



Nicotinium Dichromate Oxidation of Para-nitroacetophenone

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ABSTRACT: The kinetic study of Nicotinium dichromate oxidation of P-nitro acetophenone in 20 % (v/v) acetic acid in presence of H₂SO₄ is carried out. The probe helped in assigning the first-order rate each in [NDC] and [H⁺] and fractional-order with respect to [P-nitroacetophenone]. The solvent polarity of the medium slowed down the rate of reaction. The dissociation of existed complex occurs in the rate of measuring step as discussed in mechanism.

Keywords: Kinetics, p-nitroacetophenone, oxidation, thermodynamic parameters, Nicotinium dichromate.

I. INTRODUCTION

The toxic Cr(VI) compounds are deduced into environmentally eco-friendly and non-toxic ones by using Nicotinium dichromate (NDC). NDC is a Cr(V) complex of heterocyclic base, acting as a mild selective oxidant used in synthetic organic chemistry, [1-3] and oxidative degradation of hydroxy acids [15] ketones, [6] active methylene compounds [14], phenols [5] etc. Para-nitroacetophenone has earlier been readily studied by several oxidants such as KMnO₄ [12] SeO₂, [8] CAT, [13] H₂CrO₄, [11] etc. Para-nitro acetophenone contain carbonyl group, thus exhibiting possibility of enolisation. However, no kinetic probe involving para-nitro acetophenone with NDC has been reported so far. Although analogous related reactions have been studied as the results presented in this paper indicate that in aqueous acetic acid solvent contrasts in several ways.[10] Hence, we thought it worthwhile to study the above task of kinetics.

II. MATERIALS AND METHODS

The substrate's (Sigma A.G.) and yellow orange solid NDC [4] solutions were made in acetic acid (B.D.H.). Other miscellaneous solutions of the reagents were

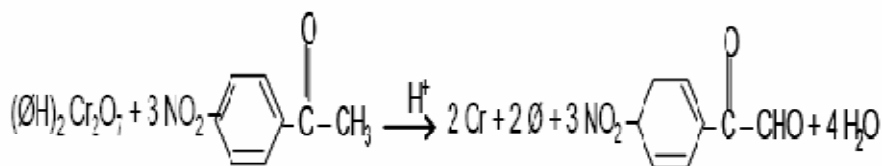
prepared in doubly distilled water and used in standardized form.

Kinetic Measurement: All the kinetic experiments were designed under pseudo first-order condition. The solutions of appropriate concentrations of oxidant (NDC) and ketone were separately and thermally equilibrated for an hour to attain the experimental temperature. The reaction was initiated by mixing two solutions, and progress of reaction was monitored by estimating the unused NDC at regular intervals of time iodometrically [7].

III. RESULTS AND DISCUSSION

(a) The stoichiometric analysis of reactions indicated that three moles of Para-nitro acetophenone was consumed for one mole of oxidant (NDC) as shown in equation.

(b) The resultant product p-nitro phenyl glyoxal was identified by physical and chemical methods and also by forming DNP derivative [9]. The rate of reaction was found to be linear, plot of log (a-x) vs. time showing first-order kinetic with respect to concentration of NDC.



Where O = Nicotinic acid

(c) The kinetic feature of the oxidation for p-nitro acetophenone under the pre-set conditions was observed of the fractional-order dependence with respect to concentration of substrate (Table 1) showing curvature for the plot k vs. [substrate] (Fig. 1). The second-order rate constant for the oxidation of substrate

does not show constancy. The study indicates the existence of complex with an electron rich transition state. This observation is quite at variance in the present case. It appears that the reaction takes place though cationic centre.

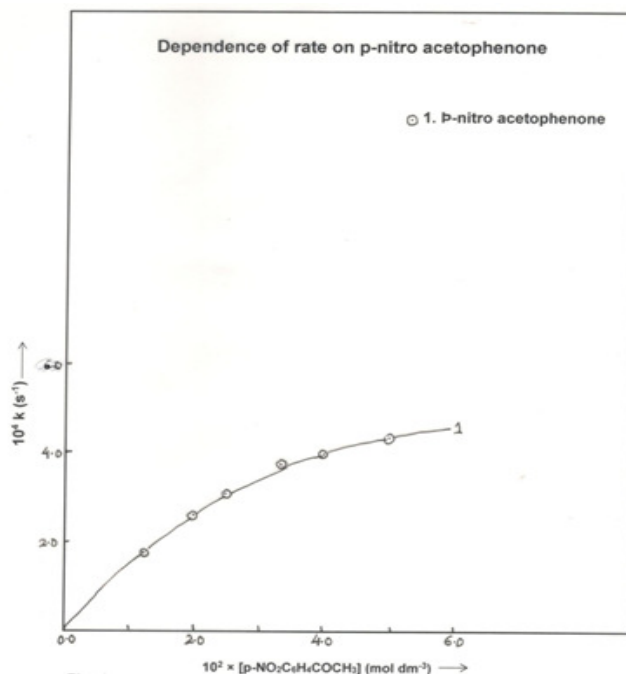


Fig. 1. Plot of log k vs log [p-nitro acetophenone] [NDC] = 2.0×10^{-3} (mol dm⁻³); [H⁺] = 3.33×10^{-3} (mol dm⁻³); HOAc-H₂O 20 % (v/v); Temp = 323 K.

Table 1: Rate of constant for the oxidation of P-nitroacetophenone- Nicotinium dichromate in aqueous acetic acid in presence of mineral acid [NDC] = 2.0×10^{-3} (mol dm⁻³); [H⁺] = 3.33×10^{-3} (mol dm⁻³); HOAc- H₂O = 20 % (v/v); Temp = 323 K.

Sr. No.	$10^2 \times [\text{p-nitro acetophenone}]$ (mol dm ⁻³)	$10^4 k$ (S ⁻¹)
1.	1.25	1.81
2.	2.00	2.62
3.	2.50	3.10
4.	3.33	3.82
5.	4.00	4.05
6.	5.00	4.31

(d) The results showing Table 2 indicate that the reaction is subject to acid catalysis, where acid catalysis could logically occur consistently the rates of reaction was determined in H₂SO₄ as depicted in Fig. 2 (Plot of log k vs. log [H⁺]). The plot is linear with unit slope

intercepting y-axis, showing that nucleophilicity and reactivity are related. The study also shows the possibility is that protonation of p-nitro acetophenone would greatly reduce the energy required to achieve the enol like transition state occur in equation (1).

Table 2: Dependence of rate constants on the concentration of acid for the oxidation of P-nitroacetophenone by Nicotinium dichromate containing acetic acid [NDC] = 2.0×10^{-3} (mol dm⁻³); [P-nitro acetophenone] = 2.0×10^{-2} (mol dm⁻³); HOAc-H₂O = 20 % (v/v); Temperature = 323 K.

Sr. No.	$10^3 \times [\text{H}_2\text{SO}_4]$ (mol dm ⁻³)	$10^4 k$ (S ⁻¹)
1.	1.00	1.29
2.	2.00	2.15
3.	2.50	2.44
4.	3.33	3.10
5.	4.00	3.78
6.	5.00	4.65

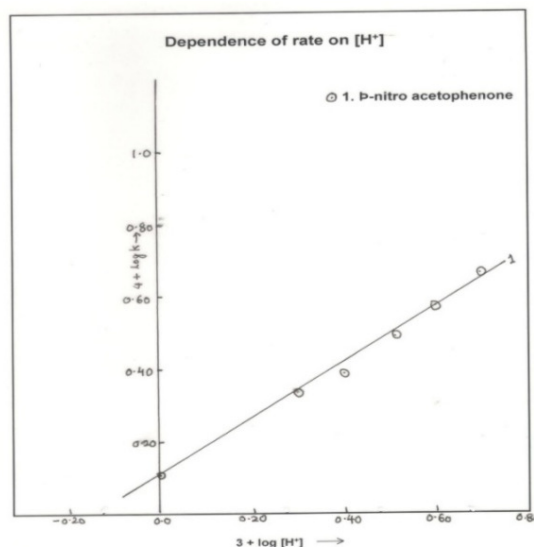
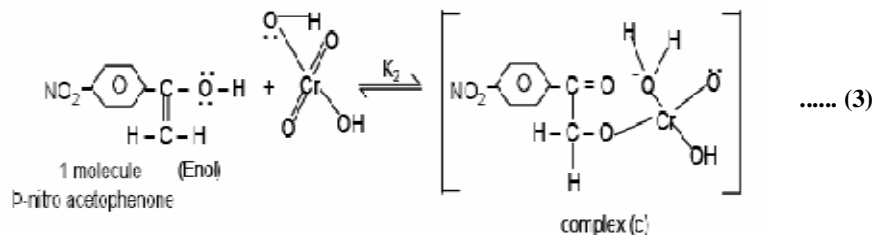
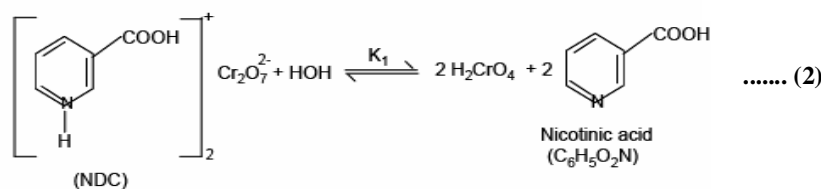
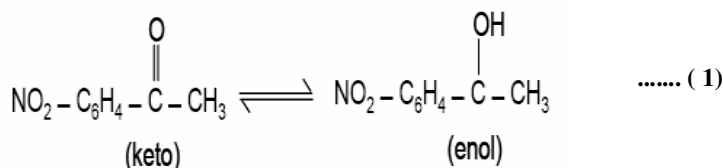


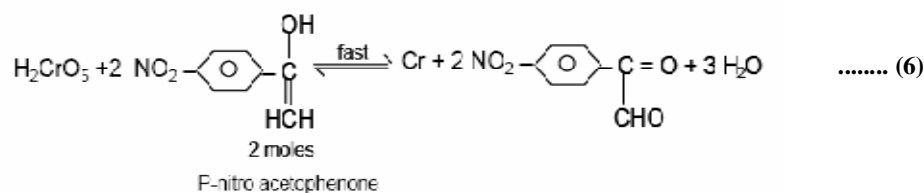
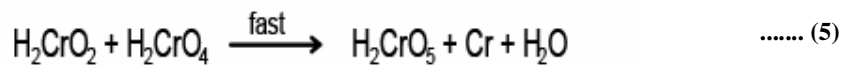
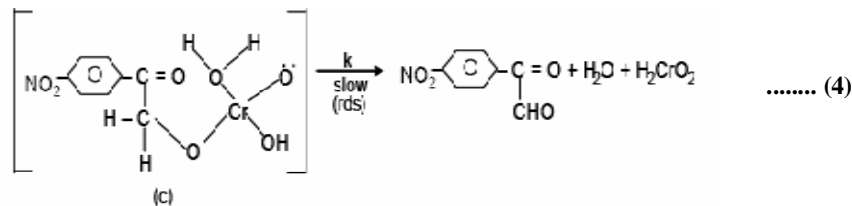
Fig. 2. Plot of $\log k$ vs $\log [H^+]$ $[NDC] = 2.0 \times 10^{-3}$ (mol dm⁻³); $[p\text{-nitro acetophenone}] = 2.0 \times 10^{-3}$ (mol dm⁻³); HOAc-H₂O 20 % (v/v); Temp = 323 K.

(e) The necessary condition for the facile oxidation of aromatic ketone in aqueous acetic acid is observed. The rate of oxidation retards gradually by increasing percentage of acetic acid (10 to 60 %) (v/v). The added neutral salt such as NaCl does not bring about any

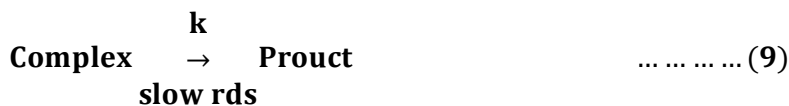
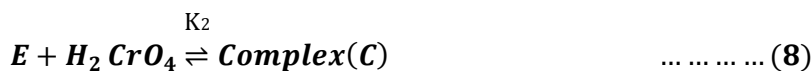
change in rate, thus ruling out the suppression in rate due to salt effect.

Mechanism: On the basis of the kinetic results, the following scanty mechanism is proposed





Rate Law:



$$\text{Rate of Reaction} = k [\text{Complex (c)}] \quad \text{..... (10)}$$

Applying steady state approximation to get k_{obs} as :

$$k_{\text{obs}} = \frac{kK_1K_2 [\text{E}][\text{H}^+]}{[\text{Nicotinic Acid}] K_1 + K_1 [\text{H}^+] K_1 K_2 [\text{E}] + [\text{H}^+]} \quad \text{..... (11)}$$

Since

$$K_1 \text{ is } \ll K_2 \quad \text{..... (12)}$$

Then the quantity written in denominator $[\text{Nicotinic acid}] K_1 + K_1 [\text{H}^+] < K_1 K_2 [\text{E}] + [\text{H}^+]$ give rise as

$$k_{\text{obs}} = k \quad \text{..... (13)}$$

The main concept of complex kinetics may be verified when equation (5) is brought in reciprocal form as:

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{Nicotinic Acid}] K_1 + K_1 [\text{H}^+] + K_1 K_2 [\text{E}] + [\text{H}^+]}{k K_1 K_2 [\text{E}] [\text{H}^+]} \quad \text{..... (14)}$$

When double reciprocal plot is drawn between $1/k_{\text{obs}}$ versus $1/[\text{p-nitro acetophenone}]$ yielded positive slope on Y-axis furnishes evidence for existence of complex.

It may be pertinent to remark that the mechanism which involves deficient cationic centre transition state is fully responsible for the fission of C-H bond, due to -I (inductive effect) and mesomeric effect shown by -NO₂ group.

The value of Arrhenius parameters have been determined. The rate law is well in accordance with kinetic findings.

CONCLUSION

The oxidation of para-nitro acetophenone by nicotinium dichromate in acidic medium has been carried out (CH₃COOH) while mineral acid was added to reaction mixture to adjust the pH of the reaction mixture. The reaction commenced by mixing appropriate molar concentrations of oxidant (NDC) and ketonic substrate and a substantive quantitative relationship suggested that for each mole of oxidant three moles of substrate were consumed and also substantiated by following the kinetic course of reaction probed by iodometric method, which indicated that reaction progressed on with a first-order rate each in [NDC] and [H⁺] and fractional-order with respect to [p-nitroacetophenone].

The polarity of the solvent had a marked effect on the rate as it got somehow decelerated. The mechanistic profile of the reaction also suggested that the oxidation of concerned ketone occurs via a formation of transition state complex which was corroborated by double reciprocal plot between $1/k_{\text{obs}}$ versus $1/[\text{p-nitro acetophenone}]$ yielded positive slope on Y-axis. It is germane to remark that the mechanism which involves scarce positive centre transition state is copiously responsible for the splitting of C-H linkage, due to -I (inductive effect) and mesomeric effect displayed by -NO₂ moiety. Thermodynamic parameters have been determined and rate law is well in accordance with kinetic course of reaction.

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Conflict of Interest. The authors declare no conflict of interest.

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