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## **Research Articles**

## OXIDATION OF ACETOPHENONE BY NICOTINIUM DICHROMATE Munauwar Ali<sup>1</sup>, Nagmani Manikpuri<sup>2</sup>

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#### Abstract

The kinetic data for the oxidation of acetophenone by Nicotinium dichromate in 20% aqueous acetic acid containing mineral acid at constant ionic strength is reported. The conducted study shows first-order kinetics with respect to concentration of oxidant and  $H^+$ , where as (-dc/ dt) rate varies as 1 to 0 power of [acetophenone]. The reaction shows retarding effect with rise of percentage composition of acetic acid. A reaction mechanism with stoichiometric ratio 1:3 for the substrate with active species  $H_2CrO_4$  has been postulated.

Key words: Acetophenone, Nicotinium dichromate, stoichiometry oxidation, phenylglyoxal.

#### **1. INTRODUCTION**

Nicotinium dichromate (NDC) a heterocyclic base is alkaline salt of Cr(VI) showed an excellent results in acidic medium in the oxidative study of phenol<sup>1</sup>, ketones,<sup>2</sup> cyclic ketones,<sup>3</sup> anilines,<sup>4</sup> active methylene compounds<sup>5</sup> and hydroxy acids.<sup>6,7</sup> NDC furnishes H<sub>2</sub>CrO<sub>4</sub>, HCrO<sub>4</sub>, and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> types of species but in presence of acid the oxidant has shown stable results since then H<sub>2</sub>CrO<sub>4</sub> ought to be assumed as a prime reacting species of oxidant.

The tautomerism exhibited by ketones due to > C=O group facilitate variety of reactions regarded as a back bone of organic chemistry. Considering the enolic form of the acetophenone, practically no kinetic study is documented with respect to the oxidation of acetophenone with NDC, hence authors report the results of above undertaken kinetic investigation.

#### 2. EXPERIMENTAL

The solvent used in all of the experiments was purified by double distillation method. The solution of commercial sample of acetophenone (Fluka A.G.) used in the study was prepared in acetic acid (B.D.H.). The oxidizing agent NDC was obtained by precipitation from  $CrO_3$  and dissolved in distilled water followed by addition of nicotinic acid to it. The solution of NDC was prepared in 100% acetic acid (B.D.H.). It was stored in the dark and was standardized with 2% KI solution followed by addition of 10 ml  $2NH_2SO_4$  and liberated iodine was estimated iodometrically.

## KINETIC MEASUREMENT

Kinetic experiments were all carried out in presence of  $H_2SO_4$ . The kinetic of reaction was monitored under pseudo first-order condition [substrate] >> [oxidant] by mixing appropriate quantity of substrate to the solution of NDC containing acetic acid maintained at constant temperature in thermostat. The unconsumed amount of NDC was determined by means of an iodometric technique. The pseudo first-order rate constant were obtained from the slopes of log a/ (a-x) or log (a-x) vs. time plots by integration and graphical methods.

## **3. RESULTS AND DISCUSSION**

Oxidative kinetic study has been comprehensively performed under the experimental conditions had the following kinetic features.

## Determination of partial order of the reagents

3.1 The dependence of rate expressed as NDC consumption on the acetophenone is determined at five-initial concentration of NDC. The investigation shows that the reaction is first-order with respect to oxidant NDC.

3.2 It is evident from the accompanying (Fig.1) which is plot of  $k^{-1}$  vs. inverse of concentration acetophenone (Table 1) that the order varies with respect to acetophenone from 1 to 0 at its higher concentration. It yields positive intercept on the Y- axis which led to Michaelis-menten kinetics and showing evidence for the formation of intermediate complex between enolic ketone and H<sub>2</sub>CrO<sub>4</sub> reacting species of oxidant NDC in rate determining step.

 Table 1 : Rate constant for the oxidation of acetophenone by Nicotinium

 dichromate in aqueous acetic acid in presence of mineral acid

 $[NDC] = 2.0 \times 10^{-3} \text{ (mol dm}^{-3}); \ [H^+] = 2.50 \times 10^{-3} \text{ (mol dm}^{-3});$ 

HOAc-H<sub>2</sub>O = 20 % (v/v) ; Temp. = 323 K

S. No.	$\frac{10^2 \times [Acetophenone]}{(mol dm^{-3})}$	$10^4 \times k \ (s^{-1})$
1.	1.25	2.53
2.	2.00	3.63
3.	2.50	4.16
4.	3.33	4.87
5.	4.00	5.36
6.	5.00	5.54



3.3 The kinetic study was performed by the successive addition of varying concentrations (0.80 to  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>) of H<sup>+</sup> ion (Table 2) on the reaction. The first-order rate was evaluated from the unit slope value for the log k vs. log [H<sup>+</sup>] linear plot (Fig.2). It is concluded that NDC led reaction of aetophenone is acid catalysed.

 Table 2 : Dependence of rate constant on the concentration of acid for the oxidation of acetophenone by Nicotinium dichromate containing acetic acid

 $[Acetophenone] = 2.0 \times 10^{-3} \text{ (mol dm}^{-3}); \text{ [NDC]} = 2.0 \times 10^{-3} \text{ (mol dm}^{-3});$ 

HOAc-H<sub>2</sub>O = 20 % (v/v) ; Temp. = 323 K

 $10^{3} \times [H_{2}SO_{4}]$ 10<sup>4</sup> k S. No.  $3 + \log$  $4 + \log k$  $(s^{-1})$  $(\text{mol dm}^{-3})$  $[H_2SO_4]$ k 1000 k = [H<sub>2</sub>SO₄] ℓ mol<sup>-1</sup> (s<sup>-1</sup>) 0.80 1.42 -0.0969 0.1522 1.77 1. 2. 1.50 2.19 0.1760 0.3404 1.46 2.00 3.05 0.3010 0.4842 1.52 3. 4. 2.50 3.63 0.3979 0.5599 1.45 0.5224 5. 3.33 4.94 0.6937 1.48 5.83 4.00 0.6020 0.7656 1.45 6.





0.20

0.20

0.60

0.80

3.4 The varying addition of the percentage composition of  $CH_3COOH-H_2O$  binary mixture (10% to 40% v/v) shows retarding effect on rate, suggested that ion-ion dipole participate in the reaction kinetic. Similar observation was also noticed by Nayak *et al.*<sup>8</sup> No substantial change was observed in the rate of oxidation by the addition of varying concentration of neutral salt (NaCl) at pre set condition.

The study completely failed to induce polymerisation<sup>9</sup> of acrylonitrile (monomer) rulesout the free radical based operative mechanism in the reaction.

3.5 The stoichiometric of the reaction has been determined by equilibrating the reaction mixture containing excess of NDC over acetophenone in varying ratio at  $50^{0}$  C for two days. The estimation of results indicated that one mole of NDC was consumed in oxidizing three moles of acetophenone according to stoichiometric reaction.

$$(\emptyset H)_2 \operatorname{Cr}_2 O_7 + 3 \bigcirc C - CH_3 \longrightarrow 2 \operatorname{Cr} + 2 \emptyset + 3 \bigcirc C - CHO + 4 \operatorname{H}_2 O$$

where  $\phi = nicotinic acid$ 

Phenyl glyoxal was identified as oxidation product of acetophenone which was confirmed by physical, chemical and spectroscopic methods. The kinetic evidence has shown  $H_2CrO_4$  as a active species of oxidant NDC. In the preset condition, the reaction is acid catalysed, proceeded by protonation of carbonyl group and de-protonation of carbonyl conjugate acid. The enolization of acetophenone was carried out by bromination method under comparable condition. The rate of enolisation was found much faster than the rate of oxidation by NDC. Hence the enol content was considered as a reacting species of substrate acetophenone.

#### Mechanism

Considering the kinetics results, the scheme of acetophenone- NDC reaction is postulated as follows : -



**Deduction of Rate law** 

NDC + HOH 
$$\leftarrow K_1 \sim 2 H_2 CrO_4 + 2 \text{ Nicotinic acid} \dots (1)$$

$$E + H_2 CrO_4 \quad \underbrace{ \overset{\kappa_2}{\longleftarrow} \quad complex (c) \quad \dots \dots (2)$$

complex 
$$\xrightarrow{k}$$
 Product ..... (3)

Obtaining the values of [NDC],  $[H_2CrO_4]$  and complex from equations (1), (2), and (3) and substituting in equation (4) we get the equation (5) on simplification.

$$k_{obs} = \frac{k K_1 K_2 [E] [H]^{\dagger}}{[\text{Nicotinic acid}] K_1 + K_1 [H^+] + K_1 K_2 [E] + [H^+]} \qquad \dots \dots (5)$$

$$K_1 \text{ is } << K_2 \qquad \dots \dots (6)$$

Then the quantity written in denominator [Nicotinic acid]  $K_1 + K_1 [H^+] < K_1 K_2$ [E] + [H<sup>+</sup>] can be neglected in comparison to  $K_1 K_2 [E] + [H^+]$ 

Hence 
$$k_{obs} = k$$
 .....(7)

The main evidence obtained when equation (5) is brought in the inverse form

$$\frac{1}{k_{obs}} = \frac{[\text{Nicotinic acid}] K_1 + K_1 [H^+] + K_1 K_2 [E] + [H^+]}{k K_1 K_2 [E] [H^+]} \qquad \dots \dots (8)$$

This equation provides basic evidence for the formation of activated complex at transition state, when a plot is made between  $1/k_{obs}$  vs. 1/ [substrate] which yielded positive intercept on Y-axis.

The thermodynamic parameters were also evaluated for the reactions under probe. The similar pattern of mechanism has also been reported in the oxidation of organic compounds containing active methylene group<sup>10</sup> by NDC which support our proposed mechanism. The reaction was found to enthalpy controlled.

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