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A KINETIC STUDY OF THE OXIDATION OF LACTIC ACID BY POTASSIUM PEROXYDISULFATE-CATALYSED BY Ag^+ IONS

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The kinetics and mechanism of the oxidation of a variety of organic and inorganic substances by potassium peroxydisulfate under uncatalysed conditions and under conditions of catalysis by Ag^+ ions have been the subject of investigation by several groups of workers (1-3). In most of the investigations of the Ag^+ catalysed oxidations of organic substrates, the rate of the reaction at any instant was found to be proportional to the peroxydisulfate concentration and to the (constant) Ag^+ ion concentration and to be independent of the concentration of the organic substrate.

In this communication we wish to report for the first time, a curious inverse relationship of the rate with the concentration of the organic substrate in the oxidation of lactic acid by peroxydisulfate under catalysis by Ag^+ in 0.1M sulphuric acid at 35^o under conditions of constant ionic strength*.

This oxidation is of the first order with respect to $S_2O_8^{--}$ and the rate increases with increasing catalyst concentration.

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* The experiments were conducted in presence of air, as earlier investigations have shown that the silver-catalysed peroxydisulfate oxidations give identical results under aerated and deaerated conditions.

But our results differ with reference to the effect of changes in concentration of the organic substrate on the rate. While at concentrations higher than 0.35M the first order rate constant is independent of the alcohol concentration (confirming the zero order dependence on substrate), at all other lower concentrations the rate of disappearance of $S_2O_8^{--}$ is inversely proportional to the alcohol concentration.

TABLE - I.

Variation in rate with changes in concentration of Lactic acid.

H_2SO_4 0.1M $K_2S_2O_8$ .0288M Temp. 35°
Ag^+ 0.001186M μ .2M

(Lactic acid)	k_1 sec^{-1} x 10^4
0.04607M	6.618
0.05062	6.1095
0.0620	5.808
0.1023	3.940
0.1446	3.160
0.2304	2.662
0.3174	2.340
0.4083	1.797
0.5061	1.638
0.6220	1.562
0.7082	1.614
1.001	1.702

A plot of k against 1/ROH (Figure 1) gives a straight line with a slope of 0.14 and an intercept of 1.6×10^{-4} on the rate axis - the rate constant that is also given at all concentrations greater than 0.35M. The rate picture thus fits into the equation.

$$\text{rate} = k\,(Ag^+)\,(S_2O_8^{--}) = k_{min.}(Ag^+)\,(S_2O_8^{--}) + \frac{k_{min.}b\,(Ag^+)\,(S_2O_8^{--})}{(ROH)}$$

where $k_{min.} = 1.6 \times 10^{-4}$ and $b = 0.14$.

At alcohol concentrations greater than 0.35M the second part of the

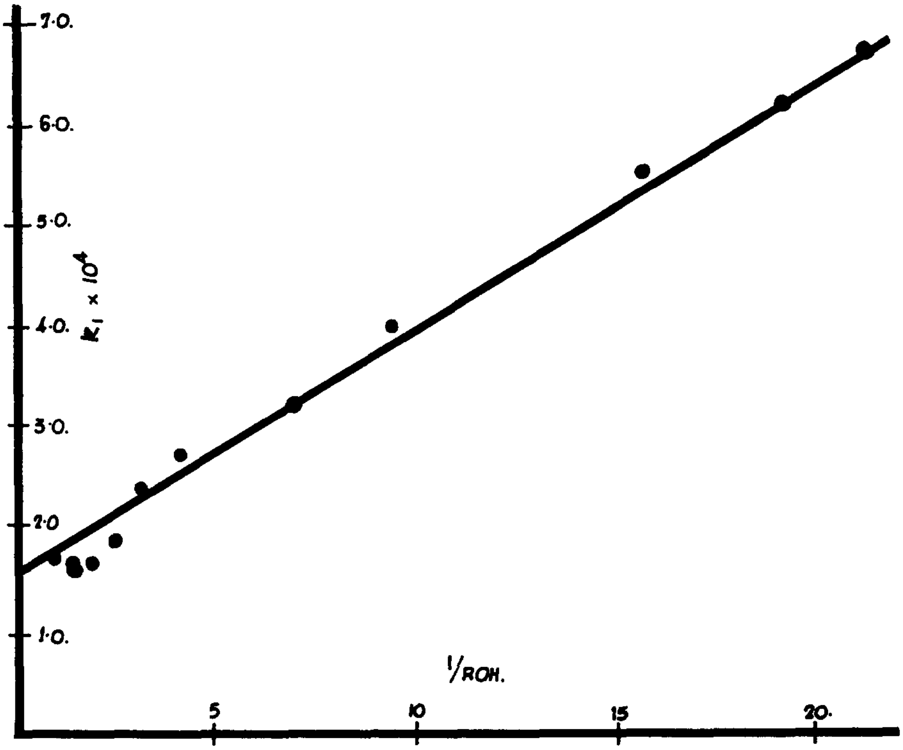

FIG: 1.

equation becomes negligible and the reaction is typically of the zero order with respect to the reductant. We feel therefore that any mechanism that is proposed for the oxidation must explain this inverse dependence on the alcohol concentration at certain concentrations and the lack of dependence on it at other concentrations.

That part of the reaction which is independent of the alcohol concentration can be explained by any one of the several mechanisms proposed already, involving either the production of Ag^{3+} or Ag^{2+} in the rate-determining step followed by a fast reaction with the organic substrate. But, for the part of the reaction that bears an inverse relationship with the alcohol concentration we feel that the general proposal of a rate-determining production of a higher valent silver species cannot be wholly correct. The application of the steady state principle to the reaction shows that the steady state concentration of the intermediate silver species is proportional to the reciprocal of the alcohol concentration and this is an indication that it is not only the production of the silver species that is rate-determining, and that at certain concentrations the consumption of the silver-species comes into the rate picture.

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