



## KINETICS AND MECHANISM OF OXIDATION OF BENZYL ALCOHOL AND 2-METHOXY BENZYL ALCOHOL BY CERIC AMMONIUM NITRATE IN ACETONITRILE AQUEOUS MEDIUM

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### ABSTRACT

The kinetics of oxidation of aromatics alcohols like benzyl alcohol and 2-methoxybenzyl alcohol to the corresponding aldehydes with ceric ammonium nitrate have been studied spectrophotometrically at  $\lambda_{\max}=400\text{nm}$ . The reaction was studied at different concentration of substrate. First order kinetics observed with respect to [substrate], [oxidant] and  $[\text{H}^+]$ . The effect of temperature and solvent composition were studied and the activation parameters have been calculated. Based on the experimental results, a probable reaction mechanism was proposed.

**Keywords:** kinetics, oxidation, aromatic alcohol, ceric ammonium nitrate (CAN)

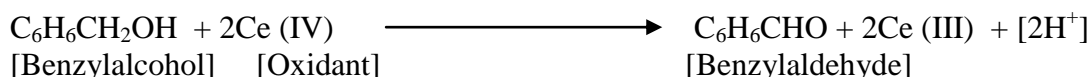
### [1] INTRODUCTION

Cerium (IV) ammonium nitrate  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  is a one-electron oxidizing agent that is oxidizes secondary alcohols into ketones and benzylic alcohols into aldehydes<sup>1</sup>. Kinetics studies in primary aliphatic alcohol Ce (IV) oxidize into aldehydes in present acetonitrile medium has been investigated by spectrophotometric method<sup>2</sup>. The study of in situ reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  a time-resolved X-ray absorption spectroscopy<sup>3</sup>. The oxidation of benzyl alcohol and 2-hydroxy benzyl alcohol by ceric ammonium nitrate has been studied spectrophotometrically, in the presence of glacial acetic acid<sup>4</sup>.

### [2] METHOD & MATERIAL

Ceric ammonium nitrate was prepared by the method of Smith et al<sup>5</sup> and its purity was checked by 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 308K in  $\text{HClO}_4$  under the condition  $[\text{alcohol}] \gg [\text{CAN}]$  in the solvent system of (V/V). The progress of the reaction was followed by measuring the absorbance of CAN at 400nm in one cm cell Placed in the compartment of systronics VISISCAN-167 spectrophotometer. The kinetics run were followed for good order kinetics were observed. The reaction products Benzylaldehyde and 2-methoxybenzylaldehyde estimated as their 2,4-dinitrophenyl hydrazone.

**[3] RESULTS AND DISCUSSION:-** Oxidation of benzylalcohol & 2-methoxybenzylalcohol by CAN in acetonitrile solvent in presence of perchloric acid under the condition  $[\text{CAN}] \ll [\text{benzylaldehyde} \& \text{2-methoxybenzylaldehyde}]$  had the following kinetics feature.



The stoichiometry of the reaction was found to correspond to the equation. The product of oxidation was identified by its 2,4-dinitrophenylhydrazine derivative.

**(i) Effect of Substrate:-** The effect of alcohol concentration on the reaction rate was studied at constant [CAN], [HClO<sub>4</sub>], temperature and acetonitrile. The rate of oxidation increased on increasing the concentration of alcohol. When the logarithms of  $k_{\text{obs}}$  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 straight line with an intercept on the rate ordinate, indicating the oxidation of both the alcohols follow Michaelis–Menten type kinetics and proceeds through the formation of a complex between the oxidant and the substrate

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

**(ii) Effect of [H<sup>+</sup>] ion:-** The effect of hydrogen ion concentration on the rate of the oxidation was studied by varying [H<sup>+</sup>] while keeping the concentration of another reactions 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  $\log k_{\text{obs}}$  against  $\log [\text{H}^+]$  is linear.

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

**(iv) 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 rate-determining step.

**(v) Effect of Temperature and determination of activation parameters:-** Rate of oxidation reaction increases with increases in temperature. (**Table-2**). Rate of reactions were determined at different temperature. In all the cases, a plot of  $\log k_{\text{obs}}$  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 57.44 and 62.22 kJ mol<sup>-1</sup>. The entropy values are all negative and high value observe. (**Table-3**).

**[4] CONCLUSION:-** The kinetics of oxidation of benzylalcohol and 2-methoxybenzylalcohol by ceric ammonium nitrate (CAN). It has found that the reaction was first order with respect to [CAN] and rate is almost independent of substrate concentration. The reaction are catalyzed by an acid [H<sup>+</sup>]. The decreases in dielectric constant increases the rate of reaction dielectric constant increases the rate of reaction with temperature and the various activation parameter 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.

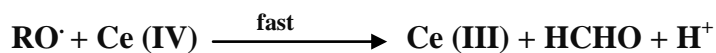
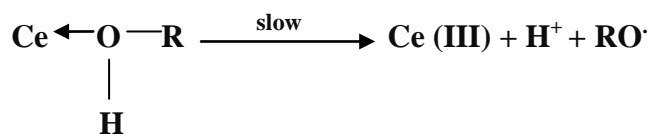
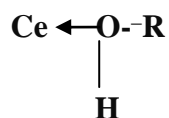
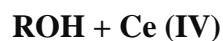


TABLE [1] EFFECT OF [SUBSTRATE], [H<sup>+</sup>], [SOLVENT], [CAN] = 3X10<sup>-3</sup> M, T=308K

[Substrate]X10 <sup>2</sup> M	[HClO <sub>4</sub> ]X10 <sup>2</sup> M	% of H <sub>2</sub> O [In Acetonitrile  WaterMix.]	k x 10 <sup>5</sup> sec-1	k x 10 <sup>5</sup> sec-1
			Benzylalcohol	2-Methoxybenzylalcohol
2	0	0	12.57	35.64
3	0	0	16.16	43.17
4	0	0	19.09	51.91
5	0	0	21.64	58.57
6	0	0	24.87	63.22
2	2	0	12.57	35.64
2	2.5	0	22.93	46.36
2	3	0	36.16	57.57
2	3.5	0	52.04	67.03
2	4	0	77.14	76.45
2	4.5	0	106.05	87.15
2	5	0	147.85	100.21
2	2	10	11.47	29.42
2	2	20	10.47	23.50
2	2	30	9.04	19.42
2	2	40	8.29	15.9
2	2	50	7.60	12.08

**TABLE [2] VARIATION OF RATE WITH TEMPRATURE [SUBSTRATE] =  $2.0 \times 10^{-2}$  M, [PERCHLORIC ACID] =  $2 \times 10^{-2}$  M, [CAN] =  $3 \times 10^{-2}$  M**

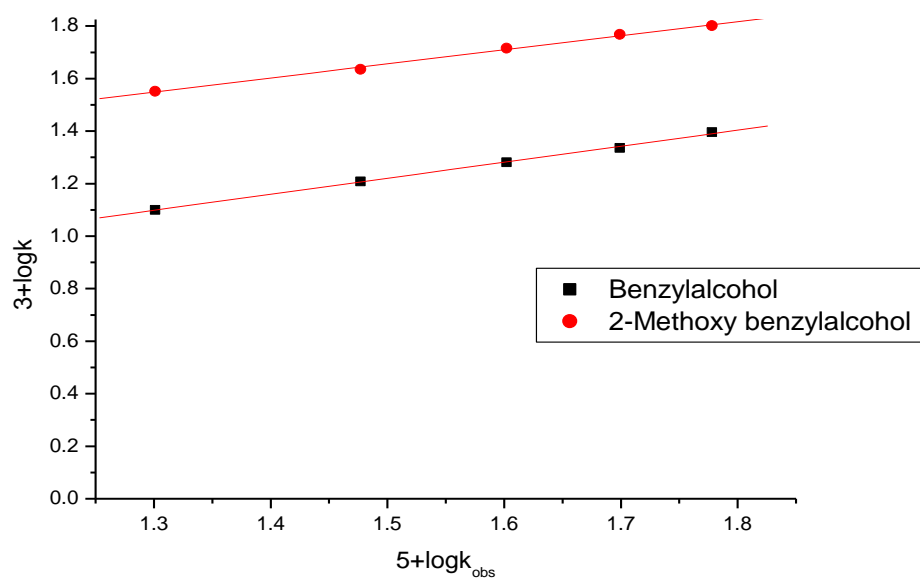
TEMPRATURE( K)	Benzyl alcohol	2-Methoxybenzylalcohol
303	12.57	35.64
308	18.78	53.05
313	26.91	75.09
318	38.61	117.13
323	52.86	168.38

**TABLE [3] THERMODYNAMIC PARAMETERS**

[SUBSTRATE]X $10^2$ M	logA	Energy of activation $\Delta E^\ddagger$ kJ mol $^{-1}$	Entropy of activation $\Delta S^\ddagger$ JK $^{-1}$ mol $^{-1}$	Free energy of activation $\Delta G^\ddagger$ kJ mol $^{-1}$	Enthalpy of activation $\Delta H^\ddagger$ kJ mol $^{-1}$
Benzylalcohol	9.4	57.44	-68.92	78.32	54.93
2-Methoxybenzylalcohol	10.67	62.22	-44.61	75.73	59.71

**Figure-1 Effect of substrate concentration log k v/s log [substrate]**

■ Benzylalcohol and ● 2-Methoxybenzylalcohol



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