

Kinetic and Thermodynamic Study of the Oxidation of Aromatic Alcohol using Polymer Supported Chromic Acid

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Abstract: Oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is an important transformation in organic chemistry. The kinetics of the oxidation of 1-Phenylethanol (PE) by Polymer supported 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 and temperature. A free radical scavenger affects the reaction rate. The stoichiometry has been found to be 1mol PE: 1mol of Chromate. Thermodynamic parameters evaluated are $[E_a] = 75\text{KJ mol}^{-1}$, $[\Delta H^\ddagger] = 54\text{ KJ mol}^{-1}$, $[\Delta S^\ddagger] = -69\text{ JK mol}^{-1}$, $[\Delta G^\ddagger] = 288\text{KJ mol}^{-1}$, and $[A] = 3.1 \times 10^{-5}\text{s}^{-1}$ results under pseudo zero order conditions are in agreement with the rate law. The reaction product acetophenone was isolated and characterized.

Keywords- Kinetics, Oxidation, Polymer supported reagent, Thermodynamics

I. INTRODUCTION

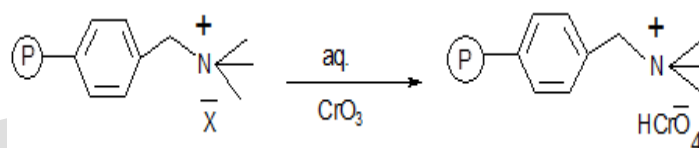
Oxidation of alcohols has been studied extensively using different oxidizing agents and in various media. One of the most commonly used oxidants is dichromate and its derivatives¹⁻⁷. In going through the literature, one finds controversial results regarding the kinetics of these reactions through all studies have proposed similar mechanism. Some reports suggested applicability of zero order kinetics with Michaelis-Menten kinetics. In the present investigation, we now report the oxidation of 1-Phenylethanol by polymer-supported sodium chromate. The polymer Amberlite IRA 410 [Cl⁻] is the strong anion exchange resin are supported on sodium chromate and used as an oxidant.

II. EXPERIMENTAL

Preparation of Chromate supported oxidizing agent

The supported oxidizing agent was prepared by reported method⁸⁻¹⁰. The Chloride form of basic anion exchange resin Amberlite IRA 410 [Cl⁻] was mixed with a solution of sodium chromate in water for 90 minutes at RT using a magnetic stirrer. The Chloride ion was readily displaced and HCrO₄⁻ form of resin was obtained in 50 min. The resin was

successively rinsed with water, acetone and THF and finally dried in vacuum at 323 K for 15hrs.



[X = Cl] polymer supported oxidizing agent

Determination of the capacity of chromate form of the polymer supported reagent¹¹⁻¹²

The capacity of the chromate form of Amberlite IRA 410 [Cl⁻] resin was 2.71 meq/mL and used for kinetic study throughout kinetic work.

Method of kinetics¹³

The reaction mixture for the kinetic run was prepared by mixing 1-PE, Polymer supported chromate and solvent. The reaction was carried out either constant stirring using magnetic stirrer and at a constant temperature $318 \pm 5\text{ K}$. 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 ml of 1, 4-dioxane and subjected to spectral analysis. The absorbance of the product formed was measured using Shimadzu UV spectrophotometer (Model Mini 1240).

Induced polymerization of acrylonitrile test¹⁴⁻¹⁵

The oxidation of alcohols, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that, a two electron oxidation, giving rise to free radicals, is unlikely in the present reaction. The formation of copious precipitate indicates formation of a free radical species in the reaction.

Product analysis¹⁶⁻¹⁷

The oxidation of 1-PE leads to the formation of acetophenone. The product formed was analyzed by their 2,4-Dinitro phenyl hydrazine derivatives. The product is then

vacuum dried, weighed and recrystallised from alcohol and determined its melting point 418K (Literature value 419K). UV spectrum (in ethyl alcohol giving absorption maxima at 197, 194, 175 and 167 μ which suggested the presence of ketone structure in the compound.

The FTIR spectrum of compound (in KBr) showed the presence of a sharp band 1720-1640 cm^{-1} indicates the presence of -C=O stretching mode, 1550 cm^{-1} indicates the presence of aromatic (-C=C-), 3065 cm^{-1} indicates the presence of (-C-H stretch).

Rate laws

The reaction is zero order with respect to Oxidant. Further the pseudo zero order rates constant. k_{obs} is independent of the initial concentrations of oxidant. The reaction is zero order with respect to the alcohol also.

III. RESULTS AND DISCUSSION

Effect of varying weights of Polymer supported Chromates

When we plots of absorbance against time were linear in all runs and observed rate constant are remains constant at various quantity of polymeric oxidizing agent at constant concentration of solvent 1:4 dioxane and 1-PE, the effect of varying weights of on Polymer supported Chromate zero order rate constant as shown in Table 1.

Table 1: Effect of varying weights of PS-Chromate on reaction rate at 318 K.

Rate constant →	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Oxidant $\times 10^{-6} \text{ kg}$ →	50	60	70	80
Amberlite IRA 410 [Cl]	1.69	1.72	1.75	1.79

Effect of varying concentrations of 1-PE

As taking various concentration of 1-PE, constant weights of polymer supported Chromate and same concentration of solvent 1: 4 dioxane, zero order rates constant was found. These results shown in table 2.

Table 2: Effect of varying concentrations of 1-PE

Rate constant →	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
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
Amberlite IRA 410 [Cl]	1.35	1.38	1.39	1.41

Effect of varying temperature

The reactions were carried out at four various temperatures. We observed that, the rate of reaction increased

with an increase in the temperature. These results shown in Table 3. The thermodynamic parameters like energy of activation [Ea], enthalpy of activation [ΔH^\ddagger], entropy of activation [ΔS^\ddagger], and free energy of activation [ΔG^\ddagger]. The high positive values of free energy of activation indicate that the transition state is highly solvated and frequency factor [A] was calculated by determining values of k at different temperatures. These results shown in Table 4.

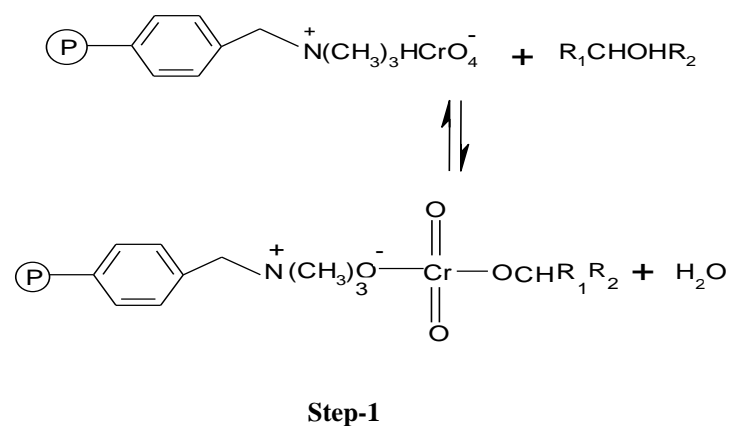
Table 3: Effect of varying temperature

Rate constant →	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Temperature K →	313	318	323	328
Amberlite IRA 410 [Cl]	1.46	1.49	1.52	1.85

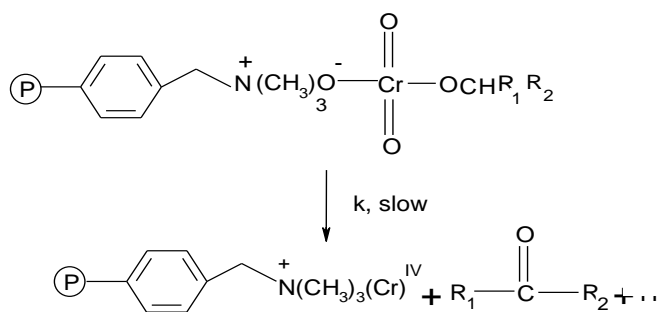
Table 4: Thermodynamic parameters for the PS-chromate oxidation of 1-PE

Temp. K	$k \times 10^{-4}$ $\text{mol dm}^{-3} \text{ s}^{-1}$	[Ea] KJ mol^{-1}	[ΔH^\ddagger] KJ mol^{-1}	[ΔS^\ddagger] JK mol^{-1}	[A] 10^7 s^{-1}	[ΔG^\ddagger] KJ mol^{-1}
313	1.36	75	54	-69	3.1	288
318	1.52					
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]

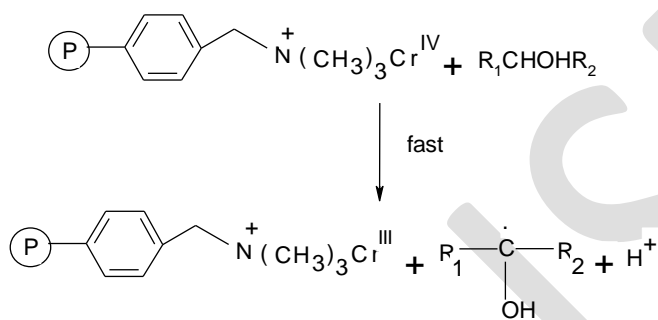


2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step. [Step-2]



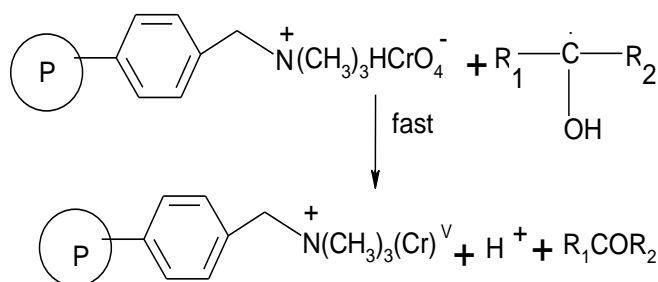
[Step-2]

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



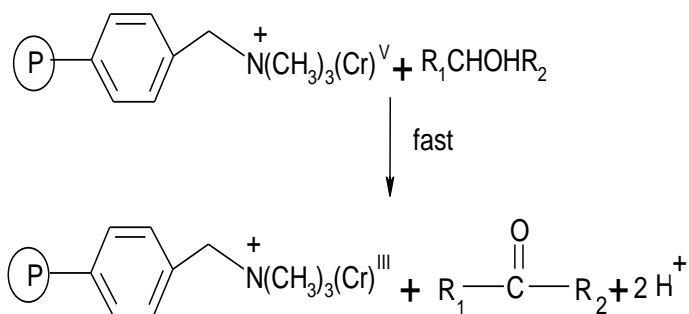
[Step-3]

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. [Step-5]

[R₁= C₆H₅- and R₂= -CH₃]

[Step-5]

Scheme-I

IV. CONCLUSION

According to various experiments, 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 was suggested¹⁸⁻²².

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