Asian Journal of Chemistry Vol. 20, No. 1 (2008), 132-136

Kinetics and Mechanism of Oxidation of 4-Bromophenyl Ethanol by Polymer Supported Chromic Acid

V.Y. SONAWANE* and N.P. HILAGE†
Department of Chemistry, B.N.College, Pen-402 107, India
E-mail: sonawane_vy@rediffmail.com

Kinetics and mechanism of oxidation of secondary alcohols by polymer supported chromic acid and the newer oxidative protocols are welcome in spite of the availability of several methods. Kinetics indicates zero order reaction in with respect to oxidant and substrate, respectively. On the basis of experimental observed kinetic finding the probable mechanism of oxidation is proposed.

Key Words: Kinetics, Mechanism, Oxidation, Chromic acid, 4-Brompophenyl ethanol.

INTRODUCTION

In continuation of our earlier analysis on oxidation of secondary alcohols by polymer supported chromic acid[1], we report kinetics and mechanism of oxidation of 4-bromophenyl ethanol by polymer supported chromic acid. The probable reaction mechanism consistent with kinetic results has also been suggested. Also the use and reuse of polymer supported oxidizing agent without loss of capacity, easy workup and safety are the major factor's of interest in the present study.

EXPERIMENTAL

The chemicals used during the investigation were AR grade.

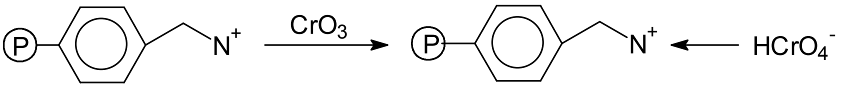
Preparation of 4-bromophenyl ethanol using sodium borohydride[2]: The calculated quantity of 4-bromoacetophenone in methanol was cooled to 0-5 ºC and sodium borohydride was added with constant stirring. The reaction mixture was slowly warmed to room temperature. The progress of reaction was monitored by thin layer chromatography. Removal of solvent gave the corresponding alcohol. It was purified by distillation and characterized by TLC and IR.

Preparation of polymer bound chromium(VI) oxide: The polymer bounded chromium(VI) oxide was prepared[3-5]. The chloride form of

---

†Department of Chemistry, Shivaji University, Kolhapur-416 004, India.

Amberlyst A-26 (Fluka 20-25 mesh) containing quaternary ammonium group was stirred with saturated aqueous solution of chromium trioxide. Chloride ions were readily displaced and $HClO_4$ form of the resin was obtained. The resin was successively rinsed with water, acetone and ether, finally dried in vacuum at 50 ºC. The dried form of the resin was stored and used throughout.



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

Capacity of chromate form of polymeric reagent[6]: The capacity of chromate form of polymeric reagents was calculated by iodometrically. The average capacity of dried resin was found to be as follows: (i) chromate form of Amberlyst A-26, 3.4 mmol/g (ii) chromate form of 3.5 % quaternary ammonium resin : 3.47 mmol/ g (iii) chromate form of 6.5 % quaternary ammonium resin : 3.42 mmol/g.

Kinetic measurments[7]: The mixture of alcohol, oxidant and solvent was stirred using magnetic stirrer at constant temperature 45 ± 1 ºC. The completion time of the reaction was monitored with the help of TLC. The course of reaction was monitored by withdrawing 10×10^{-3} dm^3 aliquot of the reaction mixture at a definite interval of time into 5×10^{-3} dm^3 of 1:4 dioxan. The optical density of all reaction mixture's measured using schimadzu 160 UV-Visual spectrophotometer.

The different variations for the kinetic study of 4-bromophenyl ethanol to 4-bromo-acetophenone were: (a) effect of polymeric reagent (b) effect of conc. of alcohol (c) effect of solvent (d) effect of temp. (e) effect of % of cross linking polymeric reagents.

The rate constants were calculated from linear plots of optical density against time. The effect of different variation's on the reaction rate is summarized in Tables 1-5.

TABLE-1
EFFECT OF POLYMERIC REAGENT

Polymeric reagent (mg)	Rate × 10^{-4} min^{-1}
50	2.20
60	2.21
70	2.22
80	2.25

TABLE-2
EFFECT OF CONCENTRATION OF ALCOHOL

Alcohol conc. × 10^{-3} dm^3	Rate × 10^{-4} min^{-1}
4.6	2.13
9.0	2.22
13.4	2.33
17.8	2.44

TABLE-3
EFFECT OF SOLVENT

Solvent (5 × 10^{-3} dm^3)	Rate × 10^{-4} min^{-1}
1:4 Dioxane	2.22
Carban tetrachloride	1.71
Cyclohexane	1.25
Chloroform	2.62

TABLE-4
EFFECT OF TEMPERATURE

Temperature (ºC)	Rate × 10^{-4} min^{-1}
40	2.00
45	2.22
50	2.75
55	3.33

TABLE-5
EFFECT OF CROSS-LINKING (%)

Cross-linking (%)	Rate × 10^{-4} min^{-1}
3.50	3.55
6.50	3.11
8.00	3.06

Product analysis: The product formed were analysed by TLC and also by their 2,4-dinitrophenyl hydrazone derivatives. After completion of reaction the resin was filtered off, washed with the solvent and the product was isolated by evaporating the filtrate under reduced pressure. The 2,4-dinitrophenyl hydrazone derivative were prepared and their melting point were as follows: 4-bromoacetophenone = 230 ºC. The yield of product was found to be above 60 %.

RESULTS AND DISCUSSION

Chromium(VI) is a oxidizing agent for the oxidation of organic compounds. The mechanism for one equivalent reducing agent, mainly inorganic ions, king and coworkers[8] proposed a sequence of three-one electron transfer steps to reduce chromium(VI) to chromium(III) with inter conversion between chromium(V) and chromium(IV) as the slow steps.

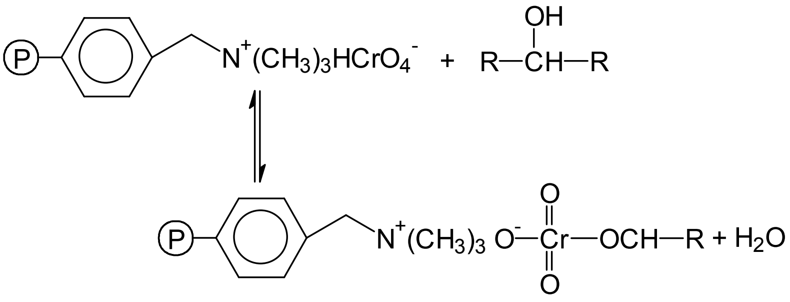
For two equivalent reducing agents, the westheimer[9] mechanism for oxidation of alcohols has been a focus for discussion and research.

$$Cr(IV) + R_2CH - OH \rightarrow Cr(III) + R_2CHO - H^+$$

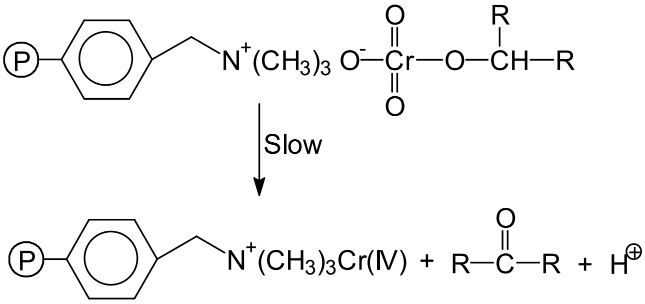
$$Cr(VI) + R_2CHO \rightarrow Cr(V) + R_2CO - H^+$$

$$Cr(V) + R_2CHOH \rightarrow Cr(III) + R_2O - 2H^+$$

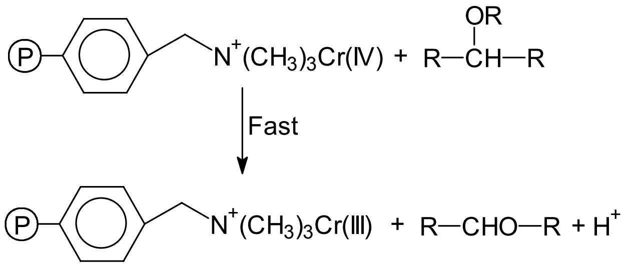
Chromium(VI) oxidation of alcohols, proceed through formation of an ester[10]. Since our oxidant was supported on a polymeric material the intermediate chromium(IV) will further oxidize another molecule of alcohol into a free radical. Therefore, on the basis of experimental result obtained for the oxidation of 4-bromophenyl ethanol which were found to be zero order, the suggested mechanism is as follows **Schemes I-V**.



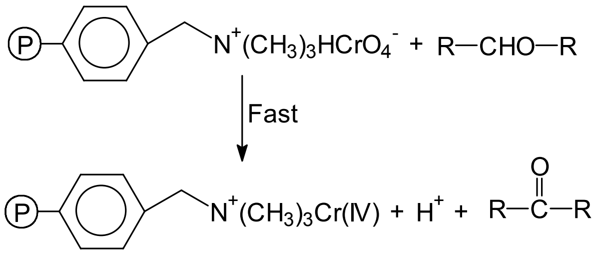
Scheme-I



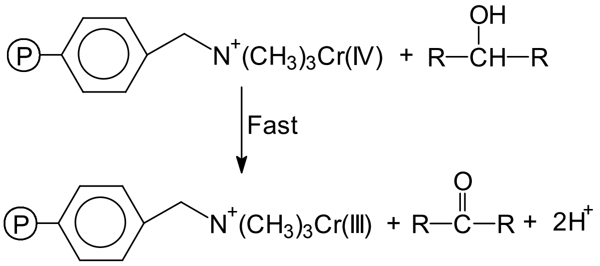
Scheme-II



Scheme-III



Scheme-IV



Scheme-V

Conclusion

According to above schemes, a second order rate law is expected. A zero order dependence is obtained with rate constant K of the second slow step in which ketone as product is formed.

REFERENCES

1. V.Y. Sonawane and N.P. Hilage, *Asian J. Chem.*, **17**, 1226 (2005).
2. A.I. Vogel's, Textbook of Practical Organic Chemistry, edn. 5 (1988).
3. J. Buglas and S.I. Waterhouse, *J. Chem. Ed.*, **64**, 3712 (1987)
4. G. Cainelli, G. Cardillo, M. Orena and S. Sandri, *J. Am. Chem. Soc.*, **98**, 6737 (1976).
5. T. Brunlet, C. Jouitteau and G. Gellhard, *J. Org. Chem.*, **51**, 4016 (1986).
6. A. Bowers, T.G. Halsall and R.H. Jones, *J. Chem. Soc.*, 2548 (1953).
7. A.L. Jawanjal and N.P. Hilage, *Indian J. Chem.*, **44A**, 1827 (2005).
8. J.Y. Tong and E.L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).
9. F.H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).
10. A.L. Jawanjal and N.P. Hilage, *Transition Metal Chem.*, **30**, 290 (2005).

(*Received*: 29 August 2006; *Accepted*: 13 August 2007) AJC-5797