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Kinetics and mechanism of Os(VIII) catalysed oxidation of 2-methyl cyclohexanol by alkaline chloramine-T

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ABSTRACT

The kinetics of Os(VIII) catalysed oxidation of 2-methyl cyclohexanol by alkaline chloramine-T has been investigated. The result indicates zero order kinetics with respect to 2-methyl cyclohexanol and first order kinetics with respect to chloramine-T, OH^- and Os(VIII) concentrations. There is insignificant effect of ionic strength, para-toluene sulphonamide (PTS) and KCl on reaction rate. The dielectric constant of the medium shows positive effect. Elevation of temperature increases the rate of reaction in oxidation of 2-methyl cyclohexanol. A suitable mechanism in conformity with the above observation has been proposed.

Key words: Kinetics, mechanism, oxidation, 2-methyl cyclohexanol, osmium tetroxide (OsO_4), chloramine-T (CAT), alkaline medium.

INTRODUCTION

The kinetics of oxidation of some cycloalcohols incorporating certain transition-metal ions viz. - Osmium (VIII)[1], ruthenium (III)[2,3], iridium (III)[4] and Palladium (II)[5] as homogeneous catalyst have been extensively investigated.

There are only few papers are reported in catalysed oxidation of cycloalcohols, but Os(VIII) catalysed oxidation of 2-methyl cyclohexanol by chloramine-T (CAT) is not reported till date. Firstly, Singh and his co-workers studied the kinetics of oxidation of 2-methyl cyclohexanol, 1,2-cyclohexane diol[6], 1,4-cyclohexane diol[7] by CAT with high redox potential (E_{red} = 1.138 V at pH 0.65) has been used in kinetic studies involving is as an oxidant both in acidic as well as in alkaline medium.

Chloramine-T is a member of aromatic sulphonyl haloamides and these are sources of halonium cations, hypophalite species and N-anion, and act both as bases and nucleophiles[8].

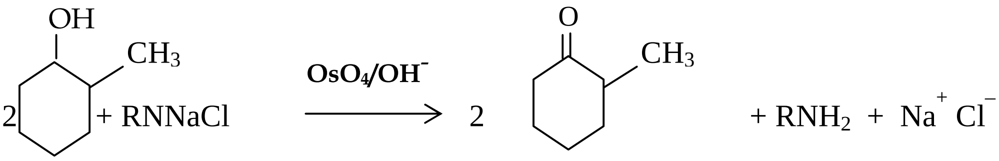
Osmium metal gives off recognizable smell due to the formation of volatile osmium tetroxide (OsO_4). OsO_4 and its various reactive species act as catalyst[9]. We have undertaken the systematic study of title reaction with a view to find out the mechanistic aspect of the reaction.

EXPERIMENTAL SECTION

Reagent grade chemicals and doubly distilled water were used in this study. Aqueous solution of CAT (E. Merk) was always prepared a fresh and standardized iodometrically. The solution of 2-methyl cyclohexanol was made in doubly distilled water. Os(VIII) oxide (Johnson & Matthey) solution was prepared by dissolving the sample in 0.1M NaOH.

A thermostatic water bath was used to maintain the desired temperature within ±0.1^{0}C. The reaction was initiated by rapid addition of CAT to the reaction mixture containing appropriate quantities of 2-methyl cyclohexanol, Os(VIII) oxide and water mixing by vigorous shaking. The progress of the reaction was monitored by estimating the amount of unconsumed CAT iodometrically at regular time intervals.

Stoichiometry and product identification. The reaction mixture containing a known amount of 2-methyl cyclohexanol, NaOH, OsO4 and known amount of [chloramine-T], were kept at 35^{0}C for 72 hrs, estimation of unreacted chloramine-T showed one mole of 2-methyl cyclohexanol consumes two moles of chloramine-T.



2-methyl cyclohexanol 2-methyl cyclohexane one

Here R is P-$CH_3C_6H_4SO_2$.

RESULTS AND DISCUSSION

The reaction was studied at several initial concentrations of the reactants and the kinetic results were reported in Table 1.

Table 1. Effect of variation of reactants concentration at 35^{0}C

[NaOH] = 1.00 × 10^{-2} mol dm^{-3}, [OsO$_4$] = 1.20×10^{-6} mol dm^{-3}

[CAT] × 10^{3} (mol dm^{-3})	[2-methyl cyclohexanol] × 10^{2} (mol dm^{-3})	[–dc/dt] × 10^{7} (mol dm^{-3} s^{-1})	k$_1$ × 10^{4} (s^{-1})
0.40	2.00	1.00	4.16
0.50	2.00	1.28	4.26
1.25	2.00	4.12	4.12
2.00	2.00	6.54	4.09
2.50	2.00	8.50	4.05
1.00	1.00	3.40	4.25
1.00	3.00	3.34	4.16
1.00	5.00	3.40	4.25
1.00	7.50	3.28	4.10
1.00	10.00	3.32	4.15
1.00[a]	2.00	1.72	2.15
1.00[b]	2.00	2.48	3.10
1.00[c]	2.00	5.28	6.60

[a] 25C; [b] 30^{0}C; [c] 40^{0}C

The plot of (–dc/dt) against the initial concentration of chloramine-T at fixed concentration of chloramine-T, 2-methyl cyclohexanol, medium and catalyst is a straight line with a slope indicating first order kinetics with respect to [CAT] (Fig. 1). The first order rate constants are independent of initial concentration of CAT. When the concentration of 2-methyl cyclohexanol is increased by keeping the concentration of other reactants constant, it is observed that the rate of reaction does not change significantly and remain practically constant (Table 1). This shows that the rate is independent of initial concentration of substrate, indicating zero order kinetics with respect to 2-methyl cyclohexanol.

Table 2. Effect of variation of [OsO$_4$], (NaOH) and μ (ionic strength) on rate constant at 35^{0}C

[CAT] = 1.00 × 10^{-3} mol dm^{-3}, [2-methyl cyclohexanol] = 2.00 × 10^{-2} mol dm^{-3}

[OsO$_4$] × 10^{6} (mol dm^{-3})	[NaOH] × 10^{2} (mol dm^{-3})	μ × 10^{2} (mol dm^{-3})	[–dc/ dt] × 10^{7} (mol dm^{-3} s^{-1})
0.40	1.00	1.00	1.12
0.80	1.00	1.00	2.28
1.60	1.00	1.00	4.52
2.00	1.00	1.00	5.68
2.40	1.00	1.00	6.74
1.20	0.50	1.00	1.58
1.20	1.25	1.00	4.14
1.20	1.50	1.00	5.00
1.20	1.75	1.00	5.66
1.20	2.00	1.00	6.72
1.20	1.00	1.50	8.46
1.20	1.00	2.00	8.52
1.20	1.00	2.50	8.48
1.20	1.00	3.00	8.56
1.20	1.00	4.00	8.50

The value of rate constant increase with the concentration of sodium hydroxide. The plot of [NaOH] vs (–dc/dt) gives a straight line indicating first order kinetics with respect to sodium hydroxide (Fig. 2). It is observed that the rate of reaction is directly proportional to the first power of concentration of OsO_4 and the plot (Fig. 3) [OsO_4] vs (–dc/dt) gives a straight line showing first order dependence on OsO4. The rate of reaction does not change on increasing the concentration of $NaClO_4$ responsible for change of ionic strength of medium[10]. The value of (–dc/dt) remains approximately constant on changing the concentration of NaClO4, showing negligible effect of ionic strength Table 2.

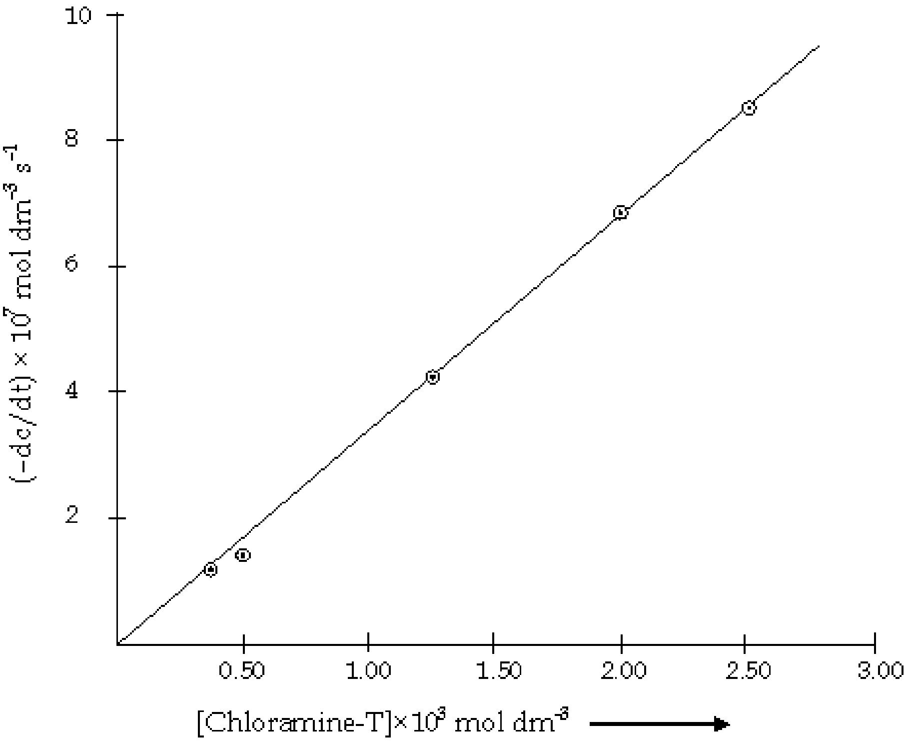


Fig. 1- Plot of (–dc/dt) Versus [CAT]

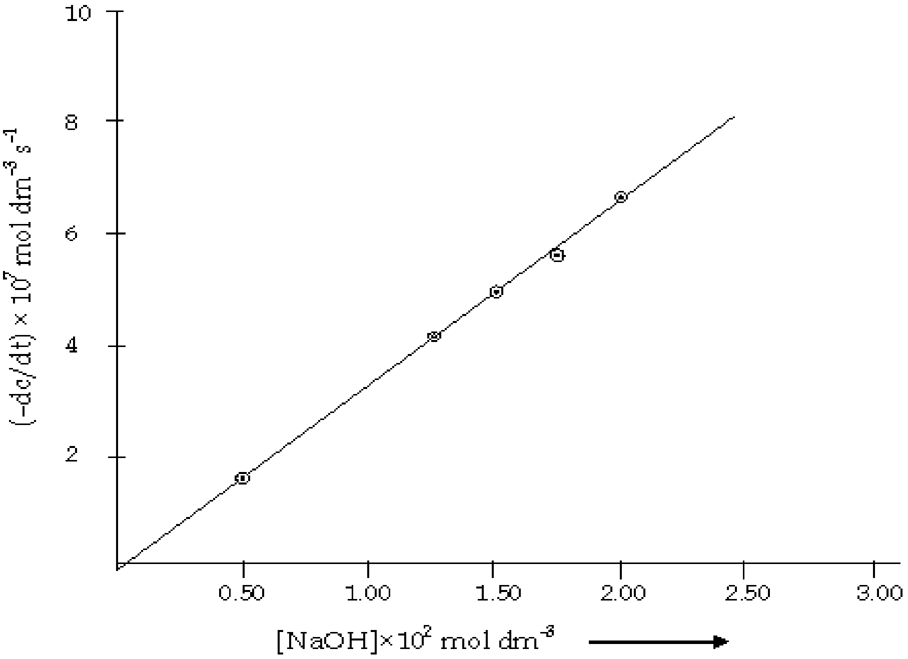


Fig. 2- Plot of (-dc/dt) Versus [NaOH]

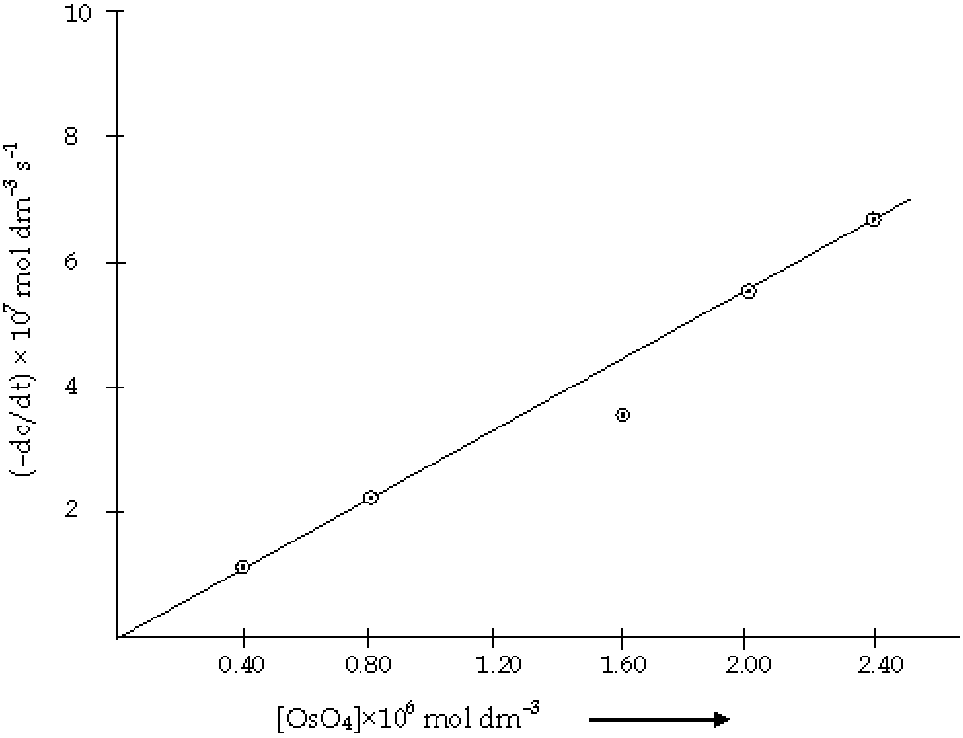


Fig. 3- Plot of (-dc/dt) Versus [OsO_4]

The reaction has been studied at 25, 30, 35 and $40^{0}C$ and the rate measurement at these temperatures lead to compute the activation parameters.

The value of E_a, □S* and □G* are found as 76.40 kJ mol^{-1}, –1.27 JK^{-1} mol^{-1}, 442 kJ mol^{-1} respectively.

The reactive species of chloramine-T and osmium tetroxide in alkaline medium is RNHCl and $[OsO_4(OH)(H_2O)]^{-1}$.

In aqueous alkaline solution chloramine-T hydrolysed as follows –

$$RNNaCl + H_2O \longrightarrow RNHCl + NaOH \qquad (a)$$

$$RNHCl + NaOH \longrightarrow RNH_2 + NaOCl \qquad (b)$$

Thus in alkaline medium, there are three probable oxidizing species of chloramine-T, NaOCl, RNHCl & chloramine-T itself.

RNHCl is a real reactive species which gives rate of reaction to be low and that explains all the observed kinetics.

In accordance with experimental results the possible proposed mechanism is given below –

$$\underset{(C_1)}{[OsO_4(OH)(H_2O)]^{-}} + OH^{-} \underset{k}{\overset{K_1}{\rightleftharpoons}} \underset{(C_2)}{[OsO_4(OH)_2]^{2-}} + H_2O \qquad (i)$$

$$C_2 + RNHCl \; X\,(Complex) \longrightarrow \qquad (ii)$$

$$X + S \; Products \xrightarrow{fast} \qquad (iii)$$

The rate of oxidation in terms of ions of concentration of chloramine-T may be written as -

$$\frac{-d[CAT]}{dt} = [C_2]\,[RNHCl] \qquad (1)$$

On applying principle of equilibrium treatment to step (i), we have

$$K_1 = \frac{[C_2]}{[C_1]\,[OH^{-}]}$$

$$\text{or, } C_2 = K_1\,[C_1]\,[OH^{-}] \qquad (2)$$

On substituting the value of $[C_2]$ from equation (2) in equation (1), we have

$$\frac{-d[CAT]}{dt} = k\,K_1\,[C_1]\,[OH^-]\,[RNHCl]$$

$$\frac{-d[CAT]}{dt} = k\,K_1\,[OsO_4]\,[CAT]\,[OH^-] \qquad (3)$$

The rate equation (3) fully explains all the observed kinetics with respect to chloramine-T, 2-methyl cyclohexanol, $[H^+]$ and osmium tetroxide.

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