

# OXIDATION OF FURFURAL BY NICOTINIUM DICHROMATE

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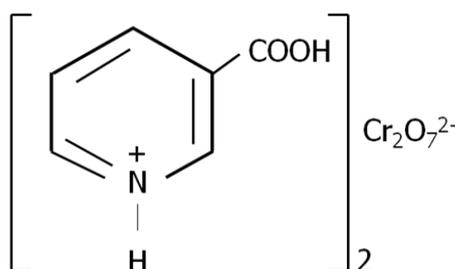
## ABSTRACT:

**The kinetics of oxidation of furfural with nicotinium dichromate (NDC) has been studied in aqueous acetic acid medium. The product of oxidation was found to be furoic acid. The reaction obeys first order with respect to oxidant and substrate and hydrogen ion concentration. There is no effect on the addition of sodium perchlorate. There is no possibility of free radical mechanism since there is no polymerization of acrylonitrile. Increase in the concentration of manganous sulphate retards the reaction rate which confirms the two electrons transfer involved in the mechanism. From the kinetic data, thermodynamic and activation parameters have been calculated and plausible mechanism has been proposed.**

**Keywords: Kinetics, oxidation, nicotinium dichromate, furfural**

## I.INTRODUCTION

**Nicotinium dichromate (NDC), one of the Cr (VI) reagent, is reported to be a neutral, stable, non-hygroscopic, mild, efficient and selective oxidant in synthetic organic chemistry[1].**



**Fig. 1. Structure of Nicotinium Dichromate**

**Kinetics of oxidation of some organic substrates [1-8]by nicotinium dichromate has already been reported. A survey into the literature on the kinetics of oxidation of**

furfural with various oxidant shows that the reactivity varies with the type of oxidant [9-10]. The present work on the oxidation of furfural by NDC is to ascertain the nature and the order of reactivity of these compounds under the given kinetic conditions.

## II. MATERIALS AND METHODS

**Materials:** The furfural was purchased from Sigma-Aldrich chemicals, NDC was prepared by the literature method [1] and its purity was checked by estimating Cr (VI) iodometrically. Acetic acid (AnalaR) was refluxed over  $\text{CrO}_3$  and distilled. All other chemicals used were AnalaR grade. The reaction mixture was homogeneous throughout the course of the reaction.

**Kinetic Measurements:** All the reactions were carried out in black coated vessels to avoid the possible photochemical reactions if any. The kinetic measurements were carried out using digital spectrometer (ELICO CL 23 MINI SPEC)  $\lambda_{\text{max}}$  at 470nm. All kinetic runs were made in aqueous acetic acid 30% (v/v) under pseudo-first order conditions by keeping the substrate always in excess over that of oxidant. The rate constants were evaluated from the linear plot of log absorbance against time by the least square method. The results were reproducible within  $\pm 3\%$  error.

**Product Analysis:** The reaction mixture containing an excess of the oxidant over furfural were kept at room temperature for sufficient time under the conditions employed for the kinetic runs. Estimation of unchanged oxidant showed that one mole of oxidant reacts with one mole of furfural. After 70% completion of the actual kinetic runs, reaction mixture was ether extracted, ether was evaporated and the residue was analyzed by thin layer chromatography, and its melting point. Furoic acid was found to be the product formed in the reaction[11].

## III. RESULT AND DISCUSSION

### *Oxidation of Furfural:*

The detailed kinetic data on the oxidation of the representative furfural is given.

**Effect of oxidant:** The oxidation of furfural by NDC was investigated at several concentrations of the oxidant [NDC], [substrate] and temperature; the plot of log absorbance *versus* time (Fig. 1) was linear indicating first order dependence of the reaction on [NDC]. The value of first order rate constant  $k_1$  (Table 1) was evaluated from the plots, according to the first order equation by the method of least squares.

**Effect of substrate:** The rate of reaction was increased steadily on increasing the concentration of the substrate as shown. The linear plot of  $\log k_1$  versus  $\log [s]$  with a slope (1.03) of unity, it clearly indicates that the reaction has unit order dependence on the concentration of the furfural.

**Effect of  $H^+$  ion:** The effect of added  $H^+$  ion on the pseudo-first order rate constant was studied by adding  $HClO_4$  in the region of 0.15 - 0.75  $\text{mol dm}^{-3}$ . The rate of reaction increased with increase the concentration of  $HClO_4$ . The plot of  $\log k$  against  $\log[H^+]$  (Fig. 2) give a straight line with unit slope 1.08 indicating that first order with respect to  $H^+$  ion concentration.

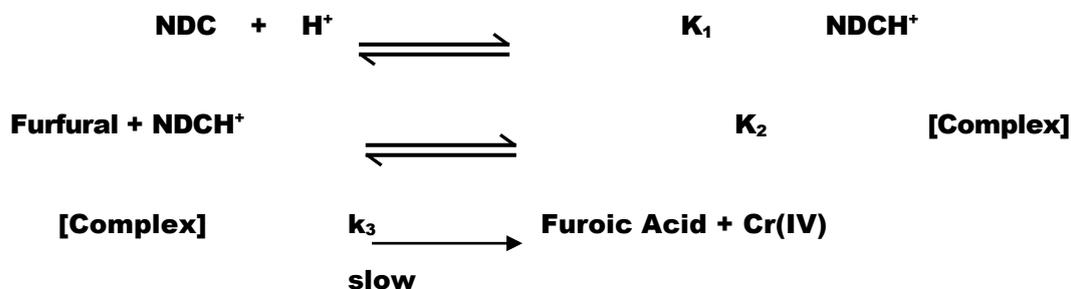
**Effect of solvent & Ionic strength:** The effect of variation of solvent composition on the pseudo-first order rate constant was also studied. The rate was found to increase when the percent content of acetic acid increases. The data in Table 2 shows that the influence of ionic strength on rate constant is not significant.

The reaction mixture showing the absence of any free radical in the reaction has ruled out the possibility of a one electron transfer during the addition of acrylonitrile. But, the rate of reaction increased with the increase in the percentage of acetic acid. The plot of  $\log k_1$  versus  $1/D$  (Fig.4) was found to be linear with a positive slope. This might be probably due to ion-dipole interaction [12-14] in the rate determining step.

**Effect of Temperature:** The reactions were studied in the temperature range 303 K-333 K for the furfural (Fig. 5). An increase in temperature had resulted in an increase in the rate of the reaction. The thermodynamic and activation parameters have been calculated using the Eyring's plot [15-16] and the least square analysis.

**Mechanism:** The furfural was oxidized by nicotinium dichromate; it was catalyzed by perchloric acid. The reaction shows first order with respect to oxidant, substrate and hydrogen ion concentration. The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical path way. But, the study on the effect of  $Mn(II)$  suggested that, the rate controlling process was produced tetravalent chromium, involving a two electron change.

In this case, the concentration of chromium (VI) is very much lower. Under this condition the active oxidizing species is  $\text{HCrO}_4^-$  [17]. Product analysis clearly indicates that the furoic acid. From these observations, the following mechanism (Scheme 1) and rate law were proposed.



**Rate law:**

$$\begin{aligned}
 \text{Rate} &= k_3 [\text{Complex}] \\
 &= k_3 K_2 [\text{Furfural}] [\text{NDCH}^+] \\
 &= k_3 K_2 K_1 [\text{Furfural}] [\text{NDC}] [\text{H}^+] \\
 -d[\text{NDC}] / dt &= k_{\text{obs}} [\text{Oxidant}] [\text{Furfural}] [\text{H}^+]
 \end{aligned}$$

The proposed mechanism and the suitable rate law support all the observations made including the effect of solvent polarity and the negative entropy of activation.

#### IV. CONCLUSION

The kinetics of oxidation of furfural with nicotinium dichromate in 30% of aqueous acetic acid medium has been studied at 313 K. The reaction obeys first order with respect to oxidant and substrate and hydrogen ion concentration. There is no possibility of free radical mechanism since there is no polymerization of acrylonitrile. Increase in the concentration of manganoussulphate retards the reaction rate which confirms the two electrons transfer involved in the mechanism. A suitable mechanism has been proposed on the basis of experimental facts and a suitable rate law was derived. The oxidation product of the reaction was corresponding furoic acid. The thermodynamic and activation parameters were calculated using Eyring's equation.

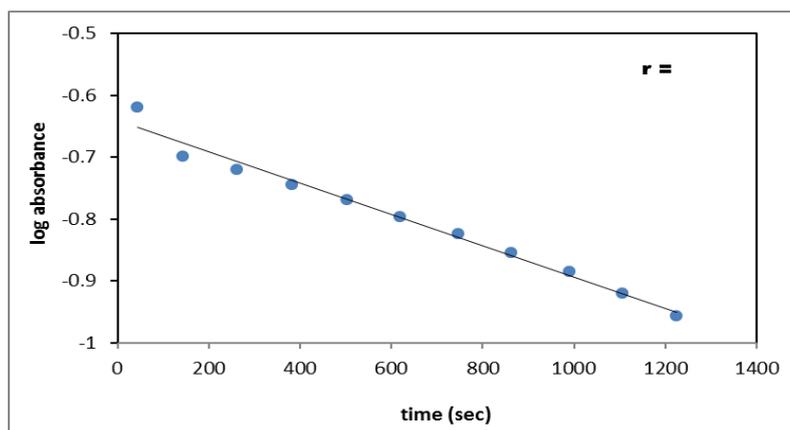
**Table 1. Rate data on the oxidation of furfural by NDC at 313 K**

[NDC] x 10 <sup>3</sup> mol dm <sup>-3</sup>	[Fur] x 10 <sup>2</sup> mol dm <sup>-3</sup>	[HClO <sub>4</sub> ] x 10 <sup>1</sup> mol dm <sup>-3</sup>	AcOH:H <sub>2</sub> O	k <sub>1</sub> x 10 <sup>4</sup> s <sup>-1</sup>
1.0 – 5.0	5.0	3.0	30:70	5.84 – 5.81
2.0	4.0 – 8.0	3.0	30:70	4.68 – 9.51
2.0	5.0	1.5 – 7.5	30:70	3.01 – 17.02
2.0	5.0	3.0	30:70 – 45:55	5.84 – 13.22

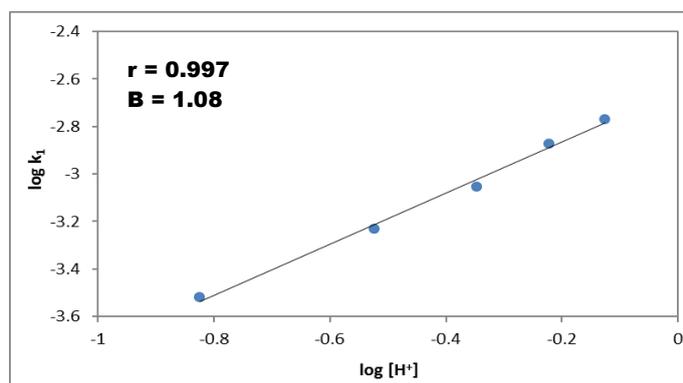
**Table 2. Rate data on the oxidation of furfural by NDC**

Temperature K	[NaClO <sub>4</sub> ] x 10 <sup>1</sup> mol dm <sup>-3</sup>	[MnSO <sub>4</sub> ] x 10 <sup>3</sup> mol dm <sup>-3</sup>	k <sub>1</sub> x 10 <sup>4</sup> s <sup>-1</sup>
303 - 333	-	-	4.12 – 12.02
313	0.00 – 20.2	-	5.87 – 5.79
313	-	0.00 – 4.08	5.87 – 3.74

[NDC] = 2.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> [Fur] = 5.0 x 10<sup>-2</sup> mol dm<sup>-3</sup> [HClO<sub>4</sub>] = 3.0 x 10<sup>-1</sup> mol dm<sup>-3</sup>



**Fig. 2. Plot of log absorbance versus time**



**Fig. 3. Plot of log k<sub>1</sub> versus log [H<sup>+</sup>]**

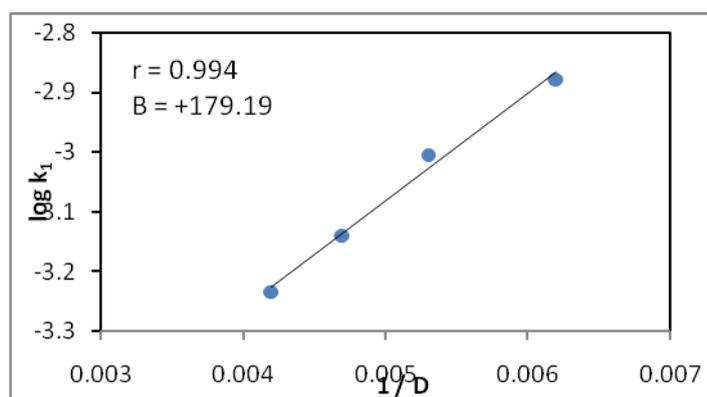


Fig. 4. Plot of  $\log k_1$  versus  $1/D$

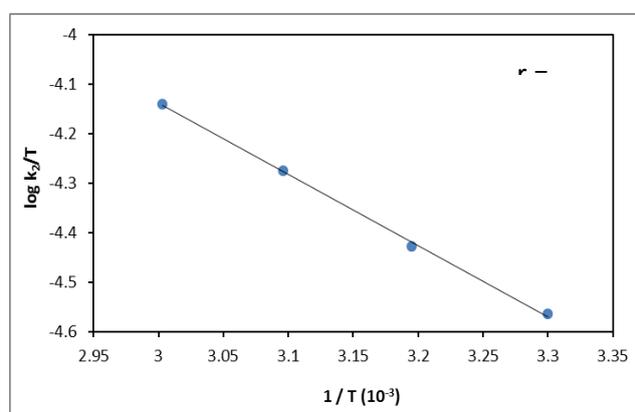


Fig. 5. Plot of  $\log k_2/T$  versus  $1/T$

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