Kinetics and mechanism of oxidation of 2-naphthol by nicotiniumdichromate

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ABSTRACT

The kinetics of oxidation of 2.Naphthol by Nicotinium dichromate has been studied in 50% acetic acid- water (v/v) medium in the presence of perchloric acid at 303K. The reaction is first order each in [oxidant], [substrate] and independent of hydrogen ion concentration $[H^+]$ and dielectric constant of the medium. Increase in Ionic strength by the addition of $NaClO_4$ has no effect on the rate constant. There is no polymerization with acrylonitrile. The reaction has been conducted at five different temperatures and activation parameters were calculated. The corresponding 1,2 Naphthoquinone 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: 2-Naphthol, oxidation, kinetics, Nicotinium dichromate, Mechanism.

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). One of these chromium (VI) reagents in NDC $(C_6H_6O_2N)_2^+ Cr_2O_7^{2-}$ which has emerged as a very useful and verstatile oxidant deserving wide spread applications(8). LFER study of the oxidation of organic sulphide with NDC (9) and Oxidation of some para, meta substituted benzaldehyde by NDC (10) were studied. Nicotinium dichromate has been used as on mild selective oxidant in synthetic organic chemistry. The kinetics and Mechanism of oxidation of 2.Naphthol by various oxidants have reported. However, the Kinetics of oxidation of 2.Naphthol by Nicotinium dichromate has not been reported.

EXPERIMENTAL SECTION

Methods and materials

2-Naphthol were purified by literature method. The oxidant Nicotinium dichromate was prepared and melting point was verified. Acetic acid was purified by standard method and the fraction distilling at 118°c was collected. All other chemicals used were of AR grade.

Kinetic Measurements:

The reaction was carried out under first order conditions [2.Naphthol] $\gg$ [NDC] in 50% (v/v) aqueous acetic acid containing perchloric acid. The course of the reaction was followed colorimetrically and the rate constants K_1 computed from the linear plots of log absorbance versus time by the least square method, were reproducible within $\pm 1\%$.

Stoichiometry and product analysis

Reaction mixture containing an excess of oxidant over 2.Naphthol were kept at room temperature in the presence of perchloric acid for 24 hr. Estimation of the unchanged oxidant showed that three mole of 2.Naphthol consumed four Mole of the oxidant. The product 1,2 Naphthoquinone was identified by IR spectra. The oxidation species Cr(VI) was observed to be reduced to Cr(III) which was identified using aluminium chloride.

RESULTS AND DISCUSSION

Oxidation of 2.Naphthol by NDC has been conducted in 50% acetic acid and 50% water medium at 303K under pseudo-first order conditions and the observed results were discussed in the subsequent pages.

The order of the reaction with respect to NDC was found to be unity as shown by the linearity of log absorbance against time plots, all the reaction were followed above 80% percentage. (Table 1)

Table 1. Rate constant for the oxidation of 2-naphthol by NDC at 303K

[2.Naphthol]x 10^2 (M)	[NDC]x 10^3 (M)	[HClO$_4$]x10^2 (M)	[NaClO$_4$]x10^4 (M)	[ACOH-H$_2$O] % v/v	K_{obs} x 10^4 s^{-1}
3--5	2.0	0.75	--	50	4.99--8.89
3.0	2--3.5	0.75	--	50	4.99--4.21
3.0	2.0	0.75--1.5	--	50	4.99--4.77
3.0	2.0	0.75	0--7.5	50	4.99--4.38
3.0	2.0	0.75	--	30--60	3.99--5.03

The concentration of NDC was varied in the range 2×10^{-3} to 3.5×10^{-3} 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 K_1 irrespective of the concentration of the NDC confirms the first order dependence on NDC.

The Substrate 2.Naphthol was varied in the range 3×10^{-2} to 5×10^{-2} Mol dm^{-3} at 303K 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 2.Naphthol, indicating first order dependence with substrate. The plot of log K_{obs} versus log[2.Naph] gave the slope of 1.1 (r= 0.998) figure, shows that the oxidation reaction was first order with respect to [2.Naph].

The perchloric acid concentration was varied in the range of 0.75×10^{-2} to 1.5×10^{-2} Mol dm^{-3} and keeping the concentrations as constant and rate were measured (Table 1). The increase in [HClO$_4$] in the oxidation reaction that there is no increases the rate of the reaction and shows a zero order dependence on [HClO$_4$].

Change in ionic strength by the addition of NaClO$_4$ has no effect on the rate constant indicating the involvement of a neutral molecule in the rate determining step and no salt effect on the rate of the reaction.

To know the effect of dielectric constant on the rate of the reaction, the reactions were studied at different composition of aqueous acetic acid keeping other factors were constant and the rate constants were determined. This data indicates that dielectric constant of the medium does not influence the rate of oxidation significantly and indicating that it may be a dipole dipole type of reaction.

The clear mixture containing 2.Naphthol and NDC when allowed to stand with a drop of acrylonitrile, no turbidity is formed suggesting the non involvement of free radical in this reaction.

Effect of Temperature:
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.

Table 2: Activation parameters for the oxidation of 2.Naphthol by Nicotiniumdichromate

SNo	Substrate	$10^4 K_{obs}$ S^{-1}					$\Delta H^{\#}$ (KJMol^{-1})	$-\Delta S^{\#}$ (JK^{-1} Mol^{-1})	$\Delta G^{\#}$ (KJMol^{-1}) At 303 K	Ea (KJMol^{-1}) At 303K
		303k	308k	313k	318k	323k				
1.	2.Naphthol	4.99	5.62	6.60	7.24	8.31	17.848	540.085	93.41	20.367

This negative valve of entropy of activation $\Delta S^{\#}$ indicates a polar transition state with an extensive charge separation which promotes high degree of solvation of the transition state compared to the reactants.

Scheme I

(N$_m$ = Nicotinium)
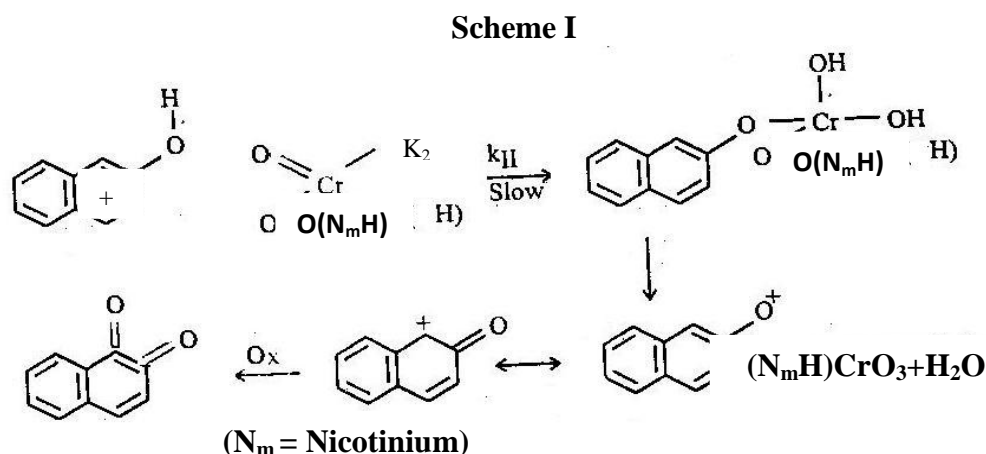
Mechanism:
Taking all these observations into consideration the possible scheme of oxidation can be written as shown in Scheme-1

From the study of solvent effect on rate of oxidation it is assumed that $H(N_mH)CrO_4$ is the active species in the present study. This interacts with the –OH of the Naphthol in the slow step to the formation of 1,2 Naphthoquinone as shown.

The above mechanism leads to the following rate law

$$\frac{-d(NDC)}{dt} = K_2\ [\ 2.\text{Naphthol}]\ [NDC]$$

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 1,2Naphthoquilone. The reaction is first order each in [substrate] [oxidant] and zero order with respect to [H^+]. The stoichiometry was found to be three mole of 2.Naphthol consuming four mole of NDC. The negative values of $\Delta S^{\#}$ provided support for the formation of a rigid activated complex.

A Mechanism in terms of active species of oxidant is proposed and the rate law is derived and verified.

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