

# Kinetics and Mechanism of the Catalysed Oxidation of Ethylenediamine by Hydrogen peroxide

G. L. AGRAWAL and ARUN K. BHATTACHARYA\*

Chemistry Department, University of Sagar, Sagar

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Kinetics of the reaction between ethylenediamine and hydrogen peroxide have been studied in presence of sodium tungstate as catalyst. The total order of the reaction is found to be two, one each with respect to oxidant and reductant. The effect of concentration of catalyst, oxidant and reductant has been studied. The change of ionic strength has no appreciable effect on the reaction rate. The activation energy and the entropy of activation is found to be 4.7 Kcals and -58.2 E.U. respectively. The probable mechanism has been suggested.

THE oxidation of several reducing ions by hydrogen peroxide has been carried out largely.

Bunton<sup>1</sup> observed the oxidation of  $\alpha$ -keto acids and  $\alpha$ -diketones with hydrogen peroxide. The oxidation of  $\alpha$ - $\beta$  unsaturated ketones<sup>2</sup>, fatty acids<sup>3</sup>, and fructose<sup>4</sup> has also been carried out. Ross<sup>5</sup> investigated the mechanism of the oxidation of triethylamine and hydrogen peroxide. Thiodialiphatic acid<sup>6,7</sup>, chloramine T<sup>8</sup> and simple aldehydes have also been studied.

Kahr and Berther<sup>10</sup> used sodium tungstate as a catalyst for the oxidation of primary amines with  $H_2O_2$ . They, however, have not carried out the kinetic study of the reactions. The present paper reports a systematic kinetic study in order to investigate the rate of the reaction between ethylenediamine and hydrogen peroxide using sodium tungstate as a catalyst.

Preliminary experiment disclosed that the velocity of the reaction in the absence of any catalyst is difficult to measure directly. However, the rate is enhanced by the introduction of sodium tungstate as a catalyst.

## Experimental

The materials employed were that of the purest quality available. Preparation of all solutions were done with redistilled water.

Calculated amounts of the reactants except  $H_2O_2$  were pipetted into 250 ml conical flasks and kept in a thermostat. The standard solution of hydrogen peroxide was kept separately in the thermostat. After allowing sufficient time for the reactants to attain the temperature of the bath, requisite amount

of hydrogen peroxide was pipetted out in the reaction flask in order to start the reaction.

Aliquots were withdrawn at suitable intervals and analysed for the amount of unreacted hydrogen peroxide using the method described by Ross<sup>5</sup>.

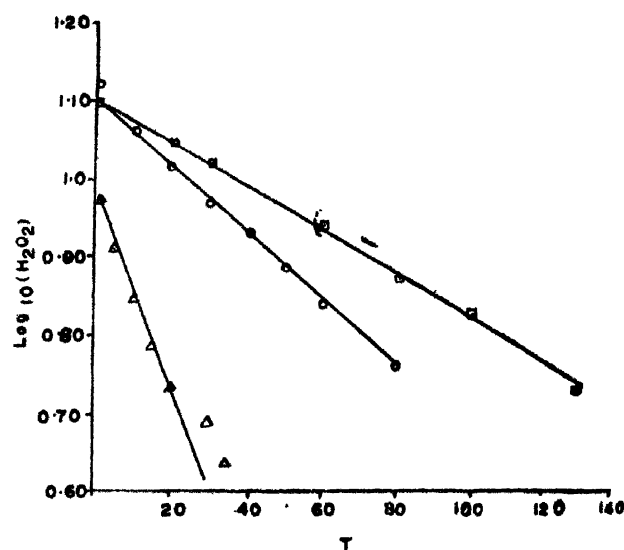


Fig. 1. Plot of  $\text{Log}_{10} (H_2O_2)$  vs Time

□ 0.0025M  
○ 0.0050M  
△ 0.0100M

## Order of reaction :

Oxidation of ethylenediamine was studied in presence of sodium tungstate. The total order of reaction was calculated employing the Ostwald's Isolation method. The experimental data are recorded in Table 1. A plot of  $\log [H_2O_2]$  vs. time for different concentrations of  $H_2O_2$  gives the straight line establishing the first order in  $H_2O_2$  (Fig. 1.).

\* Hooker Chemical Research Centre,  
M.P.O. Box 8, Niagra Falls, N.Y. 14 302 (U.S.A.)

TABLE 1

A		
Hydrogen peroxide = [0.0050 M]		
Sodium tungstate = [0.0025 M]		
Ethylenediamine	$K_1 \times 10^2 (\text{min}^{-1})$	$K_2 = \frac{K_1}{[\text{Ethylenediamine}]}$
0.0250 M	0.577	0.230
0.0500 M	1.10	0.220
0.1000 M	2.48	0.248

B		
Ethylenediamine = [0.0500 M]		
Sodium tungstate = [0.0025 M]		
Hydrogen peroxide	$K_1 \times 10^2 (\text{min}^{-1})$	
0.0025 M	0.633	
0.0050 M	1.10	
0.0100 M	2.99	

The second order rate constants have been calculated by the equation

$$K_2 = \frac{K_1}{[\text{Ethylenediamine}]}$$

where  $K_1$  is the psuedo first order rate constants in  $\text{H}_2\text{O}_2$ . Order with respect to ethylenediamine was determined with the help of the following relation :

$$n = \frac{\log \frac{K'_1}{K''_1}}{\log \frac{C'_2}{C''_2}}$$

where  $K'_1$  and  $K''_1$  are the first order rate constants obtained at two different concentrations of ethylenediamine  $C'_2$  and  $C''_2$  respectively. The relation is applicable provided the concentration of substrate is at least ten times or more than the concentration of oxidant used. The value of  $n$  is 0.9. Thus the total order of the reaction is 1.9 which may be taken as two i.e., the velocity at any instant is proportional to the concentration of  $\text{H}_2\text{O}_2$  and ethylenediamine both

*Effect of Ethylenediamine and Hydrogen peroxide concentration :*

The rate constants were obtained with different concentration of reactants. The results are recorded in Table 1. From the result it appears that the value of  $\frac{dx}{dt} \propto [\text{H}_2\text{O}_2][\text{Ethylenediamine}]$ .

*Effect of Sodium tungstate concentration :*

In order to determine the role of sodium tungstate as catalyst on the reaction rate, the value of rate constant was determined using different concentrations of sodium tungstate. It has been observed that the rate is dependent on catalyst concentration. A plot of  $\log K$  vs.  $\log \text{Na}_2\text{WO}_4$  gives a straight line.

The slope of the curve is very nearly unity showing that the rate is linearly related to sodium tungstate concentration i.e.,  $\frac{dx}{dt} \propto [\text{Na}_2\text{WO}_4]$  [Fig 2].

*Influence of ionic strength :*

The reaction was carried out in the presence of potassium sulphate in order to see the effect of ionic

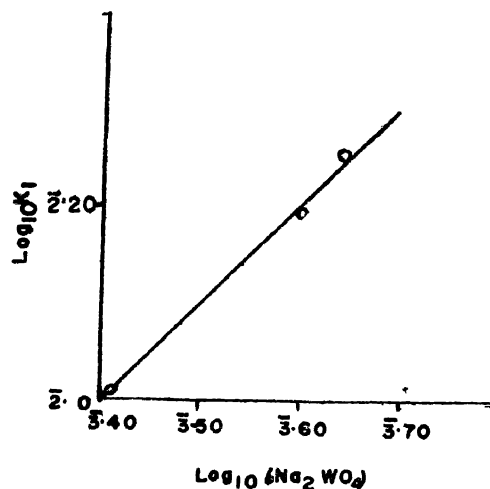


Fig. 2. Plot of  $\log_{10} K_1$  vs  $\log_{10} (\text{Na}_2\text{WO}_4)$ .

strength on the reaction. It has been observed that a four fold increase in ionic strength has an insignificant effect on the value of the rate constant  $K_1$ .

*Energy and entropy of activation :*

The average value of the energy of activation ( $E$ ) between the temperature  $20^\circ$  to  $35^\circ$  was found 4.9 Kcals. The value of entropy of activation with  $E = 4.9$  Kcals at  $20^\circ$  is  $-58.2$  E.U.

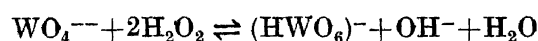
## Discussion

The total order of reaction between hydrogen peroxide and ethylenediamine in presence of tungstate ion as a catalyst is very nearly two. The observed rate equation is then

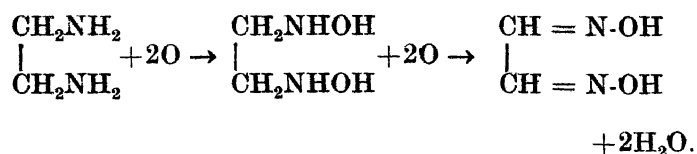
$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = K(\text{H}_2\text{O}_2)(\text{Ethylenediamine})(\text{WO}_4^{--})$$

Since the rate constant is independent of the ionic strength of the medium, the rate determining step should be between a neutral molecule and an ion i.e.,  $\text{H}_2\text{O}_2$  and  $\text{WO}_4^{--}$ .

It has also been observed<sup>11</sup> that with monotungstate, when hydrogen peroxide is weak, colourless monobasic ions with two atoms of active oxygen are formed. Thus



Thus the ethylenediamine reacts with the available oxygen in the following way :



The presence of oxime, the end product in the reaction mixture after the completion of the reaction has been confirmed by the method reported in literature<sup>12</sup>.

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