International Journal of Theoretical & Applied Sciences, 13(2): 12-16(2021)

ISSN No. (Print): 0975-1718
ISSN No. (Online): 2249-3247

Oxidation of Unsaturated Alcohols by N-chlorosaccharin in Micellar Medium

***Mamta Agnihotri*[1] *and Saras Tiwarii*[2]**
[1]Department of Chemistry, A.P.S. University, Rewa, (Madhya Pradesh), India.
[2]Head Department of Chemistry, Ishwar Chandra Vidyasagar Mahavidyalaya, Jawa,
Distt. Rewa, (Madhya Pradesh), India.

(Corresponding author: Mamta Agnihotri)*
(Received 01 July, 2021, accepted 03 September, 2021)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: The oxidative degradation of two unsaturated alcohols such as crotyl and cinnamyl alcohols with N-chlorosaccharin (NCSA) in aqueous acetic acid and micellar medium was accompanied through the complex formation stoichiometrically 1:1. The rate first-order with respect to oxidant concentration was determined. The rate of oxidation with micellar CTAB was found much faster than rate determined in case of an acid. The author formulated H_2O^+Cl active species of the oxidant lead the postulated hypothesis of the mechanism with fission of C-H bonds supported by thermodynamic parameters.

Keywords: Crotyl alcohol, Cinnamyl alcohol, CTAB, N-chlorosaccharin, oxidation.

I. INTRODUCTION

Micellar are polymer of complex organic compounds usually employed in colloidal form both as solvent and catalysts in various industrial processes. A satisfactory effect of rate when applied was observed in chemical reactions in micellar medium [12] within CMC range. The remarkable features of micellar catalysis are specificity that follow lock-and-key, Bregin's model mechanism. The micellar CTAB has been extensive used in the kinetic studies of hydroxy acids [7], and unsaturated acids [8, 9].

The unsaturated alcohols have long been known as natural products and shed valuable contribution in several bio-chemical processes occurring particularly in cellular respiration. Undoubtedly, they exhibit variety of reactions owing to presence of double bond and alcoholic group. A few studies on the unsaturated alcohols with SeO_2 [15], NDC [13], NaOCl [1, 10], and Ce(IV) [11] have already been documented.

The NCSA is a mild halo oxidant that furnishes HOCl and H_2O^+Cl species in aqueous acetic acid medium which attacks the alcoholic group and causes fission of C-H bonds. Its obscure potentiality is little realized in the study of alkanols [3], aldehydes [4], ketones [5, 14], and carboxylic acids [6] etc. However, the oxidation study of cinnamyl, and crotyl alcohols with NCSA have not been yet investigated in micellar medium.

Experimental. All the analytical grade chemicals used in kinetic study were of high degree of purity. NCSA solution was prepared in 100% CH_3COOH (B.D.H.) and was further standardized iodiometrically. The micellar CTAB (A.G.) was used directly in reaction mixture by calculating its requisite amount. Vis-à-vis other necessary standard solutions related to study were freshly prepared and used during the course of study.

Kinetic Procedure. The necessary amount of NCSA solution and unsaturated alcohols with other participating reagents were kept in separate conical flasks and placed in a well-equipped water bath maintained to equilibrate at the desire temperature for 30-45 minutes. The reaction commenced by rapid addition of NCSA solution to the rest of content of the substrate. The reaction was assessed for residual of NCSA left with standard sodium thiosulphate solution using iodiometric procedure. The rate constants (k_{obs}) was determined by integration and graphical method lying in a range of ±3%.

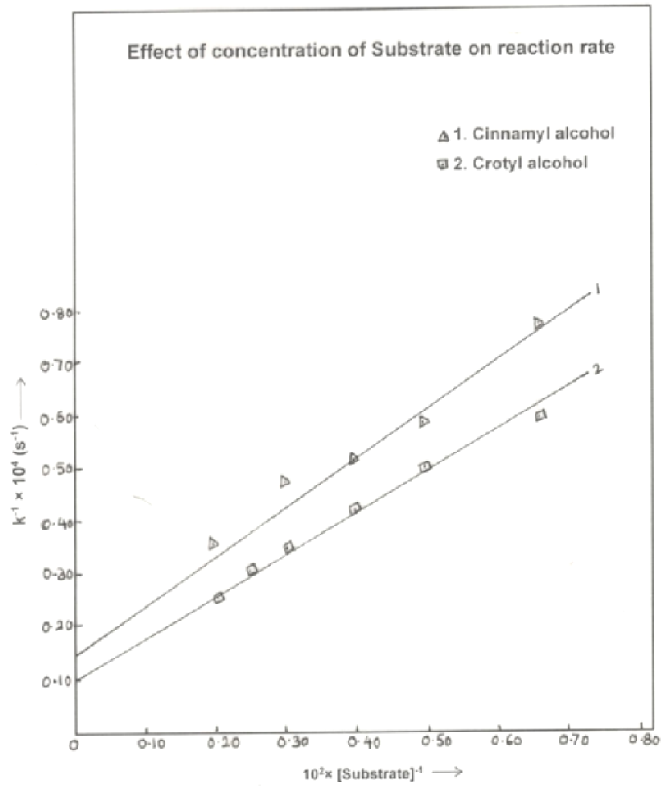
II. RESULTS AND DISCUSSION

(a) The entire kinetics study was made under the pseudo first-order condition [unsaturated alcohol] >> [NCSA]. The determinations of stoichiometry reveal 1:1 as shown in general equation

$$R - CH = CH - CH_2OH + C_6H_5COSO_2NCl \rightleftharpoons C_6H_5COSO_2NH + HCl + RCH = CHCHO$$

(b) The first-order constant (k_{obs}) was determined for the consumption of NCSA by unsaturated alcohols. The linear plots of log (a-x) against 't' yields approximately unit slope in each case. The rate remains almost constant even after variation of five-fold concentration of oxidant (NCSA).

(c) The observed data of effect of concentration of unsaturated alcohols within the range 1.50×10^{-2} to 5.0×10^{-2} (mol dm^{-3}) at 40°C was collected (Table 1). The substrates show the formation of intermediary complex itself between CTAB and protonated species of oxidant H_2O^+Cl that follow Michaelis-Menten kinetics type of fractional order. This is evidenced by plot of inverse of k_{obs} and inverse of substrates yielded positive intercepts on rate, Y-axis (Fig. 1).



$10^3 \times$ [NCSA] (mol dm^{-3}) = 2.50 (1, 2); $10^3 \times$ [CTAB] (mol dm^{-3}) = 2.50 (1, 2); CH_3COOH-H_2O %, (v/v) = 30 (1), 40(2); Temp. = 313 (1, 2)

Fig. 1. Double reciprocal plot of 1/k vs. (Substracr)$^{-1}$.

Table 1: Effect of substrate concentration on the rate of reaction.

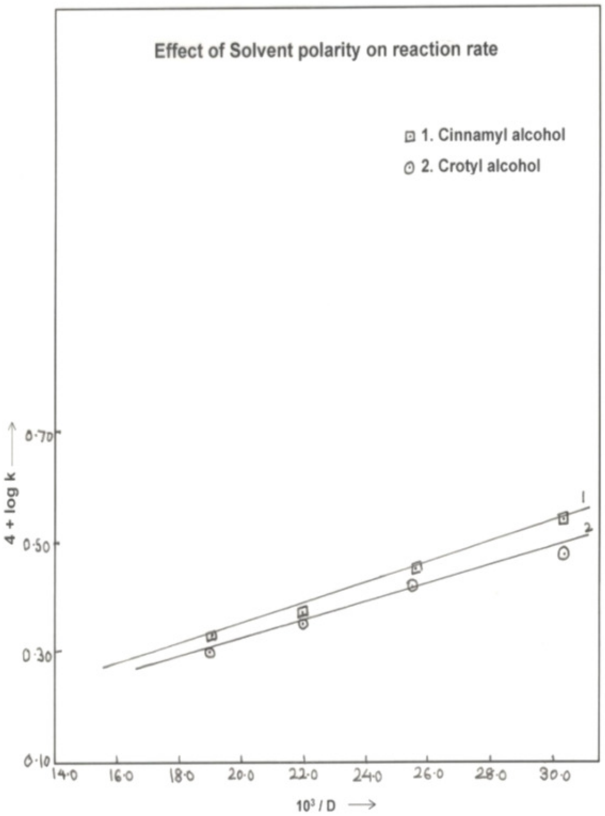
$10^2\times$ [Substrate] (mol dm^{-3})	⟵ $10^4 \times k$ (s^{-1}) ⟶	
	Cinnamyl alcohol	Crotyl alcohol
	(1)	(2)
1.50	1.29	1.69
2.00	1.72	2.01
2.50	1.95	2.35
3.33	2.05	2.84
4.00	2.71	3.15
5.00	2.73	3.72

(d) The rate of reactions are catalysed to some extent even after raising five-time more [H$^+$] but found extremely slower than the rate measured in case of micellar CTAB.

(e) The addition of acetic acid of different percentage composition to the reaction mixture, gradually increases the rate, such observation are reflected in Table 2 and demonstrated by Amis plot of log k vs. 1/D affording positive intercepts (Fig. 2).

Table 2: Effect of concentration of Dielectric constant of the medium on rate.

HOAc-H_2O % (v/v)	$10^3 \times 1/D$	⟵ $10^4 \times k$ (s^{-1}) ⟶	
		Cinnamyl alcohol	Crotyl alcohol
		(1)	(2)
30	19.15	2.05	2.15
40	21.98	2.26	2.35
50	25.64	2.66	2.86
60	30.36	2.95	3.51



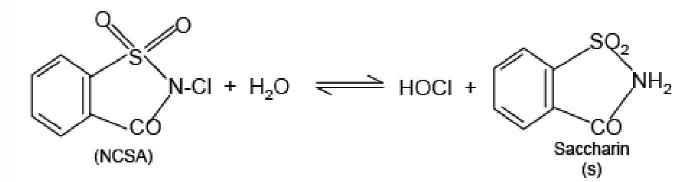
10^2 × [Substrate] (mol dm^{-3}) = 2.50 (2), 3.33 (1) ; 10^3 × [NCSA] (mol dm^{-3}) = 2.50 (1, 2) ; 10^3 × [CTAB] (mol dm^{-3}) = 1.50 (1, 2) ; Temp. = 313 (1, 2)

Fig. 2. Plot of log k vs. 103 × 1/D.

(f) The fractional order kinetics with respect to the micellar CTAB which acts both as medium and catalytic agent covers within CMC range (0.50 to 0.5 $\times 10^{-3}$ mol dm^{-3}). The rate of oxidation initially catalyses the reactions and attains a limiting value at its optimum concentration. The CTAB in presence of an acid and high dielectric constant (D) of the medium polymerized and slower the rate of oxidation followed by an intramolecular rearrangement. This fact has already been established by Beregin's model in which substrate and NCSA are preferably distributed in the stern layer of cationic surfactant CTAB having the positively charged micellar head groups. The CTAB probably provides reaction site for aggregation to show chemical activity [6] that causes increase in rate.

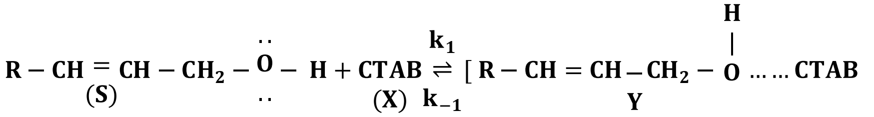
(g) The ionic strength of the medium (μ) and neutral salt had shown neutrality towards the rate whereas successive addition of reductant product saccharin of oxidant to reaction noticed marginal retarding trend in rate of oxidation.

Mechanism: The protonated reacting species H_2O^+Cl of the oxidant constitute the mechanism for two unsaturated alcohols generalised as:



……… (1)

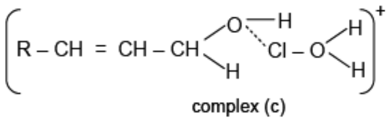
$$\mathbf{HOCl + H^+ \leftrightharpoons H_2O^+Cl} \qquad \ldots\ldots\ldots..(2)$$



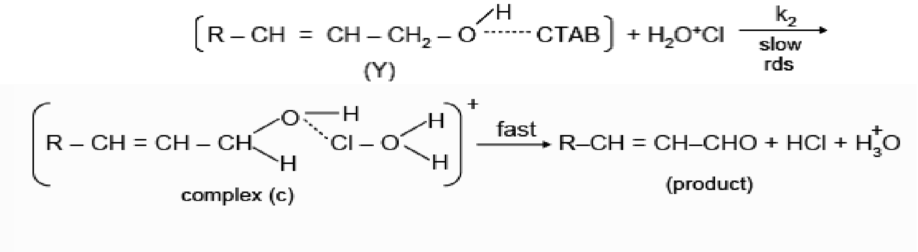
$$\mathbf{\underset{(S)}{R-CH=CH-CH_2}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H+\underset{(X)}{CTAB}\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}[\underset{Y}{R-CH=CH-CH_2-\overset{\overset{H}{|}}{O}}\ldots\ldots CTAB} \qquad \ldots\ldots\ldots(3)$$

Where S stands for substrate

Where, R = $-CH_3$ and $-C_6H_5$ for corresponding, Crotyl and Cinnamyl alcohols.



.... (4)



...... (5)

Rate equation: The rate law may be deduced in terms of consumption of [H_2O^+Cl] of oxidant as :

$$-\frac{\mathbf{d}}{\mathbf{dt}}[\mathbf{H_2O^+Cl}] = \mathbf{k_2Y} \qquad \ldots(\mathbf{6})$$

Implementing the concept of steady state approximation to the [Y],
The final rate equation is obtained as :

$$-\frac{\mathbf{d}}{\mathbf{dt}}[\,\mathbf{H_2O^+Cl} = \frac{\mathbf{K_2K_1[CTAB]_T[S]}}{\mathbf{(k_1k_2) + k_1[S]}} \qquad \ldots\ldots\ldots\ldots\ \ldots(\mathbf{7})$$

Equation (7) can be transformed as:

$$\frac{\mathbf{1}}{\mathbf{k_{obs}}}\,[\mathbf{CTAB}]_\mathbf{T} = [\,\frac{\mathbf{k_1 + k_2\,X\,1}}{\mathbf{k_2k_1[S]}} + \frac{\mathbf{1}}{\mathbf{k_2}} \qquad \ldots\ldots\ldots\ldots(\mathbf{8})$$

Where, S stands for substrate.

Equation (8) looks like a straight-line equation . The double reciprocal plots of k^{-1}_{obs} vs. $[S]^{-1}$ yielded a positive intercepts on rate axis for all the unsaturated acids, provide an evidence for the existence of complex. Equations (7), and (8) explain all the observed kinetic results satisfactorily.

A similar trend of observations in good agreement with that of advanced hypothesis made in case of unsaturated alcohol in different medium with NaOCl [13], Ce(IV) [11] and halo-oxidant [12] which support our version of mechanism. The sequence of reactivity was found as :

Crotyl alcohol > Cinnamyl alcohol

The presence of two functional groups > C = C<, and –CH = $CHCH_2OH$ having diverse array of substituent's, symmetry formation of activated complex, bulky phenyl group have shed highly polarized effect on the rate of oxidation.

The aggregated effects on chemical reactivity are generally explained by Beregin's model in a micellar pseudo phase i.e. micellars and water as separate reaction media by changing their free energy values. The CMC depends on the interactions associated with substrate to form activated complex with cationic head group which is same for all the substrates. The reactivity is least in cinnamyl alcohol due to presence of electron withdrawing phenyl group and highest value of Ea. The C-H bond fission is involved in the rate determining step due to loss to translational and rotational degree of freedom, thus driving force pushing towards a bond sufficient to cause de-protonation in the reactions which facilitate oxidation to afford products.

The products crotanaldehyde and cinnamaldehyde were identified analytically and spectroscopically. The confirmation was also made by determining their m.p.t.s. of 2:4 DNP derivatives. The addition of acrylonitrile to reaction mixture shows inertness towards free radical, non-sensitized mechanism.

A highly structured transition state also in consistent with the loss of large negative entropy of activation ($-\Delta S^\#$) in presence of CTAB leads the formations higher ordered activated complex. The compensation effect and entropy considerations are explained elsewhere [8]. The constancy in fairly high values of $\Delta H^\#$ and $\Delta G^\#$ indicate that transition is solvated and enthalpy factor to be more pre-dominating infact, the mechanism postulated envisages repulsion between two positively charged ions that support it. The reactivity sequence are well in accordance with measured value of activation energy (Ea) (Table 3), but the potential energy is not accessible. Overall summing up all the factors, it is concluded that reactions are enthalpy and entropy controlled.

Table 3: Thermodynamic parameters for the reactions unsaturated alcohols and N-chlorosaccharin in micellar medium.

Substrate	**Ea kJ ($mol^{-1)}$**	**A (s^{-1})**	**$\Delta H^\#$ kJ (mol^{-1})**	**$\Delta G^\#$ kJ (mol^{-1})**	**$-\Delta S^\#$ JK^{-1} (mol^{-1})**
Cinnamyl alcohol	64.84	1.34×10^7	63.98	90.28	83.35
Crotyl alcohol	61.19	3.78×10^6	58.95	89.21	91.26

III. CONCLUSION

Study of oxidation of crotyl and cinnamyl alcohols by N-chlorosaccharin indicated the Michaelis-Menten type of mechanism. The stoichiometric molar ratio was found 1:1. Beregin's model in micellar medium was explained. The C-H bond fission is involved in rate determining step due to loss of translational and rotational degrees of freedom. The order of reactivity and role of thermodynamic parameters was discussed in overall dealing with the study.

Acknowledgement. The authors are very thankful to the Professor and Head, Department of Chemistry, A.P.S. University, Rewa (Madhya Pradesh), India for providing Laboratory facilities.

Conflict of Interest. The authors of this manuscript hereby declare no conflict of interest.

REFERENCES

[1]. Amin, G.C. Wadekar, S.D. and Menta, H.U. (1977). *Indian J. Textile Research;* **3**, 20-23.
[2]. Agnihotri, Mamta and Tiwari Saras (2020). *Elect. J. Adv. Res.;* **6**(2), 1-9.
[3]. Khan, M.U., Tiwari, R.K., Verma, J.K., and Gupta, H.D.(1997). *Oxid. Commun;* **20**(1), 117-123.
[4]. Khan, M.U., Verma, J.K., Nigam, A., Nigam, S.K., Parihar, S.S. and Dwivedi, H.P. (1998). *Oxid. Commun;* **21**(3), 362-368.
[5]. Khan, M.U., Nigam, S.K., Nigam, A., Verma, J.K. and Chauhan, R.P.S. (1995). *Oxid. Commun;* **18**(3), 304-311.
[6]. Manna, Kausik, Panda, Amiya Kumar (2011). *J. Surfact. Deterg;* **14**, 563-576.
[7]. Patil, S, Katre, Y.R. and Singh, A.K. (2007). *J. Surfactants and Detergents;* **10**(3), 175-184.
[8]. Prajapati, Aparna, Dwivedi, Arvind Prasad, and Parihar, Surendra Singh (2019). *Int. J. Adv. Res;* **6**(8) : 1-5.
[9]. Prajapati, Aparna, Dwivedi, A.P. and Parihar, S.S. (2019). *Int. J. Chem. Sc.,* **3**(4), 9-11.
[10]. Patel, K.F., Mehta, H.U. and Shrivastava, H.C. (1974). *J. Appl. Polym. Sci.,* **18**, 389.
[11]. Rao Madhava, B, and Choudhari, U.R. (1989). *Asian J. Chem.;* **1**(4), 318-327.
[12]. Singh, Minu (2014). *J. Soft matter;* Academic Editor Ery Yoshida Hindawi Publication Corporation. Article ID 791563, p. 10.
[13]. Sekar, K.G.: *Asian J. Chem;* (2003). **15**(2) : 423-427.
[14]. Singh, Gunjan, Swami, M.N., Manikpuri, Nagmani (2016). *Elec. J. Adv. Res;* II (1), 1-8.
[15]. Valechha, N.D. and Pandey, A. (1986) : *J. Indian Chem. Soc;* **63**, 679.