Apr 2020 - Jun 2020, Vol 6, No. 2, 1-9 ISSN : 2394 -9449 Electronic Journal of Advanced Research

An International Peer review E-Journal of Advanced Research

Research Articles

OXIDATION OF POLY VINYL ALCOHOL BY N-CHLOROSAACCHARIN IN MICELLAR MEDIUM

Mamta Agnihotri¹, Saras Tiwarii²

- 1. Department of Chemistry, A.P.S. University, Rewa (M.P.) India.
- 2. Head Department of Chemistry, Ishwar Chandra Vidyasagar Mahavidyalaya, Jawa, Distt. Rewa (M.P.) India.

	Received : 11-May-2020	Revised : 17-May-2020	Accepted : 29-May-2020
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Abstract: Oxidation of poly (vinyl alcohol) is extensively studied with N-chlorosaccharin to evaluate the activation parameters in a micellar medium in presence of aqueous acetic acid, and transitory complex mechanism through established stoichiometry (1:1). The observed data indicate first-order kinetics with respect to oxidant NCSA and fractional-order to [vinyl alcohol]. The disproportionation of the complex to acetic acid is the rate determining step. The oxidation takes place with splitting of C-H bonds. A mechanism based on kinetic data has been postulated satisfying rate law.

Key words: Poly vinyl alcohol, N-chlorosaccharin, CTAB, Stoichiometry, acetic acid.

INTRODUCTION

Poly vinyl alcohol exhibits many chemical and biological activities such as antimicrobial, anti oxidant anti inflammatory etc. occurring in all cells. Owing to these properties, vinyl alcohol is of chemical, a pharmacological interest. It finds wast and wide applications in textile industries (Rayon and polymers). The molecule of this polymer possesses multiple sites for reaction e.g. methylene group and hydroxyl

group including C-C chain skeleton etc. which is attacked by active species of H_2O^+Cl of halo oxidant (N-hlorosaccharin) in aqueous acetic acid and millelar CTAB medium. Kinetic aspects of this compound is gaining importance due to its growing demand in textile industry and organic synthesis. The reacting species can cleavage either its C-C or -C-H bonds ambiguity always persists.

Involving N-chlorosaccharin oxidation in aqueous acetic acid and CTAB of likewise acetaldehyde,¹ ketones,² alcohols,^{3,4} acids,⁵ have been reported extensively. However, the oxidation of poly vinyl alcohol has not been studied in detail though few information on the kinetic studies with NaOCl,⁶ (NH₄)₂ Cr₂O₇,⁷ K₂S₂O₈,⁸ Ce(IV)⁹ are available in literature. So the author thought it worthwhile to investigate entitled reaction systematically.

MATERIALS AND METHODS

All the materials and solvents used were of high degree of analytical grade with purity. The accurately weighed sample of synthesized NCSA was dissolved in 100% acetic acid (B.D.H.) and its solution was further standardized by iodometric process. PVA solution of moisture free sample was prepared by dissolving its accurately measured quantity in double distilled water, placed at boiling water-bath. This solution was further standardized through an oxidimetric procedure as laid in literature. Other necessary reagent's employed such as H₂SO₄, Na₂S₂O₃ 2HO, CuSO₄, K₂Cr₂O₇, NaOH etc. (all A.G.) solutions were prepared in distilled water and standardized before use wherever necessary by different methods. The requisite amount of commercial sample of CTAB as such obtained is used in reaction.

KINETIC PROCEDURE

The requisite amount of oxidant NCSA and PVA along with other reagents CH_3COOH and CTAB were taken in separate conical flasks placed in a thermostat and allowed to equilibrate at the experimental temperature at $30^{\circ}C$ before mixing for half an hour. The calculated amount of NCSA is added to PVA solution to start the reaction kinetics. The entire kinetic runs were performed in a standard conical Erlenmeyer flask (250 ml) coated with a thick black paint outside. The reaction was monitored for more than 75% completion of the reaction by arresting the reaction mixture (2 ml- aliquot withdrawn quickly) with ice cold water at regular intervals of

time for un-reacted NCSA and titrated against standard hypo solution (0.001 N). The values of rate constants were evaluated by integration and graphical methods.

RESULTS AND DISCUSSION

The influences of variables on the rate of oxidation have been ascribed.

Stoichiometry of the reaction between NCSA and PVA has been determined in duplicate for its two concentrations at experimental conditions by keeping the reaction mixture for 48 hours in thermostat. The observed results indicated that one mole of PVA (monomer) requires one mole of NCSA for complete oxidation as depicted below.

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CH_2 = CH-OH + C_6H_5COSO_2NCI + H_2O = HCI + C_6H_5COSO_2NH + CH_3COOH
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The effect of initial oxidant concentration on the rate of oxidation at 30°C

The initial [NCSA] was varied from 1.25×10^{-3} to 5.0×10^{-3} (mol dm⁻³) maintaining the concentration of other reagents constant. The first-order rate constants were measured from the unit slopes of the linear plots of log (a-x) against 't'. Assessing the overall values of k_{obs} at lower and higher [NCSA] however, the rate does not change appreciably.

Effect of concentration of vinyl alcohol (monomer) on the rate of reaction

The fractional-order kinetics was observed for variation of five-fold concentrate of vinyl alcohol at fixed reaction conditions (Table 1). As the reaction progressed, the k_{obs} diminishes and drifted gradually towards X-axis. In all subsequent measurements, 0.50 to 2.5×10^{-2} (mol dm⁻³) concentration of (PVA) was used through this investigation. The inverse plot of k_{obs} against [PVA]⁻¹ yields positive intercept on Y-axis (Fig.1). proves the existence of activated complex formed between reacting molecular species of oxidant NCSA and hydrated form of PVA as acetaldehyde.

Table 1 : Effect of varying concentration of vinyl alcohol on the rate of reaction

 $[NCSA] = 2.0 \times 10^{-3} \text{ (mol dm}^{-3}); [CTAB] = 0.50 \times 10^{-3} \text{ (mol dm}^{-3});$ CH₃COOH-H₂O = 30 % (v/v); Temp. = 303 K Jan 2020 - Mar 2020, Vol 6, No. 2, 1-9 Research Articles : OXIDATION OF POLY VINYL ALCOHOL BY N-CHLOROSAACCHARIN IN MICELLAR MEDIUM

S. No.	[Vinyl alcohol] ×10 ² (mol dm ⁻³)	Rate constant (k) \times 10 ⁴ k (s ⁻¹)
1.	1.00	1.86
2.	1.25	3.01
3.	1.50	3.55
4.	2.00	4.61
5.	2.50	4.92



The reaction between PVA and NCSA was studied at several (0.25 to 1.25 $\times 10^{-3}$ mol dm⁻³) H₂SO₄ concentrations at 30^o C. Though the reaction was found acid catalysed but at its higher concentrations, rate becomes extremely slower than that of the rate determined in micellar CTAB medium.

Effect of Micellar CTAB on rate

The initial concentration of micelle CTAB was varied under CMC range (0.50 to 3.33×10^{-3} mol dm⁻³) both as medium and catalyst keeping the concentration of other participating reactants constant at fixed temperature and kinetic data are given in Table 2.

Table 2 : Effect of concentration of Micellar cetyl trimethyl ammonium bromide(CTAB) on the rate of reaction

[Poly vinyl alcohol] = 0.50×10^{-2} (mol dm⁻³); [NCSA] = 2.0×10^{-3} (mol dm⁻³);

 $CH_3COOH-H_2O = 30 \% (v/v)$; Temp. = 303 K

S. No.	[Vinyl alcohol] ×10 ² (mol dm ⁻³)	Rate constant (k) $\times 10^4$ k (s ⁻¹)
1.	0.50	1.86
2.	0.80	2.27
3.	1.25	2.60
4.	1.50	3.11
5.	2.00	3.57
6.	2.50	3.92
7.	3.33	4.31



The rate is catalysed in the initial stage and slows down as the reaction progressed at its higher [CTAB]. In presence of an acid with high dielectric constant of the medium CTAB is polymerised and slower the rate of oxidation followed by an intra molecular rearrangement. This fact is evidenced by plot of k against [CTAB] as depicted in (Fig. 2).

The rate of reaction has shown accelerating effect by increasing different composition of acetic acid whereas addition of saccharin and neutral salt (NaCl) to reaction mixture former lead to exhibit retarding trend and later insignificant effect on rate. The more negative value of entropy of activation would need greater orientation and order prior to commencement of the reaction.

MECHANISM

Vinyl alcohol undergoes isomerization to acetaldehyde shows oxidation



where, M* stands for cationic micellar CTAB.



Rate law

The derived rate law can be depicted below:

The inverse of k_{obs} may be written from equation (7) as:

$$\frac{M^*}{k_{abs}} = \frac{1}{k_1 K_1 K_2 [vinyl alcohol]} + \frac{1}{k_1 K_2} \dots \dots \dots (7)$$

This equation (7) explains all the observed results.

The unstable vinyl alcohol (monomer) isomerises into acetaldehyde. The hydrated form of acetaldehyde followed by complexation with micellar CTAB yields an intermediary complex (c). This complex (c) on further oxidation with NCSA molecular results complex(X) which finally yields acetic acid with C-H bond fission in slow process and potential energy is not accessible.

The aggregate effects of Micellar CTAB have been studied using Beregin's model. The CMC critically depends on the interactions with vinyl alcohol (monomer) to form activated complex with cationic head group of the surfactant CTAB. The loss of entropy of activation indicates that more ordered complex is (-98.33 JK⁻¹ mole⁻¹) formed and value (52.76 kJ mole⁻¹) of enthalpy ($\Delta H^{\#}$) shows that transition state is highly solvated.

Conclusion

The poly vinyl alcohol (monomer) isomerises to acetaldehyde and its hydrated form participates in the reaction with postulated molecular species NCSA and polymerized CTAB to form transitory activated complex. The complex on disproportionation by C-H bond fission yields acetic acid.

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