



Research Article

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Kinetics and Mechanism of Oxidation of Anthranyl Styryl Ketone by Nicotinium Dichromate in aqueous acetic acid media

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ABSTRACT

The kinetics of the oxidation of anthranyl styryl ketone (ASK) by nicotinium dichromate (NDC), in aqueous acid media in the presence of oxalic acid has been investigated. The reaction shows first order dependence with respect to [NDC] and $[H^+]$. The order with respect to both substrate and oxalic acid is found to be fractional. Activation parameters have been evaluated and a suitable mechanism has been proposed.

Keywords: Kinetics, oxidation, Mechanism, Chalcoess, ASK, NDC.

INTRODUCTION

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds[1-5]. Chromium especially Cr(VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisable organic functional groups. Nicotinium dichromate (NDC) a complex of Nicotinic acid & chromium trioxide is reported to be more versatile oxidant [6-10]. Nicotinium dichromate has been used as on mild selective oxidant in synthetic organic chemistry[11-18]. Now, we report the kinetics and mechanism of oxidation of Anthranyl Styryl Ketone by NDC in 70% aqueous acetic acid media.

EXPERIMENTAL SECTION

Materials

All chemicals used were of 'AnalaR' grade (Fluka). Triply distilled water was used for the preparation of solutions. NDC is prepared by improved method of Corey & Suggs [19] described by Agarwal. Acetic acid was purified by standard method and the fraction distilling at $118^{\circ}C$ was collected. Chalcone [20] were prepared and purified by literature method. NDC solution was prepared by dissolving the known amount of this compound in water and standardized iodometrically using starch as indicator.

Kinetic measurement

The reaction was carried out under pseudo-first order conditions by maintaining a large excess of chalcone over Cr(VI). The mixture was homogeneous throughout the course of the reaction. The reaction was followed titrimetrically. The rate constants were evaluated from log (titre) versus time plots.

Stoichiometry and product analysis

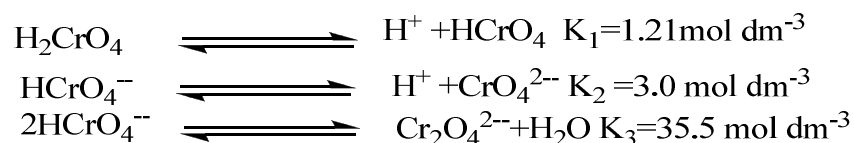
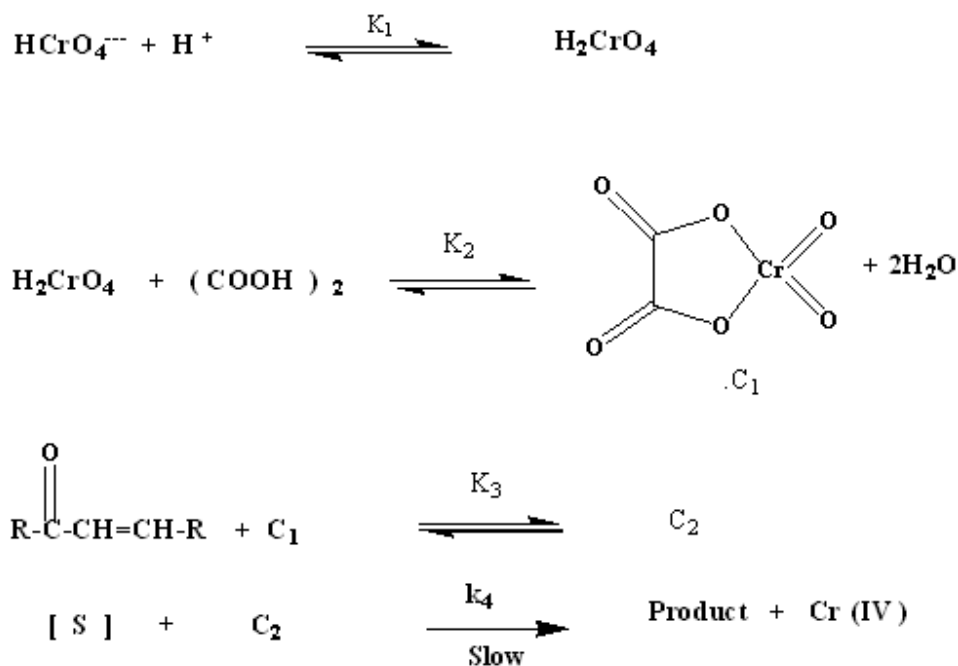
Reaction mixture containing an excess of NDC over ASK were kept at room temperature in the presence of perchloric acid for 24 hrs. Estimation of the unchanged oxidant showed that one mole of ASK consumed one mole of the NDC. The product epoxide was identified by IR spectra.

RESULTS AND DISCUSSION

At fixed $[H^+]$ with [substrate] in excess, the plot of $\log(\text{titre})$ against time was linear, indicating first order in NDC (Fig-1). The pseudo-first order rate constants were independent of the initial concentration of the oxidant (Table-1). From the observation it is clear that the reaction is showing first order dependence with respect to NDC and $[H^+]$. The order with respect to [substrate] and [oxalic] is found to be fractional (Fig-2 & 3).

The oxidation by Cr(VI) will vary with nature of Cr(VI) species used and solvent will play an important role on the rate of the reaction. In aqueous solution and in the absence of other ion the following equilibrium are existing [21] (Scheme -1). Here the dimerisation equilibrium is of considerable importance. In water the dichromate ion will be predominating species only when the concentration of Cr(VI) is greater than about 0.05 mol dm^{-3} . In this case, as the concentration of Cr(VI) is less than 0.05 mol dm^{-3} monomeric form predominates and the active oxidising species is HCrO_4^- . The reaction is acid catalysed one.

The rate increases with decrease in the dielectric constant of the medium and increase in the ionic strength has negligible effect on the rate. The reaction did not induce polymerisation of acrylonitrile indicating the absence of free radical path way (Table-2). The addition of Mn^{2+} and Al^{3+} has a noticeable catalytic effect. Based on the above observations, a suitable mechanism has been proposed (Scheme-2).

SCHEME-1**SCHEME-2**

Rate law

$$\text{Rate} = \frac{K_1 K_2 K_3 k_4 [\text{NDC}] [\text{H}^+] [\text{ASK}] [\text{Oxalic}]}{\frac{\{1+K_3[\text{ASK}]\} \{1+K_2[\text{oxalic}]\}}{K_1 K_2 K_3 k_4 \text{Cr(VI)} [\text{H}^+] [\text{ASK}] [\text{Oxalic}]}} = \frac{K_1 K_2 K_3 k_4 [\text{H}^+] [\text{ASK}] [\text{Oxalic}]}{\{1+K_3[\text{ASK}]\} \{1+K_2[\text{oxalic}]\}}$$

It is important to mention here that no investigation on oxidation of anthranyl styryl ketone(ASK) by protonated NDC which shows clearly on the mechanism of the reaction, is available in literature so far. Moreover, the system investigated by Awasthy and Rock [22] contains double bond to which are attached a number of activating alkyl groups. But the I system under consideration are chalcones which contain olefinic double bond to which strong deactivating carbonyl group attached whose polarization creates positive charge at the double bond. Under such circumstance only a mechanism involving nucleophilic attachment is probable with the formation transition state (C₂) leading to an intermediate.

Table-1

[ASK] x10 ³ mol dm ⁻³	[NDC] x10 ⁴ mol dm ⁻³	[H ⁺] x 10 mol dm ⁻³	[Oxalic] x10 ² mol dm ⁻³	[NaClO ₄]x10 ⁴ mol dm ⁻³	CH ₃ COOH- H ₂ O (% v/v)	k ₁ (10 ⁴ s ⁻¹)
0.50	1.00	2.00	5.00	-	70-30	3.16
1.00	1.00	2.00	5.00	-	70-30	5.44
1.50	1.00	2.00	5.00	-	70-30	6.87
2.00	1.00	2.00	5.00	-	70-30	8.45
1.00	0.50	2.00	5.00	-	70-30	5.98
1.00	1.00	2.00	5.00	-	70-30	5.44
1.00	1.50	2.00	5.00	-	70-30	5.26
1.00	2.00	2.00	5.00	-	70-30	5.28
1.00	1.00	1.00	5.00	-	70-30	3.43
1.00	1.00	1.50	5.00	-	70-30	4.89
1.00	1.00	2.00	5.00	-	70-30	5.44
1.00	1.00	3.00	5.00	-	70-30	12.48
1.00	1.00	2.00	0.50	-	70-30	3.02
1.00	1.00	2.00	1.00	-	70-30	4.38
1.00	1.00	2.00	1.50	-	70-30	5.22
1.00	1.00	2.00	2.00	-	70-30	5.44
1.00	1.00	2.00	5.00	2.50	70-30	2.39
1.00	1.00	2.00	5.00	5.00	70-30	2.39
1.00	1.00	2.00	5.00	7.50	70-30	2.41
1.00	1.00	2.00	5.00	10.00	70-30	2.41
1.00	1.00	2.00	5.00	-	55-45	3.48
1.00	1.00	2.00	5.00	-	60-40	4.58
1.00	1.00	2.00	5.00	-	70-30	5.44
1.00	1.00	2.00	5.00	-	75-25	17.24

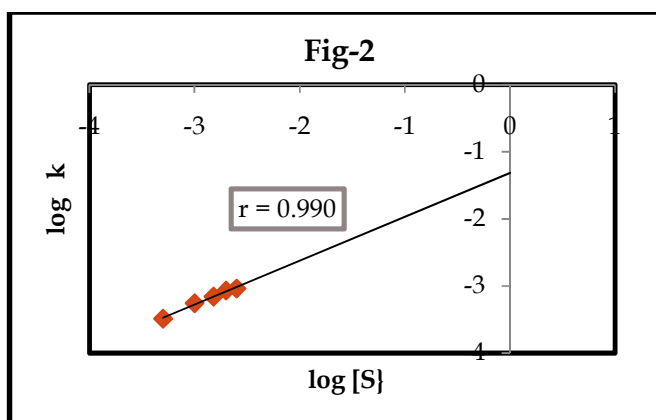
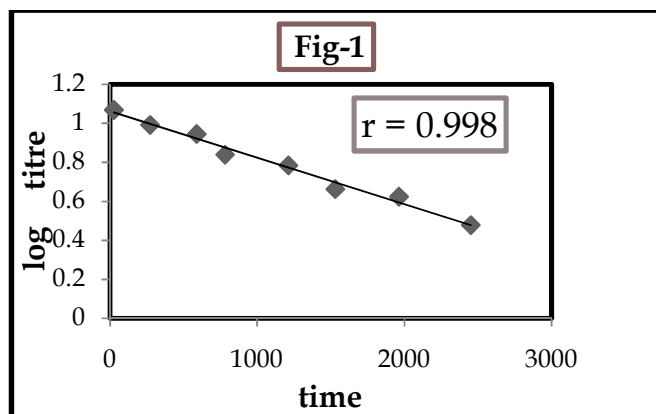
Table-2 [ASK]= 1.0×10^{-3} mol dm⁻³, [H⁺]= 2.0×10 mol dm⁻³, [NDC]= 1.0×10^{-4} mol dm⁻³, [oxalic]= 1.0×10^{-2} mol dm⁻³ Temperature:303K , Solvent:70% H₂O-CH₃COOH(v/v)

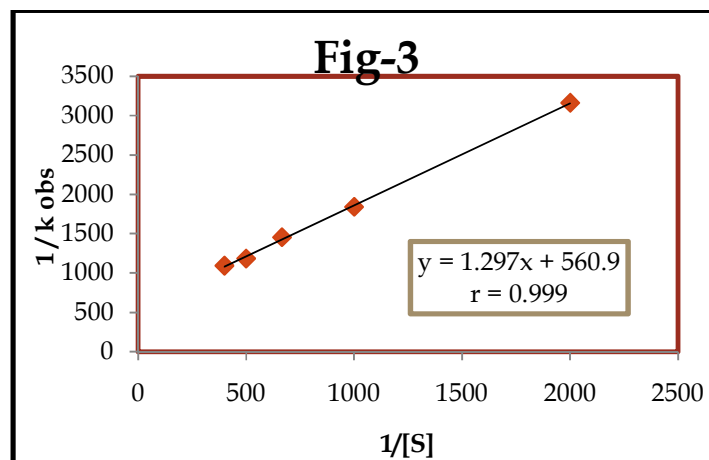
[Mn ²⁺] (10 ⁴ M) mol dm ⁻³	[Al ³⁺] (10 ⁴ M) mol dm ⁻³	[Acrylonitrile] (10 ⁴ M) mol dm ⁻³	k ₁ s ⁻¹
2.50	-	-	4.43
5.00	-	-	5.49
7.50	-	-	5.99
10.00	-	-	6.22
-	2.50	-	5.38
-	5.00	-	3.95
-	7.50	-	3.18
-	10.00	-	3.11
-	-	2.50	4.41
-	-	5.00	5.38
-	-	7.50	4.43
-	-	10.00	4.44

Effect of Temperature: The thermodynamic parameters were calculated using the Eyring's plot and the values are given in the Table 3. This negative value of entropy of activation ΔS^\ddagger indicates a polar transition state with an extensive charge separation which promotes high degree of solvation of the transition state compared to the reactants

Table-3 [ASK]= 1.0×10^{-3} mol dm⁻³, [H⁺]= 2.0×10 mol dm⁻³, [NDC]= 1.0×10^{-4} mol dm⁻³, [oxalic]= 1.0×10^{-2} mol dm⁻³ , Solvent:70% H₂O-CH₃COOH(v/v)

Substrate	298K k ₁ × 10 ⁴ s ⁻¹	303K k ₁ × 10 ⁴ s ⁻¹	308K k ₁ × 10 ⁴ s ⁻¹	ΔG^\ddagger kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger KJ mol ⁻¹
ASK	4.29	5.44	8.60	93.20	33.60	-196.79





CONCLUSION

The main product of the reaction were found to be epoxide. The reaction is first order each in $[H^+]$ and [oxidant] and fractional order with respect to [substrate] and [oxalic]. The stoichiometry was found to be one mole of chalcone consuming one mole of NDC. The negative values of ΔS^\ddagger provided support for the formation of a rigid activated complex. The proposed mechanism and the derived rate law fit well to the experimental observation.

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