

Original Article

Development of Green and Polymer-supported Periodates forms of Amberlyst a 26 and Amberlite IRA 904 for oxidation of 1-Phenyl alcohol

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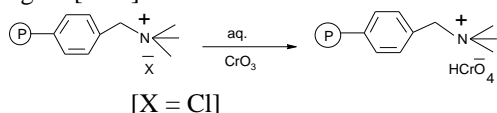
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Abstract - The periodate forms of some commercial macroporous anion-exchange resins can be used in either protic or aprotic solvents to oxidize various quinols, catechols, and glycols and also triphenylphosphine, hydrazobenzene, and benzohydroxamic acid. The reagents in methanol oxidize thioethers. Polymer-supported iodate also oxidizes quinols and catechols. The periodate anion oxidizes various functional groups, but the solubility properties of sodium and potassium periodates are such that these salts can generally be used only in hydroxylic media [1,2]. Reactions can be carried out in aprotic solvents by using periodic acid [3], sodium periodate supported on silica gel [4] or certain lipophilic quaternary ammonium salts [5,6]. We wish to report that the periodate forms of some macroporous anion exchange resins, which can be considered polymer-supported quaternary ammonium periodates, are a practically useful alternative. We have shown that they can be used in various solvents, including aprotic solvents, to oxidize various quinols, catechols, glycols, and triphenylphosphine, hydrazobenzene, and benzohydroxamic acid. Polymer-supported iodate also oxidizes quinols and catechols [7,8]. The periodate forms of Amberlyst A26 and Amberlite IRA 904, two commercial macroporous anion exchange resins, and the iodate form of Amberlyst A 26 were prepared by standard ion-exchange procedures. The dried reagents generally contained 1.2 -1.9 mmol of oxidant per g. The products of reactions with these reagents were isolated simply by filtering off the resin and evaporating the solvent from the filtrate. In many cases, the residue was essentially a pure product. Some reactions produced small amounts of iodine, but this was readily sublimed from the products

Keywords - Periodates, Amberlyst A 26, Amberlite IRA 904, Oxidation.

1. Introduction

Transition metals in the higher oxidation state generally can be stabilized by chelating with a suitable complex agent [9-10]. The kinetics and mechanism of



oxidation of periodates has been well studied. The reaction mechanism of various elementary reactions must be investigated to analyze the factors affecting selectivity. In the present investigation, we now report the oxidation of 1-Phenylethanol by polymer-supported periodate forms of Amberlyst A-26 and Amberlite IRA- 904 are used as an oxidant.

2. Experimental

All the reagents used were of the highest purity available. The aqueous solution of periodate was always prepared afresh and standardized iodometrically.

3. Preparation of Supported Oxidizing Agent

The supported oxidizing agent was prepared by the reported method [11-12]. The periodate forms of Amberlyst A26 and Amberlite IRA 904 containing a

quaternary ammonium group [10×10^{-3} kg] were stirred with a saturated solution of periodates [5×10^{-3} dm³] in water [30×10^{-3} dm³] for 30 min at room temperature using a magnetic stirrer. The periodate ion was readily displaced, and the periodate form of resin was obtained in 40 min. The resin was successively rinsed with water, acetone and THF and finally dried in a vacuum at 323 K for 5h. The dried form of the resin was stored and used throughout the kinetics Polymer supported oxidizing agent

4. Determination of the Capacity of Chromate form of the Polymeric Reagent

The capacity [13] of periodates forms of Amberlyst A 26 and Amberlite IRA 904 polymeric reagents were determined by iodometrically. The capacity of the chromate form of resin was 2.21 and 2.26 eq/L and was used for kinetic study throughout the work. The loading was also determined by elemental nitrogen analysis and was found to be 1.75 and 1.79 eq/L.

5. Chemicals and Reagents

All reagents used were of Analytical Grade, and all solutions were prepared with double distilled water.



6. Method of Kinetics

The reaction mixture [14] for the kinetic run was prepared by mixing alcohol, oxidant and solvent. The reaction was carried out either through constant stirring using a magnetic stirrer or at a constant temperature of 318 ± 1 K. At different time intervals; the reaction mixture was withdrawn using a micropipette. The aliquot thus withdrawn was taken in a stoppered test tube containing $5 \times 10^{-3} \text{ dm}^3$ of 1, 4-dioxane and subjected to spectral analysis. The absorbance of the product formed was measured using SL 159 UV-visible spectrophotometer. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 1 %.

7. Product Analysis

The oxidation of 1-Phenylethanol leads to the formation of acetophenone. The product formed was analyzed by their 2, 4-dinitrophenylhydrazine derivatives. The yield of DNP recrystallization with the DNP of acetophenone was 94%. The product was also identified either by comparison with authentic samples or by UV, FT-IR spectral and elemental analysis. The IR spectra were recorded on a Jasco FT-IR spectrophotometer using KBr pellets.[15]. UV spectrum λ_{max} 246nm. IR data: - A sharp band at 1683 cm^{-1} for $\text{-C}=\text{O}$ stretching mode, 1585 cm^{-1} aromatic ($\text{-C}=\text{C-}$), 3063 cm^{-1} (-C-H stretch) [16].

8. Results and Discussion

8.1. 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 the observed rate constant is fairly constant between 50 to $80 \times 10^{-6} \text{ kg}$ of oxidant at a constant concentration of solvent (1, 4- dioxane, $5 \times 10^{-3} \text{ dm}^3$) and 1-Phenylethanol ($12.3 \times 10^{-3} \text{ mol/dm}^3$), the effect of varying weights of oxidant on zero-order rate constant as shown in Table-1.

8.2. Effect of Varying Concentrations of 1-Phenylethanol

At a varying concentration of 1-Phenylethanol [8.20 to $20.4 \times 10^{-3} \text{ mol/dm}^3$], constant weights 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] were found.

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

Rate constant \rightarrow	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Oxidant $\times 10^{-6} \text{ kg} \rightarrow$	50	60	70	80
Periodate form of Amberlyst A-26	1.75	1.76	1.77	1.79
Periodate form of Amberlite IRA 904	1.59	1.60	1.62	1.63

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

It was found that as the dielectric constant of the medium increased, including $r^* < r$ [Where r^* and r refer to the radii of the reactant species and activated complex, respectively] at a 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 2. Effect of varying concentrations of 1- Phenylethanol

Rate constant	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
1-Phenyl ethanol	$8.20 \times 10^{-3} \text{ mol /dm}^3$	$12.3 \times 10^{-3} \text{ mol /dm}^3$	$16.4 \times 10^{-3} \text{ mol /dm}^3$	$20.4 \times 10^{-3} \text{ mol /dm}^3$
Periodate form of Amberlyst A-26	1.45	1.47	1.53	1.59
Periodate form of Amberlite IRA 904	1.55	1.57	1.59	1.60

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	2.00	2.17	2.28	4.81
Periodate form of Amberlyst A26	1.15	1.29	2.36	2.46
Periodate form of Amberlite IRA 904	1.19	1.21	1.22	1.23

8.4. Effect of Varying Temperature

It was observed that the rate of reaction increased with an increase in the temperature. [Table-4]. The activation parameters like the energy of activation [E_a], enthalpy of activation [ΔH^\ddagger], entropy of activation [ΔS^\ddagger], the free energy of activation [ΔG^\ddagger], the high positive values of free energy of activation indicate that the transition state is highly solvated. The frequency factor [A] was calculated by determining values of k at different temperatures. [Table-5].

Table 4. Effect of varying temperature

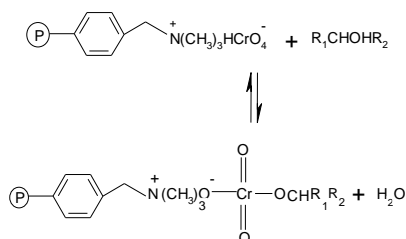
Rate constant	$k \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$			
Temperature K	313	318	323	328
Periodate form of Amberlyst A-26	1.45	1.95	2.14	2.45
Periodate form of Amberlite IRA 904	1.49	1.61	1.94	2.10

Table 5. Activation parameters

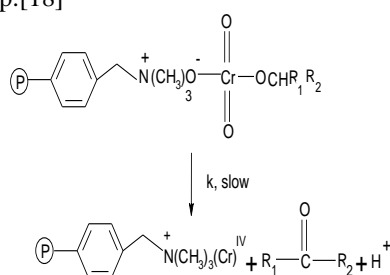
[E_a] KJ mol ⁻¹	75 ± 4	79 ± 4
[ΔH^\ddagger] KJ mol ⁻¹	55 ± 3	59 ± 3
[ΔS^\ddagger] JK mol ⁻¹	-70 ± 2	-74 ± 2
[ΔG^\ddagger] KJ mol ⁻¹	302 ± 2	305 ± 2
[A] X 10^{-5} s^{-1}	3 ± 0.5	4 ± 0.5

The mechanism is suggested in Scheme I and involves ester formation.

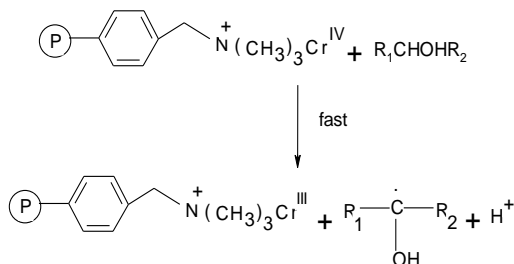
- 1) The polymer-supported reagent reacts with a molecule of alcohol to form a chromate ester. [27]



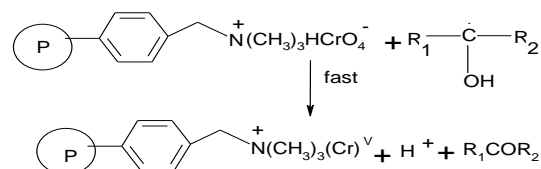
- 2) The ester formed will decompose into ketone, and the intermediate chromium (IV) will be formed in the second and slow step. [18]



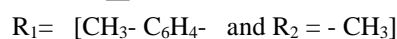
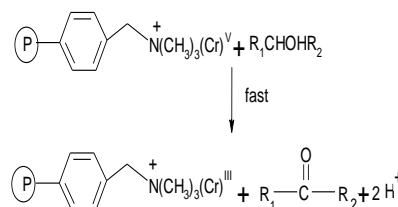
- 3) The intermediate chromium (IV) thus reacts with another alcohol molecule to produce a free radical species. [19]



- 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). [20]



- 5) The intermediate chromium (V) in the last step reacts with 1-Phenylethanol to produce acetophenone. [21]



scheme I

9. Conclusion

- The linearity of absorbance against time plots and the constancy of the zero-order rate constants indicate that neither the reaction depends on the polymeric reagents nor the alcohol concentration. [26]
- Polymer-supported oxidizing agents proved to be exclusively selective. According to Scheme I, a second-order rate law is expected. We obtained zero-order dependence with a rate constant k of the second slow step in which product acetophenone was obtained. Based on the experimental observations, a probable mechanism is suggested. [23-25]

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