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Kinetics and Mechanism of Os(VIII)-Catalyzed Oxidation of 2-Methyl propanol-1 by N-Chlorosuccinimide in Aqueous Alkaline Medium

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Kinetics of Os(VIII) catalyzed oxidation of 2-methyl propanol-1 by N-chlorosuccinimide in aqueous alkaline medium have been investigated in the temperature range 30, 35, 40 and 45 ºC. The reaction exhibited first-order in [N-chlorosuccinimide](NCS), [Os(VIII)] and [OH] and zero order in [2-methyl propanol-1]. Negligible effects of added product, succinimide and mercuric acetate on the reaction rate were observed. The variation of ionic strength of the medium showed zero effect on the reaction rate. The mechanism involving the $[OsO_4(OH)_2]^{2-}$ ion as the reactive species of the catalyst and N-chlorosuccinimide, the oxidant in the slow and rate determining step has been suggested.

Key Words: N-Chlorosuccinimide, 2-Methyl propanol-1, Oxidation, Kinetics, Mechanism.

INTRODUCTION

Kinetic studies on N-chlorosuccinimide (NCS)[1-3] oxidation of some organic compounds have been reported. N-Chlorosuccinimide has been used as on oxidizing agent and analytical reagent especially in the acid medium[4]. However, work on the oxidation reactions of N-chlorosuccinimide in alkaline medium is scanty[5]. Osmium tetroxide is known to catalyze various reactions[6]. Oxidation of 2-methyl propanol-1 by N-chlorosuccinimide is very slow in both acid and alkaline media. Osmium tetroxide did not catalyze N-chlorosuccinimide oxidiation of 2-methyl propanol-1 in acid medium, but pronounced catalysis was observed in alkaline medium. In the present communication, an attempt has been made for the systematic kinetic study of Os(VIII) catalyzed N-chlorosuccinimide oxidation of 2-methyl propanol-1 in aqueous alkaline medium with a view to find out the mechanistic aspect and to know the active forms of N-chlorosuccinimide and osmium tetroxide in alkaline medium.

EXPERIMENTAL

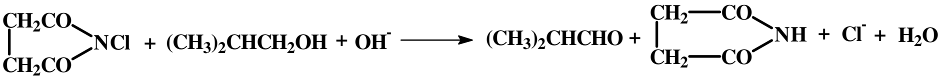
Reagent grade chemicals and doubly distilled water were used throughout. Aqueous solution of N-chlorosuccinimide (SRL) was prepared always afresh and standardized iodometrically[7]. The standard solution of 2-methyl propanol-1 (E. Merck) was prepared by dissolving its desired weighed sample in known volume of double distilled water. A osmium tetroxide stock solution was prepared by dissolving its 1 g sample (Johnson and Matthey) in 0.02 mol dm^{-3} sodium hydroxide. The prepared solution was made up to 1 L. Its concentration alongwith concentration of NaOH was noted. Stock solution of NaOH (E. Merck) was standardized with standard solution of oxalic acid (E. Merck). Standard soutions of sodium perchlorate (E. Merck) and N-chlorosuccinimide (E. Merck) were also prepared by disolving their weighed amount in water. All other reagents used were of analytical reagent grade.

Kinetic study: The reaction was carried out under preudo-first-order conditions where concentration of 2-methyl propanol-1 was always about ten-fold excess over [NCS] at constant temperature of 35 ± 0.1 ºC. The reaction was initiated by mixing the required volumes of thermally equilibrated solution of N-chlorosuccinimide and solution of 2-methyl propanol-1 which also contained the required volumes of solutions of Os(VIII), NaOH and $NaClO_4$ and $Hg(OAc)_2$. The progress of the reaction was followed by iodometric determination of the unreacted oxidant *i.e.*, N-chlorosuccinimide for its active chlorine in aliquots (5 mL each) of the reaction mixture withdrawn at regular time intervals. The pseudo-first order rate constants were obtained from the plots of log [NCS] *versus* time. Most of the kinetic runs were followed to more than 70 % completion of the reaction and rate constant were reproducible within ± 3.5 %.

RESULTS AND DISCUSSION

Different reaction mixtures containing different sets of reactant concentrations at constant alkalinity and ionic strength were kept to react for 24 h at 35 ± 0.1 ºC and then analyzed. The unconsumed N-chlorosuccinimide was estimated iodometrically for active chlorine. Succinimide was the main product as detected by the method reported, and another product 2-methyl propanaldehyde was evidenced by the test.

The results were in agreement with 1:1 stoichiometry.



$$\begin{matrix}CH_2CO\\ |\\ CH_2CO\end{matrix}\!\!>NCl + (CH_3)_2CHCH_2OH + OH^- \longrightarrow (CH_3)_2CHCHO + \begin{matrix}CH_2-CO\\ |\\ CH_2-CO\end{matrix}\!\!>NH + Cl^- + H_2O$$

Reaction order: Order of the reaction with respect to each reactant was obtained from log-log plot of rate *versus* concentration of reactant. The order in [NCS] was unity in the concentration range 0.50×10^{-3} to 2.50×10^{-3} mol dm^{-3} at fixed [Os(VIII)], [2-methyl propanol-1], [NaOH] and ionic strength. The rate constant was observed to be independent of [2-methyl propanol-1] and the order in [2-methyl propanal] was thus zero. The reaction rate increased lineraly with increase in concentration of each of osmium tetroxide and sodium hydroxide. Thus order in each of Os(VIII) and $[OH^-]$ was found to be one (Table-1). Addition of ten fold excess of the product, N-chlorosuccinimide and $Hg(OAc)_2$ at constant ionic strength did not increase the rate significantly. Change in ionic strength of the medium (μ) was also found to have negligible effect on the reaction rate (Table-2). The reaction rate measured 30, 35, 40 and 45 ºC led us to compute activation parameters, E_a (activation energy),

TABLE-1
EFFECT OF VARIATION OF [NCS], [2-MP-ol], [Os(VIII)] AND [OH^-] ON THE RATE CONSTANT OF Os(VIII) CATALYZED OXIDATION OF 2-METHYL PROPANOL-1 IN AQUEOUS ALKALINE MEDIUM AT 35 ºC (UNLESS OTHERWISE STATED)

[NCS] × 10^3 M	[2-MP-ol] × 10^2 M	[Os(III)] × 10^6 M	[OH^- × 10^2 M	$k_1 \times 10^4 \times S_{-1}$
0.50	2.00	3.84	1.00	2.90
0.80	2.00	3.84	1.00	2.94
1.00	2.00	3.84	1.00	2.84
1.67	2.00	3.84	1.00	2.92
2.00	2.00	3.84	1.00	2.88
2.50	2.00	3.84	1.00	2.86
1.00	0.50	1.92	1.00	1.46
1.00	1.0	1.92	1.00	1.42
1.00	1.50	1.92	1.00	1.48
1.00	3.00	1.92	1.00	1.40
1.00	4.00	1.92	1.00	1.46
1.00	2.00	0.96	1.00	0.70
1.00	2.00	1.92	1.00	1.44
1.00	2.00	3.84	1.00	2.84
1.00	2.00	4.80	1.00	3.62
1.00	2.00	5.76	1.00	4.30
1.00	2.00	6.72	1.00	4.98
1.00	2.00	3.84	0.50	1.39
1.00	2.00	3.84	1.00	2.84
1.00	2.00	3.84	1.25	3.60
1.00	2.00	3.84	1.50	4.28
1.00	2.00	3.84	2.00	5.64
1.00	2.00	3.84	2.50	7.08

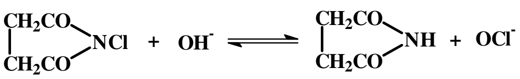
$[Hg(OAc)_2] = 3.50 \times 10^{-3}$ M.

ΔS^* (entropy change) and ΔG^* free energy change). The values of E_a, ΔS^* and ΔG^* were found as 14.76 kcal/mol, 5.03 e.u. and 12.50 kcal/mol, respectively.

In alkaline medium, osmium tetraoxide has been reported to exist as octahedral complexes of the form $[OsO_4(OH)H_2O)]^-$ and *trans*-$[OsO_4(OH)_2]^{2-}$ in an equilibrium (A) as given below:

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

Since order of the reaction with respect to [OH^-] is one, hence $[OsO_4(OH)_2]^{2-}$ is taken as active catalytic species. In alkaline medium N-chlorosuccinimide exists in the equilibrium (B) as given below:



(B)

It seems that either N-chlorosuccinimide as such or OCl^- acts as oxidizing species. On assuming OCl^- as the oxidizing species, the rate law derived requires negative effect of succinimide contrary to observed negligible effect of succinimide on the reaction rate. Therefore OCl^- as oxidizing species is ruled out. Now the only choice left is to assume N-chlorosuccinimide as such as oxidizing species. The

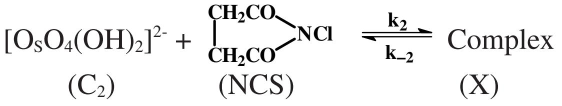
TABLE-2
EFFECT OF VARIATION OF TEMPERATURE, IONIC STRENGTH OF MEDIUM (μ) AND ADDITION OF SUCCINIMIDE (NHS) ON THE RATE CONSTANT OF Os(VIII) CATALYZED OXIDATION OF 2-METHYL PROPANOL-1 IN AQUEOUS ALKALINE MEDIUM

Temp. (°C)	[Hg(OAc) × 10^3	$\mu \times 10^2$ M	[NHS] × 10^2 M	$k_1 \times 10^4\ s^{-1}$
30	3.50	2.05	–	1.96
35	3.50	2.05	–	2.84
40	3.50	2.05	–	4.00
45	3.50	2.05	–	5.86
35	1.50	2.80	–	2.86
35	1.75	2.80	–	2.82
35	2.00	2.80	–	2.80
35	3.00	2.80	–	2.88
35	4.50	2.80	–	2.90
35	6.00	2.80	–	2.86
35	3.50	3.05	–	2.90
35	3.50	4.05	–	2.82
35	3.50	6.05	–	2.86
35	3.50	9.05	–	2.84
35	3.50	12.05	–	2.88
35	3.50	2.05	0.50	2.86
35	3.50	2.05	1.00	2.88
35	3.50	2.05	2.00	2.92
35	3.50	2.05	3.00	2.80
35	3.50	2.05	4.00	2.86
35	3.50	2.05	5.00	2.84

[NCS] = 1.00 × 10^{-3} M, [2–Methyl propanol-1] = 2.00 × 10^{-2} M, [Os(VIII)] = 3.84 × 10^{-6} M, $[\text{OH}]^-$ = 1.00 × 10^{-2} M.

rate law also derived on basis of N-chlorosuccinimide as real oxidizing species in alkaline medium conforms to all kinetic data. Therefore, N-chlorosuccinimide is taken as real oxidizing species in the present investigation zero effect of variation of $[\text{Hg(OAc)}_2]$ on rate negates the role of Hg(II) as catalyst. Experiments without using N-chlorosuccinimide and using mercuric acetate in the reaction mixture under similar conditions of all other reagent showed non-feasibility of the reaction indicating non-involvement of Hg(II) ions as oxidant. Therefore, in the present investigation mercuric acetate has limited role as Cl^- ions scavenger, to allow pure N-chlorosuccinimide oxidation and to eliminate Cl^- ions as $[\text{HgCl}_4]^{2-}$ otherwise parallel chlorine oxidation would have occurred due to formation of Cl_2 as result of interaction between N-chlorosuccinimide and Cl^- ions. Considering $[\text{OsO}_4(\text{OH})_2]^{2-}$ as reactive catalytic species of OsO_4 and N-chlorosuccinimide as such oxidizing species following reaction scheme is suggested.

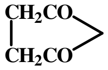
$$\underset{(C_1)}{[\text{OsO}_4(\text{OH})(\text{H}_2\text{O})]^-} + \text{OH}^- \overset{K_1}{\rightleftharpoons} \underset{(C_2)}{[\text{OsO}_4(\text{OH})_2]^{2-}} + \text{H}_2\text{O} \qquad \text{(i)}$$



$$\underset{(C_2)}{[\text{OsO}_4(\text{OH})_2]^{2-}} + \underset{(NCS)}{\begin{matrix}\text{CH}_2\text{CO} \\ | \\ \text{CH}_2\text{CO}\end{matrix}\!\!>\!\text{NCl}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(X)}{\text{Complex}} \qquad \text{(ii)}$$

Forward step is slow step

$$X + S \xrightarrow[\text{Fast}]{} \text{Product} \qquad \text{(iii)}$$

where R is  group in NCS and S is 2-methyl propanol-1 acting as substrate. Considering the above reaction scheme the rate of the reaction can be written as rate of loss of [NCS] in the form of eqn. 1.

$$\frac{-d[NCS]}{dt} = k_2[C_2][NCS] \qquad (1)$$

On applying law of chemical equilibrium to equilibrium (i) we have

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

Hence $[C_2] = K_1[C_1][OH]$ (2)

By considering eqns. (1) and (2) we have

$$\frac{-d[NCS]}{dt} = k_2K_1[C_1][OH^-][NCS]$$

Or $$\frac{-d[NCS]}{dt} = k_2K_1[Os(VIII)][NCS][OH^-]$$

The ratelaw (3) fully explains the observed kinetic results. Negligible effect of ionic strength of the medium is in agreement with interaction of negatively charged catalytic species (C_2) with diople molecule of N-chlorosuccinimide in slowest step (ii).

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