The Oxidation of Aromatic Secondary Alcohol by Polymer Supported Chromate: -A Kinetic Investigation

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Abstract

Oxidation of organic compounds is quite important from synthetic and technological view points. Many of the industrially important organic compounds like aldehydes, ketones, acids, etc. can be produced by the oxidation of related substrate by the use of suitable oxidizing agents. The kinetics of the oxidation of 1-Phenylethanol (PE) by PS-Chromate has been followed by monitoring the constant in the absorbance of reaction intermediate. The reaction followed by *zero order* behavior, being *zero order* in each reactant. The rate of reaction constant with increase in weight of oxidant, concentration, temperature and dielectric constant of the solvent. A free radical scavenger affects the reaction rate. The stiochiometry has been found to be 1mol PE: 1mol of Chromate. Thermodynamic parameters evaluated are [Ea] = 82KJ mol^{-1}, [$\Delta H^{\#}$]=60 KJ mol^{-1}, [$\Delta S^{\#}$]=-74 JK mol^{-1}, [$\Delta G^{\#}$] =302KJ mol^{-1}, and [A] =3.6 x 10^{-5}s^{-1} results under pseudo *zero order* conditions are in agreement with the rate law. Main reaction product acetophenone isolated and characterized.

Keywords: *Polymer supported Reagent, oxidation, kinetics, mechanistic*

1.   Introduction

There are few reports available on the non-Malapradin Potassium Chromate oxidation of aromatic primary ,secondary and tertiary alcohols. In continuation of our earlier studies, the results as PS-chromate oxidation of PE in 1,4 dioxane aimed at deciding the mechanism of the reaction and the rate law particularly for seeking an explanation for the unique rate PH profile observed are being presented and discussed in the present research communication.

In the present investigation, we now report the oxidation of 1-phenylethanol by polymer- supported potassium chromate. The polymer Diaion SA10A [Cl-] is the strong anion exchange Chloride form of resin was popularly used for water treatment. It is porous gel Chloride form anion is typically recommended for treatment of surface water with organic content and it was supported on Potassium dichromate and used as an oxidant.

2. Materials and Methods

The chemicals like Chloride form of anion exchange resin Diaion SA10A [Cl$^-$] is the DIAION product, Potassium dichromate $K_2Cr_2O_7$ (99.9%, BDH), acetone, THF, allyl alcohol, acrylonitrile, 1:4 dioxane, 2,4DNP solution are AR grade pure double distilled water were used throughout the research work.

2.1   Preparation   of   Chromate   supported oxidizing agent

The polymer supported oxidizing agent was prepared by reported method. The polymeric resin Diaion SA10A [Cl$^-$] was stirred with a saturated solution of potassium dichromate in double distilled water for 30 minutes at room temperature using a magnetic stirrer. The Chloride ion was readily displaced and HCrO$_4^-$ form of resin was obtained in 40 min. The resin was successively rinsed with water, acetone and THF and finally dried in vaccum at 323 K for 7hrs.

2.2 Determination of the capacity of chromate form of the polymeric reagent

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The capacity of the chromate form of Diaion SA10A [Cl$^-$] resin was 2.85 meq/mL and used for kinetic study throughout kinetic work.

2.3 Method of kinetics

The reaction mixture for the kinetic run was prepared by mixing 1-PE, PS-chromate Potassium dichromate [$K_2Cr_2O_7$] was used to prepare the required Cr(VI)solutions and distilled water was used throughout the experiment. The reaction was carried out either constant stirring using magnetic stirrer and at a constant temperature 318 ±5 K. At different time interval, the reaction mixture was withdrawn using a qualigen micropipette. The aliquot thus withdrawn was taken in a stopper test tube containing 1, 4-dioxane and subjected to spectral analysis. The absorbance of the product an acetophenone formed was measured using Shimadzu UV-VIS spectrophotometer (Model Mini 1240).

2.4 Polymerization test

Mixing of polymer supported oxidant, 1-PE and solvent at 318 K with continuous stirring did initiation of reaction. After 55 min, the reaction mixture was withdrawn in a test tube and acrylonitrile and allyl alcohol was added. The mixture after dilution with distilled water formed a copious precipitate. The precipitate formed, due to polymerization of acrylonitrile, indicates formation of a free radical species in the reaction.

2.5 Product analysis

The oxidation of 1-PE leads to the formation of acetophenone.The product formed was analyzed by their 2,4-DNP derivatives. The product is then vacuum dried, weighed and recrystallised from alcohol and determined its melting point 418K (Literature value 419K). UV –VIS spectrum (in ethyl alcohol giving absorption maxima at 195,190, 175 and 165 mu which suggested the presence of ketone structure in the compound.)

The FTIR spectrum of compound (in KBr) showed the presence of a sharp band at 1628cm^{-1} indicates the presence of -C=O stretching mode, 1560 cm^{-1} indicates the presence of aromatic (-C= C-), 3050 cm^{-1} indicates the presence of (-C- H stretch).

3. Results and discussion

3.1 Effect of varying weight

As the plots of absorbance against time were linear in all runs and observed rate constant are fairly constant at various quantity of oxidant at constant concentration of solvent and 1-PE, the effect of varying weights of on PS-Chromate *zero order* rate constant as shown in Table-3.1

Table-3.1 Effect of varying weights of Ps-chromate on reaction rate at 318 k.

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Oxidant x 10^{-6} kg →	50	60	70	80
Diaion SA10A [Cl$^-$]	1.60	1.65	1.68	1.69

3.2 Effect of varying concentration

At a varying concentration of 1-PE, constant weights of PS-Chromate and constant concentration of solvent, zero order rate constant [Table- 3.2] was found.

Table-3.2 Effect of varying concentrations of 1-PE

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
1-Phenylethanol →	8.20 x 10^{-3} mol /dm^3	12.3x 10^{-3} mol /dm^3	16.4 x 10^{-3} mol /dm^3	20.4 x 10^{-3} mol /dm^3
Diaion SA10A [Cl$^-$]	1.37	1.39	1.41	1.43

3.4 Effect of varying temperature

The reaction was carried out at four different temperatures. It was observed that, the rate of reaction increased with an increase in the temperature. [Table-3.3]. The activation parameters like energy of activation [Ea], enthalpy of activation [$\Delta H^{\#}$], entropy of activation [$\Delta S^{\#}$] free energy of activation [$\Delta G^{\#}$] the high positive values of free energy of activation indicates that the transition state is highly solved and frequency factor [A] were calculated by determining values of k at different temperatures. [Table-3.4].

Table – 3.3 Effect of varying temperature

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Temperature K →	313	318	323	328
Diaion SA10A	1.31	1.33	1.35	1.38

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[Cl⁻]				

Table -3.4 Thermodynamic parameters

Temp. K	k x 10^{-4} mold m^{-3} s^{-1}	[Ea] KJmol^{-1},	[$\Delta H^{\#}$] KJ mol^{-1}	[$\Delta S^{\#}$] JK mol^{-1}	[A] 10^{-5} s^{-1}	[$\Delta G^{\#}$] KJ mol^{-1}
313	1.39					
318	1.55	82	60	-74	3.6	302
323	1.99					
328	2.12					

It is necessary and interesting to discuss the possible molecular mechanism of the reaction. Mechanism proposed in following **(Step 1-5)**, Scheme-I shows the *zero order* as a reversible bimolecular reaction between PE and [PS-Sodium chromate]. The polymer supported reagent reacts with a molecule of 1-Phenylethanol to form a chromate ester. (**Step-1**)
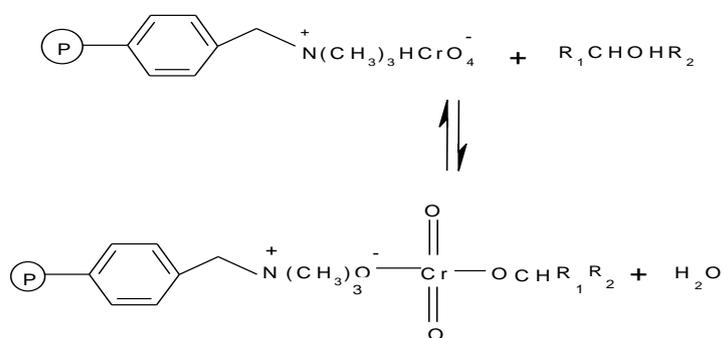
Step-1

2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step. (Step-2)
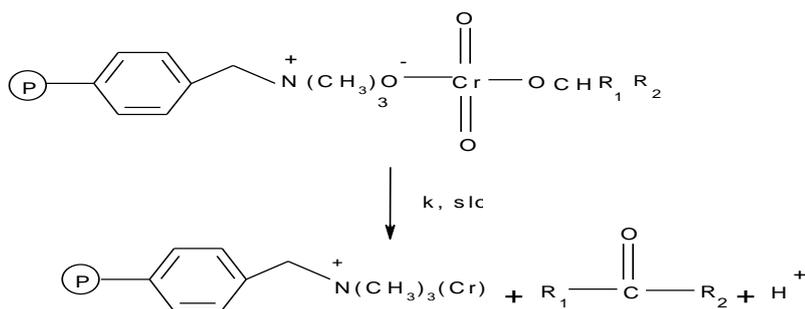
Step-2

3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. (Step-3)

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Step- 3

4) Subsequently the free radical will react with another oxidant site in the polymeric reagent in a fast step leading to the formation of chromium (V). (Step- 4)

Step- 4

5) The intermediate chromium (V) in the last step reacts with 1-phenylethanol produce acetophenone. The test for formation of chromium (V) and (IV) by the characteristic induced oxidation of iodide and manganese (II) were not probably due to heterogeneity of the reaction mixture. (Step-5)

[$R_1 = C_6H_5-$ and $R_2 = -CH_3$]

Step- 5

Scheme- I

4. Conclusion

We obtained *zero order* dependence with rate constant k of the second slow step in which product *acetophenone* was obtained. Based on the experimental observations a probable mechanism is suggested.

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