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Oxidation of Alcohol by Complex Chromates with Kinetic and Mechanistic Study

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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 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] = 79KJ mol^{-1}, [$\Delta H^{\#}$]=58 KJ mol^{-1}, [$\Delta S^{\#}$]=-72 JK mol^{-1}, [$\Delta G^{\#}$] =298KJ mol^{-1}, and [A] =3.5 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 and mechanism,*

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I. INTRODUCTION

There are few reports available on the non-Malapradin Sodium Chromate oxidation of aromatic alcohols [1-4]. In continuation of our earlier studies[5], 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, herewith report the oxidation of 1-phenylethanol by polymer- supported sodium chromate. The polymer Amberlite IRA 400 [Cl^{-}] is the strong anion exchange resin are supported on sodium chromate and used as an oxidant.

II. EXPERIMENTAL

2.1 Preparation of Chromate supported oxidizing agent

The supported oxidizing agent was prepared by reported method [6-8].The Chloride form of basic anion exchange resin Amberlite IRA 400 [Cl^{-}] was stirred with a saturated solution of sodium chromate in water for 60 minutes at RT using a magnetic stirrer. The Chloride ion was readily displaced and $HCrO_4^-$ form of resin was obtained in 30 min. The resin was successively rinsed with water, acetone and THF and finally dried in vaccum at 324 K for 5 hrs.

2.2 DETERMINATION OF THE CAPACITY OF CHROMATE FORM OF THE POLYMERIC REAGENT

The capacity of the chromate form of Amberlite IRA 400 [Cl^{-}] resin was 2.55 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 and solvent. The reaction was carried out either constant stirring using magnetic stirrer and at a constant temperature 320 ±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 formed was measured using Shimadzu UV-VIS spectrophotometer (Model Mini 1240).

2.4 POLYMERIZATION TEST

Mixing PS-oxidant, 1-PE and solvent at 318 K with continuous stirring initiation of reaction. After 30 min, the reaction mixture was withdrawn in a test tube and acrylonitrile and ethyl 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 416K (Literature value 419K). **UV –VIS** spectrum (in ethyl alcohol giving absorption maxima at194,190, 177 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 1626cm^{-1} indicates the presence of -C = O stretching mode, 1600 cm^{-1} indicates the presence of aromatic (-C= C-), 3059 cm^{-1} indicates the presence of (-C- H stretch).

III. RESULTS AND DISCUSSION

3.1 Effect of varying 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-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
Amberlite IRA 400 $[Cl^-]$	1.65	1.72	1.89	1.99

3.2 Effect of varying 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- 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
Amberlite IRA 400 $[Cl^-]$	1.35	1.41	1.49	1.52

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].

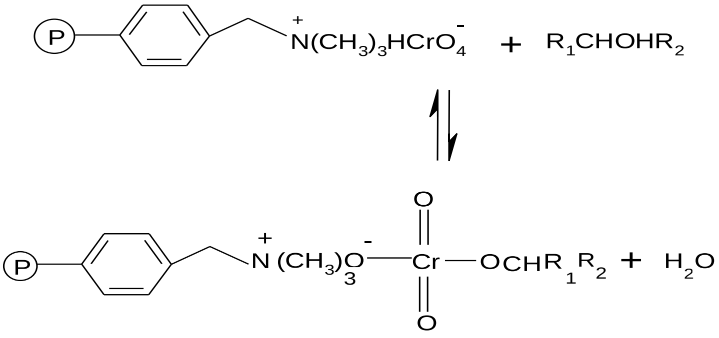
Table – 3.3 Effect of varying temperature

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Temperature K →	313	318	323	328
Amberlite IRA 400 $[Cl^-]$	1.36	1.52	1.98	2.10

Table -3.4 Thermodynamic parameters for the PS-Chromate oxidation of 1-PE

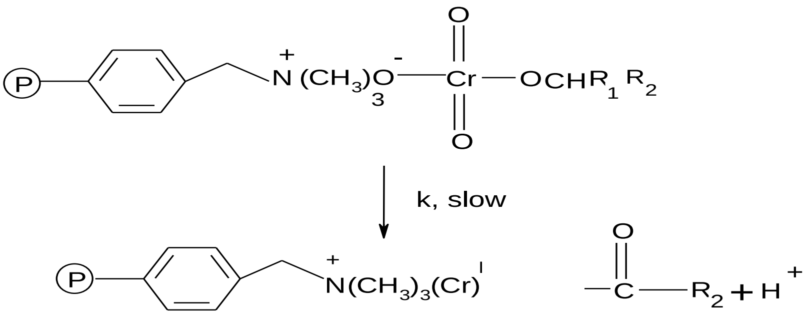
Temp. K	k x 10^{-4} moldm^{-3} s^{-1}	[Ea] KJmol^{-1},	[$\Delta H^{\#}$] KJ mol^{-1}	[$\Delta S^{\#}$] JK mol^{-1}	[A] $10^{-5}s^{-1}$	[$\Delta G^{\#}$] KJ mol^{-1}
313	1.36	75	62	-71	3.1	292
318	1.52					
323	1.98					
328	2.10					

1) 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)**[8-10].



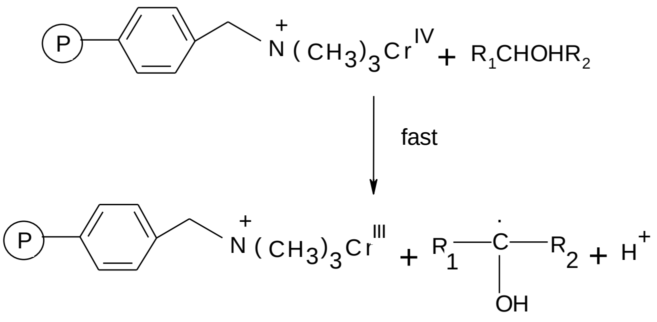
Step-1

2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step. (Step-2) [11]



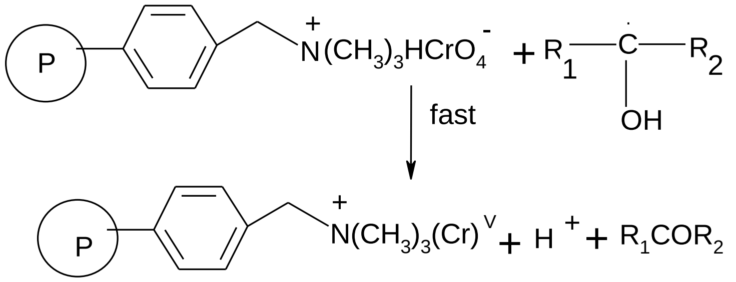
Step-2

3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. (Step-3)[12].



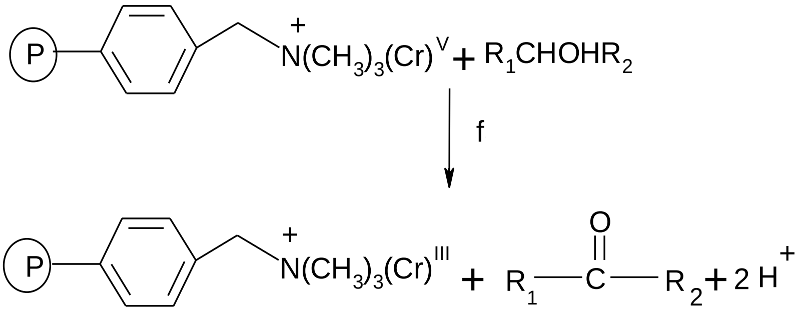
Step- 3

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) [13].



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) [14-15].



[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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REFERENCES

[1]. Hilage NP,Kakde SA,SonawaneVY, Oxidation of 4-Chlorobenzyl alcohol by polymer supported chromic acid. Journal of Indian Chemical Society (2009); 86,577-581.
[2]. Lakshmi S.and Renganathan R., Kinetics of Oxidation of certain pyrimidines by Ce (IV).International Journal of Chemical Kinetics (1996); 28,713.
[3]. Corey EJ and Schmidt G., Useful procedures for the oxidation of alcohol involving pyridiumchromate in aprotic solvent. Tetrahedron Letters (1979); 20, 399-402.
[4]. Sonawane VY, Chromium (VI) Catalyzed Oxidation of Primary alcohol by Polymer Supported Reagent: A Kinetic and Mechanistic Study. Asian Journal of Chemistry (2013); 25(7), 4001.
[5]. Cainelli G,Cardillio G, Orena M. and Sardri S. Journal of American. Chemical Society (1976); 98, 6767.
[6]. Brunlet T, Jouitteau C.and Gelhard G., Polymer Support Reagent-Oxidation of alcohol by Complex Chromates.Journal of Organic Chemistry (1986); 51 , 4016.
[7]. Mosher WA , Clement H. and Hillard RL.Journal of American Chemical Society (1993) ;29, 565 .
[8]. Watanabe W and Westheimer FH.Journal of Chemical Physics (1979); 61, 17.
[9]. M. M. Salunke, D. G. Salunke, A. S. Kanade, R. B. Mane and P. P. Wadgaonkar ,
[10]. *Synth. Commun.* **1990,** 2B**,** 1143.
[11]. J. Matsuo, A. Kawana, K. Pudhon and T. Mukaiyama, *Chem. Lett.*, **2002**, 250.
[12]. R. O. Hutchins, N. R. Natale and W. J. Cook, *Tetrahedron Lett.*, **1997**, 4167.
[13]. A. J. Buglas and J. S. Waterhouse, *J. Chem. Edu*., **1987**, 64, 3712.
[14]. J. H. Espenson, J. *Am. Chem. Soc*., **1964**, 86, 5101.
[15]. Vilas Y.Sonawane.,*Ind.J.App.Res.* , **2013**, 3(5), 60-62.
[16]. Vilas Y.Sonawane., *Int.J.Chem.Sciences*, **2013**, 1(4), 40-45.
[17]. Vilas Y.Sonawane., *Asian J.Chem*. **2013**, 25(2), 4001-4004.