Development of green and of polymer-supported chromic acid on strong anion exchange resin for oxidation of secondary alcohol - A kinetic and mechanistic study

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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 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-52 A [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.

Key words - Polymer- supported chromic acid, Oxidation, 1-Phenylethanol, Kinetic, Mechanism, Tulsion-T-52 A [Cl⁻].

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. Tertiary alcohols resist oxidation by conventional oxidizing agents unless they are dehydrated in acidic media to in alkenes, which subsequently undergo oxidation. In modern synthetic chemistry there is still a demand for mild and selective reagents for the oxidation of alcohols in presence of other oxidizable groups.

$$R_1 = -CH_3 , \quad R_2 = -C_6H_5$$
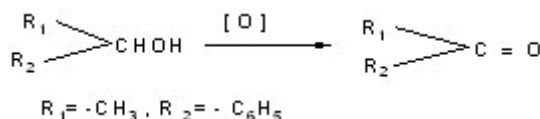
Scheme 1: Oxidation of alcohols to carbonyl compounds

In the present investigation, we now report the oxidation of 1-Phenylethanol by polymer-supported chromic acid. Tulsion-T-52 A [Cl⁻] is the

strong anion exchange resin are supported on chromium (VI) oxide and used as an oxidant.

EXPERIMENTAL

Preparation of supported oxidizing agent

The supported oxidizing agent was prepared by reported method.[8-10] The chloride form of Tulsion-T-52 A [a macro reticular anion exchange resin] containing a quaternary ammonium group [10 x 10^{-3} kg] was stirred with a saturated solution of chromium trioxide [5 x 10^{-3}dm³] in water [30 × 10^{-3}dm³] for 30 minute at room temperature using a magnetic stirrer. The $HCrO_4^-$ form of resin was obtained in 30 minute. The resin was successively rinsed with water, acetone and THF and finally dried in vaccum at 323 K. The dried form of the resin was stored and used throughout the kinetic study.

$[X = Cl]$

Polymer supported oxidizing agent
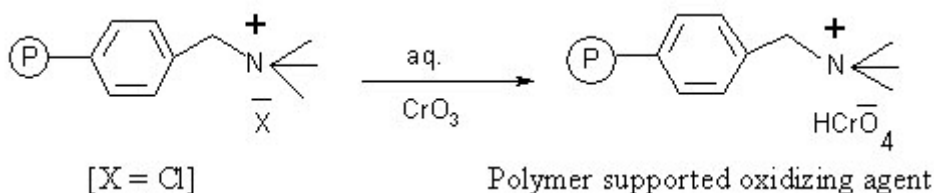
Determination of the capacity of chromate form of the polymeric reagent

The capacity of the chromate form of Tulsion-T-52 A [Cl⁻] polymeric reagent was determined by iodometrically.[11-14] The capacity of the chromate form of resin was 6.90 mmol/g and used for kinetic study throughout work. The loading was also determined by elemental nitrogen analysis and was found to be 6.98 mmol/g.

Chemicals and Reagents

All reagents used were of Analytical Grade and all solutions were prepared with double distilled water.

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} dm³ 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

Initiation of reaction was done by mixing oxidant, alcohol and solvent at 318K with continuous stirring. 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.[15] 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 intervention in the reaction.

Product analysis

The oxidation of 1-Phenylethanol leads to the formation of acetophenone. The product formed was analyzed by its 2, 4-dinitrophenylhydrazine derivative. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, the product is then vacuum dried, weighed and recrystallised from ethanol. The yield of DNP recrystallisation with the DNP of acetophenone was 96%. The product also identified either by comparison with authentic samples or by UV, FT-IR spectral, C¹³ NMR and by elemental analysis. The IR spectrum was recorded on a Jasco FT-IR spectrophotometer using KBr pellets. The melting point of 2, 4-DNP derivative of 1-Phenylethanol is 237⁰C [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).

RESULTS 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 × 10^{-3} dm^3) and 1-Phenylethanol (12.3 × 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 →	$k \times 10^{-4}$ mol dm^{-3} s^{-1}			
Oxidant x 10^{-6} kg→	50	60	70	80
Tulsion-T-52 A [Cl$^-$]	2.20	2.25	2.45	2.66

Table 2: Effect of varying concentrations of alcohol on the reaction rate at 318 K.

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
Tulsion-T-52 A [Cl$^-$]	1.70	2.18	2.56	2.89

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

Rate constant →	$k \times 10^{-4}$ mol dm^{-3} s^{-1}			
Solvent [5×10^{-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-52 A [Cl$^-$]	1.19	1.79	2.76	2.96

Table 4: Effect of varying temperature on the reaction rate

Rate constant →	$k \times 10^{-4}$ mol dm^{-3} s^{-1}			
Temperature K →	313	318	323	328
Tulsion-T-52 A [Cl$^-$]	2.0	2.22	2.75	3.33

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

Energy of activation [Ea] KJ mol^{-1}	94±5
Enthalpy of activation [ΔH$^{\#}$] KJ mol^{-1}	59±3
Entropy of activation [Δ S$^{\#}$] JK mol^{-1}	-65±2
Free energy of activation [ΔG$^{\#}$] KJ mol^{-1}	299±2
Frequency factor [A] ×10^{-5} s^{-1}	4±0.5

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 × 10^{-6} kg] and constant concentration of solvent [1,4-dioxane, 5 × 10^{-3}dm^3], zero order rate constant [Table- 2] was found.

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

It was found that, as the dielectric permittivity of the medium increased, the rate of reaction also increased at constant concentration of 1-Phenylethanol [12.3×10^{-3} mol/dm^3] and constant concentration of oxidant [70×10^{-6} Kg], solvent [5×10^{-3}dm^3] as shown in Table-3.

Effect of varying temperature on the reaction rate

The reaction was carried out at four different temperatures under the 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].
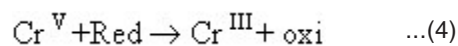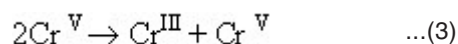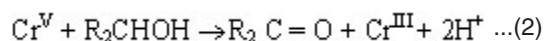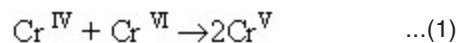
Effect of repeated use of supported oxidizing agent

The resin was filtered after the reaction and washed with 0.1 M HCl and 0.2M NaOH successively to remove CrO$_4$ 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.
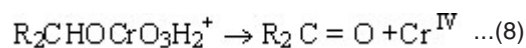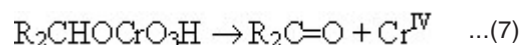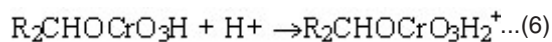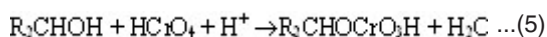
These regenerated beads were used for the reaction under identical reaction conditions. The conversion of 1-Phenylethanol was found to decrease slightly with the repeated use. There is a likelihood of having less supported agents on the resin whose pore structure could be altered by some dehydration of HCrO$_4^-$ leading to the formation of CrO$_4$ 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[16], subsequent steps must involve chromium (IV) as shown in Scheme (II) and (III).

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

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

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

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

Westheimer[16] then proposed that the oxidation of secondary alcohols proceeded via acid chromate ester intermediates.

$$R_2CHOH + HCrO_4 + H^+ \rightarrow R_2CHOCrO_3H + H_2C \quad ...(5)$$

$$R_2CHOCrO_3H + H+ \rightarrow R_2CHOCrO_3H_2^+ ...(6)$$

$$R_2CHOCrO_3H \rightarrow R_2C=O + Cr^{IV} \qquad ...(7)$$

$$R_2CHOCrO_3H_2^+ \rightarrow R_2C=O + Cr^{IV} \quad ...(8)$$

If the oxidant supported on polymer, which has certain advantages over heterogenous reaction, the intermediate chromium (IV) will further oxidize another molecule of alcohol to form a free radical species. Thus based on experimental results, obtained for the oxidation of 1-Phenylethanol by polymer support, the reaction was found to be 0th order. Initially Cr (VI) is reduced to Cr (IV). It is likely to react with another Cr (VI) to generate Cr (V) which is then reduced in a fast step to the ultimate product Cr (III). Such a sequence of reactions in Cr (VI) oxidation is well known.[17-19] The mechanism is suggested in Scheme (IV) and involves ester formation.

The polymer supported reagent reacts with a molecule of alcohol to form a chromate ester.
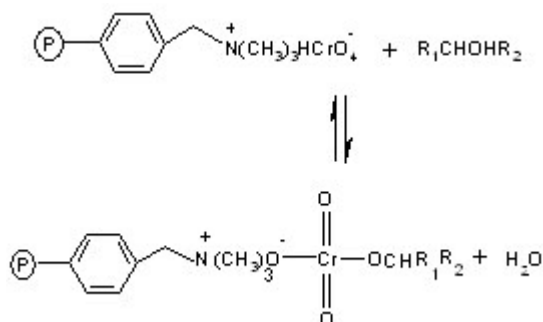
The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step.
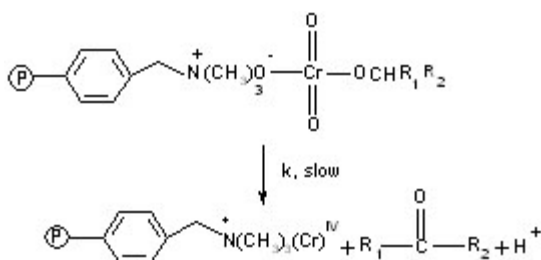

The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. The free radical species formation in the reaction was confirmed by the polymerization of added acrylonitrile or addition of acidified methanol into the reaction mixture.
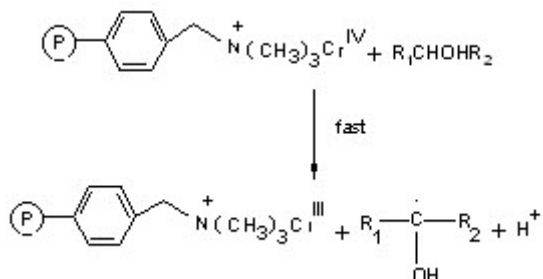
Subsequently the free radical will react with another oxidant site in the polymeric reagent in a fast step leading to the formation of chromium (V).
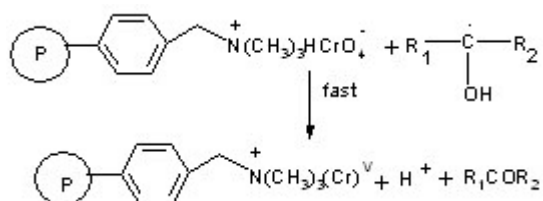
The intermediate chromium (V) in the last step reacts with 1-Phenylethanol produce acetophenone. The test for formation of chromium (V) and (IV) by the characteristic induced oxidation of iodide [20] and manganese (II) [21] were not probably due to heterogeneity of the reaction mixture.
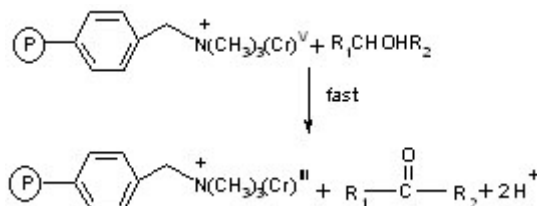
CONCLUSION

The linearity of absorbance against time plots and constancy of the zero order rate constant 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. Based on the experimental observations a probable mechanism is suggested.

ACKNOWLEDGEMENTS

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