Kinetics & Mechanism of Ag+-catalysed Oxidation of 1,3-Propanediol by Peroxydisulphate Ion — A Reinvestigation

S. P. Srivastava & Anil Kumar

Department of Chemistry, University of Roorkee
Roorkee 247672

The Ag+-catalysed oxidation of 1,3-propanediol by peroxydisulphate ion has been found to yield 3-hydroxypropionaldehyde by a first order process in the first stage, which is followed by the oxidation of this aldehyde in the next stage along with the oxidation of diol. A mechanism different from that reported by Bakore and Menghani [Curr. Sci., 37 (1968), 641] has been proposed on the basis of the product formed and kinetic study.

THE kinetics of Ag+-catalysed oxidation of 1,3-propanediol by peroxydisulphate ion was investigated by Bakore and Menghani[1] who suggested a mechanism based on the formation of formaldehyde and acetaldehyde. However, a reinvestigation of the reaction, the results of which are reported in this note, shows that the product formed is 3-hydroxypropionaldehyde, thus leading to a mechanism different from that reported by Bakore and Menghani[1].

The progress of the reaction was followed by estimating the unreacted $K_2S_2O_8$ iodometrically employing the method of Szabo et al.[2] as modified by Khulbe and Srivastava[3].

The absence of HCHO as the reaction product was confirmed by the negative chromotropic acid test in the reaction mixture as well as in the distillate obtained under reduced pressure. The solid 2,4-DNP derivative of the distillate, prepared in $HCl-H_2O$ mixture[4], melted at 151° and was found to be TLC pure (silica gel). That the 2,4-DNP derivative is not that of acetaldehyde was confirmed by the spectral data. Its NMR spectrum (chemical shift in δ-scale) showed a high field two-proton triplet 3·98 ($J = 5·0$ Hz) which might be due to methylene protons flanked on either side by a hydroxy group and another methylene group. A quartet at 2·7 ($J = 5·0$ Hz) clearly confirmed the presence of one methylene and methine groups in its neighbourhood. The total number of ten protons confirmed clearly indicated that 2,4-DNP derivative is derived from 3-hydroxypropionaldehyde

$$[OH.CH_2.CH_2.CH=N-NHC_6H_3(NO_2)_2(2,4\text{-position})]$$

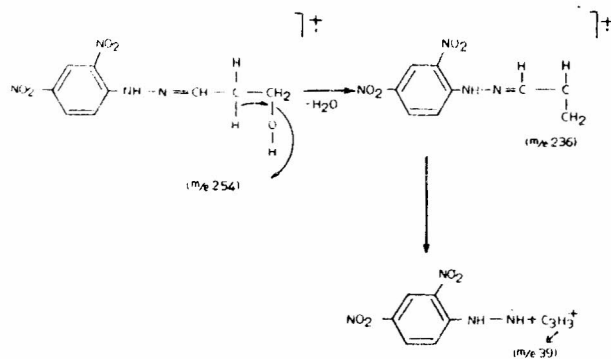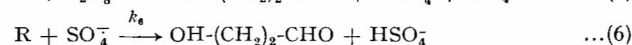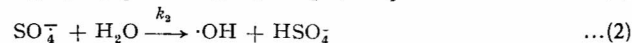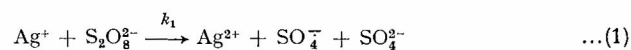The IR spectrum of the 2,4-DNP derivative showed peaks at 3280 (ν-NH) and 3600-3200 (br, ν-OH).

Chart 1

Formation of 3-hydroxypropionaldehyde was confirmed by a study of the mass spectrum of the 2,4-DNP derivative. The parent ion peak at m/e 254 agrees with the molecular weight. The base peak was found at m/e 39 $(C_3H_3^+)$. The other prominent peak was observed at m/e 236[5,6] which is due to loss of a water molecule as depicted in Chart 1.

Kinetic runs at four different temperatures showed that the reaction consists of two independent first order reactions: (i) oxidation of the diol to corresponding hydroxyaldehyde (stage-A) and (ii) oxidation of the aldehyde to corresponding hydroxy acid (stage-B). However, the rate constant for stage-B is less than that of first reaction which may be due to inhibition in later stages, but the exact nature of the inhibiting process could not be worked out. At low temperature a slight induction period was also observed.

The specific rate at four temperatures along with the energy parameters calculated therefrom are given in Table 1.

The general similarity of this reaction with other Ag+-catalysed peroxydisulphate reactions suggested that the following mechanism (Eqs. 1-6) for stage-A is followed:

$$Ag^+ + S_2O_8^{2-} \xrightarrow{k_1} Ag^{2+} + SO_4^- + SO_4^{2-} \qquad \ldots(1)$$

$$SO_4^- + H_2O \xrightarrow{k_2} \cdot OH + HSO_4^- \qquad \ldots(2)$$

$$S + Ag^{2+} \xrightarrow{k_3} R + Ag^+ \qquad \ldots(3)$$

$$S + Ag^{2+} \xrightarrow{k_4} R + H_2O \qquad \ldots(4)$$

$$R + S_2O_8^{2-} \xrightarrow{k_5} OH\text{-}(CH_2)_2\text{-}CHO + HSO_4^- + SO_4^- \qquad \ldots(5)$$

$$R + SO_4^- \xrightarrow{k_6} OH\text{-}(CH_2)_2\text{-}CHO + HSO_4^- \qquad \ldots(6)$$

where S stands for $OH\text{-}(CH_2)_3\text{-}OH$ and R stands for $OH\text{-}CH_2\text{-}CH_2\text{-}CH_2O$.

Scheme 1

TABLE 1 — ENERGY PARAMETERS

{[1,3-Propanediol] $= 1·0 \times 10^{-2}M$; $[K_2S_2O_8] = 2·0 \times 10^{-2}M$; $[AgNO_3] = 1·0 \times 10^{-3}M$; temp. $= 35°$}

Reaction stage	$k = (k_{obs.}/C_{Ag^+}) \times 10^2$ litres mole^{-1} sec^{-1}	$\Delta E\ddagger$ kcal mole^{-1}	Frequency factor (A) litres mole^{-1} sec^{-1}	$\Delta S\ddagger$ e.u.
A	13·30	(8·8 ± 0·3)	(2·50 ± 0·02) × 10^5	(−35·90 ± 0·05)
B	7·10	(11·6 ± 0·3)	(1·32 ± 0·03) × 10^7	(−28·03 ± 0·04)

Steps (1) and (2) of Scheme 1 have been proposed by a large number of workers[7-12] and the hydrogen abstraction from the organic substrate to yield the radical is considered to be the next possible step[13]. The formation of bivalent silver ion in peroxydisulphate redox processes has been shown by McMillan and Smaller[14] and the existence of SO_4^- and $\cdot OH$ in the peroxydisulphate redox reactions have recently been proved by the ESR studies[15].

It can safely be assumed that the next stage, namely the oxidation of hydroxyaldehyde to the corresponding hydroxy acid, follows a similar mechanism.

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Kinetics & Mechanism of Ag+–catalysed Oxidation of Dicarboxylic Acids by Potassium Peroxydisulphate

P. S. RADHAKRISHNAMURTI & B. R. K. SWAMY

Department of Chemistry, Berhampur University Berhampur 760007

Kinetics of oxidation of saturated dicarboxylic acids by potassium peroxydisulphate catalysed by Ag+ is reported under varying acidities, [substrate] and [Ag+]. The results indicate that these oxidations are first order in [oxidant] and [Ag+] but show zero order dependence on the [substrate]. Catalytic influence of Cu³⁺ and Hg²⁺ in H₂SO₄, HClO₄ and HCl media have also been investigated. A mechanism and rate law consistent with the results obtained is postulated.

THE kinetics of peroxydisulphate oxidations, both Ag+ catalysed[1-6] and uncatalysed[7], of a large number of organic substrates including dicarboxylic acids have been reported. We have recently reported the oxidation of saturated dicarboxylic acids by Ce^{4+} catalysed by Ag+ (ref. 8). In continuation of this work, the kinetics of Ag+-catalysed oxidation of succinic, adipic, pimelic, suberic and sebacic acids by peroxydisulphate under varying conditions are reported in this note.

Standard solution of recrystallized potassium peroxydisulphate was always prepared fresh and standardized by iodometric method. Standard solutions of recrystallized dicarboxylic acids (AR) were prepared by direct weighing. The reaction was carried out by running a calculated volume of $K_2S_2O_8$ solution into the thermostated ($\pm 0.1°$) reaction vessel containing the substrate and estimating the unreacted $K_2S_2O_8$ by the iodometric method. The decomposition of peroxydisulphate was followed separately and necessary corrections have been made in computing the rate constants. The rate constants have been computed by the usual tangential method.

The reactions are first order in peroxydisulphate as seen by the linear plots of $\log (a-x)$ versus time. The reactions are independent of the nature of the substrate and [substrate], indicating zero order dependence on the substrate (Tables 1 and 2). Though there appears to be very slight deviation in rate constants with increasing [substrate] the order with respect to substrate comes to be 0·08 which can be taken as zero order.

For a threefold increase in the [acid] there is a slight decrease in the rate (Table 1) which may be due to the increase in ionic strength. Such slight decrease was observed earlier by Gupta and Sengar[9] in the reaction between persulphate and silver ion. Surprisingly the reactions are accelerated at pH 4·5 (Table 2). Further in the absence of Ag+, the reactions in H_2SO_4 medium are very sluggish, whereas the uncatalysed reactions in the presence of HCl proceed fairly well and first order rate constants are reported in Table 3. Even in HCl medium and in the absence of catalyst the reactions are zero order with respect to the [substrate].

An increase in [Ag+] increases the rate and a plot of $\log k$ vs $\log$ [Ag+] is linear with unit slope establishing the order as unity with respect to [Ag+]. It was thought worth while to study the catalytic effect of Cu^{2+} and Hg^{2+}. Surprisingly there was no reaction in presence of Cu^{2+} and Hg^{2+} in H_2SO_4 or $HClO_4$ media. But in HCl medium though there is no positive catalytic effect due to Hg^{2+} and Cu^{2+} the reactions are facile as compared to H_2SO_4 and $HClO_4$ media. Further, there is no dramatic catalysis in presence of Ag+ in $HClO_4$ medium as in the Ce^{4+} oxidations of saturated dicarboxylic acids in $HClO_4$ medium reported earlier.

Mechanism — Present evidences in literature point to the fact that in aqueous acid solutions it is more likely that Ag^{2+} ions exist rather than Ag^{3+} ions. Allen and his associates have shown that the equilibrium $2Ag^{2+} \rightleftharpoons Ag^+ + Ag^{3+}$ lies far to the left. The fraction of Ag^{3+} (likely to exist as AgO^+ in solution) has been estimated to be 0·03% of Ag^{2+}. Further, Yost has shown that Ag^{3+} may be formed by a direct interaction of Ag+ and $S_2O_8^{2-}$ followed by a rapid reaction of Ag^{3+} with water