

OXIDATION STUDIES

I. Oxidation of Primary Alcohols by Peroxydisulfate

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ABSTRACT

Results on the oxidation of primary alcohols (methanol, ethanol, *n*-propanol, *n*-butanol and isobutanol) by peroxydisulfate in aqueous solution in the temperature range 50°–80°, under uncatalysed, Ag⁺ catalysed and deaerated conditions are presented. Oxygen was found to have a retarding effect on the rate of peroxydisulfate disappearance, $-R_{S_2O_8^{2-}}$, and the inhibition period was a maximum in the case of ethanol and isobutanol. Both under uncatalysed and Ag⁺ catalysed conditions $-R_{S_2O_8^{2-}}$ varied with $[S_2O_8^{2-}]^{3/2}$ for all the alcohols; $-R_{S_2O_8^{2-}}$ was independent of alcohol concentration for all the alcohols except for methanol and ethanol where a one-half order with respect to [alcohol] was observed. In the Ag⁺ catalysed oxidation $-R_{S_2O_8^{2-}}$ varied as $[Ag^+]^{1/2}$ with all the alcohols. The effect of [H⁺], ionic strength, temperature, initially added product of the reaction on the rate are discussed and the stoichiometries of the reactions determined. In the light of the observed results, reaction mechanisms are postulated with SO₄^{·-} as the reactive species formed by thermal decomposition of S₂O₈²⁻ under uncatalysed conditions and by the interaction of Ag⁺ and S₂O₈²⁻ under Ag⁺ catalysed conditions. The existence of Ag⁺⁺ in catalysed reactions is postulated. The values of rate constants, frequency factors, energies of activation, entropies of activation, etc., were evaluated.

I. INTRODUCTION

THE previous studies on kinetics of oxidation of alcohols by S₂O₈²⁻ were reviewed recently by House¹ and by Wilmarth and Haim.² Results of oxidation of allyl alcohol,^{3,4} methanol,^{4,5,6} ethanol^{4,5} and isopropanol⁶⁻¹¹ in aqueous solution under uncatalysed conditions were reported. An increase in the rate of thermal decomposition of S₂O₈²⁻, $-R_{S_2O_8^{2-}}$, was noticed when these alcohols were added to an aqueous solution of S₂O₈²⁻. It was observed by

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Kolthoff *et al.*,⁵ and by Wiberg⁷ that addition of a radical scavenger, *viz.*, allyl acetate to the alcohol - $S_2O_8^{2-}$ system decreased the rate to that found in the absence of alcohol and it was concluded that the thermal decomposition of $S_2O_8^{2-}$ + alcohol reaction was important as an initiation step. In the case of isopropanol Levitt *et al.*,^{9,11} proposed an ionic mechanism based on formation of SO_4 and $SO_4^{\cdot-}$ from $S_2O_8^{2-}$ and the reaction $SO_4 +$ alcohol giving a monoperoxysulfate ester. A more systematic study of isopropanol by Ball *et al.*,^{6,8} showed that thermal decomposition of $S_2O_8^{2-}$ leading to formation of $SO_4^{\cdot-}$ was the initiation step and that the presence of oxygen retarded the reaction considerably. Bartlett and Cotman³ have investigated the oxidation of Methanol and allyl alcohol under uncatalysed conditions in the presence of a phosphate buffer. A 3/2 order with respect to $[S_2O_8^{2-}]$ and a $\frac{1}{2}$ order with respect to [Methanol] were reported and the results were interpreted on the assumption that $S_2O_8^{2-}$ did not react directly with the alcohol and that $SO_4^{\cdot-}$ was responsible for the chain reaction. Kolthoff *et al.*⁵ studied the decomposition of $S_2O_8^{2-}$ in aqueous solution in buffered medium containing methanol, ethanol or allyl alcohol and the results of Bartlett and Cotman were confirmed. Bawn and Margerison¹² investigated the kinetics of dissociation of $S_2O_8^{2-}$ in ethyl alcohol-water mixture (in the presence and absence of Ag^+) by use of the free radical capturing agent, diphenyl-picrylhydrazyl. $SO_4^{\cdot-}$ and Ag^{++} were considered as the reactive species. Kinetics of oxidation of methanol and ethanol studied earlier by Bartlett *et al.*³ and Kolthoff *et al.*⁵ were extended by us to cover some of the aspects like effect of oxygen, $[H^+]$, μ , T, etc., on the rate. Ag^+ catalysed oxidation of these alcohols not investigated so far were also investigated in great detail and discussed by us. We have carried out a systematic study of the uncatalysed and Ag^+ catalysed oxidation of other primary alcohols (*n*-propanol, *n*-butanol and isobutanol) under deaerated conditions in the temperature range 50°–80° C. Mechanisms of oxidation under these conditions are discussed and the thermodynamic data are presented. Preliminary results of the oxidation of these alcohols were given by us in a note.¹³ Fuller details with regard to results of oxidation, mechanism and discussion are now presented.

II. EXPERIMENTAL

(a) *Materials.*—Most of the details appear in the other papers.¹⁴ All chemicals used in the preparation of reagents were samples of A.R. or G.R. grade. Distilled water doubly distilled over permanganate in an all-glass pyrex still followed by passage through a column of "Biodeminrolit" ion exchange resin (Permutit Co. of U.K.) was used throughout. $K_2S_2O_8$

(G.R. E. Merck grade) solution (0.2 M) freshly prepared and assayed by iodometric or ferrometric method¹⁴ was used for the experiments. Fresh stock solution (1×10^{-2} M) of AgNO_3 (B.D.H. A.R. sample) was prepared periodically. Methanol (E. Merck G.R. grade) was used without further purification. Absolute ethanol was prepared from commercial rectified spirit by adopting standard procedures. Ethanol used was always free from acetaldehyde. *n*-Propanol (B.D.H. A.R.) sample was fractionally distilled (B.P. $97^\circ\text{C}/760$ mm. Hg.) and used. *n*-Butanol (E. Merck chromatographic sample), isobutanol (B.D.H. A.R. sample) were fractionally distilled (B.P. 117.5°C . and $107.5^\circ\text{C}/760$ mm. Hg. respectively) and used. Phosphate buffer was used and its concentration was always taken in computing ionic strength. The ionic strengths refer to initial conditions only and in view of high ionic strengths (> 1.2) and low rates obtaining under our experimental conditions small changes of ionic strength were supposed to have no mechanistic significance.

(b) *Reaction Techniques*.—Details with regard to reaction vessel, deaeration technique, etc., will appear elsewhere.¹⁴ Reaction mixtures containing the requisite quantities of aqueous alcohol, salt, etc. Ag^+ (in catalysed reactions) were taken in the reaction vessel and deaerated by passing oxygen free nitrogen. The $\text{S}_2\text{O}_8^{2-}$ solution was deaerated separately. After deaeration the reaction mixture and the $\text{S}_2\text{O}_8^{2-}$ solution were kept in the thermostat (accuracy $\pm 0.1^\circ\text{C}$.) for 15 minutes to attain the experimental temperature ($50^\circ\text{--}80^\circ\text{C}$.). A known volume of the $\text{S}_2\text{O}_8^{2-}$ solution was then transferred to the reaction mixture and aliquots were removed and analysed as described below.

(c) *Rate Measurements*.—The rate of disappearance of $\text{S}_2\text{O}_8^{2-}$, $-\text{R}_{\text{S}_2\text{O}_8^{2-}}$ was followed by iodometric estimation of the unreacted $\text{S}_2\text{O}_8^{2-}$.¹⁵ Further reaction in the aliquots (5 ml.) was quenched by addition of ice-cold water containing 2 gm. of KI (25 ml.); the solution was then set aside in dark for 45 minutes, acidified with 6 N acetic acid (2 ml.) and the liberated iodine titrated against standard thiosulfate. Suitable blank corrections were made wherever thermal decomposition of $\text{S}_2\text{O}_8^{2-}$ was appreciable.

(d) *Determination of Stoichiometry*.—The reaction was allowed to 80% completion and then the residual $\text{S}_2\text{O}_8^{2-}$ was estimated, due allowance being given for the thermal decomposition of $\text{S}_2\text{O}_8^{2-}$. The formaldehyde formed in the oxidation of methanol was estimated colorimetrically using chromotropic acid.¹⁶ The colorimetric method was quite sensitive for estimating $[\text{CH}_2\text{O}] \cong 10^{-2}$ M. In the oxidation of ethanol, the acetaldehyde formed was estimated by the sodium sulfite procedure. With other primary alcohols

the corresponding aldehydes formed in each case were precipitated as their 2:4 Dinitrophenylhydrazones and estimated gravimetrically.

III. RESULTS AND DISCUSSION

General Features.—The reaction systems $S_2O_8^{2-}$ — Methanol or Ethanol were studied both under buffered (pH, 8-phosphate buffer) and unbuffered conditions (pH = 2–4). Studies on oxidations of *n*-propanol, *n*- and isobutanols were carried out under unbuffered conditions only in view of some complex features appearing with buffers in these. The uncatalysed reactions were generally studied at 60°–80° and the Ag^+ catalysed reactions at 50°–70° C. The orders with respect to the various constituents were determined from the data obtained in a series of kinetic runs under different initial concentrations of the substrates. Earlier workers^{3,5} who studied the oxidation of methanol and ethanol determined the orders from a single kinetic run. To avoid complications if any, by the products of the reaction on the oxidation, the rate was followed only up to 20–25% of the total reaction in most of the experiments. The $[substrate]/[S_2O_8^{2-}] \approx 10$ –20. It was found that there were no photochemical or heterogeneous reactions superimposed on the thermal reactions. We observed in the case of all the alcohols that the rate was generally retarded in the presence of oxygen. With ethanol as the substrate a definite inhibition period was observed and the latter increased with decreasing temperature and was also greater in buffered than in unbuffered medium. A maximum retardation in the rate was noticed with isobutanol.

(a) *Oxidation of Methanol and Ethanol.*—For the deaerated and uncatalysed system, the orders with respect to $[S_2O_8^{2-}]$ and $[alcohol]$ were 3/2 (Fig. 1, A, B) and 1/2 (Fig. 1, C, D) respectively both under buffered and unbuffered conditions. Hydrogen ion (0.1–1.0 M) did not influence the rate of oxidation. Increase of ionic strength (0.06–1.2 M) by added $KHSO_4$ or $NaClO_4$ caused a significant decrease in $-R_{S_2O_8^{2-}}$ at higher values of ionic strength, especially in the case of ethanol. With both alcohols a stoichiometry $-\Delta [S_2O_8^{2-}]/\Delta [aldehyde] = 1:1$ was obtained. Formaldehyde and acetaldehyde together with traces of acetic acid were detected as the products of oxidation of methanol and ethanol respectively. The Arrhenius equations

$$kr_1 = 1.351 \times 10^{11} \exp. (-20,140/R \times 343) \text{ lit. mole.}^{-1} \text{ sec.}^{-1} \text{ for methanol}$$

and

$$kr_2 = 2.549 \times 10^8 \exp. (-15,250/R \times 328) \text{ lit. mole.}^{-1} \text{ sec.}^{-1} \text{ for ethanol}$$

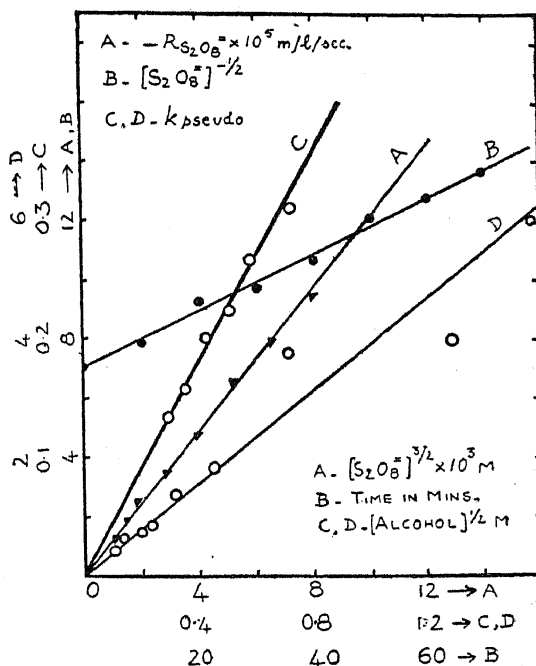
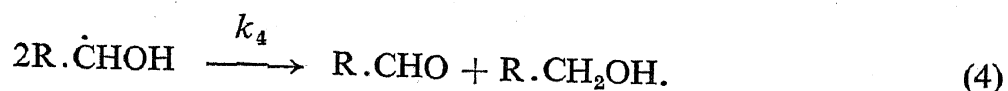
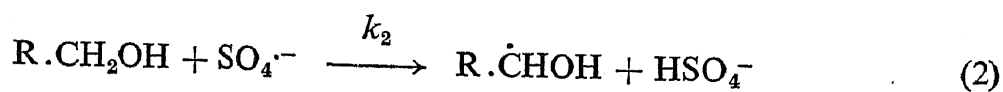
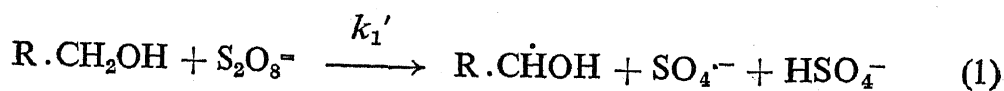


FIG. 1. Dependence of rate on $[S_2O_8^{2-}]$ and $[Alcohol]$

- A. Ethanol (0.1692 M); $\mu = 0.12 \text{ M}$; Temperature: 60° C .
 B. Methanol (0.5026 M); $[S_2O_8^{2-}] = 2 \times 10^{-2} \text{ M}$; $\mu = 0.12 \text{ M}$; Temperature: 70° C ;
 pH = 7.8 (KH_2PO_4 buffer).
 C. Methanol — $[S_2O_8^{2-}] = 2 \times 10^{-2} \text{ M}$; $\mu = 0.06 \text{ M}$; Temperature: 60° C .
 D. Ethanol — $[S_2O_8^{2-}] = 2 \times 10^{-2} \text{ M}$; $\mu = 0.06 \text{ M}$; Temp: 65° C .

were obtained. The rate law for the uncatalysed system is therefore of the form $-R_{S_2O_8^{2-}} = kr [S_2O_8^{2-}]^{3/2} [alcohol]^{1/2}$ where $kr = kr_1$ or kr_2 . Plot of $-R_{S_2O_8^{2-}}$ vs. $[S_2O_8^{2-}]^{3/2}$ (Fig. 1, A) or $[S_2O_8^{2-}]^{-1/2}$ vs. time (Fig. 1, B) were linear and a plot of $\log -R_{S_2O_8^{2-}}$ vs. $\log [S_2O_8^{2-}]$ gave a straight line with a slope of 1.5 . Plots of k_{pseudo} vs. $[alcohol]^{1/2}$ (Fig. 1, C, D) were linear without any intercept on the ordinate which indicated that water oxidation was negligible. Our results generally support the mechanism given by Bartlett *et al.*³ and Kolthoff *et al.*⁵ that the reactions are free radical in nature. A direct reaction between alcohol and $S_2O_8^{2-}$ may have to be assumed to explain the square root dependence on $[alcohol]$. If $SO_4^{\cdot -}$ produced from the thermal decomposition of $S_2O_8^{2-}$ alone is considered as the initiator it is then difficult to explain the square root dependence on $[alcohol]$. Kolthoff *et al.* suggested that the square root dependence on $[alcohol]$ might probably be due to the oxidation of products (aldehydes) by $S_2O_8^{2-}$, though no exact mechanism for such oxidation was suggested by the former. Under our experimental conditions separate experiments between $S_2O_8^{2-} +$ corresponding aldehyde showed that no appreciable oxidation of the latter to the

acid stage took place. Added aldehyde to the reaction system, $S_2O_8^{2-}$ + alcohol, also caused a decrease in the rate of the reaction. The retardation by added aldehyde through acetal formation had to be discounted in view of drastic conditions for formation of the latter and not obtaining in our experimental conditions. Further, trace of acetal if formed would easily hydrolyse in aqueous acid medium. The following mechanism therefore explains most of the observed results:



From the sequence of reactions the rate expression $-R_{S_2O_8^{2-}} = k_1' [S_2O_8^{2-}] [R \cdot CH_2OH] + k_3 (2k_1'/k_4)^{1/2} [S_2O_8^{2-}]^{3/2} [R \cdot CH_2OH]^{1/2}$ may be derived and if k_1' is considered to be small in comparison with other rate constants, the resulting rate expression equivalent to the observed rate expression could be obtained. This assumption seems to be justified since plots of $-R_{S_2O_8^{2-}}$ vs. $[S_2O_8^{2-}]^{3/2}$ (Fig. 1, A) or k_{pseudo} vs. $[R \cdot CH_2OH]^{1/2}$ (Fig. 1, C, D) are linear without any intercept on the ordinate. Kolthoff *et al.*⁵ reported that in the plot of $[S_2O_8^{2-}]^{-1/2}$ vs. time, deviation from linearity in the initial stages and perfect linearity only after 20 minutes from the start of the reaction were obtained. In our work no such deviation was noticed and up to 70% of the reaction the rate law proposed was found to obey.

The kinetics of the Ag^+ catalysed oxidation of methanol and ethanol followed more or less the same pattern as the uncatalysed reaction, the order with respect to $[S_2O_8^{2-}]$ being 3/2 and $[\text{alcohol}]$ being 1/2 (Fig. 2, A). $-R_{S_2O_8^{2-}}$ was also found to be proportional to $[Ag^+]^{1/2}$ (Fig. 2, B, C). $[H^+]$ did not affect the rate. Increase of ionic strength (0.06, -0.4 M by added $NaClO_4$) caused a significant decrease in the reaction rate (the k_{pseudo} value in the case of ethanol decreased from 0.8800 $\text{lit.}^{3/2} \text{mole.}^{-3/2} \text{sec.}^{-1}$ to 0.3399 $\text{lit.}^{3/2} \text{mole.}^{-3/2} \text{sec.}^{-1}$). In the presence of Ag^+ the Arrhenius equations

$$k_{r_3} = 3.131 \times 10^{10} \exp. (-15,740/R \times 343) \text{ lit.}^{3/2} \text{mole.}^{-3/2} \text{sec.}^{-1} \text{ for methanol}$$

and

$$kr_4 = 3.129 \times 10^7 \exp. (-10,400/R \times 328) \text{ lit.}^{3/2} \text{ mole.}^{-3/2} \text{ sec.}^{-1}$$

for ethanol

were obtained. The rate law is of the form

$$-R_{S_2O_8^{2-}} = kr [S_2O_8^{2-}]^{3/2} [Alcohol]^{1/2} [Ag^+]^{1/2}$$

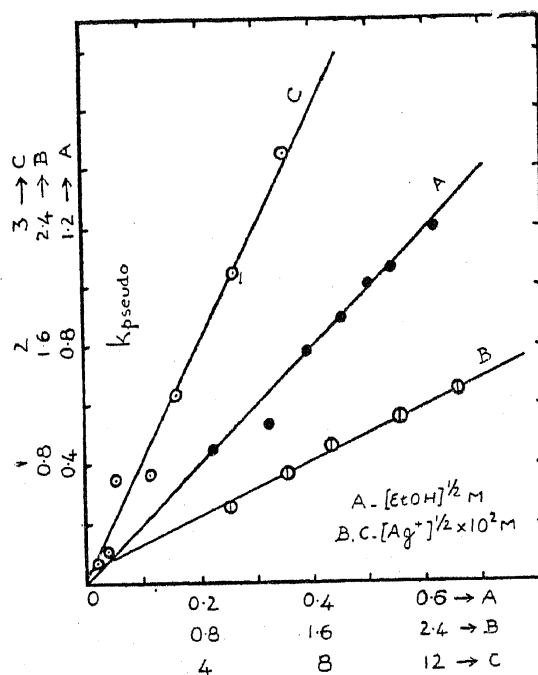
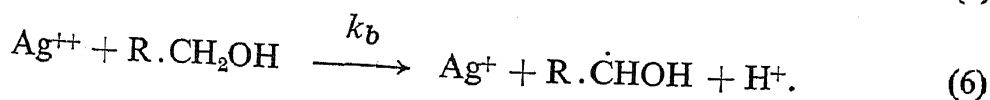
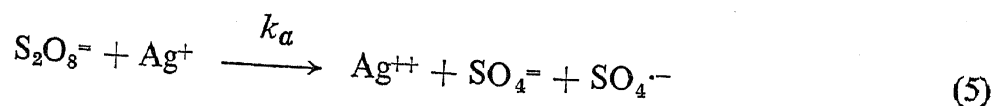


FIG. 2. Dependence of rate on [Alcohol] and $[Ag^+]$

- A. Ethanol — $[S_2O_8^{2-}] = 2 \times 10^{-2} M$; $[Ag^+] = 1 \times 10^{-4} M$; $\mu = 0.06 M$; Temperature: $50^\circ C$.
 B. Methanol ($0.3452 M$); $[S_2O_8^{2-}] = 2 \times 10^{-2} M$; $\mu = 0.06 M$; Temperature: $60^\circ C$.
 C. Ethanol ($0.1692 M$); $[S_2O_8^{2-}] = 2 \times 10^{-2} M$; $\mu = 0.06 M$; Temperature: $50^\circ C$.

where $kr = kr_3$ or kr_4 . Plot of k_{pseudo} vs. $[alcohol]^{1/2}$ (Fig. 2,A) was linear without any intercept indicating that the thermal decomposition was negligible under the experimental conditions. The plot of k_{pseudo} vs. $[Ag^+]^{1/2}$ (Fig. 2,C, D) left an intercept indicating that the uncatalysed oxidation of the alcohols also took place in the Ag^+ catalysed reactions but the former was relatively low. Here again $[alcohol]^{1/2}$ dependence can be explained only if it is assumed that $S_2O_8^{2-}$ and alcohol react directly. The catalysis by Ag^+ and the square root dependence of $-R_{S_2O_8^{2-}}$ on $[Ag^+]$ might be interpreted by considering the following steps (5) and (6) in addition to the steps (1) to (4) already suggested for the uncatalysed oxidation.



These steps seem to explain satisfactorily the observed experimental facts. Step (5) has also been suggested by Bawn and Margerison¹² in their study on the catalysed $\text{S}_2\text{O}_8^{2-}$ decomposition in presence of diphenylpicrylhydrazyl and by Allen *et al.*¹⁷ in the Ag^+ catalysed oxidation of oxalate. It may be mentioned, however, that one is not very certain about the state of oxidised Ag^+ being Ag^{++} or AgO^+ (Ag^{3+}) though the latter has to be discounted on the ground of 2-electron transfer in its formation. Catalysis was observed because steps (5) and (6) also contribute to radical production steps in addition to step (1). Step (5) being a reaction between oppositely charged ions, a negative salt effect would be expected and is in fact observed. The energies of activation were also widely different between the catalysed and uncatalysed systems indicating thereby that their mechanisms are quite different. Also the activation energy for the catalysed system (10–15 Kcal; *c.f.* $\Delta E \approx 28$ –32 Kcal for the uncatalysed^{3,12} corresponding to the fission of $-\text{O}-\text{O}-$, linkage) is of the same order as has been observed¹² for Ag^+ catalysed oxidation of water by $\text{S}_2\text{O}_8^{2-}$ ($\Delta E \approx 16$ –17 Kcal). This suggests that the reaction $\text{Ag}^+ + \text{S}_2\text{O}_8^{2-}$ and not $\text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{\cdot-}$ is the initiation step under Ag^+ catalysed conditions.

(b) *Oxidation of n-Propanol, n-Butanol and Isobutanol.*—It is found that the kinetics of oxidation of these alcohols did not conform to those of methanol and ethanol. In the uncatalysed oxidation the rate of peroxydisulfate disappearance, $-\text{R}_{\text{S}_2\text{O}_8^{2-}}$, was found to be dependent on the 3/2 power of $[\text{S}_2\text{O}_8^{2-}]$ (Fig. 3-A, B, C) and independent of [alcohol], $[\text{H}^+]$ and ionic strength (by added KHSO_4 or NaClO_4). The stoichiometry of all the three alcohols, $-\Delta [\text{S}_2\text{O}_8^{2-}] / \Delta [\text{aldehyde}] = 1:1$, was observed and the corresponding aldehydes were identified as products of the reaction mixture after completion of the reaction. Addition of product (the corresponding aldehydes) to the reaction system caused a decrease in the rate of the reaction. From the studies of temperature dependence on rates, the following Arrhenius equations were obtained:

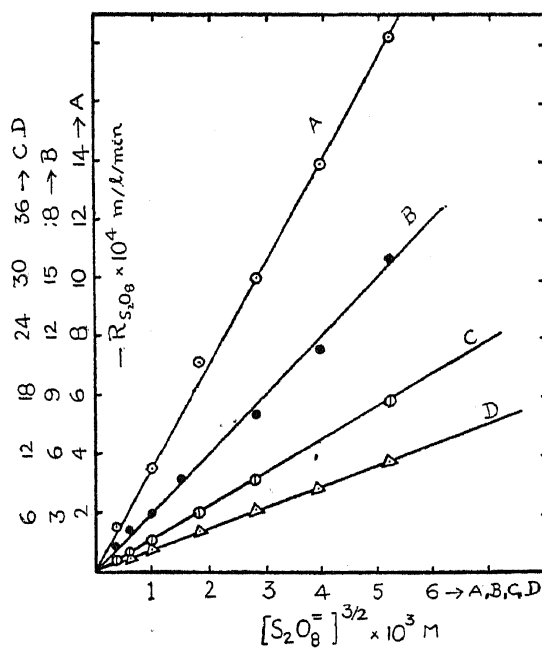
$$kr_5 = 9.181 \times 10^{15} \exp. (-28,160/R \times 343) \text{ lit.}^{\frac{3}{2}} \text{ mole.}^{-\frac{3}{2}} \text{ sec.}^{-1} \\ \text{for } n\text{-propanol}$$

$$kr_6 = 2.729 \times 10^{15} \exp. (-27,740/R \times 343) \text{ lit.}^{\frac{3}{2}} \text{ mole.}^{-\frac{3}{2}} \text{ sec.}^{-1} \\ \text{for } n\text{-butanol}$$

and

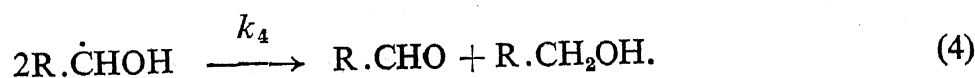
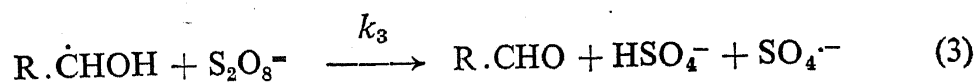
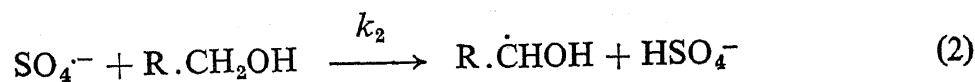
$$kr_7 = 1.888 \times 10^{14} \exp. (-25,990/R \times 343) \text{ lit.}^{\frac{1}{2}} \text{ mole.}^{-\frac{1}{2}} \text{ sec.}^{-1}$$

for isobutanol.

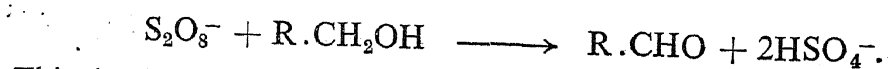
FIG. 3. Dependence of rate on $[S_2O_8^{2-}]$

- A. *n*-Propanol (0.3969 M) }
 B. *n*-Butanol (0.5400 M) } $\mu = 0.12$ M Temperature: 70° C.
 C. Isobutanol (0.5400 M) }
 D. *n*-Propanol (0.3969 M); $[Ag^+] = 1 \times 10^{-4}$ M; $\mu = 0.12$ M; Temperature: 60° C.

The experimental results would conform to the rate expression $-R_{S_2O_8^{2-}} = kr [S_2O_8^{2-}]^{3/2}$ where $kr = kr_5, kr_6$ or kr_7 . Plot of $-R_{S_2O_8^{2-}}$ vs. $[S_2O_8^{2-}]^{3/2}$ (Fig. 3, A, B, C) were linear indicating 3/2 power dependence of $[S_2O_8^{2-}]$. The most probable mechanism which explains the observed rate law is the following:



with the overall reaction



This leads to the rate expression

$$-R_{S_2O_8^{2-}} = k_1 [S_2O_8^{2-}] + k_3 (2k_1/k_4)^{1/2} [S_2O_8^{2-}]^{3/2}$$

and if $k_1 \ll k_3$, the rate expression would correspond to observed facts. This assumption seems justified because the rate of production of $SO_4^{\cdot-}$ is controlled mainly by step (3), which is the propagating step, and step (1) which initiates the reaction seems to give a few $SO_4^{\cdot-}$ by the slow thermal decomposition of $S_2O_8^{2-}$. Moreover, the first term corresponds to the water oxidation rate which was observed to be negligible (absence of intercept in the plots of $-R_{S_2O_8^{2-}}$ vs. $[S_2O_8^{2-}]^{3/2}$ (Fig. 3, A, B, C). The activation energies for the three alcohols were more or less the same and so also their rates. The ΔE values corresponded to that required for the cleavage of the $-O-O-$ bond of $S_2O_8^{2-}$. This showed that all the three alcohols had a common step of initiation, *viz.*, step (1) $S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$.

The kinetics of Ag^+ catalysed oxidation of these three alcohols were similar to the corresponding uncatalysed oxidation and in addition $-R_{S_2O_8^{2-}}$ was also dependent on $[Ag^+]^{1/2}$ (Fig. 4, A, B, C). The 3/2 order for $[S_2O_8^{2-}]$

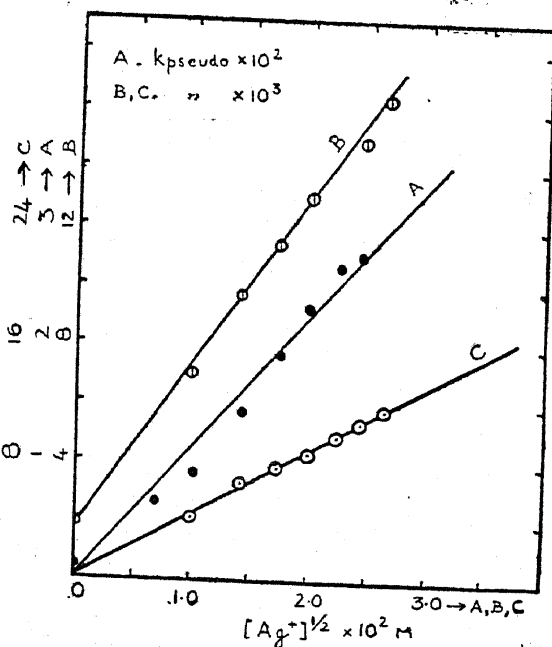


FIG. 4. Dependence of rate on $[Ag^+]$

A. *n*-Propanol (0.3969 M) }
 B. *n*-Butanol (0.5400 M) } $[S_2O_8^{2-}] = 5 \times 10^{-2} M$; $\mu = 0.015 M$; Temperature: $60^\circ C$.
 C. Isobutanol (0.5400 M) }

(Fig. 3, D) and the independence of rate on [alcohol] and $[H^+]$ were observed. Increase of ionic strength (0.1–1.00 M with added $KHSO_4$ or $NaClO_4$) decreased the rate considerably (the k_{pseudo} value in the case of isobutanol decreased from $9 \cdot 100 \times 10^{-3}$ to $1 \cdot 084 \times 10^{-3}$ lit.^{1/2} mole.^{-1/2} sec.⁻¹). The Arrhenius equations obtained for catalysed reactions were

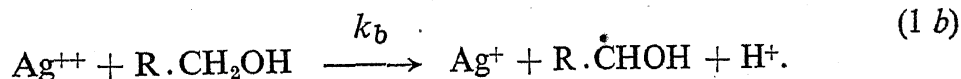
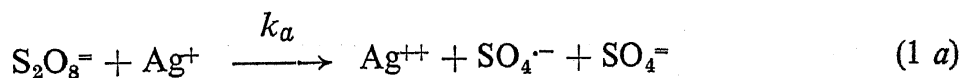
$$kr_8 = 1 \cdot 819 \times 10^{10} \exp. (-15,700/R \times 343) \text{ lit. mole.}^{-1} \text{ sec.}^{-1} \\ \text{for } n\text{-propanol}$$

$$kr_9 = 1 \cdot 917 \times 10^{10} \exp. (-16,910/R \times 343) \text{ lit. mole.}^{-1} \text{ sec.}^{-1} \\ \text{for } n\text{-butanol}$$

and

$$kr_{10} = 7 \cdot 163 \times 10^{11} \exp. (-18,640/R \times 343) \text{ lit. mole.}^{-1} \text{ sec.}^{-1} \\ \text{for isobutanol.}$$

The rate expression for the catalysed reaction is given by $-R_{S_2O_8^{2-}} = kr [S_2O_8^{2-}]^{3/2} [Ag^+]^{1/2}$ where $kr = kr_8, kr_9$ or kr_{10} . A mechanism which replaces the first step (1) in the uncatalysed oxidation of these alcohols by the two following steps (1a) and (1b) will explain the square root dependence of rate on $[Ag^+]$ if it is assumed that $ka \ll k_3$.



Plots of $-R_{S_2O_8^{2-}}$ vs. $[S_2O_8^{2-}]^{3/2}$ (Fig. 3, A, B, C) gave no intercept and also plots of the pseudo rate constant against $[Ag^+]^{1/2}$ (Fig. 4, A, B, C) were linear with an intercept on the ordinate which represented the uncatalysed substrate oxidation rate. The significant decrease in the rate with increasing ionic strength might probably be due to the first step (1 a) in which ions of opposite charges react. The activation energy values for the catalysed system were also comparable to that observed in the catalysed water oxidation wherein the step (1 a) is operative.

The values of ΔS^\ddagger are given under the corresponding substrates in Tables I and II. From a comparison of these values it is evident that they are generally positive for uncatalysed reactions (+ 4 to 12 E.U.) and negative (– 3 to 26 E.U.) for Ag^+ catalysed reactions. With Ag^+ catalysed reactions such negative values are expected because of the reaction between oppositely charged ions. With methanol and ethanol though ΔE values were less compared to those for the other alcohols there was not a great increase in the rate because of compensation by negative entropy values. The

TABLE I
Thermodynamic values (methanol and ethanol)

A: $[S_2O_8^{2-}] = 2 \times 10^{-2}$ M; Temperature: 70° C.; Ionic Strength: 0.06 M;
 B: $[S_2O_8^{2-}] = 2 \times 10^{-2}$ M; Temperature: 70° C.; Ionic Strength: 0.06 M; $[Ag^+] = 1 \times 10^{-4}$ M

	A. Uncatalysed		B. Catalysed	
	Methanol 0.3452 M	Ethanol 0.3384 M	Methanol 0.3452 M	Ethanol 0.3384 M
Rate $\times 10^5$ m/l/s ..	3.3990	8.6760	4.9690	12.690
Rate constant ..	2.045×10^{-1} $l.m^{-1}s^{-1}$	5.273×10^{-2} $l.m^{-1}s^{-1}$	2.9900 $l^{3/2}m^{-3/2}s^{-1}$	7.711 $l^{3/2}m^{-3/2}s^{-1}$
Frequency factor ..	1.351×10^{11} $l.m^{-1}s^{-1}$	2.717×10^8 $l.m^{-1}s^{-1}$	3.131×10^{10} $l^{3/2}m^{-3/2}s^{-1}$	3.244×10^7 $l^{3/2}m^{-3/2}s^{-1}$
ΔE K cal/mole ..	20.14	15.25	15.74	10.40
$\Delta S \pm$ E.U. ..	-9.8	-22.2	-12.8	-26.4
Rate uncatalysed: catalysed	1:1.462	1:1.463

TABLE II
Thermodynamic Values (n-Propanol, n-Butanol and Isobutanol)

A: $[S_2O_8^{2-}] = 5 \times 10^{-3}$ M; Temperature: 70° C.; Ionic Strength: 0.015 M;
 B: $[S_2O_8^{2-}] = 5 \times 10^{-3}$ M; Temperature: 70° C.; Ionic strength: 0.015 M; $[Ag^+] = 1 \times 10^{-4}$ M;

	A. Uncatalysed			B. Catalysed		
	n-Propanol 0.3969 M	n-Butanol 0.5400 M	Isobutanol 0.5400 M	n-Propanol 0.3969 M	n-Butanol 0.5400 M	Isobutanol 0.5400 M
Rate $\times 10^6$ m/l/s ..	2.5830	2.1000	1.9330	6.4310	3.3210	3.4170
Rate constant ..	1.054×10^{-2} $l^{1/2}m^{-1/2}s^{-1}$	5.833×10^{-3} $l^{1/2}m^{-1/2}s^{-1}$	5.320×10^{-3} $l^{1/2}m^{-1/2}s^{-1}$	1.819 $l.m^{-1}s^{-1}$	0.939 $l.m^{-1}s^{-1}$	0.966 $l.m^{-1}s^{-1}$
Frequency factor ..	9.181×10^{15} $l^{1/2}m^{-1/2}s^{-1}$	2.729×10^{15} $l^{1/2}m^{-1/2}s^{-1}$	1.888×10^{14} $l^{1/2}m^{-1/2}s^{-1}$	1.819×10^{10} $l.m^{-1}s^{-1}$	1.919×10^{10} $l.m^{-1}s^{-1}$	7.163×10^{11} $l.m^{-1}s^{-1}$
ΔE Kcal./mole ..	28.16	27.74	25.99	15.70	16.91	18.64
$\Delta S \pm$ E.U. ..	12.3	9.8	4.5	-13.9	-13.9	-6.6
Rate Uncatalysed : Catalysed	1 : 2.490	1 : 1.585	1 : 1.768

ΔS^\ddagger values of *n*-propanol, *n*-butanol and isobutanol were of the same order (5–12 E.U.) but different from those (–10 to 22 E.U.) for methanol and ethanol which indicated the difference in mechanisms between the two types. It may also be mentioned that ΔS terms for butanol and isobutanol (Table II) vary probably because of the difference in the structures of their respective transition states. The ΔE values for Ag^+ catalysed reactions were considerably less than for the uncatalysed reactions; the increase in rate in the catalysed reactions was however only 1.5 times that of the uncatalysed rate. This is evidently due to the accompanied large decrease in the ΔS^\ddagger values which indicates restricted internal freedom in the transition state compared to the reactants.

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