# Induction of Instantaneous Chain Reactions in the Peroxodiphosphate–Iron(II) System by Selected Substrates during a Titrimetric Procedure

By **Pichai Maruthamuthu** *,† and **Narayanasamy Subramanian**, Department of Chemistry, University of Madras, Autonomous Post-graduate Cente, Tiruchirapalli 620020, India

The reaction between peroxodiphosphate and iron(II) ions (in 1N-$H_2SO_4$) is instantaneous and is used to estimate the former quantitatively. But in the presence of some selected substrates such as methanol, ethanol, propan-2-ol, formaldehyde, glucose, and hypophosphite which do not react directly with peroxodiphosphate, an instaneous chain reaction is observed. This is explained by the competitive reaction between the substrate and iron(II) for the phosphate radical produced as the intermediate, and the ability of the substrate radical to reduce the oxidant, peroxodiphosphate.

REACTIONS involving $H_2O_2$–$Fe^{2+}$ and $S_2O_8^{2-}$–$Fe^{2+}$ systems in the presence and absence of substrates are generally found to be slow and measurable at ordinary temperatures and many kinetic investigations on oxidation and polymerization reactions have been carried out with these redox pairs.[1-6] On the other hand, peroxodiphosphate, $P_2O_8^{4-}$ (PDP), the phosphorus analogue of peroxodisulphate, is found to react with iron(II) ions in acid medium (1N-$H_2SO_4$) instantaneously [7,8] and quantitatively, the stoicheiometric reaction being (1). By utilizing this reaction, PDP is estimated

$$P_2O_8^{4-} + 2Fe^{2+} \xrightarrow{H^+} 2H_2PO_4^{-} + 2Fe^{3+} \qquad (1)$$

quantitatively in the presence and absence of substrates [7-11] by a titrimetric procedure using cerimetry (adding excess known concentration of $Fe^{2+}$ and back-titrating the unchanged $Fe^{2+}$ with standard $Ce^{4+}$ using ferroin indicator). During the course of our investigation of the possible thermal reactions of peroxodiphosphate with various organic and inorganic substrates, suitable concentrations of substrate and peroxodiphosphate, *e.g.* [methanol] 0.1M and [$P_2O_8^{4-}$] 0.01M, were mixed and thermostatted at 27 °C. Portions of the mixture at various intervals of time were pipetted out and analysed for the amount of PDP consumed by cerimetry. Surprisingly, it was observed that for all the portions analysed the amount of PDP which disappeared was found to be constant. But at the same time, analysis of the reaction mixture before its addition to $Fe^{2+}$ showed no evidence of any product formed except the starting material indicating the absence of any reaction between PDP and methanol, the substrate. It is certain that there is no direct reaction between $Ce^{4+}$ and methanol during titration (which was checked by separate experiments), $Ce^{4+}$ and PDP, and $Fe^{3+}$ and PDP. It is also evident that there is no self-decomposition of PDP under the present experimental conditions.[7,12] Looking at the possible explanation for the instantaneous disappearance of PDP, it is thought that the reaction (1) for the estimation of PDP may not be a one-step but a two-step reaction. Since PDP is a two-electron oxidant and $Fe^{2+}$ is a one-electron reductant, phosphate radical ($\dot{P}O_4^{2-}$ or its protonated forms) would be formed as the reactive intermediate similar to the reaction [13] of peroxodisulphate with $Fe^{2+}$. These phosphate radicals being very reactive,[14-16] would attack the substrate and set up the chain reaction. Since such a reaction was surprisingly found in the titrimetric process, it was deemed to be of interest to investigate this in detail. The present work was carried out with a view to (i) investigate the chain reactions of PDP with various substrates, (ii) find out the dependence of the concentrations of substrate as well as oxidant on the extent of the chain reaction, and (iii) propose a suitable chain mechanism involving the reactions of appropriate radicals of the oxidant and substrates in effecting the instantaneous chain reactions.

## RESULTS AND DISCUSSION

It is interesting to note the difference in the reactivity of peroxodiphosphate on the one hand, and the closely related $S_2O_8^{2-}$ and $H_2O_2$ on the other, with $Fe^{2+}$. The metal ion acts as a catalyst for the slow decomposition of the latter two peroxides whereas it reacts instantaneously and quantitatively with peroxodiphosphate (in 1N-$H_2SO_4$). Furthermore, for the $P_2O_8^{4-}$–$Fe^{2+}$ system, an instantaneous chain reaction is induced in the presence of some selected substrates such as methanol, ethanol, propan-2-ol, formaldehyde, glucose, and hypophosphite. Such a chain reaction is not observed in the presence of substrates like acetaldehyde, acetone, t-butyl alcohol, diacetone alcohol, *etc.* Though there is a possibility that other substrates like $SO_3^{2-}$, $N_3^-$, dithionite, thioglycol, *etc.*, would also induce a chain reaction due to the reducing nature of the substrate radicals, experiments involving these substrates were not successful because of the direct reaction with the titrant, $Ce^{4+}$. It is known that these substrates react with phosphate radicals and other similar radicals [16] such as $SO_4^{\cdot -}$ and $\dot{O}H$ producing very reactive reducing radicals, $SO_3^{\cdot -}$, $\dot{N}_3$, *etc.* However the titrimetric procedure was not found to be suitable for investigation of the chain reaction with these substrates.

The results of the present investigation are presented in Tables 1 and 2. It is seen that the increase of substrate concentration at constant initial concentration of PDP, $[PDP]_0$, increased the amount of the instantaneously

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† *Present address:* Institut für Strahlenchemie, Max-Planck-Institut für Kohlenforschung, Stiftstrasse 34—36, D-4330 Mulheim a.d. Ruhr 1, W. Germany.

TABLE 1

Effect of [substrate] on the instantaneous chain reaction; $[PDP]_0$ 0.01M; temperature 27 °C

| $10^2$[Substrate]/M | $\%[PDP]_r$ | | | | | Hypophosphite | |
|---|---|---|---|---|---|---|---|
| | Methanol | Ethanol | Propan-2-ol | Formaldehyde | Glucose | $10^2$[Substrate]/M | $\%[PDP]_r$ |
| 0.5 | 16 | 30 | 26 | 14 | 20 | 0.25 | 20 |
| 1.0 | 19 (20) | 41 (40) | 33 (34) | 24 (25) | 33 (34) | 0.50 | 40 |
| 1.5 | 31 | | | 32 | 41 | 0.75 | 51 (52) |
| 2.0 | 34 | 57 | 53 | 38 | 48 | 1.00 | 59 |
| 3.0 | 45 | 64 | 63 | 50 | 54 | 1.50 | 65 |
| 4.0 | 53 | 70 | 69 | 59 | 62 | | |
| 5.0 | 59 | 72 | 70 | 64 | 66 | | |
| 7.0 | 65 (67) | 80 | | 69 | 70 | | |
| 10.0 | 71 | 82 | 77 | 74 (74) | 74 | | |
| 20.0 | 74 | 87 | 87 | 82 | 79 (77) | | |
| 30.0 | 78 | 90 (88) | 89 | | | | |
| 40.0 | 81 (80) | 93 | 91 | | | | |
| 50.0 | 82 | 93 | 93 (90) | | | | |

The values given in parentheses correspond to those obtained under deaerated conditions.

TABLE 2

Effect of $[PDP]_0$ on the instantaneous chain reaction; [substrate] 0.1M; temperature 27 °C

| $10^3[PDP]_0$/M | $\%[PDP]_r$ | | | | | |
|---|---|---|---|---|---|---|
| | Methanol | Ethanol | Propan-2-ol | Formaldehyde | Glucose | Hypophosphite |
| 5 | 63 | 75 | 79 | 73 | 80 | 78 |
| 10 | 65 | 76 (75) | 78 (78) | 68 | 71 (70) | 74 |
| 15 | 65 (63) | 75 | 75 | 63 (63) | 69 | 74 (74) |
| 20 | 65 | 74 | 75 | 63 | 67 | 74 |

The values given in parentheses correspond to those obtained under deaerated conditions.

reacted PDP, $[PDP]_r$, which is expressed in terms of percentage as $\%[PDP]_r$ (Table 1). But increase of $[PDP]_0$ at constant concentration of substrate did not lead to any significant change in the value of $\%[PDP]_r$ except for a slight increase or decrease (Table 2). The variation of $[Fe^{2+}]$ ($[Fe^{2+}]$ is always greater than 2[PDP] so that there is some remaining $Fe^{2+}$ which can be back-titrated against $Ce^{4+}$) and $[H^+]$ (always greater than 1N-$H_2SO_4$ so that the reaction is complete) for constant $[PDP]_0$ and $[substrate]_0$ were found to have no effect on the extent of chain decomposition of PDP. From the similarities of structure and reactivity of peroxodiphosphate with those of peroxodisulphate [12] and also from the reactions of phosphate radicals with organic compounds,[14] the mechanism of the instantaneous chain reaction, taking propan-2-ol as the typical example for the substrate, is expressed by equations (2)—(6).

$$P_2O_8^{4-} + Fe^{2+} \xrightarrow{H^+} H_2P\dot{O}_4 + H_3PO_4 + Fe^{3+} \quad (2)$$

$$(CH_3)_2CHOH + H_2P\dot{O}_4 \longrightarrow (CH_3)_2\dot{C}OH + H_3PO_4 \quad (3)$$

$$P_2O_8^{4-} + (CH_3)_2\dot{C}OH \xrightarrow{H^+} H_2P\dot{O}_4 + H_3PO_4 + (CH_3)_2CO + H^+ \quad (4)$$

$$H_2P\dot{O}_4 + Fe_2{}^{+} \longrightarrow H_2PO_4^{-} + Fe^{3+} \quad (5)$$

$$(CH_3)_2\dot{C}OH + Fe^{3+} \longrightarrow (CH_3)_2CO + Fe^{2+} + H^+ \quad (6)$$

The phosphate radicals ($H_2P\dot{O}_4$, $HP\dot{O}_4^{-}$, and $P\dot{O}_4^{2-}$ depending upon the pH of the medium) and their p$K_a$ values are discussed in recent publications.[14,16] The formation of these radicals as transient intermediates is invoked in the slow thermal reactions of metal ions and metal complexes [9,17] and ascorbic acid [18] and in photochemical reactions.[15,19] In the proposed mechanism, equation (2) is the radical-producing step. The phosphate radicals thus produced compete for $Fe^{2+}$ [step (5)] and propan-2-ol [step (3)]. If reaction (5) is the only one taking place immediately after reaction (2), then the chain reaction would not occur. But step (3) contributes to the disappearance of peroxodiphosphate, along with step (4) wherein the substrate radical is able to reduce peroxodiphosphate-generating phosphate radicals. Under the experimental condition that the substrate concentration is increased at constant $[PDP]_0$, $[Fe^{2+}]$ used also being constant, the increase of $\%[PDP]_r$ greatly depends upon the concentration of the substrate. This is found to be true for all the substrates investigated (Table 1). In the case of alcohols, it is seen that as high as 80—90% instantaneous decomposition of PDP occurred by increasing the substrate concentration to 0.5M for $[PDP]_0$ 0.01M. The slight decrease in $\%[PDP]_r$ under the conditions of constant [substrate] and increasing $[PDP]_0$, $[Fe^{2+}]$ used also being correspondingly increased, may be due to the contribution of reaction (6) which may become predominant at high $[Fe^{3+}]$, the oxidising metal ion being formed by reactions (2) and (5). The formation of $(CH_3)_2\dot{C}OH$ and the reduction of $P_2O_8^{4-}$ are similar to the mechanism proposed in the radiolytic chain decomposition and photochemical reactions of peroxodiphosphate in the presence of various substrates.[14,19] In the present investigation, steps (3) and (4) are important in deciding the amount of PDP decomposed in the chain reaction and the feasibility of step (4) may depend upon the reducing ability of the substrate radicals. The rate constants [14] for the reaction of

$H_2P\dot{O}_4$ with methanol, ethanol, and propan-2-ol are $4.1 \times 10^7$, $7.7 \times 10^7$, and $1.4 \times 10^8$ l mol$^{-1}$ s$^{-1}$ respectively. So far, the rate constants for the reduction of PDP by the alcohol radicals have not been measured. But it has been observed that the reducing ability of these radicals increases in the order $\dot{C}H_2OH < CH_3\dot{C}HOH < (CH_3)_2\dot{C}OH$. From these observations one may conclude that for particular [alcohol] and $[PDP]_0$, the amount of PDP instantaneously decomposed should increase from methanol to propan-2-ol. Our experimental results are in good agreement with this and in fact $\%[PDP]_r$ is higher for ethanol and propan-2-ol than for methanol. However, the difference between ethanol and propan-2-ol is not significant.

In the case of other substrates, formaldehyde, glucose, and hypophosphite, the substrate radicals formed may be $H{-}\dot{C}{=}O$, $HO{-}\dot{C}H{-}(CHOH)_4CHO$, and $H\dot{P}O_2^-$, respectively. These radicals are known to be reducing in nature and the values of $\%[PDP]_r$ in the present investigation suggest the reducing ability of these radical on PDP to be in the order $H\dot{P}O_2^-$ > glucose radical > formaldehyde radical. The mechanism of reactions of these radicals would be similar to reactions (4) and (6).

In conclusion, it may be stated that among the peroxides, $H_2O_2$, $S_2O_8^{2-}$, and $P_2O_8^{4-}$ with similar properties, the behaviour of $P_2O_8^{4-}$ towards $Fe^{2+}$ is found to be unique and interesting. The $P_2O_8^{4-}$–$Fe^{2+}$ reaction, in the presence of $H^+$, is found to be instantaneous and quantitative. During this instantaneous reaction, an immeasurably fast chain reaction is set up with a selected group of substrates. Besides methanol, ethanol, propan-2-ol, formaldehyde, glucose, and hypophosphite, there may be other substrates too (which we have not tested) behaving in a similar way as in the present investigation. This was an attempt to study the instantaneous chain reaction by a simple titrimetric procedure and it served our purpose well. The results can be explained by the general behaviour of peroxides and their reaction mechanisms.

## EXPERIMENTAL

Potassium peroxodiphosphate (FMC Corporation) was converted into $Li_4P_2O_8,4H_2O$ and purified to greater than 99.5% according to the method of Chulski.[8] Methanol, ethanol, propan-2-ol, glucose, iron(II) ammonium sulphate, and sulphuric acid (B.D.H.) were AnalaR grade. Cerium(IV) ammonium sulphate and formaldehyde were from Sarabai M. Chem. and sodium hypophosphite was from SD Chemical. Lithium carbonate and perchloric acid (60%) were from E. Merck and all these chemicals were used as such except the alcohols which were distilled twice before use.

All experiments were carried out in aqueous medium at room temperature (27 °C) using various concentrations of substrate (0.005—0.5M) keeping $[PDP]_0$ constant (0.01M) and varying $[PDP]_0$ (0.005—0.02M) at constant [substrate] (0.1M). In a typical experiment, adequate volumes of particular concentrations of PDP and substrate and water (to maintain a constant total volume) were taken in a conical flask. To this, a known amount of excess concentration of iron(II) ammonium sulphate containing 1N-$H_2SO_4$ was added. The addition was done within 20 s uniformly for all experiments. The remaining unchanged $Fe^{2+}$ was titrated against $Ce^{4+}$ using ferroin indicator. From the amount of $Ce^{4+}$ consumed, the unchanged $Fe^{2+}$ and hence the amount of PDP reacted was calculated. Experiments were also done in deaerated solutions and there was no effect of oxygen on the instantaneous chain reaction. Duplicate experiments were always carried out and the results were found to be reproducible within ±5%.

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