N-chlorosaccharin oxidation of propan-2-ol: A kinetic study

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ABSTRACT

Oxidation of propan-2-ol by N-chlorosaccharin (NCSA) in aqueous acetic acid medium has been carried out. The reactions exhibit first-order in oxidant and fractional order with substrate. The rate of oxidation increases wit increase of acetic acid in medium while retarding by the addition of saccharin. This oxidation is acid catalyzed. The effect of temperature on reaction rate has also been studied. The thermodynamic parameters have been calculated. Based on all the kinetic data a possible operative mechanism has been proposed and a suitable rate law has been derived.

Key words: oxidation, kinetics, saccharin and propan-2-ol.
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INTRODUCTION

N-chlorosaccharin (NCSA) has been employed as a mild versatile oxidant in the oxidation of various organic compounds [1-9]. Literature survey reveals that the oxidation of propan-2-ol by various oxidants such as Bromamine-T [10], Quinolinium bromochromate [11], TFAIB [12], Polymer supported chromic acid [13], N-chloronicotinamide [14], Pyridinium chlorochromate [15], Quinolinium flurochromate [16], Molecular oxygen [17] has been studied. There seems to be no report on the oxidation of propan-2-ol by NCSA. Hence in the present communication authors report the oxidation kinetics of propan-2-ol by NCSA in aqueous acetic acid medium in presence of perchloric acid.

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MATERIALS AND METHODS

2.1 Materials

NCSA was synthesized by reported method [18]. The solution of NCSA was prepared by dissolving its sample in 100% acetic acid (BDH) and standardized iodometrically. Solutions of propan-2-ol (S.Merck), potassium dichromate (BDH), sodium per chlorate (AR BDH), saccharin (Sigma), were prepared by dissolving their required quantity in distilled water. The solution of sodium thiosulphate (AR BDH) and perchloric acid (E. Merck) were prepared by dissolving their appropriate quantity in distilled water and were standardized by standard methods.

2.2 Kinetic measurements

The kinetic studies were carried out under pseudo first-order conditions. The experiments were carried out in a black coated stopper glass vessel to avoid any photochemical effect. A thermo-stated water bath was used to maintain the desired temperature within $\pm 0.1 K$. Requisite volumes of all reagents, except NCSA, were introduced into a reaction vessel and equilibrated at 303 K. A measured volume of NCSA, equilibrated separately at the same temperature, was rapidly poured into the reaction vessel. The progress of the reactions was followed by estimating unconsumed NCSA iodometrically using starch as the indicator.

2.3 Stoichiometry & Product analysis

The stoichiometric results indicated consumption of 1 mol of propan-2-ol consumes 1 mol NCSA as represented by the following empirical equation:

$$CH_3\text{-}CHOH + C_6H_4COSO_2NCl + H_2O \rightarrow CH_3\text{-}C=O + C_6H_4COSO_2NH + HCl$$
$$CH_3 CH_3$$
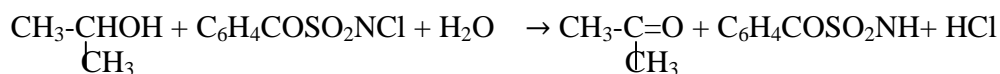
The acetone and saccharin was qualitatively identified as product of this oxidation.

RESULTS AND DISCUSSION

Oxidation of propan-2-ol by NCSA in aqueous acetic acid in presence of perchloric acid under the condition [NCSA] << [propan-2-ol] had the following kinetic feature.

3.1 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 NCSA. The pseudo first-order rate constants in NCSA 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 follows fractional order behavior with respect to the propan-2-ol concentration.

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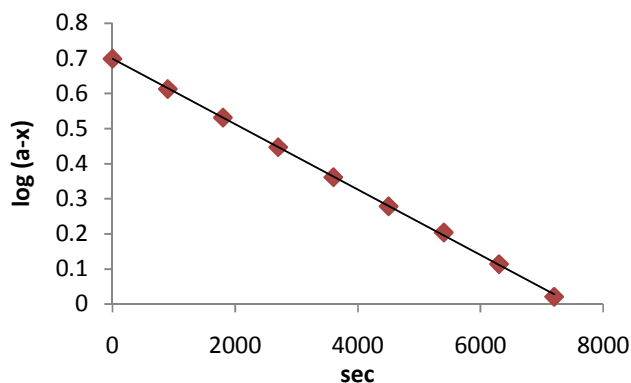
Figure 1:- The plot of log (a-x) versus time
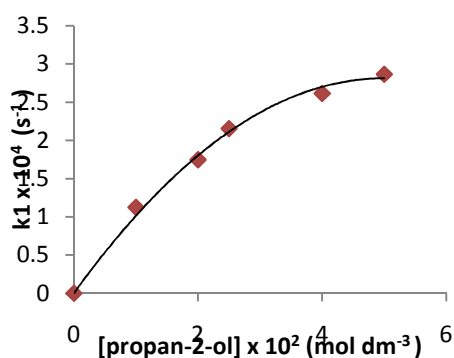
Figure 2:- Dependence of k_1 on [propan-2-ol]
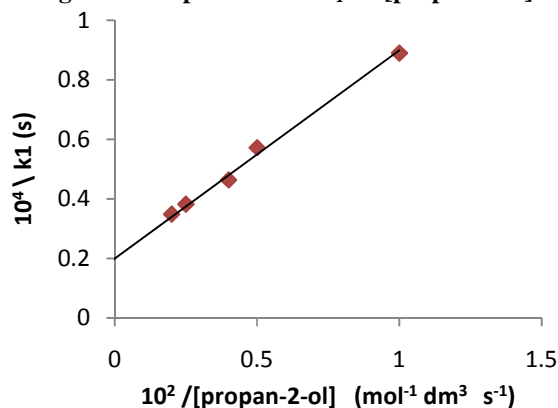
Figure 3: Double reciprocal plot depicting the dependence of the reaction rate on the concentration of propan-2-ol

3.2 Effect of variation of [H⁺]

The catalyzed 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 log [H⁺] (Figure 4) gave a straight line with negative intercept, suggesting that acid plays a complex role in the reaction system.

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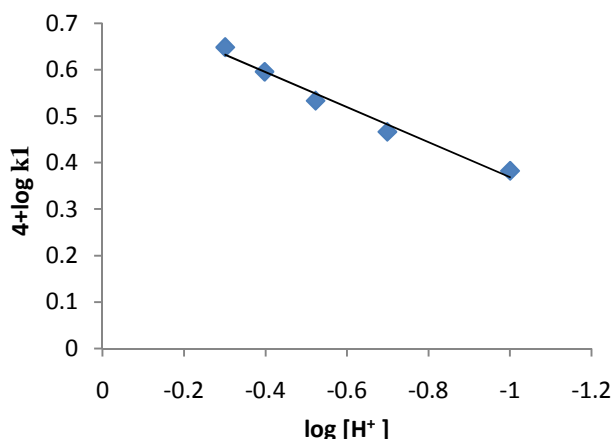
Figure 4:- Dependence of k_1 on [H$^+$]

3.3 Effect of solvent on reaction velocity

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

Table 1: Effect of variation of propan-2-ol on pseudo first order rate constant k_1 at 303K

10^2 [Substrate] (mol dm^{-3})	10^3 [NCSA] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	% HOAc - H$_2$O	$k_1 \times 10^4$ (s^{-1})
1.0	2.5	0	40	1.241
2.0	2.5	0	40	1.642
2.5	2.5	0	40	2.153
4.0	2.5	0	40	2.612
5.0	2.5	0	40	2.863
2.5	1.0	0	40	3.260
2.5	2.0	0	40	2.845
2.5	4.0	0	40	1.821
2.5	5.0	0	40	1.454
2.5	2.5	0.10	40	2.412
2.5	2.5	0.20	40	2.927
2.5	2.5	0.30	40	3.415
2.5	2.5	0.40	40	3.943
2.5	2.5	0.50	40	4.451
2.5	2.5	0	20	1.62
2.5	2.5	0	30	1.89
2.5	2.5	0	50	2.71
2.5	2.5	0	60	3.02

3.3 Effect of ionic strength, and saccharin

The reaction rate was not influenced by the addition of chemically neutral salt. Hence the ionic behavior of slow step in the reaction mechanism is ruled out. Addition of saccharin (one of the reaction products), at constant NCSA and alcohol concentration, decreases the rate of reaction. This confirms that HOCl is the main oxidizing species. The retardation of reaction rate on the addition of saccharin suggests a pre-equilibrium step that involves a process in which saccharin

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is one of the products. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of saccharin concentration.

3.4 Induced polymerization of acrylonitrile
The undertaken reactions failed to induce polymerization of acrylonitrile. This indicates the absence of free radical species during the reaction. Hence a free radical mechanism is ruled out.
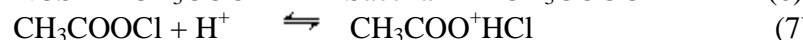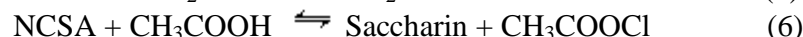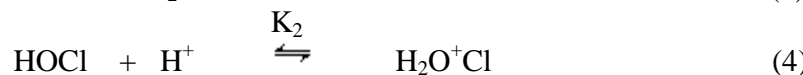
3.5 Activation Parameter
Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place. The effect of temperature on the reaction of propan-2-ol with NCSA was also studied. The value of energy of activation was calculated and the values of ΔS, ΔG were also computed. These values are summarized in Table 2 along with the other parameters.

Table 2. Thermodynamic parameters of propan-2-ol-NCSA system

Substrate	Ea (kJ mol^{-1})	A (s^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	$-\Delta S^*$ (JK^{-1} mol^{-1})
Propa-2-ol	64.358	2.45 x10^{-4}	64.04	87.12	76.48

3.6 Mechanism and Rate law
In aqueous acetic acid and in the presence of perchloric acid N-chlorosaccharin exists as molecular species [NCSA], hydrolytic product (HOCl), various protonated species and the acetyl derivatives according to following equlibria:

$$NCSA + H^+ \rightleftharpoons NCSAH^+ \qquad (1)$$
$$NCSA + H^+ \rightleftharpoons Saccharin + Cl^+ \qquad (2)$$
$$NCSA + H_2O \overset{K_1}{\rightleftharpoons} HOCl + Saccharin \qquad (3)$$
$$HOCl + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl \qquad (4)$$
$$NCSAH^+ + H_2O \rightleftharpoons H_2O^+Cl + Saccharin \qquad (5)$$
$$NCSA + CH_3COOH \rightleftharpoons Saccharin + CH_3COOCl \qquad (6)$$
$$CH_3COOCl + H^+ \rightleftharpoons CH_3COO^+HCl \qquad (7)$$
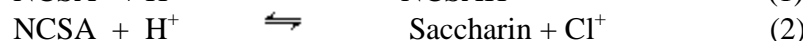
Acid catalysis and retardation of oxidation rate by added saccharin points out HOCl and H$_2$O$^+$Cl as active oxidant. The formation and participation of hypochlorous acidium ion (H$_2$O$^+$Cl) is well documented in several oxidation reactions involving halo-amides and imides as oxidants. Accordingly deprotonated (HOCl) and protonated (H$_2$O$^+$Cl) forms of oxidant species are involved in the rate controlling step.

Alcohols are nucleophilic in nature and medium effect studies also suggest that slow step is positive ion-dipole reaction. Hence, the mechanistic step involves interaction between positive oxidant species neutral alcohol molecules.

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In the present investigation, Michaelis-Menten kinetics in [alcohol] is observed. This suggests formation of hypochlorite ester in pre-equilibrium followed by its decomposition slow step. On the basis of kinetic results, stoichiometry and product analysis the following probable mechanism and rate law are proposed.

$$RCHOH + HOCl \xrightleftharpoons{K_3} RCHOCl\ (X_1^{\#}) + H_2O \qquad (8)$$
$$\overset{|}{C}H_3 \qquad\qquad \overset{|}{C}H_3$$

$$RCHOH + H_2O^+Cl \xrightleftharpoons{K_4} RCHO^+Cl\ (X_2^{\#}) + H_2O \qquad (9)$$
$$\overset{|}{C}H_3 \qquad\qquad \overset{|}{C}H_3H$$

$$RCHOCl\ (X_1^{\#}) \xrightarrow{K_5} RCHO + HCl \qquad (10)$$
$$\overset{|}{C}H_3 \qquad\qquad \overset{|}{C}H_3$$

$$RCHO^+Cl\ (X_2^{\#}) \xrightarrow{K_6} RC{=}O + HCl + H^+ \qquad (11)$$
$$\overset{|}{C}H_3H \qquad\qquad \overset{|}{C}H_3$$

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;

$$k_1 = \frac{K_1\,[alcohol]\,(\,K_3\,K_5 + K_2\,K_4\,K_6\,[H^+]\,)}{[S] + K_1\,(1 + K_3\,[alcohol]\,)} \qquad (12)$$

The above rate law equation explain fully well the experimental results obtained for the first-order kinetics, the plot of 1/[rate] versus 1/[substrate] give rise a straight line with non zero origin which gives the value of k and furnishes an evidence for the formation of complex between substrate and reactive species of the oxidant. Thus in this case the rate determining step involves C-H bond fission. This degree of agreement again shows the validity of rate law and hence confirms the proposed reaction mechanism. The values of activation energy and other thermodynamic parameters indicate that the oxidation is enthalpy controlled.

CONCLUSION

Kinetic studies demonstrate that complex of substrate and oxidant decomposes in a slow rate determining step to give acetone as main product. Stoichiometry is in good agreement. First order to oxidant and fractional order to propan-2-ol is supported by derived rate law. The negative value of ΔS* provided support for the formation of a rigid activated complex.

Acknowledgement

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