

Polymer supported reagent – chromic acid on anion exchange resin and kinetics of oxidation of alcohol to ketone

VILAS Y. SONAWANE and NANDINI P. HILAGE*

Bhauasaheb Nene College, Pen - Raigad - 402 107 (India)
Department of Chemistry, Shivaji University, Kolhapur - 416 004 (India)

(Received: April 12, 2008; Accepted: June 04, 2008)

ABSTRACT

Polymer supported oxidizing agents are very useful in organic synthesis, due to easy recovery and regeneration. The selective formation of 4- fluoro acetophenone from 4-fluorophenyl ethanol by using chromic acid supported on anion exchange resin Amberlyst A-26 (Cl) with divinylbenzene containing a quaternary functional group has been investigated in detail. It was found to be through ester formation. In a slow step the ester decomposes and produces Cr(IV). Then Cr(IV) oxidizes with another molecule of 4- fluorophenyl ethanol to generate a free radical in a fast step. The free radical reacts with another polymeric reagent to form Cr (V). Finally Cr (V) reacts with 4- ffluorophenyl ethanol to produce 4-fluoro acetophenone. We have obtained interesting results in the oxidation of alcohol to carbonyl compound by using a HCrO_4^- resin. The various activation parameters have been calculated and suitable mechanism is proposed.

Key words: Kinetics, oxidation, polymer support, chromic acid.

INTRODUCTION

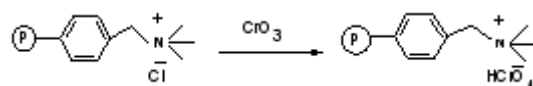
Chromium (VI) oxides and chromate salts have been widely used as oxidizing agents for a variety of substrates¹ including alcohols². Chromic acid and chromium (VI) oxide reagents are versatile oxidizing agents and typical reagents based on chromium (VI) are the Johnes, Sarett, Collins reagent etc.^{1,2}. In recent times, the oxidation of alcohols using catalytic systems has been carried out^{3,4}, while the utility of chromium oxidants has been reduced due to there hazardous toxicity. A large number of supported chromium (VI) oxidants have been reported⁵⁻⁷. The oxidation of secondary alcohol to ketone in which the polymeric reagent can be recovered and reused. This process is noteworthy because the polymeric reagent reacts with another prior to reaction with the substrate. Furthermore it is environmentally friendly since the polymers can be recycled. Polymer bound reactants have been reported for the oxidation of various alcohols⁸.

In continuation of our work on polymer supported reactions⁹, in the present communication we reports the kinetics of oxidation of 4-fluoro phenyl ethanol by using oxidant and evaluate the rate constants as well as various activation parameters calculated at 313,318,323, and 328K. Mechanistic aspects are discussed.

EXPERIMENTAL

Preparation of polymer bound – Cr (VI) oxide

Polymeric reagent (oxidant) was synthesized according to the reported procedure^{10,11,12} starting from the chloride form the Amberlyst A-26 (a macroreticular anion exchange resin)



The capacity of the chromate form of polymeric reagent was determined iodometrically. The determined average capacity of the dried resin was found to be 3.6 mmol/gm. The same of polymeric reagent was used throughout the kinetic study, other chemicals like 1;4 dioxane, cyclohexane, chloroform, carbon tetrachloride (A.R.) and 4 – fluorophenyl ethanol used were purified and stored.

Kinetic measurement

The kinetic measurement were initiated by a mixture of 4 fluorophenyl ethanol, oxidant (known amount) and solvent ($5 \times 10^{-3} \text{ dm}^3$ of 1:4 dioxane) was stirred using a magnetic stirrer at constant temp, $45^\circ + 1$. 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. The aliquot thus withdrawn in a stoppered test tube containing $5 \times 10^{-3} \text{ dm}^3$ of 1:4 dioxane at a definite interval of time and optical density of all reaction mixture was measured at different wavelengths, corresponding to the wavelength of the product ketone using ELICO – SL 159 UV – VIS spectrophotometer.

Polymerization study

The reaction mixture to which a known quantity of acrylonitrile 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 in the reaction. Also the presence of a free radical confirmed by ESR spectrum.

Product analysis

The product formed was analyzed by its 2,4 DNP derivative and UV spectra. The melting point of the 2,4 DNP hydrazone derivative of 4- fluoroacetophenone is 234°C and UV spectra max – 265 nm.

RESULTS AND DISCUSSION

Effect of oxidant

The order in oxidant is zero as the plots of absorbance against time were linear in all runs and observed rate constant are fairly constant between $50\text{-}80 \times 10^{-6} \text{ Kg}$. of the oxidant at constant concentration of solvent (1:4 dioxane, $5 \times 10^{-3} \text{ dm}^3$) and alcohol ($8.21 \times 10^{-6} \text{ mol / dm}^3$) . The effect of oxidant on the zero order rate constant as shown (Table-1)

Effect of alcohol concentration

At a concentration of 4- fluorophenyl ethanol ($5.91 - 12.8 \times 10^{-6} \text{ mol / dm}^3$), Constant concentration of oxidant ($70 \times 10^{-6} \text{ kg}$) and constant concentration of solvent (1:4 dioxane, $5 \times 10^{-3} \text{ dm}^3$), zero order rate constant (Table -2) was found.

Effect of dielectric constant

It was found that, as the dielectric constant of the solvent (medium) increased, zero order rate constant was also increased, at constant alcohol

Table 1: Effect of oxidant on zero rate constant at 45°c (solvents) $5 \times 10^{-3} \text{ dm}^3$

Oxidant $\times 10^{-6} \text{ kg}$	50	60	70	80
$k \times 10^{-4} \text{ min}^{-1}$	2.20	2.21	2.22	2.25

Table 2: Effect of alcohol conc. On zero order rate constant at 45°c (oxidant) $70 \times 10^{-6} \text{ kg}$

Alcohol conc. $\times 10^{-6} \text{ mol/dm}^3$	5.91	8.21	10.5	12.8
$k \times 10^{-4} \text{ min}^{-1}$	2.13	2.22	2.33	2.44

concentration (8.21×10^{-6} mol / dm³) and constant concentration of polymeric reagent (70×10^{-6} kg), solvent (5×10^{-3} dm³) as shown in Table 3.

Effect of temperature

It was found that, the rate of reaction increased with an increase in the temperature at constant alcohol concentration (8.21×10^{-6} mol / dm³), constant concentration of solvent (1:4

dioxone, 5×10^{-3} dm³) and constant concentration of oxidant (70×10^{-6} kg) at temperatures ranging between 313-328 K. (Table - 4).

The values of enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger), Free energy of activation (ΔG^\ddagger), energy of activation (Ea) and frequency factor (A) was calculated from log k versus 1/T plots. The values shown in Table 5.

Table 3: Effect of dielectric constant on zero order rate constant at 45°C

Solvent	Cyclohexane	CCl ₄	1:4 dioxone	Chloroform
Dielectric constant	2.0	2.2	2.2	4.8
k × 10 ⁻⁴ min. ⁻¹	1.25	1.71	2.22	2.62

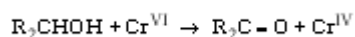
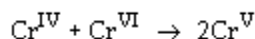
Table 4: Effect of temperature on zero order rate constant

Temperature K	313	318	323	328
k × 10 ⁻⁴ min. ⁻¹	2.0	2.22	2.75	3.33

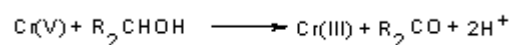
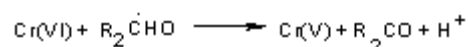
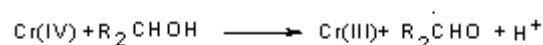
Table 5: Activation parameters

Ea KJ.mol ⁻¹	ΔH^\ddagger KJ.mol ⁻¹	ΔS^\ddagger e.u.	ΔG^\ddagger KJ.mol ⁻¹	A × 10 ⁻⁴
47.82	26.80	-54.82	100.70	3.16

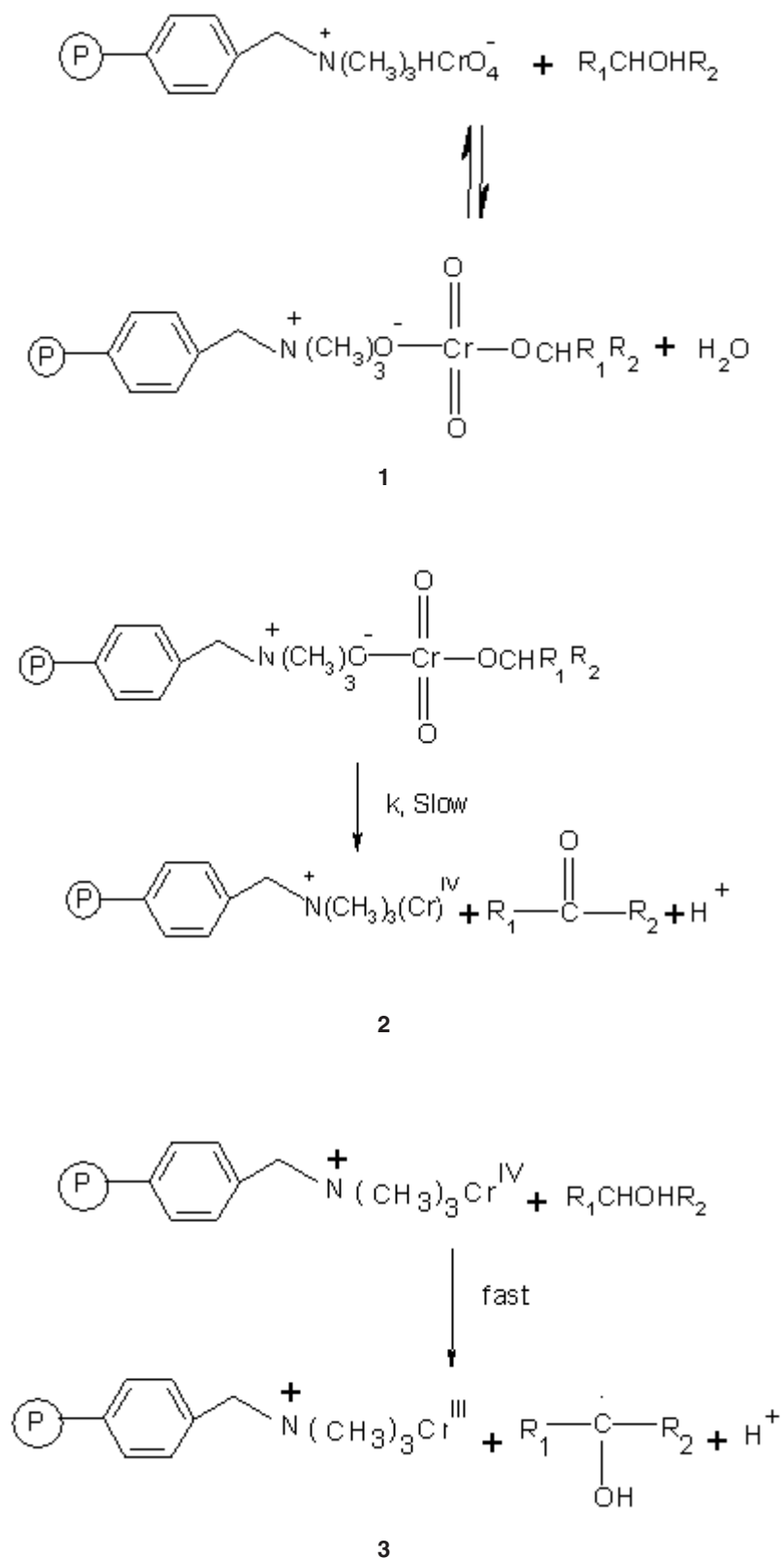
We have reported another approach to determining the relative roles of chromium (VI), (V) and (IV) in the oxidation of 4-fluorophenyl ethanol.¹³ We now wish to present a full account of this investigation. The basis of the experiment is easily seen in comparing the possible scheme. The Watanabe and Westheimer,¹⁴ subsequent step must involve chromium (IV) as shown below.

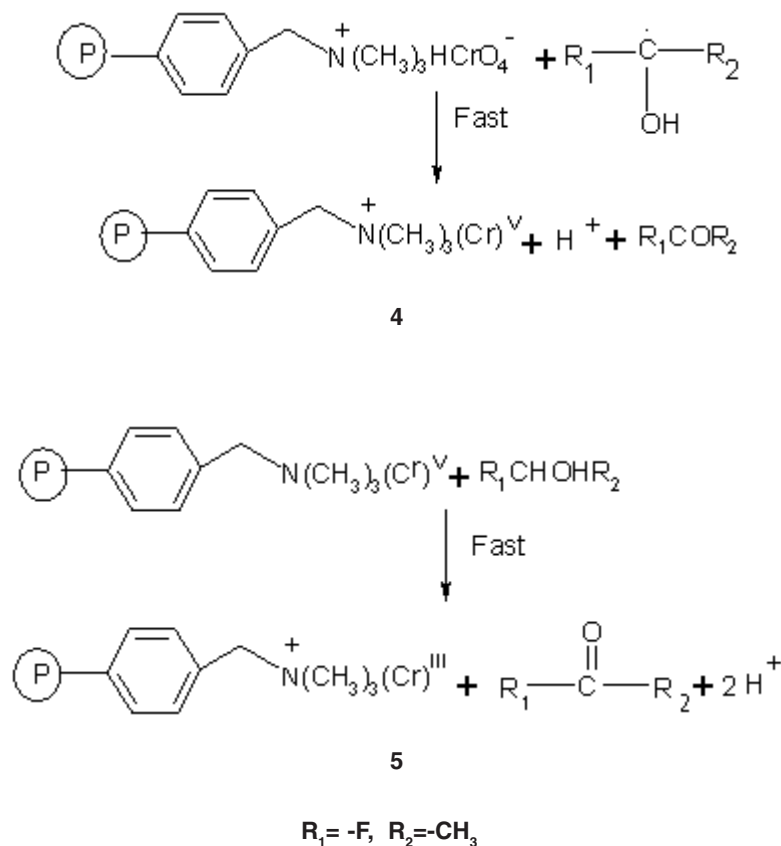


The other mechanism proposed by Westheimer¹⁵ involves production of free radical in following steps.



If the oxidant supported on polymer, which has certain advantages over homogeneous reaction, the intermediate chromium (IV) will further oxidize another molecule of alcohol produce a free radical. Thus based on the experimental results obtained for the oxidation of 4-fluorophenyl ethanol which was found to be zero order. The mechanism is suggested in Scheme 1 and involves ester formation.





Scheme 1

CONCLUSION

According to Scheme I, 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.

ACKNOWLEDGEMENTS

The authors wish to thank Shital A. Kakade and A.S. Varale for the help to carry out research work.

REFERENCES

- G. Cainelli, G. Cardillo, *Chromium oxidations in organic Chemistry*, Springer-verlag; Berlin, **19**: 118 (1984).
 - K. B. Wiberg, *Oxidation in Organic Chemistry*, Academic Press : 1965.
 - J. J. Muzart, *Bull. Soc. Chem. Fr.* **65** (d) (1988).
- G. Piancatelli, A. Scettri, M. Auria, *Synth. Commun.*, **245**: (1982).
 - J. C. Collins, W. Hess, F. J. Frank,

- Tetrahedron Lett.*, **9**: 3363 (1968).
3. E. J. Corey, E. P. Barrett, P. A. Magriotis, *Tetrahedron Lett.*, **26**: 5855 (1985)
 4. F. Shirini, I. Mahammadpoor – Baltork, Z. Hejazi, *Bull. Korean Chem. Soc.*, **24**: 517 (2003).
 5. R. P. Singh, H. N. Subbarao, S. Dev, *Tetrahedron Lett.*, **35**: 1789 (1979).
 6. M. M. Heravi, A. Ajami, K. Tabar-Heydar, *Synth Commun*; **29**: 163 (1999).
 7. B. Khadilkar, A. Chitnavis, A. Khare, *Synth. Commun*; **26**: 205 (1996)
 8. A. Matsuo, A. Kawana, K. Pudhom and T. Mukaiyama, *Chem. Lett*; 250 (2002).
 9. (a) V. Y. Sonawane and N. P. Hilage, *Asian J. Chem.*, **17**(2):1226 (2005).
(b) V. Y. Sonawane and N. P. Hilage, *Asian J. Chem*, **20**:132 (2008).
(c) Shital A. Kakade and Nandini P. Hilage, *Trans. Metal Chem*, **32**: 940-943 (2007).
 10. G. Cainelli, G. Cardillo, M. Orena and S. Sardri, *J. Am. Chem. Soc*; **98**: 9737 (1976).
 11. A. J. Buglas and J. S. Waterhouse, *J. Chem. Edu.*, **64**: 3712 (1987).
 12. J. Brunelet, C. Jouitteau and G. Gelhard, *J. org. Chem.*, **51**: 4016 (1986).
 13. K. B. Wilberg and S. K. Mukherjee, *J. Am. Chem. Soc*; **93**: 2543 (1971).
 14. W. Watanabe and F. H. Westheimer, *J. Chem. Phys.* **61**: 17 (1979).
 15. W. Watanabe, *Chem. Rev.*, **415**: 45 (1949).