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Polymer Supported Sodium Chromate Oxidation of 1-Phenylethanol: A Kinetic Mechanistic Study

Vilas Y. Sonawane[1*]

1. Department of Chemistry, B.Raghunath Arts, Commerce and Science, College, Parbhani (MS) India 431401
*[Email: sonawane _vy@rediffmail.com]

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] = 75 KJ mol^{-1}, [$\Delta H^{\#}$]=56 KJ mol^{-1}, [$\Delta S^{\#}$]=-69 JK mol^{-1}, [$\Delta G^{\#}$] =298KJ mol^{-1}, and [A] =3.4 x 10^{-5}s^{-1} results under pseudo *zero order* conditions are in agreement with the rate law. In agreement with the rate law, the 1/k_2 versus [H^+] profile passes through the minimum. Main reaction product acetophenone isolated and characterized.

Keyword: Sodium chromate, oxidation, kinetics and mechanism, Thermodynamic parameters.

1. Introduction

There are few reports available on the non-Malapradin Sodium Chromate oxidation of aromatic alcohols [1-4].There is contractioryin reagent to the ionic or free radical mechanism being followed. Now a days the development of newer chromate reagents [5, 6] for the oxidation of organic substrates continues to be of interest. In continuation of our earlier studies [7], 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. Dowex50WX8 [H^-] is the strong anion exchange resin are supported on sodium chromate and used as an oxidant.

2. Experimental

Triply distilled water was used for preparation of the solutions. Sodium chromate (Loba), 1-PE (Sigma-Aldrich), acetone, benzene, THF, carbon tetrachloride (E-Merck) and all other chemicals of analytical reagent/guaranteed reagent grade were used after redistillation /recrystillation.

2.1 Preparation of Chromate supported oxidizing agent

The supported oxidizing agent was prepared by reported method [8-10]. The hydrogen form of anion exchange resin Dowex 50WX8 [a hydrogen form anion exchange resin] was stirred with a saturated solution of sodium chromate in water for 30 minutes at RT using a magnetic stirrer. The hydrogen ion was readily displaced and $HCrO_4^-$ form of resin was obtained in 20 min. The resin was successively rinsed with water, acetone and THF and finally dried in vaccum at 323 K for 3h. The dried form of the chromate resin was stored and used kinetic study.

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

The capacity of the chromate form of polymeric reagent was determined by iodometrically. The capacity of the chromate form of Dowex 50WX8 resin was 1.75 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 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 5 x 10^{-3} dm^3 of 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 did initiation of reaction. After 45 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 [11]. It was also confirmed by ESR spectral analysis suggested the possibility of free radical interventation 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 precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off. It was filtered and solid residue was obtained that dissolved in petroleum ether and subject to TLC. 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 at 196, 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 1632 cm^{-1} indicates the presence of -C=O stretching mode, 1575 cm^{-1} indicates the presence of aromatic (-C= C-), 3063 cm^{-1} indicates the presence of (-C- H stretch). The observed values are in good agreement with the expected acetophenone.

3. Results and discussion

3.1 Effect of varying weights of PS-Chromates

The order with respect to weights PS-Chromates is zero, as the plots of absorbance against time were linear in all runs and observed rate constant are fairly constant between 50 to 80 x 10^{-6} kg of oxidant at constant concentration of solvent (1,4-dioxane , 5 x 10^{-3} dm^3) and 1-PE (12.3 x 10^{-3} mol/dm^{-3}), the effect of varying weights of on PS-Chromate *zero order* rate constant as shown in Table-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
Dowex50WX8 [H^-]	1.45	1.52	1.79	1.99

3.2 Effect of varying concentrations of 1-PE

At a varying concentration of 1-PE [8.20 to 20.4 x 10^{-3}mol/dm^3], constant weights of PS-Chromate [70x10^{-6} kg] and constant concentration of solvent [1, 4-dioxane, 5x$10^{-3}$$dm^3$], zero order rate constant [Table- 2] was found.

3.3 Effect of varying dielectric permittivity of the medium on the reaction rate

It was found that as the dielectric constant of the medium increased the rate of reaction as indicated by a linear plot between logk_2 versus 1/D, where D is the dielectric constant of the medium. It indicates the ion-dipole determining and ion-dipole type interaction in the rate determining step and the reacting ion is possibly an anion.

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
Dowex50WX8 $[H^-]$	1.45	1.59	1.63	1.82

Table 3.3 Effect of varying dielectric permittivity

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Solvent [5 x$10^{-3}dm^3$] →	THF	CCl_4	1,4-dioxane	$CHCl_3$
Dielectric constant →	2.00	2.17	2.28	4.81
Dowex50WX8 $[H^-]$	1.10	1.29	1.68	1.98

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-4]. 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-5].

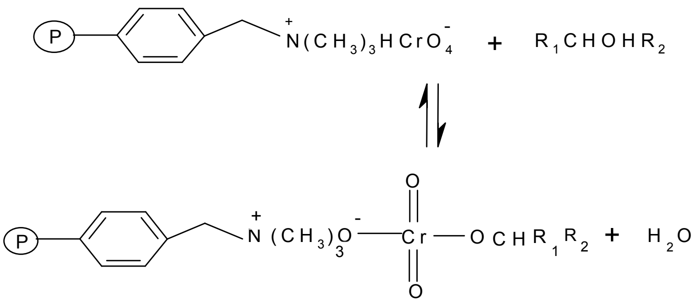
Table 3.4: Effect of varying temperature

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Temperature K →	313	318	323	328
Dowex50WX8 $[H^-]$	1.55	2.25	2.53	2.68

Table 3.5: Thermodynamic parameters for the PS-Chromate oxidation of 1-PE

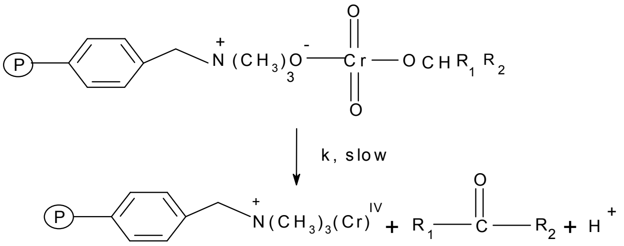
Temp. K	k x 10^{-4} $moldm^{-3}$ s^{-1}	[Ea] $KJmol^{-1}$,	[$\Delta H^{\#}$] KJ mol^{-1}	[$\Delta S^{\#}$] JK mol^{-1}	[A] $10^{-5}s^{-1}$	[$\Delta G^{\#}$] KJ mol^{-1}
313	1.55	75	56	-69	3.4	293
318	2.25					
323	2.53					
328	2.68					

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)



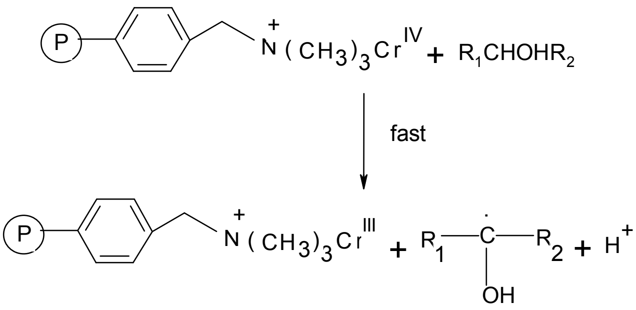
Step-1

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



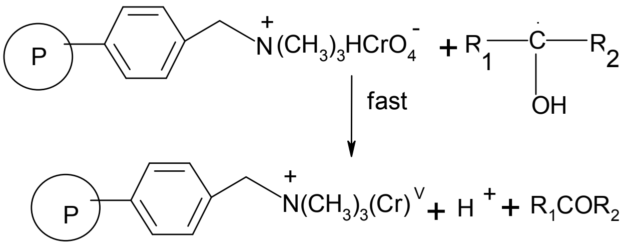
Step-2

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



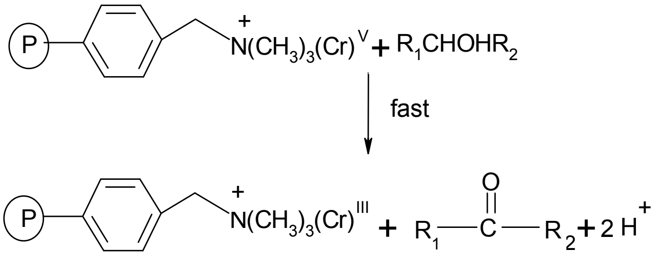
Step- 3

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 [12] and manganese (II) [13] 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

The linearity of absorbance against time plots and constancy of the *zero order* rate constants indicate that the reaction neither depends on the polymeric reagents nor on the alcohol concentration. This anomalous nature of the reaction may be because of the fact that the oxidant is taken in the form of solid supported on polymer. Polymer supported oxidizing agent proved to be exclusively selective towards the oxidation of 1-Phenylethanol, giving acetophenone as the only product.

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.

5. Acknowledgement

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