OXIDATION STUDIES

VIII. Oxidation of Some Carboxylic Acids by Peroxydisulphate Catalysed by Metal Ions

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INTRODUCTION

RESULTS of Ag^+ catalysed oxidation of a number of organic substrates by peroxydisulphates ($S_2O_8^=$) were reviewed by House[1] and Wilmarth and Haim.[2] Koishiroshinra, Kenichi, Sakurai and Takayani[3] studied the Ag^+ and Cu^{++} catalysed oxidation of mandelic acid by $S_2O_8^=$ at 25° C. to 90° C. and reported that the relative amounts of products (benzene, phenol, etc.) depended on the pH of the reaction. Mishra and co-workers,[4] Bakore and Joshi[5] and Venkatasubramanyan[6] studied oxidation of lactic acid (LA) by $S_2O_8^=$ catalysed by Ag^+. Kinetics of silver catalysed oxidation of citric acid[7] and formic acid[8] were also reported. The oxidation of *o*-phenoxy benzoic acid by $S_2O_8^=$ catalysed by Ag^+ ions was studied by Thomson and Wylie.[9] In all these cases a two electron transfer resulting in the formation of Ag^{+3} was suggested. We report in this paper results of Cu^{+2}, Mn^{+2}, Pb^{+2} and Hg_2^{+2} catalysed oxidation of lactic, malic and succinic acids by $S_2O_8^=$ in the temperature range 60°–70° C. in H_2SO_4 or HNO_3 media (depending on the catalyst) and at $\mu = 0 \cdot 2$. Our experimental results lead us to the conclusion that in all cases the total order is 2, one each with respect to $[S_2O_8^=]$ and [catalyst] and the order with respect to the substrate is zero in the rate equation for $S_2O_8^=$ disappearance. The Pb^{+2} and Mn^{+2} catalysed oxidation of malic acid are directly proportional to $[H^+]$ while Cu^{+2} catalysed oxidation of malic and succinic acids bear inverse relation to $[H^+]$, the oxidation of all the other systems being independent of $[H^+]$. Plausible mechanisms of oxidation are suggested and the kinetic parameters determined.

EXPERIMENTAL

All the reagents used are A. R. grade. The experimental procedure was as given in the previous paper[10] except for the fact that a calculated quantity of the metal ion was added in these systems as catalysts. Rates, $-R\,[S_2O_8^=]$ were usually corrected for water oxidation which was negligible

($\sim$1 % of the total rate) as found in the blank experiments. Oxidations were usually conducted for 30 min. to 3 hr., depending on the substrates and conversions of $S_2O_8^=$ were $\sim$30 to 40%. Experiments under identical conditions with substrates + metal ions but without $S_2O_8^=$ were also conducted for determining oxidation of substrates under these conditions. Rates of disappearance of the substrates were estimated by titration of the aliquots of the systems against standard NaOH ($\sim$N/50). Stoichiometries $-\Delta(S_2O_8^=)/\Delta$ (Product substrate) were determined by running the oxidation of the systems, $[S_2O_8^=] = 0{\cdot}005$ M, [Substrate] $= 0{\cdot}02$ M and the (catalyst) [Cat.] $= 0{\cdot}0001$ M for 4 hours. Product of oxidation of lactic and malic acids was acetaldehyde and that of succinic acid was formaldehyde. HCHO was identified qualitatively with chromotropic acid and all the aldehydes were estimated gravimetrically as the corresponding 2, 4-dinitro phenyl hydrozones.

RESULTS AND DISCUSSION

General.—In the case of all the systems it was observed that the oxidation was independent of the [substrate] $= (0{\cdot}5 \times 10^{-2}$ M to 22×10^{-2} M) $[HSO_4^-]$ (0·1 M to 1 M), [ionic strength] (0·1 M to 1 M). The pseudo first order rate constants ($k_{obs.}$) were calculated from the linear plots of $\log a/a-x$ *vs.* time and the second order rate constants (k) were evaluated from the plots of $k_{obs.}$ *vs.* [Cat.] (Plots A, B, C and D) (Fig. 2). The second order rate constants were either independent of $[H^+]$ or of the forms (Plots E, F and G, Figure 3 and Plots A and B, Fig. 1 *b*). $k = k_1 + k_2\,[H^+]$ or $k = k_1 + k_2'/[H^+]$. Intercepts in the plots of $k_{obs.}$ *Vs.* [Cat.] indicated the occurrence of an uncatalysed reaction though of negligible magnitude. ($\sim$ 1% of total rate). It was observed that k for all the systems increased when Cat. $\lesssim 3 \times 10^{-4}$ M, but there was a gradual decrease of k when Cat. $> 3 \times 10^{-4}$ M which may be attributed to the formation of substrate—catalyst complex and the consequent decrease in the [Cat.], the reactive species. The values for the ratio of (catalysed/uncatalysed) oxidation rates for the system of succinic acid with Cu^{+2}, Mn^{+2}, Pb^{+2} and Hg_2^{+2} respectively were 12, 17, 16 and 24; with malic acid the corresponding values were 2·6, 2·6, 2·3 and 1·5 and with lactic acid the values were 2·6, 2·6, 1·2 and 1·5. It was also found that no oxidation of the substrate took place with the metal ion alone but without persulphate. On the other hand the total order for the rate of decomposition of $S_2O_8^=$ by the catalyst without the substrates was 2, first order each with respect to $[S_2O_8^=]$ and [Cat.]. The pseudo first order rate constants being 1×10^{-5}, $1{\cdot}3 \times 10^{-5}$, $2{\cdot}8 \times 10^{-5}$ and $5{\cdot}7 \times 10^{-5}$ and ΔE values 7·8, 17·5, 18·1 and 21·4, for Cu^{+2}, Mn^{+2}, Hg_2^{+2} and Pb^{+2} respectively. The foregoing observations emphasise that the rate determining step in the oxidation of the substrates must involve the interaction of $S_2O_8^=$ – catalyst and subsequent reactions involving the substrates must be fast. The second order rate constants for catalysed lactic acid oxidations were of the order: $Hg_2^{+2} > Cu^{+2} > Pb^{+2} > Mn^{+2}$ and all were independent of [H⁺]. In the case of malic acid the trend was $Cu^{+2} > Pb^{+2} > Hg_2^{+2} > Mn^{+2}$, the magnitudes for Cu^{+2} and Mn^{+2} differed considerably from each other and the magnitude for Pb^{+2} and Hg_2^{+2} catalysed reactions of this substrate being independent of [H^+] while the Cu^{+2} catalysed reaction was inversely proportional to [H^+] and Mn^{+2} catalysed one directly proportional to [H^+]. In the case of succinic acid though Mn^{+2} and Pb^{+2} catalysed reactions were dependent directly on [H^+], unexpectedly their rate constants were found to be widely different at the same [H^+]. The ΔE values for the oxidation of substrate acids and water with different catalysts under identical conditions being generally in agreement lends support to our assumption that $S_2O_8^=$ + catalyst reaction must indeed be the rate determining step.

Lactic acid (*LA*).—The oxidation of LA catalysed by Cu^{+2}, Mn^{+2}, Pb^{+2} and Hg_2^{+2} exhibit common characteristics, the rates being independent of [Sub], [HSO_4^-], [NO_3^-], [H^+] and [ionic strength] and first order each with respect to [$S_2O_8^=$] and [Cat.]. The decreasing trend in the rate for LA $\gtrsim$ 0·35 M observed in the case of uncatalysed and Ag^+ catalysed reaction was absent here. The rate law for all the lactic acid-metal ion systems are of the form: $-R_{S_2O_8} = k\,[S_2O_8^=]\,[Cat.]$ and the Arrhenius equations obtained were:

$$k = 1\cdot120 \times 10^{9} \exp. (-13{,}450/R \times 333\cdot3) \text{ lit. mole}^{-1} \text{ sec.}^{-1};$$

$$\Delta S^{\ddagger} = -17\cdot24 \text{ e.u.}$$

$$k = 1\cdot706 \times 10^{14} \exp. (-20{,}820/R \times 333\cdot3) \text{ lit. mole}^{-1} \text{ sec.}^{-1};$$

$$\Delta S^{\ddagger} = +19\cdot05 \text{ e.u.}$$

$$k = 9\cdot245 \times 10^{2} \exp. (-4645/R \times 333\cdot3) \text{ lit. mole}^{-1} \text{ sec.}^{-1};$$

$$\Delta S^{\ddagger} = -49\cdot65 \text{ e.u.}$$

$$k = 2\cdot163 \times 10^{13} \exp. (-19{,}720/R \times 333\text{–}3) \text{ lit. mole}^{-1} \text{ sec.}^{-1};$$

$$\Delta S^{\ddagger} = +2\cdot38 \text{ e.u.}$$

with Cu^{+2}, Mn^{+2}, Hg_2^{+2} and Pb^{+2} catalysts, respectively.

The stoichiometries.—$\Delta[S_2O_8^=] : \Delta[CH_3CHO] \sim 1$ for catalysis by Hg_2^{+2} and Pb^{+2} and 2 for catalysis by Cu^{+2} and Mn^{+2} ions. Our results may be explained satisfactorily on the basis of the following mechanisms.

Hg_2^{+2} Catalysis:

$$S_2O_8^{=} + Hg_2^{+2} \xrightarrow[\text{slow}]{k} 2SO_4^{-2} + Hg^{+3} \text{ (rate determining)}$$

followed by fast reactions,

$$Hg^{+3} + CH_3CHOH\ COOH + H_2O \longrightarrow CH_3CH\begin{smallmatrix}\nearrow OH\\ \searrow OH\end{smallmatrix} + CO_2$$

$$+ 2H^{+} + Hg^{+};\quad CH_3CH\begin{smallmatrix}\nearrow OH\\ \searrow OH\end{smallmatrix} \longrightarrow CH_3CHO + H_2O$$

Pb^{+2} Catalysis:

$$S_2O_8^{=} + Pb^{+2} \xrightarrow[\text{slow}]{k} Pb^{+4} + 2SO_4^{-2} \text{ (rate determining)}$$

followed by fast reactions,

$$Pb^{+4} + CH_3CHOH\ COOH + H_2O \longrightarrow CH_3CH\begin{smallmatrix}\nearrow OH\\ \searrow OH\end{smallmatrix} + CO_2$$

$$+ 2H^{+} + Pb^{+2};\quad CH_3CH\begin{smallmatrix}\nearrow OH\\ \searrow OH\end{smallmatrix} \longrightarrow CH_3CHO + H_2O$$

Cu^{+2} and Mn^{+2} Catalysis:

$$S_2O_8^{=} + Cu^{+2} \text{ (or } Mn^{+2}) \xrightarrow[\text{slow}]{k} Cu^{+3} \text{ or } (Mn^{+3}) + SO_4^{-} + SO_4^{=}$$

followed by fast reactions.

$$CH_3CHOH\ COOH + Cu^{+3} + SO_4^{-} \longrightarrow HSO_4^{-} + Cu^{+2}$$
$$+ CH_3CHOH\ \dot{C}OO$$

$$CH_3CHOH\ \dot{C}OO + S_2O_8^{=} + H_2O \longrightarrow CH_3CH(\quad CO_2$$
$$+ 2HSO_4^{-}.$$

Succinic acid.—The total order in all the systems studied was 2 one each with respect to $[S_2O_8^{=}]$ and [Cat.] (Plot A, Fig. 1 *a*) and Plots.

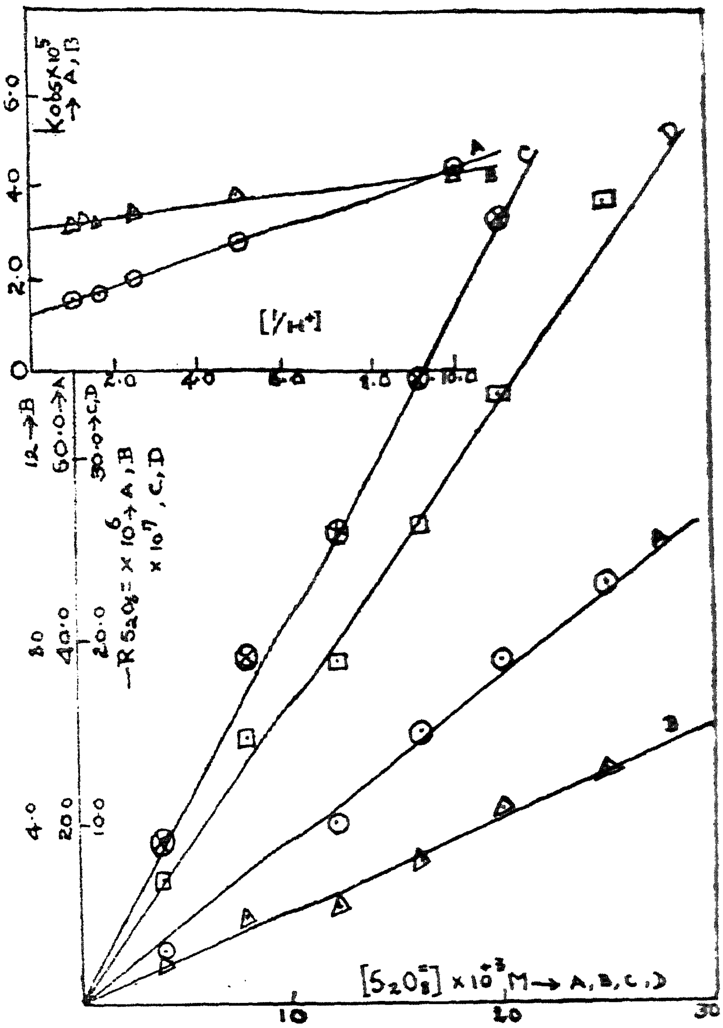

FIG. 1. (*a*) $-R_{S_2O_8^=}$ *vs.* $[S_2O_8^{=}]$ at 60° C. [Sub.] 2×10^{-2} M, [Cat.] = 1×10^{-4} M, $\mu = 0 \cdot 2$ M. (A) Succinic acid -- Pb^{+2}; (B) Malic acid -- Mn^{+2}; (C) Malic acid -- Pb^{+2}; (D) Malic acid -- Cu^{++}.

(*b*) $K_{obs.} \times 10^5$ *vs.* $[1/H^+]$; T = 60° C., $\mu = 1 \cdot 75$ M, [Cat.] = 1×10^{-4} M, [Sub.] = 2×10^{-2} M, $[S_2O_8^{=}]$ 5×10^{-3} M.

(A) Succinic acid -- Cu^{++}; (B) Malic acid -- Cu^{++}.

The rate laws are of the forms:

$$-R_{S_2O_8^=} = k_1 [S_2O_8^{=}][Cu^{+2}] + k_2' [S_2O_8^{=}][Cu^{+2}][H^+].$$

with Cu^{+2} catalyst.

$$-R_{S_2O_8^=} = k_1 [S_2O_8^{=}][Pb^{+2}] + k_2 [S_2O_8^{=}][Pb^{+2}][H^+]$$

with Pb^{+2} and Mn^{+2} catalysts.

$$-R_{S_2O_8^=} = k [S_2O_8^{=}][Hg_2^{+2}]$$ with Hg_2^{+2} catalyst.

The Arrhenius equations obtained were:

$k_1 = 1\cdot788 \times 10^1 \exp.(-8226/Rx\ 333\cdot3)$ lit. mole^{-1} sec.$^{-1}$;

$\Delta S^{\ddagger} = -52\cdot8$ e.u.

$k_2' = 2\cdot279 \times 10^9 \exp.(-22{,}820/Rx\ 333\cdot3)$ sec.$^{-1}$;

$\Delta S^{\ddagger} = 15\cdot8$ e.u. with Cu^{+2} catalyst.

$k_1 = 7\cdot977 \times 10^5 \exp.(-12{,}810/Rx\ 333\cdot3)$ lit. mole^{-1} sec.$^{-1}$;

$\Delta S^{\ddagger} = -31\cdot6$ e.u.

$k_2 = 2\cdot117 \times 10^9 \exp.(-18{,}780/Rx\ 333\cdot3)$ lit.^{2}. mole^{-2} sec.$^{-1}$;

$\Delta S^{\ddagger} = -15\cdot9$ e.u. with Mn^{+2} catalyst.

$k_1 = 6\cdot115 \times 10^1 \exp.(-7940/Rx\ 333\cdot3)$ lit. mole^{-1} sec.$^{-1}$;

$\Delta S^{\ddagger} = 43\cdot1$ e.u. with Pb^{+2} catalyst.

$k = 1\cdot219 \times 10^9 \exp.(-18{,}910/Rx\ 333\cdot3)$ lit. mole^{-1} sec.$^{-1}$;

$\Delta S^{\ddagger} = -17\cdot1$ e.u. with Hg_2^{+2} catalyst.

The stoichiometries.— $\Delta[S_2O_8^{=}]/\Delta[HCHO] = 1\cdot5$ for Hg_2^{+2}, Pb^{+2} and Cu^{+2} catalysed reactions and unity for Mn^{+2} catalysed reaction. The above results may be satisfactorily explained on the basis of the following mechanisms:

Hg_2^{+2} Catalysis:

$$S_2O_8^{=} + Hg_2^{+2} \xrightarrow[\text{slow}]{k} Hg^{+3} + 2SO_4^{=}$$

followed by fast steps.

$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} + Hg^{+3} + 2H_2O \longrightarrow Hg^{+} + \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2CO_2 + 4H^{+};$$

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \longrightarrow 2HCHO + 2H^{+}$$

Pb^{+2} Catalysis:

$$Pb^{+2} + S_2O_8^{=} \xrightarrow[\text{slow}]{k} Pb^{+4} + 2SO_4^{=}$$

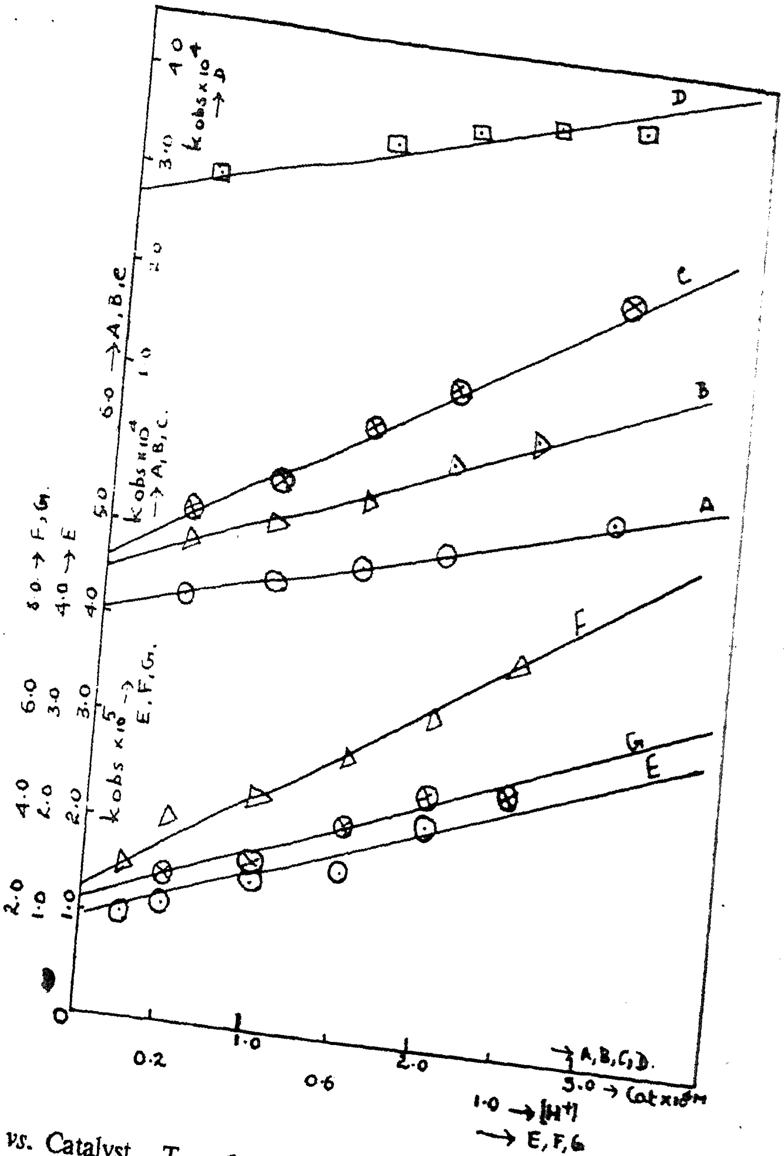

FIG. 2. $K_{obs.}$ *vs.* Catalyst, T = 60° C., $\mu = 0{\cdot}2$ M, [Sub.] $= 2 \times 10^{-2}$ M, $[S_2O_8^{=}]$ $= 5 \times 10^{-3}$ M.

(A) Lactic acid -- Mn^{+2}; (B) Lactic acid -- Pb^{+2}; (C) Lactic acid -- Hg_2^{+2}; (D) Lactic acid -- Cu^{+2}.

$K_{obs.}$ *vs.* $[H^+]$; T = 60° C., $\mu = 1{\cdot}75$ M, [Sub.] $= 2 \times 10^{-2}$ M, $[S_2O_8^{=}] = 5 \times 10^{-3}$ M, [Catalyst] $= 1 \times 10^{-4}$ M.

(E) Malic acid -- Mn^{+2}; (F) Succinic acid -- Mn^{+2}; (G) Succinic acid -- Pb^{+2}.

followed by the fast reactions

$$\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + Pb^{+4} \xrightarrow{2H_2O} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 2CO_2 + 4H^+$$

$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \longrightarrow 2HCHO + 2H^+$$

Cu^{+2}, Mn^{+2} Catalysis:

$$Mn^{+2} + S_2O_8^{=} \xrightarrow[\text{slow}]{k} Mn^{+3} + SO_4^{-2} + SO_4^{\overline{\cdot}}$$

$$\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + Mn^{+3} + SO_4^{\overline{\cdot}} \longrightarrow \begin{matrix} \dot{C}H_2COOH \\ | \\ CH_2COOH \end{matrix} + Mn^{+2} + HSO_4^{-}$$

$$\begin{matrix} \dot{C}H_2COOH \\ | \\ CH_2COOH \end{matrix} + S_2O_8^{=} \xrightarrow{H_2O} \begin{matrix} \overset{+}{C}H_2COOH \\ | \\ CH_2COOH \end{matrix} + HSO_4^{-} + SO_4^{\overline{\cdot}} + OH^{-}$$

$$\begin{matrix} \overset{+}{C}H_2COOH \\ | \\ CH_2COOH \end{matrix} + SO_4^{\overline{\cdot}} + H^{+} \longrightarrow 2CH_2COOH + SO_4^{-} + H_2O$$

$$2CH_2COOH + 2\,H_2O \longrightarrow 2CH_2OH\ COOH + 2H^{+}$$

$$2CH_2OH\ COOH \longrightarrow 2HCHO + 2CO_2 + 4H^{+}.$$

Malic acid.—The rate laws for the malic acid—metal ion systems are of the forms:

$$-R_{S_2O_8^{=}} = k_1\,[S_2O_8^{=}]\,[Cu^{+2}] + k_2'\,[S_2O_8^{=}]\,[Cu^{+2}]/[H^{+}]$$

$$-R_{S_2O_8^{=}} = k\,[S_2O_8^{=}]\,[Pb^{+2}], \quad -R_{S_2O_8^{=}} = k\,[S_2O_8^{=}]\,[Hg_2^{+2}]$$

and

$$-R_{S_2O_8^{=}} = k_1\,[S_2O_8^{=}]\,[Mn^{+2}] + k_2\,[S_2O_8^{=}]\,[Mn^{+2}]\,[H^{+}].$$

The Arrhenius equations obtained were:

Cu^{+2} Catalysis:

$k_1 = 1\cdot3790 \times 10^{22}$ exp. $(-\,39{,}760/Rx\ 333\cdot3)$ lit. mole^{-1} sec.$^{-1}$;

$k_2' = 2\cdot378 \times 10^{7}$ exp. $(-\,5751/Rx\ 333\cdot3)$ sec.$^{-1}$

ΔS_1 and $\Delta S_2' = +\,17\cdot2$ e.u.

Mn^{+2} Catalysis:

$k_1 = 7\cdot447 \times 10^{10}$ exp. $(-\,22{,}230/Rx\ 333\cdot3)$ lit. mole^{-1} sec.$^{-1}$;

$\Delta S = -\,17\cdot9$ e.u.

$$k_2 = 5\cdot118 \times 10^{23}\ \text{exp.}\ (-\ 40{,}650/\text{Rx}\ 333\cdot3)\ \text{lit.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1};$$
$$\triangle S^{\ddagger} = -\ 17\cdot9\ \text{e.u.}$$

Pb^{+2} Catalysis:

$$k = 1\cdot794 \times 10^{8}\ \text{exp.}\ (-\ 12{,}930/\text{Rx}\ 333\cdot3)\ \text{lit. mole}^{-1}\ \text{sec.}^{-1};$$
$$\triangle S^{\ddagger} = -\ 20\cdot9\ \text{e.u.}$$

Hg_2^{+2} Catalysis:

$$k = 8\cdot328 \times 10^{11}\ \text{exp.}\ (-\ 18{,}270/\text{Rx}\ 333\cdot3)\ \text{lit. mole}^{-1}\ \text{sec.}^{-1};$$
$$\triangle S^{\ddagger} = -\ 4\cdot1\ \text{e.u.}$$

The stoichiometries. $- \triangle [S_2O_8^{=}]/\triangle [CH_3CHO]$ were unity in all the 4 cases. The observed results may be explained on the basis of the following mechanisms:

Pb^{+2} Catalysis:

$$Pb^{+2} + S_2O_8^{=} \xrightarrow[\text{slow}]{k} Pb^{+4} + 2SO_4^{=}$$

$$Pb^{+4} + \begin{array}{l} \text{CHOH COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array} \xrightarrow{H_2O} Pb^{+2} + \begin{array}{l} \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array} + 2CO_2$$

$$\begin{array}{l} \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array} \longrightarrow \left[\begin{array}{l} \text{CH}_2\text{OH} \\ | \\ \text{CHO} \end{array} \right] \longrightarrow \begin{array}{l} \text{CH}_3 \\ | \\ \text{CHO} \end{array} + OH^-$$

Mn^{+2} Catalysis:

$$Mn^{+2} + S_2O_8^{=} \xrightarrow[\text{slow}]{k} Mn^{+4} + 2SO_4^{=}$$

$$\begin{array}{l} \text{CHOH COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array} + Mn^{+4} \xrightarrow{H_2O} Mn^{+2} + \begin{array}{l} \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array} + 2CO_2 + H^+$$

$$\begin{array}{l} \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array} + H^+ \longrightarrow \begin{array}{l} \text{CH}_3 \\ | \\ \text{CHO} \end{array} + H_2O$$

Hg_2^{+2} Catalysis:

$$Hg_2^{+2} + S_2O_8^{=} \xrightarrow[\text{slow}]{k} Hg^{+3} + 2SO_4^{-}$$

$$Hg^{+3} + \begin{matrix} \text{CHOH COOH} \\ \text{CH}_2\text{OH COOH} \end{matrix} \xrightarrow{H_2O} Hg_2^{+2} + \begin{matrix} \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{matrix} + 2CO_2$$

$$\begin{matrix} \text{CHOH} \\ \text{CH}_2\text{OH} \end{matrix} \longrightarrow \left[\begin{matrix} \text{CH}_2\text{OH} \\ \text{CHO} \end{matrix} \right] \longrightarrow \begin{matrix} \text{CH}_3 \\ | \\ \text{CHO} \end{matrix} + OH^-$$

Cu^{+2} Catalysis:

$$Cu^{+2} + S_2O_8^{=} \xrightarrow[\text{slow}]{k} Cu^{+3} + SO_4^{=} + SO_4^{\overline{\cdot}}$$

$$\begin{matrix} \text{CHOH COOH} \\ \text{CH}_2\text{COOH} \end{matrix} + Cu^{+3} \longrightarrow Cu^{+2} + \begin{matrix} \text{CHOH}\,\dot{\text{C}}\text{OO} \\ | \\ \text{CH}_2\text{COOH} \end{matrix} + H^+$$

$$\begin{matrix} \text{CHOH}\,\dot{\text{C}}\text{OO} \\ \text{CH}_2\text{COOH} \end{matrix} + SO_4^{\overline{\cdot}} \longrightarrow \begin{matrix} \text{CHOH}\,\dot{\text{C}}\text{OO} \\ | \\ \text{CH}_2\dot{\text{C}}\text{OO} \end{matrix} + HSO_4^-$$

$$\begin{matrix} \text{CHOH COO} \\ \text{CH}_2\text{COO} \end{matrix} \longrightarrow CH_3CHO + 2CO_2$$

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