Scientific Journal of Impact Factor (SJIF): 5.71
e-ISSN (O): 2348-4470
International Journal of Advance Engineering and Research Development
International Conference of Trends in Information, Management, Engineering and Sciences (ICTIMES)
Volume 5, Special Issue 02, Feb.-2018 (UGC Approved)

KINETICS AND MECHANISM OF CINNAMYL ALCOHOL BY BENZYLTRIMETHYL AMMONIUMDICHLOROIODATE

Dr.T.V.Reddy
Professor, Department of Humanities & Sciences, Malla Reddy College of Engineering, Secunderabad, Telangana, India,

K.Saritha,
Assistant Professor, Department of Humanities & Sciences, Malla Reddy College of Engineering Secunderabad, Telangana, India,

S.Sirisha,
Assistant Professor, Department of Humanities & Sciences, Malla Reddy College of Engineering Secunderabad, Telangana, India,

ABSTRACT

BENZYLTRIMETHYL AMMONIUM DICHLORO IODATE is used as a reagent for iodination and chloro iodination for many organic compounds because of its stable nature. However, the oxidation of alcohols, in particular unsaturated alcohols in the presence of BTMACI is not much known. In the present study, the oxidation of unsaturated alcohol, cinnamyl alcohol is carried out. The corresponding aldehyde is identified and kinetics of the oxidation reaction which is studied and found to be a first order reaction with respect to BTMACI. The effect of concentration of alcohol, oxidant and temperature on reaction rate is also studied. Depending on kinetics and activation parameters, a suitable mechanism is proposed for cinnamyl alcohol by the formation of intermediate active species between BTMACI and $ZnCl_2$.

INTRODUCTION

Synthesized BTMACI is known as a good halogenating agent (1-3). Among various Benzyltrimethyl ammonium polyhalides, BTMACI is widely used because of its stable character. Addition of Zinc Chloride makes BTMACI more soluble in acetic acid, generating a complex which serves as an excellent halogenating agent. Moriwaki et.al (4) have reported successful halogenation of aromatic acetyl derivatives by BTMACI in acetic acid in the presence of $ZnCl_2$. Fujisaki et.al (5) used BTMACI in the formation of chloroiodo adducts of alkenes. Auria et.al (5,6) reported the use of BTMACI as iodinating agent of Thiophene derivatives. The use of BTMACI in the oxidation of some Thioacids was reported by Suri et.al (7). The reaction was found to be first order with respect to Thio acids and BTMACI.

Oxidation of primary alcohols (8), hydroxy acids (9) and organic sulphides by BTMACI was studied by Jai Narain Vyas University, JODHPUR. However the use of BTMACI has not been extended to unsaturated alcohols. In the present study, the oxidation of cinnamyl alcohol in the presence of BTMACI is taken up. It is also aimed to study the effect of concentration of Substrate and oxidant and the effect of termperature on reaction rate. Based on kinetics and activation parameters a suitable mechanism is proposed for the oxidation of cinnamyl alcohol.

EXPERIMENTAL

Cinnamyl alcohol (FLUKA) is purified by recrystalisation, is used. BTMACI is dissolved in acetic acid in the presence of $ZnCl_2$ BTMACI is prepared in the following way. A solution of Benzyl Trimethyl ammonium chloride (18.6 g, 0.1 mol) in water is added to a solution of Iodine monochloride (16.2 g, 0.1 mol) in Dichloromethane (200 ml) with continuous stirring. A layer of BTMACI is separated and dried. This is recrystalised for dichloromethane – Ether mixture (3:1) to get BTMACI, yellow needle shaped crystals.

The experiment is conducted with alcohol, BTMACI and $ZnCl_2$ made up to 50 ml in Glacial acetic acid and kept in the dark for 15 hours for complete reaction. The solution is treated with 2,4-DNP in dilHCl and recrystalised form ethanol and weighed. Absorbance of experimental solutions is measured at 470 nm using HP-diode array spectrophotometer.

KINETICS MEASUREMENTS

The reactions are carried out under Pseudo First order conditions by maintaining alcohol in large excess over BTMACI. Pseudo first order rate constants Kobs were computed from the linear (r^2 >0.990) least square plots of log [oxidant] Vs time. The rates were checked by substituting values in the first order rate equation.

$$Kobs = \frac{2.303}{t} \log \frac{a}{a-x}$$

The third order rate constant K_3 of the oxidation of the alcohols by BTMACI is calculated using the equation

$$K_3 = \frac{Kobs}{[alco\,hol][ZnCl2]}$$

Ea is calculated from the linear plots between log K_3 and inverse of temperature.

Ea= -2.303 R X Slope

Change in Enthalpy is calculated from which change in entropy and change in free energy are also calculated.

RESULTS AND DISCUSSION

Kenetics of oxidation of cinnamyl alcohol has been studied at various concentrations of substrate. The rate data is given in table 1. Rate increases with increase in concentration of cinnamyl alcohol as shown in Table 1.

Table 1

Substrate variation:

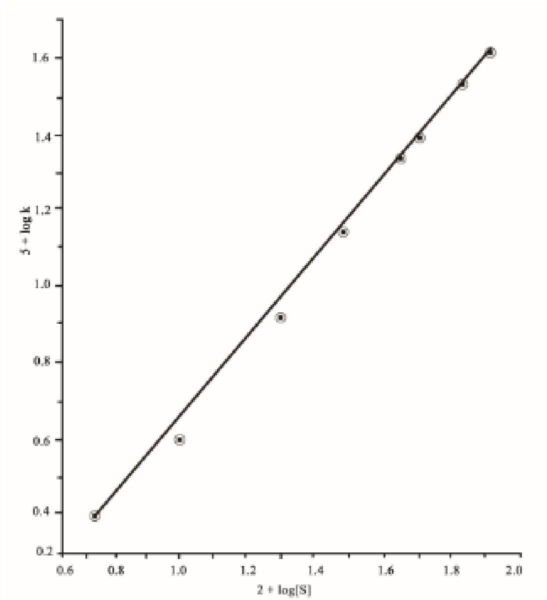
[BTMACI] = 0.001 mol dm^{-3} [$ZnCl_2$] = 0.002 dm^{-3} Temp=308K

Substrate	**[S] or [Cinnamyl Alcohol] mol dm^{-3}**	**K_{obs} X 10^5 sec^{-1}**
Cinnamyl alcohol	0.05	2.59
	0.10	4.21
	0.20	8.14
	0.30	13.30
	0.50	21.97
	0.60	26.03
	0.80	34.04
	1.00	41.14

With respect to substrate the order was found to be of first order. A plot of log K Vs log S gives a unit slope at temperature 308 K (Fig.1).

Fig.1

Cinnamyl alcohol
Log k Vs log[S]
Temperature - 308K



Rate increases with increase in concentration of cinnamyl alcohol is also found at 328 K as shown in Table .2.

Table 2

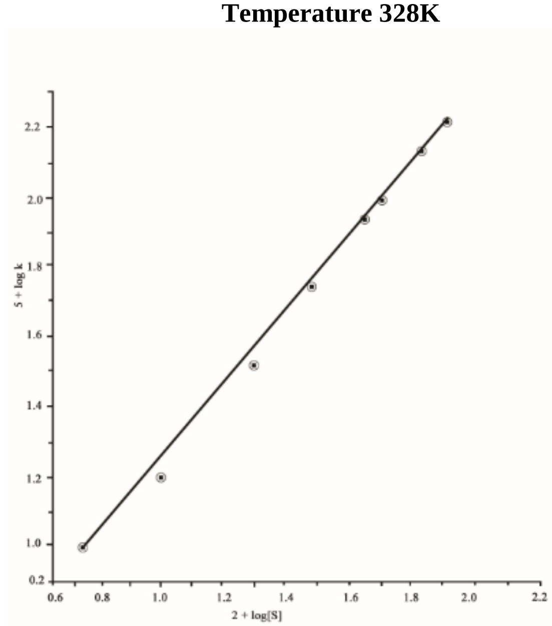
Substrate variation:

[BTMACl] = 0.001 mol dm^{-3} [$ZnCl_2$] = 0.002 dm^{-3} Temp=328K

Substrate	[S] or [Cinnamyl Alcohol] mol dm^{-3}	K_{obs} X 10^5 sec^{-1}
Cinnamyl alcohol	0.05	10.27
	0.10	16.50
	0.20	32.57
	0.30	53.27
	0.50	88.24
	0.60	103.67
	0.80	136.24
	1.00	164.74

Fig.2

Temperature 328K



Effect of change in concentration of BTMACl on reaction rate at 318 K is studied and the results are given in Table 3. It is observed that the rate of reaction has not been changed much. However, the change in the concentration of cinnamyl alcohol at 328 K shows an increase in the reaction rate.

Table 3

[Substrate] = 0.05 mol dm^{-3} [$ZnCl_2$] = 0.002 dm^{-3}

Temp=318K

Substrate	[BTMACl] Mol.dm^{-3}	K_{obs} X 10^5 sec^{-1}
Cinnamyl alcohol	1.0	8.30
	2.0	8.50
	3.0	7.10
	5.0	7.94
	8.0	7.91

Change of temperature on reaction rate is studied at three different temperatures and found that the rate increases with increase in temperature as given in Table 4.

Table 4

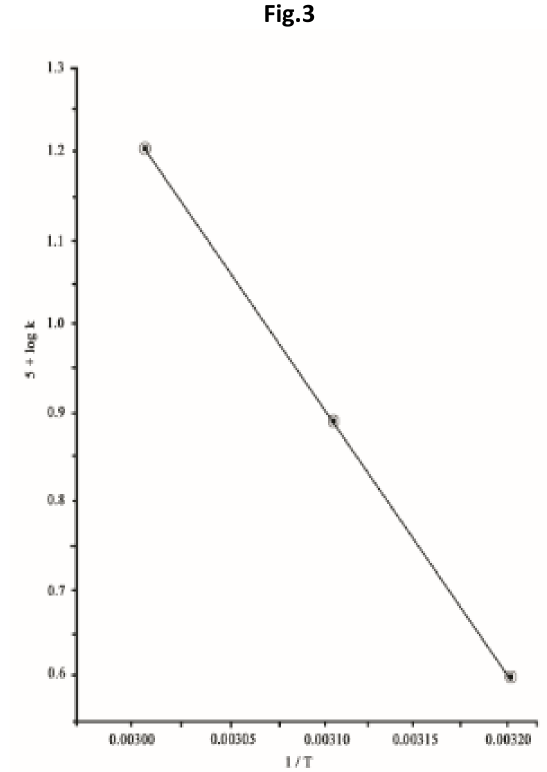
[BTMACl] = 0.01 mol dm^{-3} [$ZnCl_2$] = 0.002 dm^{-3}

[Cinnamyl alcohol] = 0.1 mol dm^{-3}

Temperature	K_{obs} X 10^5 sec^{-1}
308K	4.21
318K	8.30
328K	16.5

The relation between log K and 1/T is as shown in Fig 3.

Fig.3

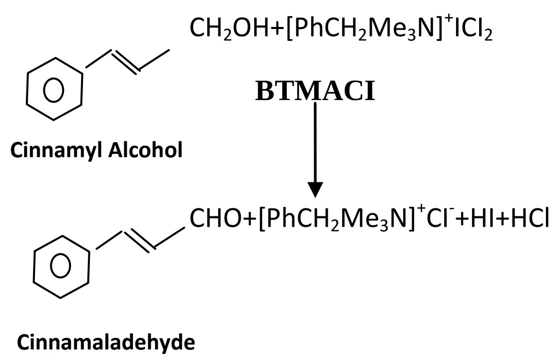


DISCUSSION:

Activation parameters for the oxidation of cinnamyl alcohol, at temperature of 318 K are calculated and given below.

ΔH^{*}=53,141.47 J.mol^{-1}
ΔS^{*}=-155.16J. mol^{-1} k^{-1}
ΔG^{*}=102.4 kj. mol^{-1}

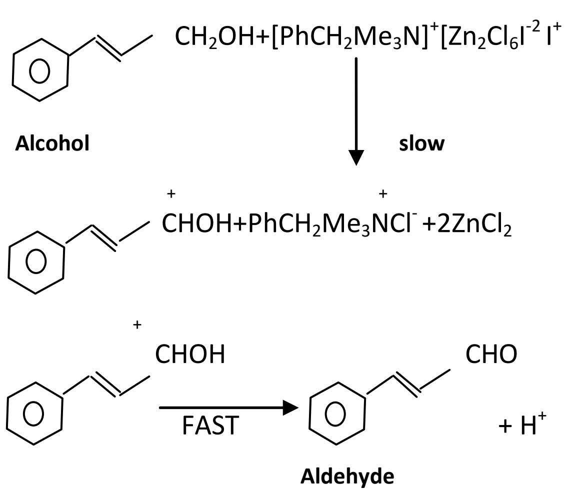
In the present investigation, the oxidation of Cinnamyl alcohol yields corresponding aldehyde as the main product. The overall reaction may be represented as follows.



The rate of oxidation is found to be first order with respect to each BTMACI, alcohol and $ZnCl_2$.
Therefore the experimental rate law will be expressed as follows.
Rate = K_3 [BTMACI] [alcohol] [$ZnCl_2$]

Mechanism:

In the present study, the oxidation of cinnamyl alcohol by BTMACI, the following mechanism is proposed and supported by the observed negative entropy of activation.



As the charge separation takes place in the transition state, the two ends becomes highly solvated. The loss in entropy can be attributed to this Solvation of the ends in the transition state.

BTMACI is reported to produce an active species A(9) as shown in the following equation, in presence of $ZnCl_2$.

$$PhCH_2Me_3N]^{+}ICl^{-}_2+ZnCl_2 \underset{}{\overset{K_1}{\rightleftharpoons}} [PhCH_2Me_3N]^{+}[ZnCl_4]^{-2}I^{+}$$

(A)

Even at low concentration of $ZnCl_2$ almost the whole of BTMACI will be in the form of complex (A) as shown in the above equation. It is observed that the rate increases linearly with increase in the concentration of $ZnCl_2$ and this point supports by further complexation of 'A' with $ZnCl_2$ to give another complex (B).

$$(A) + ZnCl_2 \overset{K_2}{\rightleftharpoons} [PhCH_2Me_3N]^{+}[Zn_2Cl_6I^{-2}I^{+}$$

(B)

The above observed dependence on the concentration of $ZnCl_2$ indicates that the equilibrium between A and B is rapid and the equilibrium constant K_2 is small and the reaction is not complete even at high concentration of $ZnCl_2$. This suggests that only the complex B is the reactive oxidizing species. The small rate enhancing effect of BTMACI suggest that Iodine monochloride is not involved in the oxidation process.

$$[PhCH_2Me_3N]^{+}ICl^{-}_2 \overset{K_3}{\rightleftharpoons} [PhCH_2Me_3N]^{+}Cl^{-}+ICl$$

The formation of the complex is supported by the spectral studies also.

CONCLUSION:

BTMACI is found to be an effective oxidant for organic compounds in particular alcohols to form corresponding aldehydes. It can be also tried for other substituted cinnamyl alcohols for further study which may give valuable information regarding mechanism and Kinetics.

REFERENCES

1. S.Kakinami, S.Kajigaeshi, H.Yamasaki and T.Okamoto
Bull, Chem., Soc.Jpn., 1988, 61,600.
2. S.Kajigaeshi, Y.Shinmasu, S.Fujisaki and T.Kakinami
Chem., Express, 1990, 5, 141.
3. S.Kajigaeshi, T.Kakinami, H.Tokiyama, T.Hirakawa and T.Okamoto
Chem.Lett., 1987, 627.
4. S.Fujisaki, S.Kajigaeshi, M.Moriwaki, T.Kakinami and T.Okamoto
Bull, Chem., Soc.Jpn., 1990, 63,3033.
5. T.Okamoto, T.Kakinami, H.Fujimoto, H.Yamasaki and S.Kajigaeshi
Bull, Chem., Soc.Jpn., 1991, 64, 2566.
6. M.D.Auria and G.Mauriello
Synthesis, 1995, 248
7. D.Suri, K.K.Banerji and S.Kothari
Int.J.Chem.Kinet., 1996, 28, 681
8. S.Goel, S.Kothari and K.K.Banerji
J.Chem.Res.(S), 1996, 230; (M) 1318
9. T.Kakinami, S.Kajigaeshi, M.Moriwaki, T.Tanaka, S.Fujisaki and T.Okamoto