

Oxidative transformations of aliphatic alcohols using Ce(IV) - Kinetic and mechanistic study

Mamta Baser^{1*}, B. K. Dangarh², Y. K. Mishra³

¹Research Scholar, Vikram University, Ujjain, Madhya Pradesh, INDIA.

²Asstt Professor, Department of Chemistry, Govt. P.G. College, Neemuch, Madhya Pradesh, INDIA.

³Professor, Department of Chemistry, Government Arts and Science College, Ratlam, Madhya Pradesh, INDIA.

Email:

Abstract

The comparative study of oxidation of methanol and ethanol by Ceric ammonium nitrate has been studied spectrophotometrically at $\lambda_{\max}=400\text{nm}$ in the presence of perchloric acid in acetonitrile-water (v/v) medium. The reactions are found first order with respect to [oxidant], [H⁺], and [substrate]. Michaelis-Menten type kinetics was observed. The reaction was studied at different temperature. A possible mechanism is proposed here. There is good agreement between the observed and calculated rate constant under different experimental conditions. The activation parameters were calculated and discussed with respect to the slow step of the proposed mechanism.

Key Word: Oxidation by alcohol, Ceric ammonium nitrate [CAN], oxidation, Kinetics.

*Address for Correspondence:

Dr. Mamta Baser, Research Scholar, Vikram University, Ujjain, Madhya Pradesh, INDIA.

Email:

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INTRODUCTION

Kinetics of cerium(IV) oxidation of aliphatic alcohol ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol were studied¹ at 30 °C in the presence and absence of surfactants in acidic medium. Ethanol can be oxidized to acetaldehyde and acetic acid². Secondary alcohols are oxidized to the corresponding kinetics tertiary alcohols³. Ceric ammonium nitrate (CAN) is a powerful oxidant that has many uses in organic synthesis⁴. CTACN has been used to oxidize some primary aliphatic alicyclic alcohols in acetonitrile medium and reaction kinetics have been investigated but spectrophotometric method⁵. Ir(III) catalyzed oxidation of ethylene glycol by Ce(IV) in sulphuric acid medium has been investigated by titrimetric technique⁶ of redox in the different temperature range. Ceria nanoparticles⁷ as a support stabilize positive

gold species in aerobic oxidation of primary and secondary alcohols. Ce(IV) support catalyst monomeric Ru(IV)⁸ ceria-zirconia supported platinum catalysts⁹ in oxidation of alcohol. The study of in situ reduction of Ce⁴⁺ to Ce³⁺ a time-resolved X-ray absorption spectroscopy¹⁰. The oxidation of Benzyl alcohol, 2-Hydroxy benzyl alcohol, methanol, ethanol by ceric ammonium nitrate has been studied spectrophotometrically, in the presence of glacial acetic acid¹¹, in acetonitrile as solvent.

METHOD AND MATERIAL

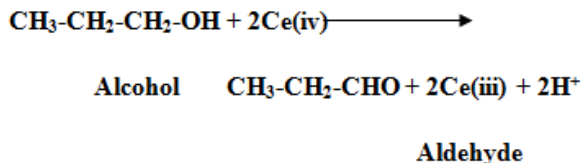
Ceric ammonium nitrate was prepared by the method of Smith *et al*¹² and its purity was checked by iodometrically and melting point. All alcohols (A.R. grade) (SRL) were used as supplied and purity was checked by its melting point. All other chemicals used in this investigation were of analytical reagent grade. The rate measurements were carried out at 35°C in HClO₄ under the condition [alcohol] >> [CAN], in the solvent system of 10-50 % (v/v) acetonitrile-H₂O. The progress of the reaction was followed by measuring the absorbance of CAN at 400 nm in one cm cell placed in the compartment of Systronics VISISCAN-167 spectrophotometer. The kinetics run were followed for good first order kinetics were observed.

RESULTS AND DISCUSSION

Stoichiometry and product analysis: The rate and experimental data were obtained for all the alcohols.

The oxidation of 1-propanol resulted in the formation of the corresponding propanaldehyde. The overall reaction may be represented as follows:

The stoichiometry of the reaction was found to correspond to the equation



Aldehyde

The Stoichiometry of the reaction was found to correspond to the equation. The qualitative product study was made under kinetic conditions i.e. with an excess of substrate over the oxidant. The product of oxidation was corresponding aldehyde i.e. aldehyde and was identified by its 2, 4-dinitro phenyl hydrazine derivative.

Effect of Substrate: The effect of alcohol concentration on the reaction rate was studied at constant [CAN], [HClO₄], temperature and acetonitrile. The reaction rate is increasing of alcohol concentrations. When the logarithms of k_{obs} values were plotted against the logarithms of the [alcohol], (figure 1) a linear plot was obtained. The plot of $1/k_{\text{obs}}$ versus $1/[\text{alcohol}]$, was found to be linear with positive intercept, indicated that Michaelis-Menten type kinetics is followed with respect to alcohol but the value of intercept is very small indicates that intermediate complex may be highly reactive so concentration will be very small at of the the rate of oxidation of some alcohols with CAN can be expresses as.

$$d[\text{CAN}] / dt = k[\text{alcohol}] [\text{CAN}] / k_M + [\text{alcohol}]$$

Effect of HClO₄: The effect of hydrogen ion concentration on the rate of the oxidation was studied by varying [H⁺] while keeping the concentration of another reactants constant. Since there is no effect of ionic strength on reaction rate therefore ionic strength was not kept constant in this experiment. A steady increase in oxidation rate with increase in the medium suggests the formation of protonated CAN in the rate determining step. The plot of log k_{obs} against log [H⁺] is linear.

Effect of Solvent composition: Effect of solvent was studied by changing proportion of acetonitrile and water; varied from 50 % acetonitrile v/v. the reaction rate increased with an increase in the percentage of acetonitrile, suggesting that a low dielectric medium favors the oxidation (Table-1). A plot of log k v/s $1/D$ (dielectric constant) in linear with a positive slope for the amino acids under study. This indicates an ion-dipole type of interaction in the rate-determining step.

Effect of Temperature and determination of activation parameters:

Rate of oxidation reactions increases with increase in temperature. Rate of reactions were determined at different temperature. In all the cases, a plot of log k_{obs} versus $1/T$ (inverse of absolute temperature) is a straight line. This shows that Arrhenius equation is valid for this oxidation. The energy of activation ranges between 54.75 and 48.19 kJ mol⁻¹. The entropy values are all negative and high value observe (Table-2).

CONCLUSION

The kinetics of oxidation of Methanol and Ethanol by Ceric ammonium nitrate (CAN), it has been found that the reactions was first order with respect to [CAN] and rate is almost independent of substrate concentration. The reactions are catalyzed by an acid [H⁺]. The decrease in dielectric constant increases the rate of reaction significantly. The rate of reaction increases with temperature and the various activation parameters are evaluated. A suitable mechanism is proposed involving the hydride ion transfer in rate determining step. The negative values of entropy of activation come under a category of slow reactions. In these oxidation reaction negative values of entropy suggest either formation of cyclic structure from non-cyclic structure or the activated state is more polar than the reactants.

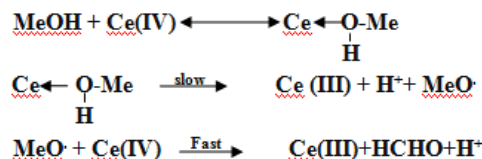


Table 1: Effect of [substrate], [h⁺], [solvent], [can] = 3 x 10⁻³ m, t = 308 k

[Substrate]X10 ² M	[HClO ₄]X10 ² M	%of H ₂ O [InAcetonitril-Water Mix.]	Methanol	Ethanol
2	0	0	128.84	82.42
3	0	0	205.49	123.85705
4	0	0	271.52	170.20
5	0	0	344.39	219.23
6	0	0	432.66	265.98
2	2	0	128.84	82.42
2	2.5	0	190.60	114.27
2	3	0	240.30	151.00
2	3.5	0	308.82	185.38
2	4	0	377.64	219.23
2	4.5	0	444.57	252.76
2	5	0	517.68	294.58
2	2	10	101.56	68.58
2	2	20	79.82	56.61
2	2	30	59.83	47.22
2	2	40	48.27	38.03
2	2	50	37.49	31.35

Table 2: Thermodynamic parameters

[SUBSTRATE] E]X10 ² M	log A	Energy of activation ΔE^\ddagger kJ mol ⁻¹	Entropy of activation ΔS^\ddagger JK ⁻¹ mol ⁻¹	Free energy of activation ΔG^\ddagger kJ mol ⁻¹	Enthalpy of activation ΔH^\ddagger kJ mol ⁻¹
Methanol	9.9 4	54.75	-58.48	72.44	52.23
Ethanol	8.6 2	48.19	-83.84	73.59	45.67

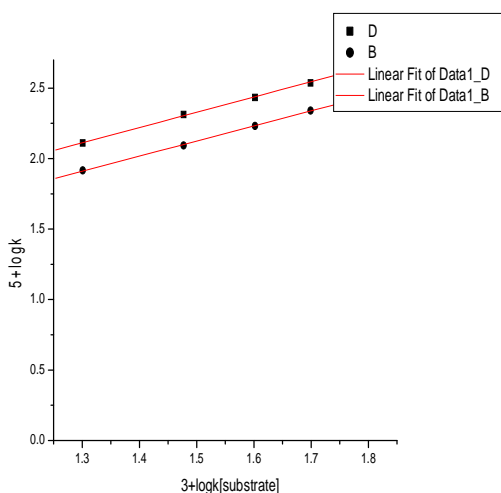


Figure 1: Effect of Substrate Concentration ■ D METHANOL, AND
 ▲ B Ethanol

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