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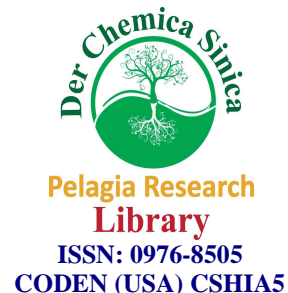
Kinetics and Mechanism of the oxidation of Cinnamyl and substituted Cinnamyl alcohols by benzyltrimethylammonium dichloroiodate

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ABSTRACT

The oxidation of Cinnamyl and substituted cinnamyl alcohol by benzyltrimethylammonium dichloroiodate (BTMACI), in the presence of zinc chloride, leads to the formation of corresponding aldehyde. The reaction is first order with respect to BTMACI, zinc chloride and alcohol. Addition of benzyltrimethylammonium chloride enhances the rate. It is proposed that the reactive oxidizing species is $[(PhCH_2Me_3N)^+ (IZn_2Cl_6)^{-1}]$. A suitable mechanism has been proposed.

Keywords: Alcohols; Benzytrimethylammonium dichloroiodate; Polyhalogens.
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INTRODUCTION

Several benzyl trimethyl ammonium polyhalides like benzyl trimethyl ammonium dichloro iodate [1-2], benzyl trimethyl ammonium tetra chloroiodate [3-5], benzyl trimethyl ammonium tribromide; etc., have been synthesized and widely used as halogenating agents.

Among various benzyl trimethyl ammonium polyhalides, benzyl trimethyl ammonium dichloriodate (BTMACI) is widely used as a reagent for the iodination and chloro iodination of many organic components. Because of its stable solid character, the bright yellow crystalline solid i.e. BTMACI (Mol. Wt 348, M.P. $125^0C – 126^0C$) can be treated quantitatively and stiochiometrically when compared to various iodine monochlorides. BTMACI can be handled and weighed on a micro and semi micro scale easily as per the requirements.

MATERIALS AND METHODS

All the alcohols (fluka or Aldrich) were purified by recrystallization process. Acetic acid was refluxed with chromium trioxide and acetic anhydride for 3h, then fractionated, The fraction

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coming over between 116^0-118^0C was collected. All other reagents used were of "analytical grade". Double distilled water was used throughout.

BTMACI is only slightly soluble in acetic acid at room temperature. However, the addition of zinc chloride renders this reagent soluble in acetic acid and reported to produce $[PhCH_2 Me_2 N]^+$ as an active species [6-7]. It is observed that in the absence of zinc chloride the strength of a saturated solution of BTMACI, in acetic acid is 0.005 mol dm^{-3}. Addition of zinc chloride (0.002. mol dm^{-3}) increased the solubility of BTMACI, and a saturated solution of BTMACI under these conditions, has a strength of 0.0016 mol dm^{-3}.

Spectral Studies:
UV-VIS spectra of [A] BTMACI (0.0005 mol dm^{-3}) alone, [B] zinc chloride (0.002 mol dm^{-3}) + BTMACI (0.0005 mol dm^{-3}) [C] zinc chloride (0.003 mol dm^{-3}) + BTMACI (0.0005 mol dm^{-3}) and [D] zinc chloride (0.006 mol dm^{-3}) + BTMACI (0.0005 mol dm^{-3}) were recorded on a HP – diode array spectrophotometer (model 8452 A) at temperature 300 $\pm$ 3K. The solvent and blank were glacial acetic acid. The scanning speed was 600 nms^{-1}.

Kinetic Measurements:
The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of alcohol (X 15 times or more) over BTMACI. The solvent was glacial acetic acid. The reactions were followed at constant temperatures ($\pm$0.1K). Lower than the ambient temperatures were obtained with the help of a refrigerated bath circulator. The reactions were carried out in the presence of zinc chloride and were followed by monitoring the decrease in [BTMACI] iodometrically for at least three half –life.

RESULTS AND DISCUSSION

In the present investigation, the oxidation of Cinnamyl alcohol, para -methyl cinnamyl alcohol, para -methoxy cinnamly alcohol and para -nitro cinnamyl alcohol yields the corresponding aldehydes as the main product. The overall reaction may be represented as follows.
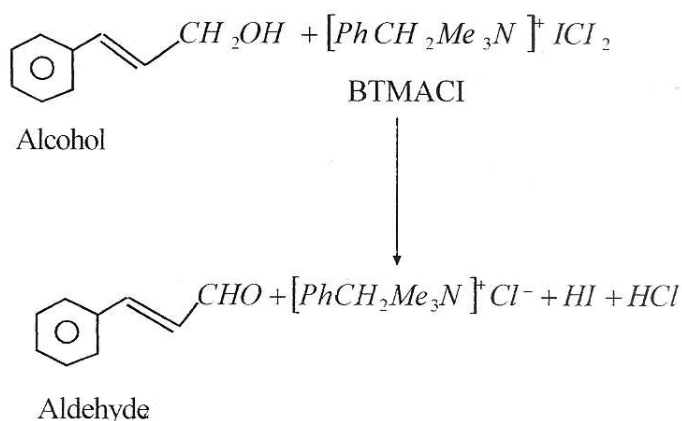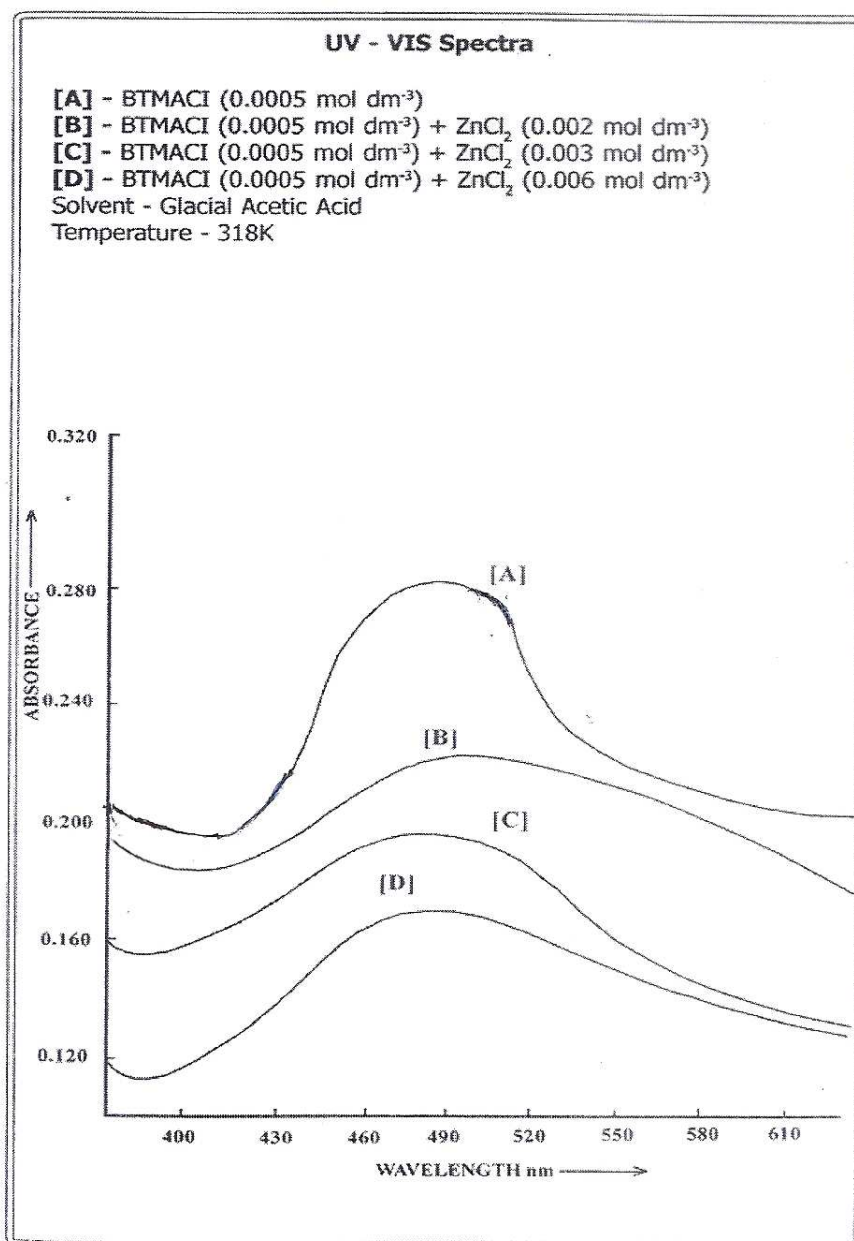
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Fig 1: Oxidation of Alcohols by Benzyl Trimethyl Ammonium Dichloroiodate

3.1   **Rate Laws:**

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] [$ZnCl_2$]

The activation parameters for the oxidation of cinnamyl and substituted cinnamyl alcohols were evaluated from the value of K_3 at 318K.

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The reaction rate increases linearly with increase in concentration of the acid (table 1). With increase in the concentration of Zinc chloride also, the reaction rate increased linearly (table 2). A plot of kobs Vs [ZnCl$_2$] is linear (r^2 > 0.9980) and passes through the origin. An addition of benzyltrimethylammonium chloride (BTMACI) enhances the reaction rate slightly (table 3).

3.3   **Effect of temperature**
Rates of oxidation of Cinnamlyl and substituted cinnamyl alcohols were determined and activation parameters were calculated at temperature 318 K as shown in table-4.

Table 1: Rate constants for the oxidation of Cinnamyl Alcohol by BTMACI at 318 K

10^3 [BTMACI] mol dm^{-3}	[Alcohol] mol dm^{-3}	10^5 k$_{obs}$ sec^{-1}
1.0	0.05	5.2
1.0	0.10	8.3
1.0	0.20	16.3
1.0	0.30	26.6
1.0	0.50	44.1
1.0	0.60	51.9
1.0	0.80	68.1
1.0	1.00	82.4
2.0	0.10	8.5
3.0	0.10	7.1
5.0	0.10	7.94
8.0	0.10	7.91

Table 2: Effect of Zinc Chloride on the rate of oxidation of Cinnamyl alcohol by BTMACI.

[ZnCl$_2$] mol dm^{-3}	K$_{obs}$ X 10^5 sec^{-1}
0.002	5.2
0.003	7.5
0.004	10.4
0.005	13.0
0.006	15.6
0.007	18.2

Table 3 : Effect of changing concentration of Benzyl trimethyl ammonium Dichloroiodate chloride on the rate of oxidation of cinnamyl alocohol
[Substrate] = 0.05 mol dm^{-3}. [ZnCl$_2$] = 0.002 mol dm^{-3} Temp = 318K

| Substrate	[BTMACI] mol dm^{-3}.	K$_{obs}$ X 105 sec^{-1}.
	1.0	8.30
	2.0	8.50
Cinnamyl Alcohol	3.0	7.10
	5.0	7.94
	8.0	7.91

3.4   **Spectral Studies**
The U.V – visible spectra of BTMACI in acetic acid and BTMACI along with different concentrations of ZnCl$_2$ in acetic acid is shown in Fig. 1. It is observed that the nature of the spectrum is not much different in the presence and absence of ZnCl$_2$. But a decrease in the absorbance of BTMACI with the increase in the concentration of ZnCl$_2$ is noted. This suggests

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that a complex is formed and its concentration increases with increase in concentration of $ZnCl_2$. Hence absorbance is measured at 470 nm in all kinetic experiments.

Table: 4 Activation parameters for the oxidation of cinnamyl and substituted cinnamyl alcohols at temperature 318K

| Substrate	ΔH^* (J mol^{-1})	ΔS^* (J $mol^{-1} k^{-1}$)	ΔG^* (KJ mol^{-1})
Cinnamyl Alcohol	53,141.4746	-155.1669	102.4
P-methyl cinnamyl alcohol	52,249.3097	-148.88	101.4
P-methoxy cinnamyl alcohol	50,677.2445	-151.768	98.9
P-nitro Cinnamyl alcohol	51,808.4902	-165.08	104.3

BTMACI is reported to produce an active species (A) [6-7] as shown in the following equation, in presence of $ZnCl_2$.

$$[PhCH_2Me_3N]+ ICI^-_2 + ZnCl_2 \leftrightarrow [PhCH_2Me_3N]+ [ZnCl_4]^{-2}I^+$$
$$(A)$$
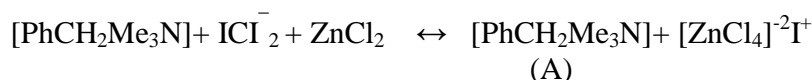
Even at low concentration of $ZnCl_2$ almost the whole of BTMACI will be in the form of complex (A) as shown in the above equation. It is observed that the rate increases linearly with increase in the concentration of $ZnCl_2$ and this point supports by further complexation of "A" with $ZnCl_2$ to give another complex (B).

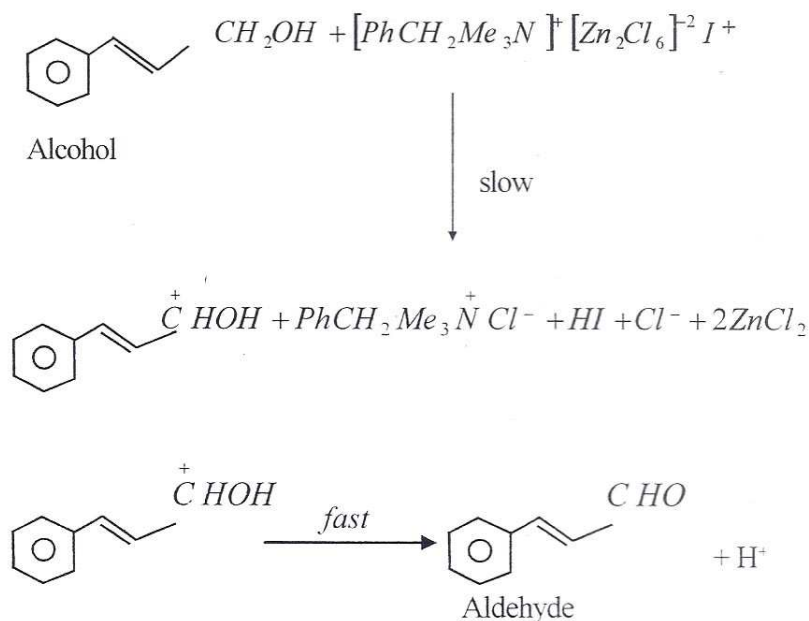$$(A) + ZnCl_2 \xrightarrow{K_2} [PhCH_2Me_3N]^+ [Zn_2Cl_6]^{-2} I^+$$
$$(B)$$
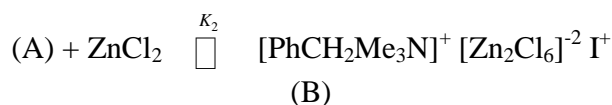
The observed dependence on the concentration of $ZnCl_2$ indicates that the equilibrium between A and B is rapid and the equilibrium constant K_2 is small and the reaction is not complete even at high concentration of $ZnCl_2$. This suggests that only the complex B is the reactive oxidizing species. The small rate enhancing effect of BTMACI suggest that Iodine monochloride is not involved in the oxidation process.

$$[PhCH_2 Me_3N]^+ ICI^-_2 \xrightarrow{K_3} [PhCH_2Me_3N]^+ Cl + IC1$$
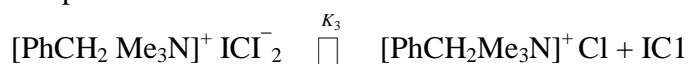
The formation of the complex is supported by the spectral studies also.

CONCLUSION

In the present study, the oxidation of Cinnamyl and substituted Cinnamly alcohols by BTMACI, the following mechanism is proposed and supported by the observed negative entropy of activation.

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$$CH_2OH + \left[PhCH_2Me_3N\right]^+ \left[Zn_2Cl_6\right]^{-2} I^+$$

Alcohol

slow

$$\overset{+}{C}HOH + PhCH_2\overset{+}{Me_3N}\,Cl^- + HI + Cl^- + 2ZnCl_2$$

$$\overset{+}{C}HOH \xrightarrow{\text{fast}} CHO \quad + H^+$$

Aldehyde

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).

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