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Kinetics of Oxidation of 3-alkanones by Nicotinium dichromate in Aqueous Acetic Acid Medium

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Abstract : The identical behaviour exhibited by nicotinium dichromate (NDC) with 3-heptanone and 3-octanone can be explained in terms of the architecture of the reactive intermediate as cyclic chromate ester involved in the oxidation. The kinetic evidences support a multi-step reaction mechanism involving a fast pre-equilibrium step leading stoichiometrically (2:3) to complex, followed a rate-determining disproportionation step. The 3-alkanones cleave the >C-H bond by loss of a proton to yield diones The reactivity follows the order 3-octanone > 3-heptanone. Overall, the dominancy of zero-order reaction rate are discussed**.**

***Key Words* - nicotinium dichromate, 3-heptanone, 3-octanone, oxidation, stoichiometry.**

I. INTRODUCTION

The oxidizing properties of hexavalent chromium (VI) compounds are becoming widely appreciated by organic chemists. [1] The wide spread utilization of one such compound is nicotinium dichromate (NDC) for the efficient oxidation of carbonyl compounds[2-5], hydroxy acids[6] and other, [7] testifies for this recent trend. Significantly NDC furnishes species of the types H_2CrO_4, $Cr_2O_7^{2-}$ and protonated NDC in presence of an acid, but stable species NDC H^+ ought to be assumed as a prime reacting species of the oxidant, performs the clean conversion of 3-alkanones to diones.

The dipolar nature of carbonyl group of 3-alkanones facilitate variety of reactions and regarded as a backbone of organic chemistry. These compounds are used in perfumery, textile industry as solvents in numerous organic synthesis, pharma- cological bio chemical processes of academic importance reaction.

The ambiguity always persists in way of their participation with no selectivity of keto or enol isomers in the oxidation of 3-alkanones. There is limited research on the oxidation of 3-alkanones, which is not facile. However, redox properties of these substrates were studied by few oxidants. [8-10]

This has motivated us to communicate the results of kinetics and mechanism of oxidation of 3-heptanone and 3-octanone by NDC in aqueous acetic acid medium.

II. EXPERIMENTAL

2.1 Materials

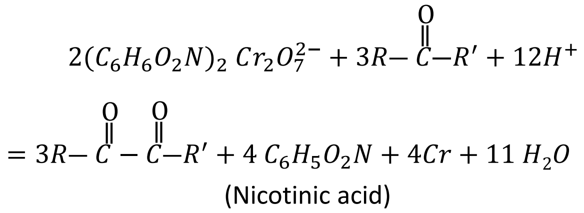
All chemicals used were of AnalaR grade. 3-heptanone and 3-octanone (E. merck) were purified by repeated distillation.[11] All other solutions were prepared in water distilled twice, and purged by nitrogen. The solution of weighed sample of synthesized [1] (Loc. cit.), NDC $(C_6H_6O_2N)_2$, Cr_2O_7 was prepared in 80% acetic acid (B.D.H.) and kept in the dark until needed and always used in standardized form for each set of experiment.

2.2 Kinetic measurements

The kinetics of oxidation of 3-alkanones were investigated under [3-alkanone] >> [NDC]. All the kinetic measurements were carried out in a glass stoppered flask, required amount of oxidant (NDC) and other ingredients alongwith a separate vessel that contained appropriate quantity of 3-alkanone kept in a well equipped thermostat water bath fitted with magnetic stirrer for temperature control with an accuracy of $\pm 0.1^0$ C. The content were mixed after the desired temperature was reached. 2 ml aliquot was withdrawn from the reaction mixture at regulator intervals for analysis. The course of the reaction for unreacted oxidant was followed iodometrically and reproducibility was found to be ± 3%. The pseudo first-order rate constant (k_{obs}) were evaluated from the slope of linear plots of ln $\frac{[NDC]_o}{[NDC]_t}$ vs. t (s).

2.3 Stoichiometry

Different sets of the reaction mixture containing amount of reactants [NDC] > [3-alkanone] were allowed to react for 6 hr. in an inert atmosphere. The means of several such estimates yielded Δ[NDC] / Δ[3-alkanone] = ⅔. Hence in view of the characterized products and the stoichiometric ratio, the reaction is expressible by equation (1).



$$2(C_6H_6O_2N)_2\, Cr_2O_7^{2-} + 3R-\overset{\overset{\displaystyle O}{\|}}{C}-R' + 12H^+ = 3R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-R' + 4\, C_6H_5O_2N + 4Cr + 11\, H_2O \quad \text{……… (1)}$$

(Nicotinic acid)

where, R = CH_3CH_2 and R' =CH_3CH_2- and CH_3 $(CH_2)_2$ CH_2- and $CH_3(CH_2)_3CH_2$- for duo 3-heptanone and 3-octanone respectively.

2.4 Product analysis

The reaction mixture was allowed to stand about 3-4 hr. at 30^0 C for completion of reaction. A portion of filtrate was treated with an excess of a satd. solution of 2,4-dinitrophenyl hydrazine in 2 mol HCl and same was left overnight in a refrigerator. The yellowish precipitates formed were separated by filtration, washed recrystallized from CH_3CH_2OH and dried. The m. pts. Of the precipitates were found match those of 2,4-DNPs of 3-alkanones. The yields of the 2,4-DNPs were in the range of 78% and also characterized by spectroscopic method.[12]

2.5 Test for free radicals

The reaction mixture degassed with nitrogen, did not produce cloudiness on treatment with acrylonitrile / acryloamide (5% v/v), thus, lacking the formation of free radicals. The addition of sodium chloride has no significant effect on the reaction rate indicating the absence of primary salt effect.

III. Results and Discussion

The kinetics of redox reaction (k_{obs}) at different concentrations 5X of nicotinium dichromate earlier at fixed conditions of other reagents and temperature were studied.

The deduced order of the reaction was found unity with respect to [NDC] from the measured slope of parallel line graphics made between $\log_{10}$ (a-x) vs. time (t). The fractional-order kinetics was observed for substrates at their higher concentrations (Table 1), with formation of protonated NDC – 3-alkanone adduct at transition state. This was proved by non-zero intercept of the plots of k_{obs}^{-1} versus [substrate]$^{-1}$ as exemplified in (Fig. 1) for 3-heptanone and 3-octanone respectively.

Table 1 : Dependence of oxidation rate on [3-alkanone] by Nicotinium dichromate at 30^0 C

10^3 × [NDC] (mol dm^{-3}) = 3.33 (a, b) ; [H$^+$] (mol dm^{-3}) = 0.001 (b), 0.002 (a);

CH_3COOH-H_2O %, (v/v) = 25 : 75 (a, b)

	10^4 × k (s^{-1})	
10^2× [Substrate] (mol dm^{-3})	3-heptanone (a)	3-octanone (b)
1.00	1.60	2.40
1.25	1.94	-
1.50	-	2.96
1.66	2.54	-
2.00	-	3.97
2.50	3.45	-
3.33	4.27	5.25
4.00	-	-
5.00	5.32	5.92
6.25	5.71	6.21

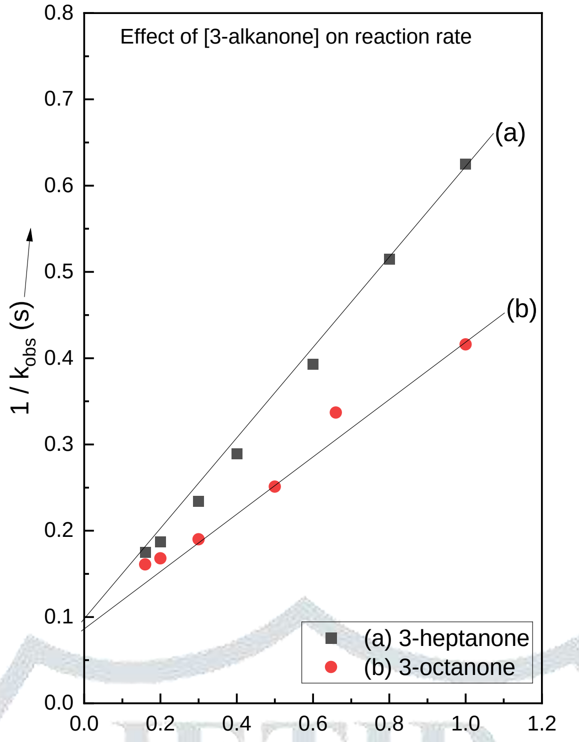


Fig. 1

Double reciprocal plot 1/k vs. 1/[3-alkanone]

$10^3 \times$ [NDC] (mol dm^{-3}) = 3.33 (a, b) ;
[H^+] (mol dm^{-3}) = 0.001 b), 0.002 (a);
CH_3COOH-H_2O %, (v/v) = 25 : 75 (a, b)
Temp. = 30^0 C

The effect of acid was investigated by varying [H^+] from 0.80 x 10^{-3} to 3.33 x 10^{-3} mol dm^{-3} at constant concentration of ketones and NDC at 303 K (Table 2). The slope of the plots of ln k_{obs} versus ln [H^+] are linear at different substrate concentration (Fig. 2) was found almost unity indicates first-order dependence with respect to H^+ ions, supporting the reactions to be catalyzed by acid. The rate slowly accelerates in protic solvent acetic acid 20% to 50% (v/v) keeping all other conditions constant with decrease in dielectric constant (D) of the medium. A plot of ln k_{obs} against D^{-1} is linear with positive slope (Fig. not given) indicating ion-dipolar interaction [13] in indicating the rate-determining step. It is presumed that intra molecular bonding that could stabilize the transition by increasing the size of $X^\#$ (activated complex)[14] by solvation is possible. The effect of divalent transition metal ions on rate was assessed as : Cu^{++} > Mn^{++} ions.

Table 2 : Dependence of rate on [H^+] for the oxidation of 3-alkanones by NDC at 30^0C

$10^3\times$[NDC] (mol dm^{-3}) =3.33 (a, b); $10^2\times$[3-alkanone] (mol dm^{-3}) =2.00 (b), 2.50 (a); CH_3COOH-H_2O %, (v/v) = 25 : 75 (a, b)

	$10^4 \times$ k (s^{-1})	
$10^3\times$ [H^+] (mol dm^{-3})	3-heptanone (a)	3-octanone (b)
0.80	-	1.68
1.00	1.59	1.97
1.25	2.07	2.44
1.50	-	2.83
1.66	2.67	-
2.00	3.45	3.97
2.50	4.14	4.76
3.33	5.61	6.31

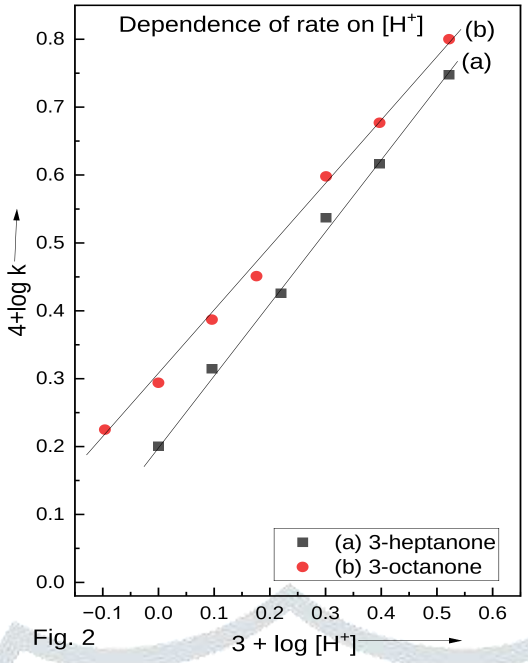


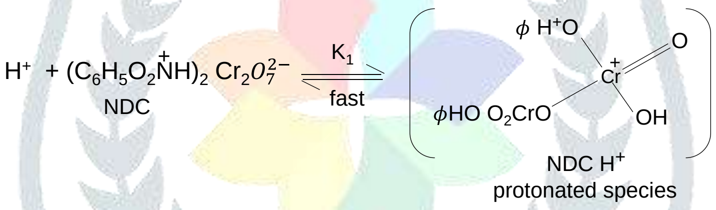
Fig. 2

Plots of log k vs. log $[H^+]$

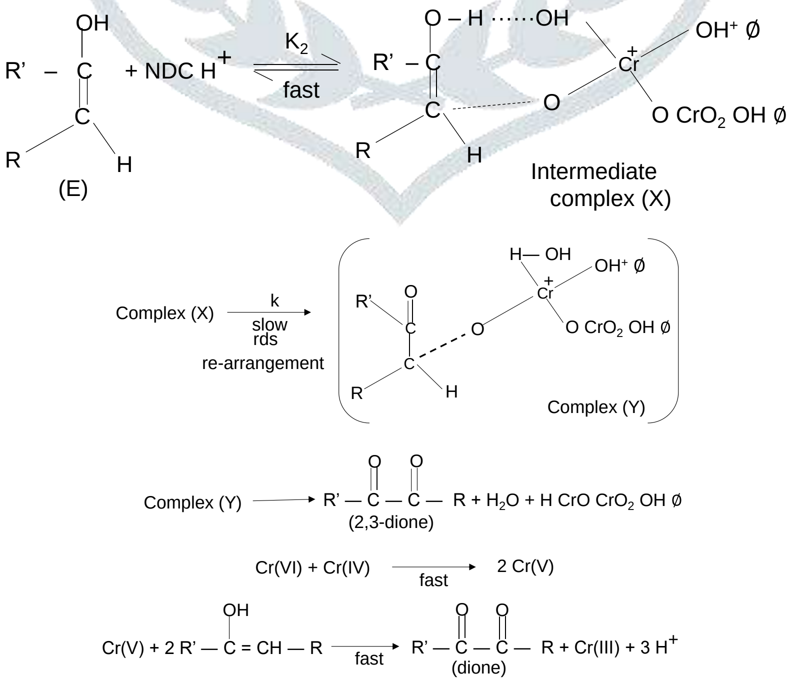
$10^3 \times$[NDC] (mol dm^{-3}) =3.33 (a, b);
$10^2 \times$[3-alkanone] (mol dm^{-3}) =2.0 (b), 2.50 (a);
CH_3COOH-H_2O %, (v/v) = 25 : 75 (a, b) ;
Temp. = 30^0 C

IV. Mechanism

Considering various experimental results, enol form of ketone and protonated species of NDC (oxidant), a plausible mechanism may be delineated as :



where, ϕ stand for $C_6H_5N^+$ (nicotinium ion)



Basing on the mechanism the rate law can be derived as :

$$Rate = k\,[complex\ (x)] \ldots\ldots (1)$$

$$Rate = k\,[complex\ (X)] \ldots\ldots (2)$$

$$Rate = k\,K_2[E][NDC] \ldots\ldots (3)$$

$$Since, [NDC]_t = [NDC] + [complex\ (X)] \ldots\ldots (4)$$

Imposing steady state hypothesis, on putting the value of equation (3) in equation (2) and further simplification results the final rate law as :

$$k_{obs} = \frac{k\,K_1K_2[E][H^+]}{1 + K_1K_2[E][H^+]} \quad \ldots\ldots\ldots (5)$$

The reciprocal of k_{obs} (equation 5) leads the expression.

$$\frac{1}{k_{obs}} = \frac{1}{[E]}\left(\frac{1}{k\,K_1K_2[H^+]}\right) + \frac{1}{k} \quad \ldots\ldots (6)$$

$\frac{1}{k_{obs}}$ is plotted against $\frac{1}{[3-alkanone]}$ a straight line is found with slope $\left(\frac{1}{k\,K_1K_2[H^+]}\right)$ and intercepts yields reciprocal of electron transfer rate constant (k) explains complex formation.

The comparative oxidation of reactivity was observed as 3-octanone > 3-heptanone. The decrease in enthalpy of activation is accompanied by decrease in degree of freedom of the reacting molecules and reorientation of solvent**[15]** molecules due to existence of complex formation**[16]** at transition state, consequently, curtailment of vibrational and rotational of the reactants occur. The fairly slow rate of 3-heptanone possesses higher activation energy (Table 3).

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

3-alkanone	ΔE^a kJ (mol^{-1})	$-\Delta S^{\#}$ JK^{-1} (mol^{-1})	$\Delta G^{\#}$ kJ (mol^{-1})	$\Delta H^{\#}$ kJ (mol^{-1})
3-heptanone	52.91	113.28	85.34	50.74
3-octanone	52.44	117.14	84.45	48.66

It appears that the reactivity increases with the 3-alkanone chain length. The higher rate constant of 3-octanone over that of 3-heptanone may be attributed to domaincy of CH_3CH_2 group sterically hindrance effect. The exhibited +I effect is sufficient enough to cleavage >C-H bond for the loss of proton. The 3-alkanones are oxidized by the similar pattern of prevailing mechanism and controlled by enthalpy of activation.

V. Conclusion

The mechanitic pathways of 3-alkanones oxidation by protonated species of oxidant stoichiometrically (2:3) occur probably through intermediate complex formation which leads further by decomposition to diones. The order of reactivity was observed as 3-octanone > 3-heptanone accompanied by a decrease in entropy of activation ($\Delta S^{\#}$).

VI. Acknowledgement

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VII. Conflict of Interest

The authors declare conflict of no interest whatsoever.

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