



Kinetic features of the oxidation of secondary alcohol by polymer - supported chromic acid

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Abstract

The oxidation of secondary alcohol was investigated 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 kinetics of oxidation of secondary alcohol with chromic acid supported on anion exchange resins like Duolite A-101[Cl⁻] and Ambersep 900[OH⁻] in 1,4-dioxane has been studied. The reaction is found to be of zero order each in concentration of alcohol and oxidant. The stoichiometric coefficient of the reaction has been found to be 2:1. The oxidation products have been isolated and characterized by their derivatives, UV and FT-IR spectral studies. The effect of substituent's on the rate of oxidation and activation parameters for the overall reactions has been computed from Arrhenius plot.

Keywords: kinetic, oxidation, secondary alcohol, polymer-supported, chromic acid.

Introduction

A variety of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group. Kinetics and mechanism of oxidation of Cr (VI) have been well studied. Although many useful procedures for oxidation of alcohols to the corresponding carbonyl compounds have been reported [1], the general problem cannot be considered definitely settled. The chief drawbacks of these procedures are the relative difficulty in the preparation of the reagents and in the working up of the reaction mixture. The use of polymer supported chromic acid has some advantages in yield, purity of product, ease of separation and selective oxidation [2]. Polymer bound reagents has been reported for the oxidation of primary and secondary aromatic alcohols [3].

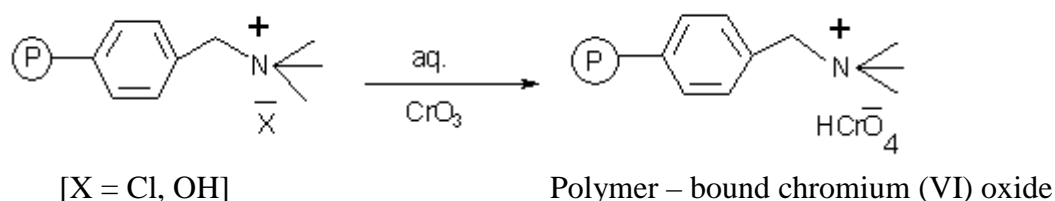
In synthetic organic chemistry, oxidation under phase transfer catalysis [4] finds wide applications, but using polymer supported oxidizing agents for kinetic and mechanistic studies are limited. In continuation of earlier our work [5-10], on polymer supported

reactions, we report herein present the oxidation of 1-Phenethyl alcohol by polymer-supported chromic acid. Duolite A-101 [Cl⁻] and Ambersep 900 [OH⁻] are the strong anion exchange resins are supported on chromium (VI) oxide and used as an oxidant.

Experimental section

Materials, methods and stoichiometry

The polymer bound chromium (VI) oxide was prepared by reported method [11, 12]. The chloride and hydroxide form of Duolite A-101 and Ambersep 900 [OH⁻] containing a quaternary ammonium group [10×10^{-3} kg] was stirred with a saturated solution of chromium trioxide [5×10^{-3} dm³] in water [30×10^{-3} dm³] for 30 min at room temperature using a magnetic stirrer. The hydroxide and chloride ions were readily displaced and HCrO₄⁻ form of resins was obtained in 30 min. The resin was successively rinsed with water, acetone and ether and finally dried in vacuum at 323 K for 5h. The dried form of the resins were stored and used throughout the kinetic study.



The capacity of the chromate form of polymeric reagent was determined by using iodometric titration. The determined average capacity of the chromate form of Duolite A-101 [Cl⁻] and Ambersep 900 [OH⁻] resins were 6.50 mmol/g and 6.55 mmol/g respectively. The loading was also determined by elemental nitrogen analysis and was found to be 6.53 mmol /g and 6.51mmol/g respectively. The 1- phenethyl alcohol was A. R. grade product and was used as supplied. Solvents like 1, 4-dioxane (A.R.), chloroform, cyclohexane, carbon tetrachloride, (Merck) were purified by the usual methods. The anion exchange resins Duolite A-101 [Cl⁻] and Ambersep 900 [OH⁻] obtained as a gift sample from the Thermax Pvt. Ltd. Bhosari, Pune. Doubly distilled water was used throughout the investigation.

Kinetic studies

The reaction mixture for the kinetic runs was prepared by mixing 1-Phenethyl alcohol [known amount], 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 aliquots from reaction mixture were withdrawn using a micropipette. The aliquot thus withdrawn was placed in a stopper test tubes containing 5×10^{-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 %. No traces of carboxylic acid or others by-products were detected in all the runs studied. The regeneration of the resins in the chloride and hydroxide form is readily accomplished by washing successively with 2N sodium hydroxide and 1N hydrochloric acid solution. The fact that the chloride and hydroxide ions in these oxidants remains firmly bound to the resins before and after the reaction maybe valuable in preventing environmental pollution.

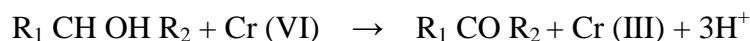
Induced polymerization test

Initiation of reaction was done by mixing oxidant, alcohol and solvent at 318 K 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 [13-15]. 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-Phenethyl alcohol 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 recrystallized from alcohol. The yield of DNP recrystallisation with the DNP of acetophenone was 79 %. The product also identified both by comparison with authentic sample and 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 acetophenone is 510 K [16]. UV spectrum λ_{\max} 245 nm.

IR data: - 1686cm^{-1} (C=O, stretching), 1587cm^{-1} (-C=C-, aromatic), 3062cm^{-1} (-C-H, stretching).



The observed stoichiometric coefficient for this reaction is 2:1 (substrate: oxidant) [17].

Results and Discussion*Effect of variation of weights of [oxidant]*

The order with respect to 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 80×10^{-6} kg of oxidant at constant concentration of solvent [1, 4- dioxane, $5 \times 10^{-3} \text{ dm}^3$] and 1-phenethyl alcohol [$12.3 \times 10^{-3} \text{ mol/dm}^3$], the effect of varying weights of oxidant on zero order rate constant as shown in Table 1.

Table 1. Effect of variation of weights of [oxidants] on reaction rate at 318 K.

Rate constant \rightarrow	$k \times 10^{-4} \text{ min}^{-1}$			
Oxidant $\times 10^{-6} \text{ kg} \rightarrow$	50	60	70	80
Duolite A-101 [Cl ⁻]	2.0	2.10	2.22	2.66
Ambersep 900 [$\bar{\text{O}}\text{H}$]	2.66	2.85	3.25	3.33

Effect of variation of [1-Phenethyl alcohol]

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

Table 2. Effect of variation of concentrations of [1-Phenethyl alcohol]on the reaction rate at 318 K

Rate constant →	$k \times 10^{-4} \text{ min}^{-1}$			
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
Duolite A-101 [Cl ⁻]	1.87	2.22	2.66	2.81
Ambersep 900 [OH ⁻]	3.20	3.25	3.29	3.31

Effect of variation of 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-Phenethyl alcohol [$12.3 \times 10^{-3} \text{ mol/dm}^3$] and constant concentration of oxidant [$70 \times 10^{-6} \text{ kg}$], solvent [$5 \times 10^{-3} \text{ dm}^3$] as shown in Table 3.

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

Rate constant	$k \times 10^{-4} \text{ min}^{-1}$			
Solvent [$5 \times 10^{-3} \text{ dm}^3$]	C ₆ H ₁₂	CCl ₄	1,4-dioxane	CHCl ₃
Dielectric constant	2.00	2.17	2.28	4.81
Duolite A-101 [Cl ⁻]	1.29	1.86	2.22	2.66
Ambersep 900 [OH ⁻]	1.33	2.31	3.25	4.0

Effect of variation of [temperature]

The reaction was carried out at four different temperatures ranging between 313 – 328 K under similar 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 temperature with increasing capacity of polymer-supported resins [Table 4]. The activation parameters like energy of activation [E_a], enthalpy of activation [ΔH^\ddagger], entropy of activation [ΔS^\ddagger] free energy of activation [ΔG^\ddagger] and frequency factor [A] were calculated from the rate measurements at 313- 328 K and these values have been recorded in Table 5.

Table 4. Effect of variation of [temperature] on the reaction rate

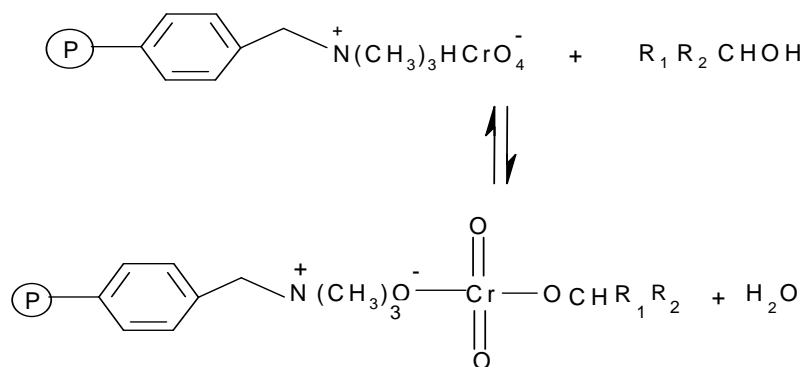
Rate constant →	$k \times 10^{-4} \text{ min}^{-1}$			
Temperature K →	313	318	323	328
Duolite A-101 [Cl ⁻]	2.0	2.22	2.75	3.33
Ambersep 900 [OH ⁻]	2.93	3.25	3.75	4.22

Table 5. Activation parameters for the oxidation of 1-Phenethyl alcohol

Activation parameters ↓	Duolite A-101 [Cl]	Ambersep 900 [OH]
Energy of activation [E _a] Kcal. mol ⁻¹	11.44 ± 0.70	10.70 ± 0.70
Enthalpy of activation [ΔH [#]] Kcal. mol ⁻¹	6.408 ± 0.6	5.948 ± 0.6
Entropy of activation [ΔS [#]] e. u.	-54.82 ± 2.0	-55.90 ± 3.0
Free energy of activation [ΔG [#]] Kcal. mol ⁻¹	24.07 ± 0.4	23.87 ± 0.5
Frequency factor [A] x 10 ⁻⁵ min ⁻¹	3.16	1.25

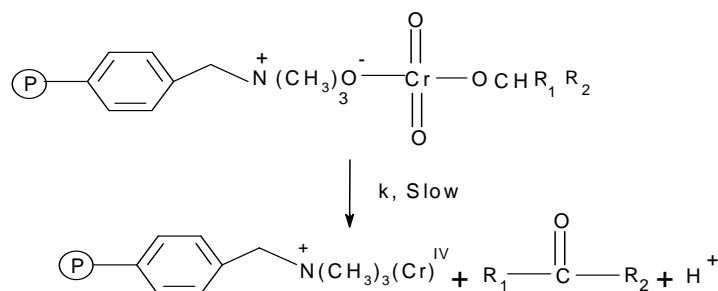
Several sets of experiments with various weights of oxidant, concentration of 1-Phenethyl alcohol and change in solvent were carried out. The reaction was found to be zero order. The proposed path for the reaction of chromium (IV) then makes possible different mechanism for oxidation of alcohols. If the oxidant supported on polymer, which has certain advantages over homogeneous reaction, the intermediate chromium (IV) will further oxidize another molecule of 1-Phenethyl alcohol to form a free radical species. Thus based on experimental results, obtained for the oxidation of 1-Phenethyl alcohol 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 [18]. The mechanism is suggested in Scheme (I) and involves ester formation.

[1st step]



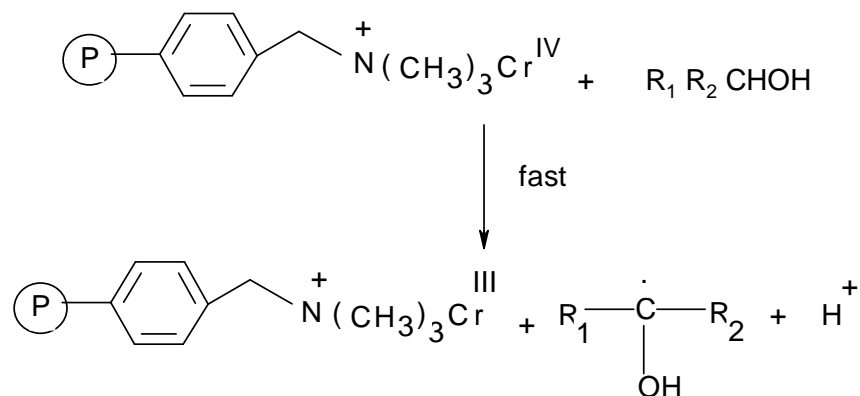
The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step.

[2nd step]



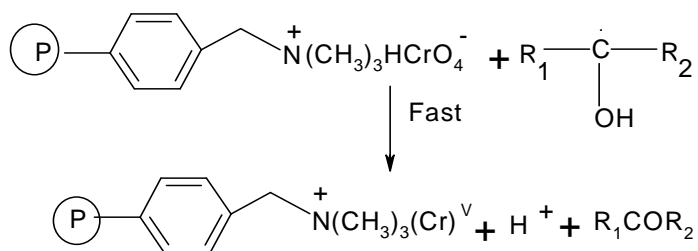
The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. The free radical species formation in the reaction was confirmed by the polymerization of added acrylonitrile or addition of acidified methanol into the reaction mixture as well as by ESR spectral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

[3rd step]



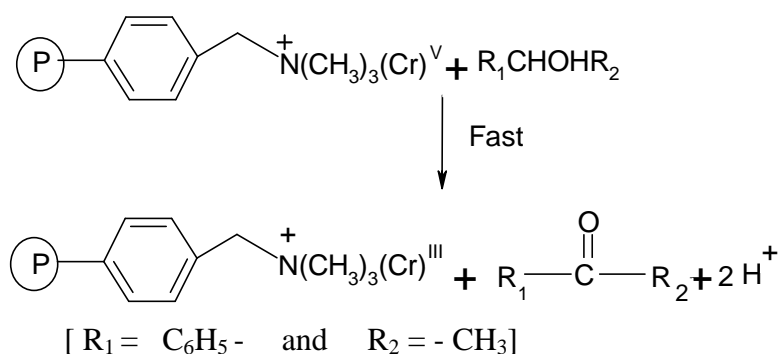
Subsequently the free radical will react with another oxidant site in the polymeric reagent in a fast step leading to the formation of chromium (V).

[4th step]



The intermediate chromium (V) in the last step reacts with 1-Phenethyl alcohol produce acetophenone. The test for formation of chromium (V) and (IV) by the characteristic induced oxidation of iodide [19] was not probably due to heterogeneity of the reaction mixture.

[5th step]



Scheme I

The conversion of Cr (IV) to Cr (III) was via a disproportionate reaction, $\text{Cr (IV)} + \text{Cr (VI)} \rightarrow 2\text{Cr (V)}$. The standard potential for the Cr (VI) – Cr (V) [20] couple was extremely favorable ($E^0 = 0.62\text{ V}$), and this reaction proceeded rapidly. The Cr (V) - (Cr III) couple ($E^0 = 1.57\text{ V}$) facilitated the conversion of Cr (V) to Cr (III), after the reaction with the substrate.

Conclusion

The kinetics and mechanism of oxidation of 1-Phenethyl alcohol by using chromic acid supported on anion exchange resins like Duolite A-101 [Cl⁻] and Ambersep 900 [OH⁻] has been studied for the first time. The reagent has been employed as a versatile reagent in organic synthesis and reagents impregnated on several solid supports have gained popularity in organic synthesis because of their selectivity. The reaction pathway involved a three electron transfer process, and the product was characterized by chemical and spectral methods. 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.

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