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Solid-Supported Reagents in Organic Synthesis

Vilas Y. Sonawane
Department of Chemistry, B.Raghunath Arts, Commerce and Science, College,
Parbhani (MS) India 431401

Abstract *-The current interest in solid-phase organic synthesis has led to a renewed interest in a Complementary technique in which solid supported reagents are used in solution phase chemistry. This technique obviates the need for attachment of the substrate to a solid-support, and enables the chemist to monitor the reactions using familiar analytical techniques. The purpose of these reviews to increase awareness of the wide range of useful transformations which can be accomplished using solid-supported reagents Oxidation of organic compounds is quite important from synthetic and technological view points. Many of the industrially important organic compounds like aldehydes, ketones, acids, etc. can be produced by the oxidation of related substrate by the use of suitable oxidizing agents. The kinetics of the oxidation of 1-Phenylethanol (PE) by PS-Chromate has been followed by monitoring the increase in the absorbance of reaction intermediate. The reaction followed by zero order behavior, being zero order in each reactant. The rate of reaction increase with increase in weight of oxidant, concentration, temperature and dielectric constant of the solvent. A free radical scavenger affects the reaction rate. The stiochiometry has been found to be 1mol PE: 1mol of Chromate. Thermodynamic parameters evaluated are* $[Ea] = 72KJ\ mol^{-1}$, $[\Delta H^{\#}] = 65\ KJ\ mol^{-1}$, $[\Delta S^{\#}] = --75\ JK\ mol^{-1}$, $[\Delta G^{\#}] = 278KJ\ mol^{-1}$, *and* $[A] = 3.9 \times 10^{-5} s^{-1}$ *results under pseudo zero order conditions are in agreement with the rate law. Main reaction product acetophenone isolated and characterized.*

Keywords*- Solid-supported reagents, solid-phase reagents, polymer-supported reagents*

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I. INTRODUCTION

Medicinal chemists in the pharmaceutical industry now routinely utilize solid-phase organic synthesis(SPOS) to prepare libraries of small organic molecules for screening.1 The advantages of this methodology have been well described in the recent literature: excess reagents can be used to drive reactions to completion, impurities and excess reagents can be removed by simple washing of the solid-phase, and enormous numbers of compounds can be created using the mix and split technique .Limitations to SPOS may include (a) the presence of a resin vestige in the final molecules (the point of attachment of the molecule to the solid support), (b) the need for two extra synthetic steps (attaching the starting material to the solid support, and removing the material from the solid support),(c) a potential scale limitation imposed by the loading level of the solid support, and (d) the need tore-optimize solution phase chemistry on the desired solid support. Recent reports indicate that pharmaceutical companies are now also increasing efforts toward high throughput solution phase synthesis using solid supported reagents (SSRs). Polymer-supported reagents have been in use since the 1960s, and have been the subject of several review articles.3 Synthesis using SSRs is attractive and suitable for parallel synthesis because the reactions are often very clean and high yielding, and the workup involves simple filtration and evaporation of the solvent. This review is prompted by the current rediscovery of the utility of these types of reagents, and exemplifies transformation

There are few reports available on the non-Malapradin Sodium Chromate oxidation of aromatic alcohols [1-4]. In continuation of our earlier studies [7], the results as PS-chromate oxidation of PE in 1,4 dioxane aimed at deciding the mechanism of the reaction and the rate law particularly for seeking an explanation for the unique rate P^H profile observed are being presented and discussed in the present communication.

In the present investigation, we now report the oxidation of 1-phenylethanol by polymer- supported sodium chromate. The polymer AmberSep 400 SO_4 is the strong base anion exchange resin are supported on sodium chromate and used as an oxidant.

II. EXPERIMENTAL

2.1 Preparation of Chromate supported oxidizing agent

The Chromate forms of AmberSep 400 SO_4 containing a quaternary ammonium group [10 x 10^{-3} kg] was stirred with a saturated solution of periodates [5 x 10^{-3} dm3] in water [30 x10^{-3} dm^3] for 30 min at room temperature using a magnetic stirrer. The sulphate ion was readily displaced and Chromate form of resin was obtained in 65 min. The resin was successively rinsed with water, acetone and THF and finally dried in vaccum at 323 K for 7-8hr. The dried form of the resin was stored and used throughout the kinetic study.

2.2 DETERMINATION OF THE CAPACITY OF CHROMATE FORM OF THE POLYMERIC REAGENT

The capacity of the chromate form of AmberSep 400 SO_4 resin was 2.75 meq/mL and used for kinetic study throughout kinetic work.

2.3 METHOD OF KINETICS

The reaction mixture for the kinetic run was prepared by mixing 1-PE, PS-chromate and solvent. The reaction was carried out either constant stirring using magnetic stirrer and at a constant temperature 318 ±5 K. At different time interval, the reaction mixture was withdrawn using a qualigen micropipette. The aliquot thus withdrawn was taken in a stopper test tube containing 1, 4-dioxane and subjected to spectral analysis. The absorbance of the product formed was measured using Shimadzu UV-VIS spectrophotometer (Model Mini 1240).

2.4 POLYMERIZATION TEST

Mixing PS-oxidant, 1-PE and solvent at 318 K with continuous stirring did initiation of reaction. After 45 min, the reaction mixture was withdrawn in a test tube and acrylonitrile and allyl alcohol 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.

2.5 PRODUCT ANALYSIS AND SPECTROSCOPIC TECHNIQUE

The oxidation of 1-PE leads to the formation of acetophenone.The product formed was analyzed by their 2,4-DNP derivatives. The product is then vacuum dried, weighed and recrystallised from alcohol and determined its melting point 416K (Literature value 419K). **UV –VIS** spectrum (in ethyl alcohol giving absorption maxima at196,191, 179 and 167 mu which suggested the presence of ketone structure in the compound.)

The FTIR spectrum of compound (in KBr) showed the presence of a sharp band at 1630cm^{-1} indicates the presence of -C = O stretching mode, 1580 cm^{-1} indicates the presence of aromatic (-C= C-), 3055 cm^{-1} indicates the presence of (-C- H stretch).

III. RESULTS AND DISCUSSION

3.1 Effect of varying weights of PS-Chromates

As the plots of absorbance against time were linear in all runs and observed rate constant are fairly constant at various quantity of oxidant at constant concentration of solvent and 1-PE, the effect of varying weights of on PS-Chromate *zero order* rate constant as shown in Table-3.1

Table-3.1 Effect of varying weights of PS-Chromate on reaction rate at 318 K.

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Oxidant x 10^{-6} kg →	50	60	70	80
AmberSep 400 SO_4	1.11	1.12	1.12	1.13

3.2 Effect of varying concentrations of 1-PE

At a varying concentration of 1-PE, constant weights of PS-Chromate and constant concentration of solvent, zero order rate constant [Table- 3.2] was found.

Table-3.2 Effect of varying concentrations of 1-PE

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
1-Phenylethanol →	8.20 x 10^{-3} mol /dm^3	12.3x 10^{-3} mol /dm^3	16.4 x 10^{-3} mol /dm^3	20.4 x 10^{-3} mol /dm^3
AmberSep 400 SO_4	1.15	1.15	1.16	1.15

3.4 Effect of varying temperature

The reaction was carried out at four different temperatures. It was observed that, the rate of reaction increased with an increase in the temperature. [Table-3.3]. The activation parameters like energy of activation [Ea], enthalpy of activation [$\Delta H^{\#}$], entropy of activation [$\Delta S^{\#}$] free energy of activation [$\Delta G^{\#}$] the high positive values of free energy of activation indicates that the transition state is highly solved and frequency factor [A] were calculated by determining values of k at different temperatures. [Table-3.4].

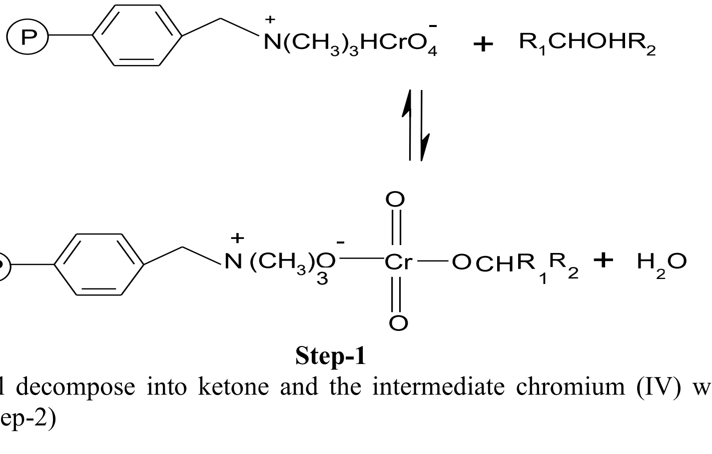
Table – 3.3 Effect of varying temperature

Rate constant →	k x 10^{-4} mol dm^{-3} s^{-1}			
Temperature K →	313	318	323	328
AmberSep 400 SO_4	1.26	1.22	1.28	1.78

Table -3.4 Thermodynamic parameters for the PS-Chromate oxidation of 1-PE

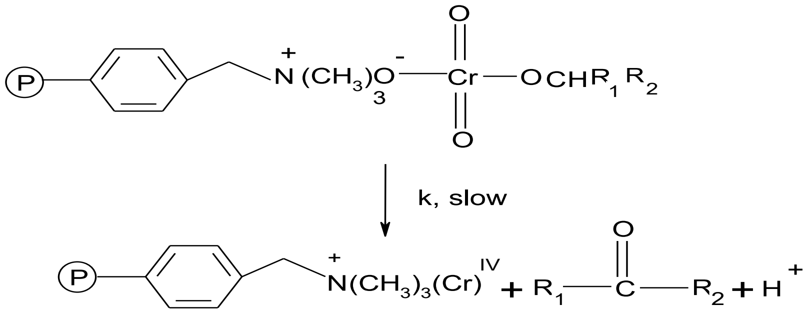
Temp. K	k x 10^{-4} $moldm^{-3}$ s^{-1}	[Ea] $KJmol^{-1}$,	[$\Delta H^{\#}$] KJ mol^{-1}	[$\Delta S^{\#}$] JK mol^{-1}	[A] $10^{-5}s^{-1}$	[$\Delta G^{\#}$] KJ mol^{-1}
313	1.26	72	65	-72	3.9	278
318	1.29					
323	1.35					
328	1.75					

It is necessary and interesting to discuss the possible molecular mechanism of the reaction. Mechanism proposed in following **(Step 1-5)**,**Scheme-I** shows the *zero order* as a reversible bimolecular reaction between PE and [PS-Sodium chromate].The polymer supported reagent reacts with a molecule of 1-Phenylethanol to form a chromate ester. (**Step-1)**



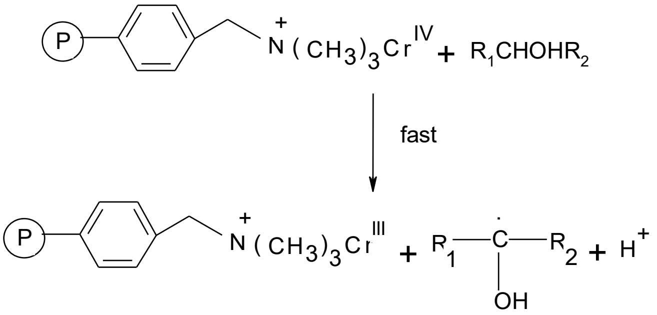
Step-1

2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step. (Step-2)



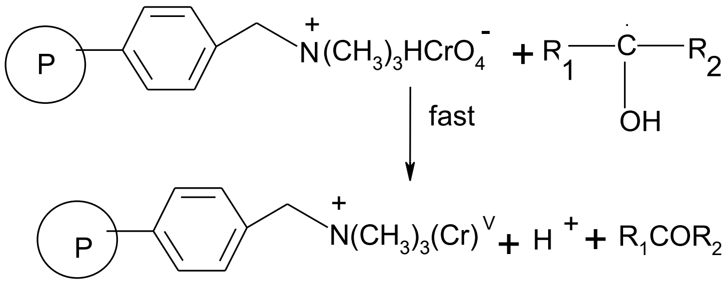
Step-2

3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. (Step-3)



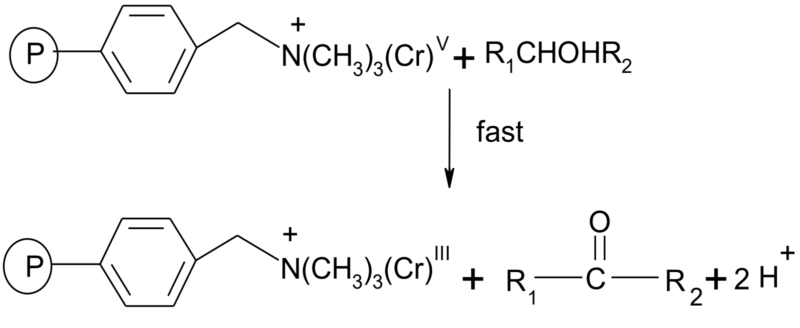
Step- 3

4) 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). (Step- 4)



Step- 4

5) 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 and manganese (II) were not probably due to heterogeneity of the reaction mixture. (Step-5)



[R_1= C_6H_5- and R_2 = - CH_3]

Step- 5

Scheme- I

IV. CONCLUSION

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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