

OXIDATIVE TRANSFORMATION OF ALIPHATIC ALCOHOLS BY CERIC AMMONIUM NITRATE (CAN) IN NON-AQUEOUS MEDIUM- KINETIC AND MECHANISTIC STUDY

Chemistry

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ABSTRACT

The oxidation of methanol and ethanol by ceric ammonium nitrate has been studied spectrophotometrically in the presence of glacial acetic acid in acetonitrile as solvent. The reaction is first order with respect to oxidant and $[H^+]$. Michaelis–Menten type kinetics is observed. The reactions exhibits positive polymerization test. The activation parameters have been evaluated.

KEYWORDS:

Kinetics, alcohols, CAN, oxidation.

Introduction

The oxidation of primary and secondary alcohols to carboxylic acids and ketones is a very important organic transformation that is extensively used in the manufacture of a wide range of products. Cerium (IV) compounds represent some of the most notable oxidants among the lanthanides reagents^[1] in various transformations of synthetic importance. The chemistry of Ce (IV) in oxidations of organic molecules is dominated by radical and radical cation chemistry. In aqueous H₂SO₄ media, Ce(IV) is both thermodynamically and kinetically weaker as an oxidising agent compared to Ce(IV) in aqueous HClO₄ media (cf. E_o = 1.7 V in 1.0 mol dm⁻³ HClO₄; E_o = 1.44 V in 1.0 mol dm⁻³ H₂SO₄).

Kinetics of Cerium (IV) oxidation of aliphatic alcohols: ethanol, 1-propanol, propan-2-ol, 1-butanol and 2-butanol were studied^[2] at 30 °C. The use of Ir (III) and Ru(III) in trace amounts as an efficient catalysts in the homogeneous reactions involving Ce(IV) as an oxidant has been reported^[3,4]. The kinetics and mechanism of trace iridium (III) catalyzed oxidation of ethylene glycol by cerium (IV) in sulphuric acid medium has been investigated by titrimetric technique^[5] of redox in the temperature range of 298-313K. The reaction is first order with respect to Ce (IV) and Ir (III).

Materials and Method-

The Methanol and Ethanol were commercial products of the highest purity available. CAN was prepared by method described by Smith et al.^[6]. Acetonitrile was purified by method given in literature^[7]. Due to the non-aqueous nature of the medium, acetic acid (AcOH) was used as a source of hydrogen ions.

The pseudo-first order conditions were attained by keeping a large excess of the alcohol over CAN. The temperature was kept constant to ± 0.1 K. The reactions progress was followed by monitoring the decrease in the concentration of CAN spectrophotometrically at 390 nm up to 80% of the reaction.

RESULTS AND DISCUSSION:

Effect of oxidant-

When alcohols were in excess, the disappearance of CAN followed the first-order rate law. The first-order rate constants are independent of the initial concentration of the [CAN] when varied in the range $(2-7) \times 10^{-3}$ mol / dm⁻³ at 303 K

Effect of Substrate-

At constant [CAN], the rate constants for oxidation were calculated at different initial concentration of alcohols and found to increase linearly with the increase in concentration of alcohols (2×10^{-2} M to 6×10^{-2} M). (Table-1). A plot of log k_{obs} against log[subs.] gives a straight line with slope nearly one revealed that the rate of oxidation is first order with respect to the substrate. It has been found that plot of $[1/k_1]$ versus $(1/[substrate])$ is straight line with an intercept on the rate ordinate, indicating the oxidation of alcohols follows Michaelis

–Menten type kinetics and proceeds through the formation of a complex between the oxidant and the substrate.

Effect of H⁺ Ion-

To study effect of hydrogen ion, glacial acetic acid was used. The rate of oxidation was studied from $[H^+] = 2$ to 5×10^{-2} M. It was observed that rate increases with increase in hydrogen ion concentration. Plot of log k_{obs} against log $[H^+]$ is a straight line in both the alcohols show first order dependence of $[H^+]$ on rate. The results are summarized in table (1).

Effect of Solvent composition-

Effect of solvent was studied by changing proportion of water and acetonitrile percentage composition was varied from 10 to 50 % acetonitrile v/v. Since there is no literature value of dielectric constants for water – acetonitrile mixture of different composition, therefore we have calculated dielectric constant using law of mixture and data for pure acetonitrile and water^[8,9] assuming a linear relationship in the limited range. Wieberg and Evans^[10] have made a similar approximation with regard to the same binary solvent system. Looking to the nature of reaction, it can be either ion-dipole or dipole-dipole^[11].

It was observed that log k_{obs}/s^{1/dielectric constant} is straight line in most of the cases with the positive slope. This indicates that reaction is ion - dipolar and further by positive slope, we can say it is cation-dipole interaction in rate determining step^[12]. Result are summarized in table-1.

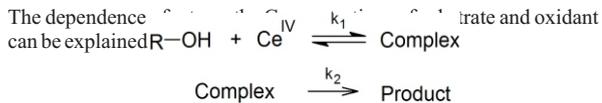
Effect of Temperature-

Rate of oxidation increases with increase in temperature. Rate of reactions were determined at different temperature (303 to 323 K) (Table- 2). In both the cases, a plot of log k_{obs} versus 1/T is a straight line. This shows that Arrhenius equation is valid for this oxidation. The energy of activation is 54.81 and 48.25 kJ mol⁻¹. The entropy values are negative and high suggesting that the transition state is more rigid. The negative entropy also suggests the formation of cyclic intermediate from acyclic species. Thermodynamic parameters have been calculated Table-3.

Conclusion:-

Oxidative transformation of methanol and ethanol is first order with respect to oxidant and $[H^+]$. Glasston^[13] has pointed out that if entropy of activation is large and positive, the reaction will be normal and fast but if it is negative, the reaction is slow. In this case, 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. Polymerization of the monomer acrylonitrile by reaction mixture was observed. This is in contradiction with Nayak et. al.^[14] Therefore reaction involve free radicals. Kemp and Waters^[15] also suggest that C-H fission must occur with Ce(IV). Thus the overall mechanism is proposed to involve the formation of a

complex in a fast pre-equilibrium and then a decomposition of the complex in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product.



[Scheme-1]

$$\text{Rate} = k_{\text{obs}} [\text{ROH}] [\text{Ce}^{\text{IV}}]$$

The kinetic data represents Michaelis - Menten type of kinetics suggesting protonation of alcohol in acid media indicating involvement of H^+ in the reaction in equilibrium step. Ce^{IV} has been found kinetically active in this study with generation of free radical in the reaction.

**Table-1 Effect of [Substrate], $[\text{H}^+]$ and [Solvent]
[CAN] = $3 \times 10^{-3} \text{ M}$ T = 308 K**

[Substrate] $\times 10^2$ M	[ACETIC ACID] $\times 10^2$ M	Percentage of H_2O [In ACN- Water Mix.]	$k_{\text{obs}} \times 10^5 \text{ sec}^{-1}$	
			Methyl alcohol	Ethyl alcohol
2.0	2.0	0	112.04	69.85
3.0	2.0	0	178.69	104.96
4.0	2.0	0	236.11	144.24
5.0	2.0	0	299.47	185.79
6.0	2.0	0	376.23	224.56
2.0	2.0	0	112.04	69.85
2.0	2.5	0	165.27	96.84
2.0	3.0	0	208.96	127.97
2.0	3.5	0	268.54	157.11
2.0	4.0	0	328.39	185.79
2.0	4.5	0	386.59	214.21
2.0	5.0	0	450.16	249.65
2.0	2.0	0	112.04	69.85
2.0	2.0	10	88.32	58.12
2.0	2.0	20	69.41	47.98
2.0	2.0	30	52.03	40.02
2.0	2.0	40	41.98	32.23
2.0	2.0	50	32.60	26.57

**Table-2 VARIATION OF RATE WITH TEMPERATURE
[SUBSTRATE] = 2.0×10^{-2} M [ACETIC ACID] = 2×10^{-2} M [CAN] = 3×10^{-3} M**

Temperature in K	$k \times 10^5 \text{ sec}^{-1}$	
	Methyl alcohol	Ethyl alcohol
303	112.04	69.85
308	173.11	102.81
313	235.68	133.41
318	330.41	182.39
323	448.54	236.25

Table-3 Thermodynamic Parameters

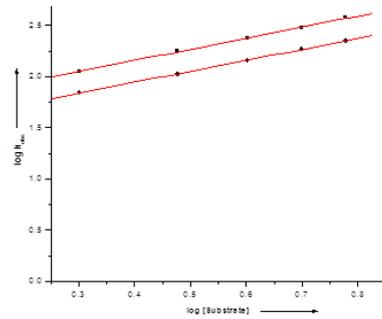
Alcohol	log A	Energy of activation E# kJ mol^{-1}	Entropy of activation S# $\text{JK}^{-1} \text{mol}^{-1}$	Free energy of activation G# kJ mol^{-1}	Enthalpy of activation H kJ mol^{-1}
Methyl alcohol	7.89	54.81	-97.73	52.29	81.90
Ethyl alcohol	6.56	48.25	-123.31	45.73	83.09

Fig-1

VARIATION OF RATE WITH SUBSTRATE CONCENTRATION

log k_{obs} v/s log [substrate]

■ METHYLALCOHOL ● ETHYLALCOHOL



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