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Kinetics of oxidation of α,β-unsaturated alcohols by pyridinium bromo chromate

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ABSTRACT

Oxidation of α,β- unsaturated alcohols (allyl, crotyl and cinnamyl alcohol) by Pyridinium bromochromate has been studied in 50% acetic acid- water (v/v) medium in the presence of perchloric acid at 303 K. The reaction is first order each in [oxidant] , [substrate] and [H^+].Decrease in dielectric constant of the medium increases the rate of the reaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate constant. There is no polymerization with acrylonitrile. The rate of the reaction has been conducted at five different temperatures and activation parameters were calculated. From the observed kinetic results a suitable mechanism with rate data has been proposed. The order of reactivity is Cinnamyl alcohol > Crotyl alcohol > Allyl alcohol.

Key words: Allyl, Crotyl and Cinnamyl alcohol, Oxidation, Kinetics, Pyridinium bromochromate

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INTRODUCTION

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds(1) Chromium especially Cr(VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisible organic functional groups(2-4). Numerous reagents and experimental procedures have been developed to carry out this transformation(5), in particular reagents containing chromium(VI) reactive species are widely used for the oxidation of alcohols to carbonyl compounds(6-7). It is a new mild, efficient and stable reagent which is able to work as oxidizing reagent. Kinetics and mechanism of oxidation of Aniline and substituted Aniline by Isoquinolinium Bromo chromate in aqueous acetic acid was studied(8).The kinetics and mechanism of oxidation of α,β-unsaturated alcohols by various oxidants have been reported.[9-11] However, the kinetics of oxidation of α,β- unsaturated alcohols by Pyridinium bromochromate has not been reported. Moreover, Pyridinium bromochromate is not is hygroscopoticy and also not suffered from photosensitivity. Hence, in the present investigation, the oxidation of α,β- unsaturated alcohols by Pyridinium bromochromate in aqueous acetic acid medium and the corresponding mechanistic aspects are discussed.

EXPERIMENTAL SECTION

E. Merck allyl alcohol was distilled[12]. The fraction at 97-98℃ was collected refluxed with anhydrous potassium carbonate for 30 minutes and distilled twice. The fraction collected at 97℃ was stored over phosphorous pentoxide in a desiccator. E. Merck Crotyl alcohol was distilled. The fraction at 119 - 120℃ was collected dried over anhydrous potassium carbonate and distilled twice. Cinnamyl alcohol was purified by distillation under reduced pressure (b.p 110℃/ 5mm). Pyridinium bromochromate were prepared[13] by literature method. Acetic acid was purified[14] by standard method and the fraction distilling at 118°C was collected. All other chemicals used were of AR grade. The solutions were prepared in triple distilled water.

Kinetic measurements

The reaction was carried out under pseudo-first order conditions [Allyl] >>[IDC] in 50% (v/v) aqueous acetic acid containing perchloric acid. The course of the reaction was followed colorimetrically at 470 nm for upto 80% of the reaction. The pseudo-first order rate constants k_1 computed from the linear plots of log absorbance versus time by the least squares method, were reproducible within ±1%.

Stoichiometry and product analysis

The reaction mixture containing an excess of oxidant over allyl alcohol were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unreacted oxidant showed that one mole of allyl alcohol consumed one mole of the oxidant.

The product acrolein was identified by spot test(15) and IR spectral data.

RESULTS AND DISCUSSION

Oxidation of allyl alcohol by Pyridinium bromochromate has been conducted in 50% acetic acid and 50% water medium at 303 K under pseudo-first order conditions and the observed results were discussed.

The order of the reaction with respect to Pyridinium bromochromate was found to be unity as shown by the linearity of log absorbance against time plots, above 80% percentage of the reaction. (Table I)

At constant concentrations of substrate and perchloric acid, the increase in concentration of Pyridinium bromochromate did not affect the rate of reaction (Table. I) The linear constancy in the value of k_1 irrespective of the concentration of the Pyridinium bromochromate confirms the first order dependence on Pyridinium bromochromate. The varying the concentration of allyl alcohol at 303 K and keeping all other reactant concentration as constant and the rates were measured (Table I). The rate of oxidation increased progressively on increasing the concentration of allyl alcohol, indicating first order dependence with substrate. The plot of log k_{obs} versus log [s] gave the slope of 0.923(r= 0.999), shows that the oxidation reaction was first order with respect to allyl alcohol.

The reaction was followed with different concentrations of perchloric acid and keeping all the concentrations as constant and rate were measured (Table 1). The rate of the reaction increases with the increasing the concentration of $[H^+]$.A plot of log k_1 vs log$[H^+]$ gave a straight line with a slope of 0.899 which indicates first order with respect to Hydrogen ion concentration. The change in ionic strength by the addition of sodium perchlorate has no effect on the rate constant indicating the involvement of a neutral molecule in the rate determining step.

The effect of solvent composition on the reaction rate was studied by varying the concentration of acetic acid 30%-60%. The reaction rate increases with the increase in the proportion of acetic acid in the medium (Table 1) when the acetic acid content increases in the medium, the acidity of the medium is increased where as the dielectric constant of the medium is decreased suggesting ion-dipole interaction(16,17) The clear mixture containing alcohol and Pyridinium bromochromate when allowed to stand with a drop of acrylonitile(18) no turbidity is formed suggesting the non involvement of free radicals in this reaction. On the other hand, the reaction rate decreases with increasing the concentration of Mn^{2+} ions confirming the involvement of two electron process in this reaction (19)

The oxidation of the other structurally related alcohols such as crotyl and cinnamyl alcohol by Pyridinium bromochromate has been studied 50% acetic acid and 50% water medium at 303 K under same pseudo-first order condition. In this case the reaction shows first order depends each on oxidant and substrates.

The rate constants were measured at five different temperature and the activation parameters were computed from a plot of ln k_2/T against 1/T of the Eyring's equation(20).(Table II).A plot of $\Delta H^\#$ against $\Delta S^\#$ (iso-kinetic plot) gives a straight line with a good correlation co-efficient (r=0.999) (21,22).Linear trend between enthalpies ($\Delta H^\#$)and entropy ($\Delta S^\#$)of activation shows that the reaction is controlled by both parameters. This negative value of entropy of activation $\Delta S^\#$ indicates a polar transition state with extensive charge separation which promote high degree of solvation of the transition state compared to the reactants.

The Exner plot also gives a straight line with a good correlation co-efficient of (r=0.999) indicating that all the three alcohols are subjected by oxidation and their mechanism is common.(23) Free energy of activation ($\Delta G^\#$) values are nearly constant. It is also suggests that all the α, β – unsaturated alcohols are oxidized by the same mechanism. The low Energy of activation (Ea) values and enthalpy of activation($\Delta H^\#$)values supports the proposed mechanism.

Table I: Rate constant for the oxidation of Allyl alcohol by Pyridinium bromochromate at 303 K.

[Allyl]× 10^1 (M)	[PBC] ×10^2 (M)	[$HClO_4$]×10^2 (M)	[$NaClO_4$]×10^3 (M)	[ACOH-H_2O] (% v/v)	[$MnSO_4$] ×10^2 (M)	k_{obs} × 10^4 s^{-1}
3.-5	2.5	1.5	-	50	-	4.89-9.22
3.0	2.5-4.0	1.5	-	50	-	4.89-4.60
3.0	2.5	1.5-3.0	-	50	-	4.89-12.58
3.0	2.5	1.5	0-9.3	50	-	4.89-4.25
3.0	2.5	1.5	-	30-60	-	2.90-8.37
3.0	2.5	1.5	-	50	0-9.3	4.89-1.38

Table II Activation parameters for the oxidation of Ally,Crotyl and Cinnamyl alcohol by Pyridinium bromochromate

[PBC] = 2.5× 10^{-2} mol dm^{-3} [$HClO_4$] = 1.5×10^{-2} mol dm^{-3}
[α,β - unsaturated alcohols]= 3.00×10^{-1}mol dm^{-3} 50% Acetic acid 50% water medium

S. No	α,β-unsaturated alcohols	$10^4 k_{obs}$ s^{-1}					$\Delta H^{\#}$ ($kJmol^{-1}$)	$-\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ ($kJmol^{-1}$) at 303 K	Ea ($kJmol^{-1}$) at 303 K
		303 K	313 K	323 K	333 K	343 K				
1.	Allyl alcohol	4.89	8.07	11.21	14.52	17.92	24.93	425.62	93.46	27.45
2.	Crotyl alcohol	7.32	9.60	12.15	15.39	18.86	17.56	937.74	92.44	20.07
3.	Cinnamyl alcohol	13.19	16.78	20.74	24.68	29.21	14.25	1079.7	91.61	16.77

Structure and Reactivity

Due to the presence of mesomeric effect and inductive effect, phenyl group of cinnamyl alcohol increases the rate of the reaction among the alcohols.

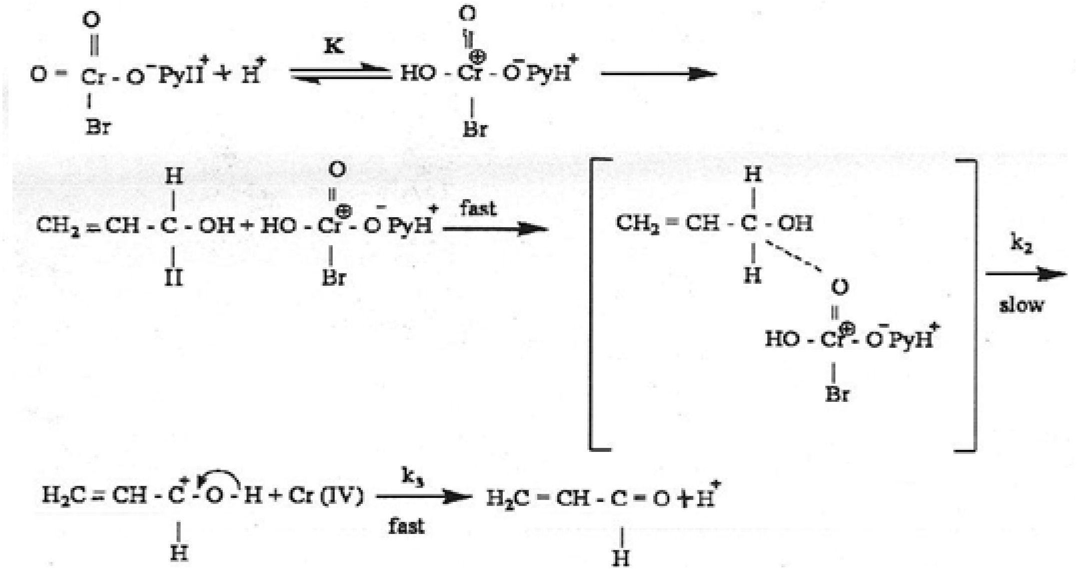
Due to the presence of inductive effect in crotyl alcohol, the rate of the reaction of crotyl alcohol faster than allyl alcohol.

Hence, the order of reactivity has been found to be Cinnamyl alcohol > Crotyl alcohol > Allyl alcohol

Mechanism and Rate law

As the reaction is showing first order dependence on the oxidant and substrate. These two species should be involved in the slow step: The large increase in rate with acidity suggests the involvement of protonated Cr^{6+} species in the rate determining step$^{(24)}$.

Scheme 1



The above mechanism leads to the following rate law

$$\frac{-d[PBC]}{dt} = Kk_2 [\ ALLYL] [PBC] [H^+]$$

$$\frac{d[PBC}{dt} = k_{obs} [ALLYL] [PBC] [H^+]$$

The proposed mechanism and the derived rate law fit well to the experimental observations.

CONCLUSION

The main product of the reaction were found to be acrolein. The reaction is first order each in [substrate], [oxidant] and hydrogen ion concentration. The stoichiometry was found to be one mole of allyl alcohol consuming one mole of Pyridinium bromochromate. The negative values of $\Delta S^{\#}$ provided support for the formation of a rigid activated complex.

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