

**Study on Micelles Catalyzed Oxidation of Methanol by N-Chlorosaccharin**Neelam Singh^{1*} and M.N. Swami²¹Department of Chemistry, Government Girls P.G. College, Rewa (Madhya Pradesh) India.²Head Department of Chemistry, Government Model College Umaria (Madhya Pradesh) India.

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ABSTRACT: This paper discusses the catalytic behaviour of cetyl trimethyl ammonium bromide (CTAB) of the oxidation of methanol by N-chlorosaccharin (NCSA) in acetic acid-H₂O medium. The degree of dissociation of CTAB Micelles complex with substrate and NCSA of the order of 1 to 0 was reported. The reaction rate was found to increase with increase in H⁺ ion concentration and dielectric constant of the medium. The ionic strength of the medium showed stationary effect on rate. The plausible mechanism and solvophobic effect was verified by rate law and activation parameters.

Keywords: Oxidation, CTAB, Methanol, N-chlorosaccharin, Catalysis.

I. INTRODUCTION

Cationic micelle *i.e.*, cetyl trimethyl ammonium bromide (CTAB) is a complex mixture of organic compound used in colloidal form in various industrial processes which include solubilization, pharmacy and biochemical research [8]. The activity of CTAB lying between homogeneous and heterogeneous catalysis. Micelles catalysed study is mainly due to the reasons that its rate is proportional to the enzyme concentration [2]. The specificity of the CTAB led to the postulate of a "lock-and-key" type of mechanism that follow Michaelis-Menten rate law depending on particular pH. The behaviour of CTAB for practical formulation in aqueous CH₃COOH media would be associated with solvophobic interactions only [6]. It is believed that such a study could provide and shed new light into understanding the catalytic behaviour of cationic surfactant CTAB in oxidation of methanol in aqueous acetic acid medium.

The catalysed studies involving surfactant CTAB systems are well documented in journals and reviews for organic compounds with different oxidants [10, 11, 16].

N-chlorosaccharin is a selective oxidant of halo group possesses ability to produce halonium ion, which an electrophilic is stabilized by resonance and used in oxidative degradation of hydroxy acids, alcohols, ketones, and amino acids [1, 4, 5, 9, 13]. A very few

reports are available for the kinetic mechanistic study of alcohols by N-bromoisonicotinamide and pyridinium hydrobromide and per bromide, etc. [3, 14].

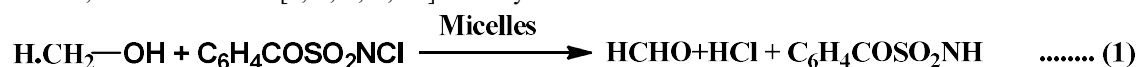
II. MATERIALS AND METHODS

The methanol and CTAB from sigma were of AG grade used without purification as such received. The solution of CH₃OH and NCSA of appropriate concentration was prepared by diluting it in doubly distilled water and acetic acid. The other solutions of reagents pertaining to the foregoing work were prepared of desired strength during the experiments.

The reaction was initiated under the condition [CH₃OH] >> [NCSA] by mixing thermostated solutions of methanol and NCSA in presence of catalyst CTAB at equilibrated desired temperature. The reaction kinetics was monitored for unreacted NCSA by iodometric process at regular intervals of time. The rate constant (k_{obs}) values were determined graphically which lie within ± 3% precision.

III. RESULTS AND DISCUSSION

(a) The stoichiometry of the reaction was determined under prevailing conditions and unconsumed NCSA was estimated iodometrically revealing that the molar ratio (oxidant: methanol) observed 1:1, as depicted in equation.



Formaldehyde was analyzed by modern technique and confirmed by forming 2:4 DNP compound (m.p. = 155°C). The free radical existence was over ruled by the addition of monomer acrylonitrile employing trapping method.

(b) The variation of [NCSA] from 1.00 × 10⁻³ to 5.0 × 10⁻³ (mol dm⁻³) on rate of reaction afford order with respect to oxidant is unity as derived from the graphic slope.

(c) A graphical presentation of the determination of five-fold concentration of CH₃OH on rate at fixed conditions of other participating reagents and temperature (Table 1) gives ample of proof for complex formation at transition state (Plot of k vs. [CH₃OH], showing 1 to 0 order reaction (Fig. 1). This was also verified by double reciprocal plot which yield positive slope on rate axis.

Table 1: Dependence of rate on variation of concentration of methanol.

Sr. No.	$[\text{CH}_3\text{OH}] \times 10^2$ (mol dm ⁻³)	$10^4 \times k$ (s ⁻¹)	$1000 k_2 = \frac{k_1}{[\text{CH}_3\text{OH}]}$ l mol ⁻¹ (s ⁻¹)
1.	1.25	1.00	0.801
2.	2.00	1.52	0.761
3.	2.50	1.68	0.674
4.	4.00	2.02	0.505
5.	5.00	2.36	0.472

[NCSA] = 2.50×10^{-3} (mol dm⁻³); [CTAB] = 2.0×10^{-3} (mol dm⁻³); HOAc-H₂O = 25 %, (v/v); Temperature = 313 K

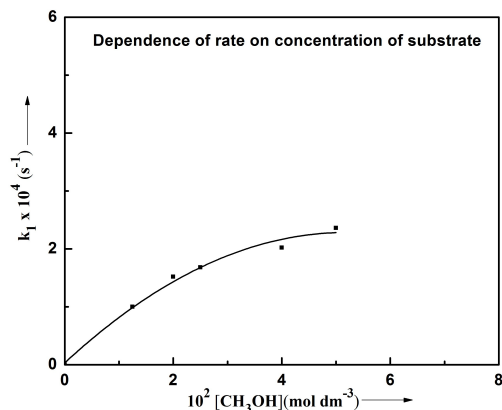


Fig. 1. Plot of k_1 Vs (Substrate).

(d) Appearances of unit slope by calculation (Table 2) catalyze the reaction and is indicative of first-order in the log k vs. log $[\text{H}^+]$ plot (Fig. 2) were found to kinetics for $[\text{H}^+]$ ions.

Table 2: Dependence of rate on the concentration of Sulphuric acid.

Sr. No.	$[\text{H}^+] \times 10^{-3}$ (mol dm ⁻³)	$10^4 \times k$ (s ⁻¹)
1.	0.00	1.52
2.	1.25	1.95
3.	2.00	2.36
4.	2.50	2.65
5.	4.00	3.22
6.	5.00	3.72

$[\text{CH}_3\text{OH}] = 2.0 \times 10^{-2}$ (mol dm⁻³); [NCSA] = 2.50×10^{-3} (mol dm⁻³); [CTAB] = 2.0×10^{-3} (mol dm⁻³); HOAc-H₂O = 25 %, (v/v); Temperature = 313 K

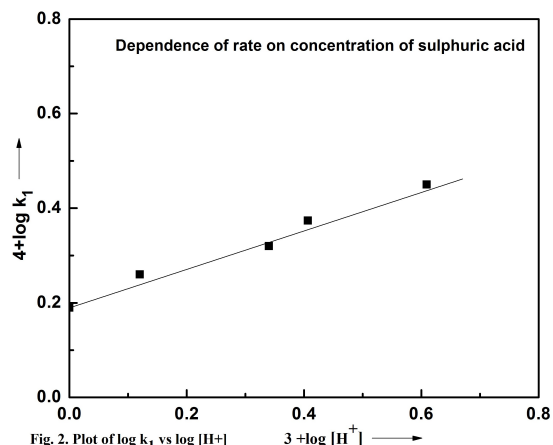


Fig. 2. Plot of $\log k_1$ vs $\log [\text{H}^+]$

$[\text{CH}_3\text{OH}] = 2.0 \times 10^{-2}$ (mol dm⁻³); [NCSA] = 2.50×10^{-3} (mol dm⁻³); [CTAB] = 2.0×10^{-3} (mol dm⁻³); HOAc-H₂O = 25 % (V/V); Temp. = 313K

(e) Acetic acid water mixtures (20-50%, (v/v)), are better solvents for this investigation and influence the permittivity of the medium. An increase in composition of acetic acid increases eventually the resulted rate. The ionic strength of the medium and salt effect on rate was assessed, which was quite negligible. The appearance of retardation in rate was observed as a common phenomenon in the presence of added saccharin, thus ignoring saccharin as a non-participating species in dealing the mechanism [12].

(f) The effect of small sub micellar aggregates of the cationic surfactant CTAB exist below CMC and interact physically with the substrate forming catalytically active entities. The increase in k_{obs} with [CTAB] may be attributed to increasing association/solubilization of the reactant species with

increase in [CTAB] and indicating fractional-order kinetics and later decreases the rate. The reason was observed by Beregin's model and other operative factors such as hydrophobicity, intramolecular rearrangement and the repulsive force between surfactant head groups, significantly in the case of charged surfactant CTAB [7, 15]. Another reason of decrease in k_{obs} could be result of counter ion inhibition.

Mechanism. The similar reaction mechanism pertaining to the present investigation has already been communicated in our previous communication emanated from this laboratory for other aliphatic alcohols [16]. However, rate expression derived, using steady state treatment may be given in the following way:



$$k_{obs} = \frac{k_2 k_1 k [\text{CTAB}] [\text{CH}_3\text{OH}]}{1 + K_1 [\text{CH}_3\text{OH}] + K_1 K_2 [\text{CH}_3\text{OH}]} \dots \dots \dots (6)$$

The equation (6) may be rearranged to equation (7) to prove the existence of complex kinetically by non-zero intercept of the double reciprocal plot of k^{-1} vs. $[\text{CH}_3\text{OH}]^{-1}$.

$$\frac{[\text{CTAB}]}{k_{(obs)}} = \frac{1}{K_2 K_1 [\text{CH}_3\text{OH}]} + \frac{1}{k K_2} \dots \dots \dots (7)$$

Various activation parameters were measured. The equation (7) accounts for all the facts.

CONCLUSION

CTAB catalyzed oxidation of methanol by NCSA was found to proceed through electrophilic attack of reacting species HOCl on alcohol, that leads to the formation of complex at transition state. The stoichiometry was observed 1:1 for the postulated mechanism of reaction between CH_3OH and NCSA. The disproportionation of intermediate in slow steps lead to formation of formaldehyde as main product identified by forming 2:4 -DNP derivative. The proposed mechanism is apparently satisfied by kinetic results.

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Conflict of Interest. None.

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