Prediction of Rate Constants for Oxidation of 3-alkanones by Nicotinium dichromate in Aqueous Acetic Acid Medium

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***Abstract*—Reaction rate constants for oxidation of 3-alkanones (3-pentanone and 3-hexanone) by nicotiniumdichromate (NDC) were measured at 308 K in aqueous acetic acid medium. The derived order each with respect to NDC and acid was found unity whereas a fractional-order kinetics is exhibited by 3-alkanones. The reaction was proceeded through 2:3 intermediate complex formed between protonated oxidant and enolic ketone in the pre-equilibrium state and subsequently deprotonation of >C-H bond at rate-determining step. The termination of reaction with acrylonitrile does not occur with free radicals. The thermodynamic characteristics of elementary steps of oxidation explaining the obtained results were calculated. The negative activation entropy showed an ordered transition state for reaction. 2,4-DNP derivative and nmr analysis revealed the products of the reaction to be 2,3-diones.**

***Index Terms*—3-pentanone, 3-hexanone, Nicotiniumdi-chromate, kinetics, oxidation.**

I. INTRODUCTION

3-alkanones are an important class of carbonyl compounds, widely applied both as solvents and fragrances. A part from applications in food industry, these compounds have various usages in the process of organic synthesis in both academic studies and industrial productions. [1] Owing to the high reactivity of carbonyl group, exhibiting tautomerism and degradation of >C-H cleavage due to loss of proton is the subject of oxidation of 3-alkanones. A considerable number of kinetic studies have been extensively investigated with variety of oxidants such as SeO_2, [2] NBSA,[3] $KBrO_3$,[4] IQBC [5] etc.
Nicotiniumdichromate (NDC) is a unique and versatile strong oxidizing agent has now been widely used for redox reactions in different media. In neutral and acidic media, NDC can exist in several different forms of species as H_2CrO_4 and $NDCH^+$. In general, the reduction of the chromate ion in acid medium goes to Cr(VI). Involving NDC, few reports in literature on oxidation of numerous organic compounds are available like ketones,[6,7] phenols,[8] anilines,[9] active methylene compounds,[10] and hydroxy acids.[11]

The oxidation of 3-alkanones (3-pentanone and 3-hexanone) by NDC has not been reported in literature. Therefore, this piece of research article is aimed to study the title reaction to shed some light on its oxidation mechanism. INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH IN TECHNOLOGY reserves the right to do the final formatting of your paper.

II. EXPERIMENTAL

Materials and methodology

Materials

3-pentanone and 3-hexanone (E. Merck, Germany) were A.R. purity. The suitability of 2-alkanones was verified by fractional distillation.[12] The oxidant nicotiniumdichromate (NDC) was synthesized as per literature. [13] The appropriate amount of the yellowish organic crystals of NDC were dissolved in the required volume of acetic acid (B.D.H.) (80% – 100%). The stock solution of NDC was standardized iodometrically. The freshly prepared solutions of all the reagents (standard form) were used in kinetic studies.

KINETIC PROCEDURE

The kinetic measurements were performed under pseudo first-order conditions [NDC] << [3-alkanones]

at constant ionic strength.

The kinetics of the oxidation process was studied in a thermostated vessel well maintained at the desire temperature. The reaction temperature was controlled within ± 0.1 K appropriate quantities of the reaction mixtures of 3-alkanones (separately) and NDC were measured and placed in the flasks alongwith ingredients kept in thermostat for at least 40 minutes. Consequently the reaction was initiated by adding requisite volume of NDC solution to substrate.

Progress of the reaction was followed by monitoring decrease in concentration of NDC as a function of time iodometrically. The pseudo first-order rate constant (k_{obs}) were evaluated from a slope of plot ln $\frac{[NDC]_o}{[NDC]_t}$ versus time.

Stoichiometry and Product Analysis

The stoichiometry was accomplished by titrimetric technique. The reaction mixture containing different initial concentrations of 3-alkanones at infinite time (35 h), were equilibrated away from light and residual [NDC] was estimated periodically. The stoichiometric ratio of $\frac{[NDC]consumed}{[3-alkanone]}$ was found to be $\frac{2}{3}$ mol. This results confirms the following equation.

$$2(C_6H_6O_2N)_2\ Cr_2O_7^{2-} + 3R-\overset{O}{\overset{\|}{C}}-R' + 12H^+$$

$$= 4Cr + 11\ H_2O + 3R-\underset{O}{\overset{O}{\overset{\|}{C}-\overset{\|}{C}}}-R' + 4\ \underset{\text{(Nicotinic acid)}}{C_6H_5O_2N} \quad \text{..... (1)}$$

where, R = CH_3CH_2 and R' = CH_3CH_2 and $(CH_2)_2\ CH_3$ for both the 3-pentanone and 3-hexanone respectively. The analyzed products pentane-2,3-dione and hexane-3,4-diones were consistent with the stoichiometric equation. The products diones were estimated quantitatively as their 2,4-DNP derivates[14] formation of a precipitate confirms the presence of diones yield 80% characterized by spectroscopic method,[15] and m.p. determination found in close agreement as reported in literature. [16]

Induced polymerization of acrylonitrile

The possibility of formation of free radicals was examined by adding 5% -10% (v/v) acrylonitrile or acryloamide to the oxidized reaction mixture in nitrogen atmosphere. No detectable induce polymerization was observed.

III. RESULTS AND DISCUSSION

The influence of NDC was studied by varying five-fold [NDC] within the range 1.25 $\times 10^{-3}$ to 6.25 $\times 10^{-3}$ (mol dm^{-3}) at fixed reaction conditions. The order is unity with respect to [NDC] as derived from the slope of slanting line graph drawn between $\log_{10}$ [NDC] against time.

The concentrations was varied at least 5X of the substrate at their prevailing experimental conditions of the reaction. The kinetic results indicate that the rate of oxidation increased appreciably with an increase in the substrate's low concentration (Table 1) but the curve inclined towards X-axis at their higher concentrations showing inhibition of rate. The linearity of Michaelis-Menten [17] plots of 1/ k_{obs} versus 1/ [3-alkanone] (Fig. 1) with a non-zero intercept on Y-axis is considered as kinetic evidence in favour of possible formation of an intermediate complex between protonated oxidant and enolic 3-alkanone. Thus, indicating that the reaction order with respect to 3-alkanone to be fractional first. However, the values of second-order (k_2) are not constant.

Table 1 : Dependence of oxidation rate of 3-alkanones by NDC at 35^0C

$10^3 \times$ [NDC] (mol dm^{-3}) = 4.0 (a, b) ; [H^+] = 0.0025 (a, b) (mol dm^{-3}) ;

HOAc-H_2O %, (v/v) = 25 (a), 30 (b)

104 × k (s-1)		
102× [3-alkanone] (mol dm-3)	3-pentanone (a)	3-hexanone (b)
1.00	1.01	-
1.25	1.29	1.57
1.50	1.41	-
2.00	1.80	2.32
2.50	-	2.82
3.33	-	3.42
4.00	2.94	3.87
5.00	3.36	4.15
6.25	3.63	4.33

The experimental error is equal to +3%.

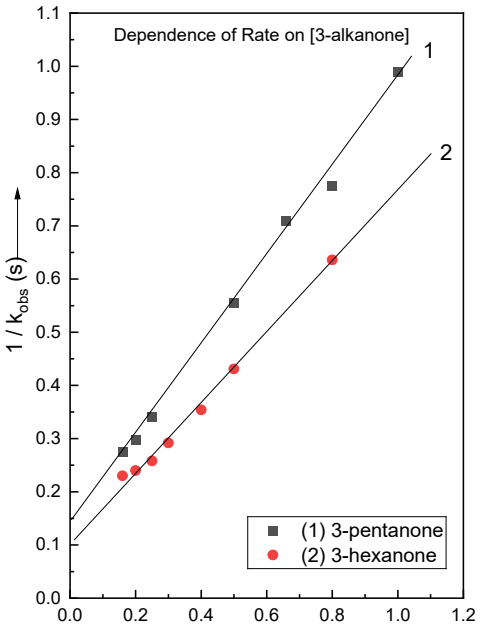


Fig. 1 Double reciprocal plot 1/k vs. 1/[3-alkanone]
(conditions are same as in table 1)

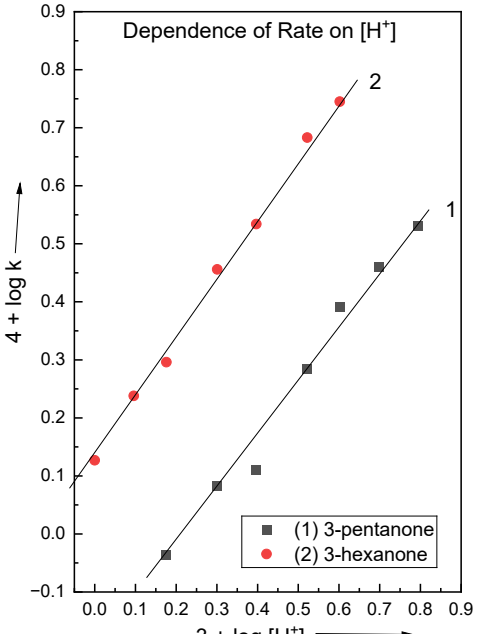


Fig. 2 Plots of log k vs. log [H$^+$]
(conditions are same as in table 2)

An increase 5X in the [H_2SO_4] was found to catalyse the reaction rate (Table 2). The linear plots of ln k_{obs} versus ln [H^+] with a unit slope 0.97 to 1.10 (Fig. 2) supported first-order dependence with respect to [H^+].

Table 2 : Dependence of reaction rate on concentration of hydrogen for the oxidation of 3-alkanones by NDC 35^{0}C
10^3×[NDC] (mol dm^{-3}) = 4.0 (a, b); 10^2×[3-alkanone] (mol dm^{-3}) = 1.25 (a), 3.33 (b); ;
HOAc-H_2O %, (v/v) = 25 (a), 30 (b)

104 × k (s-1)		
103 × [H+] (mol dm-3)	3-pentanone (a)	3-hexanone (b)
1.00	-	1.34
1.25	-	1.73
1.50	0.92	1.98
2.00	1.21	2.86
2.50	1.29	3.42
3.33	1.93	4.83
4.00	2.47	5.57
5.00	2.89	-
6.25	3.40	-

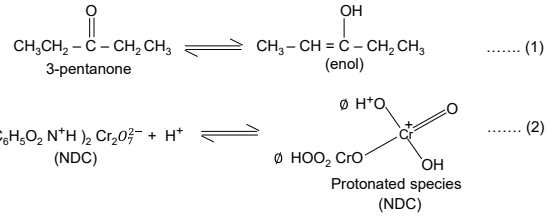
The experimental results indicate that increasing the ionic strength has no significant effect on the rate constant. The charged activated complex formed a specific influence of added transition metal ions (Cu^{++} and Mn^{++}) sulphate of selected divalent catalysts on the reaction rate may be expected. In view of this facts, the added ions of copper progressively accelerates the rate whereas a decrease in reaction rate was observed upon the addition of Mn^{++} ions in different concentrations.

The binary mixture of acetic acid and water composition 20% to 50% (v/v) showing positive rate with decrease in dielectric constant of the medium indicate that ion-ion dipole participate in the reaction mechanism.

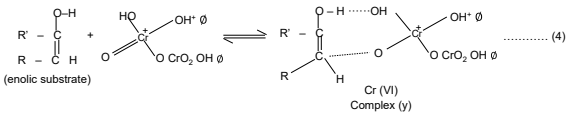
IV. MECHANISM

In view of the results obtained, a loss of proton mechanism of one electron oxidation leading to the lack of polymerization with acrylonitrile as ruled out completely the formation of free radicals. [18] The over all, mechanism is proposed considering enolic form of substrate and protonated species of NDC involves to the formation of complex in a prior equilibrium step.

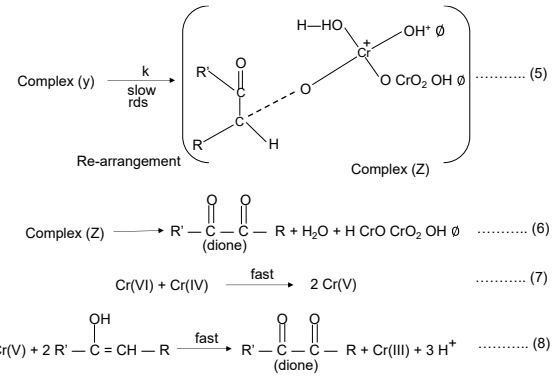
Acid-dependent path



where, Ø represents $C_6H_5O_2\ N^+$ (nicotinium ion)

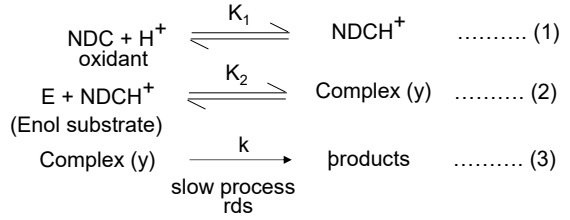


where, R = CH_3 and R' = CH_3CH_2 for 3-pentanone and 3-hexanone respectively.



Rate law

The rate of disappearance of the NDC or the formation of the intermediate complex as shown below can be expressed by



$$\text{Rate} = \frac{-d}{dt}[NDC] = k\,[\text{complex(Y)}] \ldots\ldots (4)$$

Since, the rate of complex formation (y) = $K_2[E][NDC]$ ... ... (5)

therefore, Rate = $k\,K_2[E][NDC]$ ... ... (6)

Substituting the values of [E], and [NDC]

In equation (6) and on simplification, we get

$$R = \frac{k\,K_1K_2[NDC]_t\,[H^+][E]}{1 + k\,K_1K_2[H^+][E]} \ldots\ldots\ldots (7)$$

Since. $[NDC]_t = [NDC] + [\text{complex (y)}] \ldots\ldots (8)$

Applying steady-state approximation using

$$k_{obs} = \frac{\text{Rate}}{[NDC]_t} \ldots\ldots (9)$$

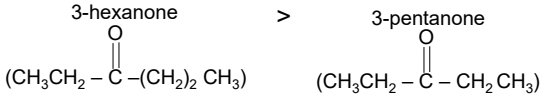
We obtain, the final equation of rate as :

$$k_{obs} = \frac{k\,K_1K_2\,[E][H^+]}{1 + K_1K_2\,[E][H^+]} \ldots\ldots (10)$$

Rearrangement of equation (10) gives the following relationship

$$\frac{1}{k_{obs}} = \left(\frac{1}{k\,K_1K_2[H^+]}\right)\frac{1}{[E]} + \frac{1}{k} \quad \ldots\ldots (11)$$

The rate law expression, equation (11) explains fully Michaelis-Menten type kinetics. The comparative order of reactivity based on rate, $\Delta H^{\#}$ and $\Delta S^{\#}$ was observed as :



The observed large negative values of $\Delta S^{\#}$ indicates an associative mechanism and compactness of rigid transition complex, [19] which is more ordered than reactants due to loss of degree of freedom and also having very small values of frequency factor (A).[20]

The charged ends of complex become highly solvated as a result of which immobilization of a large number of solvent molecules reflected in the loss of energy [21] i.e. reactions are accompanied by decrease in the entropy of activation.

On the other hand, values of thermodynamic parameters obtained, support the fact that the reaction before the rate limiting step is fairly slow and involves high activation energy[22] (Table 3). The similar values of $\Delta G^{\#}$ indicate that the kinetics of these reactions follow an identical reaction mechanism.

Table 3 : Activation parameters for the oxidation of 3-alkanones by NDC

3-alkanone	ΔS# (J mol-1 K-1)	ΔH# (kJ mol-1)	ΔG# (kJ mol-1)	ΔE# (kJ mol-1)
3-pentanone	-99.07	56.76	87.52	58.72
3-hexanone	-106.28	52.61	85.04	55.55

The parameters assessed that rate is governed by the enthalpy of activation. The slow rate of pentanone may be presumed due to presence of higher percentage of

enol content in comparison to 3-hexanone exhibiting conjugate effect and electron donating effect of methyl group showing +I effect. CH_3CH_2– group exhibits more spherically hindered effect, subsequently causes increase in enolic content and hyper conjugate effect. The +I effect pushing driving forces enough to break >C-H bond for expulsion of proton. The lengthening of the chain is also one of the reason of above order of reactivity.

V. CONCLUSION

The protonated species of NDC attacks at enolic 3-alkanone to proceed through formation of a 2:3 cyclic chromate ester complex at transition state. The final oxidation products were obtained by rupturing of >C-H bond with loss of proton to yield the products as pentane-2,3-dione and hexanone-3,4-dione which are characterized by forming their 2,4-DNP derivatives. The sequence of reactivity order was discussed.

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