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Kinetics of oxidation of allyl alcohol by imidazoliumdichromate

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ABSTRACT

The kinetics of oxidation of allyl alcohol by imidazolium dichromate has been studied in 40% acetic acid- water (v/v) medium in the presence of perchloric acid at 313 K. The reaction is first order with respect to [oxidant] and [substrate]. The reaction is acid catalysed one. The 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 reaction has been studied at four different temperatures and the activation parameters were calculated. Acrolein has been identified as the product of oxidation. From the observed kinetic results a suitable mechanism consistent with rate data has been proposed.

Key words: Allyl alcohol, oxidation, kinetics, imidazolium dichromate.

INTRODUCTION

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds [1-3] Chromium especially Cr(VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisible organic functional groups [4-6]. Numerous reagents and experimental procedures have been developed to carry out this transformation [7], in particular reagents containing chromium(VI) reactive species are widely used for the oxidation of alcohols to carbonyl compounds [8,9]. Imidazolium dichromate has been used as on mild selective oxidant in synthetic organic chemistry [10]. The kinetics and mechanism of oxidation of allyl alcohol by various oxidants have been well documented [11-13]. The literature survey reveals that the kinetics and mechanism of oxidation of allyl alcohol by imidazolium dichromate has not been reported. Hence, in the present investigation, the oxidation of allyl alcohol by imidazolium dichromate in aqueous acetic acid medium and the corresponding mechanistic aspects are discussed.

MATERIALS AND METHODS

E. Merck allyl alcohol was distilled [14]. The fraction at 97-98°C was collected refluxed with anhydrous potassium carbonate for 30 minutes and distilled twice. The freaction collected at 97°C was stored over phosphorous pentoxide in a desiccator. Imidazolium dichromate was prepared [15] by literature method. Acetic acid was purified [16] 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 first order conditions [Allyl] >>[IDC] in 40% (v/v) aqueous acetic acid containing perchloric acid. The course of the reaction was followed spectrophotometrically 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 unchanged oxidant showed that one mole of allyl alcohol consumed one mole of the oxidant.

The product acrolein was identified by spot test [17] and IR spectral data. The following stoichiometric reactions obtained from experimental results are given below



Oxidation of allyl alcohol by imidazolium dichromate has been conducted in 40% acetic acid and 60% water medium at 313 K under pseudo-first order conditions and the observed results were discussed.

The order of the reaction with respect to imidazolium dichromate was found to be unity as shown by the linearity of log absorbance against time plot.(Table 1)

$[Allyl] \times 10^3$	$[IDC] \times 10^4$	$[HClO_4] \times 10^3$	[NaClO ₄]×10 ⁴	[ACOH-H ₂ O]	$[MnSO_4] \times 10^4$	$k_{obs} \times 10^4$
(M)	(M)	(M)	(M)	(% v/v)	(M)	s ⁻¹
2.5-12.5	9.0	5.0	-	40	-	6.53-17.75
5.0	6-18	5.0	-	40	-	8.53-8.52
5.0	9.0	2.5-12.5	-	40	-	7.24-23.47
5.0	9.0	5.0	0-7.5	40	-	8.08-8.89
5.0	9.0	5.0	-	30-50	-	6.22-14.30
5.0	9.0	5.0	-	40	0-7.5	8.08-5.23

Table 1. Rate constant for the oxidation of Allylalcohol by IDC at 313K.

The concentration of imidazolium dichromate was varied in the range 6×10^{-4} to 18×10^{-4} mol dm⁻³ and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The linear constancy in the value of k₁ irrespective of the concentration of the imidazolium dihromate confirms the first order dependence on imidazolium dihromate .

The allyl alcohol was varied in the range 2.5×10^{-3} to 12.5×10^{-3} mol dm⁻³ at 313 K and keeping all other reactant concentration as constant and the rates were measured (Table 1). 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 [allyl alcohol] gave a straight line, shows that the oxidation reaction was first order with respect to allyl alcohol.

The perchloric acid concentration was varied in the range of 2.5×10^{-3} to 12.5×10^{-3} mol dm⁻³ and keeping the other concentrations as constant and rate constant were measured (Table 1). The reaction is acid catalyzed one. 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 varying solvent composition on the reaction rate was studied by varying the concentration of acetic acid 30%-50%. The reaction rate increases with the increase in the proportion of acetic acid in the medium (Table 1) is suggesting the involvement of ion-dipole interaction [18 - 20].



The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway [21, 22]. The reaction rate decreases with increasing the concentration of Mn^{2+} ions confirming the involvement of two electron process in this reaction [23].

Effect of varying temperature

The rate constants were measured at four different temperature and the activation parameters were computed from a plot of $\ln k_2/T$ against 1/T of the Eyring's equation [24].

Table 2 Activation parameters for the oxidation of allyl alcohol by Imidazolium dichromate $[IDC] = 9.00 \times 10^{-4} mol dm^{-3}$ $[HClO_4] = 5.00 \times 10^{-3} mol dm^{-3}$

[Allyl alcohol] = 5.00×10^{-3} mol dm ⁻³ 40%Acetic acid 60% water medium											
S. No	Substrate	$10^4 k_{obs}$			s ⁻¹	ΛH #	_^ a#	∆ G [#]	Ea		
		303 K	313 K	323 K	333 K	(kJmol ⁻¹)	$(JK^{-1} \text{ mol}^{-1})$	(kJmol ⁻¹) at 313 K	(kJmol ⁻¹) at 313 K		
1	Allyl alcohol	5.85	8.08	11.58	16.12	25.89	177.71	95.52	28.49		

The negative value of entropy of activation ΔS [#] indicates a polar transition state with extensive charge separation which promote high degree of solvation of the transition state compared to the reactants.

Mechanism and Rate law

The reaction is showing first order dependence on the oxidant and substrate. The large increase in rate with acidity suggests the involvement of protonated Cr^{6+} species in the rate determining step [25]. Thus a mechanism involving hydride ion transfer in the rate determining step can be postulated for the imidazolium dichromate oxidation scheme 1.

The above mechanism leads to the following rate law

$$\frac{-d[IDC]}{dt} = Kk_2 [ALLYL] [IDC]$$
$$\frac{-d[IDC]}{dt} = k_{0bs} [ALLYL] [IDC]$$

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

CONCLUSION

The main product of the reaction were found to be acrolein. The reaction is first order each in substrate and oxidant. The reaction is acid catalysed one. The stoichiometry was found to be one mole of allyl alcohol consuming one mole of imidazolium dichromate. The negative value of $\blacktriangle S^{\#}$ provides a support for the formation of a rigid activated complex.

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