POLYMER SUPPORT CHLOROCHROMATE: A NOVEL OXIDANT, KINETIC AND SYNTHETIC ASPECTS

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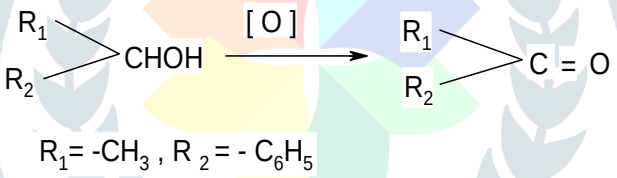
Abstract : The oxidation of 1- Phenylethanol has been studied spectrophotometrically to compare the polymer substrate supported reagent with a commercially available cross-linked polymeric reagent. The reagent supported on strong anion exchange resin was found to be more efficient in the oxidation reaction. The reagent is very easily separated from the reaction mixture and can be manually removed from the reaction mixture, which remains clear during and after the reaction. The kinetic of oxidation of 1-Phenylethanol with chromic acid supported on anion exchange resin like Tulsion T-42 [Cl^-] in 1, 4-dioxane has been studied. The reaction is found to be of zero order each in concentration of alcohol and oxidant. The oxidation product have been isolated and characterized by its derivative, UV and FT-IR and C^{13} NMR spectral studies. The effect of substituent's on the rate of oxidation and the activation parameters were determined with respect to slow step of mechanism.

Keywords - Polymer- supported chromic acid, Oxidation, 1-Phenylethanol, Kinetic, Mechanism, TulsionT-42 A [Cl^-].

I. INTRODUCTION

The kinetics and mechanism of oxidation of chromium (VI) has been well studied, chromic acid being one of the most versatile available oxidizing agents, reacting with diverse substrates. Now a day the development of newer chromium (VI) reagents [1-6] for the oxidation of organic substrates continues to be of interest. Chromium is one of the most widely distributed heavy metals in the earth's crust. It is normally found into oxidation states i.e. Cr (III) and Cr (V). Chromium is required in small quantities as an essential trace metal. Most of the biological tissues contain Cr (III) which is usually non toxic,where as Cr (VI) is a highly toxic for the metal to the organism.[7]The selective oxidation of primary alcohols and secondary alcohols into their corresponding aldehydes (or carboxylic acids) and ketones is one of the most important transformations in modern organic synthesis. A myriad of oxidizing agents have been developed to affect this transformation shown in **Scheme I.**

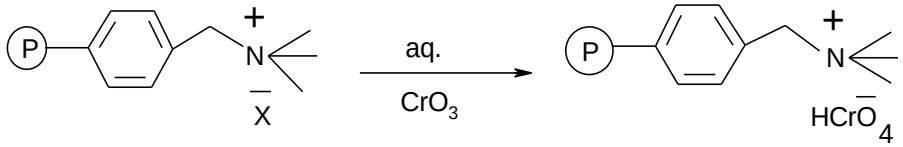


Scheme I-. Oxidation of alcohols to carbonyl compounds.

In the present investigation, here report the oxidation of 1-Phenylethanol by polymer- supported chromic acid. Tulsion T-42 [Cl^-] is the strong anion exchange resin are supported on chromium (VI) oxide and used as an oxidant.

II. EXPIRMENTAL

Preparation of supported oxidizing agent The supported oxidizing agent was prepared by reported method [8-10]. The chloride form of TulsionT-42 [a macro reticular strong anion exchange chloride form of resin] containing a quaternary ammonium group [10 x 10^{-3} kg] was stirred with a saturated solution of chromium trioxide [5 x 10^{-3} dm^3] in water [30 x10^{-3} dm^3] for 30 min 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 333 K for 4h. The dried form of the resin was stored and used throughout the kinetic study.



[X = Cl] Polymer supported oxidizing agent

Physical properties of Tulsion T-42 Tulsion A-42 (By Thermax India Ltd.Pune) is polystyrene copolymer with strong acid and it content 53 % water. It is occur in chloride form having P^H range 0-14. It is demineralization anion exchange resin.[13,14]
Determination of the capacity of chromate form of Tulsion T-42[Cl^-] The capacity of the chromate form of TulsionT-42 [Cl^-] polymeric reagent was determined by iodometrically.The capacity of the chromate form of resin was 1.32 mmol/g and used for kinetic study throughout work. The loading was also determined by elemental nitrogen analysis and was found to be 1.33 mmol/g.
Method of kinetics of oxidation procedure The reaction mixture for the kinetic run was prepared by mixing alcohol, oxidant and solvent. The reaction was carried out either constant stirring using magnetic stirrer and at a constant temperature 318 ±1 K. At different time interval, the reaction mixture was withdrawn using a micropipette. The aliquot thus withdrawn was taken in a stoppered 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 SL 159 UV-visible spectrophotometer. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3 %.

Induced polymerization test Mixing oxidant, alcohol and solvent at 318 K with continuous stirring did initiation of reaction. After 30 min, the reaction mixture was withdrawn in a test tube and acrylonitrile 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 as well as on diluting the reaction mixture with acidified methanol, a precipitate formed, suggested the possibility of free radical interventation in the reaction.

Product analysis The oxidation of 1-Phenylethanol leads to the formation of acetophenone. The product formed was analyzed by their 2, 4-dinitrophenylhydrazine derivatives. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, the product is then vacuum dried, weighed and recrystallised from alcohol. The yield of DNP recrystallisation with the DNP of acetophenone was 94%. The product also identified either by comparison with authentic samples or by UV, FT-IR spectral and elemental analysis. The IR spectra were recorded on a Jasco FT-IR spectrophotometer using KBr pellets. The melting point of 2, 4-dinitrophenylhydrazone derivative of 1-Phenylethanol is 237^0C [510 K].

UV spectrum **λmax** 245 nm.

IR data: - A sharp band at 1686 cm^{-1} for -C = O stretching mode, 1587 cm^{-1} aromatic (- C = C-), 3062 cm^{-1} (-C- H stretch).

III. RESULT AND DISCUSSION

Effect of varying weights of oxidant The order with respect to weights oxidant 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-Phenylethanol (12.3 x 10^{-3} mol/dm^{-3}), the effect of varying weights of oxidant on zero order rate constant as shown in Table-1.

Table-1. Effect of varying weights of oxidant 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
Tulsion T-42[Cl^-]	2.18	2.20	2.25	2.30

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

Table-2 Effect of varying concentrations of 1- Phenylethanol on the reaction rate at 318 K.

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
Tulsion T-42 [Cl^-]	1.50	2.08	2.36	2.59

Effect of varying dielectric permittivity of the medium on the reaction rate It was found that as the dielectric constant of the medium increased, this including r* < r [Where r* and r refer to the radii of the reactant species and activated complex respectively] at constant concentration of 1-Phenylethanol [12.3 x 10^{-3} mol/dm^3] and constant concentration of oxidant [70x 10^{-6} Kg], solvent [5 x $10^{-3}dm^3$] as shown in Table-3.

Table-3. Effect of varying dielectric permittivity of the medium on the reaction rate at 318 K.

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Solvent [5 x$10^{-3}dm^3$] →	C_6H_{12}	CCl_4	1,4-dioxane	$CHCl_3$
Dielectric constant →	2.00	2.17	2.28	4.81
Tulsion T-42[Cl^-]	1.09	1.59	2.36	2.56

Effect of varying temperature on the reaction rate The reaction was carried out at four different temperatures under otherwise similar reaction conditions to study the effect of temperatures on the rate of reaction. 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 [$\Delta G^{\#}$] and frequency factor [A] were calculated by determining values of k at different temperatures. [Table-5].

Table - 4. Effect of varying temperature on the reaction rate

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Temperature K →	313	318	323	328
Tulsion-T-42 [Cl^-]	2.01	2.12	2.45	3.13

Table -5. Activation parameters for the oxidation of 1- Phenylethanol

Energy of activation [Ea] KJ mol^{-1}	90 ± 4
Enthalpy of activation [$\Delta H^{\#}$] KJ mol^{-1}	52 ± 3
Entropy of activation [$\Delta S^{\#}$] JK mol^{-1}	-61 ± 2
Free energy of activation [$\Delta G^{\#}$] KJ mol^{-1}	279 ± 2
Frequency factor [A] X 10^{-5} s^{-1}	3 ± 0.5

Effect of repeated use of supported oxidizing agent The resin was filtered after the reaction and washed with 0.1 M HCl and 0.2M NaOH successively to remove CrO_2 deposition on the resin. The resin was then regenerated by stirring with chromic acid, followed by washing with water methanol and drying in vacuum at 333K for 5h. These regenerated beads were used for the reaction under identical reaction conditions. The conversion of 1-Phenylethanol was found to decrease slightly with the repeated use. There is a likelihood of having less supported agents on the resin whose pore structure could be altered by some dehydration of $HCrO_3^-$ leading to the formation of CrO_2 which remains inside blocking some channels. Therefore, during the third use the reduced chromate bound to the resin was directly treated with excess of chromic acid. There was an improvement in the reactivity of the supported oxidizing reagent. This suggests that the chromate salts can be effectively used on polymer supports. Several sets of experiments with various weights of oxidant, concentration of 1- Phenylethanol and change in solvent were carried out. The reaction was found to be zero order. The proposed path for the reaction of chromium (IV) then makes possible a different mechanism for oxidation of alcohols. According to Westheimer and Watanable [12], subsequent steps must involve chromium (IV) as shown in Scheme (II) and (III).

Scheme (II)

$$Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V} \quad (1)$$

$$Cr^{V} + R_2CHOH \rightarrow R_2C = O + Cr^{III} + 2H^{+} \quad (2)$$

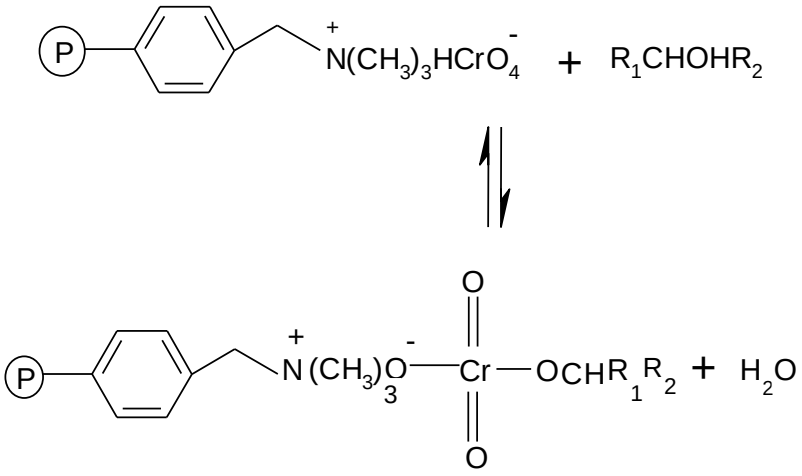
Scheme (III)

$$2Cr^{V} \rightarrow Cr^{III} + Cr^{V} \quad (3)$$

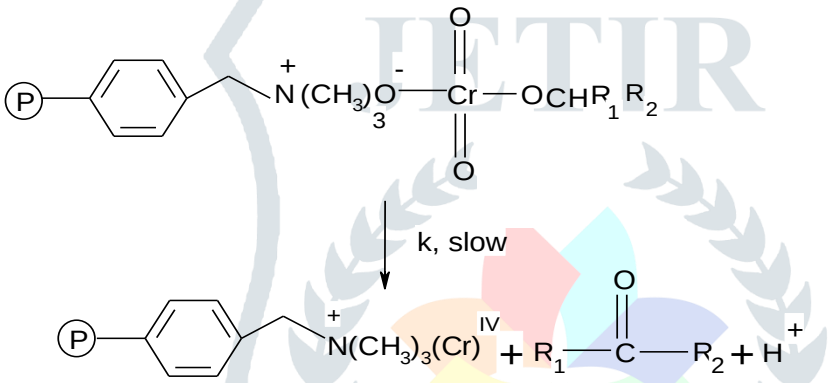
$$Cr^{V} + Red \rightarrow Cr^{III} + oxi \quad (4)$$

The mechanism is suggested in **Scheme (IV)** and involves ester formation.

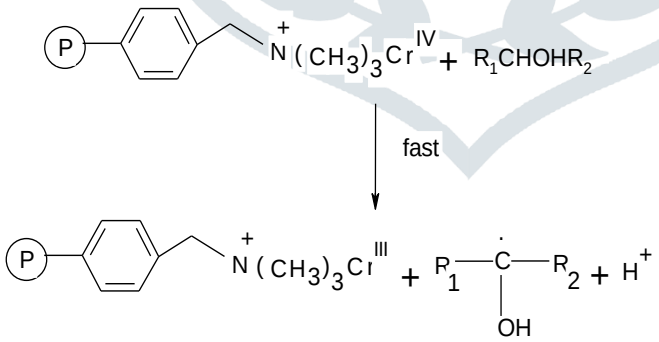
1) The polymer supported reagent reacts with a molecule of alcohol to form a chromate ester.



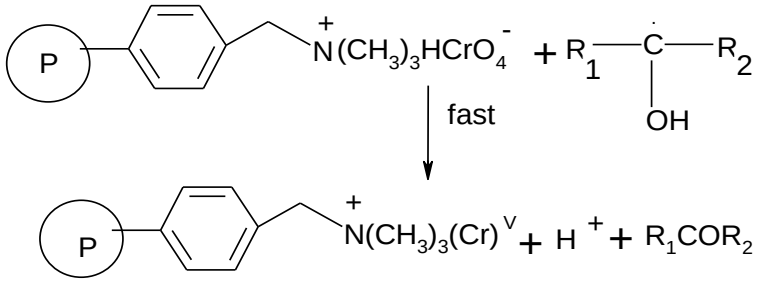
2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step.



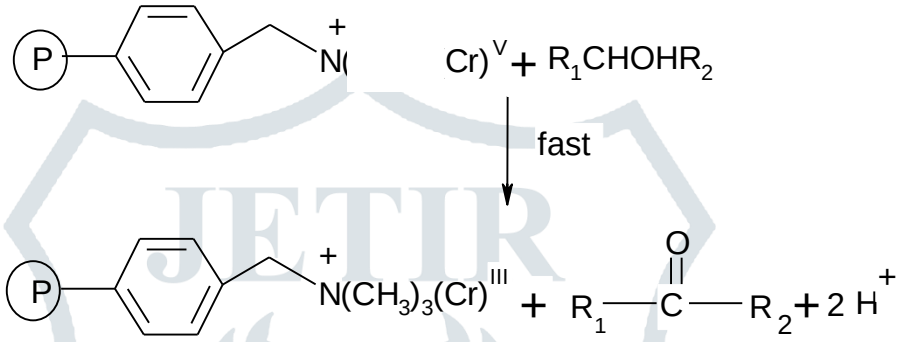
3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. The free radical species formation in the reaction was confirmed by the polymerization of added acrylonitrile or addition of acidified methanol into the reaction mixture.



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).



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.



[R_1= CH_3- C_6H_4- and R_2 = - CH_3]

Scheme IV

IV. 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. According to **Scheme IV**, a second order rate law is expected. But since the first step of ester formation occurs in solid phase and assuming that this equilibrium does not contribute to the rate of reaction. We obtained **zero order** dependence with rate constant *k* of the second slow step in which product acetophenone was obtained[15, 16]. Based on the experimental observations a probable mechanism is suggested.

V. ACKNOWLEDGMENT

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