# N-chlorosaccharin Oxidation of Allyl Alcohol in Micellar Medium

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***Abstract*— Oxidation of allyl alcohol by N-chlorosaccharin (NCSA) proceeds by a mechanism involving de-protonation in C-H bond fission via an intermediate complex stoichiometrically (1:1) to afford product. $H_2O^+Cl$ was postulated as reaction entity of the oxidant. The $-\frac{dc}{dt} \propto$ [NCSA]. The rate of oxidation in micellar (CTAB) was found much faster than rate in an acid at optimum concentration showing fraction-order kinetics to substrate.**

***Keywords* — Allyl alcohol, N-chlorosaccharin, cetyltriammoniumbromide, oxidation, kinetics.**

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## I. INTRODUCTION

Chemical kinetic vitality with rates of engineered techniques. In past three decades N-chlorosaccharin (NCSA), surged as novel halo-oxidant with two electrons system having potential +1.20 V, and producing a halonium ion which is an electrophilic reagent [1]. The chemistries of reactions pertaining to its utility with CTAB have been widely explored in the oxidation [2-8], and synthesis of several organic compounds [9]. Micellars exhibit an intermediate type of properties lying between homogeneous, and heterogeneous polymer catalyst, dominate rate, and influence the industrial production to a large extent, and some prominent micellar used as solvent [4] (Loc. cit.) in chemical reactions are cationic cetyltrimethyl- ammonium bromide (CTAB). Micellar activity is generally maximum at a definite þH when used within CMC range range at optimum temperature. The specificity of CTAB shows Lock, and key model mechanism. The results are still treated to be fragmentary in nature [10]. The reactions are accelerated by addition of [CTAB] as catalysts [11-13] which might be adsorbed on the positive charged surface of the micelles i.e. in the juncture of Gouy–man stem layer of the micelles due to aggregation of the micellar by polymerization that exists below CMC in several redox reactions [14]. Allyl alcohol largely distributed in fruits, vegetable, and mainly used in textile industry, and pharmacological interest as exhibit many biological activities in all cells. The conjugated double bond with alcoholic group of this substrate is completely delocalized by $\pi$ electron, and can also form site of de-polymerization [15]. Now-a-days allyl alcohol is gaining importance, and growing demand in the field of textile industry in organic synthesis, and extensively, and kinetics by different oxidants [16-18]. There, seems to be no reports available on the kinetic study of oxidation of allyl alcohol by NCSA not yet been documented in literature for the formation of proposed mechanism. Therefore, inspired from the aforementioned facts, the dynamics of allyl alcohol with NCSA in micellar medium was taken as task of kinetic study.

## II. EXPERIMENTAL

The analytical grade sample of allyl alcohol was used as such obtained in reaction, its solution may also be prepared by diluting its requisite amount in doubly distilled water. The accurately weighed amount of NCSA (across) sample was dissolved in 100% acetic acid (E-Merck), and standardized iodometrically. The requisite amount of commercial A.G. sample of (CTAB) micelles was used as such obtained.

The reaction was studied under pseudo-first-order condition keeping large excess (X 10 or greater) of allyl alcohol over NCSA. The temperature was maintained constant ± 0.1 K. The kinetics of reaction was initiated by mixing two solutions- NCSA oxidant, and allyl alcohol, and other participating reagent in equilibrated thermostat at 303 K. The reaction was followed by disappearance of [NCSA] up to 80% of the reaction. The pseudo first-order reaction rate constant ($k_{ob}$s)was evaluated graphically, and by integration method from the linear plot of log [NCSA] against time. Duplicate kinetic runs of reaction showed that $k_{obs}$ was reproducible within ± 3%. The stoichiometry was determined for allyl alcohol - NCSA reaction can be formulated as :

$$CH_2 = CH - CH_2OH + \underset{\text{(NCSA)}}{C_6H_5COSO_2\,NCl} \rightleftharpoons \underset{\text{(saccharin)}}{C_6H_5COSO_2NH} + HCl + \underset{\text{(acrolein}}{CH_2 = CH \cdot OH} \quad \ldots\ldots(1)$$

The product analysis for was carried out under kinetic conditions. The acrolein, the oxidation product of allyl alcohol was identified by chemical method, and also characterized by forming its phenyl hydrazine in ether to yields phenyl pyrazoline M.P. $51^0C$.

## III. RESULTS AND DISCUSSION

Before The oxidation of allyl alcohol by NCSA in an stream of nitrogen failed to induce the polymerization of acrylonitrile, clearly indicating that NCSA undergoes a two electron change. The rate of reaction remains unaffected by ionic strength, and successive addition of neutral salt (sodium chloride) thus showing that neutral species participates in reaction. Likewise the added quantity of reduction product saccharin of oxidant showed a nominal change in oxidation. Thus, ruling out its participation as species in proposed mechanism.

The reaction is found to be of first-order in NCSA. The kinetic runs obeyed first-order in NCSA. The linear plots of lg $\frac{[NCSA]_o}{[NCSA]_t}$ against time yields unit slope further showed that pseudo first-order rate constants ($k_{obs}$) do not depend on the initial concentration of NCSA.

The reaction dynamics reveals that a reaction between reacting species of NCSA and substrate at transition state exists showing fractional-order kinetics (Tabel 1). The Michaelis-Menten type. Kinetics was observed when linear plot of $k_{obs}$ against [allyl alcohol] (Figure 1) was made, which can also be proved by a double reciprocal plot of $k_{obs}^{-1}$ versus [allyl alcohol]$^{-1}$ with positive intercept on Y-axis. The values of second-order rate ($k_2$) are not constant. Exactly, in the same manner, the micellar CTAB also showed maximum rate at optimum concentration of CTAB (Table 2). The enzyme catalysis obeys here as Michaelis-Menten type kinetics (linear plots of $\frac{1}{k_{obs}}$ vs. $[\frac{1}{CTAB}]$, with a positive intercept on Y-axis (Figure 2). Thus, CTAB showing fractional-order kinetics, behaving both as solvent and a catalysis.

**Table 1: Rate constants for the oxidation of allyl alcohol by NCSA at 303 K**
[NCSA] = $2.0 \times 10^{-3}$ (mol dm$^{-3}$) ; [CTAB] = $1.25 \times 10^{-3}$ (mol dm$^{-3}$) ;
$H_3COOH : H_2O = 30 : 70$ %, (v/v).

| **[allyl alcohol] ×10$^2$(mol dm$^{-3}$)** | **10$^4$ $k_{obs}$ (s$^{-1}$)** | $100k_2 = \frac{k_{obs}}{[allyl\ alcohol]}$ $\ell\ mol^{-1}\ s^{-1}$ |
|---|---|---|
| 0.50 | 1.31 | 2.62 |
| 1.00 | 2.15 | 2.15 |
| 1.25 | 2.44 | 1.95 |
| 2.00 | 3.64 | 1.25 |
| 4.00 | 5.01 | 1.10 |
| 5.00 | 5.50 | 1.10 |

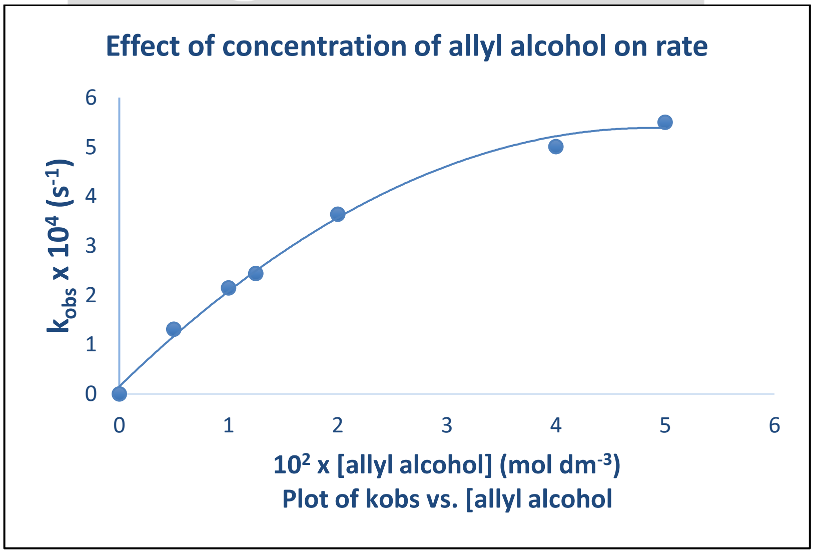


**Fig. 1** [NCSA] = $2.0 \times 10^{-3}$ (mol dm$^{-3}$) ;
[CTAB] = $1.25 \times 10^{-3}$ (mol dm$^{-3}$) ;

$H_3COOH:H_2O$ = 30 : 70 %, (v/v)

**Table 2: Effect of concentration of micellar (CTAB) on rate at 303 K**
[allyl alcohol] = 1.25 × $10^{-2}$ (mol $dm^{-3}$); [NCSA] = 2.0 ×$10^{-3}$ (mol $dm^{-3}$); $CH_3COOH:H_2O$ = 30 : 70 %, (v/v)

| Micellar [CTAB] × $10^{-3}$ (mol $dm^{-3}$) | $10^4$ $k_{obs}$ (s-1) | $10^4 \times \frac{1}{k_{obs}}$ | $10^3 \times \frac{1}{[CTAB]}$ $mol^{-1}$ $dm^3$ |
|---|---|---|---|
| 0.50 | 1.26 | 0.7936 | 0.20000 |
| 1.00 | 1.96 | 0.5102 | 1.0000 |
| 1.25 | 2.44 | 0.4098 | 0.8000 |
| 1.50 | 2.71 | 0.3690 | 0.6666 |
| 2.00 | 3.17 | 0.3154 | 0.5000 |
| 5.50 | 3.36 | 0.2976 | 0.4000 |

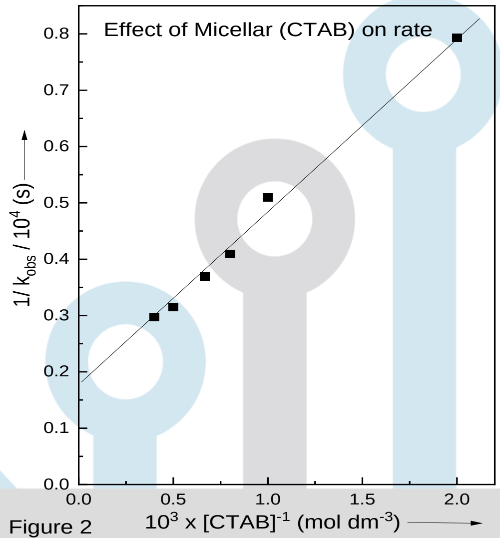


Figure 2

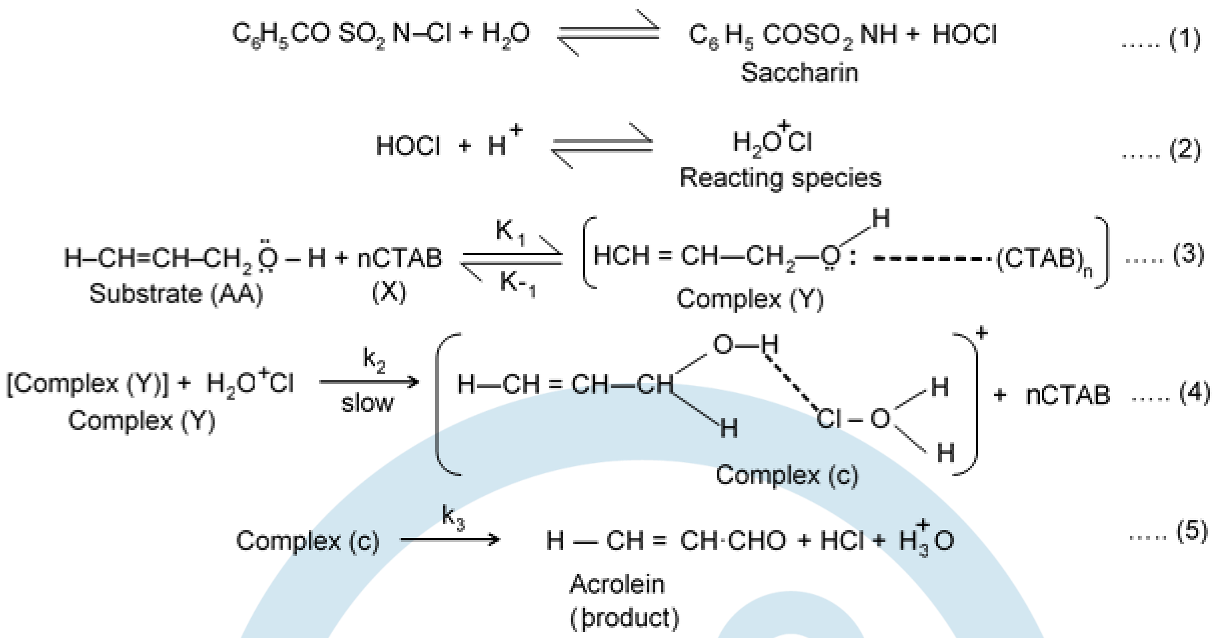
Plot of 1/ $k_{obs}$ vs. 1 / [CTAB]

[allyl alcohol] = 1.25 × $10^{-2}$ (mol $dm^{-3}$) ;
[NCSA] = 2.0 × $10^{-3}$ (mol $dm^{-3}$) ;
$CH_3COOH$: $H_2O$ = 30 : 70 %, (v/v)
Temp. = 303 K

## IV. MECHANISM

HOCl produced as hydrolytic product of NCSA undergoes protonation to form $H_2O^+Cl$ considered fit to cover the mechanism of substrate. The allyl alcohol contains > C= C < and -$CH_2OH$ and is in conjugation makes it susceptible to undergo for oxidation.

The $H_2O^+Cl$ interact with allyl alcohol in micellar cationic CTAB solvent in pre-equilibrium, lead to the formation of the complex to constitute the postulated mechanism. The presence of substantial kinetic results confirm the de-protonation in cleavage of C-H bond in the rate-determining step. The mechanism is also supported by the major role of cation solvating power of the solvents.



The rate low corresponding to proposed mechanism can be enumerated as :

$$\frac{-d}{dc}[H_2O^+Cl] = k_2 \qquad \ldots\ldots(5)$$

Employing the hypothesis of steady-state approximation to the [Y], we have

$$\frac{dc}{dt}[Y] = K_1[X][AA] - K_{-1}[Y] - k_2\,[Y] \qquad \ldots\ldots(6)$$

when, $\frac{dc}{dt}\,[Y] = O$ , then on simplification, we have

$$[Y] = \frac{K_1[AA][X]}{(K_{-1}) + k_2} \qquad \ldots\ldots\ (7)$$

In collaboration of equation (7), and equation (5), we get

$$\frac{-dc}{dt}\,[H_2O^+Cl] = \frac{k_2k_1\,[X]\,[AA]}{K_{-1} + K_2} \qquad \ldots\ldots(8)$$

From equation (8), and equation (9), we obtain the rate of reaction as :

$$k_{obs} = \frac{-dc}{dt}\,[H_2O^+Cl] = \frac{k_2k_2[CTAB]_t[AA]}{(k_{-1} + k_2) + K_1[AA]} \qquad \ldots\ldots\ldots(9)$$

The equality takes the form, on assuming $K_2 >> K_{-1} + K_1[AA]as$ :

$$k_{obs}=k_2[CTAB]_t[AA] \qquad \ldots\ldots\ldots(10)$$

but reciprocal of equation (10) might be tested for Michaelis-Menten type kinetics as :

$$\frac{1}{k_{obs}} \times [CTAB]_t = \left\{\frac{(k_{-1} + K_1)}{k_2K_1[AA]}\right\} + \frac{1}{k_2} \qquad \ldots\ldots\ldots(11)$$

The deduced rate equation (12) is able to explain all the kinetic parameters as determined earlier for the oxidation of allyl alcohol-NCSA system. The fission of C-H bond in oxidation is facile due to driving force existence in the molecule pushing towards bond sufficient to de-protonation followed by asymmetric arrangement of the atom. The activation parameters have been measured for the reaction. The similar mechanistics routes have also been reported by eminent authors employing different oxidizing agent viz. Ce(IV) [19], and $k_2S_2O_8$ [20] etc.

## CONCLUSION

The The rupturing of C-H bond involved in rate-determining step via disproportionation of complex. The cationic cetyl- trimethyl ammonium chloride (CTAB) acts both as a solvent and catalysis, and has ability to form complex. The reaction follows Michaelis-Menten type kinetics, and catalyzed by hydrogen ions.

## V. ACKNOWLEDGEMENT

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## VI. CONFLICT OF INTEREST

The authors of this manuscript hereby declare no conflict of interest

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