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Kinetics and Mechanistic approach to Chromic acid Oxidation by Amberlite 400[Cl^-]

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Abstract:
The kinetics 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 kinetics of oxidation of 4-Bromophenylethanol,4-Cholophenylethanol and 4-Iodophenylethanol with chromic acid supported on anion exchange resins like Amberlite 400 [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 thermodynamic parameters with respect to the first step of the suggested mechanism were evaluated and discussed.

Keywords: *Kinetics, Mechanism, Alcohol, Chromates.*

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I. Introduction

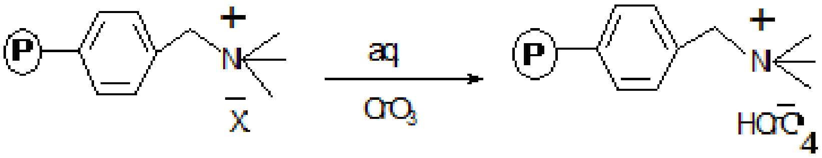
Chromium compounds have been used in aqueous and non-aqueous medium for oxidation of variety of organic compounds. Chromium compounds especially chromium (VI) reagent are capable of oxidizing almost all the oxidative organic functional groups. The development of newer chromium (VI) reagents for the oxidation of organic subtracts continues to be chromium containing compounds like tri/tetra alkyl ammonium halochromates have been used as oxidant for the oxidation of various organic subtracts. Some of the newly alkylammoniumhalochromates like tetraethylammoniabromochomate, tributylammonoiaumchlorochromates, tripropylammoniafluorochromate and triethylammoniumchlorochoromate have been used to study the kinetics of oxidation of various organic compounds[9-12]. In the present investigation, herewith report the oxidation of secondary aromatic alcohols by polymer supported chromic acid on Amberlite 400[Cl^-] It was supported on Chromium VI oxide and it used as an oxidant.

II. Experiment:

Reagent grade Chemicals and doubly distilled water were used throughout the work. All other reagents used were of analytical grade and their solutions were prepared by dissolving requisite amount of the sample in doubly distilled water.

Preparation of supported oxidizing agent

The supported oxidizing agent was prepared by reported method [13-15]. The chloride form of Amberlite 400[Cl^-] [a macro reticular anion exchange resin] congaing 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 $HCrO4^-$ form of resin was obtained in 40 min. The resin was successively rinsed with water, acetone and THF and finally dried in vacuum at 323 K for 5 hrs. The dried form of the resin was stored and used throughout the kinetic study.



[X = Cl$^-$]

Determination of the capacity of chromate form of the polymeric reagent

The capacity of the chromate form of Amberlite 400 [Cl$^-$] polymeric reagent was determined by iodometrically. The capacity of the chromate form of resin was 1.75eq/L and used throughout work. The loading was also determined by elemental nitrogen analysis and was found to be 3.015 eq/L.

Kinetic Measurements

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 k. At different time interval, the reaction mixture was withdrawn using a micropipette. The aliquot thus withdrawn was taken in a stopper test tube containing 5 x 10^{-3} dm^3 of 1,4-dioxane and subjected to spectral analysis. The absorbance of the product formed was measured using Schmadzu 1800 UV- visible spectrophotometer kinetic study.

Product analysis

Melting point of 2,4DNPhydrazone 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

III. Results and Discussion:

Influence 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 ,5x10-^{3}dm^3) and aromatic secondary alcohols (24.6 x 10^{-3} mol/dm^3), the effect of varying weights of oxidant on zero order rate constant as shown in Table-1

Influence of varying concentrations various aromatic secondary alcohols

At a varying concentration of alcohols, constant weight of oxidant [140x10^{-6} kg] constant concentration of solvent [1,4-dioxane,5 x 10^{-3} dm^3] zero order rate constants shown in the Table-2] was found.

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

It is found that as the dielectric constant of 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/dm^3] and constant concentration of oxidant [140 x 10^{-6} kg] solvent [5x 10^{-3} mol/dm^3] as shown in Table -3.

Influence of varying temperature

The reaction was carried out at four different temperatures under otherwise similar reaction condition to study the effect of temperatures on the rate of reaction. It was observed that, the rate of reaction increased with an increase in temperature.[Table-4].The activation parameters like energy of activation[Ea].enthalpy of activation [$\Delta H^{\#}$] , entropy of activation [$\Delta S^{\#}$] free energy of activation [ΔG#]the high positive value of free energy of activation state is highly solved and frequency factor[A] were calculated by determining value of K at different temperature[Table-5]on the bases 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. Influence of varying weights of oxidant on reaction rate at 318K.

Rate constant →	k X 10 $^{-4}$mol dm-^{3}s^{-1}			
Oxidant X 10^{-6} Kg →	100	120	140	160
4-Bromoacetophenone	1.25	1.24	1.25	1.29
4-Chloroacetophenone	1.52	1.55	1.85	1.87
4-Iodoacetophenone	1.98	2.05	2.10	2.12

Table 2. Influence of varying concentration of various aromatic secondary alcohols

Rate constant →	k X 10 $^{-4}$mol dm-^{3}s^{-1}			
Concentration of alcohol →	16.40 x 10^{-3} mol dm^{3}	24.6 x 10^{-3} mol dm^{3}	40.8 x 10^{-3} mol dm^{3}	20.4 x 10^{-3} mol dm^{3}
4-Bromoacetophenone	1.45	1.49	1.50	1.52
4-Chloroacetophenone	1.55	1.59	1.52	1.62
4-Iodoacetophenone	1.68	1.60	1.62	1.65

Table 3. Influence of varying dielectric permittivity

Rate constant →	k X 10 $^{-4}$mol dm-^{3}s^{-1}			
Solvent[5x 10^{-3}dm^{3} →	C_6H_{12}	CCl_4	1,4-dioxane	$CHCl_3$
Dielectric constant	1.98	2.07	2.18	4.11
4-Bromoacetophenone	1.29	1.37	1.40	1.61
4-Chloroacetophenone	1.39	1.42	1.43	1.55
4-Iodoacetophenone	1.45	1.48	1.49	1.55

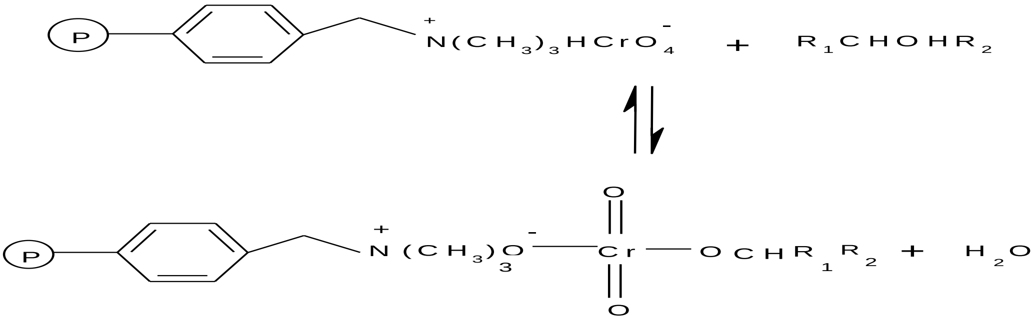
Table 4. Influence of varying temperature

Rate constant →	k X 10 $^{-4}$mol dm-^{3}s^{-1}			
Temperature K →	313	318	323	328
4-Bromoacetophenone	1.55	2.01	2.13	2.28
4-Chloroacetophenone	2.25	2.27	2.30	2.34
4-Iodoacetophenone	2.28	2.31	2.38	2.39

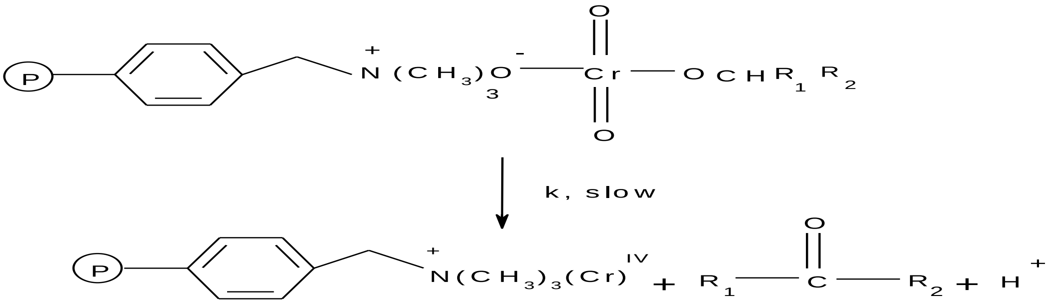
Table 5. Thermodynamic Parameters

Thermodynamics Parameters →	[Ea] KJ Mol-3	$[\Delta H^{\#}]$ KJ Mol-3	$[\Delta S^{\#}]$ KJ Mol-3	$[\Delta G^{\#}]$ KJ Mol-3	[A]X10-3 S^{-1}
4-Bromoacetophenone	73	56	-76	316	4.4
4-Chloroacetophenone	94	77	-89	319	5.8
4-Iodoacetophenone	95	78	-99	322	5.8

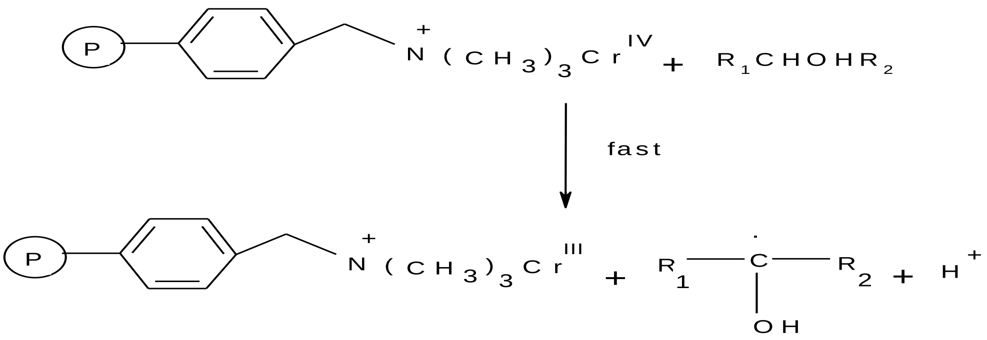
1) The polymer supported reagent reacts with a molecule of alcohol to form a chromate ester.



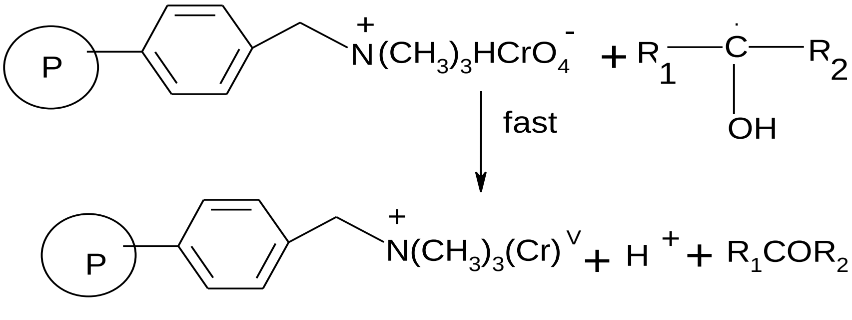
2) The ester formed will decompose into ketone and the intermediate chromium (VI) will be formed in the second step.



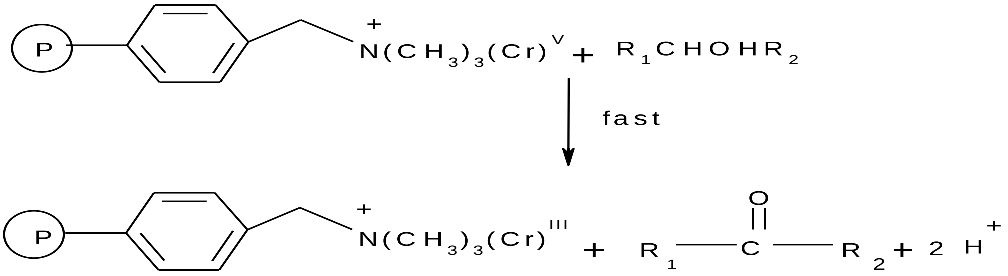
3) The intermediate chromium (VI) thus reacts with another alcohol molecule to produce a free radical species. The free radical species formation in the reaction was confirmed by the polymerization of added acrylonitride or addition of acidified methanol into the mixture.



4) Subsequently the free radical will react with another site in the polymweric 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 iodide and manganese (II) were not probably due to heterogeneity of the reaction mixture. (Step-5)



[R_1= CH_3-C_6H_4- and R_2 = - CH_3]

Step- 5

Scheme- I

IV. Conclusion:

The linearly of absorbance against time plots and constancy of the zero order rate constant 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 product[16].

According to **scheme-1**, 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 obtain 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.

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