

Mechanistic approach of Os(VIII) catalysed oxidation of 2-methylbutan-1-ol by chloramine-T

Nilima* and Parashuram Ram

*Assistant Professor Guest Faculty, B.S College, Danapur, Patna-12

E-mail- nilimak16@gmail.com, dr.p.prasad.chem@gmail.com

Manuscript received online 02 March 2024, accepted on 28 March 2024

Abstract : The oxidation kinetics of 2-Methyl butanol-1 have been studied by alkaline solution of Chloramine-T in presence of Os(VIII) catalyst. The order of reaction with respect to Chloramine-T, 2-methyl butan-1-ol Osmium tetroxide has been studied respectively. Effect of temperature variation on the reaction rate has been observed. Zero effect of addition of paratoluene sulphonamide (PTS) on reaction rate was observed. A possible mechanism confirming to all the observed kinetic data have been collected and suitable mechanism has been suggested. The rate law derived on the basis of proposed mechanism is as $-d[\text{chloramine-T}] / dt = K[\text{chloramine-T}][\text{OsO}_4][2\text{-methyl butan-1-ol}]$

(Keywords : 2-methyl butan-1-ol, chloramine-T, Oxidation kinetics, order of reaction).

Introduction

Redox reaction are most frequently investigated from kinetic point of view. Several oxidizing agents have been used for oxidation of organic substances. These oxidants are

Potassium permanganate
Potassium dichromate
N- Bromosuccinimide
N-chlorobenzomide
Ceric sulphate
Hydrogen peroxide
Chloramine-B etc.

In the catalyzed reactions several short lived intermediate, involving catalyst may be

formed. Therefore mechanism of the catalyzed reactions may be entirely different that of uncatalyzed reactions.

A number of catalysts have been attempted to study various reactions of industrial importance. A few of them are Cu(II) 1, Ag(II) 2, Cr(III) 3, Mn(II) 4 etc.

Kalvoda 5 has employed an interesting method for regenerating Os(VIII) electrochemically, where Os(VIII) is used as catalyst in oxidation of alcohol and formic tetra chloramine-T in acidic and alkaline media 6-8. Here an attempt has been done to investigate the kinetics of oxidation of 2- methyl butan-1-ol by alkaline solutions of sodium salt of P-toluene sulphonamide in presence of Osmium tetroxide used as homogeneous catalyst 9-20 .The kinetic data have been collected and suitable mechanism has been suggested.

Experimental method:

The solution of 2 methyl butan-1-ol was prepared by dissolving weighted amount of sample in known volume of water. Chloramine-T was dissolved in known volume of distilled water. Further it's solution was standardized iodometrically. For this solution of osmium tetroxide as well as that of sodium hydroxide was calculated in 1000ml and their strengths were noted. Aqueous solution of sodium hydroxide was prepared by dissolving it's weighted sample

in distilled water and standardized by oxalic acid. The solution of chloramine- T was prepared by dissolving it's weighted sample in distilled water. Sodium perchlorate solution (to maintain ionic sample of sodium compound) was prepared by dissolving it's weighted amount in distilled water. 1% starch solution was used as an indication.

Method for kinetic studies:

It was observed that reaction between chloramine-T and 2- methyl butan-1-ol did not proceed in alkaline medium with measurable velocity. While when reaction is carried out in presence of osmium tetroxide, the reaction proceeds with measurable velocity. Hence it was decided to study the kinetics of oxidation 2-methyl butan-1-ol by chloramine-T in presence of osmium tetroxide.

The reaction was studied at constant temperature.

The requisite volume of 2- methyl butan-1-ol Osmium tetrachloride, sodium hydroxide, sodium perchlorate and water were taken in a reaction vessel which was placed in thermostatic water both for thermal equilibrium chloramine-T in requisite quantity was taken and this bottle was placed in the same thermostatic water both at desired temperature (I 0.1o C) was used.

The solution of both bottles were mixed and time for mixing was noted. Immediately after mixing these solutions , 5ml of reaction mixture was taken and was estimated for unconsumed chloramine-T iodometrically using sodium thiosulphate as titrant and starch solution as indicator.

The progress of reaction was followed by estimating unconsumed chloramine-T 5 ml of reaction mixture was transferred to a titrating flask 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 indicator.

The estimation for unconsumed chloramine-T was carried at different intervals of time.

From the titre value the order of reaction was titre value the ,order of reaction was calculated with respect to Chloramine-T. After determination of order of reaction , the reaction was studied at different concentration of substrate, Osmium tetroxide, NaOH etc one by one keeping constant of all other reagent.

Determination of dependence of reaction on chloramine-T concentration.

The order of reaction was determined with respect to chloramine-T.

Table 1.1

[Chloramine-T] = 4.00×10^{-4} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH]= 1.00×10^{-2} M, $\frac{1}{4}$ = 2.00
 $\times 10^{-2}$ M, Temp.= 35°C

Time (min.)	ml. of Hypo solution (8.42×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	3.80	2.32
5	3.62	
10	3.46	
15	3.22	
20	3.00	
25	2.76	
30	2.56	
35	2.36	
40	2.20	
50	2.06	

[Chloramine-T] = 3.00×10^{-4} M at which $(-dc/dt)$ was determined.

Table 1.2

[Chloramine-T] = 5.00×10^{-4} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00$
 $\times 10^{-2}$ M, Temp. = 35°C

Time (min.)	ml. of Hypo solution (8.42×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	4.76	2.86
5	4.14	
10	3.52	
15	2.94	
20	2.46	
25	2.22	
30	2.00	
35	1.86	
40	1.60	
50	1.42	

[Chloramine-T] = 4.00×10^{-4} M at which
 (-dc/dt) was determined.

Table 1.3

[Chloramine-T] = 8.00×10^{-4} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00$
 $\times 10^{-2}$ M, Temp. = 35°C

Time (min.)	ml. of Hypo solution (11.90×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	6.72	4.60
5	6.62	
10	4.90	
15	4.08	
20	3.64	
25	3.06	
30	2.58	
35	2.14	
40	1.76	
50	1.38	

[Chloramine-T] = 4.00×10^{-4} M at which
 (-dc/dt) was determined.

Table 1.4

[Chloramine-T] = 10.00×10^{-4} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00$
 $\times 10^{-2}$ M, Temp. = 35°C

Time (min.)	ml. of Hypo solution (11.90×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.40	5.92
5	7.28	
10	6.38	
15	5.64	
20	4.86	
25	4.24	
30	3.56	
35	3.06	
40	2.54	
50	2.02	

[Chloramine-T] = 9.00×10^{-4} M at which
 (-dc/dt) was determined.

Table 1.5

[Chloramine-T] = 16.67×10^{-4} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00$
 $\times 10^{-2}$ M, Temp. = 35°C

Time (min.)	ml. of Hypo solution (20.84×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.00	9.42
5	7.00	
10	6.20	
15	5.64	
20	4.80	
25	4.14	
30	3.50	
35	2.88	
40	2.24	
50	1.92	

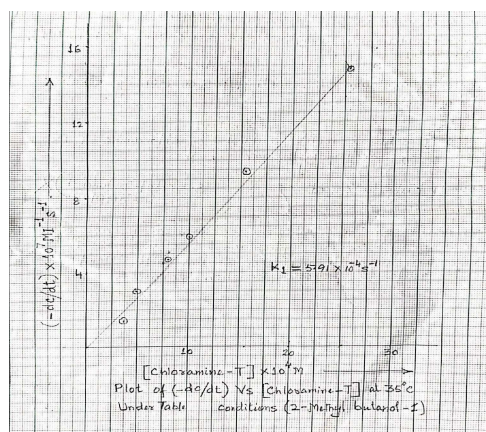
[Chloramine-T] = 15.00×10^{-4} M at which
 (-dc/dt) was determined.

Table 1.6

[2-Methyl butanol-1]	$= 2.00 \times 10^{-2} \text{ M}$
[Os(VIII)]	$= 4.82 \times 10^{-6} \text{ M}$
[NaOH]	$= 1.00 \times 10^{-2} \text{ M}$
$2.00 \times 10^{-2} \text{ M}$, Temp. = 35°C	

[Chloramine-T] $\times 10^4 \text{ M}$	$(-dc/dt) \times 10^7 \text{ M l}^{-1} \text{ s}^{-1}$	$K_1 \times 10^4 \text{ s}^{-1} = (-dc/dt) / [\text{Chloramine-T}]$
4.00	2.32	5.80
5.00	2.86	5.72
8.00	4.60	5.75
10.00	5.92	5.92
16.67	9.42	5.96
25.00	14.74	5.89

Average $k_1 = 5.84 \times 10^{-4} \text{ s}^{-1}$

**Graph 1.1**

On close examination of data indicates on increasing the concentration of chloramine-T, the value of rate constant (k_1) does not change significantly. This indicates first order dependence of reaction of chloramine-T which is used as oxidant. When a graph is plotted between value of $(-dc/dt)$ and chloramine-T as a straight out is obtained. Determination of dependence of reaction on concentration of 2-methyl butan-1-ol.

The experiment at different concentration of 2-methyl butan-1-ol have been performed keeping concentration of all reagents is constant.

Table 2.1

[Chloramine-T]	$= 10.00 \times 10^{-4} \text{ M}$,
[2-methyl butanol-1]	$= 0.50 \times 10^{-2} \text{ M}$,
[Os(VIII)]	$= 4.82 \times 10^{-6} \text{ M}$,
[NaOH] = $1.00 \times 10^{-2} \text{ M}$, $\mu = 2.00 \times 10^{-2} \text{ M}$, Temp. = 35°C	

Time (min.)	ml. of Hypo solution ($8.60 \times 10^{-4} \text{ N}$)	$(-dc/dt) \times 10^7 \text{ M l}^{-1} \text{ s}^{-1}$
0	11.66	3.82
5	9.94	
10	8.90	
15	7.96	
20	6.94	
25	5.66	
30	4.44	
40	3.42	
50	2.28	
60	1.76	

Table 2.2

[Chloramine-T]	$= 10.00 \times 10^{-4} \text{ M}$,
[2-methyl butanol-1]	$= 0.50 \times 10^{-2} \text{ M}$,
[Os(VIII)]	$= 4.82 \times 10^{-6} \text{ M}$,
[NaOH] = $1.00 \times 10^{-2} \text{ M}$, $\mu = 2.00 \times 10^{-2} \text{ M}$, Temp. = 35°C	

Time (min.)	ml. of Hypo solution ($8.60 \times 10^{-4} \text{ N}$)	$(-dc/dt) \times 10^7 \text{ M l}^{-1} \text{ s}^{-1}$
0	11.66	3.86
5	9.94	
10	8.92	
15	7.96	
20	6.94	
25	5.64	
30	4.48	
35	3.42	
40	2.34	
50	2.02	

Table 2.3

[Chloramine-T] = 10.00×10^{-4} M,
 [2-methyl butanol-1] = 0.50×10^{-2} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (8.60×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	11.66	3.90
5	9.98	
10	8.84	
15	7.86	
20	6.98	
25	6.36	
30	4.68	
35	3.78	
40	3.46	
50	2.88	

Table 2.4

[Chloramine-T] = 10.00×10^{-4} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (8.60×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	11.66	3.82
5	9.82	
10	8.86	
15	7.92	
20	6.92	
25	6.38	
30	5.30	
35	4.72	
40	2.38	
50	1.82	

Table 2.5

[Chloramine-T] = 10.00×10^{-4} M,
 [2-methyl butanol-1] = 3.50×10^{-2} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (8.60×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	11.66	3.88
5	9.86	
10	8.78	
15	7.86	
20	6.92	
25	6.38	
30	5.16	
35	4.68	
40	3.38	
50	2.10	

Table 2.6

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

[2-Methyl butanol-1] $\times 10^2$ M	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹	$K^1 \times 10^4$ s ⁻¹
0	11.66	3.88
5	9.86	
10	8.78	
15	7.86	
20	6.92	
25	6.38	
30	5.16	
35	4.68	
40	3.38	
50	2.10	

From the kinetic results summarized in table 8.6 that the value of $(-dc/dt)$ as well as value of first order rate constant (k_1) do not change significantly and remain practically constant at different concentration of 2-methyl butan-1-ol is zero order.

9. Determination of dependence of reaction on the concentration of Osmium tetroxide used as catalyst. Various experiments have been carried out at different concentration of Osmium tetroxide at fixed concentration of all other reagents. The results of such experiments have been recorded in tables 9.1-9.4 and 9.5.

Table 3.1

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 0.96×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{s}^{-1}$
0	8.00	0.69
10	7.56	
20	7.08	
40	6.36	
60	5.48	
80	4.86	
100	4.32	
120	3.76	
140	3.00	

Table 3.3

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 3.84×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{s}^{-1}$
0	8.00	2.82
10	7.30	
20	6.80	
40	6.04	
60	5.20	
80	4.52	
100	4.00	
120	3.36	
140	2.70	

Table 3.2

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 1.98×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{s}^{-1}$
0	8.00	1.44
10	7.42	
20	6.92	
40	6.18	
60	5.34	
80	4.72	
100	4.18	
120	3.58	
140	2.86	

Table 3.4

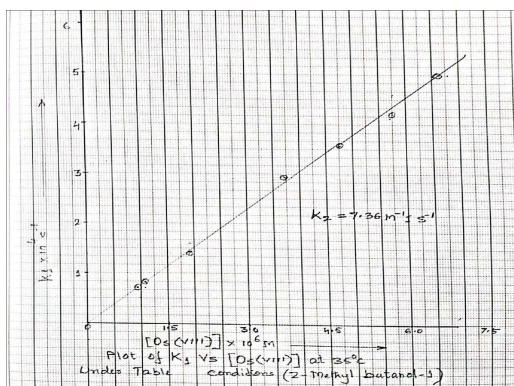
[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{s}^{-1}$
0	8.00	3.48
10	7.16	
20	6.68	
40	5.88	
60	5.06	
80	4.40	
100	3.86	
120	3.20	
140	2.54	

Table 3.5

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

[Os(VIII)] $\times 10^6 \text{ M}$	$(-dc/dt)$ $\times 10^7 \text{ l}^{-1} \text{ s}^{-1}$	$k_1 \times 10^4 \text{ s}^{-1}$	$k_2 \times 10^4 \text{ K}_1$ /[Os(VIII)]
0.96	0.69	0.69	7.19
1.92	1.44	1.44	7.50
3.84	2.82	2.82	7.34
4.82	3.48	3.48	7.22
5.76	4.40	4.40	7.64
6.72	5.02	5.02	7.47

**Graph 3.1**

From the data it has been observed that the value of k_2 is constant showing first order dependence of the reaction on concentration of Osmium tetroxide.

When a graph is plotted between value of rate constant and concentration of Osmium tetroxide, a straight is obtained which indicates the first order reaction.

10. Determination of dependence of the reaction on the concentration of sodium hydroxide. Various experiments have been carried out at different concentration of sodium hydroxide at fixed concentration of all reagents. Results of such experiments have been recorded in following tables.

Table 4.1

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 0.50×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{ s}^{-1}$
0	8.84	3.00
5	8.48	
10	8.00	
15	7.58	
20	7.00	
30	6.64	
40	6.26	
50	5.82	
80	4.92	

Table 4.2

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.25×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{ s}^{-1}$
0	8.84	7.36
5	8.00	
10	7.26	
15	6.40	
20	5.92	
30	5.22	
40	4.56	
50	4.00	
75	3.64	

Table 4.3

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 0.50×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.84	8.86
5	7.82	
10	7.06	
15	6.24	
20	5.80	
30	5.00	
40	4.40	
50	3.84	
75	3.46	

Table 4.5

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 2.25×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.84	13.18
5	7.52	
10	6.70	
15	5.90	
20	5.54	
30	4.70	
40	4.06	
50	3.42	
65	3.16	

Table 4.6

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.00×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

NaOH $\times 10^2$ M	$(-dc/dt) \times 10^7$ l ⁻¹ s ⁻¹	$k_1 \times 10^4$ s ⁻¹	$K_1 \times 10^2$ M ⁻¹ s ⁻¹ = $k_1 \times 10^2 / [\text{Os(VIII)}]$
0.50	3.00	3.00	6.00
1.00	5.92	5.92	5.92
1.25	7.36	7.36	5.89
1.75	8.86	8.86	5.91
2.00	10.28	10.28	5.87
2.25	13.18	13.18	5.86

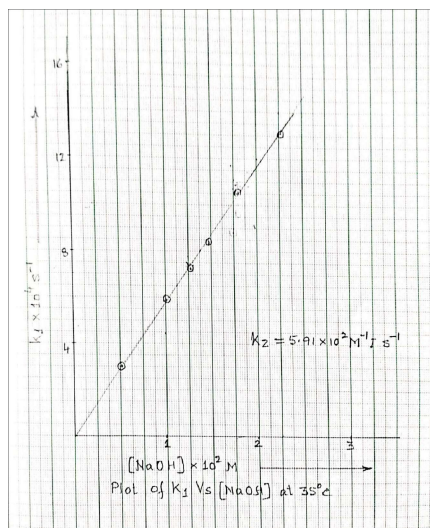
Table 4.4

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.75×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.84	10.28
5	7.70	
10	6.86	
15	6.06	
20	5.68	
30	4.86	
40	4.28	
50	3.54	
65	3.36	

From the kinetic data, it is clear that the value of first order rate constant (k_1) increases linearly with increase the concentration of [OH⁻] this indicates the reaction is first order with respect to NaOH.

A graph is plotted between k_1 values and concentration of sodium hydroxide, a straight is obtained.

**Graph 4.1**

11. Determination of effect of variations of temperature on rate constant of reaction. To study the effect of temperature on reaction rate a series of experiment at different temperature. V12 30°C, 40°C, 41°C have been carried out at fixed concentration of all reagent.

Table 5.1

[Chloramine-T] = 10.00×10^{-4} M,
[Os(VIII)] = 4.82×10^{-6} M,
[2-methyl butanol-1] = 2.00×10^{-2} M,
[NaOH] = 2.25×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
Temp. = 30°C

Time (min.)	ml. of Hypo solution (11.90×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.40	4.00
10	6.68	
20	5.84	
30	4.94	
40	3.98	
50	3.14	
60	2.76	
70	2.24	
80	1.82	

Table 5.2

[Chloramine-T] = 10.00×10^{-4} M,
[Os(VIII)] = 4.82×10^{-6} M,
[2-methyl butanol-1] = 2.00×10^{-2} M,
[NaOH] = 2.25×10^{-2} M, $\mu = 1.00 \times 10^{-2}$ M,
Temp. = 40°C

Time (min.)	ml. of Hypo solution (11.90×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.40	8.80
5	7.02	
10	6.18	
15	5.36	
20	4.68	
30	3.40	
40	2.56	
50	2.00	
60	1.46	

Table 5.3

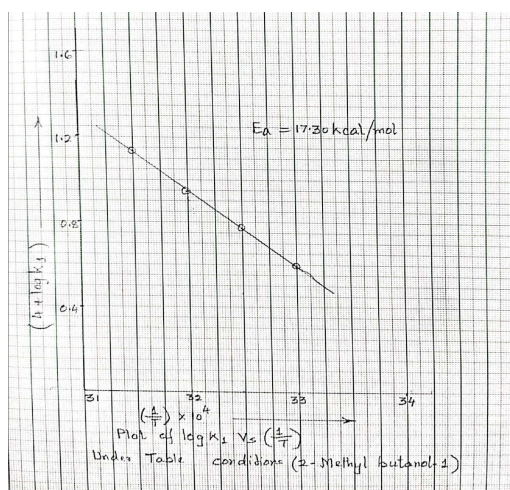
[Chloramine-T] = 10.00×10^{-4} M,
[Os(VIII)] = 4.82×10^{-6} M,
[2-methyl butanol-1] = 2.00×10^{-2} M,
[NaOH] = 2.25×10^{-2} M, $\mu = 1.00 \times 10^{-2}$ M,
Temp. = 40°C

Time (min.)	ml. of Hypo solution (11.90×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.40	12.78
5	6.46	
10	5.82	
15	4.94	
20	4.22	
25	3.64	
30	2.92	
35	2.56	
40	2.02	

Table 5.4

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 2.25×10^{-2} M, $\mu = 1.00 \times 10^{-2}$ M,
 Temp. = 40°C

Temp. $^\circ\text{C}$	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{s}^{-1}$	$K_1 \times 10^4 \text{s}^{-1} = (-dc/dt)$ [Chloramine-T]
30	4.00	4.00
35	5.92	5.92
40	8.80	8.80
45	12.78	12.78

**Graph 5.1**

From the kinetic data, it has been observed that the reaction rate increases with increasing the temperature, showing the marked effect of temperature variations on rate of reaction. A graph is plotted between $\log k_1$ and $(1/T)$, a straight line is obtained, where slope gives the value of $ea/2.303R$. Where ea is energy of activation. The energy of activation for the oxidation of 2-methyl butan-1-ol was found as 17.30 kcal/mole. Effect of para toluene sulphonamide (PTS) on rate of reaction. Para toluene sulphonamide is the reduction produced of the oxidant Chloramine-T. Therefore it's effect was observed by different experiments. The results obtained have been recorded in following tables.

Table 6.1

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 2.25×10^{-2} M, $\mu = 1.00 \times 10^{-2}$ M,
 Temp. = 40°C

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{s}^{-1}$
0	8.84	7.40
5	8.02	
10	7.24	
15	6.42	
20	5.90	
30	5.22	
40	4.58	
50	4.06	
75	3.68	
100	3.14	

Table 6.2

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 2.25×10^{-2} M, $\mu = 1.00 \times 10^{-2}$ M,
 Temp. = 40°C

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	$(-dc/dt) \times 10^7$ $\text{M l}^{-1} \text{s}^{-1}$
0	8.84	7.42
5	8.04	
10	7.20	
20	5.96	
30	5.24	
40	4.56	
50	4.00	
80	3.58	
100	3.16	

Table 6.3

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [PTS] = 3.00×10^{-3} M, [NaOH] = 2.25×10^{-2} M
 $\mu = 2.00 \times 10^{-2}$ M, Temp. = 40°C

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	(-dc/dt) $\times 10^7$ M l ⁻¹ s ⁻¹
0	8.84	7.38
5	8.04	
10	7.26	
20	5.98	
30	5.26	
40	4.52	
50	4.02	
60	3.86	
80	3.60	
100	3.18	

Table 6.5

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [PTS] = 4.00×10^{-3} M, [NaOH] = 2.25×10^{-2} M
 $\mu = 2.00 \times 10^{-2}$ M, Temp. = 40°C

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	(-dc/dt) $\times 10^7$ M l ⁻¹ s ⁻¹
0	8.84	7.34
5	8.00	
10	7.28	
20	5.92	
30	5.24	
40	4.58	
50	4.08	
60	3.82	
80	3.64	
100	3.20	

Table 6.6**Table 6.4**

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [PTS] = 3.00×10^{-3} M, [NaOH] = 2.25×10^{-2} M
 Temp. = 40°C $\mu = 2.00 \times 10^{-2}$ M,

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	(-dc/dt) $\times 10^7$ M l ⁻¹ s ⁻¹
0	8.84	7.42
5	8.02	
10	7.24	
15	6.42	
20	5.90	
30	5.22	
40	4.58	
50	4.06	
75	3.68	
100	3.14	

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [PTS] = 1.00×10^{-3} M, [NaOH] = 2.25×10^{-2} M
 Temp. = 40°C $\mu = 2.00 \times 10^{-2}$ M,

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	(-dc/dt) $\times 10^7$ M l ⁻¹ s ⁻¹
0	8.84	7.42
5	8.02	
10	7.24	
15	6.42	
20	5.90	
30	5.22	
40	4.58	
50	4.06	
75	3.68	
100	3.14	

The results of 6.1 to 6.6 have been summarized in the table 6.7

Table 6.7

[Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.25×10^{-2} M, $\mu = 2.00 \times 10^{-2}$ M,
 Temp. = 35°C

[PTS] $\times 10^{-3}$ M	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹	$K_1 \times 10^4$ s ⁻¹
0.00	7.36	7.36
1.00	7.40	7.40
2.00	7.42	7.42
3.00	7.38	7.38
4.00	7.34	7.34
5.00	7.38	7.38

It is quite clear that the values of k_1 was not changed which indicates that increasing of (PTS) in the reaction mixture there were no changed values of k_1 and rate $(-dc/dt)$ Effect of variation of Ionic strength of the medium on rate of reaction.

The Ionic strength has been varied by adding different amounts of sodium perchlorate in the reaction mixture. The results obtained have been recorded in the following tables.

Table 7.1

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 1.92×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaClO₄] = 1.00×10^{-3} M, [NaOH] = 2.25×10^{-2} M
 Temp. = 35°C $\mu = 2.00 \times 10^{-2}$ M,

Time (min.)	ml. of Hypo solution (11.30×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.00	1.48
10	7.42	
20	6.92	
30	6.48	
40	6.18	
60	5.34	
80	4.72	
100	4.18	
120	3.58	
100	3.14	

Table 7.2

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 1.92×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaClO₄] = 2.00×10^{-3} M, [NaOH] = 2.25×10^{-2} M
 Temp. = 35°C $\mu = 2.00 \times 10^{-2}$ M,

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.00	1.45
10	7.44	
20	6.94	
30	6.46	
40	6.18	
50	5.76	
60	5.32	
80	4.74	
100	4.12	

Table 7.3

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 1.92×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaClO₄] = 4.00×10^{-3} M, [NaOH] = 1.00×10^{-2} M
 Temp. = 35°C $\mu = 5.00 \times 10^{-2}$ M,

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	$(-dc/dt) \times 10^7$ M l ⁻¹ s ⁻¹
0	8.00	1.48
10	7.72	
20	6.96	
30	6.48	
40	6.20	
60	5.32	
80	4.74	
100	4.08	

Table 7.4

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 1.92×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaClO₄] = 6.00×10^{-3} M, [NaOH] = 1.00×10^{-2} M
 Temp. = 35°C $\mu = 7.00 \times 10^{-2}$ M,

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	(-dc/dt) $\times 10^7$ M l ⁻¹ s ⁻¹
0	8.00	1.46
10	7.76	
20	6.94	
40	6.18	
60	5.36	
80	4.74	
100	4.12	
120	3.62	
140	3.18	

Table 7.5

[Chloramine-T] = 10.00×10^{-4} M,
 [Os(VIII)] = 1.92×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaClO₄] = 1.00×10^{-3} M, [NaOH] = 1.00×10^{-2} M
 Temp. = 35°C $\mu = 2.00 \times 10^{-2}$ M,

Time (min.)	ml. of Hypo solution (12.50×10^{-4} N)	(-dc/dt) $\times 10^7$ M l ⁻¹ s ⁻¹
0	8.00	1.48
10	7.42	
20	6.92	
30	6.48	
40	6.18	
60	5.34	
80	4.72	
100	4.18	
120	3.58	

The results of 13.1 to 13.5 have been summarized in table 13.6

Table 7.6

[Chloramine-T] = 10.00×10^{-4} M
 [Os(VIII)] = 4.82×10^{-6} M,
 [2-methyl butanol-1] = 2.00×10^{-2} M,
 [NaOH] = 1.00×10^{-2} M,
 Temp. = 35°C

[NaClO ₄] $\times 10^3$ M	$\mu \times 10^{-2}$ M	(-dc/dt) M l ⁻¹ s ⁻¹	$K_1 \times 10_4$ S ₋₁
0.00	1.00	1.44	1.44
1.00	2.00	1.48	1.48
2.00	3.00	1.45	1.45
4.00	5.00	1.48	1.48
6.00	7.00	1.46	1.46
8.00	9.00	1.51	1.51

From the above table It has been observed that the values of (-dc/dt) as well as k₁ remain practically constant at different Ionic strength of medium.

This indicates that there was no effect of change in Ionic strength of medium on reaction rate.

14. Conclusions:

The following are results obtained through kinetic studies.

- * The reactions were first order kinetics with respect to Chloramine-T.
- * The reactions followed zero-order with respect to 2methyl butanol-1.
- * First order dependence of all the reaction on concentration of sodium hydroxide was observed.
- * All the reactions showed first order kinetics with respect to Osmium tetroxide.
- * Negligible effect of Ionic strength of the medium on reaction rates for the reactions was observed.
- * A zero-effect of addition of para toluene Sulphonamide (PTS) on the reaction rates.
- * Marked effect of temperature variation on the reaction rate was observed.

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

References

1. J.A Christiansen, *Z Physical Chem*, 10882(1924)
2. C.N Davis, 'Progress in Reaction Kinetics,' Vol.I, P 161, Pergamon Press, Oxford (1961).
3. C.Scatzhard, *Chem. Rev.*, 10229 (1932).
4. J.Smidt, *Chem. Ind (London)*, **59** (1962)
5. P.K Prakash and B.Sethuram, *J.Indian Chem. Soc.***11**(2), 11(1973)
6. M.G.Reddy and T.N Rao, *Indian J.Chem*, **17A**, 378(1979)
7. M.P.Rao, B.Sethuram and T.N.Rao, *Indian J.Chem*, **19A**, 582 (1980)
8. P.E.Hardy, *H. Chem. Soc.*, **2089** (1970)
9. A.V.R.Moorthy and V.S.Rao, *Proc.Indian Acad. Science, A* **35**, 69(1952)
10. M.C. Agarwal and S.P Mushrooms, *Z. Naturforsch*, 27401(1972)
11. G.Shiemann and P.Novak, *Angela Chem.*, **40**, 1032(1968)
12. K.Weber and H.Valic, *Z.physical Chem.* **239**, 24(1968)
13. S.P. Mushran, M.C .Agarwal and B.Prasad, *J. CHEM, Soc.B*, 1712(1971)
14. V.Laximnarayan and A.R.V. Moorthy, *Chemist-Analyst*, **54**, 9(1954)
15. D.K.Padma and A.R.V.Moorthy, *Curr. Science*, **37**,343(1968)
16. Wilhelm, *Pogg. Ann.* **81**, 413(1850)
17. F.W Ostwald, *J.Practice.Chem*; **29**, 385(1884)
18. C.P.Wenyel, *Lehre Vonder Verwandtschaft Der Korper Dresden* (1777)
19. P.E.M Berthelot and L.P. De Saint Gills, *Ann. Chem. Phys.*, **63**(3), 385(1832)
20. M.P.Rao et al, *Indian J.Chem* **16A**, 440(1978)