



Kinetics and Mechanism of Oxidation of Aromatic Secondary Alcohols by Chromate Ion

Vilas Y. Sonawane

Department of Chemistry, B.Raghunath Arts, Commerce and Science, College,

Parbhani – 431 401, Maharashtra (India).

E-mailID: sonawane_vy@rediffmail.com

Abstract

The kinetic of chromium (VI) catalyzed oxidation of aromatic secondary alcohols has been studied by the rate of disappearance of [Cr(VI)]. The reaction is zero order with respect to [Cr(VI)]. The reagent supported on anion exchange resin was found to be more efficient in the oxidation reaction. The reagent is very easily separated from the reaction mixture and can be manually removed from the reaction mixture, which remains clear during and after the reaction. The kinetic of oxidation of 4-Bromophenylethanol, 4-Chlorophenylethanol and 4-Iodophenylethanol with chromic acid supported on anion exchange resin like Amberjet1500 [Cl⁻] in 1, 4-dioxane has been studied. The reaction is found to be of zero order each in concentration of alcohol and oxidant. The reaction constants involved in the mechanism and the activation parameters have been calculated.

Keywords: Kinetics, mechanism, alcohol, chromate ion

1. Introduction

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds. Chromium compounds especially chromium^{VI} reagents and capable of oxidizing almost all the oxidative organic functional groups. The development of newer chromium^{VI} reagents for the oxidation of organic substrates continues to be of interest¹⁻⁸. In recent years, a number of chromium^{VI} containing compounds like tri/tetralkylammonium halochromates have been used as oxidant for the oxidation of various organic substrates. Some of the newalkylammoniumhalochromateliketertaethylammoniumbromochromate, tributylammoniumchlorochromate, tripropylammoniumfluorochromate and triethylammoniumchlorochromate have been used to study the kinetics of oxidation of various organic

compounds⁹⁻¹². In the present investigation, we now report the oxidation of secondary aromatic alcohols by polymer- supported chromic acid on Amberjet1500 [Cl⁻] strong anion anion exchange resin are supported on chromium^{VI} oxide and it used as an oxidant.

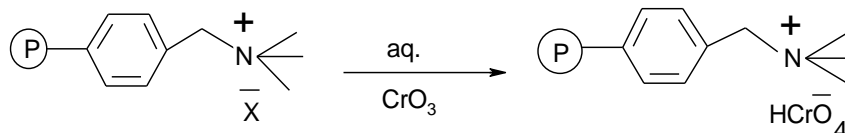
2. Experimental

All the chemicals used were of reagent grade and doubly distilled water was used throughout. The resin Amberjet1500 [Cl⁻] as Thomas Baker used.

Preparation of supported oxidizing agent

The supported oxidizing agent was prepared by reported method¹³⁻¹⁵. The chloride form of Amberjet1500 [Cl⁻] [a macro reticular anion exchange resin] containing a quaternary ammonium group was stirred with a saturated solution of chromium trioxide in water for 30 min at room temperature using a magnetic

stirrer. The chloride ion was readily displaced and HCrO_4^- form of resin was obtained in 40 min. The resin was successively rinsed with water, acetone and THF and finally dried in



[X = Cl]

Determination of the capacity of chromate form of the polymeric reagent

The capacity of the chromate form of Amberjet1500 [Cl] polymeric reagent was determined by iodometrically. The capacity of the chromate form of resin was 1.75 eq/L and used for kinetic study throughout work. The loading was also determined by elemental nitrogen analysis and was found to be 3015eq/L.

Kinetic study

Product analysis

Melting point of 2,4 DNP hydrazone Derivative	K	Yield in %	UV λ_{max}	Lit. UV λ_{max}
4-Bromoacetophenone	237	95	242	245
4-Chloroacetophenone	245	95	259	263
4-Iodoacetophenone	274	98	278	276

3. Results and Discussion

Effect of varying weights of oxidant

The order with respect to weights oxidant is zero, as the plots of absorbance against time were linear in all runs and observed rate constant are fairly constant between 100 to 160 x 10⁻⁶ kg of oxidant at constant concentration of solvent (1, 4-dioxane, 5 x 10⁻³ dm³) and aromatic secondary alcohols (24.6 x 10⁻³ mol/dm³), the effect of varying weights of oxidant on zero order rate constant as shown in Table-1.

Effect of varying concentrations of various aromatic secondary alcohols

At a varying concentration of alcohols, constant weights of oxidant [140 x 10⁻⁶ kg] and constant concentration of solvent [1,4-dioxane, 5 x 10⁻³dm³], zero order rate constant [Table-2] was found.

vacuum at 323 K for 5h. The dried form of the resin was stored and used throughout the kinetic study.

Polymer supported oxidizing agent

The reaction mixture for the kinetic run was prepared by mixing aromatic secondary alcohol, oxidant and solvent. The reaction was carried out either constant stirring using magnetic stirrer and at a constant temperature 318 ±1 K. At different time interval, the reaction mixture was withdrawn using a micropipette. The aliquot thus withdrawn was taken in a stoppered test tube containing 5 x 10⁻³ dm³ of 1, 4-dioxane and subjected to spectral analysis. The absorbance of the product formed was measured using Schmadzu 1800 UV-visible spectrophotometer

Effect of varying dielectric permittivity of the medium on the reaction rate

It was found that as the dielectric constant of the medium increased, this including $r^* < r$ [Where r^* and r refer to the radii of the reactant species and activated complex respectively] at constant concentration of various aromatic secondary alcohol [24.6 x 10⁻³ mol/dm³] and constant concentration of oxidant [140x 10⁻⁶ Kg], solvent [5 x 10⁻³dm³] as shown in Table-3.

Effect of varying temperature

The reaction was carried out at four different temperatures under otherwise similar reaction conditions to study the effect of temperatures on the rate of reaction. It was observed that, the rate of reaction increased with an increase in the temperature. [Table-4]. The activation parameters like energy of activation [Ea], enthalpy of activation [ΔH^\ddagger],

entropy of activation $[\Delta S^\ddagger]$ free energy of activation $[\Delta G^\ddagger]$ the high positive values of free energy of activation indicates that the transition state is highly solvated and frequency factor $[A]$ were calculated by determining values of k at different temperatures. [Table-5].

On the basis of above experimental results the following reaction scheme is proposed for Cr (VI) catalyzed oxidation of various aromatic secondary alcohols. The mechanism is suggested in **Scheme (I)** and involves ester formation^{12,13}.

Table-1. Effect of varying weights of oxidant on reaction rate at 318 K.

Rate constant →	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Oxidant $\times 10^{-6} \text{ kg}$ →	100	120	140	160
4-Bromophenylethanol	1.25	1.24	1.25	1.29
4-Chlorophenylethanol	1.52	1.55	1.85	1.87
4-Iodophenylethanol	1.98	2.05	2.10	2.12

Table-2 Effect of varying concentrations of various aromatic secondary alcohols

Rate constant →	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Conc. of alcohol →	$16.40 \times 10^{-3} \text{ mol /dm}^3$	$24.6 \times 10^{-3} \text{ mol /dm}^3$	$40.8 \times 10^{-3} \text{ mol /dm}^3$	$20.4 \times 10^{-3} \text{ mol /dm}^3$
4-Bromophenylethanol	1.45	1.49	1.50	1.52
4-Chlorophenylethanol	1.55	1.59	1.52	1.65
4-Iodophenylethanol	1.68	1.60	1.62	1.65

Table-3. Effect of varying dielectric permittivity

Rate constant →	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Solvent [$5 \times 10^{-3} \text{ dm}^3$] →	C_6H_{12}	CCl_4	1,4-dioxane	CHCl_3
Dielectric constant →	1.98	2.07	2.18	4.11
4-Bromophenylethanol	1.29	1.37	1.40	1.61
4-Chlorophenylethanol	1.39	1.42	1.43	1.55
4-Iodophenylethanol	1.45	1.48	1.49	1.55

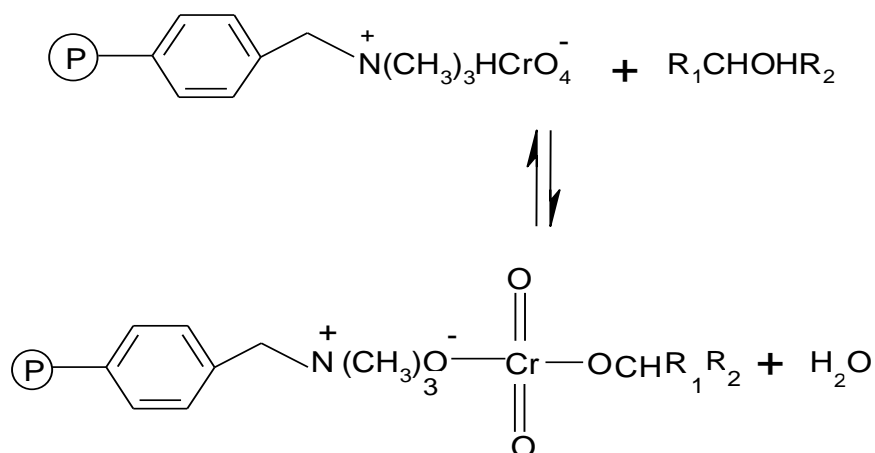
Table - 4. Effect of varying temperature

Rate constant →	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Temperature K →	313	318	323	328
4-Bromophenylethanol	1.55	2.01	2.13	2.28
4-Chlorophenylethanol	2.25	2.27	2.30	2.34
4-Iodophenylethanol	2.28	2.31	2.38	2.39

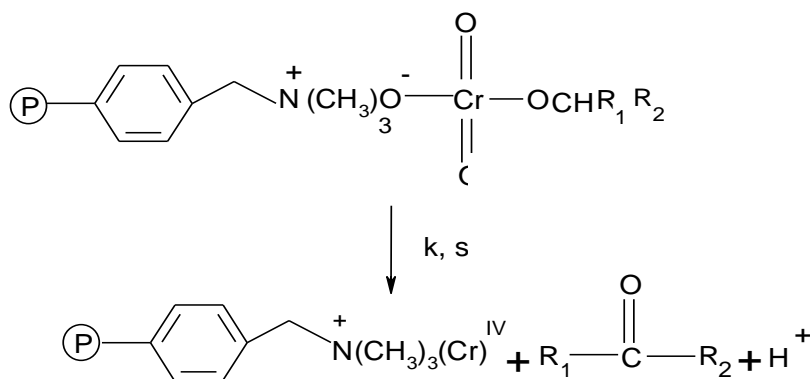
Table -5. Thermodynamic Parameters

Thermodynamic Parameters	[Ea] KJ mol ⁻¹	[ΔH [#]] KJ mol ⁻¹	[ΔS [#]] KJ mol ⁻¹	[ΔG [#]] KJ mol ⁻¹	[A] X 10 ⁻⁵ s ⁻¹
4-Bromophenylethanol	75	55	-77	315	4.5
4-Chlorophenylethanol	95	75	-88	320	5.7
4-Iodophenylethanol	97	79	-96	3230	5.9

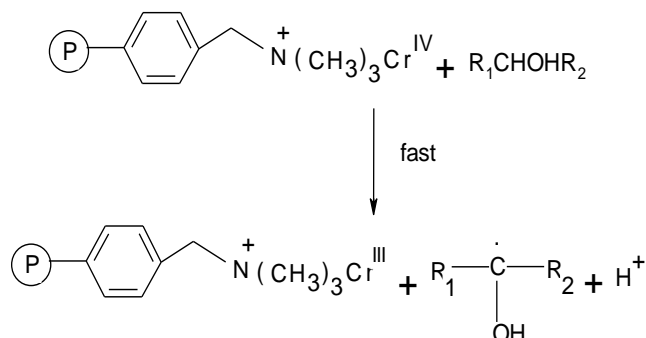
1) The polymer supported reagent reacts with a molecule of alcohol to form a chromate ester.



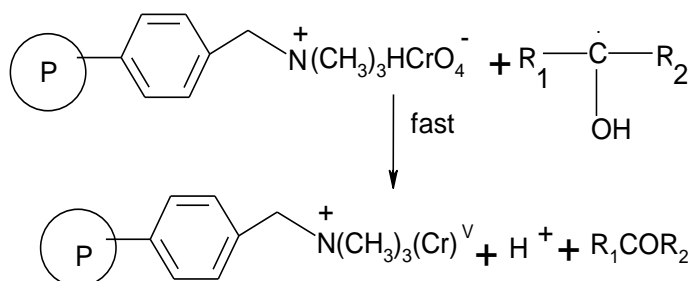
2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second and slow step.



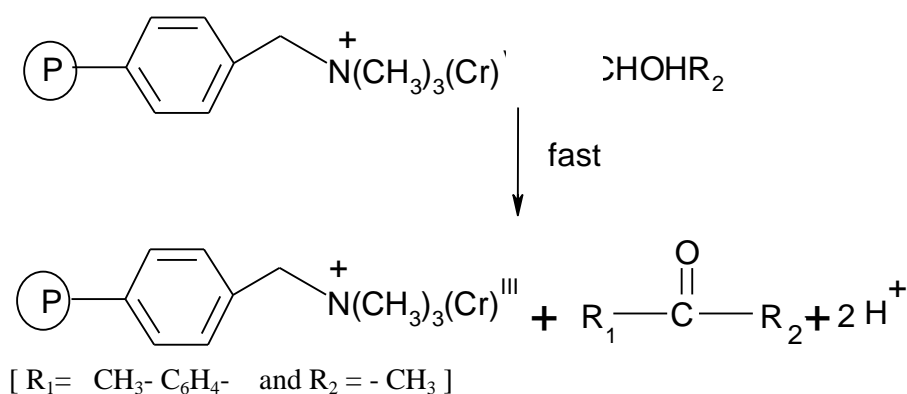
3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. The free radical species formation in the reaction was confirmed by the polymerization of added acrylonitrile or addition of acidified methanol into the reaction mixture.



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).



5) The intermediate chromium (V) in the last step reacts with aromatic secondary alcohols produce corresponding acetophenone. The test for formation of chromium (V) and (IV) by the characteristic induced oxidation of iodide¹⁴ and manganese (II)¹⁵ were not probably due to heterogeneity of the reaction mixture.



Scheme I

4. Conclusion

The linearity of absorbance against time plots and constancy of the zero order rate constants indicate that the reaction neither depends on the polymeric reagents nor on the alcohol concentration. This anomalous nature

of the reaction may be because of the fact that the oxidant is taken in the form of solid supported on polymer. Polymer supported oxidizing agent proved to be exclusively selective towards the oxidation of aromatic



secondary alcohols, giving corresponding acetophenone as the only product¹⁶.

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 acetophenone was

obtained. Based on the experimental observations a probable mechanism is suggested.

5. Acknowledgement

The author is thankful to the University Grants Commission, New Delhi, India for the financial support of this major research project sanctioned F.No.42-253/2013(SR).

5. References

1. Song W Y, Li W K and Jia C P *Chem.J.Univ.*1999, **20**,1767.
2. Song W Y and Liu H M *Chin. J.Inorg.Chem.* 2000, **16**,607.
3. Shan J H Qian Q and Zhai T Y *Chin. J.Inorg.Chem.*2003, **19**, 843.
4. Lakshmi S and Renganathan R *Int.J.Chem.Kinet.* 1996, **28**, 713.
5. Corey E J and Schmidt G , *Tetrahedron Lett.* 1979, **20**, 399.
6. Bhattacharjee M N and Choudhari M.K., Dasgupta S D, Roy N and Khating D T *Synthesis.*1982 , **58**.
7. Corey E J , Barette E P and Margrious P A. *Tetrahedron Lett.* 1985, **24**, 5855.
8. Climinale F,Camporeale M,Mello R,Troisi L and Curci R,*J.Chem.Soc.,Perkon Trans.*, 1989, **2**, 417.
9. Sharma G G and Mahanti M K , *Bull. Soc. Chem. Fr.* 1991,**128**,449.
10. Balasubramanian K and Pratibha V, *Indian J. Chem., Sec. B*, 1986, **25**,**326**.
11. Narayana B and Tam Cherian, *J. Braz. Chem. Soc.* 2005, **16** 167.
12. Buglas A J and Waterhouse J S, *J. Chem. Edu*, 1987, **64**, 3712.
13. Cainelli G,Cardillio G, Orena M and Sardri S, *J. Am. Chem. Soc.* 1976,**98**,6767.
14. Brunlet T, Jouitteau C and Gelhard G, *J. Org. Chem.*1986, **51**,**4016**.
15. Mosher W A Clement H and Hillard R L ,*J. Am .Chem. Soci.* 1993, **29**,**565**.
16. Matsuo J ,Kawana A, Pudhon K and Mukaiyama T, *Chem. Lett.* 2002,250.