Kinetics of Oxidation of Acetaldehyde, Propionaldehyde & n-Butyroaldehyde by Peroxydiphosphate

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The oxidation of acetaldehyde, propionaldehyde and n-butyraldehyde by peroxypophosphate (PP) have been studied kinetically in aq. H₂SO₄ medium ([H⁺] = 0.1 to 0.5M) at constant ionic strength (μ = 0.85M) in the temperature range, 20-50°C. The important experimental observations are as follows: (1) The oxidation is subject to remarkable catalysis by H⁺, order with respect to [H⁺] being equal to unity; (2) a zero-order dependence on aldehyde and a first order dependence on PP have been observed; (3) the reaction stoichiometry, PP : aldehyde is found to be 1:1, the product of oxidation being the respective carboxylic acid in each case; (4) evidence for free radical intermediates has been obtained by the initiation of vinyl polymerization. The results seem to be explained in the best plausible way by a free radical mechanism involving phosphate radical ion intermediates, the dissociation of H₃PO₄ being the rate-determining step. The kinetic and thermodynamic parameters evaluated for all the three oxidations are discussed and a comparison is made with similar reactions involving peroxysulphate.

EXCEPT for the photochemical oxidation of ethanol and 2-propanol by peroxypophosphate (PP) due to Edwards et al. and preliminary notes by us, the kinetics of oxidation of organic substrates by PP have not been investigated as extensively as those by peroxysulphate. As a part of our programme to study the kinetics and mechanism of oxidation of a variety of organic substrates by PP, the results of our kinetic study on the PP oxidation of acetaldehyde (AA), propionaldehyde (PA) and n-butyraldehyde (BA) are presented in this paper.

Materials and Methods

K₂P₂O₇ (purity, 96.5%) obtained from FMC Corporation, USA, was converted into lithium peroxysulphate, Li₄P₂O₇·4H₂O (purity, 99.1%) and the purification was accomplished according to the method of Chulski. AA, PA (Riedel) and BA (E. Merck) were used as such. Other chemicals used were of analar grade. All the preparations of reagents and solutions were done with doubly distilled water.

Experiments were carried out in aqueous sulphuric acid medium at constant [H⁺] = 0.5M (by added H₂SO₄; the dissociation of HSO₄ and the ionic strength, μ = 0.85M, adjusted with NaHSO₄. [Substrate] ≥ [PP] was generally employed and [PP] (μM) always denotes the total concentration of peroxypophosphate) was varied from 2.5×10⁻³ to 20×10⁻³M, [substrate] from 0.025 to 2.0M, the temperature range studied being 20-50°C. The effect of [H⁺] was investigated by varying [H⁺] from 0.1 to 0.5M at constant strength (0.85M). There was no significant change in the acidity of the solution before and after the reaction, checked by measuring the pH of the solution.

The concentrations of PP (initial and during the experiments) were determined by the addition of excess known amount of Fe²⁺ to aliquots of the reaction mixture and estimating the unused Fe²⁺ by vanadometry using diphenylamine indicator. Experiments carried out under deaerated conditions showed that the presence or absence of oxygen in the reaction system did not produce any significant change in the rates. The reaction stoichiometry in the oxidation of all the three aldehydes was estimated by 2,4-dinitrophenylhydrazone method gravimetrically. Under the condition [substrate] ≥ [PP], since PP reacted completely, the reaction mixture would contain the unreacted carbonyl compound. The latter was converted into 2,4-dinitrophenylhydrazone by adding Borsche's reagent and estimated. Product analysis was done by GLC.

Duplicate experiments were carried out to estimate the experimental error. The rate constants are reproducible with a precision of ±2%.

Results and Discussion

Oxidations of all the three aldehydes obeyed first-order kinetics, the order with respect to [PP] being unity and that due to [aldehyde] being zero. The linearity of the plots of log ([a] - [x]) vs time (up to 85% conversion of PP) and the independence of pseudo-first order rate constant, k' (sec⁻¹) on the initial [PP] (0-0.025 to 0-0.02M) indicated first-order dependence on PP. k' (sec⁻¹) was found to be independent of [substrate] (Table 1) and hence the overall first-order rate constant, k₁ (sec⁻¹) and k' (sec⁻¹) are the same. Increase in [H⁺] (0-1 to 0-5M) at constant μ (0.85M) increased the rate of oxidation significantly and plots of k' vs [H⁺] (Fig. 1)
TABLE 1 — Zero-order Dependence on [Aldehyde]

\[
\begin{array}{cccc}
\text{[AA]} & \kappa \times 10^4 & \text{[PA]} & \kappa \times 10^4 \\
M & \text{sec}^{-1} & M & \text{sec}^{-1} \\
2.5 & 2.36 & 3.0 & 2.00 \\
5.0 & 2.35 & 6.0 & 1.98 \\
7.5 & 2.45 & 9.0 & 1.98 \\
10.0 & 2.25 & 12.0 & 1.98 \\
12.5 & 2.37 & 15.0 & 1.98 \\
\end{array}
\]

were found to be linear passing through origin showing the order with respect to \([H^+]\) as unity and the reaction to be completely acid-dependent. The rate law is of the form

\[
\frac{-d[PP]}{dt} = k_1[PP] = k_0[PP][H^+] 
\]

In all the three oxidations, evidence for the formation of free radicals was obtained by the initiation of vinyl polymerization which occurred with a short induction period compared to the initiation by PP alone. In our study on the self-decomposition of peroxydiphosphate, IR spectrum of the polymer, polyacrylonitrile, indicated the presence of phosphate grouping in the polymer and hence it may be concluded that phosphate radical ions are produced as intermediates. Formation of \(PO_2^-\) was suggested earlier by Edwards and coworkers in the thermal oxidations of \(VO^{2+}\) and \(Fe(II)\) complexes and photochemical oxidation of water, ethanol and 2-propanol by peroxydiphosphate. In the case of \(Ag^{+}\)-catalysed oxidation of water and oxidation of hexacyanoferrate (II) by peroxydiphosphate, we have also invoked the formation of \(PO_2^-\) as the reaction intermediate.

The evidence for the formation of free radical intermediates coupled with the fact that PP is a two-electron oxidant, indicates clearly its functioning as a one-electron oxidant.

From a knowledge of the concentrations of the various species of PP as a function of \(pH\), it is evident that \([PP]_{total} = [H_2P_2O_7^-] + [H_4P_2O_8] + [H_3P_2O_7] + [H_5P_2O_8] \) under the present experimental conditions \([H^+] = 0.1 \text{ to } 0.5M\). If \(H_2P_2O_7^-\) is the active species, the rate law would correspond to

\[
\frac{-d[PP]}{dt} = k_0[H_2P_2O_7^-] = \frac{k_0[PP]_T}{1 + K_{14}[H^+] + K_{13}K_{14}[H^+]^2} 
\]

where \(K_{14}\) and \(K_{14}\) are the equilibrium constants for the protonation of \(H_2P_2O_7^-\) and \(H_4P_2O_8\), respectively. In view of the arguments given by us in the self-decomposition of PP, assuming \(K_{14}[H^+] + K_{13}K_{14}[H^+]^2\) to be negligible compared to unity, the above rate law would simplify to

\[
\frac{-d[PP]}{dt} = k_0[H_3P_2O_7^-] = k_0[PP]_T 
\]

Similarly, if the active species is \(H_3P_2O_7^-\), the rate law would correspond to

\[
\frac{-d[PP]}{dt} = k_0[H_3P_2O_7^-] = k_0[PP]_T[H^+] 
\]

Both \(H_2P_2O_7^-\) and \(H_3P_2O_7^-\) as the active species would lead to the rate law

\[
\frac{-d[PP]}{dt} = k_0[H_2P_2O_7^-] + k_0[H_3P_2O_7^-] 
\]

The same simplifications, for \(H_3P_2O_7^-\) as the active species, would yield the following rate equation,

\[
\frac{-d[PP]}{dt} = k_0[H_3P_2O_7^-] = k_0[K_{14}K_{13}][PP]_T[H^+]^2 
\]

Experimental data on the effect of \([H^+]\) on the rate are in accordance with rate law (4). The plots of \(-d[PP]/dt\) or \(k'\) vs \([H^+]\) (Fig. 1) are linear passing through origin with a simple first order dependence on \([H^+]\) indicating \(H_2P_2O_7^-\) as the only active species of PP in the oxidation of aldehydes. In other words, the reaction proceeds via an acid-dependent path only.

It is rather abnormal that aldehydes are oxidized by acid-dependent route only whereas ketones are oxidized by both acid-dependent and acid-independent routes. The unusual experimental observation is understandable in terms of the difference in the reaction centre on the carbonyl compound. The reactivity of the carbonyl group is generally electron-accepting, involving the electron-deficient carbon as the reaction centre. But in a redox reaction where the carbonyl compound acts as a reducing agent, it has to function necessarily as an

\[\text{Fig. 1 — First-order dependence on } [H^+] \text{ in PP-aldehyde reaction } (\mu = 0.85M; [PP] 0.0025 \text{ to } 0.02M; [aldehyde] 0.025 \text{ to } 0.2M)\]
electron-donor, donating electrons to the oxidant and hence the attack of the oxidant on the carbonyl compound would be expected to occur only at an electron-rich centre of the latter, namely the carbonyl oxygen. Such an attack of PP on the carbonyl oxygen can be visualized when the reaction is a homooligomolecular one obeying second-order kinetics, first order in PP and first order in the carbonyl compound, as in the case of PP-ketone reaction. But the same argument cannot hold good for a reaction which is first order in PP and zero order in the carbonyl compound, i.e. for PP-aldehyde reaction. The kinetic data show evidently that only PP is involved in the rate-determining step and the first order dependence on $[H^+]$ indicates $H_3P_2O_6$ to be the active species of PP. It is interesting to note that the reaction is wholly acid-dependent with a simple first order dependence on $[H^+]$ for all the reactions wherever zero order dependence on substrate has been encountered. Furthermore the self-decomposition of PP is also wholly acid-dependent obeying similar kinetics with a rate law corresponding to Eq. (I). The fact that the active species of PP and the kinetics for aldehyde oxidation differs from those for ketone oxidation makes it reasonable to suppose the reaction site on the carbonyl compound also to be different. On the basis of the mechanism postulated for the oxidation of aldehydes by most of the metal ions, C-H bond may be visualized as the reaction centre. Evidence from studies on kinetic isotope effects cannot be sought regarding this point since C-H bond cleavage is not involved in the rate-determining step. But it is evident from product analysis that alkyl group of the aldehyde remains intact and hence alkyl group is not the reaction centre.

The kinetic data coupled with a reaction stoichiometry of PP: aldehyde = 1:1, and the evidence for free radical intermediates can be correlated in the best possible way by the mechanism shown in Scheme 1, involving the attack of hydroxyl radical

\[
\begin{align*}
H_3P_2O_6 + H^+ & \rightarrow H_3P_2O_4 & (7) \\
H_3P_2O_4 & \rightarrow HPO_4^2 + H_2PO_4^- & (8) \\
HPO_4^2 + H_2O & \rightarrow H_2PO_4^- + OH^- & (9) \\
(H_2PO_4^- + H_2O & \rightarrow H_2PC_4^- + OH^- + H^+) & (10) \\
R-C & \rightarrow O+OH^- & \rightarrow R-C = O + H_2O & (11) \\
R-C & \rightarrow O + H_3P_2O_4 & \rightarrow R-C = O + H_2PO_4^- + HPO_4^2^- & (12) \\
R-C & \rightarrow O + HPC_4^- & \rightarrow R-C = O + HPC_4^- & (13) \\
R-C & \rightarrow O + H_2O & \rightarrow R-C = O + H^+ & (14)
\end{align*}
\]

(Both HPO_4^2- and H_2PO_4^- will act as chain carriers. But for the sake of simplicity, only HPO_4^2- is represented as the chain carrier since the kinetics will be the same in either case).

Scheme 1

The fact that the active species of PP and the kinetics for aldehyde oxidation differs from those for ketone oxidation also makes it reasonable to suppose the reaction site on the carbonyl compound also to be different. On the basis of the mechanism postulated for the oxidation of aldehydes by most of the metal ions, C-H bond may be visualized as the reaction centre. Evidence from studies on kinetic isotope effects cannot be sought regarding this point since C-H bond cleavage is not involved in the rate-determining step. But it is evident from product analysis that alkyl group of the aldehyde remains intact and hence alkyl group is not the reaction centre.

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\]

(Both HPO_4^2- and H_2PO_4^- will act as chain carriers. But for the sake of simplicity, only HPO_4^2- is represented as the chain carrier since the kinetics will be the same in either case).

Scheme 1
aldehydes by PP follows the order, aldehydes > ketones, in accordance with the general reactivity trend.

The overall first order rate constants, $k_1$ (sec$^{-1}$), for aldehyde oxidation and the thermodynamic parameters are presented in Table 2. The overall energy of activation, $E_a$, increases in the order for AA < PA < BA. On the basis of the rate Eq. (14), $E_a = (E_1 + E_2 + E_3 - E_0)$. The activation energy, $E_1$, for the radical-radical reaction (12) is negligible and $E_2$ and $E_3$ for the reactions (8) and (9) would be the same and independent of the substrate. Hence the only difference in $E_a$ would be due to reaction (11). In other words, the reactivity of the organic free radical, $R - C = O$, with PP may be expected to be in the order, CH$_2$-C=O>CH$_3$-C=O>CH$_2$+C=O = O and hence the same decreasing order of reactivity for the corresponding parent compounds. But all of them were found to be oxidized almost at the same rate (Table 2). This may be explained in terms of the reverse trend observed in the entropy of activation. For instance, $E_A$ for AA oxidation is more favourable but $\Delta S^f$ is highly negative or unfavourable. The compensation of the two factors may result in almost the same order of reactivity.

A comparison with similar reactions involving $S_2O_8^2-$ shows that peroxydisulphate$^{19,20}$ requires the presence of catalysts like Ag$^+$ to effect appreciable oxidation of aldehydes and the oxidizing trend observed is peroxydisulphate > peroxydisulphate. The same order of reactivity was observed in the oxidation of VO$^{2+}$ by Edwards et al.$^8$. On the basis of the redox potential, $-2.07$ V for peroxydisulphate$^{21}$ and $-2.01$ V for peroxydisulphate$^{22}$, the oxidizing capacity of these two isoelectronic peroxides may not be greatly different from one another. But the kinetic studies involving the two oxidants show a large difference in reactivity and this difference, as Edwards et al.$^8$ have pointed out, may be a kinetic rather than a thermodynamic one.

### Table 2 — Kinetic and Thermodynamic Parameters for PP-Aldehyde Reaction

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>$k_1 \times 10^4$ sec$^{-1}$ at</th>
<th>$E_a$ kcal/mol</th>
<th>$A$ Sec$^{-1}$</th>
<th>$\Delta S^f$ e.u.</th>
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<td>20°</td>
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<td>5.01</td>
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<td>5.86</td>
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### References