Research Article

Kinetics of silver(I)-catalyzed oxidation of allyl alcohol by peroxodiphosphate in acetate buffers

Priyamvada SHARMA, Riya SAILANI, Deepmala PAREEK, Chandra Lata KHANDELWAL[*]
Department of Chemistry, University of Rajasthan, Jaipur, India

Abstract: The kinetics and mechanism of silver(I)-catalyzed oxidation of allyl alcohol with peroxodiphosphate in acetate buffers have been studied. The rate is independent of allyl alcohol concentration. The effect of other reaction parameters such as hydrogen and acetate ions has also been studied. The rate law accounting for all experimental observations corresponds to the proposed mechanism. The energy and entropy of activation have also been evaluated by employing Eyring plots.

Key words: Kinetics, mechanism, oxidation, allyl alcohol, peroxodiphosphate

1. Introduction

Peroxodiphosphate (PDP) is considered to be isoelectronic and isostructural to peroxydisulfate.[1] PDP has been found to act as an oxidizing agent both in acid[2−13] and alkaline[14] media. Authors have extensively reviewed oxidation reactions of PDP and also the nature of its pH-dependent species and their interactions with various types of inorganic substrates.[15−21] Trace-metal ion catalysts including silver(I) are also reported in oxidation reactions of PDPs.[22−30] Since oxidation of water catalyzed by silver(I) in PDP oxidation reactions has been reported,[31] silver(I) catalysis of other substrates in such reactions has been of much interest.

Hepatotoxicity of allyl alcohol involves its bioactivation to acrolein and subsequent protein sulfhydryl loss and lipid peroxidation. Exposure of yeast cells to allyl alcohol results in intracellular production of acrolein.

However, operation of silver(I) as a catalyst is still not well defined. From the studies reported so far, the following three important factors are required to be attended to in much more detail.

1) Are silver(I)-catalyzed reactions of PDP in acid medium controlled by a hydrolytic step of PDP?

2) PDP undergoes hydrolysis in acid medium yielding the hydrolyzed product peroxomonophosphate, which itself is also a strong oxidizing agent. Thus, under acidic conditions, the rate should be controlled by a hydrolytic step rather than the interaction between PDP and the substrate.

3) Acetate is considered to be a medium of choice in which negligible hydrolysis of the oxidant occurs. Thus, the reactions of PDP have been kinetically analyzed in acetate buffers where the catalytic role of silver(I) can be exclusively delineated. In oxidation of allyl alcohol PDP has been chosen in acetate buffers to understand the role of silver(I) as a catalyst.

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[*]Correspondence: khandelwal_cl@yahoo.in

Most of the kinetic studies of oxidation of unsaturated alcohols have been made in the presence of heterogeneous catalysts.[32−34] Transition metal ions such as Ru(III),[35,36] Os(VIII), Pd(III),[37] and Ru(II) were also employed as homogeneous catalysts. There is ambiguity regarding the oxidation products of these unsaturated alcohols with metal ion oxidants in solution.

These were certain observations that prompted us to undertake the kinetic study of the title reaction with the purpose of finding out the kinetic pattern of the oxidation of allyl alcohol by PDP apart from identification of its oxidation products and dependence of the rate on hydrogen ion concentration.

2. Results and discussion

2.1. Preliminary test

Reaction did not occur for 24 h in the absence of Ag(I); however, the addition of Ag(I) made the reaction proceed at a measurable rate. The kinetics of the catalyzed reaction were studied under pseudo-order conditions with the substrate at least at 10 times in excess over PDP.

2.2. Peroxodiphosphate dependence

The dependence of k_{obs} on PDP was studied by varying in the range of 1.0–5.0 $\times$ 10^{-3} mol dm^{-3}. The k_{obs} values did not depend on PDP, confirming first-order dependence in PDP (Figure 1) in agreement with the experimental rate law:
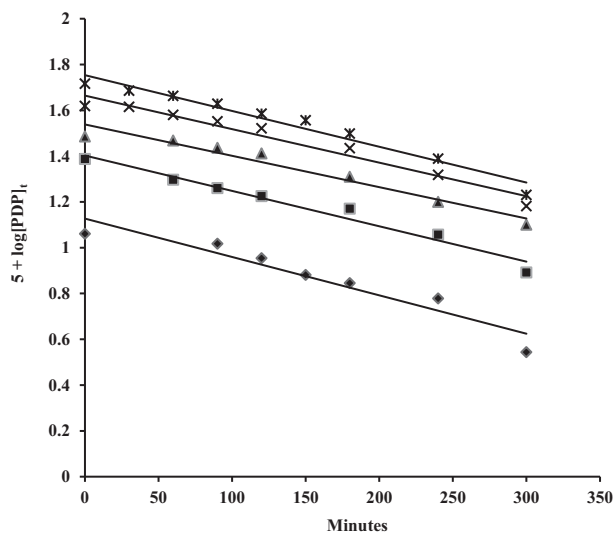
$$-\frac{d[PDP]}{dt} = k_{obs}[PDP]_t$$

Figure 1. Pseudo-first-order plots in silver(I)-catalyzed oxidation of allyl alcohol by peroxodiphosphate. [Allyl Alc.] = 0.1 mol dm^{-3}; [Ag(I)] = 1 $\times$ 10^{-3} mol dm^{-3}; pH = 4.68. [PDP] = (1) 1.0 $\times$ 10^{-3}; (2) 2.0 $\times$ 10^{-3}; (3) 3.0 $\times$ 10^{-3}; (4) 4.0 $\times$ 10^{-3}; (5) 5.0 $\times$ 10^{-3} mol dm^{-3}; T = 45 $^{\circ}$C.

2.3. Allyl alcohol dependence

A variation in allyl alcohol from 3 $\times$ 10^{-2} to 7.5 $\times$ 10^{-2} mol dm^{-3} showed the rate of the reaction to be independent of allyl alcohol, showing zero order with respect to alcohol.

2.4. Silver(I) dependence

A variation in Ag(I) showed the first order in Ag(I) and the plot of k_{obs} versus Ag(I) was passing through the origin (Figure 2) in agreement with $k_{obs} = k_{cat}$ [Ag(I)]. Thus, the rate law includes [PDP], [Ag(I)], and allyl alcohol:

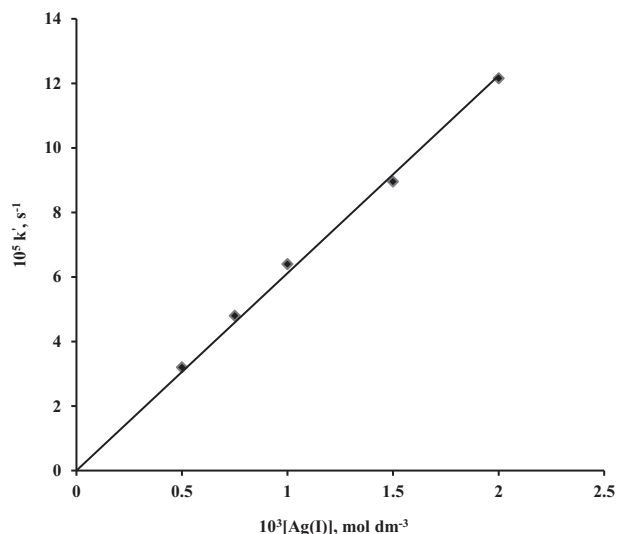$$-\frac{d[PDP]}{dt} = k_{obs}\,[PDP]\,[Ag(I)]$$

Figure 2. Variation of silver(I) in allyl alcohol and peroxodiphosphate reaction. [Allyl Alc.] $= 0.1$ mol dm^{-3}; [PDP] $= 2 \times 10^{-3}$ mol dm^{-3}; pH $= 4.68$; T $= 45$ °C.

2.5. pH dependence

The reaction was also studied at different pH levels by changing the ratio of acetic acid and acetate ions, fixing the concentration of acetate ions at 40, 45, and 50 °C. The rate increases with increasing pH.

2.6. Variation of sodium acetate

Sodium acetate was varied under first-order conditions of the reaction taking silver(I) to be 2×10^{-3} mol dm^{-3} at [I] $= 1.0$ mol dm^{-3} (ionic strength (I) was maintained constant by employing NaNO$_3$) at pH levels of 4.68, 5.02, and 5.20, respectively. The rate of the reaction increases with increasing concentration of sodium acetate. However, pH variation (Figure 3) was limited for two main reasons: first, pH cannot be taken >5.20 in view of the fact that white turbidity appeared in the reaction due to precipitation of silver phosphate. Second, pH of <4.68 cannot be taken as the hydrolysis of PDP ensues.

2.7. Effect of ionic strength

The effect of ionic strength was studied by employing sodium nitrate (NaNO$_3$) (0.2 to 1.0 mol dm^{-3}) keeping fixed concentrations of other reaction ingredients at pH 4.68 and 45 °C. The rate decreases with increasing ionic strength (Figure 4).
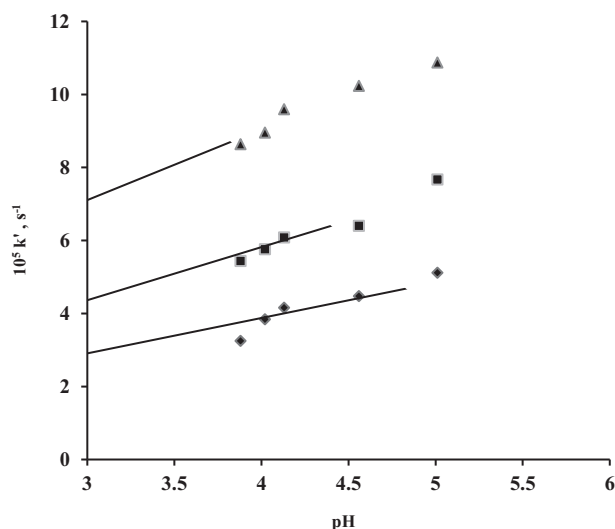
Figure 3. Variation of pH in silver(I)-catalyzed oxidation of allyl alcohol by peroxodiphosphate. [Allyl Alc.] = 0.1 mol dm^{-3}; [PDP] = 2 × 10^{-3} mol dm^{-3}; [Ag(I)] = 2 × 10^{-3} mol dm^{-3}; [I] = 1.0 mol dm^{-3}; T= 40 45, and 50 °C.
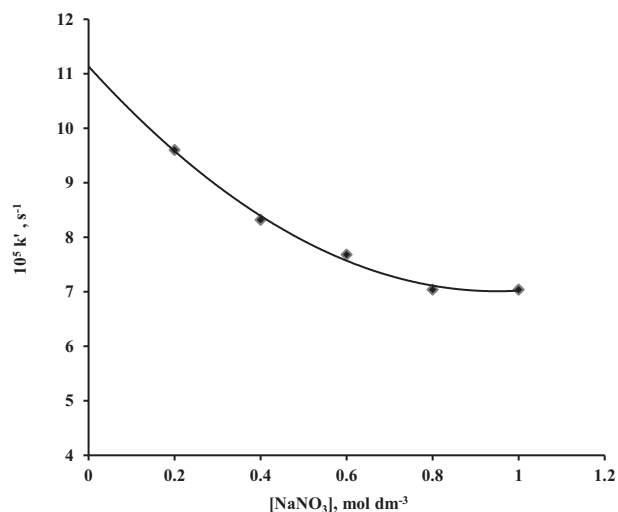
Figure 4. Ionic strength dependence in silver(I)-catalyzed oxidation of allyl alcohol by peroxodiphosphate. [Allyl Alc.] = 0.1 mol dm^{-3}; [PDP] = 2 × 10^{-3} mol dm^{-3}; [Ag(I)] = 2 × 10^{-3} mol dm^{-3}; T = 45 °C.

2.8. Effect of temperature

The effect of temperature on the rate of the reaction was studied at 40, 45, and 50 °C respectively, keeping constant concentrations of other reaction ingredients at pH 4.68. The energy and entropy of activation were calculated by employing the Eyring equation to be 58.2 ± 0.34 kJ mol^{-1} and –92.8 ± 1.8 J K^{-1} mol^{-1}, respectively (Figure 5).
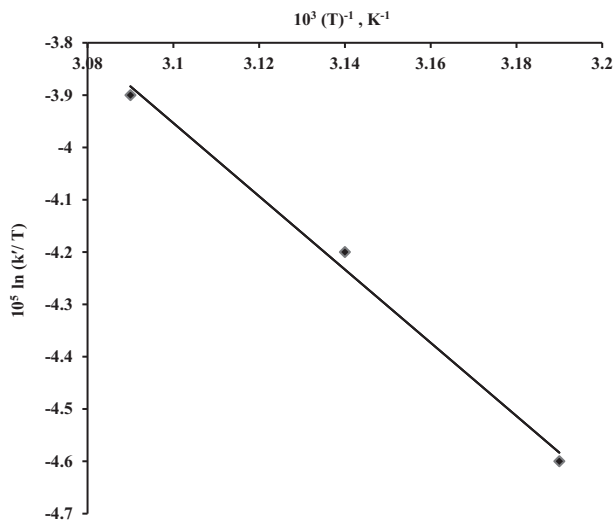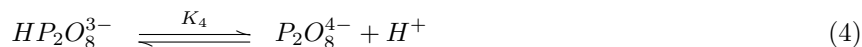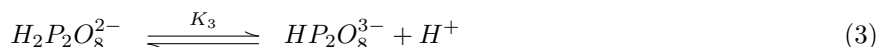

Figure 5. Eyring plot of (T)$^{-1}$ versus ln (k′ / T). [Allyl Alc.] = 0.1 mol dm^{-3}; [PDP] = 2 × 10^{-3} mol dm^{-3}; [Ag(I)] = 2 × 10^{-3} mol dm^{-3}; [I] = 1.0 mol dm^{-3} and pH 4.68.

2.9. Test of free radicals

The test of free radicals was negative as the substrate itself, being an unsaturated monomer, does not undergo polymerization. This was further tested by adding an excess concentration of acrylic acid but without any white sediment, which further ruled out any possibility of participation of free radicals under the experimental conditions of the reaction.

2.10. Discussion

PDP species are pH-dependent and are governed by equilibrium as in Eqs. (1)–(4) in aqueous solutions.
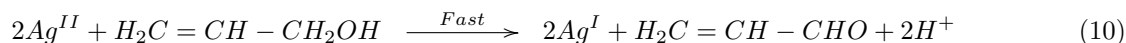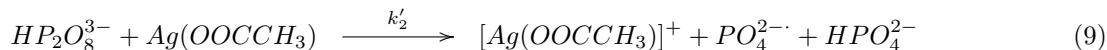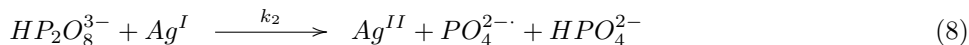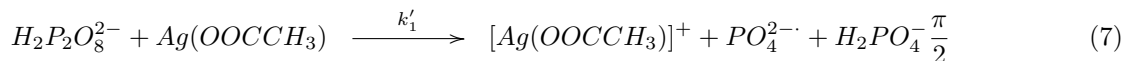
$$H_4P_2O_8 \quad \underset{\longleftarrow}{\overset{K_1}{\rightleftharpoons}} \quad H_3P_2O_8^- + H^+ \tag{1}$$

$$H_3P_2O_8^- \quad \underset{\longleftarrow}{\overset{K_2}{\rightleftharpoons}} \quad H_2P_2O_8^{2-} + H^+ \tag{2}$$

$$H_2P_2O_8^{2-} \quad \underset{\longleftarrow}{\overset{K_3}{\rightleftharpoons}} \quad HP_2O_8^{3-} + H^+ \tag{3}$$

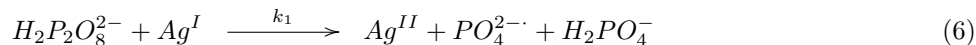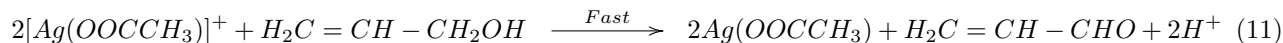$$HP_2O_8^{3-} \quad \underset{\longleftarrow}{\overset{K_4}{\rightleftharpoons}} \quad P_2O_8^{4-} + H^+ \tag{4}$$
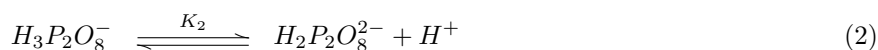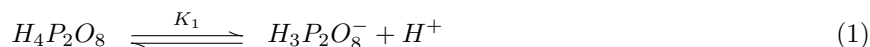
If pH is any guide and K_{3is} reported[38] to be $6.6 \pm 0.3 \times 10^{-6}$ mol dm^{-3} at 25 °C, $HP_2O_8^{3-}$ is more reactive than $H_2P_2O_8^{2-}$ species. Furthermore, the acetate ion affects the rate of the reaction via an equilibrium step as in Eq. (5), and the $Ag(OOCCH_3)$ species is more reactive than $Ag(I)$.

$$Ag^+ + {}^-OOCCH_3 \quad \underset{\longleftarrow}{\overset{K}{\rightleftharpoons}} \quad Ag(OOCCH_3) \tag{5}$$

Here K is 5.4 dm^3 mol^{-1}.

Since allyl alcohol is not protonated under experimental conditions and the rate is also independent of alcohol concentration, the following mechanism consisting of the steps in Eqs. (6)–(11) can be envisaged to account for the kinetics observations of the title reaction.

$$H_2P_2O_8^{2-} + Ag^I \quad \xrightarrow{k_1} \quad Ag^{II} + PO_4^{2-\cdot} + H_2PO_4^- \tag{6}$$

$$H_2P_2O_8^{2-} + Ag(OOCCH_3) \quad \xrightarrow{k_1'} \quad [Ag(OOCCH_3)]^+ + PO_4^{2-\cdot} + H_2PO_4^- \frac{\pi}{2} \tag{7}$$

$$HP_2O_8^{3-} + Ag^I \quad \xrightarrow{k_2} \quad Ag^{II} + PO_4^{2-\cdot} + HPO_4^{2-} \tag{8}$$

$$HP_2O_8^{3-} + Ag(OOCCH_3) \quad \xrightarrow{k_2'} \quad [Ag(OOCCH_3)]^+ + PO_4^{2-\cdot} + HPO_4^{2-} \tag{9}$$

$$2Ag^{II} + H_2C = CH - CH_2OH \quad \xrightarrow{Fast} \quad 2Ag^I + H_2C = CH - CHO + 2H^+ \tag{10}$$

$$2[Ag(OOCCH_3)]^+ + H_2C = CH - CH_2OH \xrightarrow{\quad Fast \quad} 2Ag(OOCCH_3) + H_2C = CH - CHO + 2H^+ \quad (11)$$

Acrolein was characterized to be the oxidation product of alcohol, which was not further oxidized under the experimental conditions.

Such a mechanism leads to the rate law of Eq. (12) or (13).

$$-\frac{d[PDP]}{dt} = \frac{(k_1[H^+] + k_2 K_3) + \{\left(k_1' K[H^+] + k_2' K K_3\right)[^-OOCCH_3]\}[PDP][Ag^I]}{(K_3 + [H^+])\left(1 + K[^-OOCCH_3]\right)} \quad (12)$$

Here [PDP] and [Ag^I] are the gross analytical concentrations of PDP and silver(I), respectively.

$$k = \frac{(k_1[H^+] + k_2 K_3) + \left(k_1' K[H^+] + k_2' K K_3\right)[^-OOCCH_3]}{(K_3 + [H^+])\left(1 + K[^-OOCCH_3]\right)} \quad (13)$$

Here k is an observed second-order rate constant.

A plot of k $(K_3 + [H^+])$ $(1 + K[^-OOCCH_3])$ versus $[^-OOCCH_3]$ was made at different concentrations of pH, which yielded a straight line with nonzero intercepts (Figure 6). The intercept (I) and gradient (G) from this plot were evaluated as given by Eqs. (14) and (15), respectively:
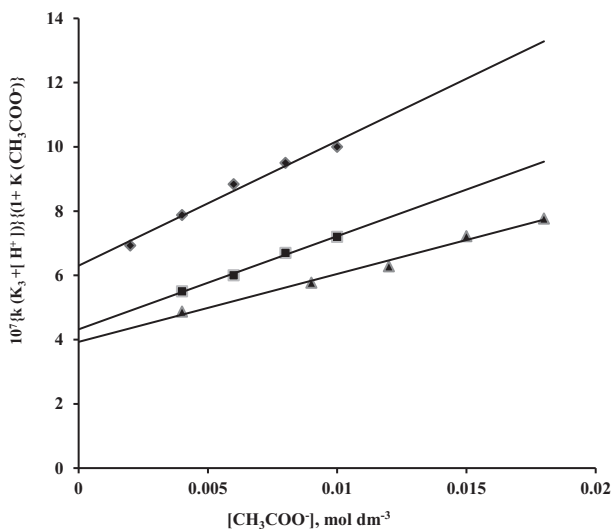

Figure 6. A plot of $\{$k $(K_3 + [H^+])\}\{(1 + K (CH_3COO^-)\}$ versus $[CH_3COO^-]$ in silver(I)-catalyzed oxidation of allyl alcohol by peroxodiphosphate. [Allyl Alc.] = 0.1 mol dm^{-3}; [PDP] = 2 × 10^{-3} mol dm^{-3}; [Ag$^+$] = 2 × 10^{-3} mol dm^{-3}; [I] = 1.0 mol dm^{-3}; pH = 4.68 5.02 5.20; T = 45 °C.

$$I = k_1[H^+] + k_2 K_3 \quad (14)$$

$$G = k_1' K[H^+] + k_2' K K_3 \quad (15)$$

Further plots of (I) versus $[H^+]$ from Eq. (14) and (G) versus $[H^+]$ from Eq. (15) respectively were made, which also yielded straight lines with nonzero intercepts in each case (Figures 7 and 8). k_1 and $k_2 K_3$ from the slope and intercept of Figure 7 were calculated to be 1.67×10^{-2} s^{-1} and 2.81×10^{-7} dm^3 mol^{-1} s^{-1}, respectively. Similarly, $k'_1 K$ and $k'_2 KK_3$ were calculated from the slope and intercept of Figure 8 respectively to be 1.11 s^{-1} and 1.61 dm^3 mol^{-1} s^{-1} at 45 $^\circ$C and I = 1.0 mol dm^{-3} (Table).
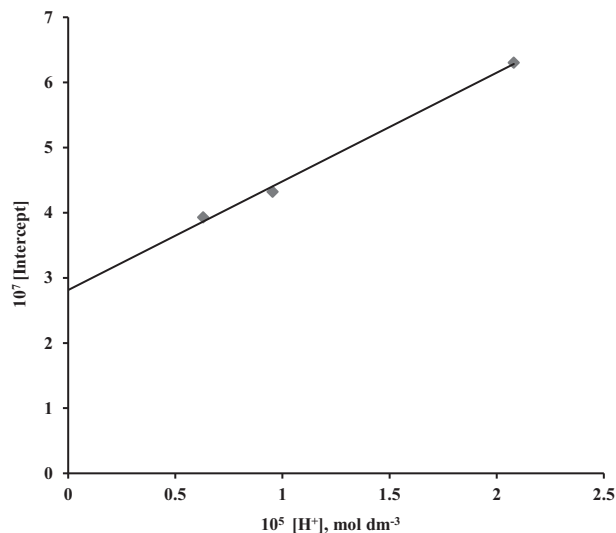

Figure 7. A plot of intercept versus hydrogen ion concentration in silver(I)-catalyzed oxidation of allyl alcohol by peroxodiphosphate.
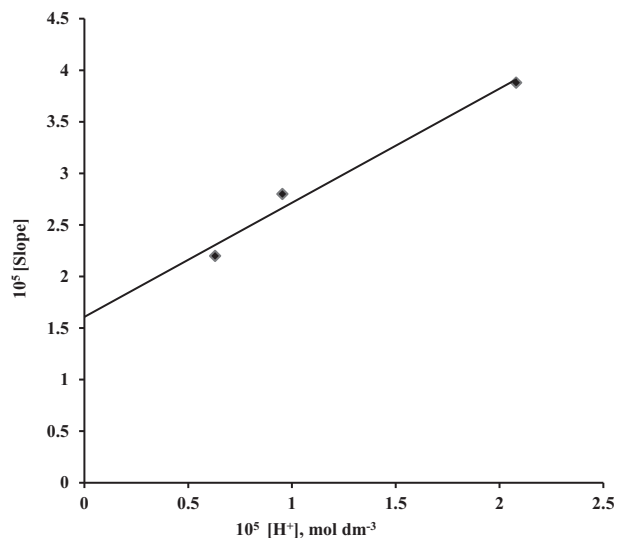

Figure 8. A plot of slope (G) versus hydrogen ion concentration in silver(I)-catalyzed oxidation of allyl alcohol by peroxodiphosphate.

Table. Pseudo-first-order (k', s^{-1}) and second-order rate constants (k, dm^3 mol^{-1} s^{-1}) in silver(I)-catalyzed oxidation of allyl alcohol by peroxodiphosphate in acetate buffers at pH 4.68 and 45 $^\circ$C.

10^3 [PDP] mol dm^{-3}	10^3 [Ag^I] mol dm^{-3}	10^5 (k$'$) s^{-1}	10^2 (k) dm^3 mol^{-1} s^{-1}
1.0	1.0	6.39	6.39
2.0	1.0	6.39	6.39
3.0	1.0	6.39	6.39
4.0	1.0	6.39	6.39
5.0	1.0	6.39	6.39
2.0	0.5	3.198	6.4
2.0	0.75	4.797	6.4
2.0	1.0	6.397	6.4
2.0	1.5	8.958	6.2
2.0	2.0	12.154	6.1

These results are quite comparable to those obtained earlier for the decomposition of water. Since the rate is independent of the concentration of allyl alcohol, the operation of catalyst redox cycle Ag^I/Ag^{II} appears to exhibit the rate to be independent of the substrate concentration. Furthermore, the rates of oxidation of water[31] as well as that of allyl alcohol with PDP respectively are nearly in agreement if temperature and ionic strength are taken into account.

Kinetic evidence[39] for the complexation between Ag(I) and PDP was reported earlier. The rate increases

with decreasing hydrogen ion concentration that certainly corresponds to increased reactivity of $HP_2O_8^{2-}$ species of PDP.

Silver(III) is known to be formed via disproportionation of silver(II).

$$2Ag(II) \rightleftharpoons Ag(I) + Ag(III) \tag{16}$$

The oxidation of allyl alcohol by Ag(III) through hydride ion transfer from α-carbon of alcohol is also a possibility, but such a possibility was abandoned in view of the following facts:

1) The rate is not retarded by Ag(I). Moreover, the concentration of silver(I) employed in the reaction will push back this equilibrium as in Eq. (16) to silver(II) to a large extent with lesser probability of formation of silver(III). Also, the acid concentrations employed in the reaction are such that Ag(III) cannot be stabilized and no stabilizing agent is present. As soon as it is formed, it immediately reacts with silver(I) in the solvent cage to form Ag(II) and has no chance to diffuse out of the cage.

2) When 2,2'-bipyridyl was added to the reaction mixture in acetate buffers at ice-cold temperature, an orange color appeared for a fraction of a second, probably indicating formation of Ag^{II} – bipyridyl transient species, whereas no such color was observed in the absence of silver(I) or in the presence of allyl alcohol. Since silver(II) and silver(III) both are known to give an orange complex with 2,2'-bipyridyl, the distinction between Ag(II) and Ag(III) is difficult, the temperature being significantly low. However, it will not oxidize silver(I) to silver(III). Thus, it is possible that the orange color is only due to the formation of silver(II).

Thus, ruling out the possibility of formation of silver(III), the mode of electron transfer from the substrate to the oxidant via the Ag(I)/Ag(II) catalyst redox cycle appears to be a reasonable mode of reaction. The reaction events can be understand by the following Scheme.
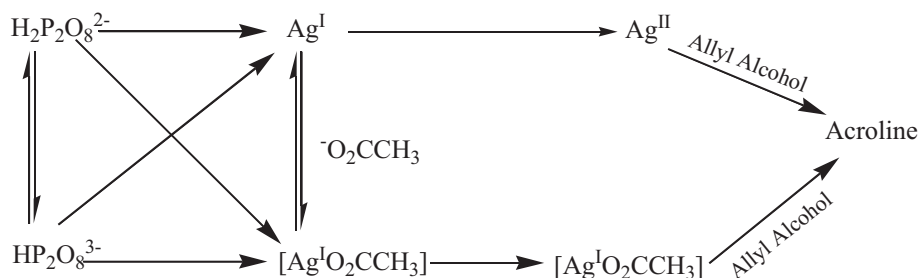
Scheme. Reaction events.

3. Experimental

3.1. Materials and methods

PDP was a gift sample from the FMC Corporation (USA). Its solution was prepared by dissolving a requisite amount of PDP salt in doubly distilled water. Since the solution is not stable, it was always prepared fresh. Then it was standardized iodometrically.[40]

Other reagents such as allyl alcohol were used after distillation under vacuum and then kept in a glass-stoppered bottle painted black from the outside to block the effect of diffused light.

3.2. Kinetic procedure

The reactions were carried out taking all the reagents except PDP in glass-stoppered Erlenmeyer flasks, which were painted black from the outside. These flasks were suspended in a water-bath thermostated at ± 0.1 °C until and unless stated otherwise. The requisite amount of temperature-preequilibrated solution of PDP was added to the reaction mixture and the time of initiation was noted when 50% of the solution from the pipette was discharged into the reaction flask.

The reaction mixture was shaken well and then a known aliquot (5 cm^3) of the reaction mixture was withdrawn periodically for assaying the remaining PDP iodometrically in the presence of a mixed catalyst [Cu(II) + Fe(III)]. The iodine liberated by the catalyst was accounted for in subsequent calculations of PDP concentrations.

Since the reaction was studied under pseudo-first-order conditions and thus plots of log[PDP]$_t$ versus time were made, pseudo-first-order rate constants were calculated.

3.3. Stoichiometry and product analysis

Stoichiometry of the reaction was studied under kinetic conditions by measuring PDP iodometrically at different times. The results indicate that a mole of PDP is required for a mole of substrate and thus the stoichiometry of the reaction corresponds to the reaction as represented by Eq. (17).
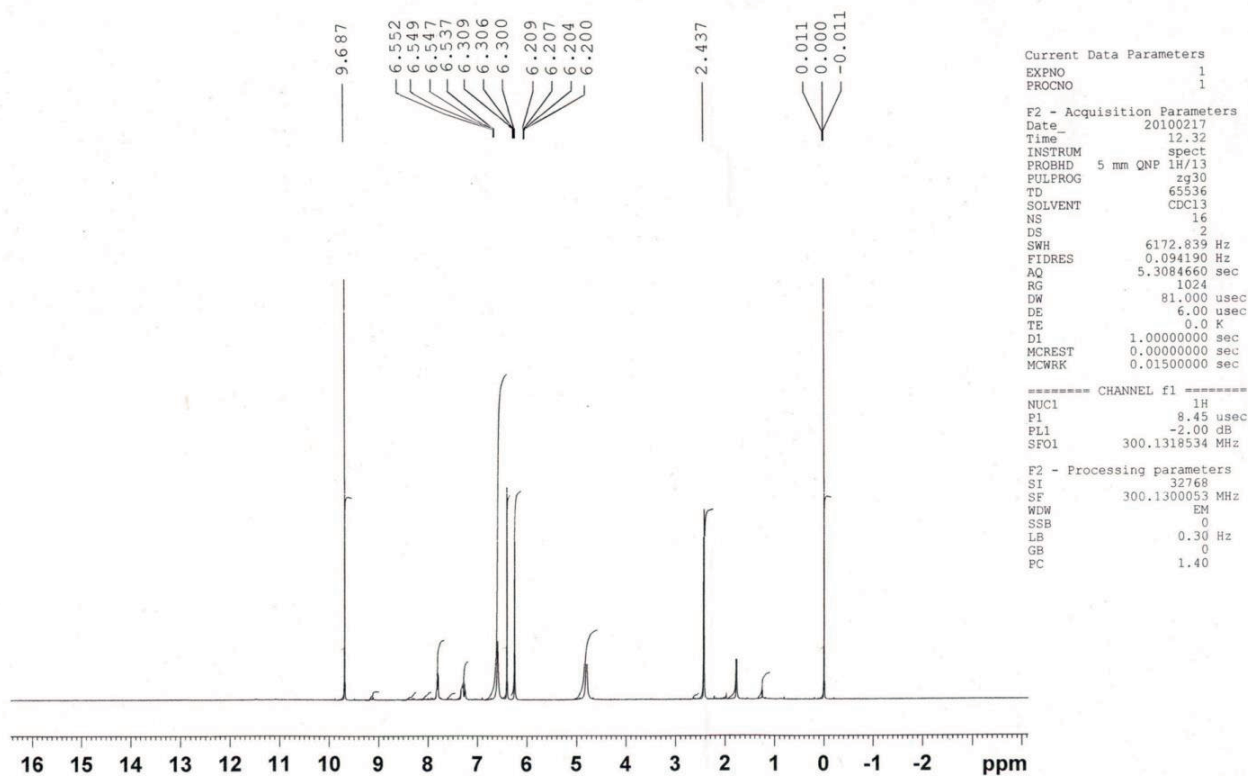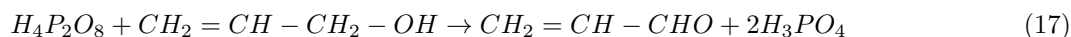
$$H_4P_2O_8 + CH_2 = CH - CH_2 - OH \rightarrow CH_2 = CH - CHO + 2H_3PO_4 \qquad (17)$$

Figure 9. ^{1}H NMR spectrum of acrolein.

The oxidation product of allyl alcohol was qualitatively established to be allyl aldehyde by testing with 2,4-dinitrophenyl hydrazine, which yielded a yellow-orange precipitate of 2,4-dinitrophenylhydrazone derivative and was established spectrally. Acrolein was less susceptible to further oxidation because of the stability provided by the resonance.

$$CH_2 = CH - CH = O \quad \rightleftharpoons \quad \overset{+}{C}H_2 - CH = CH\overset{-}{O} \tag{18}$$
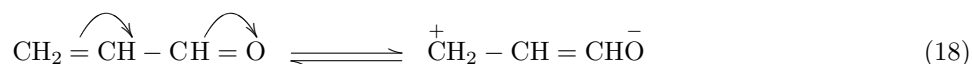
The ^{1}H NMR spectrum of acrolein was obtained in CDCl$_3$ employing a 300 MHz spectrometer using TMS as a reference. The NMR signal at $\delta 9.687$ (s) ppm is due to the -CHO group of aldehyde. One singlet at $\delta 6.3$ ppm is due to the -CH group trans to the aldehydic group. Two singlets are obtained at $\delta 6.209$ ppm and $\delta 6.207$ ppm, showing the presence of the -CH group (Figure 9).

IR spectra of 2,4-dinitrophenylhydrazone of acrolein were obtained, in which 3280 cm^{-1} was due to the -NH group; 3080 cm^{-1} was due to unsaturation; 1600 cm^{-1} was due to the -C=N group; and 1500, 1420, and 1340 cm^{-1} (aromatic peaks) and 920, 840, and 720 cm^{-1} were due to the -CH group (Figure 10).
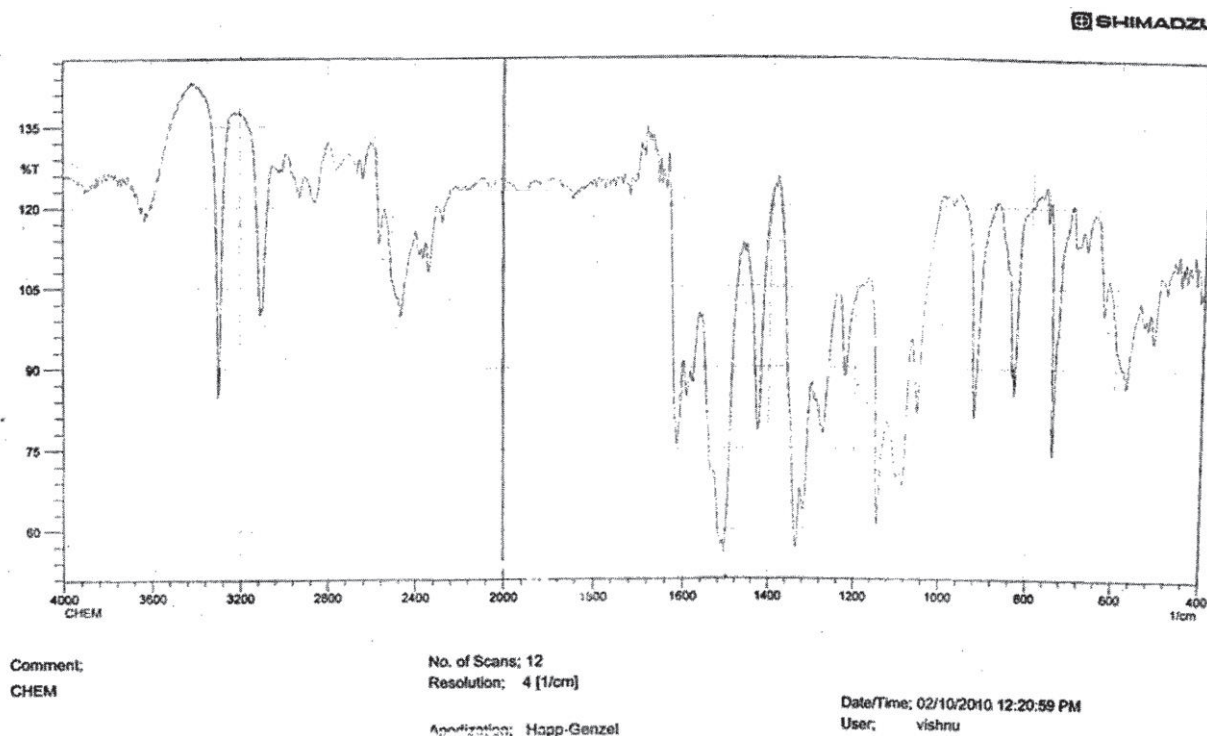

Figure 10. IR spectrum of 2,4-dinitrophenylhydrazone of acrolein.

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