

## Kinetics of Oxidation of Acetaldehyde, Propionaldehyde & *n*-Butyraldehyde by Peroxydiphosphate

P. MARUTHAMUTHU & M. SANTAPPA

Department of Physical Chemistry, University of Madras, A.C. College Campus, Madras 600025

Received 28 June 1976; accepted 12 October 1976

The oxidation of acetaldehyde, propionaldehyde and *n*-butyraldehyde by peroxydiphosphate (PP) have been studied kinetically in aq.  $H_2SO_4$  medium  $\{[H^+] = 0.1 \text{ to } 0.5M\}$  at constant ionic strength ( $\mu = 0.85M$ ) in the temperature range, 20-50°. 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  $H_3P_2O_8$  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 peroxydisulphate.

EXCEPT for the photochemical oxidation of ethanol and 2-propanol by peroxydiphosphate (PP)<sup>1</sup> due to Edwards *et al.*<sup>2</sup> and preliminary notes by us<sup>3,4</sup>, the kinetics of oxidation of organic substrates by PP have not been investigated as extensively as those by peroxydisulphate. 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

$K_4P_2O_8$  (purity, 96.5%) obtained from FMC Corporation<sup>5</sup>, USA, was converted into lithium peroxydiphosphate,  $Li_4P_2O_8 \cdot 4H_2O$  (purity, 99.1%) and the purification was accomplished according to the method of Chulski<sup>6</sup>. 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  $H_2SO_4$ ; the dissociation of  $HSO_4^-$  and the alkalinity of PP solution being taken into account) and ionic strength,  $\mu = 0.85M$ , adjusted with  $NaHSO_4$ .  $[Substrate] \gg [PP]$  was generally employed and  $[PP]$   $\{[PP]$  always denotes the total, initial concentration of peroxydiphosphate $\}$  was varied from  $2.5 \times 10^{-3}$  to  $20 \times 10^{-3}M$ ,  $[substrate]$  from 0.025 to 0.2M, the temperature range studied being 20-50°. The effect of  $[H^+]$  was investigated by varying  $[H^+]$  from 0.1 to 0.5M at constant ionic 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  $Fe^{2+}$  to aliquots of the reaction mixture and estimating the unused  $Fe^{2+}$  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  $[substrate] \gg [PP]$ , 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  $\pm 2\%$ .

### 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  $[PP]$  (0.0025 to 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,  $k_1$  ( $sec^{-1}$ ) and  $k'$  ( $sec^{-1}$ ) are the same. Increase in  $[H^+]$  (0.1 to 0.5M) at constant  $\mu$  (0.85M) increased the rate of oxidation significantly and plots of  $k'$  vs  $[H^+]$  (Fig. 1)

TABLE 1—ZERO-ORDER DEPENDENCE ON [ALDEHYDE]  
 {[H<sup>+</sup>]=0.5M; μ=0.85M; [PP]=0.0025M; temp.=30°}

[AA] ×10 <sup>2</sup> M	k' × 10 <sup>4</sup> sec <sup>-1</sup>	[PA] ×10 <sup>2</sup> M	k' × 10 <sup>4</sup> sec <sup>-1</sup>	[BA] ×10 <sup>2</sup> M	k' × 10 <sup>4</sup> sec <sup>-1</sup>
2.5	2.36	3.0	2.00	2.5	2.18
5.0	2.35	6.0	1.96	5.0	2.21
7.5	2.47	9.0	1.98	7.5	2.19
10.0	2.25	12.0	1.98	10.0	2.15
12.5	2.37	15.0	1.88	12.5	2.22

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

$$\frac{-d[PP]}{dt} = k_1[PP] = k_b[PP][H^+] \quad \dots(1)$$

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<sup>7</sup>, 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<sub>4</sub><sup>2-</sup> was suggested earlier by Edwards and coworkers<sup>8-10</sup> in the thermal oxidations of VO<sup>2+</sup>

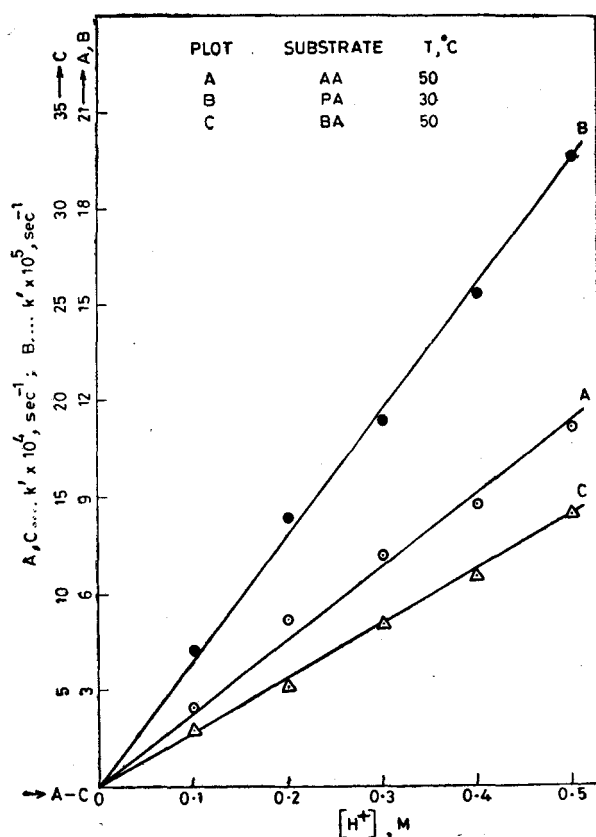


Fig. 1—First-order dependence on [H<sup>+</sup>] in PP-aldehyde reaction {μ=0.85M; [PP] 0.0025 to 0.02M; [aldehyde] 0.025 to 0.2M}

and Fe(II) complexes and photochemical oxidation of water, ethanol and 2-propanol by peroxydiphosphate. In the case of Ag<sup>+</sup>-catalysed oxidation<sup>11</sup> of water and oxidation of hexacyanoferrate (II)<sup>12</sup> by peroxydiphosphate, we have also invoked the formation of PO<sub>4</sub><sup>2-</sup> 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<sup>13</sup> of the concentrations of the various species of PP as a function of pH, it is evident that [PP]<sub>total</sub> = [H<sub>2</sub>P<sub>2</sub>O<sub>8</sub><sup>2-</sup>] + [H<sub>3</sub>P<sub>2</sub>O<sub>8</sub><sup>-</sup>] + [H<sub>4</sub>P<sub>2</sub>O<sub>8</sub>] under the present experimental conditions {[H<sup>+</sup>] = 0.1 to 0.5M}. If H<sub>2</sub>P<sub>2</sub>O<sub>8</sub><sup>2-</sup> is the active species, the rate law would correspond to

$$\frac{-d[PP]}{dt} = k_a[H_2P_2O_8^{2-}] = \frac{k_a[PP]_T}{1 + K_{13}[H^+] + K_{13}K_{14}[H^+]^2} \quad \dots(2)$$

where K<sub>13</sub> and K<sub>14</sub> are the equilibrium constants for the protonation of H<sub>2</sub>P<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>3</sub>P<sub>2</sub>O<sub>8</sub><sup>-</sup> respectively. In view of the arguments given by us<sup>8</sup> in the self-decomposition of PP, assuming K<sub>13</sub>[H<sup>+</sup>] + K<sub>13</sub>K<sub>14</sub>[H<sup>+</sup>]<sup>2</sup> to be negligible compared to unity, the above rate law would simplify to

$$\frac{-d[PP]}{dt} = k_a[H_2P_2O_8^{2-}] = k_a[PP]_T \quad \dots(3)$$

Similarly, if the active species is H<sub>3</sub>P<sub>2</sub>O<sub>8</sub><sup>-</sup>, the rate law would correspond to

$$\frac{-d[PP]}{dt} = k'_a[H_3P_2O_8^-] = k'_aK_{13}[PP]_T[H^+] = k_b[PP]_T[H^+] \quad \dots(4)$$

Both H<sub>2</sub>P<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>3</sub>P<sub>2</sub>O<sub>8</sub><sup>-</sup> as the active species would lead to the rate law

$$\frac{-d[PP]}{dt} = k_a[H_2P_2O_8^{2-}] + k'_a[H_3P_2O_8^-] = k_a[PP]_T + k'_aK_{13}[PP]_T[H^+] = \{k_a + k_b[H^+]\}[PP]_T \quad \dots(5)$$

The same simplifications, for H<sub>4</sub>P<sub>2</sub>O<sub>8</sub> as the active species, would yield the following rate equation,

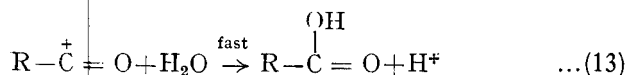
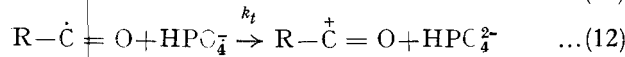
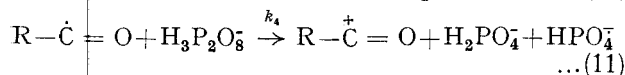
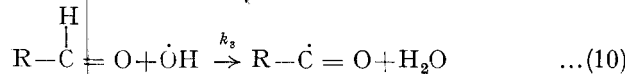
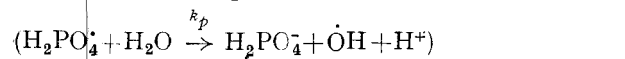
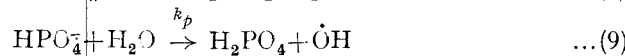
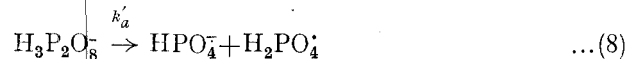
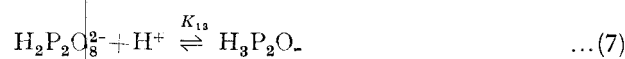
$$\frac{-d[PP]}{dt} = k''_a[H_4P_2O_8] = k''_aK_{13}K_{14}[PP]_T[H^+]^2 = k_c[PP]_T[H^+]^2 \quad \dots(6)$$

Experimental data on the effect of [H<sup>+</sup>] on the rate are in accordance with rate law (4). The plots of -d[PP]/dt or k' vs [H<sup>+</sup>] (Fig. 1) are linear passing through origin with a simple first order dependence on [H<sup>+</sup>] indicating H<sub>3</sub>P<sub>2</sub>O<sub>8</sub><sup>-</sup> 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

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 bimolecular one obeying second-order kinetics, first order in PP and first order in the carbonyl compound, as in the case of PP-ketone reaction<sup>4,14</sup>. 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<sup>+</sup>] indicates H<sub>3</sub>P<sub>2</sub>O<sub>8</sub><sup>-</sup> 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<sup>+</sup>] for all the reactions<sup>14</sup> wherever zero order dependence on substrate has been encountered. Furthermore the self-decomposition<sup>7</sup> of PP is also wholly acid-dependent obeying similar kinetics with a rate law corresponding to Eq. (1). The fact that the active species of PP and the kinetics for aldehyde oxidation differs from those for ketone oxidation<sup>15</sup> 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<sup>15</sup>, 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



(Both HPO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PC<sub>4</sub><sup>2-</sup> will act as chain carriers. But for the sake of simplicity, only HPO<sub>4</sub><sup>-</sup> is represented as the chain carrier since the kinetics will be the same in either case).

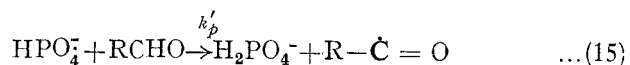
Scheme 1

on C-H bond of the aldehyde. The aldehydic hydrogen can function effectively as a reducing agent with respect to  $\dot{O}H$  as the oxidizing species since the simultaneous transfer of an electron and a proton or hydrogen atom transfer can be accomplished in the reaction. The reaction of R- $\dot{C}=\overset{O}{O}$  radical with PP would increase the overall rate of the reaction and this will not change the kinetics of the reaction.

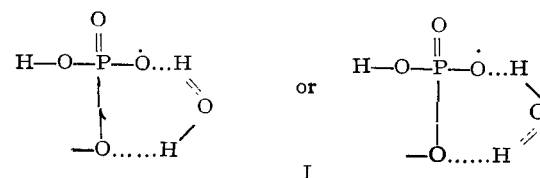
Assuming  $k'_a$  to be negligible, on the basis of steadystate hypothesis, the rate Eq. (14), which is in good agreement with the experimentally observed one, can be derived.

$$\begin{aligned} \frac{-d[PP]}{dt} &= \left( \frac{k'_a k_p k_4}{k_t} \right)^{1/2} [H_3P_2O_8^-] \\ &= k_b [PP]_T [H^+] = k_1 [PP]_T \quad \dots(14) \end{aligned}$$

The above rate equation is derived making use of some simplifying assumptions like  $k_p > k'_p$  where  $k'_p$  is the rate constant for the reaction of the phosphate radical ion with the aldehyde.

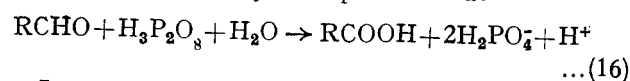


This trend of reactivity is not unusual. A similar trend has been noticed in oxidations involving peroxydisulphate<sup>16</sup> also. In peroxydisulphate-initiated vinyl polymerization<sup>17</sup>, end-group analysis of the polymer showed that the ratio of sulphate to hydroxyl end-group on the polymer decreases sharply to less than unity in acid media indicating  $\dot{O}H$  to be the major initiating species in acid solution. This observation also justifies the assumption that  $k_p > k'_p$ . In view of the higher bond energy<sup>18</sup> associated with O-H bond involved in reaction (9) compared to that of C-H bond involved in reaction (15), energetic considerations would warrant  $k'_p > k_p$ . The reverse trend, which seems to be operative, may probably be explained in terms of the relative stability of the activated complex involved in reactions (9) and (15). A six-membered cyclic transition state (I) stabilized by hydrogen bonding may be involved in reaction (9)



whereas such a stabilization of the transition state by hydrogen bonding is not possible for reaction (15).

The product of oxidation in each case was identified to be exclusively the respective carboxylic acid, i.e. acetic acid, propionic acid and *n*-butyric acid in the oxidation of AA, PA and BA respectively. The stoichiometric equation for the oxidation of aldehyde by PP may be represented as



In spite of the difference in the kinetic behaviour, the relative rates of oxidation of ketones<sup>15</sup> and

TABLE 2 — KINETIC AND THERMODYNAMIC PARAMETERS FOR PP-ALDEHYDE REACTION

$$\{[H^+] = 0.5M; \mu = 0.85M; [PP] = 0.0025 \text{ to } 0.02M; [\text{Aldehyde}] = 0.025 \text{ to } 0.2M\}$$

Aldehyde	$k_1 \times 10^4 \text{ sec}^{-1}$ at				$E_a$ kcal/mol	$A$ Sec <sup>-1</sup>	$\Delta S^\ddagger$ e.u.
	20°	30°	40°	50°			
AA	1.14	2.36	5.01	11.11	14.3	$4.9 \times 10^6$	-30.0
PA	0.73	1.96	4.82	10.09	16.6	$1.8 \times 10^8$	-23.0
BA	0.80	2.19	5.86	13.96	18.1	$2.4 \times 10^9$	-17.8

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

The overall first order rate constants,  $k_1$  (sec<sup>-1</sup>), 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),  $E_a = \frac{1}{2}(E'_a + E_p + E_A - E_t)$ . The activation energy,  $E_t$ , for the radical-radical reaction (12) is negligible and  $E'_a$  and  $E_p$  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,  $R-\dot{C}=O$ , with PP may be expected to be in the order,  $CH_3-\dot{C}=O > CH_3-CH_2-\dot{C}=O > CH_3-CH_2-CH_2-\dot{C}=O$  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  $\Delta S^\ddagger$  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<sup>19,20</sup> requires the presence of catalysts like  $Ag^+$  to effect appreciable oxidation of aldehydes and the oxidizing trend observed is peroxydiphosphate > peroxydisulphate. The same order of reactivity was observed in the oxidation of  $VO^{2+}$  by Edwards *et al.*<sup>9</sup> On the basis of the redox potential, -2.07 V for peroxydiphosphate<sup>21</sup> and -2.01 V for peroxydisulphate<sup>22</sup>, 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.*<sup>9</sup> have pointed out, may be a kinetic rather than a thermodynamic one.

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