

Oxidative Transformation of Propan-1-ol Ce (IV) Oxidants (CAN) in Acetonitrile-Water medium, A Kinetic and Mechanistic Study

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Abstract

Oxidation of Propan-1-ol by Ceric Ammonium Nitrate(CAN) in Acetonitrile-Water medium leads to the formation of aldehyde. The reaction is first order with respect to [substrate] concentration in . Michaelies-Menten type of kinetics is observed with respect to the Propan-1-ol.. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has taking the form $k_{obs} = a + b [H^+]$. The oxidation of Propan-1-ol has been studied in different organic solvents. The solvent effect has been observed by using Kamlet's and Swain's multiparametric equations.all experiments were operated at 400 nm.

Keywords: propan-1-ol, kinetics, mechanism, oxidation,

INTRODUCTION

Salts of Ce(IV) have long been used as oxidizing reagents in synthetic organic chemistry.kinetics of oxidation of propan-1-ol by pyridinium chloro chromate(PCC) hve been studied in acetonitrile medium in the presence of PTSA at 308 K .The reaction shows first order with respect to [Substrate]and $[H^+]$.The rate of oxidation increases with decrease in dielectric constant in solvent ^[1] Kinetic

of oxidation of aliphatic alcohol by various oxidizing agents has been well studied^[2]. Kinetic study of methanol, ethanol and propanol by Ce(IV) in presence of HClO₄ in acetonitrile medium.^[3] Kinetics study of Cerium (IV) oxidation of ethanol, 1-propanol, propan-2-ol, 1-butanol and 2-butanol were studied^[4] at 30°C.

MATERIALS AND METHODS

The propan-1-ol and glacial acetic acid were commercial products and were used as such. All reagents were A.R. grade which we use for analysis. CAN was prepared by method described by Smith et al^[5]. The purity of oxidants was checked by spectral analysis. Propan-1-ol was used with 99% pure. Glacial acetic acid was used as a source of [H⁺] ions. The kinetics of alcohol was studied in various acetonitrile-water mixtures at different temperatures. Acetonitrile is used as a medium polarity solvent that is miscible with water. The solution of oxidant, alcohol in aqueous solvent in acidic medium follows Beer Lambert's law i.e. plot of absorbance v/s oxidant is a straight line. The reaction conditions are arranged as pseudo first order. The reaction mixture was prepared by mixing the required amount in a thermostatic bath maintained at constant temperature (308K ± 0.1) for reaction. The optical density of the reaction mixture was measured by spectrophotometer at 400 nm by using Systronics VISISCAN 167 spectrophotometer.

Stoichiometry

Product analysis was carried out under kinetic conditions. After completion of reaction, whole reaction mixture was treated with 2,4-dinitrophenylhydrazine. The oxidation of Propan-1-ol by CAN leads to the formation of Propionaldehyde. Confirmation of carbonyl (aldehyde/ketone) compound was done by melting point, IR and nitrogen percentage analysis of precipitate obtained.

Kinetic Measurements : Beer Lambert's law was followed by reaction mixture of Oxidant, Alcohol in Aqueous solvent in acidic medium. So, plot between absorbance v/s Oxidant gives a straight line. The reaction conditions are arranged as pseudo first order. The pseudo-first-order rate constant k_{obs} was computed from the linear least-squares plot of $\log v/s$ time. All reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions. The reaction mixture was prepared by mixing the required amount in a thermostatic bath maintained at constant temperature (± 0.1K) for reaction. The optical density of the reaction mixture was measured by spectrophotometer at 400 nm by using Systronics VISISCAN 167 spectrophotometer.

RESULTS AND DISCUSSION-

Effect of oxidant concentration - The reactions are of first order with respect to Ceric Ammonium Nitrate (CAN) i.e. log absorbance versus time is straight line for more than 85% reaction. The first-order rate constants are independent of the initial concentration of the [CAN] when varied in the range $(2-7) \times 10^{-3} \text{ mol/dm}^{-3}$ at 30 °C.

Effect of substrate concentration - The rate of oxidation increased by increasing the concentration of alcohols. The plot of $\log k_{\text{obs}}$ v/s $\log [s]$ is a straight line. The effect of substrate (alcohol) concentration on this reaction rate was studied at constant [CAN], [acetic acid], temperature and acetonitrile. this oxidation proceeds through the formation of a complex between the oxidant and the substrate. and follows Michaelis-Menten-type kinetics. [Table1]

Effect of [H⁺] ion concentration - The reaction was studied at different acidities by adding varying amount of Glacial acetic acid(AcOH) to the reaction mixtures. Since there is no effect of ionic strength on reaction rate, therefore, ionic strength was not kept constant in this experiment. The hydrogen-ion dependence has the form $k_{\text{obs}} = a + b [H^+]$. The rate of oxidation was studied from $[H^+] = 2 \text{ to } 5 \times 10^{-2}$ the rate increases with an increase in hydrogen ion concentration. [Table1]

Effect of Solvent composition- The study effect of solvent was changing proportion of water and acetonitrile percentage composition was varied from 10 to 50 % acetonitrile [6]. At constant [H⁺] the rate of oxidation changes in the percentage of water in acetonitrile. changing proportion of water and acetonitrile percentage composition was varied from 40 to 60 % Rate of oxidative transformation enhanced with increasing the percentage composition of acetonitrile. The rate of oxidation increases with decrease in dielectric constant. acetonitrile v/v. a plot of $\log k$ v/s $1/D$ in liner with a positive slope for alcohols understudy this slope an ion-dipole type of interaction^[7] in the rate determined step^[8] [Table1]

Effect of temperature- Rate of oxidation of 1-propanol was studied at various temperature The rate of oxidation increases with an increase in temperature. the variation in 1-propanol concentration was studied in (303 K to 323 K) temperatures and the plot of $\log k_{\text{obs}}$ v/s $1/T$ is a straight line. The negative value suggests the formation of a cyclic intermediate from non cyclic reactants in the rate determining step^[9] This shows that the Arrhenius equation is valid for this oxidation. ([Table-2] The thermodynamic parameters for the complex formation are calculated in table 3.

CONCLUSION- The kinetics of Propan-1-ol was studied in acetonitrile. The rate of oxidation increases by increasing substrate concentration. The reaction is found to be first order in respect of CAN. Plot of $\log k_{\text{obs}}$ vs. $\log [\text{Substrate}]$ gave a straight-line with

slope ≈ 1 showed first order dependence over substrate. study of Propan-1-ol is first-order kinetics with respect to oxidant and hydrogen ions this reaction is catalyzed by $[H^+]$ ions the reaction exhibited Michaelis-Menten type kinetics with respect to the aliphatic alcohol. entropy of activation is large and positive, the reaction will be normal and fast but if it is negative, the reaction is slow ^[10]The reaction was studied at different temperatures (308K to 323K). The negative values of entropy indicates that the complex is more orderd than reactant .

TABLE NO. 1
Effect of [Substrate], $[H^+]$ and [Solvent]
CAN= 3×10^{-2} T= 308K

Substrate $\times 10^2 \text{ Mol dm}^{-3}$	[Acetic acid] $\times 10^2 \text{ Mol dm}^{-1}$	Percentage of H ₂ O in acetonitrile	$K_{\text{obs}} \times 10^5 \text{ sec}^{-1}$ Propan-1-ol
2.0	2.0	50	11.19
3.0	2.0	50	13.73
4.0	2.0	50	15.19
5.0	2.0	50	17.03
6.0	2.0	50	18.63
2.0	2.0	50	11.19
2.0	3.0	50	13.21
2.0	4.0	50	15.2
2.0	5.0	50	15.89
2.0	6.0	50	17.03
2.0	2.0	50	11.89
2.0	2.0	40	17.01
2.0	2.0	30	21.19
2.0	2.0	20	33.19
2.0	2.0	10	48.18

TABLE NO. 2

[SUBSTRATE] = 2.0×10^{-2} M [ACETIC ACID] = 2×10^{-2} M

Temperature(K)	303 K	308 K	313 K	318 K	323 K
Propan-1-ol	11.19	18.13	23.19	32.54	45.62

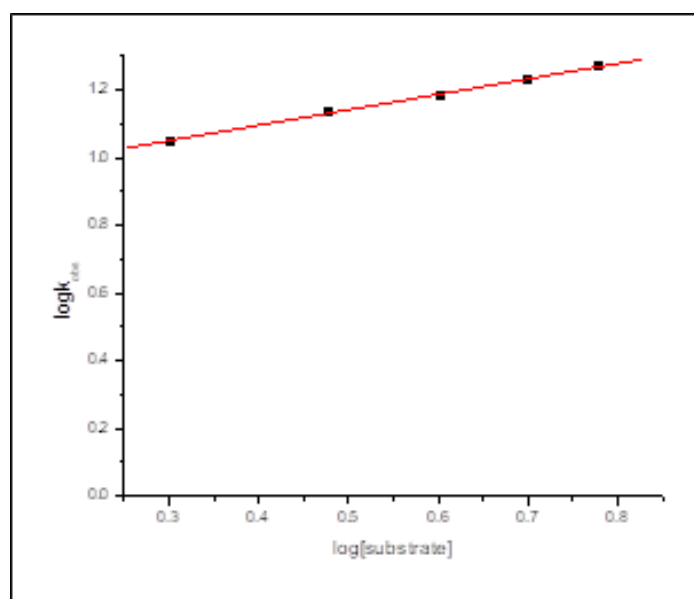


Figure1: Effect of Substrate Concentration

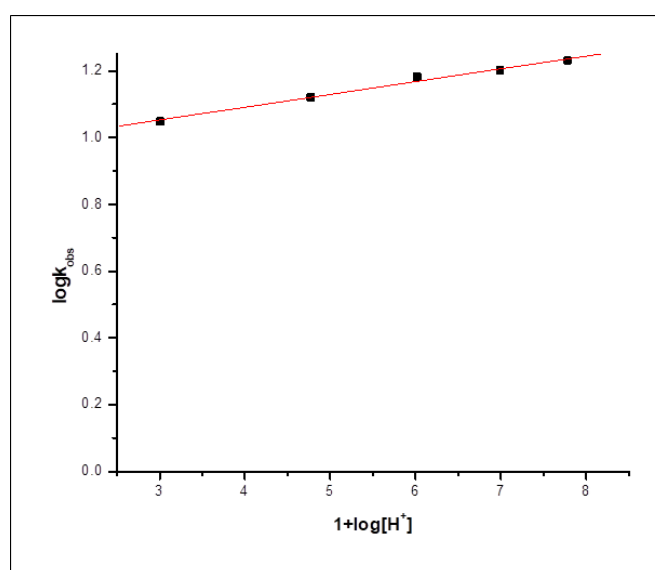


Figure2: Effect of acid Concentration

TABLE NO. 3

Thermodynamic parameters:-

Substrate	Thermodynamic parameter				
	Ea KJ mol ⁻¹	Log A	ΔS J mol ⁻¹ K ⁻¹	ΔH KJ mol ⁻¹	ΔG KJ mol ⁻¹
Propan-1-ol	54.37	8.81	-80.04	51.85	76.10

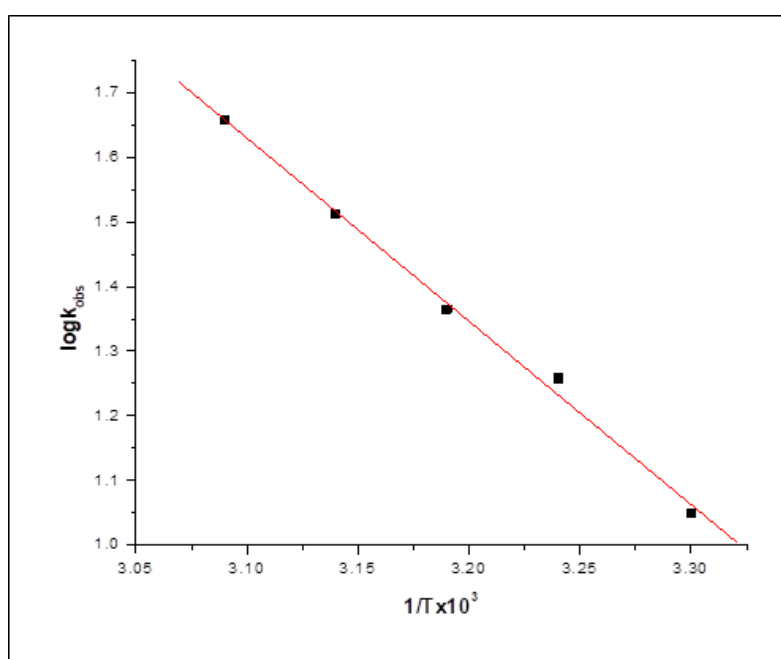


Figure3: Variation of rate with Temperature

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