



Oxidation of Aromatic Secondary alcohol by Polymer Supported Reagent: A Kinetic and Mechanistic Approach

KEYWORDS

Kinetics, Reaction mechanism, Oxidations, Chromium (VI)

Vilas Y. Sonawane

Department of Chemistry, B. Raghunath Arts, Commerce and Science College, Boralkar nagar, Jintur Road, Parbhani. At./Post./Tal/ Distt.- Parbhani, Maharashtra, 431 401, India.

ABSTRACT The kinetics of chromium (VI) catalyzed oxidation of 1-Phenylethanol 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 kinetic of oxidation of 1-Phenylethanol with chromic acid supported on anion exchange resin like Amberjet-9900 [OH⁻] 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. There is a good agreement between observed and calculated rate constants under different experimental conditions. Acetophenone was detected as end product.

Introduction

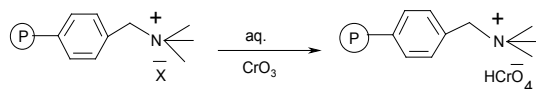
Recently, many researchers are interested in the study of the highest oxidation state of transition metals which in a higher oxidation state generally can be stabilized by chelating with suitable ligands¹⁻⁴. The kinetics and mechanism of oxidation of chromium (VI) has been well studied, chromic acid being one of the most versatile available oxidizing agents, reacting with diverse substrates. Now a day the development of newer chromium (VI) reagents⁵⁻¹¹ for the oxidation of organic substrates continues to be of interest.

In this paper, oxidation of 1-Phenylethanol by polymer-supported chromic acid reported. Amberjet-9900 [OH⁻] is the strong basic anion exchange resin was supported on chromium (VI) oxide and used as an oxidant.

Experimental

Preparation of supported oxidizing agent

The supported oxidizing agent was prepared by reported method¹²⁻¹⁵. The hydroxide form of Amberjet- 9900 [a macro reticular anion exchange resin] containing a quaternary ammonium group [10 x 10⁻³ kg] was stirred with a saturated solution of chromium trioxide [10x 10⁻³ dm³] in water [60 x10⁻³ dm³] for 30 min at room temperature using a magnetic stirrer. The hydroxide ion was readily displaced and HCrO₄⁻ form of resin was obtained in 30 min. The resin was successively rinsed with water, acetone and THF and finally dried in vacuum at 323 K for 5h. The dried form of the resin was stored and used throughout the kinetic study.



[X = OH] Polymer supported oxidizing agent

Determination of the capacity of chromate form of the polymeric reagent

The capacity of chromate form of Amberjet- 9900 polymeric reagent was determined by iodometrically. The capacity of chromate form of resin was 2.65 eq/L found and used for kinetic study throughout work. The loading was also determined by elemental nitrogen analysis and was found to be 2.69 eq /L.

Kinetics measurements and product analysis

The reaction mixture for the kinetic run was prepared by mixing 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 10 x 10⁻³ dm³ of 1, 4-dioxane and subjected to spectral analysis. The absorbance of the product formed was measured using UV-visible spectrophotometer. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 1 %.

The product of was identified as ketone by its characteristic spot test¹⁶ and spectrophotometrically.

Results and Discussion

A) 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 50 to 80 x 10⁻⁶ kg of oxidant at constant concentration of solvent (1, 4-dioxane, 5 x 10⁻³ dm³) and 1-Phenylethanol (12.3 x 10⁻³ mol/dm³), the effect of varying weights of oxidant on zero order rate constant as shown in Table-1.

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

Rate constant →	k x 10 ⁻⁴ mol dm ⁻³ s ⁻¹			
Oxidant x 10 ⁻⁶ kg →	100	120	140	160
AMBERJET- 9900 [OH ⁻]	2.20	2.24	2.26	2.29

B) Effect of varying concentrations of 1-Phenylethanol

At a varying concentration of 1-Phenylethanol [16.40 to 40.8 x 10⁻³ mol/dm³], constant weights of oxidant [70 x 10⁻⁶ kg] and constant concentration of solvent [1,4-dioxane, 5 x 10⁻³ dm³], zero order rate constant [Table- 2] was found.

Table-2 Effect of varying concentrations of 1- Phenylethanol

Rate constant →	k x 10 ⁻⁴ mol dm ⁻³ s ⁻¹			
1-Phenylethanol →	16.40 x 10 ⁻³ mol /dm ³	24.6 x 10 ⁻³ mol /dm ³	32.8 x 10 ⁻³ mol /dm ³	40.8x 10 ⁻³ mol /dm ³
AMBERJET-9900 [OH ⁻]	1.54	1.56	1.59	1.62

C)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 1-Phenylethanol [$12.3 \times 10^{-3} \text{ mol/dm}^3$] and constant concentration of oxidant [$70 \times 10^{-6} \text{ Kg}$], solvent [$5 \times 10^{-3} \text{ dm}^3$] as shown in Table-3.

Table-3. Effect of varying dielectric permittivity

Rate constant \rightarrow	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Solvent [$5 \times 10^{-3} \text{ dm}^3$] \rightarrow	C_6H_{12}	CCl_4	1,4-dioxane	CHCl_3
Dielectric constant \rightarrow	2.00	2.17	2.28	4.81
AMBERJET-9900 [OH] \rightarrow	1.89	2.12	2.76	2.96

C) 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 [ΔS^\ddagger] free energy of activation [ΔG^\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].

Table - 4. Effect of varying temperature

Rate constant \rightarrow	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Temperature K \rightarrow	313	318	323	328
AMBERJET-9900 [OH] \rightarrow	2.25	2.31	2.59	3.15

Table -5. Activation parameters

Energy of activation [Ea] KJ mol^{-1}	95 ± 4
Enthalpy of activation [ΔH^\ddagger] KJ mol^{-1}	75 ± 3
Entropy of activation [ΔS^\ddagger] JK mol^{-1}	-86 ± 2
Free energy of activation [ΔG^\ddagger] KJ mol^{-1}	358 ± 2
Frequency factor [A] $\times 10^{-5} \text{ s}^{-1}$	3.5 ± 0.5

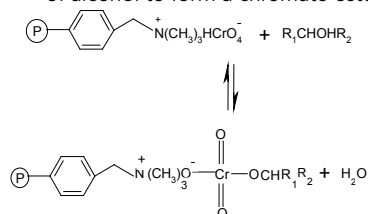
E) Effect of repeated use of supported oxidizing agent

The reaction was found to be zero order. The proposed path for the reaction of chromium (IV) then makes possible a different mechanism for oxidation of alcohol.

Thus based on experimental results obtained, for the oxidation of 1-Phenyl ethanol by polymer support, the reaction was found to be zero order. Initially Cr (VI) is reduced to Cr (IV). It is likely to react with another Cr (VI) to generate Cr (V) which is then reduced in a fast step to the ultimate product Cr (III). Such a sequence of reactions in Cr (VI) oxidation is well known¹⁷⁻¹⁹.

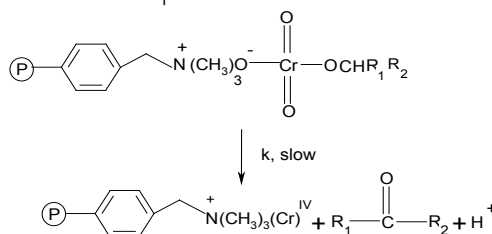
On the basis of above discussion and experimental results, the following reaction Scheme (I) is proposed for Cr (VI) catalyzed oxidation of 1-Phenylethanol and involves ester and free radical formation.

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

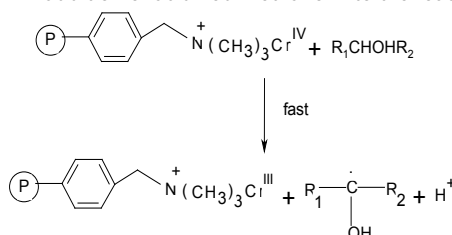


- 2) The ester formed will decompose into ketone and the intermediate chromium (IV) will be formed in the second

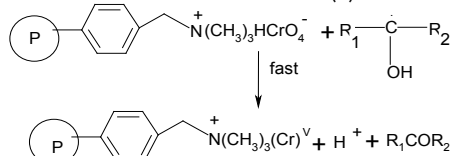
and slow step.



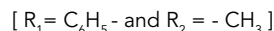
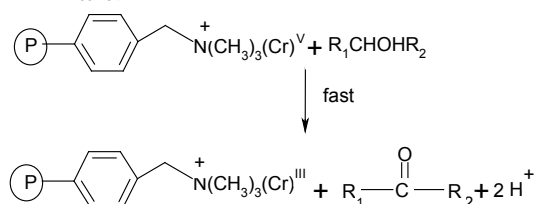
- 3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. The free radical species formation in the reaction was confirmed by the polymerization of added acrylonitrile or addition of acidified methanol into the reaction mixture.



- 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 1-Phenylethanol produce acetophenone. The test for formation of chromium (V) and (IV) by the characteristic induced oxidation of iodide²⁰ and manganese (II)²¹ were not probably due to heterogeneity of the reaction mixture.



Scheme I Conclusion

Based on the former discussion and results we know that 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. Polymer supported oxidizing agent proved to be exclusively selective towards the oxidation of 1-Phenylethanol, giving ketone as the only product.

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 dependence²² with rate constant k of the second slow step in which product ketone was obtained.

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