

OXIDATION STUDIES—VI

Oxidation of Some Mono- and Di-basic Acids by Peroxy Disulphate

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ABSTRACT

Uncatalysed oxidation of malonic, maleic, succinic, malic, mandelic and lactic acids by peroxydisulphate have been studied at 60°–80° C. Rates of oxidation and E values are reported. Probable mechanisms are proposed.

INTRODUCTION

WORK on the oxidation of a variety of organic and inorganic substrates by peroxy disulphate up to 1962 was reviewed by House¹ and Wilmarth and Harim.² Koshiroshinra, Kenichi, Sakurai and Takayani³ reported that in the oxidation of mandelic acid by $S_2O_8^{=}$ catalysed by Ag^+ and Cu^{++} at 25° C. to 90° C. the relative amounts of the products (benzene, phenol, etc.) depended upon the pH of the reaction. Mishra and co-workers⁴ as well as Venkatasubramanyan⁵ studied Ag^+ catalysed oxidation of lactic acid by $S_2O_8^{=}$. The latter authors found that the rate of $S_2O_8^{=}$ disappearance decreased for $[lactic\ acid] \gtrsim 0.35\ M$ and for higher concentrations of the latter the rate remained constant. Kinetics of Ag^+ catalysed $S_2O_8^{=}$ oxidations of citric⁶ and formic acid⁷ and uncatalysed oxidation of tartaric acid⁸ were also reported. In this paper the kinetic results of $S_2O_8^{=}$ oxidation (without any catalyst like Ag^+ , etc.) of malonic, maleic, succinic, malic, mandelic and lactic acids in the range 60°–80° C. in H_2SO_4 medium at constant ionic strength ($\mu = 0.2-0.25\ M$) are presented; mechanisms of oxidations are discussed in the light of rate laws and kinetic parameters derived. Oxidation of malic acid was also studied in $HClO_4$ medium for the purpose of comparison of results in H_2SO_4 medium. Oxidation of malonic acid was carried out in heavy water also and the kinetic isotopic effects k_{H_2O}/k_{D_2O} were evaluated at 60° and 70° C. Our results led us to the general conclusion that in the case of all acids the order of $[S_2O_8^{=}]$ for rate of disappearance of persulphate, $-R_{S_2O_8^{=}}$, was unity and the order for each substrate was

zero exception being mandelic acid for which the order was unity. Oxidation of malic acid was found to be catalysed by SO_2 . Kinetic features of lactic acid oxidation were found to be exceptional in regard to the inverse dependence of the former on the rate. Mandelic acid and lactic acid oxidation rates were found to vary with $[\text{I}^-]$ and $[\text{H}^+]$ respectively.

EXPERIMENTAL

(a) *Reagents.*— $\text{K}_2\text{S}_2\text{O}_8$ (G. R. ; E. Merck) solution (0.1 M) was always freshly prepared and assayed by iodometry before use in the experiments. Lactic acid (M & B; reagent grade); Succinic acid (M & B, reagent grade), malic acid (Riedel), maleic acid (Riedel), malonic acid (Riedel), mandelic acid (Mallinck rodt., U.S.A. XII) were used. Water distilled over alkaline KMnO_4 twice in all glass still followed by passage through an ion exchange resin (Bioclemin rolin, Permuti Co., U.K.), was used in the preparation of all the solutions. Heavy water (99.9% purity, Atomic Energy, Bombay) was used for malonic acid oxidations.

(b) *Rate measurements.*—The system containing the substrate acid (0.02 M in the case of all the acids except lactic acid and 0.15 M to 0.45 M in the case of lactic acid) at $\mu = 0.2$ M was taken in a flask (250 ml. cap) thermostated (60° – 70°). Aqueous $\text{K}_2\text{S}_2\text{O}_8$ solution in a separate flask (100 ml. cap) was also kept in the same thermostat maintained by a toluene regulator and a relay to an accuracy of $1^\circ\text{C} \pm 0.1^\circ\text{C}$. A known volume of $\text{K}_2\text{S}_2\text{O}_8$ solution was transferred to the flask containing the substrate system and the time at transfer of one-half volume of the former was reckoned as the start of the oxidation reaction. Aliquots (10 ml.) of the reaction mixture were withdrawn at 5–30 min. intervals depending upon the substrate, quenched in ice cold water containing KI (~ 2 gm.) for about 40 minutes; acetic acid (2 ml. of 6.0 N) was then added and titrated against standard sodium thiosulphate ($\sim \text{N}/40$ N). Unreacted $[\text{S}_2\text{O}_8^{2-}]$ and therefore the rate of disappearance of persulphate, $-\text{R}_{\text{S}_2\text{O}_8^{2-}}$, was computed. Rates were usually corrected for water oxidation (usually 10% of total rate) conducted simultaneously in the blank experiments. Oxidations were usually conducted for 30 min. to 3 hr. depending on the substrate and conversions of $\text{S}_2\text{O}_8^{2-}$ were $\sim 30\%$. The pHs of the reaction mixtures measured both before and after the experiments in a pH meter (Leeds and Northrup Cat. No. 7666) indicated small variations of $[\text{H}^+]$ during the experiments. The iodometric method for the computation of $-\text{R}_{\text{S}_2\text{O}_8^{2-}}$ compared well with other methods based on addition of excess of standard $[\text{Fe}^{2+}]$ to the aliquots and

back titrating with standard $k\text{MnO}_4$ or ceric sulphate. All these analytical methods may be considered to yield rates accurate to $\pm 1\%$.

(c) *Stoichiometries*.—The system, $[\text{S}_2\text{O}_8^{=}] = 0.005 \text{ M}$ to 0.015 M ; [substrate] = 0.005 M to 0.015 M was thermostated at $60^\circ \text{ C.} \pm 0.1^\circ \text{ C.}$ for 4 hr. Stoichiometries were determined from $-\Delta [\text{S}_2\text{O}_8^{=}] / [\text{Product substrate}]$. Product of oxidation of mandelic acid was benzaldehyde; of succinic acid was formaldehyde; of malonic acid was formic acid and for the rest of the acids acetaldehyde was the product. The aldehydes were estimated after conversions to the corresponding 2–4 dinitrophenyl hydrozones and formic acid was estimated after reduction to formaldehyde (Al + HCl) and estimating the latter by the corresponding 2–4 dinitrophenyl hydrozone.

RESULTS AND DISCUSSIONS

(1) Malonic, maleic and succinic acids exhibit certain common kinetic features. Under conditions, [substrate acid] $>$ $[\text{K}_2\text{S}_2\text{O}_8]$ ($[\text{K}_2\text{S}_2\text{O}_8] = 0.005 \text{ M}$, [Malonic acid] = 0.02 M (pH = 1.8–2.0); [Maleic acid] = 0.2 M (pH = 1.8–1.9); [succinic acid] = 0.02 M (pH = 1.9–2.0)) at $\mu = 0.2 \text{ M}$, $\log (a - x)$ vs. t plots were linear both at 60° C. and 70° C. (Fig. 1 a: A, B and C) and from the slopes of these plots the pseudo first order rate constants k_s for the acids were evaluated. The k_s in all cases were independent of substrate (zero order), $[\text{H}^+]$ ($= 0.1 \text{ M}$ to 1.0 M); $[\text{HSO}_4^-]$ ($= 0.1 \text{ M}$ to 1.0 M); $[\text{SO}_4^{=}]$ ($= 0.1 \text{ M}$ to 1.0 M) and μ ($= 0.1 \text{ M}$ to 1 M by adding KHSO_4). It may therefore be assumed that the rate law for the three acids is of the form $-\text{R}_{\text{S}_2\text{O}_8} = k [\text{S}_2\text{O}_8^{=}]$, the k values of course differing for the three acids. The Arrhenius equations are:

$$k_m = 2.55 \times 10^{11} \exp. (-29,150/R \times 333.3) \text{ sec.}^{-1} \text{ (Malonic acid)}$$

$$k_M = 8.12 \times 10^{12} \exp. (-24,680/R \times 343.3) \text{ sec.}^{-1} \text{ (Maleic acid)}$$

$$k_s = 4.01 \times 10^7 \exp. (-16,180/R \times 333.3) \text{ sec.}^{-1} \text{ (Succinic acid)}$$

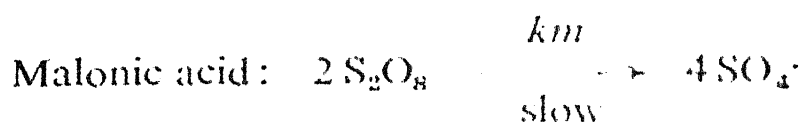
(ii) The stoichiometries

$$-\Delta [\text{S}_2\text{O}_8^{=}] / \Delta [\text{H COOH}] = 2 \text{ for malonic acid.}$$

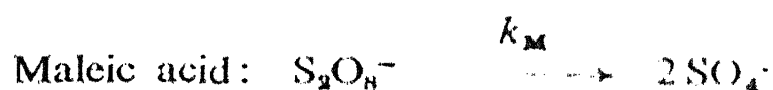
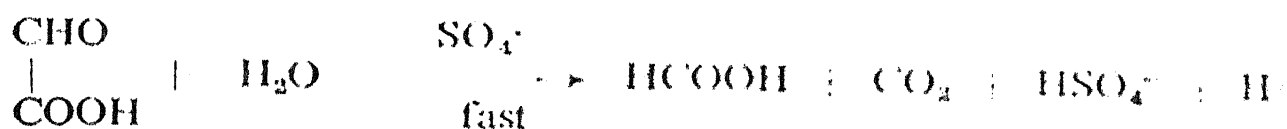
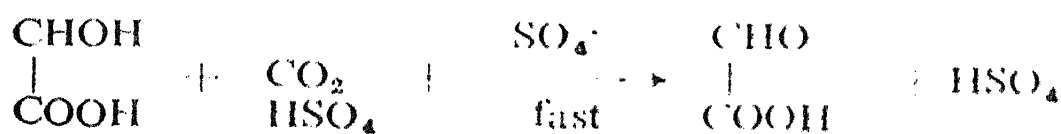
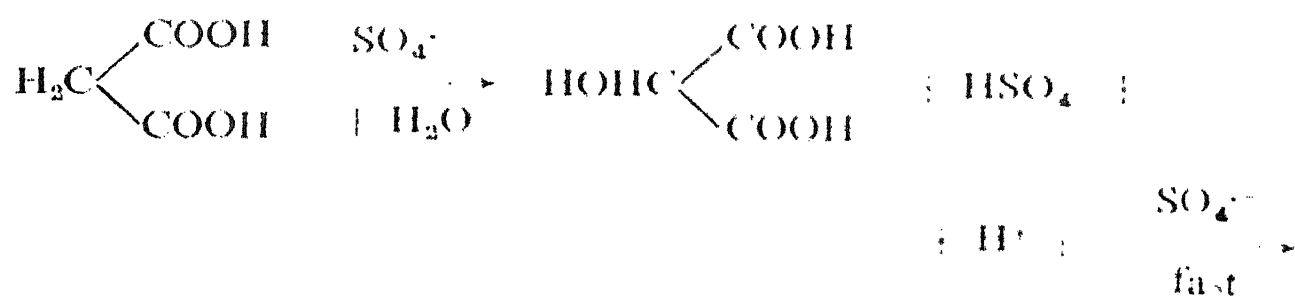
$$-\Delta [\text{S}_2\text{O}_8^{=}] / \Delta [\text{CH}_3\text{CHO}] \approx 1 \text{ for maleic acid and}$$

$$-\Delta [\text{S}_2\text{O}_8^{=}] / \Delta (\text{HCHO}) \approx \frac{1}{2} \text{ for succinic acid were obtained.}$$

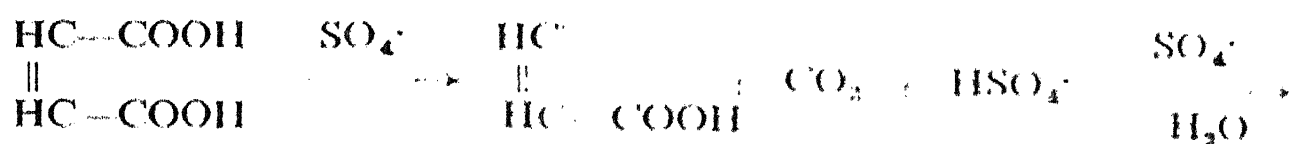
The foregoing results may be satisfactorily explained on the basis of the following mechanisms:



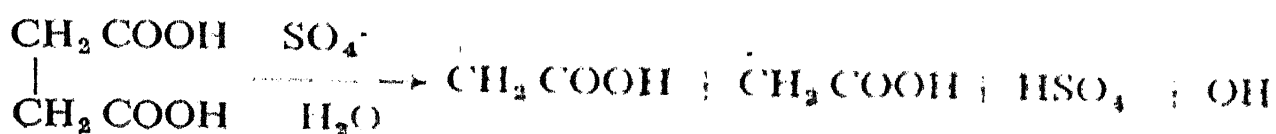
followed by fast reactions;

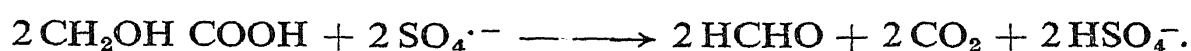
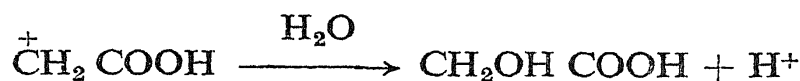
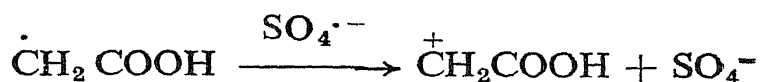
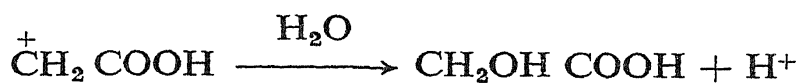


followed by fast reactions;



followed by fast reactions:





The different ΔE values for the acids obtained are to be understood in terms of pH effect upon the homolysis of S_2O_8^- or oxidation of water by S_2O_8^- (cf. Part V of our paper in the series).

(2) *Malic acid*: The system $\text{K}_2\text{S}_2\text{O}_8$ (0.005 M), Malic acid (0.02 M) at $\mu = 0.2$ M, $\text{pH} \approx 2.5$ exhibited first order dependence of $[\text{S}_2\text{O}_8^-]$ on $-\text{R}_{\text{S}_2\text{O}_8^-}$ and zero order for [malic acid] at 60°C . and 70°C . Rate was also observed to be independent of HSO_4^- , ($[\text{HSO}_4^-] = 0.01$ M to 1 M), $[\text{H}^+]$ ($[\text{H}^+] = 0.1$ M to 1 M) and μ (0.1 M to 1 M). Rate was found to be susceptible to $\text{SO}_4^{\cdot-}$ catalysis. Addition of ZnSO_4 (0.1 to 1 M) increased the rate by $\sim 20\%$. The rate law in the absence of added $\text{SO}_4^{\cdot-}$ was of the form

$$-\text{R}_{\text{S}_2\text{O}_8^-} = k_{ma} [\text{S}_2\text{O}_8^-]$$

and

$$k_{ma} = 3.791 \times 10^{18} \exp. (-33,320/\text{R} \times 333.3) \text{ sec.}^{-1}$$

was obtained. The rate in the presence of the $\text{SO}_4^{\cdot-}$ was of the form

$$-\text{R}_{\text{S}_2\text{O}_8^-} = k_1 [\text{S}_2\text{O}_8^-] + k_2 [\text{S}_2\text{O}_8^-] [\text{SO}_4^{\cdot-}]$$

and

$$k_1 = 3.1 \times 10^{19} \exp. (-34,770/\text{R} \times 333.3) \text{ sec.}^{-1}$$

and

$$k_2 = 52.97 \exp. (-8420/\text{R} \times 333.3) \text{ lit. mole}^{-1} \text{ sec.}^{-1}$$

were obtained. It was found that there was no $\text{SO}_4^{\cdot-}$ catalysis in HClO_4 medium and the rate law is of the form:

$$-\text{R}_{\text{S}_2\text{O}_8^-} = k_{mb} [\text{S}_2\text{O}_8^-].$$

And

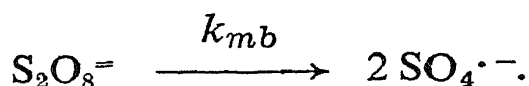
$$k_{mb} = 1.83 \times 10^{13} \exp. (-25,700/R \times 333.3) \text{ sec.}^{-1}.$$

The stoichiometry

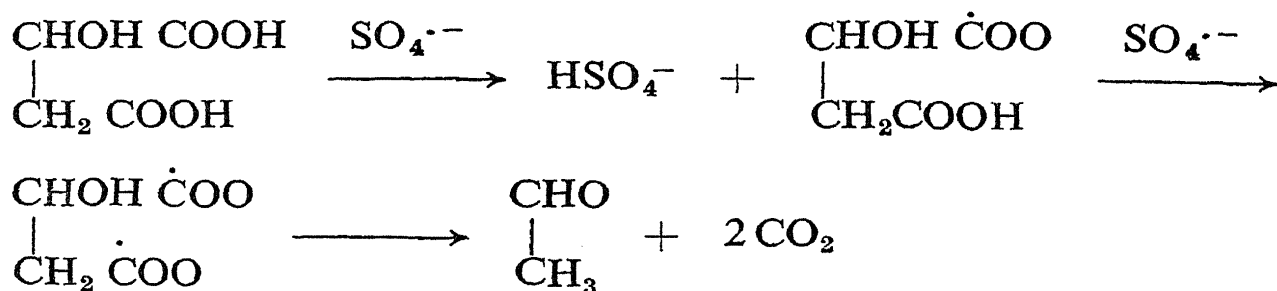
$$-\Delta [\text{S}_2\text{O}_8^{2-}] / \Delta [\text{CH}_3\text{CHO}] \approx 1$$

in HClO_4 and $\frac{1}{2}$ in H_2SO_4 medium was obtained.

The mechanism in HClO_4 may be as follows



And fast reactions:



(3) *Mandelic acid*.—Under conditions of $[\text{K}_2\text{S}_2\text{O}_8] = 0.005 \text{ M}$; $[\text{Mandelic acid}] = 0.02 \text{ M}$; $\text{pH} \approx 2.5$ and $\mu = 0.2 \text{ M}$, plots of $\log(a-x)$ vs. t were linear both at 60° and 70° C . (Fig. 1 a, Plot E) and the pseudo first order rate constants k_{obs} evaluated for each concentrations of the acid were proportional to the latter. The rate was therefore first order each in $(\text{S}_2\text{O}_8^{2-})$ and $[\text{Mandelic acid}]$. The rate was also found to vary inversely with $[\text{H}^+]$ Plots of $-\text{R}_{\text{S}_2\text{O}_8^{2-}}$ vs. $[\text{S}_2\text{O}_8^{2-}]$ or $[\text{substrate}]$ (Fig. 1 b, Plot A) left no intercepts on the ordinate while plots of $-\text{R}_{\text{S}_2\text{O}_8^{2-}}$ vs. $[1/\text{H}^+]$ (Fig. 1 b, Plot B) did leave intercepts. The rate law therefore was of the form

$$-\text{R}_{\text{S}_2\text{O}_8^{2-}} = k_a [\text{S}_2\text{O}_8^{2-}] [\text{Acid}] + k_b \frac{(\text{S}_2\text{O}_8^{2-}) [\text{Acid}]}{[\text{H}^+]}$$

The acid independent and dependent rate constants were evaluated from intercepts and slope of the plot of k_{obs} vs. $1/[\text{H}^+]$ respectively and the Arrhenius equations were:

$$k_a = 3.7 \times 10^9 \exp. (-18,850/R \times 333.3) \text{ lit. mole}^{-1} \text{ sec.}^{-1}$$

and

$$k_b = 15.9 \exp. (-5,128/R \times 333.3) \text{ sec.}^{-1}$$

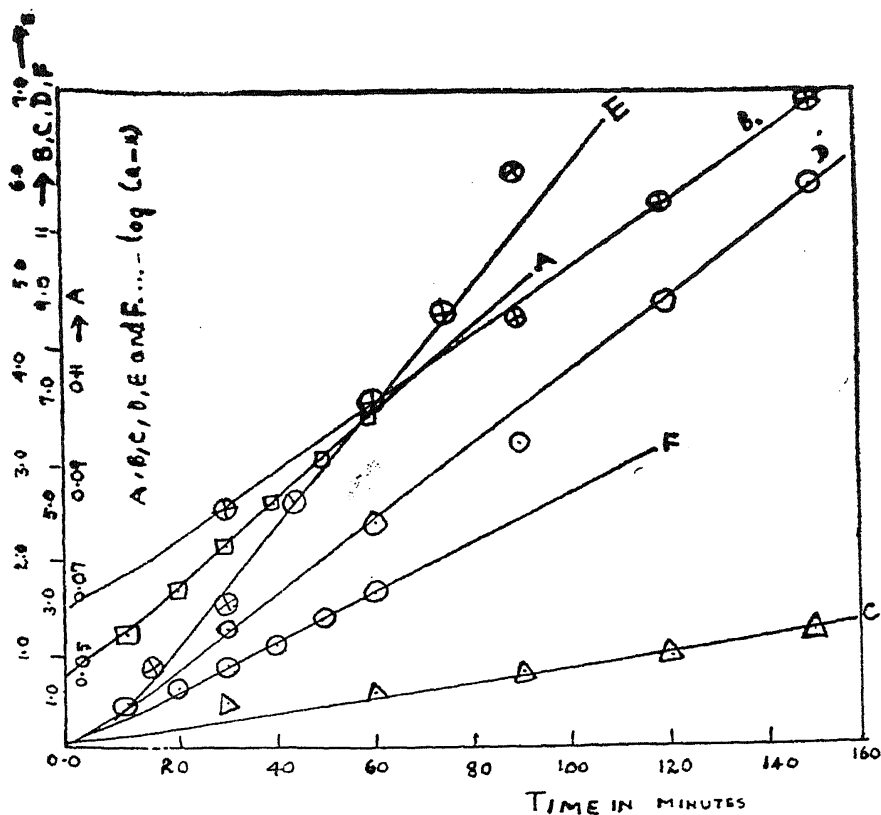


FIG. 1 a. Plot A, B, C, D, E and F: $\log(a - x)$ vs. time. A, Malonic acid; B, Maleic acid; C, Succinic acid; D, Malic acid; E, Mandelic acid; and F, Lactic acid.

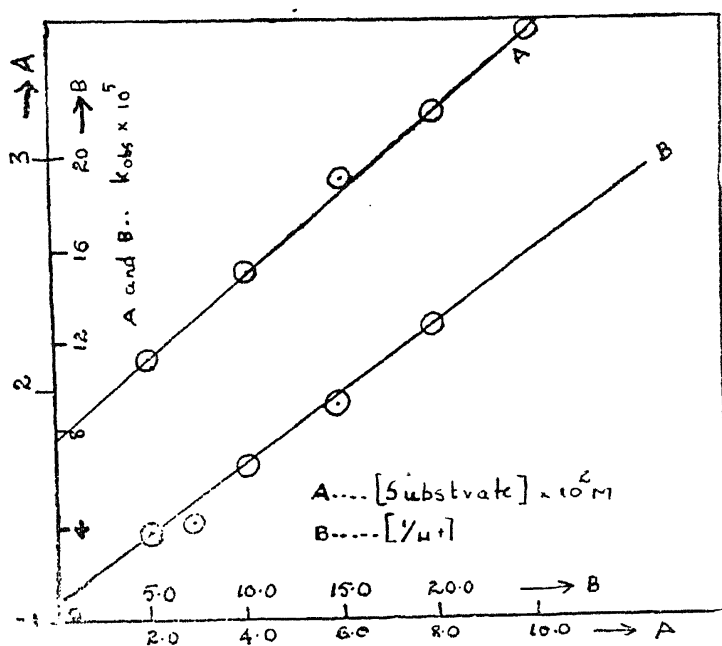
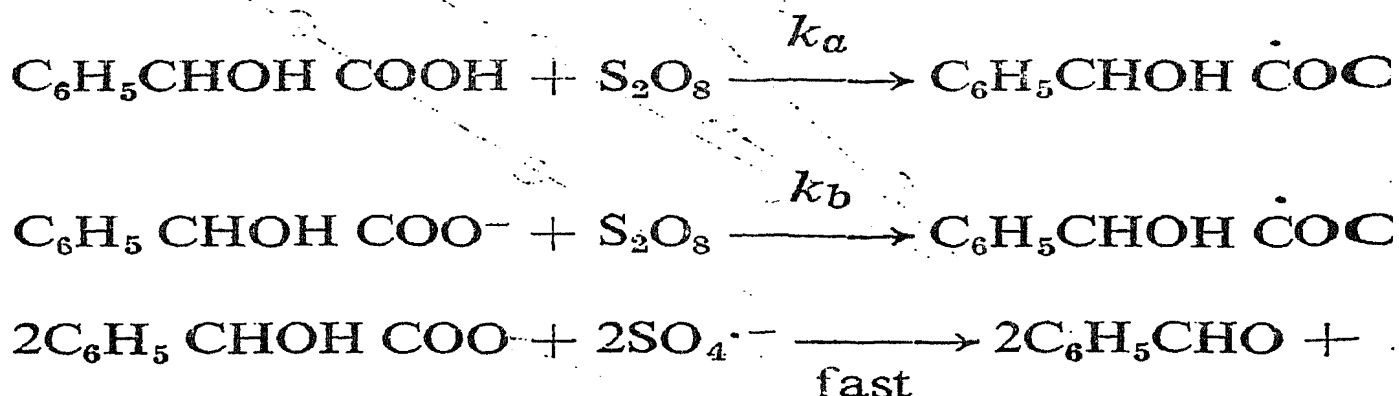


FIG. 1 b. Plot A.—Pseudo first order rate constant k_{obs} vs. (Substrate) (mandelic acid). Plot B: k_{obs} vs. (H^+) (mandelic acid).

Benzaldehyde was the product of oxidation and $-\Delta(S_2O_8^{2-})/\Delta(\text{Benzaldehyde}) = 1$ was found. The reaction stood in terms of the mechanism:



(4) *Lactic acid*.—Under conditions $[\text{K}_2\text{S}_2\text{O}_8] = 0.00 \leq 0.35 \text{ M}$; $\text{pH} = 2.14$ the rate decreased steadily and $> 0.35 \text{ M}$ ($\text{pH} 1.9$) the rate remained steady. These were observed by earlier workers⁵ in the Ag^+ catalysed lactic acid but no explanation was offered. We observed concentration of 0.35 M for lactic acid was reduced to ionic strength of the medium was reduced from $\mu = 0.25$. Kinetic studies were made with $[\text{Lactic acid}] < 0.35 \text{ M}$ was of the form

$$-R_{\text{S}_2\text{O}_8^{2-}} = k_1 [\text{S}_2\text{O}_8^{2-}] + k_2 \frac{[\text{S}_2\text{O}_8^{2-}] [\text{H}^+]}{[\text{L}]}$$

k_1 and k_2 were evaluated by 3 different methods:

(i) $-R_{\text{S}_2\text{O}_8^{2-}}$ was plotted against $[\text{S}_2\text{O}_8^{2-}]$ at const. $[\text{L}]$ and $[\text{H}^+]$. The slope of such plots, $(k_1 + k_2 [\text{H}^+])$, were plotted against $[\text{H}^+]$ at const. $[\text{L}]$ (Fig. 2, A) and slopes of these latter plots k_1 and k_2 were evaluated.

(ii) $-R_{\text{S}_2\text{O}_8^{2-}}/[\text{S}_2\text{O}_8^{2-}]$ vs. $[1/\text{L}]$ plots at constant $[\text{H}^+]$ slope, $k_2 [\text{H}^+]$ and intercept on the ordinate k_1 .

(iii) The pseudo first order rate constant $k_{\text{obs.}} = k_1 + k_2 [\text{H}^+]/[\text{L}]$ plotted against $[\text{H}^+]/[\text{L}]$ and k_2 and k_1 were evaluated from slopes and intercept respectively. k_1 and k_2 evaluated by these methods agreed. Kinetic studies conducted with $[\text{L}] > 0.35 \text{ M}$ conformed

$$-R_{\text{S}_2\text{O}_8^{2-}} = k_3 [\text{S}_2\text{O}_8^{2-}] + k_4 [\text{S}_2\text{O}_8^{2-}] [\text{H}^+]$$

From plots similar to those under (i) to (iii) k_3 and k_4 were evaluated. From experiments conducted at 60° C. and 70° C., the Arrhenius equations were derived:

$$k_1 = 7.4 \times 10^{-1} \exp. (-5540/R \times 333.3) \text{ sec.}^{-1}$$

$$k_2 = 2.29 \times 10^{-1} \exp. (-5130/R \times 333.3) \text{ sec.}^{-1}$$

$$k_3 = 1.74 \times 10^7 \exp. (-16,010/R \times 333.3) \text{ sec.}^{-1}$$

$$k_4 = 2.2 \times 10^7 \exp. (-16,200/R \times 333.3) \text{ lit. mole}^{-1} \text{ sec.}^{-1}$$

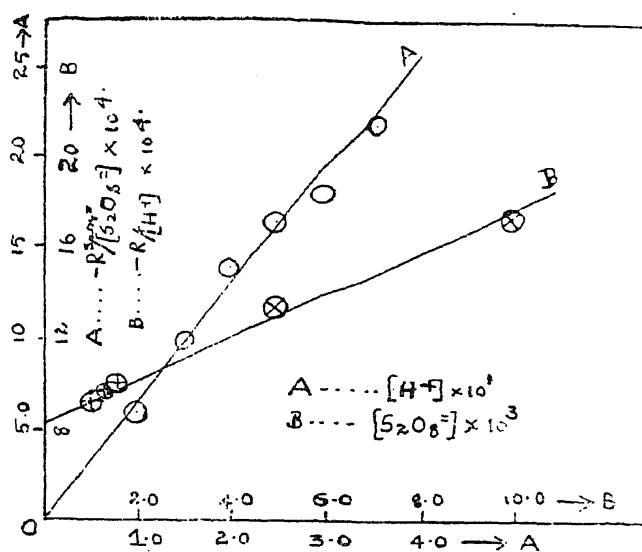


FIG. 2. Plot A: $-R_{S_2O_8^{2-}}/[S_2O_8^{2-}]$ vs. $[H^+]$ (Lactic acid). Plot B: $-R_{S_2O_8^{2-}}/[H^+]$ vs. $[S_2O_8^{2-}]$ (Lactic acid).

Oxidation was also studied by following the rate of disappearance of lactic acid $-R_L$ (titrimetry with standard NaOH), under conditions $[K_2S_2O_8] = 0.005$ M, $L = 0.003$ M, $\mu = 0.25$ M at 60° C. and 70° C. and it was found that the rate law was of the form

$$-R_L = k_5 [L] + k_6 [L] [S_2R_8^-] [H^+].$$

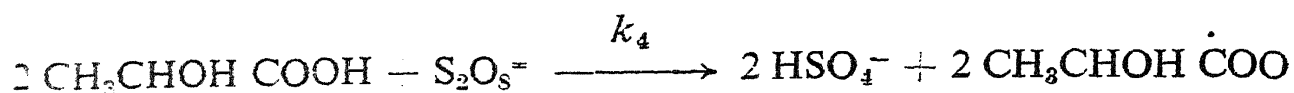
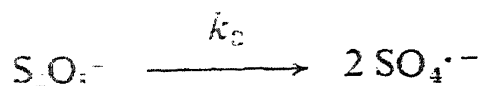
From plots of $-R_L$ vs. $[L]$ at constant $[S_2O_8^{2-}]$; $[H^+]$, etc., k_5 and k_6 were evaluated and the Arrhenius equations derived.

$$k_5 = 9.0 \times 10^{-1} \exp. (-5988/R \times 333.3) \text{ sec.}^{-1}$$

$$k_6 = 8.867 \exp. (-6939/R \times 333.3) \text{ lit.}^2 \text{ mole}^{-2} \text{ sec.}^{-2}$$

A stoichiometry of $-\Delta [S_2O_8^{2-}]/\Delta (CH_3CHO) \approx 1$ was observed. The results under conditions of $[L] > 0.35$ M may be satisfactorily explained

on the basis of the mechanism involving the dissociated lactic acid as the active species:



followed by water oxidation reaction

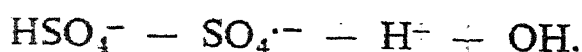
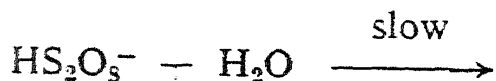


The decrease of $-R_{S_2O_8^{2-}}$ with increased $[L]$ (≥ 0.35 M) appears to be due to the effect of ionic strength involving the interactions of specific ions like $S_2O_8^{2-}$ and H_3O^+ .

(5) *Oxidation studies in D₂O*.—Malonic acid whose oxidation was found to be independent of $[H^-]$ was taken as a typical acid for oxidation studies in heavy water, under conditions $K_2S_2O_8 = 0.005$ M in D_2O ; [Malonic acid] = 0.02 M in D_2O and $\mu = 0.2$ M. The rate law was of the form $-R_{S_2O_8^{2-}} = k_{D_2O} [S_2O_8^{2-}]$, and from experiments conducted at 60° and 70° C. the Arrhenius equation was derived.

$$k_{D_2O} = 2.429 \times 10^{12} \exp. (-24,020/R \times 333.3) \text{ sec.}^{-1}$$

The kinetic isotopic effect $k_{H_2O}/k_{D_2O} = 1.52$ at 60° C. and 1.84 at 70° C. were obtained, k_{H_2O} being same as k_m under (1) above. On the basis of kinetic isotopic effects connected with substrates involving C-H bond, $k_{H_2O}/k_{D_2O} > 1$ would indicate proton transfer (or deuteron) in the rate determining step.



Radicals $SO_4^{\cdot -}$ and OH oxidise the substrate molecules to products.

ACKNOWLEDGEMENT

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