Oxidation Kinetics of Some Cyclonols by N-bromosuccinimide in Aqueous Acetic Acid and Micellar medium

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Abstract- **The kinetic oxidation of cycloheptanol and cyclooctanol were described with an emphasis of correlation of structure and reactivity. The reaction were first-order with respect to loss of [NBS] N-bromosuccinimide and reaction are [H⁺] that follow $k_{obs} = a + b\,[H^+]$. However, Michaelis-Menten type kinetics were observed for the cyclonols. The micellar CTAB exhibited the existence of ternary complex behaviours between oxidant species and substrate at transition state. Based on kinetic data, thermodynamic parameters and reacting species HOBr of oxidant with 1:1 stoichiometry a mechanism was pastulated with the expulsion of α-H hydride anion.**

Key words: **N-bromosuccinimide, cycloheptanol, cyclooctanol, cetyltrimethlammonium- bromide (CTAB), oxidation.**

1. INTRODUCTION

In the past few decade N-bromosuccinimide an halooxidant, N-bromosuccinimide's hidden potentiality was realised for the first time in the oxidation of aliphatic/ aromatic secondary alcohols.[1] It is n oxidant of two electron system, which provides positive halogen ions. The hydrolytic and protonated product of NBS giverise HOBr and H_2O^+Br the prime reacting species which are very useful in transformation of amino acids,[2] benzhydrols,[3] in synthetic organic chemistry. In the present investigation, the study has been performed in micellar cationic CTAB) medium, which is enzyme catalyst[4-7] mainly functions below CMC in several reactions aggregates of the surfactant are responsible for variation of the rate of redox reaction.[8] Several reports on oxidation of cyclonones by different oxidising agents such as NCP[9], CAT,[10] NBP,[11] NCS,[12] etc. have been documented in acetic acid and micellar medium. The present probe was undertaken, primarily to discuss the kinetics and mechanistic aspect along with structure-reactivity corelation in the oxidation of cycloheptanol, and cyclooctanol in acetic acid and micellar medium as solvent, in addition to this, the plan of the present work to be opted to determine kinetic parameters and to evaluate the rate laws.

2. EXPERIMENTAL

Materials : The micellar cationic (CTAB) Aldrich was used as such received (purity 99% sp conductivity 1- 2.8 ms cm⁻¹) without further purification a solution was prepared in demenerized water. The cycloheptanol and cyclooctanol both belongs to B.D.H. were used and their solution was, made in acetic acid. The N-bromosuccinimide[13] (Across) sample was used and dissolved in 80 to 90% acetic acid (B.D.H.). Its purity was checked iodometrically.

Kinetic measurement

The reaction kinetics were carried out under pseudo first-order conditions by keeping excess of the cyclonol (10- fold or higher) over [NBS]. One flask containing in gradient CTAB, cyclonol and acetic acid, while another one NBS. Both the flasks were suspended in thermostated water bath at 35 ± 0.1^0C. When the solutions attend the desire temperature, the reactions were followed upto 80% conversion by monitoring the decrease in [NBS] iodometrically at different intervals of time. The pseudo first-order rate constant k_{obs} was computed from the linear plot of log [NBS] vs. time employing integration method. The values were reproducible in duplicate rate measurement to within $\pm 4\%$.

The oxidation of cyclonols by NBS leads to the formation of corresponding cyclonols characterized by 2,4-DNP derivatives and TLC method. The stoichiometric ratio (Δ[NBS] / Δ[cyclonol]) was found 1:1. The overall reaction may be written as :
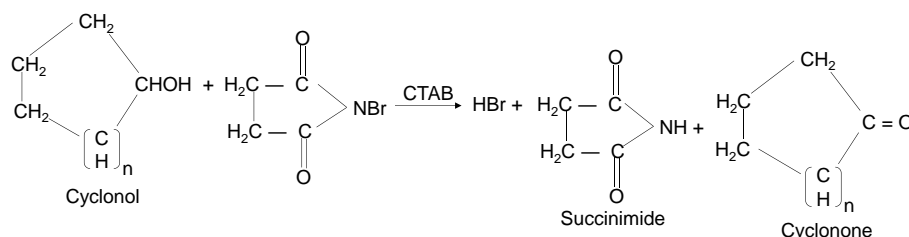
where, n = 3 and 4 for cycloheptanol and cyclooctanol respectively.

3. RESULTS AND DISCUSSION

The reactions were found to be of first-order with respect to [NBS]. In individual kinetics run, plots of log [NBS] vs. time were linear ($r^2 > 0.997$). Further pseudo first-order rate constant do not depend on the enolic concentration of [NBS].

The kinetic data at the cost of prevailing conditions of the reactions were collected. The order with respect to cyclonols was found less than one (Table 1). The downward curvature of the plot suggests, the existence of complex formed between substrate, CTAB and reacting species of oxidant, which is judged by graphic plot of $1/k_{obs}$ vs. $1/$ [cyclonol] was linear with an positive intercept on the rate ordinate (Fig. 1). Thus, above version of study also verify Michaelis-Menten model of kinetics with respect to cyclonol at transition state.

Table 1: Dependence of Rate on Cyclonols

$10^3 \times$ [NBS] (mol dm^{-3}) = 3.33 (1, 2) ; $10^2 \times$ [H$^+$] (mol dm^{-3}) = 1.0 (1, 2) ;
$10^3 \times$ [CTAB] (mol dm^{-3}) = 1.25 (2), 1.66 (1) ; CH$_3$COOH-H$_2$O %, (v/v) = 30(1, 2) ; Temperature K = 308 (1, 2)

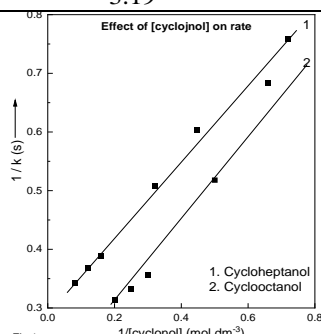| $10^2 \times$[cyclonol] (mol dm^{-3})	10^4 k (s^{-1})	
	Cycloheptanol (1)	Cyclooctanol (2)
1.00	-	1.64
1.50	1.46	2.20
2.00	1.93	2.79
3.33	2.80	4.17
4.00	3.01	4.56
5.00	3.19	5.20

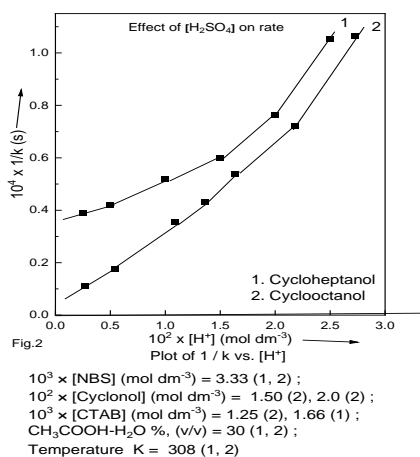Fig.1 Plot of k_{obs}^{-1} vs. [cyclonol]$^{-1}$

$10^3 \times$ [NBS] (mol dm^{-3}) = 3.33 (1, 2) ;
$10^2 \times$ [H$^+$] (mol dm^{-3}) = 1.0 (1, 2) ;
$10^3 \times$ [CTAB] (mol dm^{-3}) = 1.25 (2), 1.66 (1) ;
CH$_3$COOH-H$_2$O %, (v/v) = 30(1, 2) ;
Temperature K = 308 (1, 2)

The reaction is not sensitised by [H$^+$] (Table 2). The hydrogen ion dependence has the following form, $k_{obs} = a + b$ [H$^+$], and the values of a and b were derived for cyclonols. The graphic plots $1/k$ vs. [H$^+$], (Fig. 2) shows limiting value of k_{obs} at low concentration.

Table 2: Dependence of Rate on Acidity

$10^3 \times$ [NBS] (mol dm^{-3}) = 3.33 (1, 2) ; $10^2 \times$ [Cyclonol] (mol dm^{-3}) = 1.50 (2), 2.0 (2) ;
$10^3 \times$ [CTAB] (mol dm^{-3}) = 1.25 (2), 1.66 (1) ; CH$_3$COOH-H$_2$O %, (v/v) = 30(1, 2) ; Temperature K = 308 (1, 2)

$10^2 \times$ [H$^+$] (mol dm^{-3})	10^4 k (s^{-1})	
	Cycloheptanol (1)	Cyclooctanol (2)
0.25	2.56	2.86
0.50	2.37	2.65
1.00	1.93	2.20
1.25	-	2.05
1.50	1.67	1.87
2.00	1.31	1.63
2.50	0.95	1.31

Fig.2
Plot of 1 / k vs. [H⁺]
$10^3 \times$ [NBS] (mol dm^{-3}) = 3.33 (1, 2) ;
$10^2 \times$ [Cyclonol] (mol dm^{-3}) = 1.50 (2), 2.0 (2) ;
$10^3 \times$ [CTAB] (mol dm^{-3}) = 1.25 (2), 1.66 (1) ;
CH$_3$COOH-H$_2$O %, (v/v) = 30 (1, 2) ;
Temperature K = 308 (1, 2)

The oxidation of cyclonols by NBS was studied in two solvents in the composition range 10% to 50% (v/v). The solubility of the reactants and the reaction of NBS with cyclonols was limited with the choice of the solvent. The kinetics were identical in all the solvents and no reaction was observed with the choosen solvent. The kinetic data of solvent effect shows that k_{obs} gradually decreases by increasing composition of solvent polarity.

Amis plots of log k vs. 1/D were found linear with negative slope supporting rate limiting step with charge dispersal. The rates of oxidation of cyclonols in two solvents showed an excellent correlation in Swain equation[14] with the cation solvating power playing the major role.

The cationic micellar cetyltriammoniumbromide (CTAB) behaves / simultaneously as a solvent as well as a catalyst, when added to the reaction mixture in five-fold concentrations to the reaction initially increases the rate of oxidation to a optimum concentration of CTAB showing first-order kinetics and catalysed the reaction, but at its higher concentration, order falls from 1 to 0 when used under CMC condition.

The ionic strength of the medium (μ) and salt effect have shown negligible effect on the rate of reaction and the study supports dipole-dipole interactions suggesting that one of the reactants involved in the rate-determining step.

The reactions between cyclonols and NBS in an aqueous acetic acid and micellar medium in an atmosphere of nitrogen unable to induce polymerisation of acrylonitrile confirming the absence of free radicals in the reaction path. This is further proved when reaction was caried out with 2,4-di-t-butyl-1,4-methyl phenol which was recovered unchanged.

Succinimide, a reduction product of NBS when added to the reaction between cyclonols and NBS 5 X times in concentrations, shows the gradual retardation in rate. The plot of 1/ k_{obs} vs. [succinimide] yielded straight line with positive slop clearly shows that it can not be a reacting species in the mechanism.

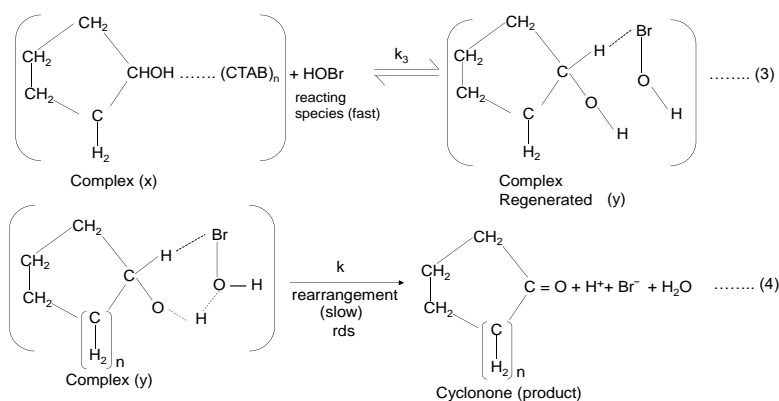**Reaction Mechanism**
Based on kinetic data, stoichiometry and reacting species of oxidant leads to the postulation of over all mechanism.
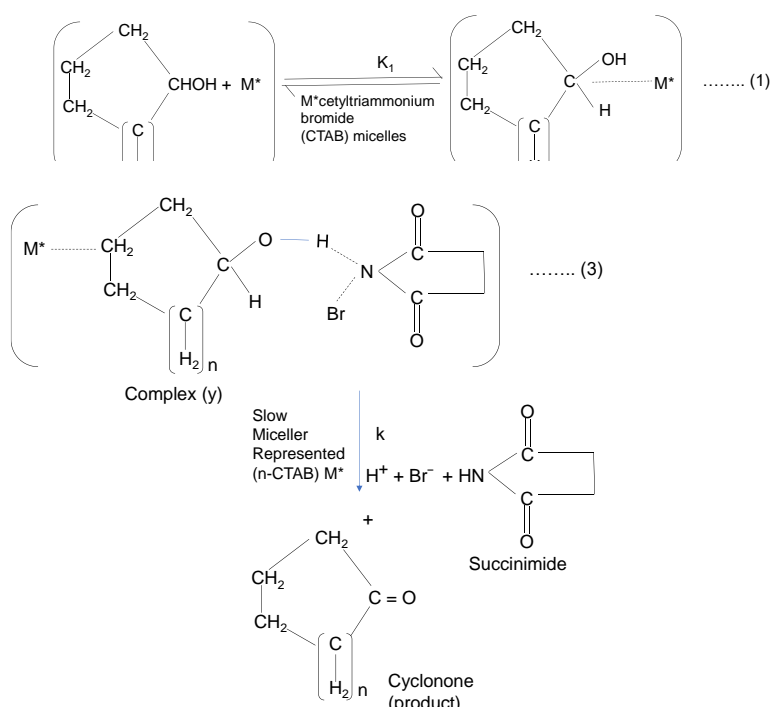**Scheme-1**
Acid independent path
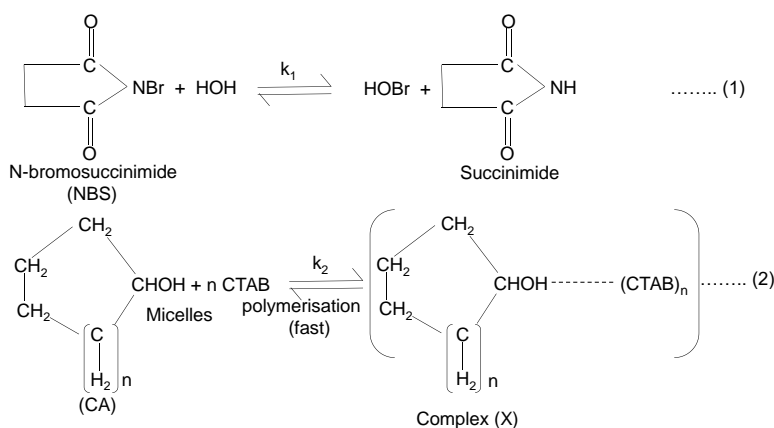
Scheme-2

Acid dependent path : An alternative mechanism based on acid dependent path may be illustrated as :

Rate law

The rate law may be obtained applying steady-state approximation.

$$-\frac{d}{dt}[NBS] = k[(y)] \ldots\ldots (1)$$

Since, $[Y] = [NBS] + [Y]$ …….. (2)

On substituting the values of [NBS] and [Y] in equation (1) and simplification results equation (3)

$$k_{obs} = \frac{k\,K_1 K_2 [M^*][CA]}{1 + K_1[CA] + K_1 K_2[CA]} \ldots. (3)$$

Equation (3) can be transferred into rearranged equation (4) at fix [S].

$$\frac{M^*}{Rate\ k} = \frac{1}{k\,K_1 K_2 [CA]} + \frac{1}{k\,K_2} \ldots. (4)$$

Similar rate law have also been suggested by different authors during the probe of reactions.

The equation (4) explains all the kinetics aspects, Michaelis-Menten type of kinetics.

Structure and Reactivity

The order of reactivity in the present investigation is cyclooctanol > cycloheptanol. The alternation of the reactivity is due to steric chemical effect experienced by the molecules during transformation of tetrahedral sp^3 hybridized carbon of alcohol to the sp^2 hybridized orbitals of ketonic carbon, further the presence of non-bonded interaction in the 7 and 8, membered ring which is not found in the ground state. Our finding suggest that k_{obs} increases with the increase in ring size of the cyclonols under, investigation. The energy of activation (Ea) is found higher for 7 and lowest for 8, this account for the slow approach of the rate of oxidation of cycloheptanol (Table 3).

Table 3: Thermodynamic activation parameters for the reaction between cyclonols and NBS

Cyclonol	Ea (kJ/ mol)	$\Delta H^{\#}$ (kJ/ mol)	$\Delta G^{\#}$ (kJ/ mol)	$-\Delta S^{\#}$ (JK^{-1} mol^{-1})
Cycloheptanol	36.52	33.04	87.87	176.60
Cyclooctanol	33.14	29.35	86.82	185.08

The $\Delta S^{\#}$ value are in the reverse order of reactivity were as $\Delta H^{\#}$ in the order of reactivity. This specifically indicating the reaction is enthalpy controlled. The proceed mechanism is however, supported by the observed negative ($\Delta S^{\#}$) value as the charge separation takes place in the transition state. The molecules becomes highly solvated, reflected in the loss of ΔH, which restricts the translational and rotational freedom of the molecule. In light of above mentioned point, removal of α-H hydride anion occurs, hence above order of reactivity. Similar reactivity of order was also reported earlier by a group of eminent scientists[15-17]. Consequently, the negative polar reaction constant occur with the net flow of the electrons towards the oxidant. The constancy in Gibbs-free energy ($\Delta G^{\#}$) suggests that identical reaction path in both the cyclonols studied was found.

Conclusion

The reaction is proposed to proceed via expulsion of α-H hydride anion from cyclonols to the oxidant. Reactivity and structure was discussed the oxidation reaction is accompanied by decrease in entropy of activation ($\Delta S^{\#}$). The mechanism is supported by cations solvating power of the solvent. The micellar CTAB acts as both solvent and catalyst, forms ternary complex between oxidant and substrate. The reaction is acid catalysed and follows $k_{obs} = a + b\ [H^+]$. The order with respect to oxidant were as fractional-order exhibited by cyclonols verifying Michaelis-Menten types of kinetic model with stoichiometry 1:1.

Conflict of Interest

The author declare conflict of no interest whatsoever.

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