Kinetic Study of Silver-Catalysed Oxidation of α-Hydroxy Monocarboxylic Acids - dl-Atrolactic, Isobutyric, Mandelic and Benzilic Acid by Potassium Peroxydisulphate

HAMBIR SINGH* and J. C. GOVIL

D. S. College, Aligarh

and

S. C. SAKSENA

Hindu College, Moradabad

The oxidation of dl-atrolactic, benzilic, mandelic and α-hydroxy isobutyric acids by peroxydisulphate in the presence of Ag(I) shows first order dependence on $[S_2O_8^{2-}]$ and [Ag(I)] and zero order dependence on [acid]. The first order specific reaction rate in case of all the acids decreases with an increase in $K_2S_2O_8$ concentration and increases with an increase in Ag(I) concentration. Allyl acetate and H^+ ion exert an inhibitory effect on the oxidation rate of the acids. The salt effect is negative and of exponential type. Various metal ions inhibit the reaction rate in the order $K^+ > Na^+ > Zn^{+2} > Mg^{+2} > Al^{+3}$. The stoichiometry in the reaction between the hydroxy acids and $S_2O_8^{2-}$ ion is 1:1. Various energy parameters have been calculated for all acids. The results have been explained by suitable reaction mechanism that the oxidation of α-hydroxy acids proceeds through C-C bond fission which results in decarboxylation giving rise to a carbonyl compound.

A survey of literature reveals that oxidation of α-hydroxy acids has been carried out by different oxidising agents[1-7]. The oxidation of mandelic acid[8], lactic acid[8,9] and malic acid[10] by peroxydisulphate ion catalysed by Ag^+ has also been reported. We undertook a systematic kinetic study of Ag^+ catalysed oxidation of mandelic acid (M.A.), α-hydroxyisobutyric acid (α-OH-I.B.A.), atrolactic acid (A.L.A.) by $S_2O_8^{2-}$ ion in aqueous medium and of benzilic acid (B.A.) in dioxane-water system because benzilic acid was sparingly soluble in H_2O.

Materials and Methods : All chemicals used were of AnalaR grade and the methods adopted for studying the oxidation rates were the same as described in our previous studies[11]. The specific reaction rate constant (k) has been evaluated by subtracting the specific rate (k_3) for silver catalysed self decomposition of peroxydisulphate from the observed specific rate (k_1) for the reaction. The concentration of all acids in the kinetic study was 0.1 M except α-hydroxyisobutyric acid which was 0.001 M.

Results

It was observed that a plot of log C vs time in case of each acid at four temperatures varying from 30 to 45° was linear which established the first order behaviour of reactions. A representative plot between log C vs time at 35° for each reaction is given in Fig. 1.

All the reactions showed first order dependence with respect to $[S_2O_8^{-2}]$ and $[Ag^+]$ and zero order with respect to [acid]. However, the first order specific

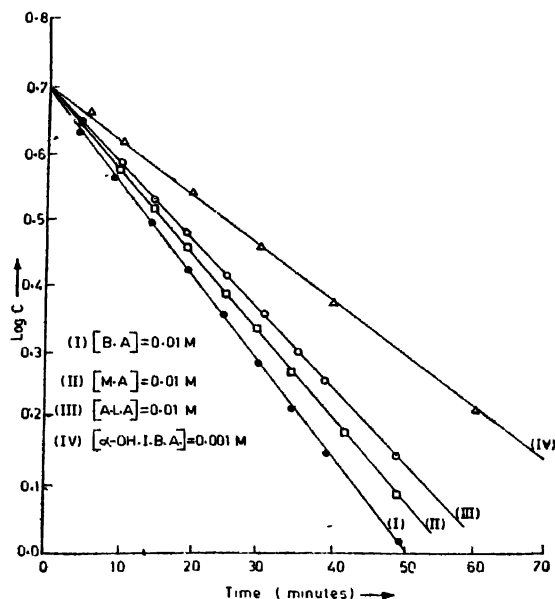reaction rate constant (k) in general maintains a decreasing tendency with increase of $[K_2S_2O_8]$ and

Fig. 1 : Temp. = 35°; $[K_2S_2O_8]$ = 0.01 M; $[AgNO_3]$ = 0.001 M

the following relationship is obeyed :

$$-\log k = a + m_1 \, [S_2O_8^{-2}]_0$$

where a is intercept and m_1 is the slope of the linear curve for a particular acid. Similar relation has also

TABLE 1

[AgNO₃]=0.001 M, [M.A.]=[A.L.A.]=[B.A.]=0.01 M
[α-OH.I.B.A.]=0.001 M   Temp.=35°

Reductant	a	m_1	$k_0 \times 10^8 min^{-1}$	m
M.A.	1.505	6.13	15.6	11.8
α-OH.I.B.A.	2.108	9.50	6.42	0.684
A.L.A.	1.552	13.71	17.4	4.00
B.A.	1.405	10.76	23.4	7.69

been obtained by Singh and Srivastava[11-13] in other silver catalysed oxidation reaction by peroxydisulphate ion. Keeping the concentration of $AgNO_3$ unchanged (0.001M), a and m_1 have been evaluated (Table 1) at 35°. In order to calculate the order of reaction with respect to $S_2O_8^{-2}$ ion, the concentration of K^+ ion was kept constant by adding calculated amounts of K_2SO_4. It was observed that the specific reaction rate increased with increase of $S_2O_8^{-2}$ ion concentration in case of

0.01 M $K_2S_2O_8$ and 0.001 M $AgNO_3$ for the reactions are shown in Table 2 along with the various energy parameters. The concentration of all acids were 0.01 M except α-hydroxyisobutyric acid which was 0.001 M. The rate of oxidation of the acids was found to follow the order B.A.>M.A.>A.L.A>α-OH.I.B.A.

All the reactions are characterised by a large negative entropy of activation and since the free energy of activation values are almost the same, the primary steps involved in all reactions should be the same as in other reactions[11-13] involving $S_2O_8^{2-}$ ion in presence of Ag(I) as catalyst.

Stoichiometry and analysis of products : It was found that one mole of $S_2O_8^{-2}$ reacted with one mole of different acids. The intermediate and final products of different reactions identified and isolated are as given below.

α-hydroxy acid	Products identified	Isolation of aldehyde or ketone (product) as
M.A.	Benzaldehyde and CO_2	benzaldehyde-2,4-dintrophenylhydrazone (m p. 239°)
α-OH-I.B.A.	Acetone and CO_2	acetone-2,4-dintrophenylhydrazone (m.p. 127°)
A.L.A.	Acetophenone and CO_2	acetophenone-2,4-dintrophenylhydrazone (m p. 245°)
B.A.	Benzophenone and CO_2	benzophenone-2,4-dintrophenylhydrazone (m.p. 236°)

all the acids at constant K^+ concentration. The specific reaction rate has been found to be linearly related to the concentration of $AgNO_3$ and follows the expression :

$$k = k_0 + m [Ag^+]$$

The values of k_0 and m obtained for different cases at 35° are also recorded in Table 1.

Effect of added salts : The effect of added salts in the oxidation of each acid was found to be negative and of primary exponential type. The specific inhibitory effect of the cations at constant ionic strength for each reaction was in the order, $K^+>Na^+>Zn^{+2}>Mg^{+2}>Al^{+3}$ in agreement with our studies[8,11-13]. Added H_2SO_4 was found to decrease the rate.

Effect of allyl acetate : Small amount of allyl acetate viz. $1\times10^{-4}M$ considerably retarded the rate of oxidation of the acid as well as the self decomposition of peroxydisulphate ion in each case. This retardation of reaction rates by allyl acetate is attributed to its established capacity to capture[14] SO_4 which is formed by the catalysed decomposition of peroxydisulphate ion and leads to polymerisation of allyl acetate.

Energy parameters : In order to evaluate the energy parameters, the reactions were studied at different temperatures ranging from 303 to 318°A. The values of specific rate constant (k) in presence of

From the above results it is clear that the oxidation of α-hydroxy acids proceeds through decarboxylation giving rise to a carbonyl compound. These experimental findings are in agreement with the results obtained by other workers[2].

Discussion and Mechanism

Taking a general formula, RR_1-C(OH)-COOH for the reductant the steps involved in the proposed mechanism are presented in the scheme :
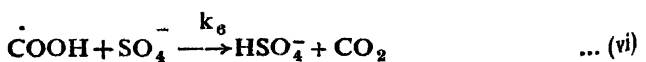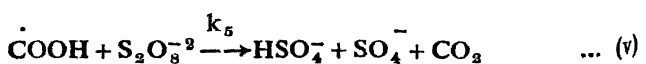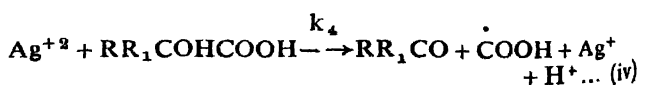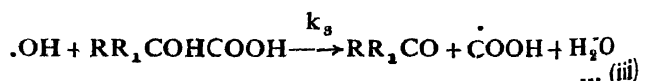
$$Ag^+ + S_2O_8^{-2} \xrightarrow{k_1} Ag^{+2} + SO_4^- + SO_4^{-2} \quad ... (i)$$

$$SO_4^- + H_2O \xrightarrow{k_2} HSO_4^- + .OH \quad ... (ii)$$

$$.OH + RR_1COHCOOH \xrightarrow{k_3} RR_1CO + \overset{.}{C}OOH + H_2O \quad ... (iii)$$

$$Ag^{+2} + RR_1COHCOOH \xrightarrow{k_4} RR_1CO + \overset{.}{C}OOH + Ag^+ + H^+ \quad ... (iv)$$

$$\overset{.}{C}OOH + S_2O_8^{-2} \xrightarrow{k_5} HSO_4^- + SO_4^- + CO_2 \quad ... (v)$$

$$\overset{.}{C}OOH + SO_4^- \xrightarrow{k_6} HSO_4^- + CO_2 \quad ... (vi)$$

TABLE 2

Reductant	$k \times 10^3 min^{-1}$				ΔE K Cal. mole⁻¹	$A \times 10^{-8}$ litre mole⁻¹ sec⁻¹	$-\Delta S^{\ddagger}$ E.U.	$\Delta G^{\ddagger}$ K. Cals. mole⁻¹	$\Delta H^{\ddagger}$ K. Cals. mole⁻¹
	303	308	313	318					
M.A.	20.72	27.00	35.82	48.77	10.64	16.3	41.3	22.73	10.26
α-OH.I.B.A.	5.56	7.03	8.59	11.14	8.84	0.123	51.2	23.58	7.78
A.L.A.	17.41	21.59	28.36	34.25	9.20	1.24	46.21	23.51	8.56
B.A.	22.65	30.65	39.53	50.56	10.20	8.93	21.5	22.70	9.15

It may be pointed out that the first two steps have also been proposed by Bawn and Margerison[15] and supported by Srivastava and Singh[11-13] in the Ag^+ catalysed oxidation reactions by $S_2O_8^{-2}$ ion. Applying the steady state treatment to the radicals .OH, $\overline{SO_4}$, $\overset{.}{COOH}$ and Ag^{+2} the rate of disappearance of $S_2O_8^{-2}$ comes out to be,

$$\frac{-d[S_2O_8^{-2}]}{dt} = k[Ag^+][S_2O_8^{-2}]$$

where k is the observed reaction rate constant. The mechanism furnishes a sound explanation of the salient kinetic features of the data obtained in the oxidation of all the reactions studied.

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