

Polymer Supported Reagents: - Kinetics of Oxidation of Aromatic Secondary Alcohols by Chromic acid.

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Abstract: Polymer supported oxidizing agent are very useful in organic synthesis, due to easy recovery and regeneration. The selective formation of ketones from secondary alcohols by using chromic acid supported on Amberlyst A-26 (Cl⁻) containing a quaternary ammonium functional group has been investigated in detail. There were total selectivity for ketones and reduced chromate species can be regenerated. The kinetics of oxidation of monosubstituted aromatic secondary alcohols by polymer supported chromium (VI) has been studied spectrophotometrically. The oxidation of secondary alcohols was found to proceed through ester formation. Thus ester decomposes and produces Cr (IV) in a slow step. Cr (IV) oxidizes another molecule of secondary alcohol and generates a free radical in a fast step. The free radical react with another oxidant site in a polymeric reagent in fast step and form Cr (V). Finally intermediate Cr (V) reacts with secondary alcohol to produce ketone. 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.

Keywords: Kinetics, oxidation, chromic acid, and polymer supported reagent.

Introduction :-

The introduction of supported reagents has produced attractive options for organic synthesis. These reagents not only modify the activity but may also impart specific product selectivity [1]. They also reduce difficulty in product isolation. A large number of supported chromium (VI) oxidants have been reported. [2-4] However, there is still scope to develop a reagent which has an easy method of preparation, a longer shelflife without any special condition of storage and better activity. The polymer supported reagent showed a high efficiency in the oxidation of alcohols to the corresponding carbonyl compounds. Insoluble polymer supported reagents are convenient from the practical view point for solving many problems in organic synthesis. [5]

Chromium (VI) oxides and chromic acids have been widely used as oxidizing agents for a variety of substrates [6] including alcohols. [7] In recent times, the oxidation of alcohols using catalytic systems has been carried out [8,9] while the utility of chromium oxidants have been reduced due to their hazardous toxicity. The oxidation of secondary alcohol to ketone in which the polymeric reagent can be recovered and reused. Oxidation is certainly one of the most commonly employed reactions

especially for oxidation of secondary alcohols. Furthermore, it is environmentally friendly, since the polymer can be recycled and used in medicinal chemistry parallel synthesis procedures.

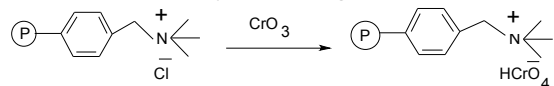
In continuation of our work on polymer supported reactions [10] in the present communication we report kinetics of oxidation of aromatic secondary alcohols by polymer supported chromic acid and evaluated the rate constant as well as various activation parameters. Mechanistic aspects were discussed.

Experimental:-

General procedure for the Preparation of supported oxidizing agent

The polymeric reagent was prepared [11-13] starting from the chloride form of Amberlyst A-26, a macroreticular anion exchange resin. In the present work, Amberlyst A-26[Cl⁻] was washed with acetone and methanol to remove traces of impurities present on the catalyst, 7.5 gm of chromic acid was dissolved in 25 cm³ of water and slurry of resin was prepared by using this solution which was stirred 30 minutes. The resin was filtered off and washed successfully with water, methanol and diethyl ether until an excess of chromic acid was

removed from the surface. The resin was then dried under vacuum for 5 hrs. at 50°C. The capacity of chromate form of resin was determined by iodometrically. The capacity was found to be 3.6 mmol of HCrO_4^- per gram of the dry resin. The resin so obtained did not lose activity on storing in air at room temperature.



Other chemicals like 1:4 dioxane, chloroform, cyclohexane, carbon tetrachloride, benzene and aromatic secondary alcohols are used. All chemicals used in this investigation were of analytical reagent grade. Double distilled water was used throughout the investigation.

Kinetics studies:

The kinetics studies was initiated by the mixture of reactant (alcohol), oxidant (known amount) and solvent ($5 \times 10^{-3} \text{ dm}^3$ of 1:4 dioxane) was stirred using a magnetic stirrer at constant rate, and at a constant temperature, $45 \pm 1^\circ\text{C}$. The completion time of reaction was monitored with the help of TLC. The course of reaction was monitored by withdrawing a known amount of aliquot with the help of micropipette (Care was taken, that no solid particles were removed along with the aliquot). The aliquot thus withdrawn was placed in a stoppered test-tube containing $5 \times 10^{-3} \text{ dm}^3$ of 1:4 dioxane at definite interval of time and subjected to spectral analysis. The optical densities of all the reaction mixture were measured at different wavelengths, corresponding to the wavelengths of the ketones using ELICO-SL 159 UV-VIS spectrophotometer.

Polymerization study:

Test for free radical

The reaction was initiated by mixing oxidant, alcohol and solvent at 45°C 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 copious precipitate. Also the addition of acidified methanol into the reaction mixture formed white precipitate. The precipitation due to polymerization of acrylonitrile indicates that the formation of a free radical in the reaction. The presence of the free radical intermediate was also confirmed by ESR spectrum.

Product Analysis

The product (Ketone) was analyzed by its 2:4 dinitrophenyl-hydrazone derivative. The melting points of 2:4 DNP derivatives of ketones were recorded by open capillary method and uncorrected. (Table-1).

Table 1

Ketone	M.P.
(1)4-Methoxy acetophenone	264°C
(2)4-Methyl acetophenone	258°C
(3)Acetophenone	237°C

Results:-

Effect of oxidant

The order of reaction with respect to oxidant is zero as the plots of absorbance against time were linear in all runs and the observed rate constants are fairly constant between 50 to $80 \times 10^{-6} \text{ kg}$ of the oxidant at constant concentration of solvent (1:4 dioxane $5 \times 10^{-3} \text{ dm}^3$) and alcohols. The effect of oxidant on the zero order rate constant is shown in Table-2.

Table 2 Effect of oxidant concentration on the zero order rate constant at 45°C [solvent] $5 \times 10^{-3} \text{ dm}^3$

Alcohols	$k \times 10^{-4} \text{ min}^{-1}$			
	Resin weight $\times 10^{-6} \text{ (Kg)}$			
	50	60	70	80
4-Methoxy phenyl ethanol	1.16	1.20	1.25	1.21
4-Methyl phenyl ethanol	1.41	1.51	1.60	1.66
1- Phenyl ethanol	1.77	1.83	1.86	1.87

Effect of alcohol concentration:-

Effect of concentration of alcohol was checked by varying the concentration of alcohol and the amount of polymer supported chromic acid and solvent were kept

constant. It was observed that the rate remain constant with change in concentration of alcohol . The zero order rate constant shown in Table 3

Table – 3: Effect of alcohol concentration on the zero order rate constant at 45⁰[oxidant] 70 x 10⁻⁶ Kg, temperature 45⁰C

4-Methoxy phenyl ethanol	Alcohol conc. x 10 ⁻⁶ mole.dm ⁻³	6.08	9.16	12.1	15.1
	k x 10 ⁻⁴ (min ⁻¹)	1.11	1.25	1.28	1.42
4-Methyl phenyl ethanol	Alco. conc. x 10 ⁻⁶ mole.dm ⁻³	6.05	8.95	11.85	14.75
	k x 10 ⁻⁴ (min ⁻¹)	1.60	1.60	1.62	1.86
1- Phenyl ethanol	Alco.conc x10 ⁻⁶ mole.dm ⁻³	5	7.5	10.0	12.5
	k x 10 ⁻⁴ (min ⁻¹)	1.83	1.86	1.90	1.92

Effect of dielectric constant:-

It was found that the zero order rate constant increases with increase in dielectric constant of the medium indicating $r^* < r$ (where r^* and r refer to the radii

of the reactant species and activated complex respectively) at constant alcohol concentration and constant concentration of oxidant and solvent. (5x10⁻³dm³) shown in Table 4

Table-4: Effect of dielectric constant on the zero order rate constant at 45⁰C

Solvents	Dielectric constants	k x10 ⁻⁴ min. ⁻¹		
		4-Methoxy phenyl ethanol	4-Methyl phenyl ethanol	1- Phenyl ethanol
Cyclohexane	2.0	0.8	1.11	1.25
CCl ₄	2.2	1.11	1.27	1.50
1:4 dioxane	2.2	1.25	1.60	1.86
Chloroform	4.8	1.77	1.86	2.16

Effect of Temperature:-

It was found that the rate constant increases with increase in the temperatures. The reactions were carried out at constant concentration of oxidant [70 x10⁻⁶ Kg], constant concentration of solvent [1:4 Dioxane, 5 x10⁻³ dm³] and constant concentration of alcohols. The zero order rate constant was shown in Table 5.

Using the Arrhenius equation the activation energies E_a values were calculated from the plots of log k versus 1/T. Other activation parameters such as $[\Delta H^\ddagger]$, $[\Delta S^\ddagger]$, $[\Delta G^\ddagger]$ and frequency factor [A] were also calculated. The activation parameters are computed in Table- 6.

Table-5 Effect of temperature on the zero order rate constant

Alcohols	$k \times 10^{-4} (\text{min}^{-1})$			
	40 ^o	45 ^o	50 ^o	55 ^o
4-Methoxy phenyl ethanol	1.0	1.25	1.71	2.41
4-Methyl phenyl ethanol	1.28	1.60	1.95	2.54
1- Phenyl ethanol	1.66	1.86	2.22	2.66

Table-6: Activation parameters:

Activation Parameters	Substrates		
	4-Methoxy phenyl ethanol	4-Methyl phenyl ethanol	1- Phenyl ethanol
Enthalpy of activation [ΔH^\ddagger] KCal.mol ⁻¹	9.533	7.321	6.534
Entropy of activation [ΔS^\ddagger] e.u.	-46.55	-52.98	-54.60
Free energy of activation [ΔG^\ddagger] KCal.mol ⁻¹	24.38	24.29	24.20
Activation energy [Ea]Kcal	12.95	12.70	12.43
Frequency factor[A] x 10 ⁴	6.3	5.0	3.9

Discussion :-

Chromium (VI) is a common reagent for the oxidation of organic compounds. The mechanism for one equivalent reducing agent, mainly inorganic ions, King and co-workers [14] proposed a sequence of three-one electron transfer steps to reduce chromium (VI) to chromium (III) with interconversion between chromium (V) and chromium (IV) as the intermediates.

For two equivalent reducing agents, the Westheimer [15] mechanism for oxidation of alcohols has been a focus for discussion and research.

The negative value of [ΔS^\ddagger] suggest that, the rate determining step involves the association of molecules and there is loss of freedom of motion which reveals that the transition state is more ordered than the reactant molecules.

The values for the free energy of activation (ΔG^\ddagger) for all reactions almost the same. These suggest that probably the same mechanism prevails in all the reactions.

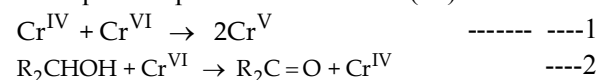
The activation energy (E_a) determined from the slope of Arrhenius plots of log k versus 1/T and other parameters computed are given in Table-6. Thus, the trend in E_a values and order of reactivity reveal that, the activation energy value is the highest for the slowest reaction and vice versa.

The above result shows that the rate of oxidation goes on increasing from 4-methoxy phenyl ethanol to 1-phenyl ethanol. Hence it is evident that the reaction is

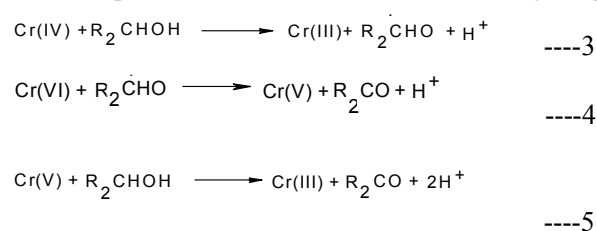
facilitated by electron withdrawing group at para position.

The several sets of experiments with various effects of oxidant, alcohols concentration, and change in solvent were carried out. The reaction was found to be zero order.

There were several paths proposed for subsequent reaction of chromium (IV), thus making possible different mechanism for the oxidation of alcohols. The Westheimer and Watanable[16], shows subsequent step involve chromium (IV) as shown below.



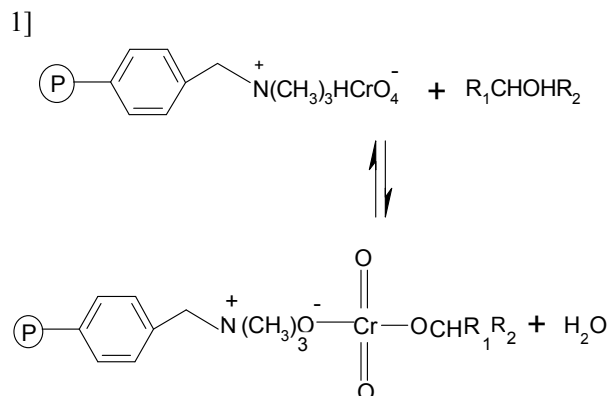
The other mechanism proposed by Westheimer [15] involves production of free radical in followings steps.



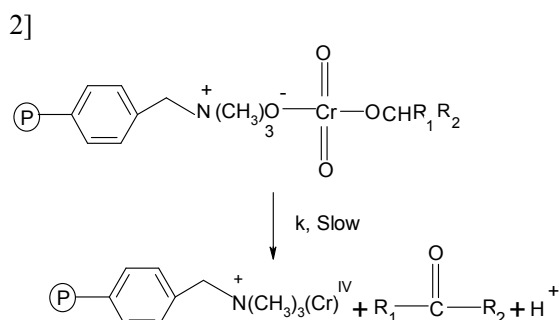
Now our oxidant was supported on polymer, then the intermediate chromium (IV) will further oxidize another molecule of alcohol to produce a free radical.

Thus based on experimental results, for the oxidation of substituted 1-phenyl ethanol was found to be of zero order.

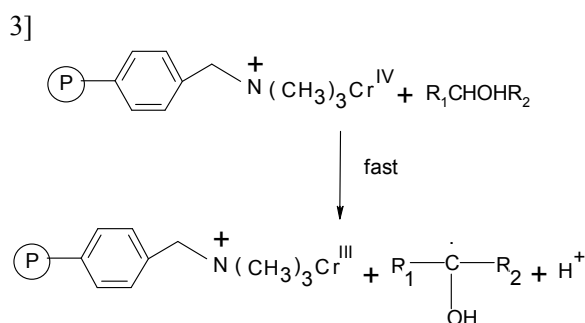
The mechanism is suggested in **Scheme 1** and involves ester formation. [17-20]



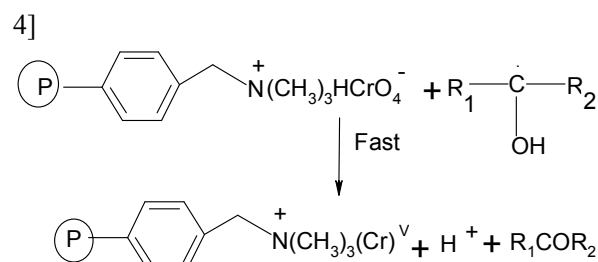
The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step.



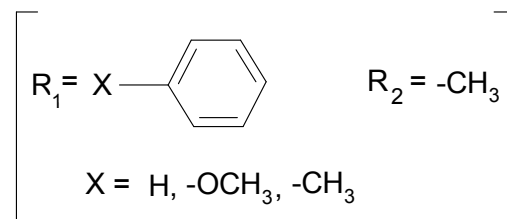
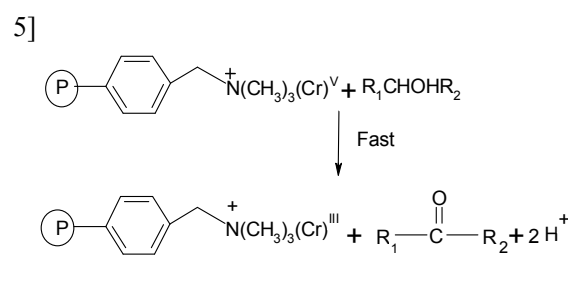
The intermediate chromium (IV) thus formed will further react with another alcohol molecule to produce a free radical. The free radical formation in the reaction was confirmed by the polymerization of added acrylonitrile as well as acidified methanol to the reaction mixture.



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 react with alcohol to produce ketone.



Scheme - 1

Conclusion:-

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

According to Scheme 1, 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 ketone is formed.

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