Mechanism of Os (VIII) Catalysis in N-Chlorosuccinimide oxidation of 3-Methyl butanol-1in aqueous alkaline solution: A Kinetic study

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Abstract

Kinetics of oxidation of 3-methyl butanol-1by N-Chlorosuccunimide (NCS) in presence of alkaline solution of osmium tetroxide has been investigated at 35^0. The result shows first order kinetics with respect to [NCS], [Os (VIII)], and [OH^-]. While zero order dependence on [3-methyl butanol-1]. Addition of succinimide [NHS] and variation of ionic strength of medium had zero effect on rate constant. A negligible effect of addition of mercuric acetate on rate was observed. A complex of [$OsO4(OH)_2$-----CLN<]$^{2-}$ formed between the reactive species of NCS and Osmium tetroxide prior to rate determining step, is suggested. A suitable mechanism in full agreement with kinetic observation was proposed.

***Keywords**: Kinetics, oxidation Os (VIII), 3-methyl butanol-1 N-Chlorosuccinimide.*

Introduction-

N-halosuccnimides are the source of positive halogens and these reagents have been exploited as oxidant for variety of substrates[1-2] in aqueous solutions. Transition metal-catalysed redox reactions involving N-halo succinimide as oxidant in alkaline medium have been scantly repprted[3-5]. The role of osmium (VIII) as a catalyst in redox system have been reviewed in oxidation of a number of organic compounds[6-11]. Oxidation of 3-methyl butanol-1 by N-chlorosuccinimide is very slow in both acidic and alkaline medium and Os (VIII) does not catalyse the reaction in acidic medium. Thus in present paper a systematic kinetic study of the title reaction with a view to know the active species of NCS and Os (VIII) in alkaline medium have been probed and propose a reaction mechanism consistent with observed kinetic data.

Experimental-

Materials:-

N-chlorosuccinimide (E-Merck) solution was always prepared afresh and its strength was checked iodometrically. Solution of 3-methyl butanol-1 (E-Merck) was prepared by weighing the sample and dissolved in appropriate volume of doubly distilled water. Succinimide, sodium hydroxide, sodium perchlorate of AnalR Grade and E-Merck Germany, sample of $Hg(OAc)_2$ were used for preparing their standard solution in doubly distilled water. A 1g-samle of osmium tetroxide (Johnson and Matthey) was first dissolved in 200 ml of 0.01 N NaOH Solution and thereafter the volume was raised to 1000ml. The final strength of Osimum tetroxide and that of Sodium Hydroxide was calculated in 1000ml and these strength were noted.

Procedure:- The reaction was carried out under pseudo first order conditions where concentration of 3-methyl butanol-1 was always about ten folds excess over [NCS] at constant temperature $35^0 + 0.1^0$. The reaction was initiated by mixing the requisite bolums of thermally equilibrated solution of N-chlorsuccinimide, and solution of 3-methyl butanol-1, which also contained the required volumes of Os (VIII), NaOH, $NaclO_4$ and $Hg(OAc)_2$. The progress of the reaction was followed by iodometric estimation of unconsumed NCS in a aliquots (5ml.each) of the reaction mixture withdrawn at regular time intervals. The rate of reaction (-dc/dt) was calculated from the slope of the curve obtained from the plots of unreacted [NCS] vs. time. The rate constants (k_{obs}) was calculated by using formula k_{obs} = [-dc/dt/[NCS^*] where NCS^* is the concentration of NCS at which –dc/dt hve been determined. Most of the kinetic runs were followed to more than 70%k com;lition of the reaction and rate constant, were reproducible within + 3.5%.

Result and Discussion-

The kinetic investigation were carried out at several initial concentration of reactants Pseudo first order rate constant, k_{obs}, where kobs =- dc/dt/[NCS*] remains nearly identical at several initial [NCS]. The rate constant remains almost constant with increase in [3-methyl butanol-1] was found to be zero. The order of the reaction was found to be unity in [Os (VIII)], which was calculated from the plot of log k_{obs} verses log [Os (VIII)] (figure not shown). The linear increase in rate constant with increase in [OH^-] shows first order. Addition of mercuric acetate, succinimide [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. Mercuric acetate 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.

Catalytic species of Osmium tetroxide in alkaline medium-

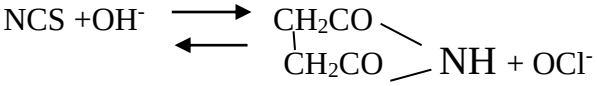
In alkaline solution osmium tetroxide exists in octahedral complexes of the form $[OsO_4 (OH) H_2O]^-$ and Trans $[OsO_4 (H_2O)]^{2-}$ and these species exist in following equilibria.

$$[OsO_4 (OH) H_2O]^- + OH^- \rightleftharpoons [OsO_4 (OH_2)]^{2-}$$

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 these two species $[OsO_4 (OH_2)]^{2-}$ is assumed as real reactive catalytic species of osmium tetroxide in the present investigation.

Oxidising Species of N-Chlorosuccinimide (NCS)-

In alkaline medium NCS has been reported[12] to exist according to following equilibrium



OCl^- has been taken as reactive species of NCS in alkaline medium in oxidation of allyl alcohol. Ramachandran et.al[2] have ruled out the possibility of OCl^- as reactive species of kNCS in alkaline medium in oxidation of amino acids. In view of contrasting opinions about the reactive species of NCS in alkaline medium, we have undertaken the study of this reaction with an aim to decide the real reactive species of NCS. The observed first order is observed in $[OH^-]$ and zero order effect of addition of succinimide helps to suggest that the oxidizing species is NCS itself. When NCS as such is taken as reactive species then rate law derived on its basis confirms to all observed kinetic data. Hence NCS was finally assumed as reactive species of N-chlorosuccinimide in alkaline medium.

Elucidation of reaction mechanism and derivation of rate law-

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

$$[OsO_4(OH)(H_2O)]^- + OH^- \underset{K-1}{\overset{K_1}{\rightleftharpoons}} [OsO_4(OH_2)]^{2-} + H_2O \quad \text{---- (i)}$$
$$(C_1) \qquad\qquad (C_2)$$

$$[OsO_4(OH_2)]^{2-} + NCS \xrightarrow{K_2} \left[OsO_4\text{-------}ClN\langle \begin{matrix} O\text{-}H \\ O\text{-}H \end{matrix} \right]^{2-} \quad \text{----- (ii)}$$
$$(C_2) \qquad\qquad (C_3)$$

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

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

$$[OsO_3(OH)_2]^{2-} + >NCl + H_2O \xrightarrow{fast} [OsO_4(OH_2)]^{2-} + > NH + HCl \quad \text{--(v)}$$

The rate of reaction may be written in terms of loss of [NCS] as eq. (1)

Rate = $r = k [C_3]$ ------(1)

From step (ii) we have

$$K_2 = \frac{[C_3]}{[C_2](NCS)}$$

Hence $[C_3] = K_2 [C_2] [NCS]$ ------(2)

From eq. (1) and (2)

$r = k K_2 [C_2] [NCS]$ -------(3)

On applying steady state appropriation to $[C_2]$

$$[C_2] = \frac{K_1 [C_1] [OH^-]}{K\text{-}1 [H_2O] + K_2 [NCS]} \quad \text{-------(4)}$$

From eq. (3) and (4)

$$r = \frac{k K_2 [NCS] k_1 [C_1] [OH^-]}{K\text{-}1 [H_2O] + K_2 [NCS]} \quad \text{------- (5)}$$

On assuming the inequality $K_1 >> K_2 [NCS]$

We have

$$r = \frac{k K_1 K_2 [NCS] [C_1] [OH^-]}{[H_2O]} \quad \text{------- (6)}$$

$$r = k.\ a.\ [NCS]\ [Os\ (VIII)]\ [OH^-] \quad \text{-------- (7)}$$

Where $a = \frac{K_1 K_2}{[H_2O]}$

The rate law (7) is in complete agreement with the observed kinetic results.

Table-1 Effect of variation of [NCS], [3-methyl butanol-1], [Os(VIII)] and $[OH^-]$ on the rate constant of the reaction at 35^0

$[NCS] \times 10^3$ M	[3-methyl butanol-1] $\times 10^2$M	[Os(VIII)] $\times 10^6$M	$[OH^-] \times 10^2$M	$k_1 \times 10^4 S^{-1}$
0.5	2.00	3.84	1.00	5.90
0.8	2.00	3.84	1.00	5.86
1.0	2.00	3.84	1.00	5.86
1.67	2.00	3.84	1.00	5.86
2.00	2.00	3.84	1.00	5.93
2.50	2.00	3.84	1.00	5.86
1.00	0.50	1.92	1.00	5.28
1.00	1.00	1.92	1.00	5.30
1.00	2.00	1.92	1.00	5.28
1.00	3.00	1.92	1.00	5.34
1.00	4.00	1.92	1.00	5.30

1.00	**2.00**	**0.96**	**1.00**	**1.15**
1.00	**2.00**	**1.92**	**1.00**	**2.40**
1.00	**2.00**	**3.84**	**1.00**	**4.89**
1.00	**2.00**	**4.80**	**1.00**	**5.86**
1.00	**2.00**	**5.76**	**1.00**	**6.67**
1.00	**2.00**	**6.72**	**1.00**	**8.04**
1.00	**2.00**	**3.84**	**0.50**	**2.91**
1.00	**2.00**	**3.84**	**1.00**	**5.86**
1.00	**2.00**	**3.84**	**1.25**	**7.42**
1.00	**2.00**	**3.84**	**1.50**	**10.35**
1.00	**2.00**	**3.84**	**2.00**	**11.64**
1.00	**2.00**	**3.84**	**2.50**	**13.03**

$[Hg(OAc)_2] = 3.50 \times {}^{-3}$ M

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