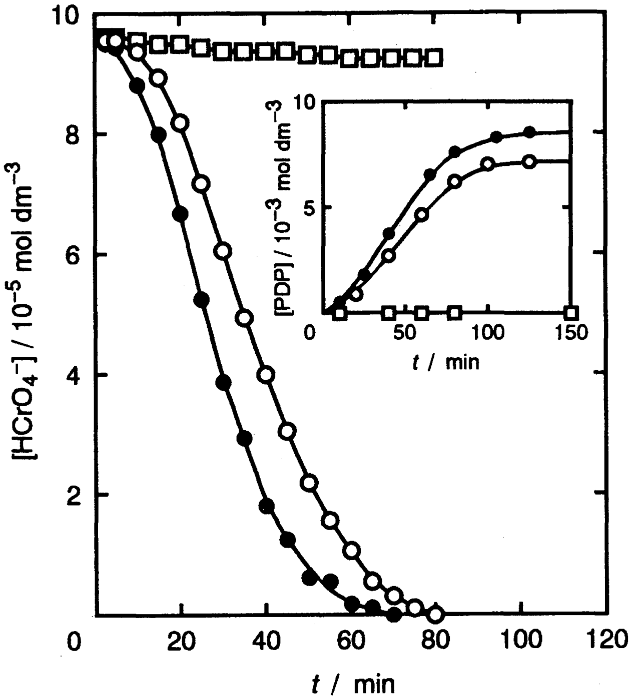

Fig. 1. Plots of $[HCrO_4^-]$ vs. t for the reaction between $PH_2O_2^-$ (0.40 $mol\,dm^{-3}$) and $HCrO_4^-$ (9.7×10^{-5} $mol\,dm^{-3}$) at 25 °C and pH 2.57 (H_2SO_4). □: N_2-sat., ○: air-sat., and ●: O_2-sat. Inset shows the formation of PDP during the reaction between $PH_2O_2^-$ and $HCrO_4^-$, where the conditions with symbols are the same as those for the plots $[HCrO_4^-]$ vs. t, but the concentration of $HCrO_4^-$ is 1.0×10^{-5} $mol\,dm^{-3}$.

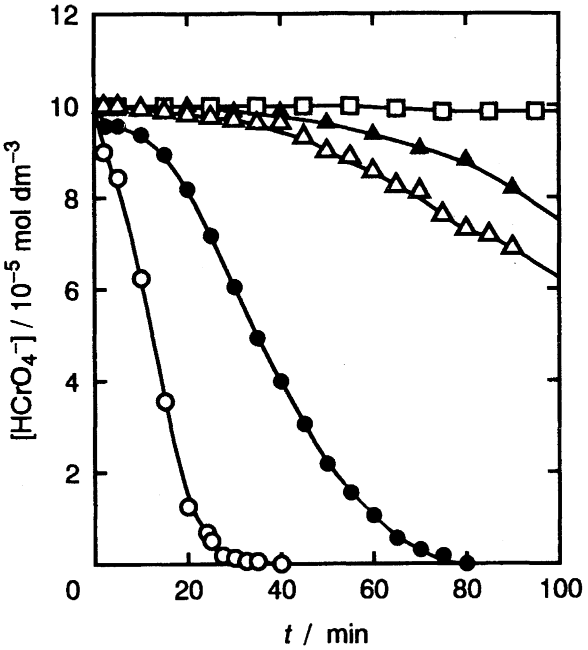

Fig. 2. Effect of pH on the decay of $HCrO_4^-$ as a function of time at 25 °C. Initial concentrations of $PH_2O_2^-$ and $HCrO_4^-$ are 0.40 and 1.0×10^{-4} $mol\,dm^{-3}$, respectively. ○: pH 1.97, ●: pH 2.57, △: pH 3.13, ▲: pH 3.48, and □: pH 3.91.

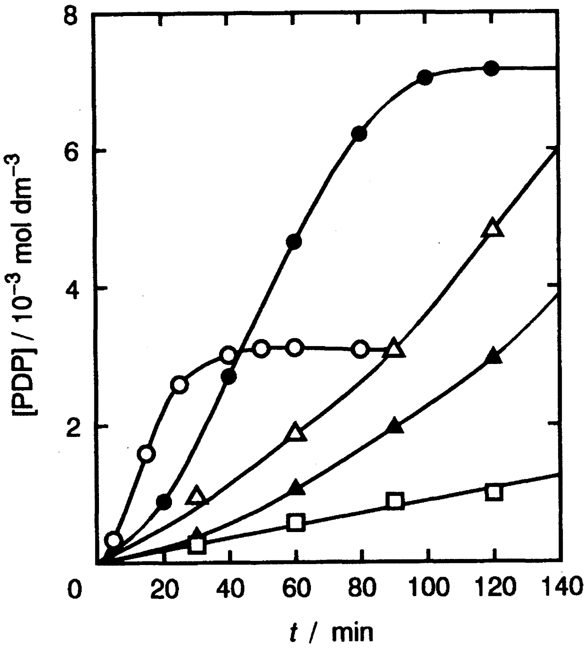

Fig. 3. Effect of pH on the PDP formation as a function of time at 25 °C. Initial concentrations of $PH_2O_2^-$ and $HCrO_4^-$ are 0.40 and 1.0×10^{-5} $mol\,dm^{-3}$, respectively. Each symbol indicates the same pH value as in Fig. 2.

of PDP formed in the presence of 1% acrylonitrile were less than half of those without a radical scavenger. These results indicate that PDP formation could have occurred by a chain reaction involving radical species, and that the chromate(VI) or its reduced-chromate species could act as a catalyst.

Effect of Acidity. Not only the reduction rate of $HCrO_4^-$ by $PH_2O_2^-$, but also the formation rate of PDP, were extremely dependent on the acidity of the reaction solution (see Figs. 2 and 3). It is noted that PDP formation stopped at the same time when the chromate ion had completely disappeared. These results indicate that a rapid cycle, such as Cr^{VI}/Cr^{V} and Cr^{V}/Cr^{IV}, should occur to make a chain reaction in solutions. The chromate ions of the larger oxidation number must be reduced by a reducing species, such as $PH_2O_2^-$ and $O_2^{-\bullet}$, and those having a smaller oxidation number should be oxidized by the oxidizing species, such as O_2, $PH_2O_2^+$, and PDP, in the reacting solution. Although the Cr^{III}/Cr^{II} cycle is most capable of being a possible cycle, our preliminary experiments showed that the chromium(III) ion is not a catalyst for the formation of PDP. This fact indicates that the phosphinate ion did not reduce Cr^{III} to Cr^{II}. Further, this is consistent with the fact that PDP formation stopped at the time when the added chromate(VI) disappeared completely.

Reaction Mechanisms. From the redox-potential diagram for the chromate species and the redox potentials for the species of oxygen and phosphinic acid in acidic aqueous solutions,[7,8]

$$Cr^{VI}\xrightarrow{0.55\text{ V}}Cr^{V}\xrightarrow{1.34\text{ V}}Cr^{IV}\xrightarrow{2.1\text{ V}}Cr^{III}\xrightarrow{-0.41\text{ V}}Cr^{II} \quad \text{(A)}$$

$$O_2+e^-\rightleftarrows O_2^{-\bullet} \qquad [E^\circ=-0.56\text{ V}] \quad \text{(B)}$$

$$O_2 + H^+ + e^- \rightleftarrows HO_2^{\bullet} \qquad [E^\circ = -0.13\ \text{V}] \quad (C)$$

$$H_3PO_3 + 2H^+ + 2e^- \rightleftarrows HPH_2O_2 + H_2O \qquad [E^\circ = -0.50\ \text{V}] \quad (D)$$

any step except for Cr^{II} to Cr^{III} seems to be hard to be simply oxidized by O_2. Considering that PDP formation continued up to the complete disappearance of $HCrO_4^-$ (see Figs. 1, inset, and 2) and then stopped, and that the molar concentrations of the formed PDP were much larger than those of the initially added $HCrO_4^-$, the following mechanism is assumed.

$$PH_2O_2^- + O_2 \rightleftarrows PH_2O_2^{\bullet} + O_2^{-\bullet} \qquad [\text{initiation}] \quad (1)$$

$$HO_2^{\bullet} \rightleftarrows O_2^{-\bullet} + H^+ \qquad [\text{p}K_a = 4.8]^{9)} \quad (2)$$

$$2PH_2O_2^{\bullet} \rightleftarrows PH_2O_2^+ + PH_2O_2^- \quad (3)$$

$$Cr^{VI} + O_2^{-\bullet}\ (\text{or } HO_2^{\bullet}) \rightarrow Cr^{V} + O_2 \quad (4)$$

$$2Cr^{V} \rightleftarrows Cr^{IV} + Cr^{VI} \quad (5)$$

$$PH_2O_2^- + Cr^{V} \rightarrow PH_2O_2^{\bullet} + Cr^{IV} \quad (6)$$

$$PH_2O_2^- + Cr^{IV} \rightarrow PH_2O_2^+ + Cr^{2+} \quad (7)$$

$$O_2 + Cr^{2+} \rightarrow O_2^{-\bullet} + Cr^{3+} \quad (8)$$

$$Cr^{3+} + PH_2O_2^+ \rightarrow Cr^{IV} + PH_2O_2^{\bullet} \quad (9)$$

$$PH_2O_2^+ + O_2^{-\bullet}\ (\text{or } HO_2^{\bullet}) \rightarrow H_2PO_4^{\bullet} \quad (10)$$

$$2H_2PO_4^{\bullet} \rightarrow H_2P_2O_8^{2-}\ (\text{or PDP}) + 2H^+ \quad (11)$$

All of the reactions, except Eq. 1, might be very fast; thus, both plots of $[HCrO_4^-]$ vs. t and [PDP] vs. t were rectilinear at intermediate periods of t after the induction time. As stated before, only the induction periods were slightly longer in the air-saturated solution than those in the O_2-saturated one (see Fig. 1). These facts may be due to the rapid reactions of Eqs. 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11. The rapid chain-cycle in Eqs. 7, 8, and 9 is considered to occur during the occurrence of the reduction reactions of Cr^{VI}. The rate of chromate(VI) decay in Fig. 2 would be dependent on that of reaction 4. Interestingly, the reactions in Eqs. 4, 5, 6, 7, 8, and 9 containing chromate species are induced by the reaction of Eq. 1, and the overall reaction of (7)+(8)+(9) is $PH_2O_2^- + O_2 \rightarrow PH_2O_2^{\bullet} + O_2^{-\bullet}$, which corresponds to Eq. 1. Consequently, the chromium(VI) ion acts as a catalyst for reaction 1, and almost the same rates in the air- and O_2-saturated solutions after the induction periods in Fig. 1 may be caused by reaction 7 or 9 being much slower than reaction 8. The rate of Eq. 9, which competes with reactions 10 and 14, might control the overall reaction rate and the amounts of PDP formation. The formation rate of PDP greatly increased with decreasing pH (see Fig. 3). Such a pH dependence was similar to that on the chromate(VI) decay rate in Fig. 2. Judging from the redox potentials in (B), (C), and (D), $HO_2^{\bullet}$ is a weaker reductant than $O_2^{-\bullet}$, and phosphinic acid HPH_2O_2 becomes a stronger reductant by decreasing the acidity. Therefore, the conditions of pH increase are more favorable for the reactions in Eqs. 1, 4, 6, and 7, despite the fact that the reaction became slower with increasing pH (see Figs. 2 and 3). Accordingly, the slower rate at larger pH is not thought to be due to the species of superoxide and phosphinate, but is thought to be mainly caused by decreasing the oxidizing capability of the chromium species (Cr^{VI}, Cr^{V}, and Cr^{IV}).

On the other hand, the maximum formation of PDP was less at a lower pH. This means a chain-shortening or the turnover-number decrease in reactions 7—9. It is noted that the pH dependences in the present reaction seem to be very complex, because the redox capabilities of not only the species, such as $PH_2O_2^-$, $O^{-\bullet}$, and Cr^{VI}, but also other radicals, such as $PH_2O_2^{\bullet}$ and $H_2PO_4^{\bullet}$, are apt to depend on the acidities in the reacting solution. For example, the rate constants corresponding to reaction 13 are 3.9×10^8, 5.9×10^7, and 7.9×10^7 dm^3 mol^{-1} s^{-1} for $H_2PO_4^{\bullet}$, $HPO_4^{-\bullet}$, and $PO_4^{2-\bullet}$, respectively.[10)]

When N_2 gas was bubbled through the reacting solution after the PDP formation had ceased and remained constant, the once-formed PDP began to decrease. The rate of such a PDP decomposition appeared to be indifferent to not only the acidity, but also to the added chromate concentrations.

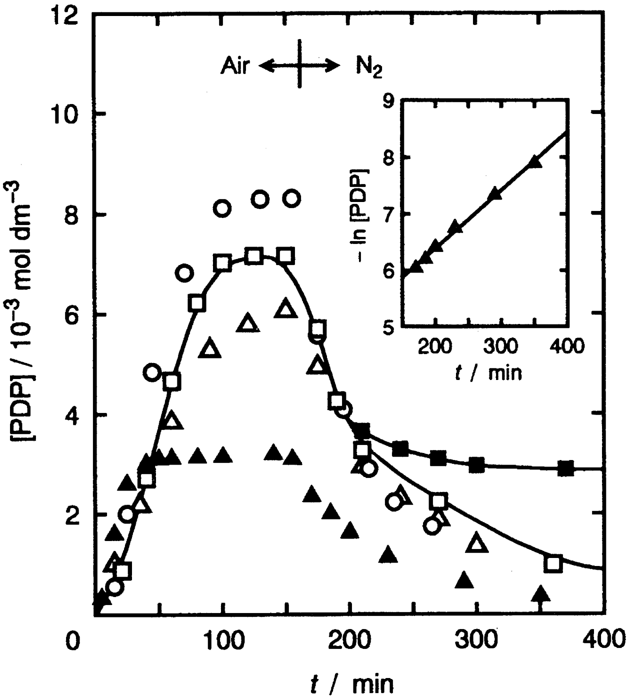

Fig. 4. Profile of the formation and decomposition of PDP for the reaction of $PH_2O_2^-$ with $HCrO_4^-$ at 25 °C, 0.40 mol dm^{-3} $PH_2O_2^-$, and pH 2.57. The reaction solution was saturated with air for 160 min, and was then saturated with N_2. The symbols of ○, □, and △ indicate the runs in the initial concentrations of $HCrO_4^-$ of 2.0×10^{-5}, 1.0×10^{-5}, and 5.0×10^{-6} mol dm^{-3}, respectively, and the plots ▲, the results under the conditions of 1.0×10^{-5} mol dm^{-3} $HCrO_4^-$ at pH 1.97. Plots ■ indicate results when the reacting solution was again saturated with air at t=210 min under the same conditions as in □. Inset shows the plots of −ln [PDP] vs. t under the same conditions as in ▲ (i.e., $[HCrO_4^-]=1.0\times10^{-5}$ mol dm^{-3} at pH 1.97).

Moreover, the decomposition of PDP is of first order (see Fig. 4, inset). Interestingly, when the solution was again bubbled through by the air on the way of the PDP decrease, such a decrease of PDP stopped once again (see Fig. 4, plot ■). These facts can be accounted for by the following mechanisms:

(In the case without O_2)

$$H_2P_2O_8^{2-} + PH_2O_2^- \rightarrow HPO_4^{2-} + HPO_4^{-\bullet} + PH_2O_2^{\bullet} \quad (12)$$

$$HPO_4^{-\bullet} + PH_2O_2^- \rightarrow HPO_4^{2-} + PH_2O_2^{\bullet} \quad (13)$$

$$2PH_2O_2^{\bullet} \rightleftarrows PH_2O_2^- + PH_2O_2^+ \quad (3)$$

$$PH_2O_2^+ + H_2O \rightarrow H_2PO_3^- + 2H^+ \quad (14)$$

Thus, the overall reaction is

$$H_2P_2O_8^{2-} + PH_2O_2^- + H_2O \rightarrow 2HPO_4^{2-} + H_2PO_3^- + 2H^+.$$

(In the case with O_2)

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

$$H_2P_2O_8^{2-} + PH_2O_2^- \rightarrow HPO_4^{2-} + HPO_4^{-\bullet} + PH_2O_2^{\bullet} \quad (12)$$

$$HPO_4^{-\bullet} + PH_2O_2^- \rightarrow HPO_4^{2-} + PH_2O_2^{\bullet} \quad (13)$$

$$2PH_2O_2^{\bullet} \rightleftarrows PH_2O_2^- + PH_2O_2^+ \quad (3)$$

$$PH_2O_2^+ + O_2^{-\bullet} \rightarrow H_2PO_4^{\bullet} \quad (10)$$

$$2H_2PO_4^{\bullet} \rightarrow H_2P_2O_8^{2-} + 2H^+ \quad (11)$$

The latter case is different from the former one in the occurrence of Eqs. 1, 10, and 11. The reaction rate of Eq. 10 competes with that of Eq. 14, and the equivalent formation and decomposition of PDP could occur in Eqs. 11 and 12.

Namely, the overall reaction, 2(1)+(12)+(13)+2(3)+2(10)+(11), is $2PH_2O_2^- + 2O_2 \rightarrow 2HPO_4^{2-} + 2H^+$. Consequently, the PDP concentrations remained constant in the latter case of O_2 presence. In the case without O_2, reaction 12 would be a rate-determining step, and the rate of the PDP decay follows the first-order rate law of $-d[\mathrm{PDP}]/dt = k_{\mathrm{obsd}}[\mathrm{PDP}]$ (where $k_{\mathrm{obsd}} = k_{12}[PH_2O_2^-]$) under the condition $[\mathrm{PDP}] \ll [PH_2O_2^-]$. Actually, plots of $-\ln[\mathrm{PDP}]$ vs. t were rectilinear (see Fig. 4, inset).

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