Oxidation of Alcohol by using Weak base Anion Exchange Resin Duolite A568:- A Kinetic Study

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Abstract: *The Oxidation of alcohol by using polymer supported oxidizing agent has been studied experimentally. The kinetics of the oxidation of 1-Phenylethanol (PE) by PS-Chromate has been followed by monitoring the increase in the absorbance of reaction intermediate. The reaction followed by zero order behavior, being zero order in each reactant. The rate of reaction increase 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 $[Ea] = 85KJ\ mol^{-1}$, $[\Delta H^{\#}]=62\ KJ\ mol^{-1}$, $[\Delta S^{\#}]=-75\ JK\ mol^{-1}$, $[\Delta G^{\#}] =315KJ\ mol^{-1}$, and $[A] =3.7\ x\ 10^{-5}s^{-1}$ results under pseudo zero order conditions are in agreement with the rate law. Main reaction product acetophenone isolated and characterized.*

Keywords*: Oxidation, Alcohol, Resin, Kinetics study, Duolite A568*

I.   Introduction :

There are few reports available on the non-Malapradin Sodium Chromate oxidation of aromatic 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 P^H profile observed are being presented and discussed in the present communication.

In the present investigation, we now report the oxidation of 1-phenylethanol by polymer- supported sodium chromate. The polymer Duolite A567 [OH⁻] is the weak basic anion exchange resin are supported on sodium chromate and used as an oxidant. This observation prompted us to investigate the above mentioned reaction in the title. The main objective of the present study to check the reaction rate of aromatic alcohol towards polymer supporting oxidizing agent.

II.   Experimental Methodology:

Materials used:

All the chemicals used in this experiment were of laboratory grade and the solutions were prepared by dissolving the requires amount of the samples in distilled water. All reagents were used AR grade.

2.1 Preparation of Chromate supported oxidizing agent

The supported oxidizing agent was prepared by reported method. The hydroxyl form of basic anion exchange resin Duolite A567 [OH⁻] was stirred with a saturated solution of sodium chromate in water for 70 minutes at RT using a magnetic stirrer. The hydroxyl 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 5 hrs.

2.2 Capacity of chromate form of the polymeric reagent

The capacity of the chromate form of Duolite A567 [OH⁻] resin was > 1.22 eq/L and used for kinetic study throughout kinetic work. Total pore volume is 0.78- 1Ml/g, it s physical form is Gren-gray with particle size μm and particle density is 1.10-1.14 g/mL.

Method of kinetics:

The reaction mixture for the kinetic run was prepared by mixing 1-PE, PS-chromate and solvent. 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

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absorbance of the product formed was measured using Shimadzu UV-VIS spectrophotometer (Model Mini 1240).

Polymerization :

In the reaction mixture acrylonitrile and methyl alcohol was added and kept for 10 minutes, on diluting the reaction mixture white precipitate is obtained, seems to be generation of free radical in the reaction. It shows that the reaction took place under free radical mechanism

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 416K (Literature value 419K). UV –VIS spectrum (in ethyl alcohol giving absorption maxima at196,191, 179 and 167 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 $1624cm^{-1}$ indicates the presence of -C = O stretching mode, $1570 cm^{-1}$ indicates the presence of aromatic (-C= C-), $3054 cm^{-1}$ indicates the presence of (-C- H stretch).

III. Results and discussion:

3.1 Effect of weights of PS-Chromates

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 no 3.1

Table no 3.1 Effect of weights of PS-Chromate on reaction rate at 318 K.

Rate constant →	$k \times 10^{-4}$ mol dm^{-3} s^{-1}			
Oxidant $\times 10^{-6}$ kg →	50	60	70	80
Duolite A567 [OH⁻]	1.55	1.62	1.79	1.89

3.2 Effect of concentrations of 1-PE

At a varying concentration of 1-PE, constant weights of PS-Chromate and constant concentration of solvent, zero order rate constant [Table no 3.2] was found.

Table no 3.2 Effect of concentrations of 1-PE

Rate constant →	$k \times 10^{-4}$ mol dm^{-3} s^{-1}			
1-Phenylethanol →	8.20×10^{-3} mol /dm^{3}	12.3×10^{-3} mol /dm^{3}	16.4×10^{-3} mol /dm^{3}	20.4×10^{-3} mol /dm^{3}
Duolite A567 [OH⁻]	1.25	1.31	1.39	1.42

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 no 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 no3.4].

Table no 3.3 Effect of temperature

Rate constant →	$k \times 10^{-4}$ mol dm^{-3} s^{-1}			
Temperature K →	313	318	323	328
Duolite A567 [OH⁻]	1.26	1.32	1.78	1.92

*Table no 3.4 Thermodynamic parameters for the PS-Chromate oxidation of 1-PE*

| Temp. K	$k \times 10^{-4}$ moldm^{-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	1.36					
318	1.52	85	62	-75	3.7	315
323	1.98					
328	2.10					

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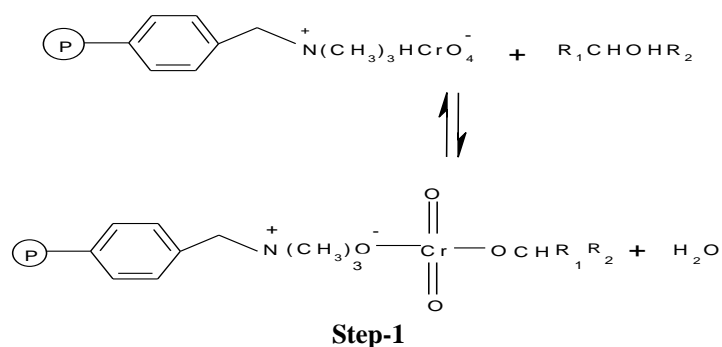
2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step. (Step-2)

**Step-2**
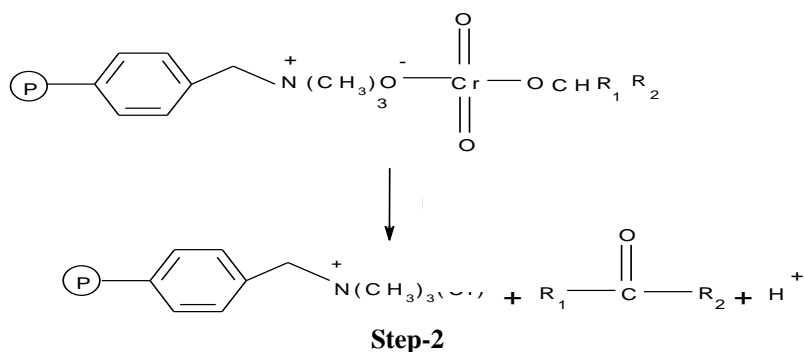
3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. (Step-3)

Step- 3
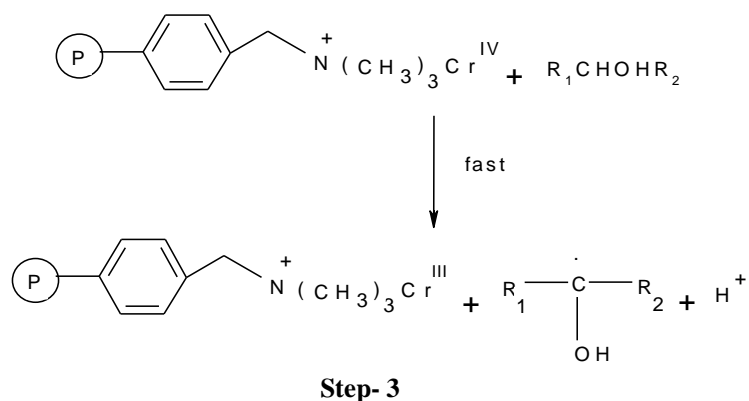
4) Subsequently the free radical will react with another oxidant site in the polymeric reagent in a fast step leading to the formation of chromium (V). (Step- 4)

Step- 4
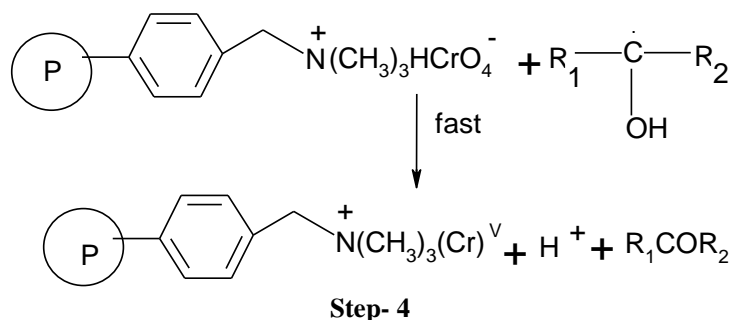
5) The intermediate chromium (V) in the last step reacts with 1-phenylethanol produce acetophenone. The test for formation of chromium (V) and (IV) by the characteristic induced oxidation of iodide and manganese (II) were not probably due to heterogeneity of the reaction mixture. (Step-5)

[$R_1 = C_6H_5-$ and $R_2 = - CH_3$]
Step- 5
Scheme- I
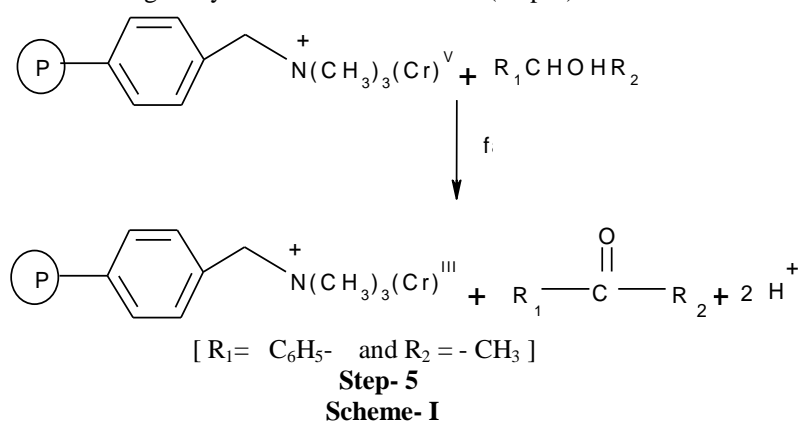
IV. Conclusion :

Practically 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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