

## Effect of various factors and kinetic study of oxidation of 4-chloro phenyl ethanol by polymer supported Cr(VI)

VILAS Y. SONAWANE\*, A.S. VARALE<sup>1</sup> and N.P. HILAGE<sup>2</sup>

\*Bhauasaheb Nene College, Pen, Raigad (India).

<sup>1,2</sup>Department of Chemistry, Shivaji University, Kolhapur (India).

(Received: April 12, 2009; Accepted: May 22, 2009)

### ABSTRACT

The kinetic behaviour of oxidation of 4-Chloro phenyl ethanol by polymer supported Cr (VI) studied spectrophotometrically and observe the effect of solvents and temperature. The study described the effect of concentration of Cr (IV), the 34-chloro phenyl ethanol and polymer supported reagent on the rate of reaction to arrive at a suitable rate expression. The rate law shows zero order with respect to concentration of polymer supported Cr(VI). The influence of solvents of the medium on the rate has been studied to find out the possible involvement of the oxidizing species in the reaction. The study shows that the reaction was unaffected by changes in the ionic strength of the medium, the effect of temperature on the rate showed the Arrhenius equation and use to evaluate the different activation parameters of the reaction. It has been also observed that this oxidation reaction induces polymerization of acrylonitrile.

**Key words:** Factors, Polymer supported, Kinetic, Oxidation, 4-Chloro phenyl ethanol.

### INTRODUCTION

Requirements in the pharmaceutical industry for parallel synthesis of libraries of organic compounds has led to the development of simple, high yielding chemical transformation using polymer-supported reagents, scavengers, catalysts and reagents that are amenable to automation. After reaction using insoluble polymer – supported species a simple filtration process allow the product in solution to be recovered with high yield and purity. Recovery of the spent reagent retained on the support allows recycling, thus fulfilling the requirements of environmentally friendly chemistry.

Chromium (VI) is one of the versatile oxidant which normally behaves as a three electron oxidant. The major use of Cr (VI) reagents in synthetic chemistry is to oxidize alcohols to carbonyl compounds. As a result; alcohol oxidation with these was extensively investigated. The introduction of

supported species has produced attractive options for organic synthesis. These reagents not only modify the activity but may also impart specific product sensitivity<sup>1</sup>. They also reduce difficulties in product isolation. A large number of supported Chromium (VI) oxidants have been reported<sup>2-4</sup>. However, there is still to develop a reagent which has an easy method of preparation, a longer shelf life without any special conditions of storage and better activity. The oxidation of alcohols by chromium (VI) has been employed as oxidant for the oxidation of crotyl alcohol<sup>5,6</sup>. Despite the use of various oxidized agents the detailed kinetic study on the mode of oxidation of 4-chlorophenyl ethanol by polymer supported Cr (VI) is lacking. Hence the paper reported the kinetics of above oxidation reaction.

### EXPERIMENTAL

The polymeric reagent (oxidant) was prepared according to reported procedure<sup>7-9</sup> starting

from the chloride form of Amberlyst A-26. The dried form of the resin was stored and used throughout the kinetic study. The capacity of the chromate form of Amberlyst A-26 was determined by iodometrically. The capacity of the chromate form of resin 3.5 mmol per gram. All the reagents used were A. R. grade. Redistilled water was used in all the preparation.

### Kinetic Measurement

The oxidation kinetics were determined the Cr(VI) content spectrophotometrically. Reaction mixture containing appropriate quantity of 4-chloro phenyl ethanol, oxidant and solvent (a:4 dioxane) were stirred using a magnetic stirrer at constant temperature  $45^{\circ}\text{C} \pm 1$ .

The completion time of reaction was monitored with the help of TLC. The course of reaction was followed by measuring the optical density of the aliquots withdrawn at appropriate interval of the time with help of ELICO SL- 159 UV-VIS spectrophotometer and determined the optical density of all reaction mixture at different wavelength corresponding to the wavelength of 4-chloroacetophenone. The initial rates were determined from the slope of the tangent to the optical density – time using the plane mirror method.

### Induced polymerization of acrylonitrile:

Acrylonitrile, a free radical scavenger<sup>11</sup> when added to the reaction mixture a white precipitate is formed. The precipitation due to polymerization of acrylonitrile indicates the formation of a free radical<sup>12</sup>. The presence of a free radical also confirmed by ESR spectrum.

### Product analysis:

The product formed was analyzed by its 2, 4 DNP derivative UV spectra and IR spectra. The melting point of 2, 4 DNP derivative of 4-chloroacetophenone is  $232^{\circ}\text{C}$  indicating its authenticity and UV spectrum  $\lambda_{\text{max}}$  260 nm.

### Variation in concentration of 4-chlorophenyl ethanol

Chromium (VI) oxidation of 4-chlorophenyl ethanol studied at different concentration range from  $5.32 \times 10^{-3}$ – $15.5 \times 10^{-3}$  mol/dm<sup>3</sup> of substrate in the reaction mixture. The concentration of other reactants was fixed.

### Variation in concentration of oxidant:

The initial rates were measured at several weights of the oxidant in the range  $50 \times 10^{-3}$  –  $80 \times 10^{-3}$  kg keeping the concentration of solvent and alcohol constant.

### Variation in solvent polarity:

The effect of change in solvent polarity has been studied by carrying the reactions at different solvents like benzene, carbon tetrachloride, 1:4 dioxanes and chloroform. Other conditions remaining constants.

### Variation in temperature:

The reaction were studied at four different temperatures and initial rates are calculated at these temperature. The activation parameters have been evaluated from temperatures dependent rates.

## RESULT AND DISCUSSION

The obedience to Beers law of the absorption of polymer supported chromium (VI) at 260 nm used has been tested by obtaining a linear graph relating optical density and time.

### Effect of varying concentration of oxidant:

It was observed that the rate do not vary significantly with the change in initial weight of chromium (VI). The data was presented in Table-1. This suggestion that the reaction is strictly zero order with respect to oxidant. This also suggests that polymer supported chromium (VI) weight is not involved in the final rate expression.

### Effect of varying 4-chloro phenyl ethanol concentration

The variation in 4-chlorophenyl ethanol concentration shows that, the rate constant zero with increase in the concentration of substrate or alcohol at other reactant. The plot (Fig. 1) of absorbance against time was linear in all runs and passing through origin. This shows that the reaction is zero order to concentration of 4-chlorophenyl ethanol (The data recorded in Table-2).

### Effect of varying solvents

It was observed that, the rate constant increased with increase in dielectric constants of

**Table 1: Effect of oxidant on the rate of reaction**

Oxidant	:	$50 \times 10^{-3}$ - $80 \times 10^{-3}$ kg
Alcohol	:	$12.1 \times 10^{-6}$ moles/dm <sup>3</sup>
Solvent	:	1:4 Dioxane, $5 \times 10^{-3}$ dm <sup>3</sup>
Temperature	:	45°C

Oxidant	50	60	70	80
$k \times 10^{-6} \text{ sec}^{-1}$	2.38	2.40	2.41	2.44

**Table 2: Effect of [Alcohol] on the rate of reaction**

Oxidant	:	$70 \times 10^{-6}$ kg
Alcohol	:	$5.30 \times 10^{-3}$ $15.5 \times 10^{-3}$ kg
Solvent	:	1:4 Dioxane, $5 \times 10^{-3}$ dm <sup>3</sup>
Temperature	:	45°C

Alcohol	5.30	8.72	12.1	15.5
$k \times 10^{-6} \text{ sec}^{-1}$	2.40	2.41	2.45	2.50

**Table 3: Effect of varying of solvent on the rate of reaction**

Oxidant	:	$70 \times 10^{-6}$ kg
Alcohol	:	$12.1 \times 10^{-6}$ kg
Solvent	:	Different Solvents, $5 \times 10^{-3}$ dm <sup>3</sup>
Temperature	:	45°C

Solvent	C <sub>6</sub> H <sub>6</sub>	CCl <sub>4</sub>	1:4 dioxane	CHCl <sub>3</sub>
$k \times 10^{-6} \text{ sec}^{-1}$	1.66	2.0	2.41	2.83

**Table 4: Effect of temperature on the rate of reaction**

Oxidant	:	$70 \times 10^{-6}$ kg
Alcohol	:	$12.1 \times 10^{-6}$ kg
Solvent	:	1:4 Dioxane, $5 \times 10^{-3}$ dm <sup>3</sup>
Temperature	:	45°C-55°C

Temperature	40°C	45°C	50°C	55°C
$k \times 10^{-6} \text{ sec}^{-1}$	2.13	2.41	2.92	3.62

**Table 5: Activation parameters**

Parameters	Unit	Calculated values
Energy of Activation	Ea (K. J. mole <sup>-1</sup> )	46.40
Enthalpy of Activation	$\Delta H^*$ (K. J. moel <sup>-1</sup> )	23.93
Entropy of Activation	$\Delta S^*$ (J. K <sup>-1</sup> mole <sup>-1</sup> )	-57.14
Free Energy of Activation	$\Delta G^*$ (KJ. mole <sup>-1</sup> )	100.49
Frequency Factor	A (Sec <sup>-1</sup> )	$2.51 \times 10^4$
Temperature coefficient	$K_s (T + 10) / K_s (T)$	1.43

**Table 6: Comparison between rates of substituted and unsubstituted 1-phenyl ethanol**

1-Phenyl ethanol	4-Chlorophenyl ethanol
$1.86 \times 10^{-6} \text{ sec}^{-1}$	$2.41 \times 10^{-6} \text{ sec}^{-1}$

the medium. There was no reaction of the solvents with the oxidant. The rate constant are fairly constants. (The data recorded in Table-3).

**Effect of varying temperature**

The experimental results presented in Table-4 shows that the rates of reaction constant (The data recorded in Table 4) with an increased in temperature. The activation parameters such as energy of activation, enthalpy of activation, entropy of activation, free energy of activation, frequency factor and temperature coefficient are calculated from temperature dependent rates data and presented in the Table 5. Arrhenius law was found to be obeyed and large negative value of entropy of activation is obtained. It was found that zero order

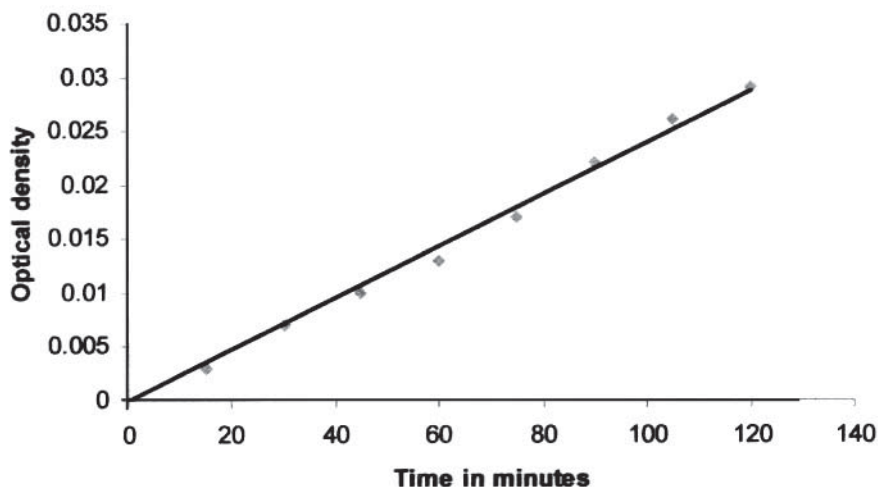


Fig. 1:

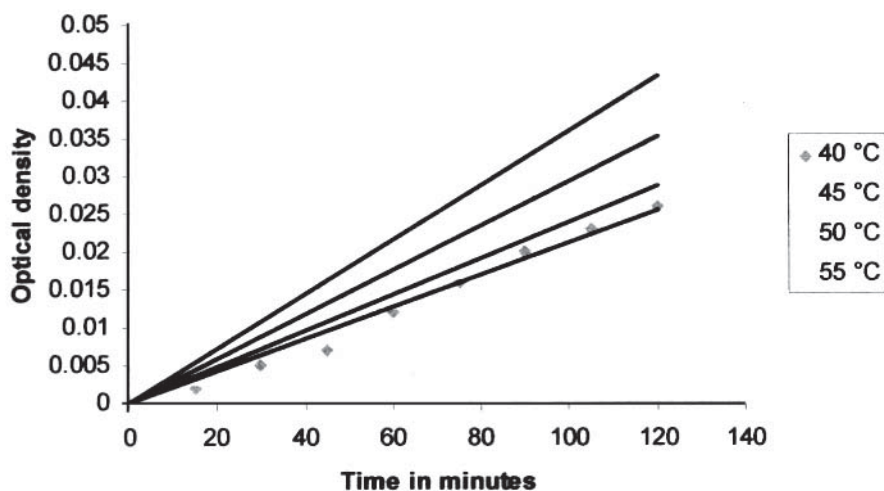


Fig. 2: Effect of temperature on the rate of reaction

rate constant depends on the reaction temperature. (Fig. 2). The above result shows that the rate of oxidation goes on increasing when compared with other substituted aromatic secondary alcohol<sup>13-17</sup>. (Table 6).

#### Complex formation

No complex formation takes place during the course of reaction, confirmed by the spectroscopic analysis. All the rates lead to the conclusion that rate of oxidation was independent of concentration of oxidant. So the implied rate law is  $-d(a-x)/dt = k$

Arrhenius law is obeyed and reaction is entropy controlled. Negative  $\Delta S^*$  value indicated that the transition state are more ordered the reactants due to increase in number of degree of freedom. The oxidation reaction induces the polymerization of acrylonitrile and there is no spectroscopic evidence for the intermediate complex formation.

#### CONCLUSION

The linearity of absorbance against plots and constancy of the zero order rate constants indicates that the reaction neither depends on the

polymeric reagent nor the alcohol concentration. This anomalous nature of the reaction may be because the oxidant 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 phase i.e. solid phase. This was observed in earlier study of benzoin oxidation by polymer supported N-bromosulphonamide<sup>18</sup>.

In previous work<sup>19</sup> we reported the kinetics of oxidation of 4-methoxy phenyl ethanol by Cr (VI)

supported on Amberlyst A-26 (Cl<sup>-</sup>). In the present study due to electron donating effect of chlorine group in 4-chlorophenyl ethanol the rate of oxidation increases. (Table 6).

#### ACKNOWLEDGMENTS

The authors are thankful to Head, Department of Chemistry, Shivaji University, Kolhapur, Shital S. Kakade and H. A. Awaskar, Bhausaheb Nene College, Pen – Raigad for providing laboratory facilities and encouragements, during the present research work.

#### REFERENCES

1. F. Shirini, M. A. Zolfigo, M. Khaleghi, *Bull Korean Chem. Soc.*, **24**: 1021 (2003).
2. R. P. Singh, N. H. Subbarau, S. Dev., *Tetrahedron Lett.*, **35**: 178 (1979).
3. M. M. Haveri, A. Ajami, K. Tabar-Heydar, *Synth. Commun.*, **29**: 163 (1999).
4. B. Khadilkar, A. Chitnavis, A. Khare, *Synth. Commun.*, **26**: 105 (1996).
5. S. T. Nandibewar and J. R. Raju., *J. Ind. Chem. Soc.*, **55**: 1284 (1978).
6. M. Saraf, G. Garg and S. Saraf, *Oriental J. Chem.*, **21**(3): 495-500 (2005).
7. A. J. Buglas, J. S. Waterhouse, *J. Chem. J. Elu.*, **64**: 3712 (1987).
8. G. Cainelli, G. Cardillio, M. Orena and S. Sardri, *J. Am. Chem. Soc.*, **98**: 6737 (1976).
9. T. Brunlet, C. Jouitteau and G. Gelhard., *J. Org. Chem.*, **51**: 4016 (1986).
10. M. Latshaw, *J. Am. Chem. Soc.*, **47**: 793 (1925).
11. C. Walling, "Free Radicals in Solution", *John Wiley and Sons, New York*, (1957).
12. W. A. Mosher, H. Clement, R. L. Hilliard, *J. Am. Chem. Soc.*, **51**: 81 (1965).
13. V. Y. Sonawane, N. P. Hilage, *Asian J. Chem.*, **17**(2): 1226 (2005).
14. V. Y. Sonawane, N. P. Hilage, *Asian J. Chem.*, **20**(1): 32 (2008).
15. V. Y. Sonawane, N. P. Hilage, *Oriental J. Chem.*, **24**(3) (2008).
16. V. Y. Sonawane, N. P. Hilage, *Oriental J. Chem.*, **25**(2) (2009).
17. S. Kakade, A. S. Varale, V. Y. Sonawane and N. P. Hilage, *J. Indian Chem. Soc.*, **86** (2009).
18. A. S. Kanade, G. S. Gokavi and M. M. Salunke, *Eur. Polym. J.*, **29**: 565 (1993).
19. V. Y. Sonawane, N. P. Hilage, *Indian Council of Chem.*, **25**(2) (2008).