Kinetics And Mechanism Of 2-Hexanone by Pyridinium Dichromate in Aqueous Acetic Acid Medium

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***Abstract*—The potential role of acid catalysed in the form of protonated species of pyridiniumdichromate (PDC) in enol ketone reaction n has been explored as possible pathway in mechanism. The rate is independent of concentration of oxidant, kinetic evidence for the formation of Cr (VI) - ketone 2:3 complex has been obtained. Negative entropy of activation ($\Delta S^{\#}$) revealed the existence of symmetrical transition state for the reaction. The rate limiting step of oxidation reaction involves the cleavage of the α-C-H bond in the associated reaction kinetics is assigned.**

***Index Terms*—kinetics. Oxidation, mechanism, 2-hexanone, pyridinium dichromate.**

I. INTRODUCTION

Pyridiniumdichromate[1] (PDC) is a moderate oxidant of Cr(VI) complex of heterocyclic base, [2] used in synthesis of various compounds.[3] The common mechanism of the reaction is the formation of an intermediate Cr(VI) substrate complex in the pre-equilibrium step has been assumed, [4] that decomposes in the rate limiting step to Cr(IV) and oxidation products of the substrate. Though a large number of oxide metal ion catalyzed oxidation of ketones by various oxidants exhibiting quite different mechanisms have been reported. [5-9]

Some question arises about the nucleophilic addition or substitution on the α-C-H bond atom which is featured with the oxidation. Therefore, need was felt to explore this task to reach with some logical inferences.

Moreover, the interactions of PDC with ketone to produce controversy between keto or its enol forms to be reactive forms was discussed.

Since such environmental influences appear to affect the rate and perhaps even the mechanism of Cr (VI) oxidations. Therefore, it was worthwhile to carry out a systematic investigation of these effects.

The present probe describes the kinetics and mechanism of oxidation of 2-hexanone by PDC in aqueous acetic acid medium.

II. EXPERIMENTAL

Pyridinium dichromate solution was prepared by dissolving weighed sample AnalaR reagent grade of CrO_3 in pyridine and methylene chloride by reported method [10,11] and standardized by iodometric process. The hexanone (E-Merck) was distilled under reduced pressure and solution was prepared in acetic acid (C.D.H.). Other chemicals used were of reagent grade. Water used was redistilled from alkaline $KMnO_4$ in an all glass still. Reaction vessel glass stoppered flasks containing required volumes of reactants was kept in a thermostat maintained at the desired temperature to within ± 0.1^0 C. Pseudo first-order conditions were maintained in all the runs by using al large excess of 2-hexanone > five-ten-fold than PDC. The requisite volume of temperature pre-equilibrated PDC solution was added to initiate the reaction. An aliquot (2 cm^3) of the reaction mixture was sucked out and kinetics of the reaction was followed by estimating unconsumed PDC at different intervals of time iodometrically.

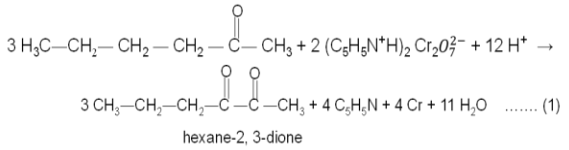
Initial rates were computed employing integration and graphical methods. The duplicate rate measurements were reproducible to within ± 5%.

III. STOICHIOMETRY AND PRODUCT ANALYSIS

The stoichiometry was estimated with excess of PDC concentration over under 2-hexanone under kinetic

conditions. The reaction was allowed to stand for 10 h to ensure completion of the reaction. The residual PDC was determined, showed that the stoichiometry is 3:2 i.e., three moles of 2-hexanone are consumed by two moles of oxidant, PDC.

The stoichiometry suggested the overall reaction.



The product dione was identified by forming its 2,4-dinitrophenyl hydrazone (DNP) and established by comparing the m.p. of the 2,4-DNP derivative with literature value.

IV. RESULTS AND DISCUSSION

(a) The reaction was found to be first-order kinetics with respect to PDC, as evidenced by strictly its kinetic runs. The graphic plot of lg [PDC] versus time was found linear ($r^2 > 0.997$). Further the pseudo first-order rate coefficients did not vary with the initial concentrations of PDC.

(b) The rate constants for the variation of 5X concentration of 2-hexanone at fixed condition was determined (Table 1). It has been noticed that rate increased non-proportionality with [2-hexanone]. The second-order rate constant (k_2) is variant showing inconstancy diminishing trend in values. The two-fold proportional plot between 1/ k_{obs} against 1/ [substrate] (Fig. 1), yields positive slope on Y-axis with parametric evidence for fractional-order kinetics. This fact follows Michaelis-Menten type kinetics and confirms the formation of complex between enol substrate and protonated species of oxidant, PDC at transition state.

Table 1: Effect of [2-hexanone] on the observed rate constants for the redox reaction between PDC and 2-hexanone

[PDC] = 4.00 ×10^{-3} (mol dm^{-3}) ; [H^+] = 00025 (mol dm^{-3}) ;
CH_3COOH: H2O = 30: 70 %, (v/v) ; t = 35^0 C

[2-hexanone] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	$\frac{10^3 k_2}{l\ mol^{-1}\ s^{-1}} = \frac{k_{obs}}{[2-hexanone]}$
1.25	1.21	9.68
1.66	1.54	9.27
2.00	1.86	9.30
2.50	2.27	9.08
3.33	2.98	8.94
4.00	3.41	8.52
5.00	3.76	7.52
6.25	4.40	7.04

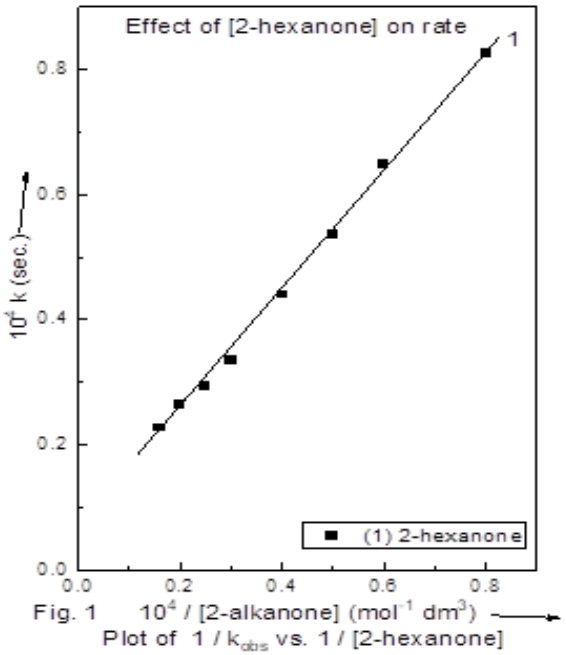


Fig. 1 Plot of 1 / k_{obs} vs. 1 / [2-hexanone]

The rate of oxidation was sensitized apparently with an increase in acidity. This was affirmed by straight (Table 2) plot of lg k_{obs} vs. lg [H^+] (Fig. 2) with slope value > 0.982 characterized by nearly order unity with respect to [H^+].

Table 2: Effect of Hydrogen ion on the observed rate constant

[PDC] = 4.00 ×10^{-3} (mol dm^{-3}) ; CH_3COOH:H_2O = 30 : 70 %, (v/v) ; t = 35^0 C

[2-hexanone] × 10^2 (mol dm^{-3})	10^3 [H^+] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
3.33	0.80	1.16
3.33	1.00	1.33
3.33	1.50	1.89
3.33	2.00	2.56
3.33	2.50	2.98
3.33	3.33	4.21
3.33	4.00	4.87

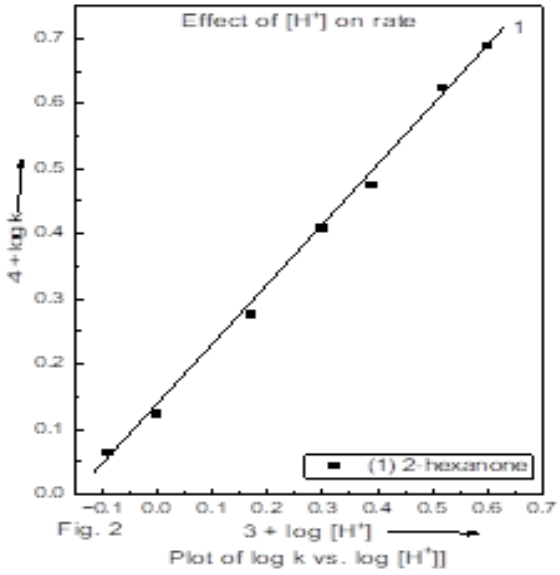


Fig. 2

Plot of log k vs. log [H+]]

To contemplate impact of solvent polarity on the rate, the designed experiments with blended acetic acid (20% to 60% v/v) at pre-set conditions of the reaction was performed. The results shows that pace of oxidation impeded with increment in the rate with decline in dielectric constant of the medium. The solvent effect suggests the positive intercept of ln k_{obs} vs. 1/D plot with cogent evidence that the reaction is ion-dipole type.

The oxidation of 2-hexanone by PDC in an atmosphere of nitrogen as detected by conventional trap method, failed to induce polymerization of acrylonitrile. Thus, rules out a one-electron oxidation giving rise to free radicals is unlikely to participate in mechanism.

The observed hydrogen ion catalyzed rate dependence suggests that PDC to yield protonated Cr (VI) species which is kinetically stronger oxidant and electrophile or chromate ester.

$$(C_5H_5N^+H)_2\,Cr_2O_7^{2-} + H^+ \rightleftharpoons (Py\,H^+O)^2 + O\,Cr\,O_2\,Cr\,(OH) \quad \ldots\ldots\ldots (2)$$

(PDC H+ species)

From this clue, it was accepted that protonated species of oxidant Cr (VI) may initiate the reaction. [13]

In order to remove the controversy that persists whether keto or its enol to be of reactive form, the rate of enolization of substrate was determined by halogenation method under earlier set conditions of the reaction and result showed that rate of enolization was found much faster than the oxidation. This concludes that enol form of 2-hexanone is most probably participate in rate-determining step.

The ionic strength (I) and neutral salt at maintained steady consistent of temperature have shown non substantial effect on rate.

V. MECHANISM

The most important of elucidation of the reaction mechanism in oxidation of 2-hexanone by PDC pertains to the enol species of ketone in the rate-determining step involving protonated species of oxidant PDC the following mechanism being inconformity to the experimental observations can be envisaged.

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \rightleftharpoons CH_3{-}CH_2{-}CH_2{-}CH=\underset{\underset{OH}{|}}{C}{-}CH_3 \quad \ldots\ldots (1)$$

2-hexanone (Enol)

$$PDC + H^+ \underset{\text{protonation}}{\overset{K_1}{\rightleftharpoons}} PDC\,H^+ \quad \ldots\ldots (2)$$

Cr(IV) protonated species of oxidant

$$2\text{-hexnone} + PDC\,H^+ \overset{K_2}{\rightleftharpoons} \text{Complex (c)} \quad \ldots\ldots (3)$$

cyclic chromate ester complex

$$\text{Complex (c)} \xrightarrow[\text{slow rds}]{k} \text{dione} + Cr(IV) + Py \quad \ldots\ldots (4)$$

$$Cr(IV) + Cr(VI) \xrightarrow{\text{fast}} 2\,Cr(V) \quad \ldots\ldots (5)$$

$$Cr(V) + 2\ \text{reductant (E)} \longrightarrow Cr(III) + 6H^+ + \text{products} \quad \ldots\ldots (6)$$

The rate law was worked out as:

$$Rate = k\,[Complex\ (C)] \ldots\ldots\ldots (7)$$

$$[Cr(VI)]_t = \frac{K_2[E][Cr(VI)] + K_1[H^+][Cr(VI)[C]}{[C]} \qquad (8)$$

Comparing equation (7), with equation (8) and applying steady-state approximation we get

$$k_{obs} = \frac{k\,K_1K_2[E][H^+]}{1 + K_1K_2[H^+][E]} \ldots. \qquad (9)$$

Equation (9) can be rewritten as equation (10)

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

The two-fold proportional plot of $\frac{1}{k_{obs}}$ against $\frac{1}{[E]}$ yields positive intercept on Y-axis confirms, the complex formation between protonated species of oxidant, PDC and enol 2-hexanone at transition state in pre-equilibrium steps before electron transfer. The mechanism is followed by cleavage of α-C-H bond to release proton. The negative value of $\Delta S^{\#}$ (entropy of

activation) reduces randomness of molecule and causes loss of rotational freedom in the kinetic process, that is, responsible for breaking of above bond. The temperature coefficient was computed as 1.39 and 1.95 at rise of 5^0 C and 10^0 C temperature respectively. Activation parameters were determined as (E_a= 55.98, kJ mol^{-1}, $\Delta H^{\#}$ = 50.71 kJ mol^{-1}, $\Delta G^{\#}$ = 87.92 kJ mol^{-1} and $\Delta S^{\#}$ = -119.84 JK^{-1} mol^{-1}). The derived rate law is well in accordance with kinetic observations.

VI. CONCLUSION

In analysis of the results can supply information about the mode of action on rection condition. The mechanistic pathways of 2-hexanone oxidation occur probably through an intermediate of enol ketone and protonated species of oxidant PDC in lack of free radicals which leads further by decomposition to dione. The reaction was found first-order w.r.t. PDC and fractional each in substrate and [H^+]. The complex was corroborated by double reciprocal plot between k_{obs}^{-1} vs. [2-hexanohe]$^{-1}$. It is germane to remark that the mechanism which involved scarce positive centre transition state is copiously responsible for the splitting of α-C-H bond. The complex followed 2:3 stoichiometry. The mechanism is followed by cleavage of α-C-H bond o eliminate proton. The rate law derived is in conformity with the kinetic observations.

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CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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