Kinetic Study of Oxidative Degradation of Butan- 2- OL BY N-Chloroisonicotinamide in Aqueous Acetic Acid Medium.

Sanjay K Singh[1], Deepti Pandey, Shalinee Singh[1*], Arti Tiwari

1.Department of Chemistry Govt.T.R.S. College Rewa
* Corresponding author: shalinee.singh85@gmail.com

ABSTRACT:
The oxidation of Butan-2-ol by a mild and selective oxidizing agent N-chloroisonicotinamide (NCIN) leads to the formation of corresponding ketones. The reaction found first order in NCIN. Oxidation resulted in the formation of ketonic compounds. The reaction follows Arrhenius relationship with respect to Butan-2-ol. A retarding effect of acetic acid is observed. The aliphatic alcohols are widely used as diluents in the Perfumery industry. Various thermodynamic parameters have been computed. No evidence of Polymerization of acrylonitrile showed no effect of free radical on the rate of reaction. Suitable reaction mechanism has been suggested for the oxidation of the alcohols in the absence and presence of transition metal ions. Stoichiometric study revealed 1:1 mole ratio. On the basis of thermodynamic parameters and stoichiometry a feasible mechanism has been proposed and rate law has been derived.
Keywords: ASA, Kinetics, Butan-2-ol, Mechanism, NCIN, Oxidation.

I. INTRODUCTION

Organic reaction mechanism not only deals with the relationship between the molecular structure and chemical properties but tells us about the rate constants. Alcohols are emitted to atmosphere by anthropogenic (fuels additives, industrial solvents) and biogenic (vegetation) sources.[1-4]

N-chloroisonicotinamide (NCIN) is a new member of the N-halo family. NCIN, the derivative of Isonicotinamide is a mild, stable, efficient, and inexpensive oxidant for organic substates [5]. The elemental analysis and physical propertiesof NCIN affirm the presence of the N-X bond. For this reason, it is possible that the compound serving as an effective source of halonium ion. The study of benzyl ethers, benzaldehyde di-N-butyl acetal, and its derivatives [6-10] reveals the mildness and selectiveness of NCIN [11-12].

The oxidation kinetics of secondary alcohol has been extensively studied. They have substantially helped to our understanding of mechanistic pathway for reaction. Oxidation of alcohols to the related aldehydes and ketones is one of the most transformations in organic synthesis and numerous methods are available in the literature [13-14].

Aliphatic secondary alcohol (ASA) has an essential role in cosmetics, fragrance and pharmaceutical industries. The kinetics of ASA with different oxidants has been reported [15-22]. This paper deals with the kinetics of oxidation of the aliphatic secondary alcohols 2-Butanol in the temperature range 303K and the effect of ionic strength on the oxidation rate of the alcohols using K_2SO_4.

Aliphatic secondary alcohols (ASA) are studied with various oxidants and follows first order kinetics [23-28]. Butan-2-ol is a secondary alcohol also studied individual with various oxidants [29-34].

The general review of the literature explored that no works have been reported about the oxidation of Butan-2-ol with NCIN; so, this prompted for the present investigation and evaluate kinetic parameters as well as correlation analysis. All the data collected has been collated and suitable reaction mechanisms have been suggested for the oxidation of the aliphatic secondary alcohols in the presence and absence of metal ions.

II.   MATERIALS AND METHODS

2.1 Chemicals
Chemicals employed in this study were of A.R. grade. Double distilled water used throughout the study. The solutionswere prepared without any further purification of chemicals. The solution of NCIN prepared by reported method.

2.2 Kinetic experiment
The experiments were performed under pseudo-first-order conditions by keeping an excess of the substrate over NCIN. The experiments were carried out in a black-coated stopper glass vessel to avoid any photochemical effect. A thermo-stated water bath maintained the desired temperature within ± 0.1K (308K).Requisite volumes of all reagents, except NCIN, were introduced into a reaction vessel and equilibrated at 308K. A measured volume of NCIN, equilibrated separately at the same temperature, was rapidly poured into the reaction vessel. The progress of the reactions was monitored by examining aliquots of the reaction mixture for unconsumed NCIN iodometrically using starch as the indicator.

2.3   Product analysis
The end product from the oxidation of Butan-2-olwas ketone and its presence confirm by existing conventional methods. The analysis of end product was carried out under kinetic conditions i.e., with the excess of Butan-2-ol was taken over NCIN. After completion of reaction the solution is treated with an excess (200ml) of saturated solution of 2,4- dinitrophenylhydrazine (DNPH) in 2 mol/dm^3 HCl and kept in refrigerator for 24 hours. The precipitate of 2,4- dinitrophenylhydrazone (DNP) filtered, dried and weighed respectively. recrystallize the crystal of DNP with ethanol and weighed again. The DNP was found identical (m.p. and mixed m.p.) with DNP of Butan-2-ol.

III.   RESULT AND DISCUSSION
The oxidation of Butan-2-ol was carried out by NCIN in PTA at 308K under pseudo first order condition. The rate of Butan-2-ol and other experimental data were obtained. Oxidation of Butan-2-ol by NCIN in presence of PTA under the condition [NCIN] << [Butan-2-ol] had the following kinetic feature.

3.1   Stoichiometric studies
The stoichiometric studies of oxidation of Butan-2-ol by NCIN were carried out with excess of oxidant (NCIN) and maintaining other parameters constant (HOAc-H$_2$O = 30 % (v/v), Temperature = 308K).The stoichiometric results indicated 1 mole of Butan-2-ol consumes 1 mole NCIN as represented by the following empirical equation:

$$CH_3\text{-}\underset{\underset{R}{|}}{C}HOH + C_5H_5NCONHCl \rightarrow CH_3\text{-}\underset{\underset{R}{|}}{C}=O + HCl + C_5H_5NCONH_2$$
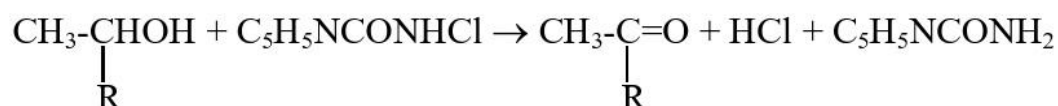
R = CH$_2$-CH$_3$ for butan-2-ol
There is first order rate constant is unchanged with an increase in the NCIN.

3.1.1   Order with respect to [oxidant] [substrate]
When the Butan-2-ol are inlarge excess, the plots of log (a-x) vs time **(Figure 1)** are found to be linear, indicating first-order dependence on NCIN. The pseudo first-order rate constants in NCIN calculated at different initial concentrations of the reactants are found to be independent of the substrate concentration. The plot of k$_1$*vs* [Butan-2-ol] is initially linear passing through origin and tends to obtain limiting value, bending towards horizontal axis **(Figure 2).** Hence the reaction follows fractional order behaviour with respect to the Butan-2-olconcentration.
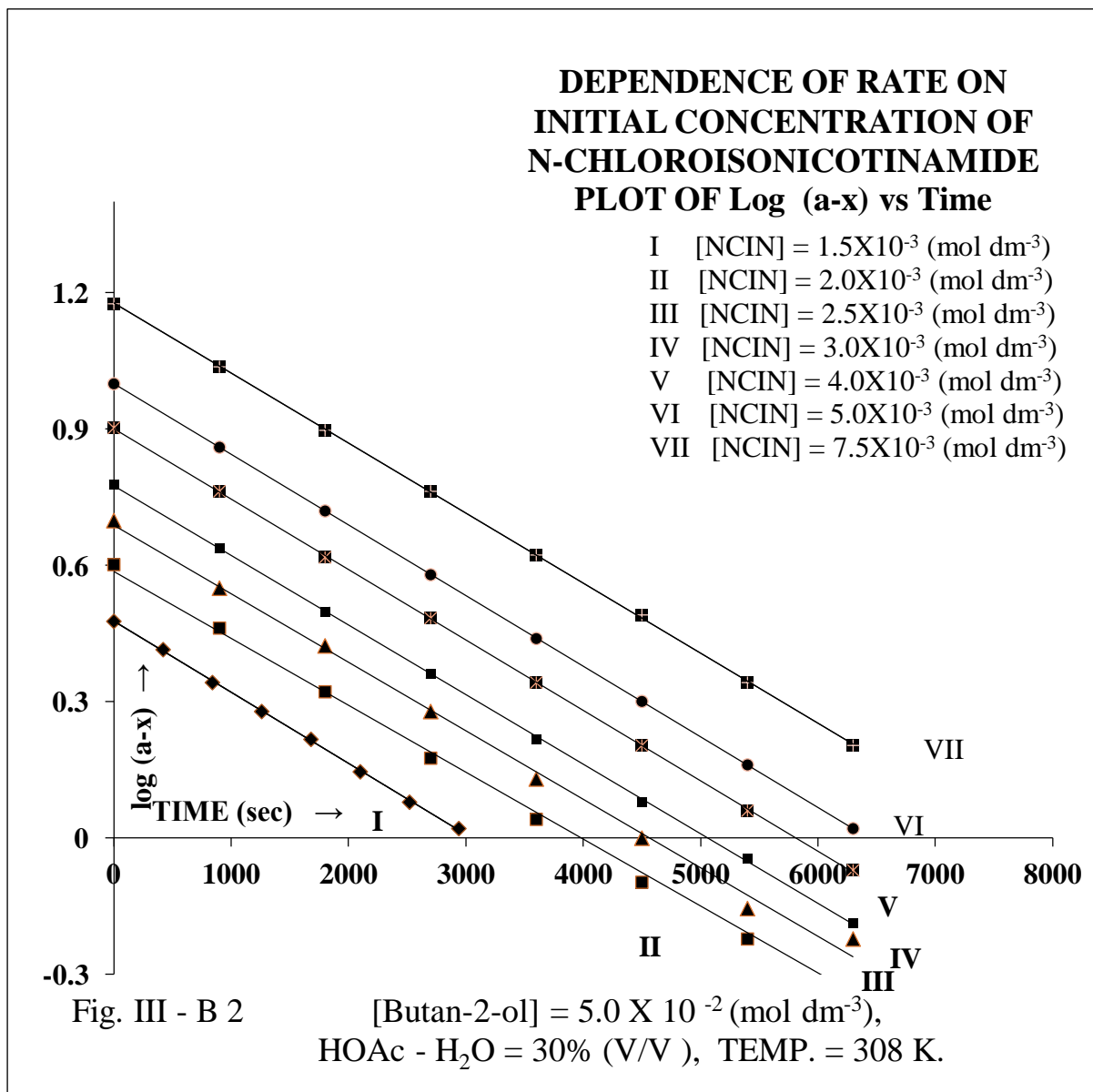
DEPENDENCE OF RATE ON INITIAL CONCENTRATION OF N-CHLOROISONICOTINAMIDE PLOT OF Log (a-x) vs Time

I $[NCIN] = 1.5 \times 10^{-3}$ (mol dm^{-3})
II $[NCIN] = 2.0 \times 10^{-3}$ (mol dm^{-3})
III $[NCIN] = 2.5 \times 10^{-3}$ (mol dm^{-3})
IV $[NCIN] = 3.0 \times 10^{-3}$ (mol dm^{-3})
V $[NCIN] = 4.0 \times 10^{-3}$ (mol dm^{-3})
VI $[NCIN] = 5.0 \times 10^{-3}$ (mol dm^{-3})
VII $[NCIN] = 7.5 \times 10^{-3}$ (mol dm^{-3})

Fig. III - B 2 $[\text{Butan-2-ol}] = 5.0 \times 10^{-2}$ (mol dm^{-3}), HOAc - H_2O = 30% (V/V), TEMP. = 308 K.

Figure 1: The plot of log (a-x) versus time. Conditions are given in Table 1.

DEPENDENCE OF RATE ON THE CONCENTRATION OF SUBSTRATE
PLOT OF k_1 VS SUBSTRATE
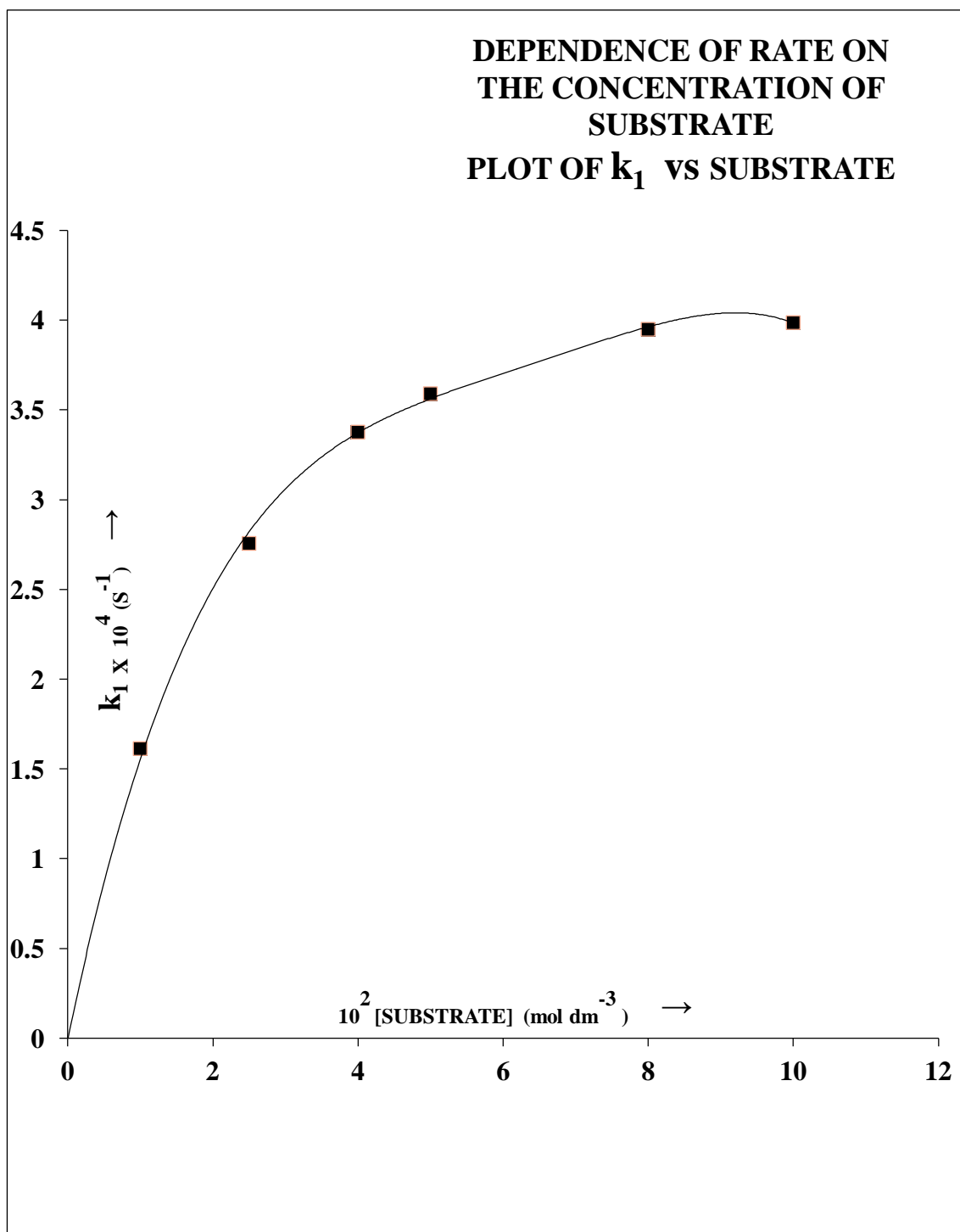
Figure 2: Dependence of k_1 on [Butan-2-ol]. Conditions are given in Table

Table 1: Effect of variation of reactants on pseudo-order rate constant k_1 at 308K

10^2 [Substrate] (mol dm^{-3})	10^3 [NCIN] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	% HOAc - H$_2$O	$k_1 \times 10^3$ (s^{-1})
1.00	2.50	-	30	0.1614
2.50	2.50	-	30	0.2757
4.00	2.50	-	30	0.3377
5.00	2.50	-	30	0.3591
8.00	2.50	-	30	0.3950

10.00	2.50	-	30	0.3987
5.00	1.50	-	30	0.3589
5.00	2.00	-	30	0.3538
5.00	2.50	-	30	0.3592
5.00	4.00	-	30	0.3587
5.00	5.00	-	30	0.3579
5.00	2.50	0.0	30	0.3591
5.00	2.50	0.1	30	0.4342
5.00	2.50	0.15	30	0.4731
5.00	2.50	0.2	30	0.5065
5.00	2.50	0.25	30	0.5254
5.00	2.50	0.3	30	0.5484
5.00	2.50	0.4	30	0.5912
5.00	2.50	0.5	30	0.6116
5.00	2.50	-	10	0.2921
5.00	2.50	-	20	0.3254
5.00	2.50	-	30	0.3591
5.00	2.50	-	40	0.3814
5.00	2.50	-	50	0.4271

3.1.2 Effect of variation of [H^+]:

The catalysed kinetics was observed by the addition of perchloric acid. On varying perchloric acid concentration there is an increase in reaction rate (**Table 1**). The plot of log k_1 versus [H^+] (**Figure 3**) gave a straight line with positive intercept, suggesting that acid pPropane-2-olys a complex role in the reaction system.
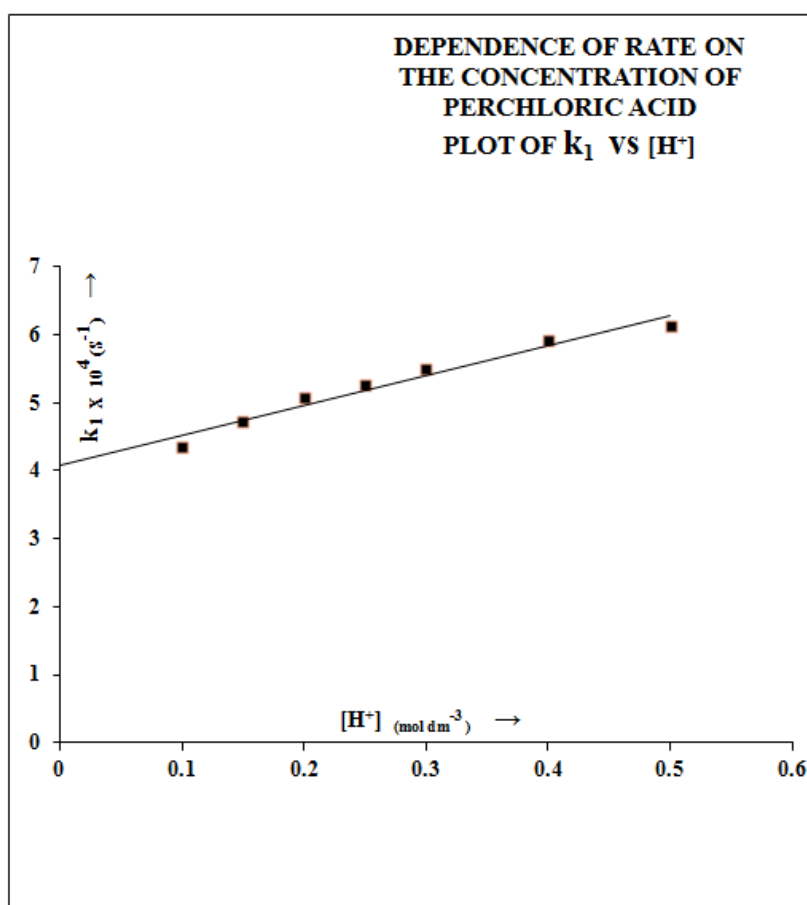

Figure 3: Dependence of k_1 on [H^+]. Conditions are given in Table 1.

3.1.3 Effect of solvent on reaction velocity:

The rate was studied at different concentrations of the solvent. It is observed that the rate decreases with increasing concentration of acetic acid.

3.1.4 Effect ofionic strength and isonicotinamide:

The reaction rate was not influenced by the addition of chemically neutral salt. Hence the ionic behaviouron slow step in the reaction mechanism is ruled out. Addition of isonicotinamide (one of the reaction products), at constant NCIN and Butan-2-ol concentration, decreases the rate of reaction.The retardation of reaction rate on the addition of isonicotinamide suggests a pre-equilibrium step that involves a process in which isonicotinamide is one of the products. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of isonicotinamide concentration.

3.1.5 Effect of Product and Free Radical Inhibitor:

The reaction under study failed to induce polymerization of added acrylonitrile discarding the presence of free radicals and free radical path.

3.1.6 Effect of temperature:

The effect of temperature on the reactions of Butan-2-ol with NCIN in was also studied. The value of energy of activation, $\Delta S, \Delta H$ & ΔG were computed. These values are summarized in **Table 2** along with the other parameters.
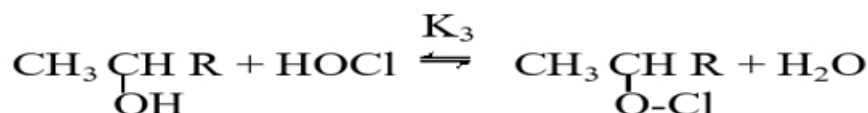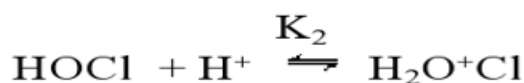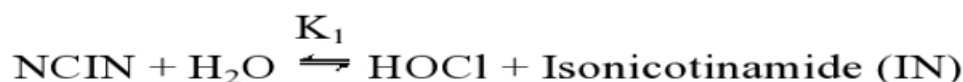
Table 2: Thermodynamic parameters of BUTAN-2-OL-NCIN system

Substrate	E_a (kJ mol^{-1})	A (s^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	$-\Delta S^*$ (JK^{-1} mol^{-1})
BUTAN-2-OL	68.58	1.05×10^8	66.002	88.859	70.119

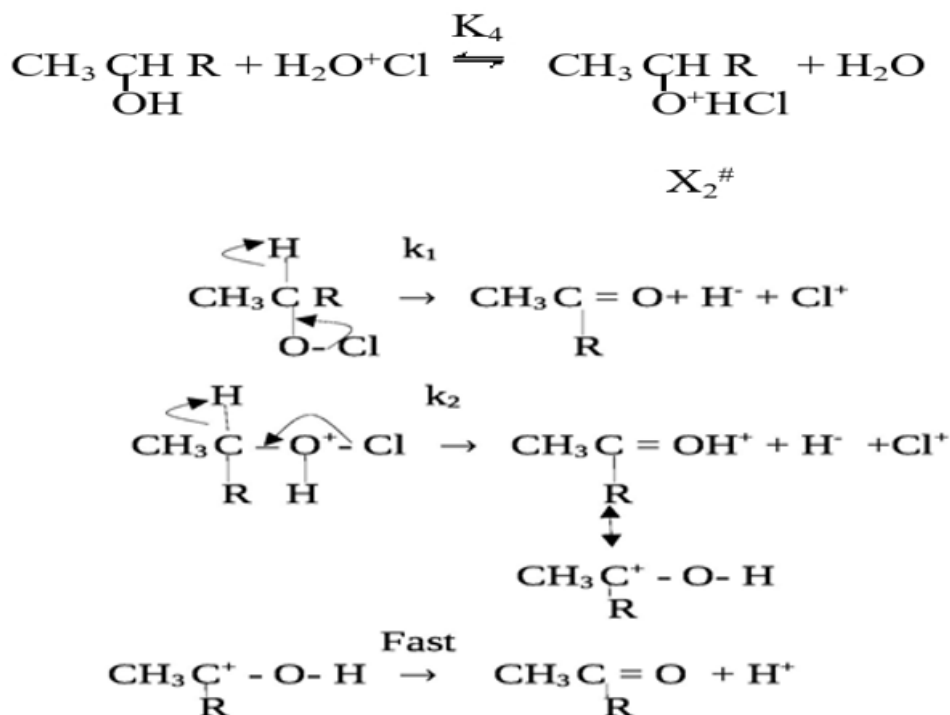## IV. MECHANISM

The concentration of NCIN was found to be constant over a period of time.So, it was found that there was no appreciable reaction between acid and NCIN.

Retarding effect of INA & solvent and positive effect of H+ clearly ruled out the NCIN, CH3COOCl, CH3COO+HOCl are not prime reactive species from the list of possible reactive species. Thus, the only choice and possibility that is left as a remote prime active species more probable is for HOCl. Our kinetic finding also suggests to us to assume that HOCl is to be considered as the most predominant, fertile reacting species. This leads to the postulation of the following overall mechanism and rate law.

$$NCIN + H_2O \overset{K_1}{\rightleftharpoons} HOCl + \text{Isonicotinamide (IN)}$$

$$HOCl + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl$$

$$NCIN + H^+ \rightleftharpoons NCINH^+$$

$$NCINH^+ + H_2O \rightleftharpoons H_2O^+Cl + \text{Isonicotinamide}$$

$$CH_3 \underset{OH}{CH} R + HOCl \overset{K_3}{\rightleftharpoons} CH_3 \underset{O-Cl}{CH} R + H_2O$$

$$X_1^{\#}$$

$$CH_3\overset{|}{\underset{OH}{C}}H\ R + H_2O^+Cl \overset{K_4}{\rightleftharpoons} CH_3\overset{|}{\underset{O^+HCl}{C}}H\ R + H_2O$$

$$X_2{}^{\#}$$

$$CH_3\overset{\curvearrowleft H}{\underset{O\text{-}Cl}{C}}R \overset{k_1}{\rightarrow} CH_3\overset{|}{\underset{R}{C}} = O + H^- + Cl^+$$

$$CH_3\overset{\curvearrowleft H}{\underset{R\ \ H}{C}}O^+\text{-}Cl \overset{k_2}{\rightarrow} CH_3\overset{|}{\underset{R}{C}} = OH^+ + H^-\ +Cl^+$$

$$\downarrow$$

$$CH_3\overset{+}{\underset{R}{C}}\text{- O- H}$$

$$CH_3\overset{+}{\underset{R}{C}}\text{- O- H} \overset{Fast}{\rightarrow} CH_3\overset{|}{\underset{R}{C}} = O\ + H^+$$

Where R=CH$_2$-CH$_3$ for Butane-2-ol

On the basis of the aforementioned steps involved in the proposed mechanism and at steady state approximation condition, the final rate Propane-2-olw is derived as;

$$k_{obs} = \frac{K_1\ [SA]\ (k_1 K_3 + k_2 K_2 K_4\ [H^+])}{[IN] + K_1 + K_1 K_3\ [SA]} \qquad (18)$$

This proposed rate law explained all experimental facts.

V.   CONCLUSION

Butan-2-ol is an aliphatic secondary alcohol. At first substrate formed a complex which is attacked by HOCl, an active species of NCIN. Just like the oxidation of aliphatic secondary alcohols with NCSA [35-36] and NBIN [37], NCIN also exhibits similar kinetics with aliphatic secondary alcohols. An intermediate complex formed which is decomposes in a slow rate determining step and give the product. The reaction obeys Arrhenius relationship. The proposed mechanism is in good accordance with experimental findings.

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