

In other words, pyruvic acid will be the first oxidised product. We have, however, seen that pyruvic acid in presence of peroxodisulphate and silver ions of the concentration used at the temperatures of these experiments is oxidised very slowly and it does not yield aldehyde easily. It may therefore be concluded that oxidation of lactic acid occurs mainly, as shown by equation (2), i.e., the COOH is detached as CO_2 and an OH group is substituted as shown in the equation.

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CHEMICAL LABORATORIES,
UNIVERSITY OF JABALPUR,
JABALPUR, M.P.

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Kinetics of Oxidation of Glycerol by Potassium Peroxodisulphate in Presence of Silver Ions

D. D. Mishra and S. Ghosh

Oxidation of glycerol by peroxodisulphate by itself is slow even at 45° , but in presence of silver ions it proceeds with a measurable velocity. Kinetic study reveals that the rate is proportional to the concentration of the catalyst (silver ions) and that its order is unity with respect to the oxidant, but it is of zero order with respect to the reducing substrate. The products of oxidation of glycerol have been found to be formaldehyde, formic acid, acetaldehyde, and acetic acid, depending on the concentration of glycerol and temperature of the reaction. A mechanism for the catalytic action of silver ions has been suggested and the various oxidation compounds formed are ascribed to two side reactions. The energy and entropy of activation between 30° and 35° have also been determined.

Kinetics of the oxidation of organic compounds by peroxodisulphate has been little studied. According to King and Steinbach¹, the oxidation of oxalic acid by this oxidant is erratic and is susceptible to impurities. In the present investigation, by the use of re-distilled water as the medium, fairly reproducible results have been obtained. Among several oxidising agents tried, the kinetics of the oxidation of glycerol by peroxodisulphate, catalysed by silver ions, has been reported in this communication.

EXPERIMENTAL

The experimental procedure adopted was the same as reported in an earlier paper^{1a}. Measured volumes of the reaction mixture were withdrawn at different intervals and un-

1. *J. Amer. Chem. Soc.*, 1930, **52**, 4779.

1a. This issue, p. 307.

consumed oxidant was estimated according to Szabo *et al.*² In most of the experiments a few earlier first-order constants were found to vary and the rest, to fairly agree. The results are, however, reproducible. The data of one typical experiment have been recorded in Table I.

TABLE I

Glycerol = 0.1*N*. $K_2S_2O_8 = 0.02M$. $AgNO_3 = 0.001M$. Temp. = 35°.

Time.	Hypo.	$K/2.303 \times 10^4 \text{ min}^{-1}$	Time.	Hypo.	$K/2.303 \times 10^4 \text{ min}^{-1}$
0 min.	5.00 ml	..	150 min.	3.06 ml	14.15
30	4.46	14.71	180	2.78	14.01
60	4.08	14.28	210	2.54	14.04
90	3.72	14.17	240	2.30	14.11
120	3.38	14.12	270	2.08	14.16

Av. 14.18

$$K = 32.68 \times 10^{-4} \text{ min}^{-1}.$$

Effect of Peroxodisulphate Concentration

To ascertain the order of the reaction with respect to peroxodisulphate, the rate of oxidation was studied with different concentrations of this oxidant. In all the cases the concentration of glycerol was kept high. The results on the reaction rate have been summarised in Table II.

TABLE II

Initial conc. of the oxidant (<i>M</i>)	..	0.01	0.02	0.04
$K \times 10^4 \text{ min}^{-1}$..	37.42	32.68	29.38

Thus, with the increase in the concentration of peroxodisulphate, the rate constants decrease. Similarly, Schimb and Ruttner³ noted the effect of the initial concentration of this oxidant on its self-decomposition by sonic energy. This decrease in the rate constants may be ascribed either to the increase in the ionic strength by the use of higher concentrations of peroxodisulphate or to the specific decreasing effect of the K^+ ions. If the former is prominent, the rate constants for one particular reaction should have also decreased with the progress of the reaction, because the reduction of one bivalent peroxodisulphate yields two bivalent sulphate ions, leading to the increase in the ionic strength with the progress of the reaction. As we have not found this to be the case, the inhibiting action of the increase in the initial concentration of peroxodisulphate may be ascribed to the specific effect of K^+ ions, as has been suggested by Gupta and Ghosh⁴ for the oxidation of oxalic acid by peroxodisulphate.

Variation of Glycerol Concentration

The kinetics of this reaction with different concentrations of glycerol was also studied to determine its total order. The results are recorded in Table III.

2. *Z. anal. Chem.*, 1952, **135**, 269.

3. *J. Amer. Chem. Soc.*, 1940, **62**, 3416.

4. *This Journal*, 1958, **35**, 483.

TABLE III

Initial conc. of glycerol (N)	0.8	0.4	0.2	0.1
$K \times 10^4 \text{ min}^{-1}$	26.05	27.15	30.42	32.68

As the initial concentration of the glycerol is very high, specially where 0.8N and 0.4N glycerol have been used, in comparison to the concentration of the oxidant, the order with respect to glycerol may be calculated from the relation:

$$n = \frac{\log K_1/K_2}{\log c_1/c_2}$$

where K_1 and K_2 are the rate constants calculated for the loss of the oxidant for the initial concentrations of the organic substrate, c_1 and c_2 . The order of the reaction with respect to glycerol is thus found to be -0.06 , i.e., slightly negative. If the reaction is strictly of zero order with respect to glycerol, the values of the constants should remain to be the same for the various initial concentrations of glycerol. Table III shows that the reaction rate decreases with the increasing concentration of glycerol, i.e., the reaction is of zero order with respect to glycerol, glycerol having a slight inhibitory effect on its oxidation by the oxidant.

Table III also shows that the first-order constants, calculated from the loss of the concentration of peroxodisulphate, slightly decrease with increase in the initial concentration of glycerol. Similar experiments at different temperatures with different initial concentrations of glycerol showed that in all the cases slightly negative values for its order were obtained, as reported in Table III, and that the average order with respect to glycerol tended to approach zero as the temperature was increased. Thus the inhibitory effect of glycerol appears to be less at higher temperatures.

Effect of Concentration of Silver Nitrate

The catalytic effect of three different concentrations of silver nitrate was investigated. Table IV shows the average values of the rate constants for three different concentrations of AgNO_3 at different temperatures.

TABLE IV

Initial conc. of Ag^+ ions.	First-order constants ($K \times 10^4$) at			
	30°.	35°.	40°.	45°.
0.001M	25.08	32.68	47.95	65.54
0.002	48.85	55.90	93.85	127.72
0.004	93.15	111.30	187.81	249.19

Table IV shows that with increasing Ag^+ ions, the rate constants increase and bear a linear relationship.

Energy and Entropy of Activation

These values have been calculated using the average ones of the constants for the different ranges of temperatures for different concentrations of the catalyst, silver ions. The average values of heat of activation and their variation with different concentrations

of silver nitrate appear to be negligible. The average value of energy of activation calculated, when 0.001*M* silver nitrate has been used as catalyst, is found to be 12370 cal. mole⁻¹. The frequency factor and the entropy of activation, calculated from this average value of heat of activation, are found to be 3664×10^4 litres mole⁻¹ sec⁻¹ and -29.93 e.u. respectively.

DISCUSSION

Several oxidation products of glycerol containing the same number of carbon atoms have been reported and such compounds are formed by the fission of one or both the C-C bond of the glycerol molecule.

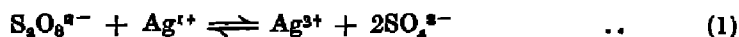
The oxidation of glycerol by peroxodisulphate yields formaldehyde, formic acid, acetaldehyde, and also acetic acid. The proportion of these oxidised products depends on the conditions of oxidation, viz., the concentration and the temperature. The rupture of the valency bonds of all the carbon atoms thus appears to occur during oxidation when glycerol concentration is low or the temperature is high (above 35°); but there are also traces of acetaldehyde under these conditions. If, however, the concentration of glycerol is high and temperature is below 35°, an appreciable amount of acetaldehyde is formed. These conclusions we have arrived at by the estimation of acetaldehyde left after the complete reduction of peroxodisulphate. Thus it is clear that the step of oxidation of glycerol by the oxidant differs for different concentrations of glycerol.

The oxidation of glycerol, leading to complete fission of the molecule, usually occurs under drastic conditions by the use of strong oxidising agents at higher temperatures. It seems that peroxodisulphate with silver ion as a catalyst can lead to the breaking of all the C-C bonds when the concentration of glycerol is low and the temperature is above 35°.

Various mechanisms for the catalytic action of Ag⁺ ion for the oxidation of organic compounds by peroxodisulphate have been suggested in which the role of higher valent silver, either bivalent or trivalent, has been emphasised. Thus for the silver-catalysed reactions of peroxodisulphate, the loss of the oxidant may be expressed by the relation:

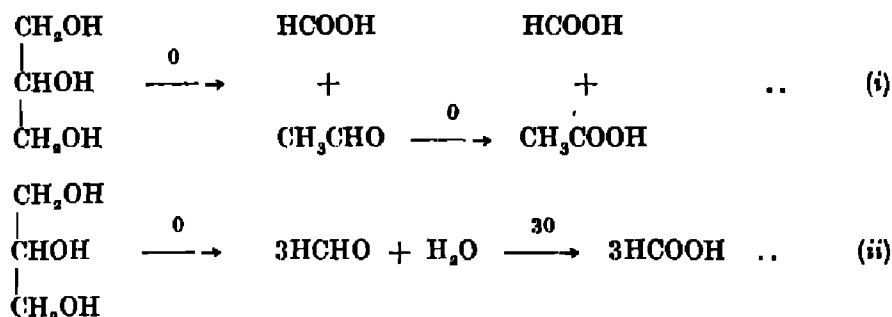
$$\frac{-d[S_2O_8^{2-}]}{dt} = K [S_2O_8^{2-}] [Ag^+]$$

This indicates that order of the reaction with respect to the reducing substrate is zero. Our experimental data reveal that the increasing concentrations of glycerol have a depressing effect on the rate of the reaction. The following mechanism of the catalysed oxidation of glycerol by peroxodisulphate is suggested:

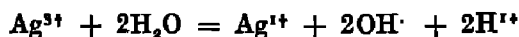


This step involves two-electron transfers for the formation of Ag³⁺. This is against the views of Haber and Weiss⁵. The formation of Ag³⁺ in two steps of oxidation by S₂O₈²⁻ may, however, be easily postulated.

The results of our identification of the oxidation products indicate that two side reactions occur concurrently. It is also clear that in the oxidation of glycerol, yielding either formaldehyde and formic acid or acetaldehyde and formic acid, oxygen is necessary for the oxidation process. Thus



It should be noted here that the oxidation of the aldehydes by peroxodisulphate is slow and hence the oxidation does not proceed to completion, specially because in most of our experiments concentrations of glycerol used are very high compared to the concentration of the oxidant present, majority of which being used up in the first step of oxidation. We are also of the opinion that oxygen is made available for the oxidation process by the interaction of Ag (III) or Ag (II) and the solvent water, yielding the radical OH.



Further work in this direction is in progress.

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