Oxidative Degradation of Propan-2-Ol by N-Chloroisonicotinamide in Aqueous Acetic Acid Medium; a Kinetic Study

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

1.Department of Chemistry Govt.T.R.S. College Rewa

ABSTRACT:
The oxidation of Propan-2-ol by a mild and selective oxidizing agent N-chloroisonicotinamide (NCIN) leads to the formation of corresponding ketones. The reaction found first order with respect to NCIN. The reaction follows Michaelis-Menten kinetics. A retarding effect of acetic acid is observed. Various thermodynamic parameters have been computed. No evidence of polymerization of acrylonitrile found. 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, Propan-2-ol, Mechanism, NCIN, Oxidation.

I.   INTRODUCTION

N-chloroisonicotinamide (NCIN) is a new member of N-halo family. NCIN, the derivative of Isonicotinamide is a mild, stable, efficient, and inexpensive oxidant for organic substates [1]. The elemental analysis and physical properties of 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 [2-6] reveals the mildness and selectiveness of NCIN [7-8].

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 [9-10].

Aliphatic secondary alcohol (ASA) has an essential role in cosmetics, fragrance and pharmaceutical industries. The kinetics of ASA with different oxidants has been reported [11-18]. Aliphatic secondary alcohols (ASA) are studied with various oxidants and follows first order kinetics [19-24]. Propan-2-ol is widely used for oxidation by various oxidants [25-30].

The general review of the literature explored that no works have been reported about the oxidation of Propan-2-ol with NCIN; so, this prompted for the present investigation and evaluate kinetic parameters as well as correlation analysis.

II.   MATERIALS AND METHODS

1.1.   Chemicals

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

1.2.   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 reaction was monitored by examining aliquots of the reaction mixture for unconsumed NCIN iodometrically using starch as the indicator.

1.3.   Product analysis

The end product from the oxidation of Propan-2-ol was 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 Propan-2-ol was taken over NCIN. After completion of reaction the solution is treated with an excess (200 ml) of saturated solution of 2,4- dinitrophenylhydrazine

(DNPH) in 2 mol/dm³ 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 Propan-2-ol.

III. RESULT AND DISCUSSION

The oxidation of Propan-2-ol was carried out by NCIN at 308K under pseudo first order condition. Oxidation of Propan-2-ol by NCIN under the condition [NCIN] << [Propan-2-ol] had the following kinetic feature.

1.4. Stoichiometric studies

The stoichiometric studies of oxidation of Propan-2-ol by NCIN were carried out with excess of oxidant (NCIN) and maintaining other parameters constant (HOAc-H_2O = 30 % (v/v), Temperature = 308K).The stoichiometric results indicated 1 mole of Propan-2-ol consumes 1 mole NCIN as represented by the following empirical equation:

$$CH_3\text{-}CHOH + C_5H_5NCONHCl \rightarrow CH_3\text{-}C\text{=}O + H$$
$$\quad\;| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\quad\,R \qquad\qquad\qquad\qquad\qquad\qquad\qquad\;\; R$$

R = CH_3 for propan-2-ol

1.4.1. Order with respect to [oxidant] [substrate]

When the Propan-2-ol are in large 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 [Propan-2-ol] is initially linear passing through origin and tends to obtain limiting value, bending towards horizontal axis (**Figure 2**). Hence the reaction shows complex formation with respect to the Propan-2-ol concentration.
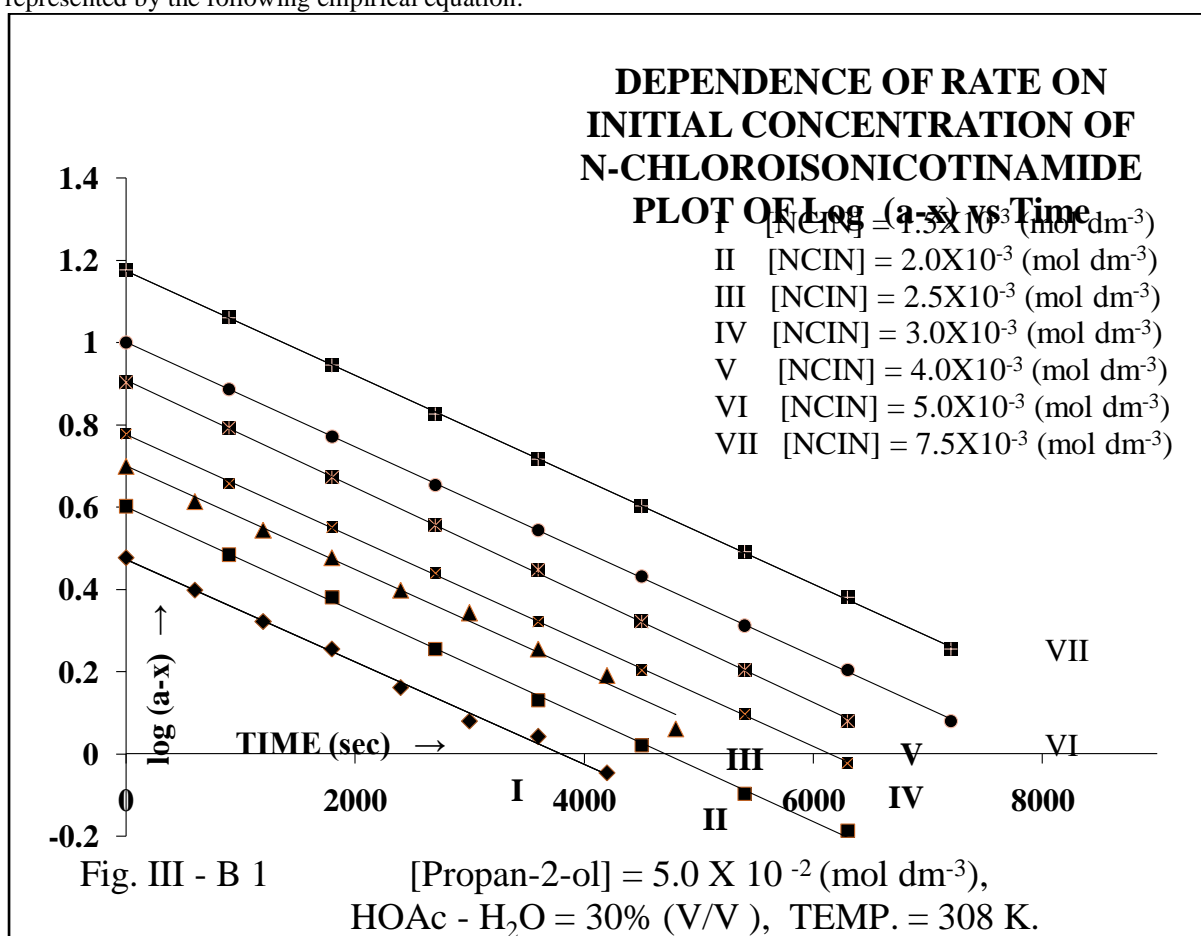

DEPENDENCE OF RATE ON INITIAL CONCENTRATION OF N-CHLOROISONICOTINAMIDE PLOT OF Log (a-x) vs Time

I   [NCIN] = 1.5X10⁻³ (mol dm⁻³)
II   [NCIN] = 2.0X10⁻³ (mol dm⁻³)
III   [NCIN] = 2.5X10⁻³ (mol dm⁻³)
IV   [NCIN] = 3.0X10⁻³ (mol dm⁻³)
V   [NCIN] = 4.0X10⁻³ (mol dm⁻³)
VI   [NCIN] = 5.0X10⁻³ (mol dm⁻³)
VII   [NCIN] = 7.5X10⁻³ (mol dm⁻³)

Fig. III - B 1   [Propan-2-ol] = 5.0 X 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
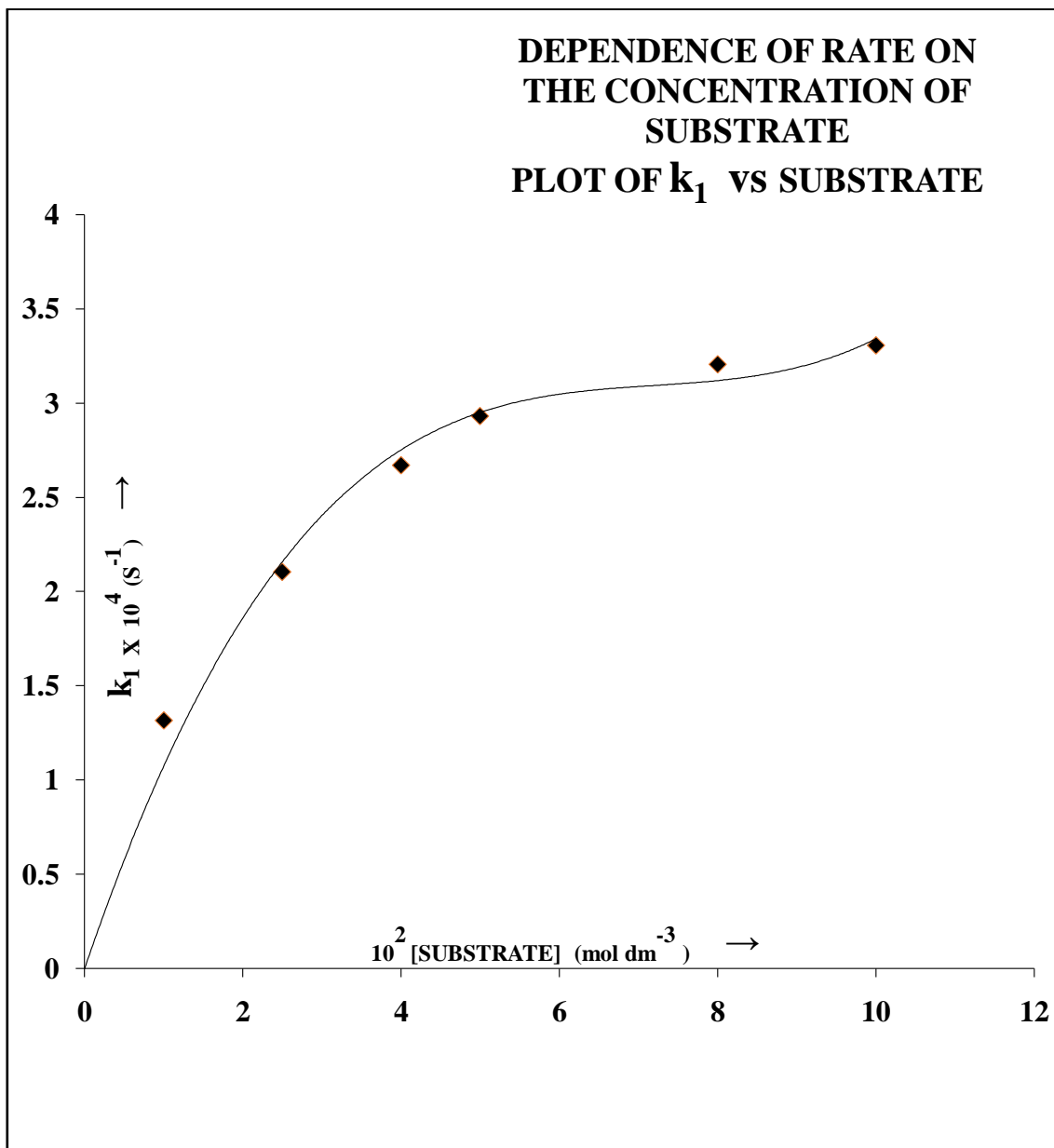## PLOT OF k_1 VS SUBSTRATE

Figure 2: Dependence of k_1 on [Propan-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	0.1314
2.50	2.50	-	30	0.2104
4.00	2.50	-	30	0.2669
5.00	2.50	-	30	0.2929
8.00	2.50	-	30	0.3204
10.00	2.50	-	30	0.3306
5.00	1.50	-	30	0.2941
5.00	2.00	-	30	0.2952
5.00	2.50	-	30	0.2929
5.00	4.00	-	30	0.2947

5.00	5.00	-	30	0.2926
5.00	2.50	0.0	30	0.2929
5.00	2.50	0.1	30	0.3013
5.00	2.50	0.15	30	0.3319
5.00	2.50	0.2	30	0.3519
5.00	2.50	0.25	30	0.3754
5.00	2.50	0.3	30	0.3902
5.00	2.50	0.4	30	0.4354
5.00	2.50	0.5	30	0.4602
5.00	2.50	-	10	0.2574
5.00	2.50	-	20	0.2752
5.00	2.50	-	30	0.2929
5.00	2.50	-	40	0.3201
5.00	2.50	-	50	0.3864

1.4.2.   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 plays a complex role in the reaction system.
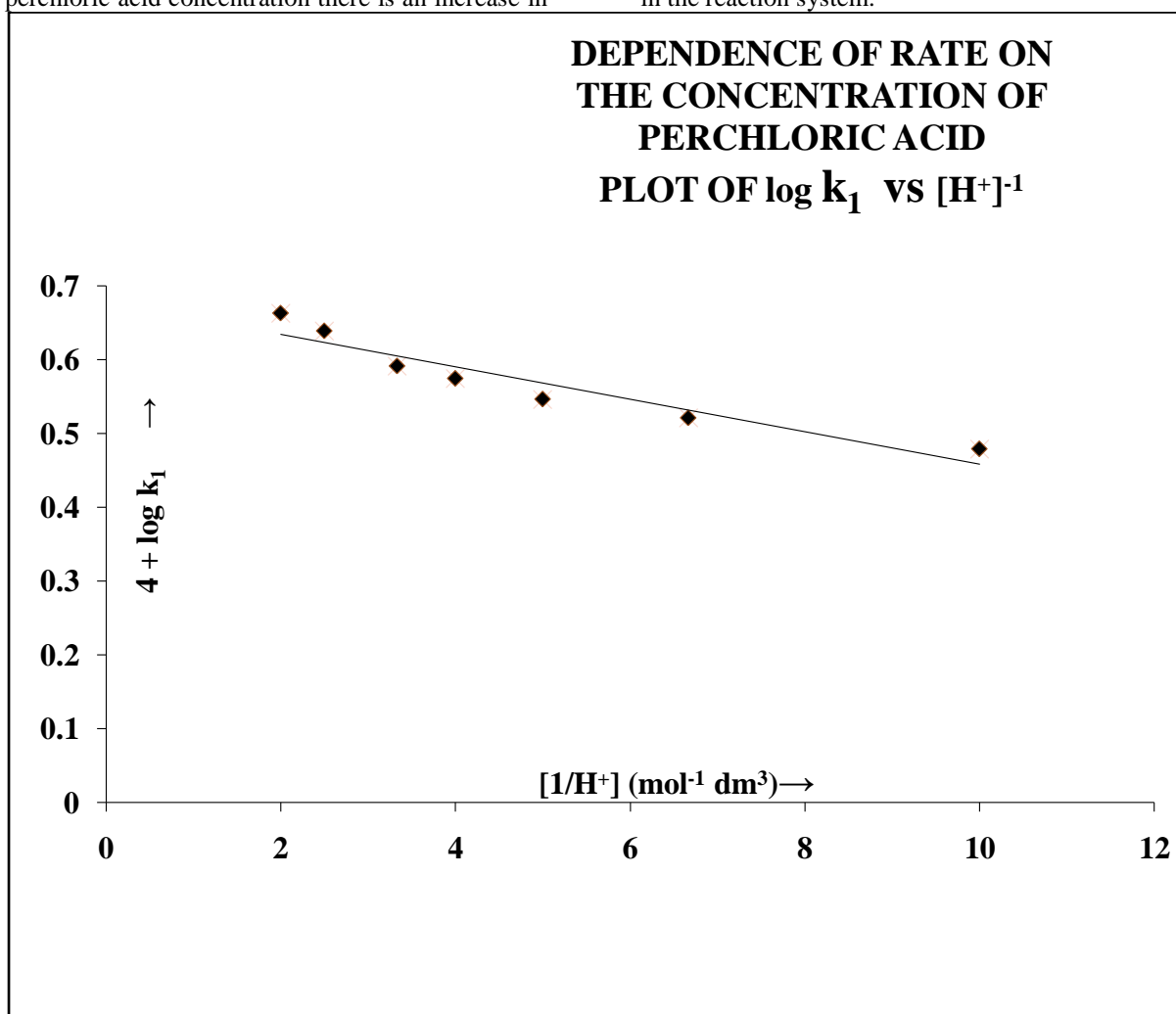

Figure 3: Dependence of k_1 on [H⁺]. Conditions are given in Table 1.

1.4.3.   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.

1.4.4.   Effect of ionic strength and isonicotinamide:

The reaction rate was not influenced by the addition of chemically neutral salt. Hence the ionic behaviour on slow step in the reaction mechanism is ruled out. Addition of isonicotinamide (one of the reaction products), at constant NCIN and Propan-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 product. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of isonicotinamide concentration.

1.4.5.   Effect of Free Radical Inhibitor:

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

1.4.6.   Effect of temperature:

The effect of temperature on the oxidation of Propan-2-ol with NCIN was also studied. The value of energy of activation, ΔS, ΔH & ΔG were computed. These values are summarized in **Table 2** along with the other parameters.

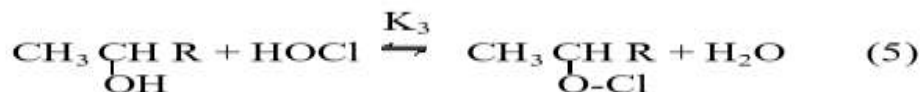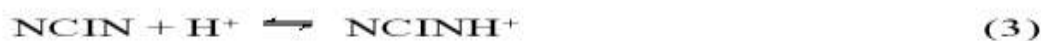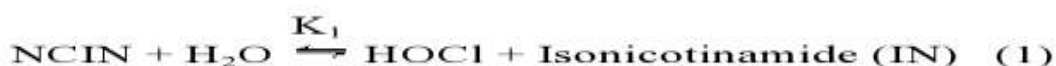**Table 2: Thermodynamic parameters of PROPAN-2-OL-NCIN system**

Substrate	E_a (kJ mol^{-1})	A (s^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	$-\Delta S^*$ (JK^{-1} mol^{-1})
PROPAN-2-OL	71.323	0.99×10^8	67.436	89.029	69.0118

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 solvent & end product of oxidation was observed while positive effect of [H^+] clearly ruled out the NCIN, CH_3COOCl,
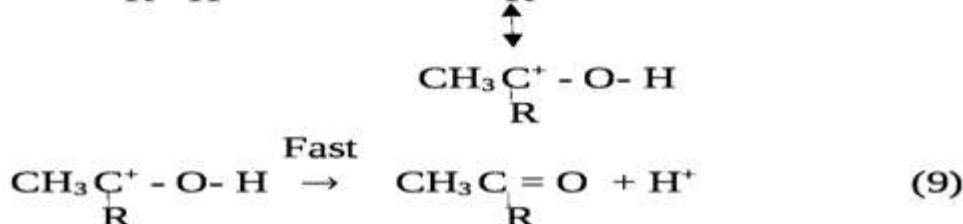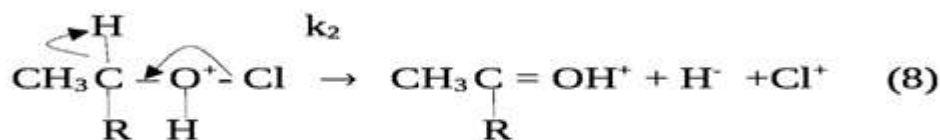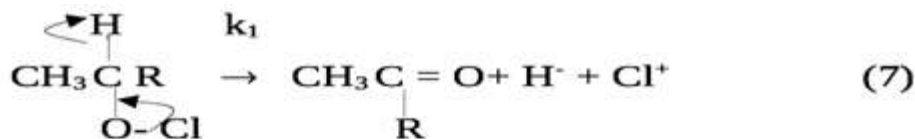
CH_3COO^+HOCl as a prime reactive species from the list of possible reactive species. Thus, the only choice and possibility that is left is HOCl as a remote prime active species. Our kinetic finding also suggests to us to assume that HOCl is to be considered as the most predominant, fertile reacting species. This leads to the postulation of the following overall mechanism and rate law.

$$NCIN + H_2O \xrightleftharpoons{K_1} HOCl + \text{Isonicotinamide (IN)} \quad (1)$$

$$HOCl + H^+ \xrightleftharpoons{K_2} H_2O^+Cl \quad (2)$$

$$NCIN + H^+ \rightleftharpoons NCINH^+ \quad (3)$$

$$NCINH^+ + H_2O \rightleftharpoons H_2O^+Cl + \text{Isonicotinamide} \quad (4)$$

$$\underset{OH}{CH_3\,CH\,R} + HOCl \xrightleftharpoons{K_3} \underset{O\text{-}Cl}{CH_3\,CH\,R} + H_2O \quad (5)$$

$$X_1{}^\#$$

$$\underset{OH}{CH_3\,CH\,R} + H_2O^+Cl \xrightleftharpoons{K_4} \underset{O^+HCl}{CH_3\,CH\,R} + H_2O \quad (6)$$

$$X_2{}^\#$$

$$CH_3 \overset{H}{\underset{O-Cl}{C}} R \xrightarrow{k_1} CH_3 \underset{R}{C} = O + H^- + Cl^+ \qquad (7)$$

$$CH_3 \underset{R \quad H}{C} O^+ - Cl \xrightarrow{k_2} CH_3 \underset{R}{C} = OH^+ + H^- + Cl^+ \qquad (8)$$

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

$$CH_3 \underset{R}{C^+} - O - H \xrightarrow{Fast} CH_3 \underset{R}{C} = O + H^+ \qquad (9)$$

Where R=CH$_3$

On the basis of the aforementioned steps involved in the proposed mechanism and at steady state approximation condition, the final rate law 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

Propan-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 hydroxy acid with NCSA [35-36] and NBIN [37], NCIN also exhibits similar kinetics with aliphatic hydroxy acid. 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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