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Kinetics and Mechanism of Oxidation of 1-Phenyl Ethyl Alcohol by Polymer Supported Chromic Acid

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Kinetics and mechanism of oxidation of 2-phenyl ethyl alcohol by polymer supported chromic acid has been extensively studied. Kinetic findings indicated zero order reaction kinetics in oxidants, substrates respectively. On the basis of experimental observed kinetic findings, the probable mechanism involving generation of free radical is suggested.

Key Words: Kinetics, Mechanism, Oxidation, 1-Phenyl ethyl alcohol, Chromic acid.

INTRODUCTION

The oxidation of alcohols into carbonyl compounds is an important transformation in organic synthesis[1]. Although a large number of reagents are known in the literature[2], for such transformation there still appears a need either to improvise the existing oxidation methods[3] or to introduce newer reagents[4] to permit better selectivity under mild conditions and with easy work up procedures. Oxidation is certainly one of the most commonly employed reactions especially for oxidation of secondary alcohols[5].

In the present paper, the kinetics of oxidation of 1-phenyl ethyl alcohol by polymer supported chromic acid has been reported. The effect of polymeric reagent, alcohol concentration, change in solvent and percentage of cross-linking in polymeric reagent on the reaction at 45°C has been studied. The probable reaction mechanism consistent with the kinetic results has also been suggested.

EXPERIMENTAL

All the chemicals used during the investigation were of BDH, E. Merck or AR grade of extra pure quality.

Preparation of 1-phenyl ethyl alcohol by reduction method using sodium borohydride in acetophenone[6] : A solution of acetophenone in methanol was cooled to 0–5°C and sodium borohydride was added in small portions with constant stirring. Acetophenone was distilled before use and the fraction boiling at 202–203°C collected. The stirring was continued for 2 h. The reaction mixture was slowly warmed to room temperature. The progress of reaction was monitored by thin-layer chromatography. After completion of reaction, methanol was removed under reduced pressure, followed by addition of saturated solution of ammonium chloride and extraction with ether. The ether reaction was washed with brine and dried over anhydrous sodium sulphate. Removal of solvent gave the corresponding alcohol which was purified by distillation (b.p. 103°C) and characterized by TLC and IR.

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Preparation of polymer bound chromium(VI) oxide: The polymer bounded chromium(VI) oxide was prepared[7–9]. The chloride form of Amberlyst A-26 (Fluka 20–25 mesh) containing quaternary ammonium group was stirred with saturated aqueous solution of chromium trioxide in 15 mL of water for 30 min at room temperature using a magnetic stirrer. Chloride ions were readily displaced and $HClO_4$ form of the resin was obtained in 30 min. The resin was successively rinsed with water, acetone and ether and finally dried in vacuum at 50°C for 5 h. The dried form of the resin was stored and used throughout.

The resin form 3.5 and 6.5% cross-linked quaternary ammonium resin was prepared by the same procedure.

Determination of capacity of chromate form of polymeric reagent: The capacity of chromate form of polymeric reagents was determined iodometrically. The average capacity of polymeric reagent was found as: (a) Amberlyst A-26 (3.4 mmol/g); (b) 3.5% quaternary ammonium resin (3.5 mmol/g); (c) 6.5% quaternary ammonium resin (3.45 mmol/g).

Method of kinetics of oxidation reaction[10]: The kinetic measurement was initiated by mixture of 2-phenyl ethyl alcohol and 1 : 4 dioxane (E. Merck) was stirred using magnetic stirrer at a constant temperature 45°C. The completion time of the reaction was monitored with the help of thin-layer chromatography. The course of reaction was monitored by withdrawing a known aliquot of the reaction mixture at a definite interval of time and optical density of all the reaction mixture measured using Schimadzu 160 UV-Vis spectrophotometer.

The different variations for the kinetic study of 2-phenyl ethanol to acetophenone were: (a) concentration of polymeric reagent, (b) concentration of phenyl ethanol, (c) solvent, and (d) percentage of cross-linking in polymeric reagents.

The rate constants were evaluated from linear plots of optical density against time. The effect of different variations on the reaction rate is summarized in Tables 1–4.

TABLE-1
POLYMERIC REAGENT EFFECT ON RATE OF OXIDATION

Polymeric reagent (mg)	Rate × 10^{-4} (s^{-1})
50	1.600
60	1.770
70	1.245
80	1.111

TABLE-2
ALCOHOL CONCENTRATION ON RATE OXIDATION

Alcohol concentration × 10^3 (mL)	Rate × 10^{-4} (s^{-1})
5.0	1.55
7.5	1.70
10.0	1.20
12.5	1.12

TABLE-3
SOLVENT EFFECT ON RATE OF OXIDATION

Solvent	Rate × 10^{-4} (s^{-1})
Cyclohexane	1.66
1 : 4 dioxan	1.245
Carbon tetrachloride	1.10

TABLE-4
PERCENTAGE OF CROSS-LINKING EFFECT ON RATE OF OXIDATION

% of cross linking	Rate × 10^{-4} (s^{-1})
3.5	2.75
6.5	2.83

The catalytic effects are to be decreased as the cross-linked ratio increases[11] which indicates that there is strong diffusional control. It is known that at increased cross-linked density, there is a steric interference at the catalytic site[12].

Product analysis: The product acetophenone was characterized by its 2,4-dinitrophenyl hydrazone (DNP), oxime, phenyl hydrazone and semicarbazone derivatives and recrystallized from ethyl alcohol, dried and melting point determined. The melting points of the above derivatives[6] are as follows:

Compound	Derivative m.p. (°C)			
	2,4-DNP	Oxime	Phenyl hydrazone	Semicarbazone
Acetophenone	237	59	105	199

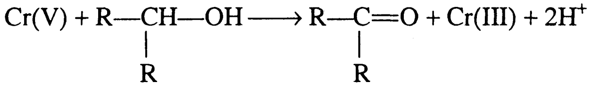
RESULTS AND DISCUSSION

Several sets of experiments with various effects of polymeric reagent, alcohol concentration, change in solvents and percentage of cross-linking in polymeric reagents over the polymer supported chromium troixide were carried out. The order of reaction was found to be of zero order.

The linearity of absorbance against time plots and constancy of the zero order rate constants indicates that the reaction neither depends on the concentration of polymeric reagent nor on the concentration of alcohol. Such a type of conclusion has been reported in earlier study of benzoin oxidation of polymer supported N-bromo sulphonamide[13].

The proposed path for the reaction of chromium(IV) then makes possible different mechanisms for oxidation of alcohols. According to Westheimer and Watanabe[12], subsequent steps must involve chromium(VI) as shown below:

$$\mathrm{Cr(VI)} + \mathrm{Cr(IV)} \longrightarrow 2\mathrm{Cr(V)} \qquad (1)$$



$$\mathrm{Cr(V)} + \mathrm{R{-}\underset{\displaystyle R}{\underset{|}{C}}H{-}OH} \longrightarrow \mathrm{R{-}\underset{\displaystyle R}{\underset{|}{C}}{=}O} + \mathrm{Cr(III)} + 2\mathrm{H}^+ \qquad (2)$$

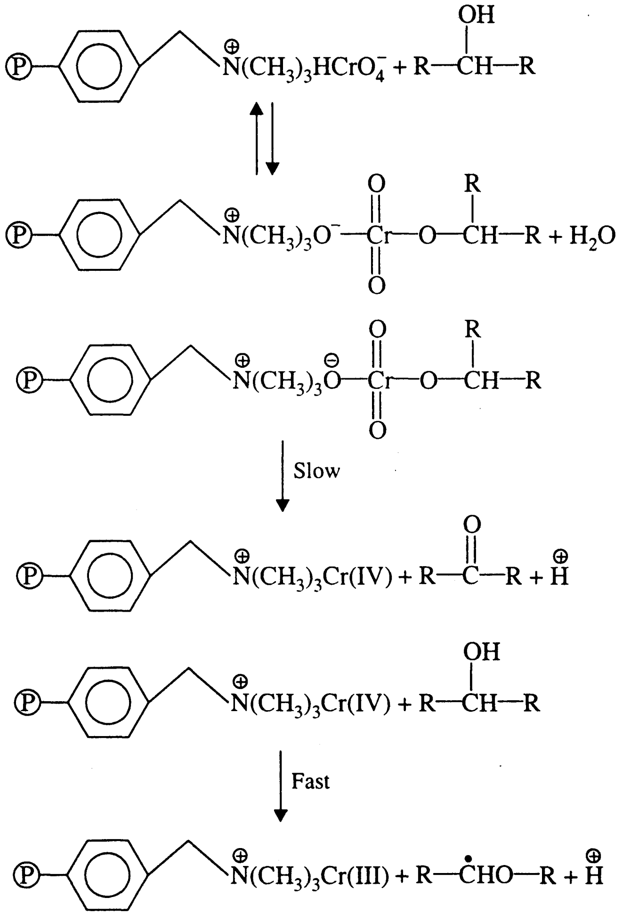
The other mechanism proposed by Westheimer[14] involves production of free radical in (3) to (5):

$$\mathrm{Cr(IV)} + \mathrm{R_2CH{-}OH} \longrightarrow \mathrm{Cr(III)} + \mathrm{R_2\dot{C}HO} + \mathrm{H}^+ \qquad (3)$$

$$\mathrm{R_2\dot{C}H{-}O} + \mathrm{Cr(VI)} \longrightarrow \mathrm{Cr(V)} + \mathrm{R_2C{=}O} + \mathrm{H}^+ \qquad (4)$$

$$\mathrm{Cr(V)} + \mathrm{R_2CH{-}OH} \longrightarrow \mathrm{Cr(III)} + \mathrm{R_2C{=}O} + 2\mathrm{H}^+ \qquad (5)$$

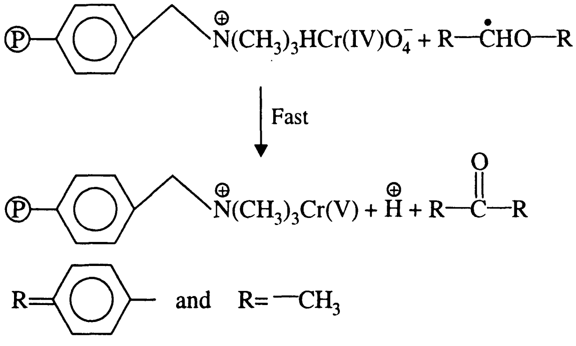
If the oxidant is supported on polymer, which has certain advantages over homogeneous reactions, the intermediate chromium(IV) will further oxidize another molecule of alcohol to a free radical. Thus based on experimental results obtained for the oxidation of 1-phenyl ethanol, the reaction was found to be of zero order. The mechanism is suggested in **Scheme-1** and it involves ester formation (6) to (9) as



(6)

(7)

(8)



(9)

where

Scheme-1

The ester formed will decompose into ketone and the intermediate chromium(IV) will be formed in the second and slow step (eqn. 7).

The intermediate chromium(IV) thus formed will further react with another alcohol molecule to produce a free radical (eqn. 8). The free radical formation in the reaction was confirmed by the polymerization of the added acrylonitrile to the reaction mixture.

Then free radical will react with another oxidant site in the polymeric reagent in a steps leading to the formation of chromium(V) (eqn. 9).

According to **Scheme-1** (eqns. 6–9), a second order rate law is expected. But since the first step (eqn. 6) of ester formation occurs in the solid phase and assuming that this equilibrium does not contribute to the rate of the reaction. We obtained a zero order dependence with rate constant K of the second slow step in which the product ketone is formed.

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