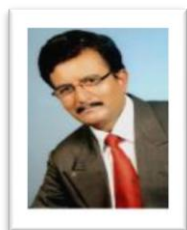


Sodium Tungstate Catalysed Oxidation of Triethanolamine by Hydrogen Peroxide



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Abstract

Result of the investigation on the reaction of triethanolamine and hydrogen peroxide catalysed by sodium tungstate in order to determine the mechanism of this reaction. Dependence on Triethanolamine and hydrogen peroxide, dependence on catalyst concentration and Influence of ionic Strength have been evaluated. The result show that the total order of sodium tungstate catalysed oxidation of triethanolamine by hydrogen peroxide is very nearly two.

Keywords: Sodium Tungstate, Triethanolamine, Order of Reaction, Dependence, Catalyst, Hydrogen Peroxide, Rate Constant.

Introduction

Reaction of hydrogen peroxide with various chemical species have been studied^{1, 2}. From the chemical point of view, the redox reaction of hydrogen peroxide has been the subject matter of many investigations. The reaction often utilized in the kinetic method of analysis is the oxidation by hydrogen peroxide, of which the rate depends on the concentration of catalyst in solution³.

Recently the interest developed in using a number of substances as a catalyst for the oxidation of organic as well as inorganic substances by hydrogen peroxide. Ascorbic acid has been oxidized by H₂O₂ in the presence of methyleneblue⁴ and EDTA-Fe(III) complex⁵. W(VI)⁶ and Mo(VI)⁷ were used as a catalyst for the kinetic study of the reaction between iodide and hydrogen peroxide. A macromolecular organometallic catalyst using insoluble polymeric tungsten for the oxidation of maleic acid was carried out by Graham and Neogi⁸. Agrawal et al⁹⁻¹⁰ studied the sodium tungstate catalysed oxidation ethylenediamine and hexamethylenetetramine. Epoxidation of maleic acid with hydrogen peroxide in presence of sodium tungstate and molybdate has also been carried out¹¹.

This paper reports the result of the investigation on the reaction of triethanolamine and hydrogen peroxide catalysed by sodium tungstate in order to determine the mechanism of this reaction. Preliminary experiments 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

All the chemicals used were of high grade purity and their solution were prepared in redistilled water.

Calculated amount of the reactants were equilibrated at the desired temperature, mixed and aliquots withdrawn at suitable time intervals and analysed for the amount of un reacted hydrogen peroxide using the method described by Ross¹².

Order of Reaction

Sodium tungstate catalysed oxidation of triethanolamine was studied. Ostwald's isolation method has been used to determine the total order of reaction. Table 1 records the experimental data. A plot of log₁₀[H₂O₂] Vs time for different concentrations of H₂O₂ gives the straight line establishing the first order dependence [H₂O₂] (Fig.1).

Order with respect to triethanolamine was determined with the help of following reaction

$$n = \log \frac{k'1/k''1}{C'2/C''2}$$

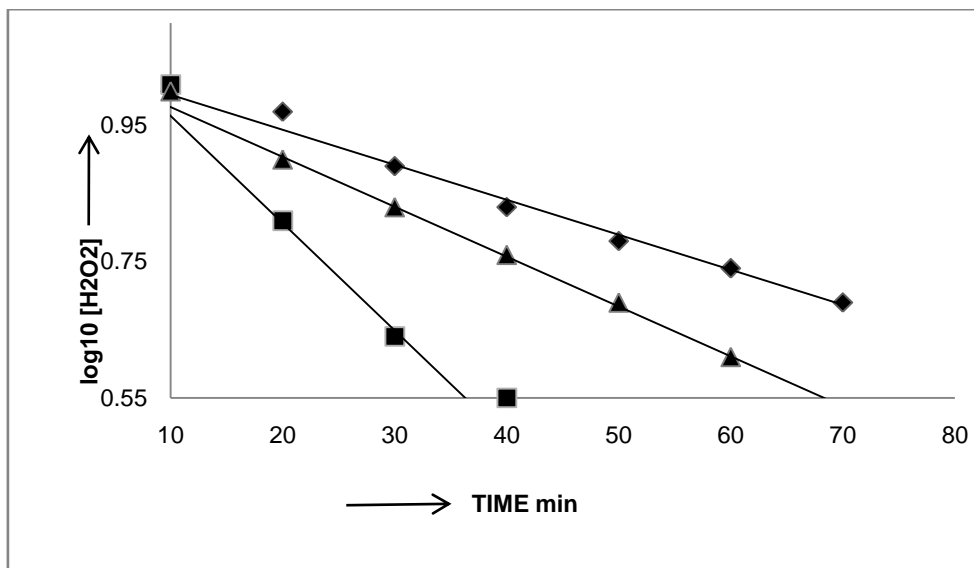


Fig. 1 : Plot of Log₁₀ [H₂O₂] Against Time

for hydrogen peroxide oxidation of triethanolamine catalysed by sodium tungstate at 20⁰. Concentrations : 0.025 M triethanolamine, 0.002 M Na₂WO₄.

Where k₁ and k₁' are the first order rate constants obtained at two different concentrations of triethanolamine C₁ and C₂ respectively. The relation is applicable provided the concentration of substrate

is at least ten times or more than the concentration of the oxidant used.

The value of n is 0.82. A plot of log₁₀ k₁ Vs log₁₀ [Triethanolamine] gives a straight line whose slope also comes out to be around 0.8 (Fig. 2). Thus the total order of reaction is 1.8 which may be taken as two. It is unity with respect to each i.e. triethanolamine and hydrogen peroxide.

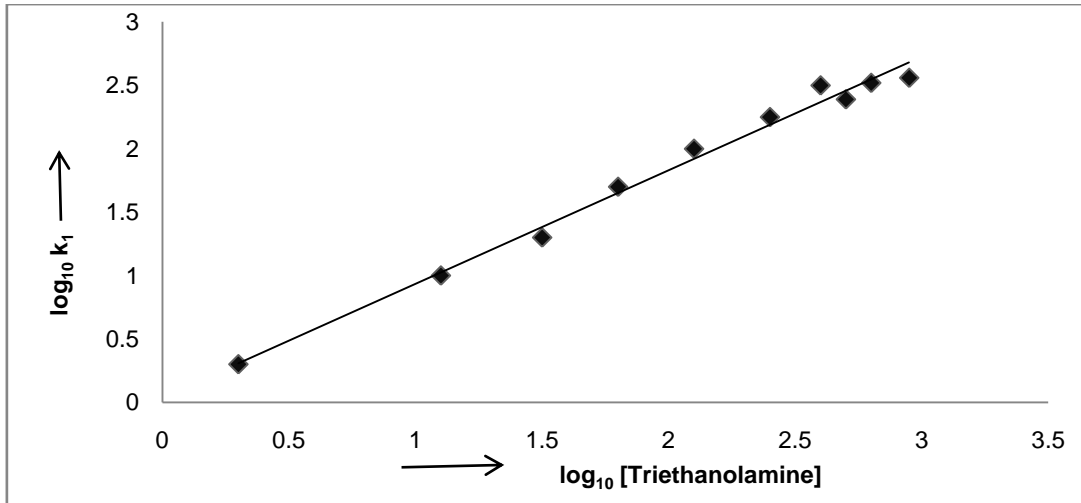


Fig.2 : Plot of log₁₀ k₁ Against log₁₀ [Triethanolamine]

for hydrogen peroxide oxidation of triethanolamine catalysed by sodium tungstate at 20⁰. Concentrations : 0.0025 H₂O₂, 0.0020 M Na₂WO₄.

Dependence on Triethanolamine and Hydrogen Peroxide

The rate constants obtained at different concentrations of substrate and oxidant recorded in Table 1 show that the :

$$-\frac{d[H_2O_2]}{dt} \propto [H_2O_2] [Triethanolamine]$$

Dt

Dependence on Catalyst Concentration

In order to decide the role of sodium tungstate as catalyst on the reaction rate, the value of rate constants were obtained at different concentrations of catalyst.

A plot of log₁₀ k₁ Vs log₁₀[Na₂WO₄] gives a straight line indicating that the rate is linearly related to [Sodium tungstate] i.e.

$$\frac{d[H_2O_2]}{dt} \propto [WO_4] \dots \dots \dots (Fig. 3)$$

Influence of Ionic Strength

The reaction was carried out in the presence of potassium chloride, potassium sulphate and

sodium sulphate in order to see the effect of ionic strength on the reaction. Rate data are presented in Table 2.

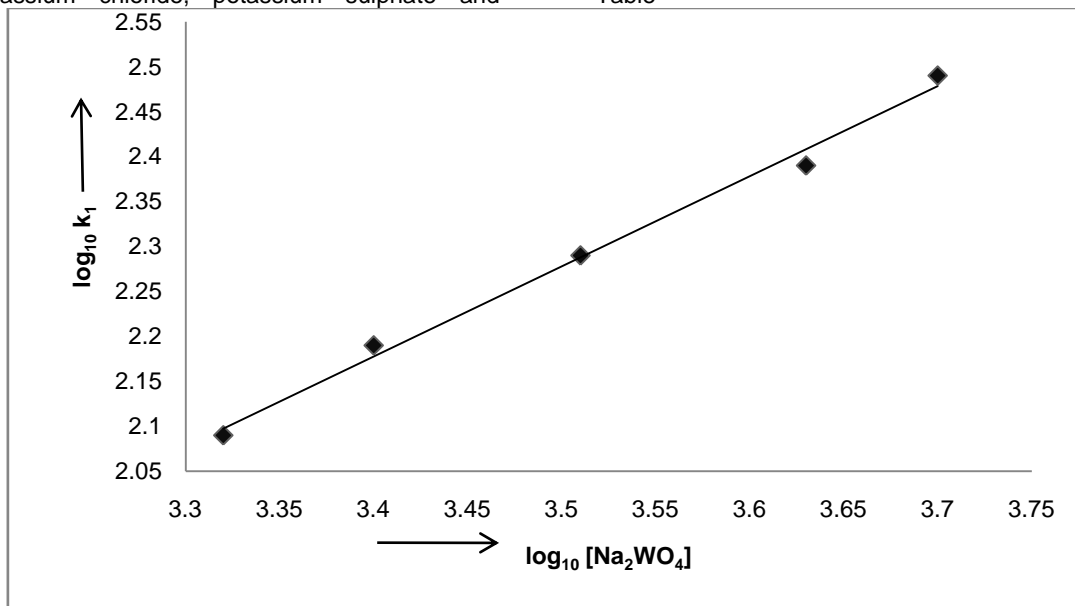


Fig.3 : Plot of $\log_{10} k_1$ Against $\log_{10} [\text{Na}_2\text{WO}_4]$

for hydrogen peroxide oxidation of triethanolamine catalysed by sodium tungstate at 20°. Concentrations : 0.0025 H₂O₂, 0.025 M triethanolamine.

Table : 1 – First order rate constant in the Oxidation of Triethanolamine by H₂O₂

[H ₂ O ₂] X 10 ³ M	[Triethanolamine] X 10 ² M	[Na ₂ WO ₄] X 10 ³ M	K ₁ X 10 ³ (min ⁻¹)	n
TEMP. = 15°				
2.50	1.25	2.0	06.11	
2.50	2.50	2.0	09.52	
TEMP. = 20°				
2.50	1.25	2.0	06.50	
2.50	2.50	2.0	12.20	0.90
2.50	5.00	2.0	23.60	
2.50	6.25	2.0	27.90	
2.50	12.50	2.0	48.20	
1.25	2.50	2.0	09.24	
5.00	2.50	2.0	17.10	
2.50	2.50	2.5	15.50	
2.50	2.50	4.0	24.66	
2.50	2.50	5.0	28.50	
TEMP. = 25°				
2.50	1.25	2.0	09.45	
2.50	2.50	2.0	15.80	0.74
TEMP. = 30°				

2.50	1.50	2.0	10.80	
2.50	2.50	2.0	19.42	0.84

TABLE : 2 - Effect of varying Ionic Strength on the reaction rate.

[Triethanolamine] = 0.0250 M, [H₂O₂] = 0.0025 M, [Na₂WO₄] = 0.0020 M : Temp = 20°

KCl X 10 ³ M	K ₁ X 10 ² (min ⁻¹)	[K ₂ SO ₄] X 10 ³ M	K ₁ X 10 ² (min ⁻¹)	[Na ₂ SO ₄] X 10 ³ M	K ₁ X 10 ² (min ⁻¹)
0.00	1.22	0.00	1.22	0.00	1.22
2.50	1.13	5.00	1.25	5.00	1.25
5.00	1.24	20.00	1.37	10.00	1.12
10.00	1.20	25.00	1.20	20.00	1.26

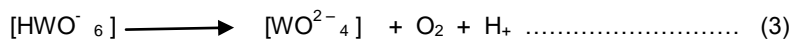
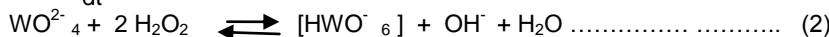
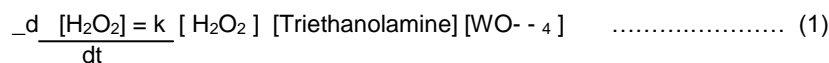
It is observed that the reaction rate is virtually insensitive to change in ionic strength. A brown precipitate is developed almost instantaneously by the addition of Manganous sulphate.

Activation Parameters

The value of frequency factor A with E = 6.18 Kcal/mole at 20° C was found to be 1.98 X 10³. The value of entropy of activation with E = 6.18 Kcal/mole was - 45.39 cal mole⁻¹ deg⁻¹.

Discussion

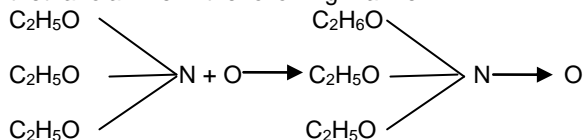
The total order of sodium tungstate catalysed oxidation of triethanolamine by hydrogen peroxide is very nearly two. Equation (1) gives the observed rate.



Since the reaction rate is virtually independent of the changes in ionic strength of the medium, the reaction may be between a neutral molecule and an ion i.e. H_2O_2 and WO_4^{--} .

It has been observed that colourless monobasic ions with two atoms of active oxygen are formed with monotungstate at low $[\text{H}_2\text{O}_2]$ (Equn 2 & 3)

The available oxygen reacts with triethanolamine in the following manner .



The presence of an amine oxide, the end product in the reaction mixture after the completion of the reaction has been tested by the method reported in literature.

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