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Oxidation of α, β-Unsaturated Alcohols by Nicotinium Dichromate: A Kinetic Study

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Kinetics of oxidation of α, β-unsaturated alcohols by nicotinium dichromate (NDC), have been studied in 50% acetic acid-water medium. The reaction is first order each in the concentration of oxidant and substrate. Increase in acidity increases the rate of the reaction. Increase in ionic strength has appreciable effect on the reaction rate. The rate of the reaction decreases with increase in the dielectric constant of the medium. The reaction does not induce the polymerization of acrylonitrile. The retardation of the rate by the addition of Mn^{2+} ions confirms that a two electron transfer process is involved in the reaction. The reaction rates have been determined at different temperatures and the activation parameters calculated and a suitable mechanism has been proposed. The order of reactivity is allyl alcohol < crotyl alcohol < cinnamyl alcohol.

Key Words: Kinetics, Oxidation, Unsaturated alcohols, Nicotinium dichromate, Activation parameters.

INTRODUCTION

Recently some neutral Cr(VI) reagents[1, 2] have been developed for effective oxidation under mild conditions. Nicotinium dichromate (NDC) is an effective oxidizing agent to oxidize alcohols into carbonyl compounds[3]. In part of the investigations on the oxidation of allyl alcohol with various oxidants[4, 5] the oxidation of α,β-unsaturated alcohols with NDC has been studied extensively.

EXPERIMENTAL

Nicotinium dichromate was prepared by literature method[3]. All the α,β-unsaturated alcohols such as allyl alcohol, crotyl alcohol and cinnamoyl alcohol (Fluka grade) were used as such. Acetic acid was refluxed over chromium trioxide for 6 h and then fractionated[6]. All other chemicals used were of AR grade. The solutions were prepared in triple distilled water.

The reaction was carried out under pseudo-first order conditions ([Allyl] >> [NDC]) in 50% (v/v) aqueous acetic acid medium. The kinetic measurements were made by estimating the aliquots of reaction mixtures for the oxidant iodometrically using starch as indicator. The rate constants (k_1) evaluated from the linear plot of log [NDC] against time by least-squares method were reproducible within ±2%.

Reaction mixtures containing an excess of the oxidant over α, β-unsaturated alcohol were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unreacted oxidant proved that one mole of oxidant consumed one mole of the substrate.

The product, acrolein, was identified by spot test[7] and IR spectral data.

RESULTS AND DISCUSSION

The order of the reaction with respect to NDC was found to be unity as shown by the linearity of log (a – x) against time plots, over 70% of the reaction. The pseudo-first order rate constants were found to be independent of the initial concentration of NDC. The reaction was found to be first order in substrate as evidenced by the unit slope (r = 0.997) of the plot of log k_1 against log [Allyl]. The second order rate constant k_s (= k_1/[Allyl]) obtained by dividing the pseudo-first order rate constants by the respective substrate concentration were found to be constant indicating the first order dependence on substrate (Table-1).

TABLE-1

EFFECT OF CONCENTRATION OF REACTANTS ON REACTION RATES AT 302 K

$[H^+] = 2.0 \times 10^{-1}$ mol dm^{-3}, 50% acetic acid-water (v/v)

10^3 [Allyl] (mol dm^{-3})	10^3 [NDC] (mol dm^{-3})	10^4 k_1 (s^{-1})
7.5	1.00	2.63
10.0	1.00	3.62
12.5	1.00	4.36
15.0	1.00	5.01
17.5	1.00	6.16
20.0	1.00	7.24
10.0	0.75	3.17
10.0	1.25	3.96
10.0	1.50	3.58
10.0	1.75	3.70

There was no appreciable change in the rate with the change in ionic strength of the medium[8]. At constant concentrations of the reactants the reaction rate increased with increase in the concentration of the hydrogen ion. But the plot of log k_1 against log $[H^+]$ did not give an ideal slope of unity indicating simply the reaction is an acid-catalyzed one[5] (Table-2).

TABLE-2

EFFECT OF VARYING $[H^+]$ AND IONIC STRENGTH ON THE RATE OF OXIDATION AT 302 K

[Allyl] = 10.0×10^{-3} mol dm^{-3}, [NDC] = 1.0×10^{-3} mol dm^{-3}, 50% acetic acid-water (v/v)

10^3 [KNO_3] (mol dm^{-3})	10^4 k_1 (s^{-1})	[$HClO_4$] (mol dm^{-3})	10^4 k_1 (s^{-1})
0.00	3.62	0.15	2.57
0.25	3.56	0.20	3.62
0.50	3.49	0.25	4.67
0.75	3.41	0.30	5.62
1.00	3.37	0.35	6.96

The rate of acid-catalyzed oxidation of allyl alcohol decreases with an increase in the dielectric constant of the medium. A plot of log k_1 against inverse of dielectric constant is linear with a positive slope suggesting an interaction between a positive ion and a dipole. This confirms the involvement of protonated chromium(VI) species in the rate-determining step[9] (Table-3).

TABLE-3
EFFECT OF CONCENTRATION OF SOLVENT ON REACTION RATES AT 302 K IN ACID MEDIA

[Allyl] = 10.0×10^{-3} mol dm^{-3}, [NDC] = 1.0×10^{-3} mol dm^{-3}, [H$^+$] = 2.0×10^{-1} mol dm^{-3}

Acetic acid-water (% v/v)	45	50	55	60	65
Dielectric constant	59.60	56.00	50.80	45.50	42.00
$10^4 k_1$ (s^{-1})	3.16	3.62	4.36	5.65	6.92

The reaction mixture when allowed to stand with acrylonitrile does not induce polymerisation suggesting the absence of free radical mechanism. On the other hand, the addition of Mn^{2+} ions retarded the reaction rate showing the two electron transfer process in the reactions[10] (Table-4).

TABLE-4
EFFECT OF CONCENTRATION OF MANGANESE SULFATE ON REACTION RATES AT 302 K

[Allyl] = 10.0×10^{-3} mol dm^{-3}, [NDC] = 1.0×10^{-3} mol dm^{-3}, [H$^+$] = 2.0×10^{-1} mol dm^{-3}, 50% acetic acid-water (v/v).

10^4 [MnSO$_4$] (mol dm^{-3})	0.00	2.50	5.00	7.50	10.00
$10^4 k_1$ (s^{-1})	3.62	1.25	1.18	1.09	1.02

The rate constants were measured at four different temperatures and the activation parameters have been determined. In this case, the third order rate constant should be evaluated as $k_t = k_1/[\text{Allyl}][H^+]$ and then Eyring's plot of log (k_t/T) against 1/T by the least-squares method (Table-5).

TABLE-5
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE OXIDATION OF α, β-UNSATURATED ALCOHOLS WITH NDC

Substrate	$k_1\ 10^4$ (s^{-1})				$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J K^{-1}mol^{-1})
	302 K	309 K	316 K	323 K		
Allyl	3.62	4.20	4.57	5.11	4.70	186.46
Crotyl	9.58	10.26	10.98	12.02	3.03	206.91
Cinnamyl	28.90	30.98	33.94	37.16	2.58	212.40

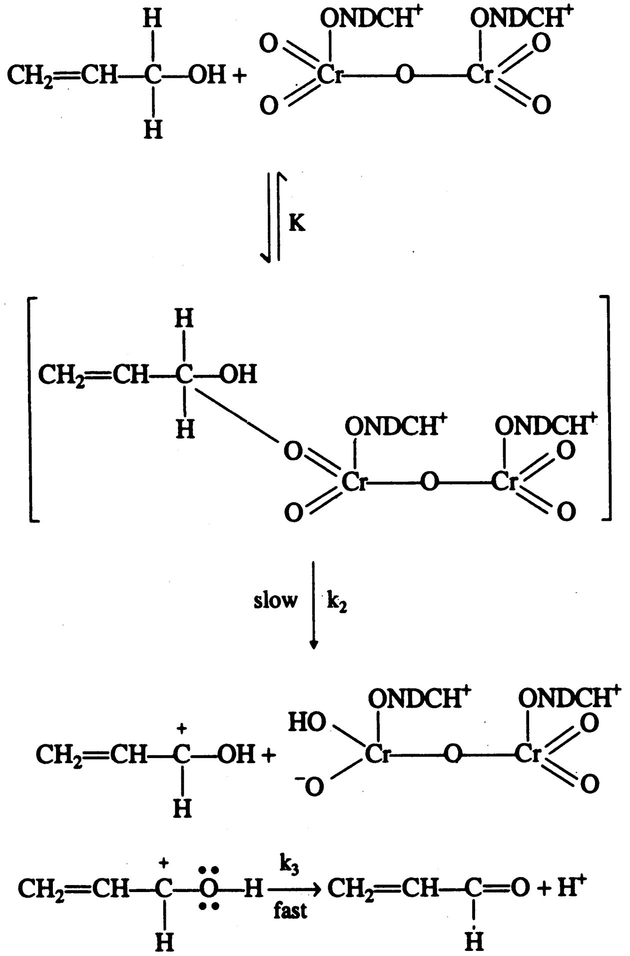
A plot of $\Delta H^{\#}$ against $\Delta S^{\#}$ (isokinetic plot) gave a straight line with a very fine correlation coefficient[11]. The Exner plot also gave a straight line with a very fine correlation coefficient indicating that all the α, β-unsaturated alcohols are undergoing oxidation by a common mechanism[12].

The enthalpy of activation $\Delta H^{\#}$ values are very low suggesting a concerted mechanism as proposed[13]. The entropies of activation $\Delta S^{\#}$ are all negative indicating extensive solvation of the transition state over the reactants.

The rate of oxidation of cinnamyl alcohol is much faster compared to other unsaturated alcohols, because the phenyl group is present.

Mechanism and rate law

It is clear that reaction is first order dependence on oxidant and substrate. The large increase in rate with acidity suggests the involvement of a protonated oxidizing species in the rate determining step. Thus a mechanism involving hydride ion transfer[14] in the rate determining step can be postulated for the NDC oxidation of allyl alcohol.



The above mechanism leads to the following rate law,

$$-\frac{d[NDC]}{dt} = Kk_2[Allyl][NDC][H^+]$$

$$-\frac{d[NDC]}{dt} = k_{obs}[Allyl][NDC][H^+]$$

This rate law explains all the observed experimental facts.

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