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Kinetic and Mechanistic Study of N-Chlorosuccinimide Oxidation of 2-Methyl butanol-1 in the Presence of Osmium Tetroxide as Homogeneous Catalyst in Aqueous Alkaline Solution

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The kinetic study of osmium tetroxide catalyzed oxidation of 2-methyl butanol-1 by aqueous alkaline solution of N-chlorosuccinimide shows first-order kinetics with respect to each [N-chlorosuccinimide], [Os(VIII)] and [OH^-] and zero order kinetics with respect to [2-methyl butanol-1]. Negligible effect of variation of ionic strength of the medium on the rate of the reaction was observed. Addition of succinimide and mercuric acetate did not affect the rate constant of the reaction. Activation parameter, Ea, $\Delta S^{\#}$ and $\Delta G^{\#}$ were calculated by the rate contents observed of 30, 35, 40 and 45 ºC. A suitable mechanism in agreement with kinetic observation was proposed.

Key Words: 2-Methyl butanol-1, N-Chlorosuccinimide, Osmium tetraoxide, Kinetic, Oxidation.

INTRODUCTION

N-Chlorosuccinimide (NCS) has been used as an oxidizing agent and analytical reagent especially in the acid medium[1-3]. However, work on oxidation kinetic involving N-chlorosuccinimide as oxidant in alkaline medium is scanty[4-7]. In some investigations, palladium(II) chloride[3,6] has been used as catalysts in N-chlorosuccinimide oxidation kinetics. The role of Os(VIII) as a catalyst is some redox reaction have been reviewed[8]. Osmium(VIII) catalysis in redox reaction involve several complexities[9] due to formation of different intermediate complexes and different oxidation states of osmium, *etc*. Since oxidation of 2-methyl butanol-1 by N-chlorosuccinimide, both in the presence or absence of either Pd(II) or Os(VIII) does not take place in acid medium, we have investigated the kinetic of oxidation of 2-methyl butanol-1 by N-chlorosuccinimide in the presence of Os(VIII) as homogeneous catalyst in alkaline medium in order to propose the reaction mechanism.

EXPERIMENTAL

N-Chlorosuccinimide (E. Merck) and 2-methyl butanol-1 (E. Merck) were used as supplied. A 1 g sample of osmium tetroxide (Johnson and Matthey) was first dissolved in 200 mL of 0.01N NaOH solution and there after the volume was raised to 1000 mL. The final strength of osmium tetroxide and that of sodium hydroxide was calculated in 1000 mL and these strength were noted. All other reagents *viz*. NaOH, mercuric acetate and succimimide of A.R. grade were used and their solutions

were prepared in double distilled water. An aqueous solution of N-chlorosuccinimide was freshly prepared daily.

A thermostated water bath was used to maintain the desired temperature within ± 0.1 ºC. Reaction was initiated by addition of N-chlorosuccinimide solution to the reaction vessel containing desired volumes of solution of 2-methyl butanol-1, osmium tetroxide, sodium hydroxide and mercuric acetate *etc*. all maintained at 35 ºC. The progress of the reaction was followed by determining N-chlorosuccinimide iodometrically in aliquots withdrawn after suitable time intervals.

Stoichiometry: The reaction mixtures containing a known excess of [NCS] over [2-methyl butanol-1] were hept in the presence of NaOH, $Hg(OAc)_2$ and OsO_4 at 35 ºC for 72 h. Estimation of unreacted N-chlorosuccinimide showed that one mole 2-methyl butanol-1 consumes one mole of N-chlorosuccinimide. The results may be represented by the following stoichiometric equation:

$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH + >NCl \xrightarrow{OsO_4/OH^-} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO + >NH + HCl \quad (1)$$

The presence of $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO$ as product was confirmed by forming its 2,4-dinitrophenyl hydrazone derivative[10] and m.p. compare with an authentic sample.

RESULTS AND DISCUSSION

The kinetic of Os(VIII) catalyzed oxidation of 2-methyl butanol-1 by N-chlorosuccinimide was investigated at several initial concentrations of the reactants. The first order kinetics with respect to N-chlorosuccinimide was observed which is evident by the constant values of first-order rate constant, k_1 obtained at different initial concentration of N-chlorosuccinimide. Constant values of k_1 at different initial concentrations of 2-methyl butanol-1 indicates zero-order kinetics with respect to substrate. Linear increase in the k_1 values with increase in $[OsO_4]$ and [NaOH] indicates that reaction follows first-order dependence on both $[OsO_4]$ and [NaOH] as is evident from Table-1.

Addition of mercuric acetate, succinimde (NHS) and variation of ionic strength of the medium (adjusted by $NaClO_4$ addition) had an insignificant effect on k_1 observed in each case (Table-2) rate measurements at 30, 35, 40 and 45 ºC led us to compute the value of energy of activation (Ea), which was found to be 15.27 Cal/mol.

The role of mercuric acetate is to eliminate Cl^- which might interact with N-chlorosuccinimide to produce chlorine which may further set Cl_2 oxidation of 2-methyl butanol-1, mercuric acetate traps Cl^- to form $[HgCl_4]^{2-}$ and pure N-chlorosuccinimide oxidation is facilitated. It has need observed that $Hg(OAc)_2$ does not play either catalytic role or co-catalytic role as it shows zero effect on rate. The reaction does not proceed in its presence without using N-chlorosuccinimide, then negating its role as oxidant.

TABLE-1
EFFECT OF VARIATION OF [NCS], [2-MB-Ol][Os(VIII)] AND [OH^-] ON THE RATE CONSTANT OF Os(VIII) CATALYZED OXIDATION OF 2-METHYL BUTANOL-1 IN AQUEOUS ALKALINE MEDIUM AT 35 °C [$Hg(OAc)_2$] = 3.50×10^{-3} M

[NCS] × 0^3 M	[2-MB-ol] × 10^2 M	[Os(VIII)] × 10^6 M	[OH^-] × 10^2 M	$k_1 \times 10^4$ s^{-1}
0.40	2.00	4.80	1.00	6.51
0.50	2.00	4.80	1.00	6.57
0.80	2.00	4.80	1.00	6.48
1.00	2.00	4.80	1.00	6.49
1.67	2.00	4.80	1.00	6.54
2.50	2.00	4.80	1.00	6.54
1.00	0.50	4.80	1.00	5.82
1.00	1.00	4.80	1.00	5.86
1.00	2.00	4.80	1.00	5.84
1.00	3.00	4.80	1.00	5.84
1.00	4.00	4.80	1.00	5.84
1.00	5.00	4.80	1.00	5.86
1.00	2.00	0.96	1.00	1.29
1.00	2.00	1.92	1.00	2.60
1.00	2.00	3.84	1.00	5.06
1.00	2.00	4.80	1.00	6.49
1.00	2.00	5.76	1.00	7.83
1.00	2.00	6.72	1.00	8.98
1.00	2.00	4.80	0.50	3.22
1.00	2.00	4.80	1.00	6.48
1.00	2.00	4.80	1.25	8.06
1.00	2.00	4.80	1.75	11.31
1.00	2.00	4.80	2.00	13.00
1.00	2.00	4.80	2.25	14.55
1.00[a]	2.00	4.80	1.00	4.42
1.00[b]	2.00	4.80	1.00	9.75
1.00[c]	2.00	4.80	1.00	14.11

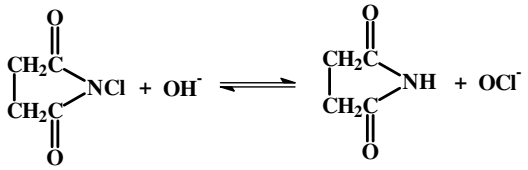
a → 30 °C, b → 40 °C and c → 45 °C.

In alkaline solution osmium tetroxide exists in octahedral complexes of the forms $[OsO_4(OH)(H_2O)]^-$ and *trans* $[OsO_4(H_2O)]^{2-}$ and these species exist in the following equilibrium.

$$[OsO_4(OH)(H_2O)]^- + OH^- \rightleftharpoons [OsO_4(OH)_2]^{2-} \quad (2)$$

In view of first-order kinetics with respect to [OH^-], on increasing [OH^-] more of $[OsO_4(H_2O)]^{2-}$ is formed. Hence out of there two species $[OsO_4(OH)_2{}^{2-}]$ is assumed as reactive catalytic species of osmium tetroxide in the present investigation.

In aqueous alkaline medium N-chlorosuccinimide[6] is reported to exist in the following equilibrium.



(3)

TABLE-2
EFFECT OF VARIATION OF IONIC STRENGTH OF MEDIUM, ADDITION OF SUCCINIMIDE (NHS) AND MERCURIC ACETATE ON THE RATE CONSTANT OF OS(VIII) CATALYSED OXIDATION OF 2-METHYL BUTANOL-1 IN AQUEOUS ALKALINE MEDIUM AT 35 ^{O}C

$(\mu) \times 10^2$ M	[NHS] $\times 10^2$ M	$[Hg(OAc)_2] \times 10^3$ M	$k_1 \times 10^4$ s^{-1}
0.80	–	1.00	3.20[a]
1.30	–	1.00	3.24[a]
1.80	–	1.00	3.27[a]
2.80	–	1.00	3.21[a]
3.80	–	1.00	3.22[a]
5.80	–	1.00	3.19[a]
8.30	–	1.00	3.20[a]
10.80	–	1.00	2.22[a]
	0.25[b]	3.50	10.97
	0.50[b]	3.50	10.93
	1.00[b]	3.50	10.95
	1.50[b]	3.50	10.88
	2.00[b]	3.50	10.84
	3.00[b]	3.50[c]	10.91
	4.00[b]	3.50[c]	10.93
		3.50[c]	6.560
		3.50[c]	6.540
		4.50[c]	6.520
		6.00[c]	6.530
		9.00[c]	6.590
		12.00[c]	6.550
		15.00[c]	6.570
		18.00[c]	6.530

[NCS] = 1.00×10^{-3} M(a), 1.67×10^{-3} M(b) and 2.50×10^{-3} M(c).
[NaOH] = $0 .50 \times 10^{-2}$ M(a), 1×10^{-2} M(b and c).
[Os(VIII) = 4.80×10^{-6} M and [2-methyl butanol-1] = 2.00×10^{-2} M.

This it is evident that either N-chlorosuccinimide or OCl^- may act as oxidizing species. When OCl^- is assumed to be active species of N-chlorosuccinimide then rate law would require negative effect of succinimide (NHS) contrary to the observed negligible effect of [NHS] on the rate of reaction. Thus OCl^- is ruled out as reactive oxidizing species of N-chlorosuccinimide. Under the given condition the only choice left is to assume N-chlorosuccinimide itself as oxidizing species. Hence in the present investigation, N-chlorosuccinimide itself is assumed as oxidising species.

Considering reactive species of N-chlorosuccinimide and OsO_4 in alkaline medium and kinetic results, the following mechanism is suggested.

$$\underset{(C_1)}{[OsO_4(OH)(H_2O)]^-} + OH^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \underset{(C_2)}{[OsO_4(OH)_2]^{2-}} + (H_2O) \qquad \text{(i)}$$

$$\underset{(C_2)}{[OsO_4(OH)_2]^{2-}} + >NCl \xrightarrow{K_2} \underset{(C_3)}{\left[OsO_4 \begin{matrix} OH \\ O-H \end{matrix} \!\!-\!\!- ClN< \right]^{2-}} \qquad \text{(ii)}$$

$$(C_3) \xrightarrow[\text{Slow and rate determining step}]{k} [OsO_4(OH)(OCl)]^{2-} + >NH \quad \text{(iii)}$$

$$[OsO_4(OH)(OCl)]^{2-} + RCH_2OH \xrightarrow[\text{Fast}]{} [OsO_3(OH)_2]^{2-} + RCOOH + HCl \quad \text{(iv)}$$

$$[OsO_3(OH)_2]^{2-} + >NCl + H_2O \xrightarrow[\text{Fast}]{} [OsO_4(OH)_2]^{2-} + >NH + HCl \quad \text{(v)}$$

The rate of the reaction may be written in terms of rate of loss of N-chlorosuccinimide as eqn. 4.

$$\text{Rate} = \frac{-d(NCS)}{dt} = k[C_3] \quad (4)$$

Form step (II) we have $[C_3] = K_2[C_2][NCS]$ (5)

On applying steady steady state approximation to $[C_3]$, we have

$$d[C_2]/dt = K_1[C_1][OH^-] - K_{-1}[H_2O]\,[C_2] - K_2[C_2][NCS] = 0$$

Or
$$[C_2] = \frac{K_1[C_1](OH^-]}{K_{-1}[H_2O] + K_2(NCS)} \quad (6)$$

By considering eqns. 4, 5 and 6 we have

$$\frac{-d[NCS]}{dt} = \frac{kK_1K_2[C_1][NCS][OH^-]}{K_{-1}[H_2O] + K_2[NCS]} \quad (7)$$

Further on assuming $K_{-1}[H_2O] >> K_2[NCS]$, eqn. 7 become eqn. 8 in which $K'_1 = K_1/K_{-1}[H_2O]$

$$\frac{-d[NCS]}{dt} = kK'_1K_2[NCS][OH^-][Os(VIII)] \quad (8)$$

The rate law (8) fully explains the observed kinetics. Hence proposed mechanism is valid.

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