

Kinetic studies of oxidation of 3-methyl butan-1-ol by alkaline solution of chloramineT in present of catalyst

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Abstract : In the present work, an attempt has been done to investigate the kinetics of oxidation of 3-methyl butan-1-ol by alkaline solution of chloramine-T ($\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{N-NaCl}$) sodium salt of p-toluene sulphonamide in presence of osmium tetroxide used as homogeneous catalyst. The Kinetic data have been collected and suitable mechanism has been suggested. The rate law derived on the basis of proposed mechanism is as $-\frac{d[\text{Chloramine-T}]}{dt} = K [\text{Chloramine-T}] [\text{Os (VIII [3-methyl] butan-1-ol)}]$

(Keywords : 3-methyl butan-1-ol, chloramine-T, Osmium Tetroxide, Sodium hydroxide)

Introduction

A number of catalyses such as Cu(II)^1 , $\text{Ag}^2(\text{I})$, Cr(III)^3 , Mn(II) etc have been attempted to study various reactions of industrial importance. Os (VIII)⁵ is used as catalyst in the oxidation of alcohol. Reagent chloramine-T is most commonly used as oxidant as its solution is stable. It is a strong electrolyte and strong oxidant in both acidic and alkaline media⁶⁻⁸. In present work, an attempt has been done to investigate the kinetic of oxidation of 3-methyl butan-1-ol by alkaline solution of sodium salt of p-toluene sulphonamide (ChloramineT) in presence of Osmium tetroxide used as homogenous catalyst⁹⁻²⁰. The authentic data have been collected and suitable mechanism has been suggested.

Experimental

- The solutions of 3-methyl butan-1-ol and chloramine-T were prepared by dissolving weighed amount of sample in known volume about 5% solution of KI was prepared of distilled

water. Further, its solution was standardized iodometrically.

A sample of Osmium tetroxide was first dissolved in 200ml of 0.01M NaOH solution and thereafter its volume was raised to 1000ml. The final strength was calculated. Sodium perchlorate solution (to maintain ionic strength medium constant) was prepared by dissolving its weighed amount in distilled water. 1% starch solution was used as an indicator. About 5% solution of KI was prepared.

Method for kinetic studies:- It was observed that reaction b/w chloramine-T and 3-methyl butan-1-ol did not proceed in alkaline medium with measurable rate while when reaction is carried out in presence of chloramine-T in presence of Osmium tetroxide the reaction proceeded with measurable rate. Hence it was decided to study the kinetics of oxidation of 3-methyl butan-1-ol by chloramineT in presence of Osmium tetroxide. The reaction was studied at constant temp.

The requisite volume of 3-methyl butan-1-ol, osmium tetroxide, sodium hydroxide, sodium perchlorate and water were taken in a reaction vessel and placed in thermostat water bath. In another bottle chloramine-T in requisite quantity was taken and this bottle was placed in the same thermostatic water bath as desired temp. (± 0.100).

The solution of both bottles were mixed and time of moving was noted. Immediately after

mixing these solution, 5ml of reaction mixture was taken and estimated for unconsumed chloramine-T, iodometrically.

The progress of reaction was followed by estimating unconsumed chloramine-T, 5ml of reaction mixture was transferred to a titrating flask containing 5% KI acidified solution. The unconsumed chloramine-T liberated an equivalent amount of iodine. The liberated iodine was titrated against standard solution of sodium thiosulphate using starch as a indicator.

The estimation of unconsumed chloramine-T was carried out at different intervals of time. From the titre values, the order of reaction was calculated with respect to chloramine-T. After

determining the order of reaction, the reaction was studied at different concentration of 3-methyl butan-1-ol, osmium tetroxide, sodium hydroxide etc one by one keeping constant all other reagents.

Results and Discussion

(i) Determination of dependence of reactions on chloramine-T concentration. An attempt has been made to study the order of reaction with respect to chloramine-T and 3-methyl butan-1-ol. For this purpose the reactions have been studied at constant temp. With various concentration of chloramine-T and keeping concentration of all other reagents fixed. The result have collected in table (7.1)

Table – 7.1

$$[3\text{-methyl butan-1-ol}] = 2.00 \times 10^{-2} \text{ M}$$

$$1. [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{Os (VIII)}] = 4.82 \times 10^{-6} \text{ M}$$

$$\mu = 2.00 \times 10^{-2} \text{ M. Temp. } 35^{\circ}\text{C}$$

Chloramine-T X 10 M	$(-dc/dt) \times 10^7 \text{ ML}^{-1} \text{ S}^{-1}$	$K_1 \times 10^4 \text{ s}^{-1} = -dc/dt$ [Chloramine-T]
5.00	2.50	5.00
6.67	3.42	5.13
8.00	4.06	5.07
10.00	5.12	5.12
16.67	8.42	5.05
25.00	12.80	5.12

$$\text{Average } K_1 = 5.08 \times 10^{-4} \text{ s}^{-1}$$

From close examination of above table, It has been observed that on increasing the concentration of chloramine-T, the value of first order rate constant does not change significantly indicating first order dependence of the reaction on chloramine-T. When a graph is plotted b/w value of $(-dc/dt)$ and [Chloramine-T], a st. line is obtained.

(ii) Determination of dependence of reactions on concentration of reducing alcohol.

An experiment at different concentration of 3-methyl butan-1-ol has been performed keeping concentration of all other reagent constant. The result of experiment has been recorded in table 7(ii)

Table – 7.1

Chloramine-T
[NaOH] = 1.00×10^{-2} M

[Os (VIII)] = 4.82×10^{-6} Ml.
 $\mu = 2.00 \times 10^{-2}$ M. Temp. 35°C

[3-Methyl butan-1-ol] $\times 10^2$ M	$(-dc/dt) \times 10^7 \text{ ML}^{-1} \text{ S}^{-1}$	$K_1 \times 10^4 \text{ S}^{-1}$
0.50	3.48	3.48
1.00	3.56	3.56
1.50	3.54	3.54
2.00	3.52	3.52
4.00	3.50	3.50
5.00	3.54	3.54

Average $K_1 = 3.53 \times 10^{-4} \text{ sp}^{-1}$

It is quite obvious from the kinetic result that the values of $(-dc/dt)$ as well as values of K_1 do not change significantly. This indicates that the reaction is zero order with respect to 3-methyl butan-1-ol.

An experiment has been carried out at different concentration of osmium tetroxide at fixed concentration of all other reagents. The result of experiment has been recorded in table 7(iii) the value of K_2 is calculated by

$$K_2 = [\overline{\text{OSK(viii)}}]$$

(iii) Determination of Dependence of reaction on concentration of Osmium Tetroxide.

Where K_2 is the 2nd order rate constant

Table –7.21

[Chloramine-T] = 10.00×10^{-4} M
[3-Methyl butan-1-ol] = 2.00×10^{-2} M

[NaOH] = 1.00×10^{-2} M
 $\mu = 2.00 \times 10^{-2}$ M. Temp. 35°C

Os (viii) $\times 10^6$ M	$(-dc/dt) \times 10^7 \text{ ML}^{-1} \text{ S}^{-1}$	$K \times 10^4 \text{ s}^{-1}$	$K_2 \times 10 \text{ ML}^{-1} \text{ S}^{-1}$
0.96	0.58	0.58	6.04
1.92	1.20	1.20	6.25
3.84	2.38	2.38	6.20
4.82	2.98	2.98	6.18
5.76	3.66	3.66	6.35
6.72	4.16	4.16	6.19

The result of table 7(iii) indicates that the values of K_2 are nearly constant showing first order dependence of the reactions on [OS VIII].

different concentration of sodium hydroxide but concentration of all other reagents were constant. The result of experiment has been recorded in table 7 (iv).

(iv) **Determination of sodium hydroxide.**
An experiment has been performed at

Table – 7.4

[Chloramine-T] = 10.00×10^{-4} M
 [3-Methyl butan-1-ol] = 2.00×10^{-2} M

[Os (viii)] = 4.82×10^{-6} M
 $\mu = 2.00 \times 10^{-2}$ M. Temp. 35°C

[NaOH] $\times 10^2$ M	$(-dc/dt) \times 10^7 \text{ ML}^{-1} \text{ S}^{-1}$	$K \times 10^4 \text{ s}^{-1}$	$K_2 \times 10 \text{ ML}_1\text{S}_1 / K_1 [\text{NaOH}]$
0.50	2.52	2.52	5.04
1.00	5.12	5.12	5.12
1.25	6.32	6.32	5.06
1.25	8.92	8.92	5.10
2.00	10.16	10.16	5.08
2.25	11.28	11.28	5.01

It is clear from the kinetic data of Table 7 (iv) that the value of first order rate constant increases linearly with increasing the concentration of sodium hydroxide showing the first order with respect to [OH].

(v) Determination of effect of variation of temperature on rate constant of reaction: Here,

the effect of variation of temperature on the rate constant of oxidation of 3-methyl butan-1-ol by chloramines-T was studied.

For this purpose, a series of experiments at different temp. viz 30° , 35° have been carried out at fixed concentration of all other reagents.

Table – 7.5

[Chloramine-T] = 10.00×10^{-4} M
 [3-Methyl butan-1-ol] = 2.00×10^{-2} M
 $\mu = 1.00 \times 10^{-2}$ M. Temp. 35°C

[Os (VIII)] = 4.82×10^{-6} M
 [NaOH] = 1.00×10^{-2} M

Temperature $^\circ\text{C}$	$(-dc/dt) \times 10^7 \text{ ML}^{-1} \text{ S}^{-1}$	$K \times 10^4 \text{ s}^{-1}$
30	3.52	3.52
35	5.12	5.12
40	7.26	7.26
45	10.86	10.86

Discussion:-

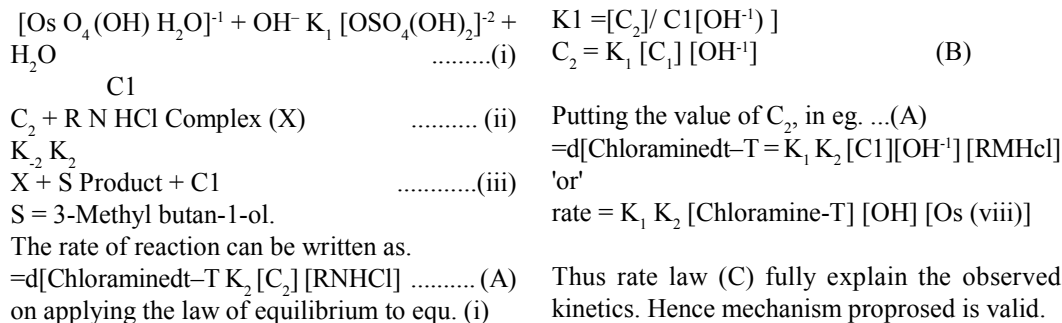
The followings are results obtained through kinetic studies.

- The reaction was first order kinetics with respect to chloramines-T.
- The reaction followed zero order kinetics with respect to 3-Methyl butan-1-ol.
- First order reaction was observed with respect to sodium hydroxide and Osmium tetroxide.

- Marked effect of temperature variation on the reaction rate was observed.

All these kinetic results have been taken into consideration while preparing the reaction mechanism.

Mechanism:- The following reaction steps are suggested for the little reaction. The reaction followed zero order Kinetic with respect to 3-Methyl butan-1-ol the mechanism. Is suggested as.



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