

Catalysed Oxidation Study of Primary Alcohols (propanol and butanol) by N-chloroisonicotinamide in Aqueous Acetic Acid Medium

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Abstract: Keggin-type phosphotungstic acid catalyzed oxidation of (propanol and butanol) by N-chloroisonicotinamide have been investigated in aqueous acetic acid medium in presence of mineral acid H₂SO₄ to afford corresponding products aldehydes. The redox reaction indicates a first-order dependence in [NCIN] and fractional order on alcohol and PTA. The existence of complex was established and substantiated by Michaelis-Menten equation. The variation of H⁺ ion, isonicotinamide and neutral salts have insignificant effect on rate on oxidation based on observed results two plausible mechanism are postulated one protonated in slow step and the other non-protonated of reacting species in the slow step. The stoichiometry 1:1 and thermodynamic parameters supports the proposed mechanism and rate law.

Key words: Propanol, Butanol, N-chloroisonicotinamide, Phosphotungstic acid, Kinetics.

1. INTRODUCTION

Nowadays under ordinary conditions oxidation of organic substrate is slow and requires various metals, ions, with higher oxidation state and redox potential more than 1.0 volt as a catalysts^[1] for feasibility of the reaction. It has long been known that tungston compounds and their polyoxometallates are efficient catalyst^[2] for oxidation because having high electron density. Owing to outer-sphere electron transfer reagent^[3] and the properties of the metal ions gets altered increasing its stability considerably in aqueous solution^[4] along with it can be recycled without loss of its activity PTA is a catalyst of prime importance in the oxidation of organic compounds, such as alcohols,^[5-7] amines,^[8] hydroxy acids,^[9] amines,^[10] styrene,^[11] etc.

NCIN is a mild and versatile oxidant widely used in biotechnology with reference to analysis of antimicrobial activity and acts as source of positive halogen ions. The literature shows that it produces HOCl has a powerful prime reacting species of this reagent. This potential oxidant plays very important role in biochemical processes occurring in cellular respiration.

The review of the literature reveals that very few kinetic studies of organic compounds are documented for alcohols,^[12] acids,^[13] amines,^[14] hydroxy acids,^[15] etc. with NCIN. The kinetics and mechanistic investigations of the oxidation of primary aliphatic alcohols by various oxidizing agents (QCC,^[16] PBC,^[17] CAT.^[18] etc.) have been earlier. The present work aims to explore the kinetics and mechanism of PTA catalyzed oxidation of propanol and butanol by N-chloroisonicotinamide in aqueous acetic acid medium.

2. EXPERIMENTAL

The oxidant NCIN (Across Sample) was used and its solution was prepared in acetic acid (B.D.H.) purified by the literature and standardized iodometrically. To avoid photochemical effect this solution was stored in a dark place. Its strain was checked iodometrically^[19] before using in experiment. The standard solution of propanol and butanol (B.D.H. sample) was prepared in distilled water and in acetic acid.

PTA solution was prepared by dissolving its known weight in boiling water acidified with HCl of known concentration in order to maintain pH few drops of acetones are also added to established in solution.

Its strength was checked time to time by the standard as laid down in literature.^[20] Several useful solutions related to kinetic investigation were also prepared and used in standardized form wherever necessary.

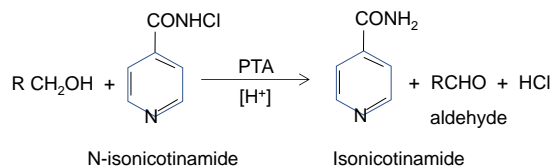
Kinetic measurements

The kinetic study was performed at temperature 313 and 318 K respectively in a thermostated water bath ($\pm 0.1^\circ\text{C}$). The calculated volume of oxidant, NCIN was contained in a conical vessel immersed in a water bath maintained at desire temperature the rest of the reagents solutions including PTA, alcohol, H⁺ ion, acetic acid were contained in a another flask kept in a same water bath for half an hour to attend the equilibrium temperature, The reaction was initiated by mixing solution of NCIN oxidant to substrate solution.

The kinetics were followed under pseudo first order condition with [alcohol] in excess. The progress of the reaction was followed by measuring the concentration of NCIN unused periodically at different intervals of time. The rate constant of each reaction was calculated by integration and graphical methods. The first-order rate constant were obtained from the linear plot of [NCIN] vs. time, For about 80% completion of the reaction the values of k_{obs} were reproducible within $\pm 3\%$.

4. Results and Discussion

The stoichiometry of both the reaction were determined under laid down previous conditions of the reactions. The results indicates that 1 mole of oxidants, NCIN had reacted with 1 mole of primary alcohols according to equation-1.



where, R = CH₂CH₃ and -CH₂CH₂CH₃ for propanol and butanol respectively.

The end products of the reactions were found propionaldehyde and butyraldehyde which were identified chromatographically and also by forming their 2,4-diphenylhydrazine further characterization was done by determination of their melting points. On treatment of reaction mixture with equil-amide does not cause to produce polymerization, Hence presence of free radicals based mechanism is completely ruled out.

(a) The reaction order was assigned from the plots of log [NCIN] vs. time. The order with respect to NCIN in the 1.25 × 10⁻³ to 5.0 × 10⁻³ mol dm⁻³ concentration range was found to be unity at constant reagents temperature and ionic strength of the medium for about 80% completion of the reaction.

(b) The order with respect to aliphatic primary alcohols was determined by varying their concentration [1.00 × 10⁻²] to [6.25 × 10⁻²] mol dm⁻³ maintaining the concentration of oxidant ionic strength and temperature constant. The rate of oxidation indicates first-order dependence on substrate but at intermediate concentrations its shows fractional- order. The study reveals the formation of complex between reacting species of oxidant and alcohol at open point of transition states. The effect of initially added products isonicotinamide, neutral salts, and H⁺ ion in wide range of concentrations observed that they had no any significant effect on the reaction rate, the order for H⁺ ion concentration was derived to be the less than unity.

(c) The formation of complex was also proved kinetically by the non-zero intercept obtained from the plot of $\frac{1}{k_{obs}}$ vs. $\frac{1}{[PTA]}$ (Fig. 1) i.e. the effect of Keggin anion PTA shows fractional-order kinetics (Table 1). Though proton is released during the reaction by PTA is not sufficient and responsible for protonation of oxidant. During formation of complex the outer sphere reagents of PTA is used by the replacement of one of the water molecules of hydration in transition state under tungstate framework.

Table 1: Effect of Dielectric constant of the medium on rate

10³ × [NCIN] (mol dm⁻³) = 2.50 (1, 2); 10⁵ × [PTA] (mol dm⁻³) = 2.0 (1, 2);

10² × [Primary alcohol] (mol dm⁻³) = 2.0 (2), 2.50 (1); [H⁺] (mol dm⁻³) = 0.20 (1, 2); CH₃COOH-H₂O %, (v/v) = 30 (1), 40 (2); Temperature K = 318 (1), 313 (2)

CH ₃ COOH-H ₂ O % (v/v)	10 ⁵ × 1/D	← 10 ⁴ k (s ⁻¹) →	
		CH ₃ CH ₂ CH ₂ OH	CH ₃ (CH ₂) ₃ OH
20	17.17	-	-
30	19.15	2.43	3.15
40	21.98	2.94	3.71
50	25.64	3.74	4.39
60	30.36	5.03	5.95

1. Propanol, 2. Butanol.

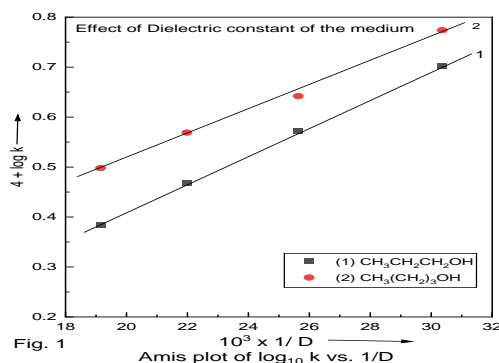


Fig. 1

Amis plot of log₁₀ k vs. 1/D
 10³ × [NCIN] = (mol dm⁻³) = 2.50 (1, 2);
 10² × [Primary alcohol] (mol dm⁻³) = 2.0(2), 2.50 (1);
 [H⁺] (mol dm⁻³) = 0.20 (1, 2);
 10⁵ [PTA] (mol dm⁻³) = 2.0 (1, 2);
 Temp. K = 318(1), 313 (2)

(d) The oxidation rate of alcohol was collected by varying solvent composition range (30% to 60%, (v/v)). The result envisaged the rate of reaction accelerated by decrease in dielectric constant of the medium (Table 2). The linear plot of $\log k$ vs. $\frac{1}{D}$ or $\frac{D-1}{2D+1}$ (Fig. 2) yields positive slopes shows that reaction is ion-ion dipole type the results was found in good agreement with the Amis concept of solvent systems.

Table 2: Dependence of rate on [PTA] catalyst

$10^2 \times [\text{alcohol}]$ (mol dm⁻³) = 2.0 (2), 2.50 (1) ; $10^3 \times [\text{NCIN}]$ (mol dm⁻³) = 2.50 (1, 2) ;
 [PTA] (mol dm⁻³) = 2.0 (1, 2) ; CH₃COOH-H₂O %, (v/v) = 40 (1, 2) ;
 Temperature K = 313 (1), 318 (2)

10 ⁵ [PTA] (mol dm ⁻³)	6 + log [PTA]	CH ₃ (CH ₂) ₂ OH		CH ₃ (CH ₂) ₃ OH	
		10 ⁴ k (sec ⁻¹)	4 + log k	10 ⁴ k (sec ⁻¹)	4 + log k
1.00	1.0000	2.40	0.3802	2.75	0.4393
1.50	1.1760	2.69	0.4297	3.36	0.5263
2.00	1.3010	2.94	0.4683	3.71	0.5693
2.50	1.3979	3.23	0.5092	3.95	0.5965
3.33	1.5224	3.48	0.5415	4.21	0.6242
4.00	1.6020	3.51	0.5453	4.15	0.6180
5.00	1.6989	-	-	-	-

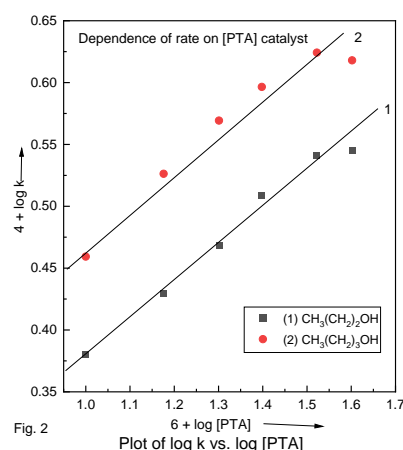


Fig. 2

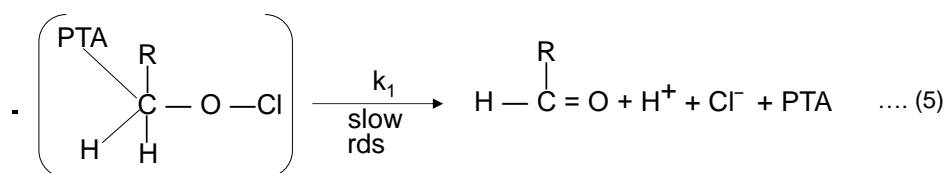
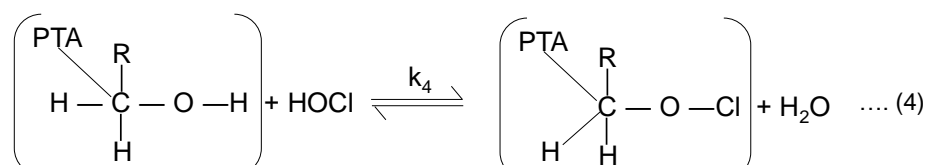
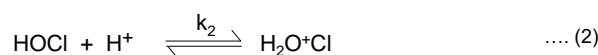
Plot of $\log k$ vs. $\log [\text{PTA}]$
 $10^2 \times [\text{alcohol}]$ (mol dm⁻³) = 2.0 (2), 2.50 (1) ;
 $10^3 \times [\text{NCIN}]$ (mol dm⁻³) = 2.50 (1, 2) ;
 $[\text{H}^+]$ (mol dm⁻³) = 0.20 (2), 0.25 (1) ;
 $10^2 \times [\text{PTA}]$ (mol dm⁻³) = 2.0 (1, 2) ;
 CH₃COOH-H₂O %, (v/v) = 40 (1, 2) ;
 Temp. K = 313 (1), 318 (2)

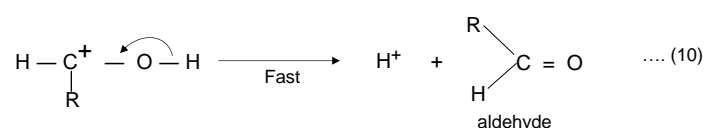
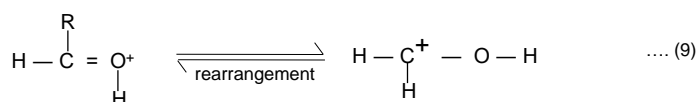
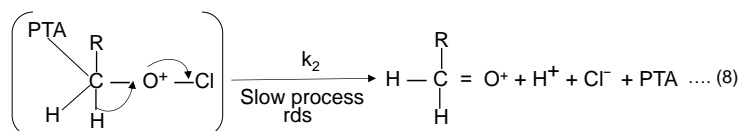
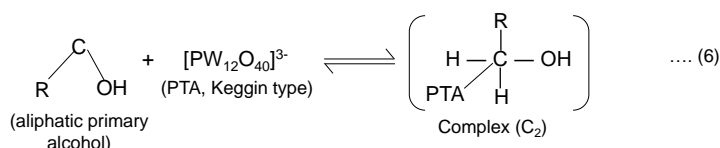
The authors have been chosen HOCl and protonated form H₂O⁺Cl of species of oxidant NCIN based on assessing the earlier cited kinetic results of the reactions for the mechanism.

Reaction Mechanism

The experimental results, stoichiometry (1:1) and reacting species HOCl and H₂O⁺Cl leads the formulation of the proposed mechanism in two schemes.

Scheme-1 (Non protonated path)



Scheme-2 (Protonated path of the reaction)

and

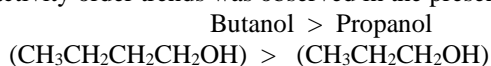
$$k_{obs} = \frac{[Rate]}{[NCIN]_t} \dots \dots (14)$$

Substituting the values of $[X_1^{**}]$ and $[X_2^{**}]$ From equation (11) to equation (14) in order to get final expression for rate law.

$$k_{obs} = \frac{k_1 k_3 [substrate] [PTA] (k_1 k_4 + k_2 k_3 [H^+])}{[Isonicotinamide] + k_1 + k_1 k_3 k_4 [PTA]} \dots \dots (15)$$

Equation (15) is in good agreement with the kinetic results obtained for the said reactions, the rate law also validities Michaelis-Menten equation.

The reactivity order trends was observed in the present investigation is



The reactivity and structure trend have been justified based on several operational factor operating in them like polar nature differing in chain length configuration co-related with rate, inductive effect, size of the molecules, and thermodynamic parameters etc. It has been earlier reported that faster rate of the butanol was found by decreasing chain length and propanol has the lowest alcoholic percentage content whereas butanol has the highest.

The above order of reactivity and complex formation may also be explained by thermodynamically as under the large negative value of entropy of activation reveals that polar and solvated complex is formed at the transition state ΔS^\ddagger values is lost in transitional energy and presents the rotational freedom of the molecule, besides this the value of energy of activation is lower than that of propanol (Table 3). In addition to this almost similar gives free energy indicates that similar mechanism appears in the present reaction paving the way to conclude that reactions are enthalpy controlled.

Table 3. Activation parameters for NCIN-alcohol systems

Alcohol	E_a (kJ/mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
CH ₃ CH ₂ OH (Propanol)	52.96	50.88	89.96	121.87
CH ₃ (CH ₂) ₃ OH (Butanol)	50.70	41.14	86.61	144.17

Conclusion

PTA [Keggin type anion] forms the complex between substrate and to reacting species HOCl and protonated H₂O⁺Cl stoichiometrically (1:1), which then disproportionate in slow process to yield corresponding aldehydes. The reactions provides test for Michaelis-Menten of kinetics, the order with respect to oxidant is unity whereas fractional-order was observed each to catalyst [PTA] [H⁺] ions etc. Two schemes of mechanism non-protonated and protonated paths were assigned which were supported by physical and it activation parameters.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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