

Kinetics & Mechanism of Ag^+ -catalysed Oxidation of Glycerol by Peroxydisulphate—An Analysis of Consecutive Reactions

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Ag^+ -catalysed oxidation of glycerol by peroxydisulphate has been found to yield formaldehyde and glycolaldehyde by a first order process in the first stage, which is followed by the oxidation of the two aldehydes to yield formic and glycollic acids respectively by two independent first order reactions. A complete analysis of the two consecutive reactions has been made and the products have been characterized. The above findings are different from those reported previously for this reaction [J. Indian chem. Soc., 41 (1964), 402].

MISHRA and Ghosh¹ earlier showed that like other Ag^+ -catalysed oxidations by $\text{S}_2\text{O}_8^{2-}$, oxidation of glycerol is also first order with respect to oxidant and catalyst Ag^+ , and is of zero order with respect to glycerol. They identified formaldehyde, acetaldehyde, formic acid and acetic acid as the products of oxidation. However, neither any kinetic evidence was put forth for the formation of these compounds by side or consecutive reactions nor the reaction sequence worked out. It appears that this reaction, unlike the oxidations of other organic substrates by $\text{S}_2\text{O}_8^{2-}$ is a complex reaction consisting of side as well as consecutive reactions. In view of this we were prompted to reinvestigate this reaction to study the influence of side and consecutive reaction on the overall kinetics, and to identify the oxidation products. The uncatalysed oxidation of glycerol by peroxydisulphate has been reported by Vasudeva and Wasif².

Materials and Methods

All the chemicals used were of AR quality. Potassium peroxydisulphate was used after recrystallization.

The progress of the reaction was followed by estimating the unreacted $\text{K}_2\text{S}_2\text{O}_8$ iodometrically by the method of Szabo, Csanyi and Galiba³ as modified by Khulbe and Srivastava⁴.

The progress of the reaction was also followed kinetically by estimating the amount of total aldehyde formed⁵ as well as the amount of formaldehyde formed by spectrophotometric method⁵. In the above method the reaction was quenched by the addition of 5 ml of a saturated solution of KCl in each aliquot of 5 ml and centrifuged before applying the spectrophotometric method.

Results and Discussion

Product analysis and stoichiometry — Formaldehyde and glycolaldehyde were detected in the reaction mixture in earlier stages of the reaction by chromotropic acid test and diphenylamine test⁶, respectively.

It may be noted that acetaldehyde is not formed as reported by Mishra and Ghosh¹. This erroneous finding might perhaps have been due to the sodium nitroprusside and morpholine test used to characterize acetaldehyde which is also positive for glycolaldehyde. Further confirmation of the presence of glycolaldehyde is provided by a study of the NMR and IR spectra of 2,4-diphenylhydrazone of the TLC separated product. Further, the presence of a hydroxy acid (obviously glycollic acid) detected in the later stages of the reaction by sym. 1,5-diphenyl carbazide test⁷ confirms the formation of glycolaldehyde in the earlier stage.

The total amount of aldehyde formed at various intervals of time was estimated spectrophotometrically⁵ at 560 nm (characteristic of the complex between Schiff's reagent and the aldehyde at pH 2.7). The amount of formaldehyde at different intervals of time was also estimated spectrophotometrically but with the help of sodium salt of chromotropic acid at 570 nm⁵. The amount of glycolaldehyde was evaluated by difference. The quantities of aldehydes formed at three different temperatures are recorded in Table 1. It is apparent from Table 1 that the oxidation of glycerol by peroxydisulphate is a case of consecutive reaction since the [total aldehyde] starts decreasing after a certain interval of time. Formaldehyde and glycolaldehyde are formed nearly in equimolar amounts.

The mole ratio in the first stages of the reaction up to the formation of aldehydes has been found to be equal for the glycerol-peroxydisulphate reaction. The maximum yield in terms of total aldehyde formation is 85% at 35°.

Kinetic behaviour — The results of typical kinetic runs at three different temperatures followed by the estimation of the unreacted peroxydisulphate are graphically presented in Fig. 1. In these kinetic runs five-fold excess of $\text{S}_2\text{O}_8^{2-}$ has been employed so as to study the next stage of the reaction also. It appears from the data in Fig. 1 that the reaction consists of two first order consecutive reactions,

TABLE 1 — AMOUNTS OF FORMALDEHYDE AND GLYCOLALDEHYDE FORMED AT DIFFERENT STAGES OF REACTION AND AT DIFFERENT TEMPERATURES

{[Glycerol] = 0.01M; [K₂S₂O₈] = 0.05M; [AgNO₃] = 0.001M}

Time min	Temp. 35°C			Temp. 40°C			Temp. 45°C		
	[Total aldehyde] (M × 10 ³)	[HCHO] (M × 10 ³)	[Glycol- aldehyde] (M × 10 ³)	[Total aldehyde] (M × 10 ³)	[HCHO] (M × 10 ³)	[Glycol- aldehyde] (M × 10 ³)	[Total aldehyde] (M × 10 ³)	[HCHO] (M × 10 ³)	[Glycol- aldehyde] (M × 10 ³)
5	1.12	0.57	0.55	1.29	0.64	0.65	1.66	0.72	0.94
10	2.71	1.42	4.29	2.56	1.56	1.00	3.41	2.06	1.35
15	3.58	1.98	1.60	4.46	2.41	2.05	4.75	2.90	1.85
20	4.61	2.55	2.06	5.40	2.94	2.47	—	3.68	—
25	5.41	—	—	6.37	3.61	2.76	6.82	—	—
30	6.20	3.33	2.87	7.16	4.11	3.05	7.37	4.53	2.84
35	—	—	—	—	—	—	7.37	—	—
40	7.39	4.11	3.28	7.64	4.85	2.79	6.98	—	—
50	7.91	4.61	3.30	8.27	4.99	3.28	5.39	3.47	1.92
60	8.58	4.89	3.69	7.00	4.99	2.01	2.77	—	—
70	8.58	—	—	5.73	—	—	0.87	—	—
75	—	5.17	—	—	3.61	—	—	—	—
80	8.42	—	—	—	—	—	—	—	—
90	7.79	4.82	2.97	—	—	—	—	—	—

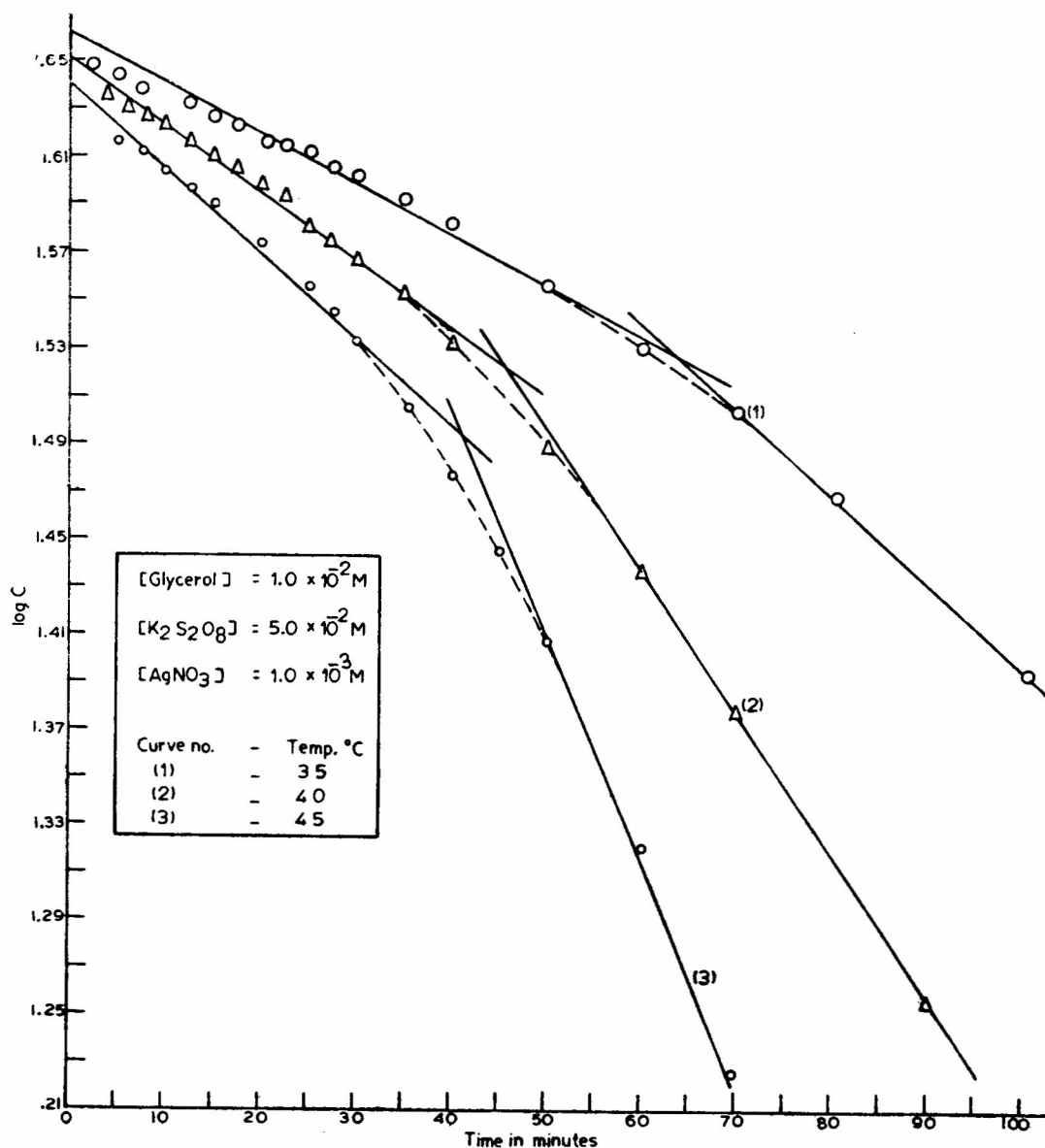


Fig. 1 — Plots of log C versus time (t) at different temperatures {[Glycerol] = 0.01M; [K₂S₂O₈] = 0.05M; [AgNO₃] = 0.001M}

TABLE 2 — SPECIFIC RATES OF OXIDATION OF REACTIONS (A) AND (B)

 $\{[\text{Glycerol}] = 0.01M; [\text{K}_2\text{S}_2\text{O}_8] = 0.05M; [\text{AgNO}_3] = 0.001M\}$

Temp. °C	$k_1^{(a)}$ (litres mol ⁻¹ min ⁻¹)	$k_1^{(b)}$ (litres mol ⁻¹ min ⁻¹)	$k_2^{(c)}$ (litres mol ⁻¹ min ⁻¹)	Sp. rate of oxidn of		$C_x (M \times 10^3)$		$C_y (M \times 10^3)$	
				HCHO (litres mol ⁻¹ min ⁻¹)	glycolaldehyde (litres mol ⁻¹ min ⁻¹)	Obs.	Calc.	Obs.	Calc.
35	4.96	6.40	8.30	4.95	3.35	5.17	3.14	3.70	2.87
40	6.47	8.36	13.65	5.43	8.22	4.99	3.15	3.28	2.54
45	8.42	11.76	21.82	6.28	15.54	4.53	2.63	2.84	2.45

(a) Refers to rate of consumption of $\text{S}_2\text{O}_8^{2-}$ (reaction-A). (b) Refers to rate of formation of formaldehyde (reaction-A). (c) Rate of oxidation of aldehydes. (d) $[\text{HCHO}] = 0.005M$; $[\text{S}_2\text{O}_8^{2-}] = 0.05M$; $[\text{Ag}^+] = 0.001M$. (e) Refers to rate of oxidation of glycolaldehyde (reaction-B).

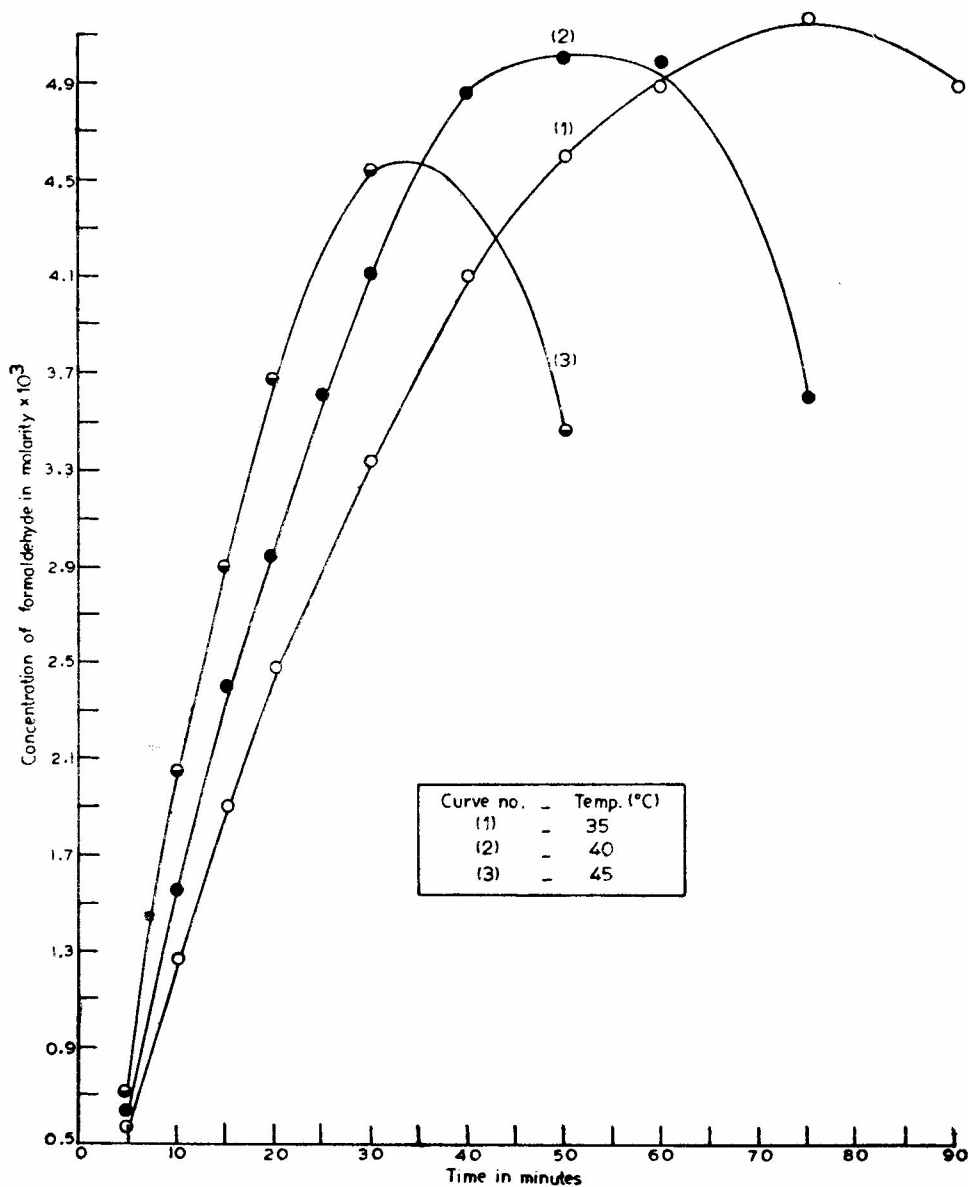


Fig. 2 — Plot of amount of HCHO formed versus time (t) at different temperatures $\{[\text{Glycerol}] = 0.01M; [\text{K}_2\text{S}_2\text{O}_8] = 0.05M; [\text{AgNO}_3] = 0.001M\}$

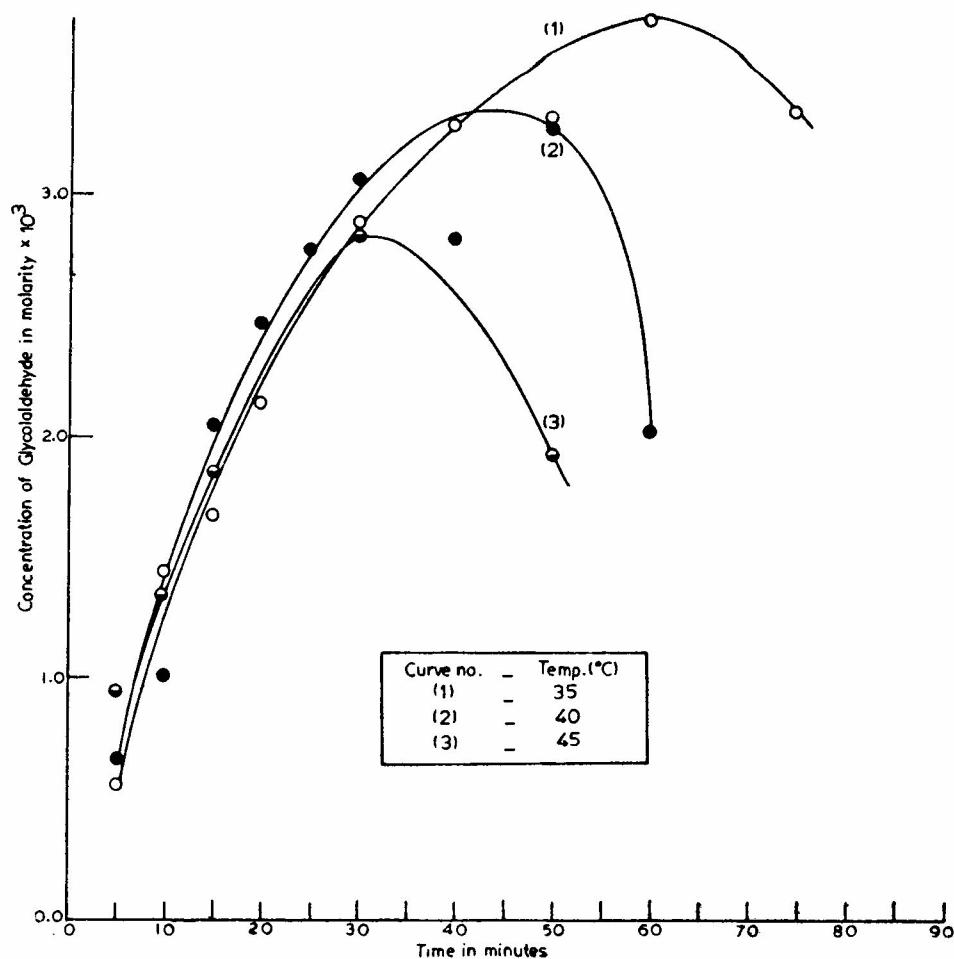


Fig. 3 — Amount of glycolaldehyde formed versus time (t) at different temperatures {[Glycerol] = 0.01M; $[K_2S_2O_8]$ = 0.05M; $[AgNO_3]$ = 0.001M}

designated as A and B. The specific rate (k_1) for the reaction-A was computed by estimating the amount of formaldehyde formed at different intervals of time and on the basis that one molecule of glycerol gives one molecule of formaldehyde and one molecule of glycolaldehyde. The specific rate (k_1 or k_2) reported was obtained by dividing the observed rate constant by the $[Ag^+]$ employed as catalyst, i.e. k_1 or $k_2 = k_{obs} / [Ag^+]$.

A perusal of the results given in Table 2 shows that the specific rate (k_1) for the reaction-A by formaldehyde determination and by peroxydisulphate consumption are of the same order of magnitude. In reaction-B the two aldehydes formed are getting oxidized into their products through two independent reactions. The specific rate for formaldehyde oxidation (k_2') into formic acid was determined separately also under identical conditions by taking formaldehyde nearly equal to the maximum amount, $C_x(\max)$ obtained in glycerol oxidation. The specific rate (k_2'') for glycolaldehyde oxidation was then evaluated by subtracting k_2' from the specific rate k_2 for second stage of oxidation of glycerol, assuming that the second stage consists of two parallel first order reactions. The values of k_2' and k_2'' thus obtained were used to calculate the value of

maximum concentration of formaldehyde, $C_x(\max)$ and glycolaldehyde, $C_y(\max)$ formed in the glycerol oxidation by employing the expressions (1) and (2)

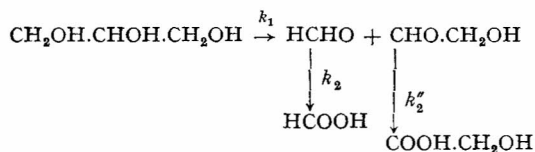
$$C_x(\max) = \frac{ak_1}{k_2' - k_1} [e^{-k_1 t} - e^{-k_2' t}] \quad \dots(1)$$

$$C_y(\max) = \frac{ak_1}{k_2'' - k_1} [e^{-k_1 t} - e^{-k_2'' t}] \quad \dots(2)$$

The amounts of formaldehyde and glycolaldehyde formed at various intervals of time (as given in Table 1), when plotted against time (Figs. 2 and 3) gave characteristic curves for consecutive reactions. The values of $C_x(\max)$ and $C_y(\max)$ extrapolated from these curves are tabulated along with the calculated values in Table 2. Taking into account the possible errors in such estimations, there seems to be rather good agreement between the calculated and observed values.

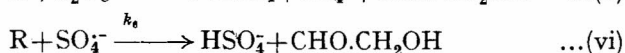
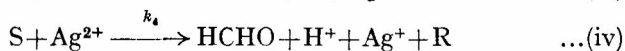
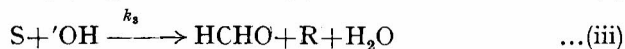
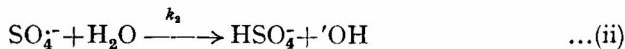
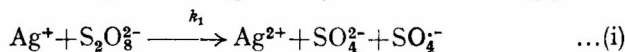
The energy parameters for reaction-A as calculated from the rate constant values are of the same order of magnitude as those reported by Mishra and Ghosh¹.

Mechanism — On the basis of the above results the different stages of the Ag^+ -catalysed peroxydisulphate oxidation of glycerol may be represented as shown in Scheme 1.



Scheme 1

Taking into account the general similarity in kinetic behaviour of this reaction with other Ag^+ -catalysed redox reactions of $\text{S}_2\text{O}_8^{2-}$, we propose the reaction mechanism shown in Scheme 2 for the first stage of the Ag^+ -catalysed oxidation of glycerol.



where S stands for glycerol and R stands for $\text{CHOH}\cdot\text{CH}_2\text{OH}$.

Scheme 2

Applying steady state treatment to the radicals $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, Ag^{2+} and R the rate expression for the consumption of peroxydisulphate comes out to be

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = k_1 [\text{Ag}^+][\text{S}_2\text{O}_8^{2-}] + \left(\frac{k_1 k_2 k_5}{k_6}\right)^{1/2} [\text{S}_2\text{O}_8^{2-}] [\text{Ag}^+]^{1/2}$$

Since $k_6 \gg k_1$ or k_2 or k_5 , because k_6 refers to a radical-radical reaction, hence the second term is much smaller than the first term and kinetically not distinguishable and apparently the reaction follows first order behaviour in $[\text{S}_2\text{O}_8^{2-}]$ and $[\text{Ag}^+]$.

It is pertinent to point out that the first two stages have been proposed by a large number of workers⁸⁻¹³ and the hydrogen abstraction from the organic substrate to yield the radical is considered to be the next probable step. The existence of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ in peroxydisulphate redox reactions has recently been proved by the ESR studies of Chawla and Richard¹⁴ while the formation of Ag^{2+} in peroxydisulphate redox processes has been shown by the ESR studies of McMillan and Smaller¹⁵.

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