

Kinetic and mechanistic study on oxidation of 1- Phenyl ethanol by polymer supported Cr (VI) A free radical intervention

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ABSTRACT

The reaction of 1- phenyl ethanol was found to proceed through ester formation. The ester thus decomposes in a slow step to produce chromium (IV). Since our oxidant was supported on Ambersep 900 (OH⁻), the intermediate chromium (IV) will further oxidize another molecule of 1- phenyl ethanol generating a free radical in a fast step. The free radical subsequently reacts 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- phenyl ethanol to produce acetophenone. There is no evidence of any systematic investigation in the literature on the kinetics of 1- phenyl ethanol by polymer supported chromic acid. Hence, the present work is undertaken with a view to seek the reaction kinetics and the activation parameters have been computed with respect to the slow step.

Key words: Kinetics, mechanistic, 1-phenyl ethanol, polymer supported, free radical, oxidation.

INTRODUCTION

The chromium-based reagents are widely used and powerful oxidation reagents for the oxidation of alcohols to the corresponding carbonyl compounds^{1,2}. Oxidation of organic compounds like aldehydes, ketones, carboxylic acids etc. can be produced by the oxidation of related substrate by the use of suitable oxidizing agents. Chromium trioxide has attracted wide interest in view of its utility for a variety of reactions.³ The easy handling, high selectivity and mild reaction conditions employed utilizing this reagent are of much advantage.⁴ An increasing number of polymeric reagents have been designed^{5,6}. One of them being the easier separation of the products from the mixture.

Most of this reagent is involved in a one step process leading to a discrete chemical modification of a substrate in solution, as the excess of reagent and spent reagent remains on the polymer, the workup is greatly facilitated. By percolating a substrate through a series of different

polymeric reagent, it is possible to follow a sequence of chemical modification to obtain the desired molecule (Cascade modification)⁷.

Oxidation is certainly one of the most commonly employed reactions especially for oxidation of secondary alcohols⁸. Therefore, in continuation of our investigation, in the present communication, we report on a simple preparation of a convenient polymeric reagent for oxidation of 1-phenyl ethanol on the basis of commercially available anion exchange resin like *Ambersep 900* (OH⁻).

EXPERIMENTAL

Preparation of supported oxidizing agent

Various techniques have been employed for impregnating the oxidizing agent on different supports.⁹⁻¹³ The most commonly used technique is the "Wet impregnates" method in which the oxidizing agent is first dissolved in solvent and mixed with the solid support.

In the current work, 5×10^{-3} kg of the water and a slurry of hydroxide form of *Ambersep* 900 (OH^-) was prepared by using solution which was stirred for 30 minutes at room temperature using a magnetic stirrer. Then resin was filtered off and washed successively with water and acetone. The resin was then dried under vacuum for 5h at 50°C .

The hydroxide ion was readily displaced by HCrO_4^- ion. The resin supported reagent has a general structure $\text{P}[\text{Ph-CH}_2\text{-N}^+(\text{CH}_3)_3\text{HCrO}_4^-]$ and was henceforth referred to as $\text{P}[\text{Q}^+\text{HCrO}_4^-]$. The capacity of the resin was determined by stirring 0.5 gm of resin with $10 \times 10^{-3}\text{dm}^3$ of 2 N aqueous potassium hydroxide for 12h, filtering off and titrating iodometrically the obtained chromate solution. The capacity was found to be 6.53 mmole of HCrO_4^- per gm of the resin. The resin so obtained did not lose activity on storing in air at room temperature. Thus, the exchange of OH^- ions by HCrO_4^- ions. Other chemicals like 1: 4 dioxane, chloroform, cyclohexane, carbon tetrachloride, benzene and 1-phenyl ethanol used. All the chemicals used in this investigation were of analytical reagent grade. Double distilled water was used throughout the investigation.

Ambersep 900 (OH^-)

Ambersep 900 (OH^-) anion exchange resin was used as polymer support basic anion exchange resin being in OH^- form. *Ambersep* 900 (OH^-) was purchased from Across Organics Company. The basic resin hydroxide styrene cross linked with divinyl benzene. The structure of *Ambersep* 900 (OH^-) was macro reticular having decomposition temperature 140°F , composition is approximately 35-55 % quaternary amine divinyl benzene / styrene copolymer of OH^- form and 45-65%water.

Kinetic studies

The kinetics measurement was initiated by a mixture of 1-phenyl ethanol, oxidant and solvent ($5 \times 10^{-3}\text{dm}^3$ of 1:4 dioxane) was stirred using a magnetic stirrer at constant temperature 45°C . The completion time of reaction time of reaction was monitored with help of thin layer chromatography. The course of reaction was monitored by withdrawing a known amount of aliquot with the help of micropipette (care was taken, so that no solid

particles were removed along with the aliquot). The aliquot was withdrawn in a stoppard test tubes containing $5 \times 10^{-3}\text{dm}^3$ of 1:4 dioxane at a definite interval of time and optical density of all reaction mixtures were measured at different wavelengths corresponding to the wavelength of product acetophenone using SL 159-UV visible spectrophotometer keeping the zero time reading as reference. The wavelength of 1-phenyl ethanol was determined by diluting 0.1dm^3 of sample of 1-phenyl ethanol in 100 ml of 1:4 dioxane, keeping 1:4 dioxane as a reference. The values reported were the mean of at least duplicate runs and were reproducible within $\pm 3\%$.

RESULTS

Induced polymerization of acrylonitrile

The reaction was initiated by mixing oxidant, 1-phenyl ethanol and 1:4 dioxane at 45°C continuous stirring. After 30 minutes, the reaction mixture was withdrawn in a test-tube and acrylonitrile was added. Then mixture on dilution with double distilled water formed copious precipitate which indicates the formation of a free radical in the reaction. The presence of a free radical in reaction mixture confirmed by addition of 4-5 drops of acidified methanol to form white precipitate,¹⁴ the precipitation due to polymerization of acrylonitrile. The presence of a free radical in reaction mixture also conformed by ESR spectrum.

Product analysis

The product obtained was analyzed by its 2:4 dinitrophenyl hydrazones derivative. After completion of the reaction (02 hours), the resin was filtered off, washed with the solvent and product was isolated by evaporating the filtrate under reduced pressure. The residue was then treated with an excess of a freshly prepared saturated solution of 2:4 DNP in H_2SO_4 to form the orange yellowish crystals of 2:4 DNP derivative of acetophenone. The melting point of its 237°C . The percentage yield of the product was found to be more than 90%. The product was characterized by comparison of its UV and IR. The UV spectrum $\lambda_{\text{max}} = 245 \text{ nm}$, IR shows at 1710 cm^{-1} .

Effect of weight of oxidant on the rate

Different weight of oxidant was used. The

rate of reaction has no appreciable effect as the weight of oxidant increases. This clearly indicates that, the rate is independent on the weight of oxidant is zero as the plots of absorbance against time were linear in all runs. The results are recorded in Table 1.

Different concentration of alcohol was used. It was found that the zero order rates constant remains fairly constant. The results are given in Table 2.

Table 1: Effect of weight of oxidant on the zero order rates constant

Alcohol – 7.5×10^{-3} mol dm³, Solvent -1:4
Dioxane 5×10^{-3} dm³, Temp. -318K

Oxidant x 10 ⁻⁶ kg	50	60	70	80
k x 10 ⁻⁴ sec ⁻¹	2.66	2.85	3.25	3.50

Table 2: Effect of alcohol concentration on the zero order rates constant

Oxidant- 70×10^{-6} kg, Solvent – 1:4 dioxane 5×10^{-3} dm³, Temp. - 318K

[Alcohol] x 10 ⁻⁶ mol dm ³	5	7.5	10	12.5
k x 10 ⁻⁴ sec ⁻¹	3.20	3.25	3.29	3.31

Table 3: Effect of dielectric constant on the zero order rates constant

Alcohol- 7.5×10^{-3} mol dm³, Oxidant – 70×10^{-6} kg,
Solvent 1:4 dioxane 5×10^{-3} dm³, Temp. - 318K

Solvent 5×10^{-3} dm ³	C ₆ H ₁₂	CCl ₄	1:4 dioxane	CHCl ₃
Dielectric constant	1.9	2.2	2.2	4.8
k x 10 ⁻⁴ sec ⁻¹	1.33	2.31	3.25	4.0

Table 4: Effect of % of cross-linking on the zero order rates constant

Alcohol - 7.5×10^{-3} mol dm³, Oxidant- 70×10^{-6} kg,
Solvent -1: 4 dioxane 5×10^{-3} dm³ Temp.-318K.

	k x 10 ⁻⁴ sec ⁻¹		
1-phenylethanol	4%	6%	6.5%
	4.66	3.25	2.66

Effect of dielectric constant on the rate

Different solvents were used. It was found that increase in dielectric constant of the solvent with increasing zero order rates constant. The results are recorded in Table 3.

Effect of percentage of cross-linking on the rate

The effect of % of cross-linking in polymeric resin (oxidant) was studied between 4%, 6.5% (Cross-linked with DVB). It was found that the zero order rate constants increases as the percentage of cross-linking in polymeric resin decreases.¹⁵ The observation indicates that there is a strong diffusion control, because the acid sites in the resin are least accessible in the larger and more cross-linked resin. Due to increased cross-linked density, there is a steric interference at the catalytic site¹⁶, these results are recorded in Table-4.

Effect of temperature on the rate

The reaction was studied at four different temperatures ranging from 313K to 328K and from the data, the activation parameters were calculated. The reaction is found to obey Arrhenius relationship. These results are recorded in Table 5 and 6.

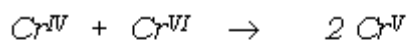
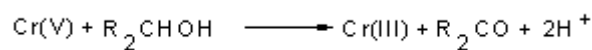
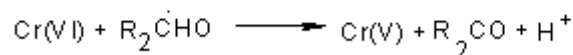
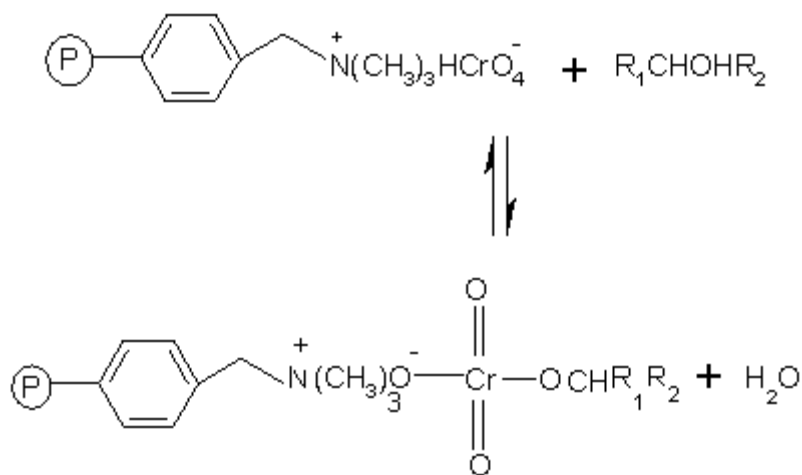
Table 5: Effect of temperature on the zero order rates constant

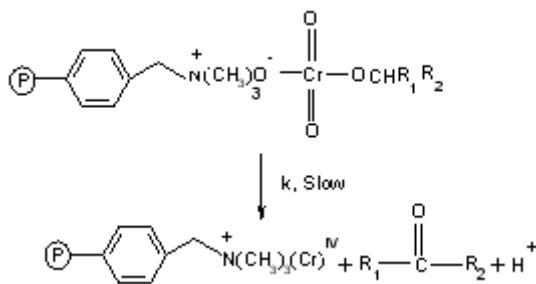
Alcohol -7.5×10^{-3} mol dm³, Oxidant -70×10^{-6} kg,
Solvent -5×10^{-3} dm³

Temp.	313 K	318 K	323 K	328 K
$k \times 10^4 \text{sec}^{-1}$	2.91	3.25	3.75	4.22

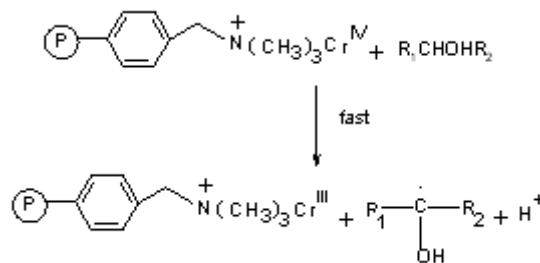
Table 6: Activation parameters

Energy of activation [Ea] Kcal. mol ⁻¹	9.152
Enthalpy of activation [H* *] Kcal. mol ⁻¹	5.948
Entropy of activation [S* *] e.u.	-55.90
Free energy of activation [G**] Kcal. mol ⁻¹	23.87
Frequency factor [A]	5.01×10^2
Temperature coefficient	1.293

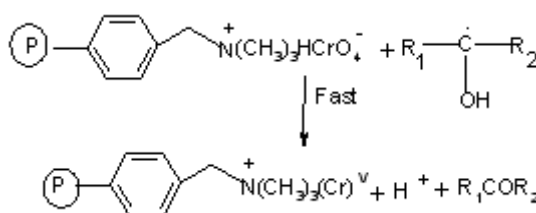
**Scheme 1****Scheme 2****Scheme 3 (1)**



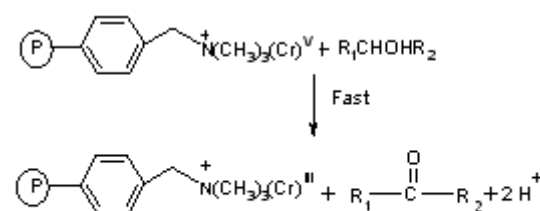
Scheme 3(2)



Scheme 3 (3)



Scheme 3 (4)



Scheme 3 (5)



DISCUSSION

The role of chromium (IV) in chromic acid oxidation has been the subject of a number of investigations. Rocek and Radkowsky¹⁷ found that the chromium (IV) generated by the reaction of vanadium (IV) with chromium (VI) causes oxidative cleavage of cyclobutanol. Nave and Trahanavsky¹⁸ found the oxidative cleavage of alcohols which occurs during chromium (VI) oxidation to have characteristics similar to ceric ion oxidation of these alcohols.

We have reported another approach to determining the relative roles of chromium (VI), (V) and (IV) in the oxidation of 1-phenyl ethanol.^{19, 20} We now wish to present a full account of this investigation. The basis of the experiment is easily seen in comparing two possible schemes. (Schemes 1 and 2) for the chromium (VI)

If we consider only the reactions up through the formation of chromium (V), the first

scheme gives an acetophenone, Cr (V) ratio of 1:2 where as the second scheme gives the products in the ratio of 2:1. Thus an examination of the stoichiometry of the oxidation by chromium (V) is slower than that by chromium (VI) should reveal which of the schemes is correct. Now our oxidant supported on polymer, which has certain advantages over homogeneous reaction. There follow two successive oxidation steps in which chromium (VI) is first converted to chromium(V), and then chromium (V) is converted to chromium (III). Thus based on experimental results obtained for the oxidation of 1-phenyl ethanol which was found to be zero order, the mechanism may be suggested as per **scheme-3** [equations(1)-(5)]

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

The intermediate Chromium (IV) thus formed will further react with another molecule of 1- phenyl ethanol to produce a free radical. The free radical formation in the reaction was confirmed

by the polymerization of added acrylonitrile as well as 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 another molecule of 1- Phenyl ethanol to produce product acetophenone.

Thus the linearity of absorbance against time plots and constancy of the zero order rate constants indicate that the reaction neither depends on the polymeric reagent nor the alcohol concentration. This anomalous nature of reaction may be because the oxidant is taken in the form of a solid supported on polymer. Therefore, the prior equilibrium, before the rate determining or the step

in which actual reaction takes place giving the product does not seem to contribute to the total rate since they are occurring in different phase i.e. solid phase. This was observed in earlier study of the benzoin oxidation by polymer supported N-Bromo sulphonamide²¹.

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