Kinetics of Oxidation of 2-Pentanone by Nicotinium Dichromate

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Abstract: **Now-a-days Nicotinium dichromate (NDC) has drawn the attention to several laboratories and is of academic interest due to its vast and wide application in allyl alcohols, kinetic and Non-kinetics oxidations of compounds. Nicotinium dichromate (NDC) is non-hazardous and easy to handle. The most important advantageous feature of this oxidant is that the potential of this industrial oxidants is about + 1.101 V being a moderate strong oxidant, it consumes little time, gives maximum products yields. The advantage to employ NDC in oxidation kinetics, its easy preparation and stable nature has leaded us to choose for the present investigation as an oxidant. Owing to possessing of reactive carbonyl group and tautomer phenomenon ketones are the subject of the interest. The relevant literature pertaining to the undertaken 2-butanone reveal that oxidations carried out by an NDC is very rare and scanty and none of the researcher acclaimed the use of NDC in probing the oxidation kinetics of 2-pentanone with it, thus the author has chosen NDC as an oxidant for kinetics study of ketones. The tautomer equimolecular ketoenol dynamic equilibrium creates complication and interesting mechanism due to structural change such as methyl etc. in presence of electron releasing and electron attracting groups with the enol from of the substrate. In this equilibrium shifting of α-halogen atom takes place to carbonyl oxygen to produce reacting enol and lengthening of the straight chain will enable me to take above text of task for study in view of explaining the kinetics of 2-pentanone.**

Keywords: **Kinetics of Oxidation, 2-PENTANONE and Nicotinium dichromate (NDC).**

INTRODUCTION

The kinetics remains one of the most important tool even this day in finding out the underline mechanism of the reaction. Thus due to developments of modern physical techniques viz. n.m.r., i.r., u.v., visible, absorption spectroscopy, mass spectra, epr. Thermo gravimetry, colourometry, polarography, chromatography etc. and wide and vast applicability of hi-tech, super-tech, has shed a new light and horizons on reaction mechanism and provide the complete picture of the reactions.

Dichromate have been used as mild and selective oxidizing reagent in synthetic organic chemistry.[1] A variety of compounds containing Chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group. The kinetics and mechanism involving Cr (VI) has been recently well study.

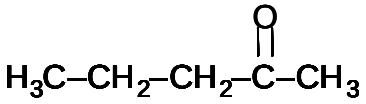
A number of new chromium containing compounds like pyridinium dichromate[2], chlorochromate,[3] 2,2-bipyridinium chlorochromate[4], pyridinium fluorochromate[5], nicotinium fluorochromate[6], nicotinium dichromate bromochromate[7], nicotinium dichromate[8], pyridinium fluorochromate[9], imadazolium fluorochromate[10] have been used to study the kinetics and mechanism of oxidation of various organic compounds. However, most of the reagents developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, hydroscopicity, low selectivity, long reaction time and need for large excess of reagent.

Now-a-days Nicotinium dichromate (NDC) an eco-friendly oxidant has been synthesised and employed in the oxidation of substituted.

In proposed study, 2-pentanone are actually ketones containing keto functional group at 2-carbon as, exhibited variety of chemical reaction with different oxidants viz. selenium dioxide[11], bromamine-T[12], NBSA[13], Acid-bromate[14], hexacyanoferrate(III)[15], chromic acid[16] and NCSA.[17]

The study of such reaction is of great significance and of interest because of its vast implication in under-standing the nature of chemical processes involved.

In the present investigation, NDC has been employed as an oxidant. Thus in view of exploring the kinetics of 2-pentanone with this particular oxidant and also in order to throw light insight the reaction path, and its vital activity the 2-pentanone has been selected for oxidation study:



(2–pentanone)

METHODS AND MATERIALS

2-Naphthol was purified by literature method. The oxidant Nicotinium dichromate was prepared and melting point was verified. Acetic acid was purified by standard method and the fraction distilling at 118^{o}C was collected. All other chemicals used were of AR grade.

Kinetic Measurements:

The reaction was carried out under first order conditions [2.Naphthol] >> [NDC] in 50% (v/v) aqueous acetic acid containing perchloric acid. The course of the reaction was followed calorimetrically and the rate constants K1 computed from the linear plots of log absorbance versus time by the least square method were reproducible within ±1%.

Stoichiometry and product analysis

Reaction mixture containing an excess of oxidant over 2.Naphthol were kept at room temperature in the presence of perchloric acid for 24 hr. Estimation of the unchanged oxidant showed that three mole of 2.Naphthol consumed four Mole of the oxidant. The product 1,2 Naphthoquinone was identified by IR spectra. The oxidation species Cr(VI) was observed to be reduced to Cr(III) which was identified using aluminium chloride.

RESULT AND DISCUSSION

Kinetics of oxidation of 2-pentanone have been studied in binary solvent mixture of aqueous acetic acid with NDC. The following results were obtained :

(a) The kinetics data have been collected for five-fold concentration of oxidant (NDC) at fixed concentration of other reactants and temperature. The linear plots of log (a-x) vs. time, suggested that the first-order rate was observed with respect to oxidant.

(b) The reactions follow first-order kinetics at lower concentration of substrate which tends toward zero-order at higher concentration, showing limiting value of rate constant. The substrate understudy, obey first-order kinetics and the value of pseudo first-order constant is nearly constant. The plots of log (a-x) vs. time is linear with nearly constant slope (Fig. 1) It is therefore, concluded that the order is one with respect to oxidant

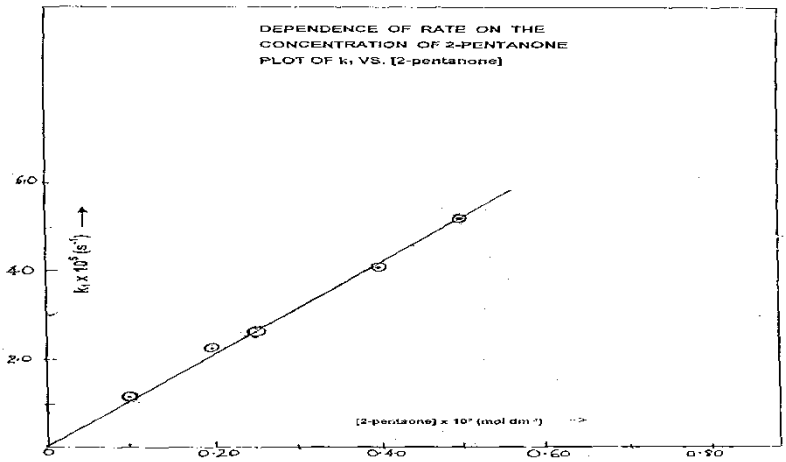


Fig. 1 [NDC] = 2.50 × 10^{-3} (mol dm^{-3}) ; [H^{+}] = 1.0 × 10^{-1} (mol dm^{-3}) ; HOAc-H_2O = 50% (v/v) ; TEMP. = 303 K

Table : 1

Dependence of rate on the variation of the concentration of 2-pentanone

[NDC] = 2.50×10^{-3} (mol dm^{-3}) ;
$[H^+]$ = 1.0×10^{-3}(mol dm^{-3}) ;
$HOAc\text{-}H_2O$ = 50 % (v/v) ;
Temp. = 303° K

Sr. No.	[2-pentanone] $\times 10^3$ (mol dm^{-3})	$10^4 k_1$ (s^{-1})
1.	1.00	1.26
2.	2.00	2.35
3.	2.50	2.65
4.	4.00	4.16
5.	5.00	5.20

(c) The reactions are fully acid catalyzed. The plot of k_1 vs. substrate are obtained linear with unit slope (Fig. 2) confirming that the order with respect to substrate is one.

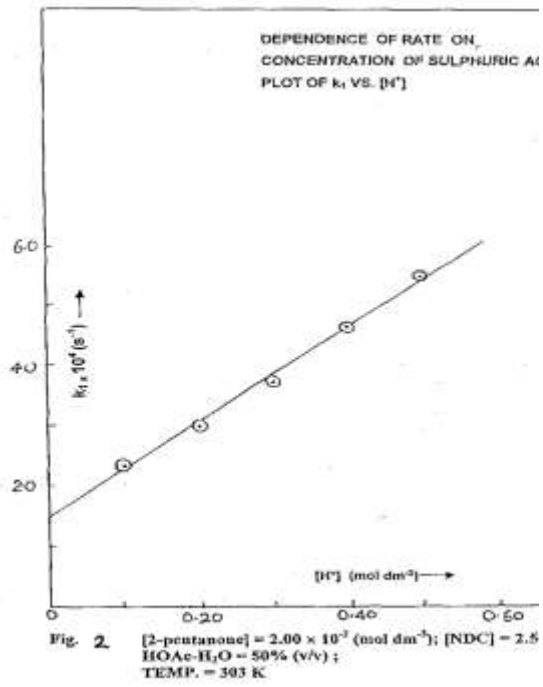


Fig. 2. [2-pentanone] = 2.00 × 10^{-3} (mol dm^{-3}); [NDC] = 2.5
HOAc-H_2O = 50% (v/v) ;
TEMP. = 303 K

Table : 2

Summary : Dependence of rate on the concentration of Sulphuric acid

[2-pentanone] = 2.00×10^{-2} (mol dm^{-3}) ;
[NDC] = 2.50×10^{-2} (mol dm^{-3}) ;
$HOAc\text{-}H_2O$ = 50 % (v/v)
Temp. = 303° K

Sr. No.	$[H^+] \times 10^3$ (mol dm^{-3})	2-pentanone $10^4 k_1$ (s^{-1})
6.	0.10	2.35
7.	0.20	3.02
8.	0.30	3.73
9.	0.40	4.71
10.	0.50	5.55

(d) The first-order rate constant increases with increasing composition of acetic acid i.e. rate slightly accelerated with decrease in dielectric constant of the medium. The plot of log k_1 vs. 10^3/D were obtained linear with positive slope in each substrate (Fig. 3).

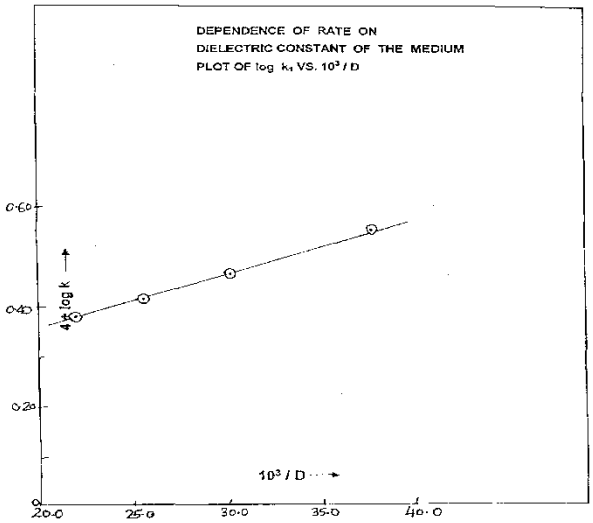


Fig. 3 [NDC] = 2.50×10^{-3} (mol dm^{-3}) ; [2-pentanone] = 2.00×10^{-2} (mol dm^{-3}); $[H^+]$ = 0.10 (mol dm-3) ; TEMP. = 303 K

Table : 3
Dependence of rate on dielectric constant of the medium

[2-pentanone] = 2.00×10^{-2} (mol dm^{-3});
[NDC] = 2.50×10^{-3} (mol dm^{-3});
$[H^+]$ = 0.10×10^{-1} (mol dm^{-3});
Temp. = 303° K

Sr. No.	[HOAc-H_2O] % (v/v)	$\underline{10^3}$ D*	2-pentanone $10^4 k_1$ (s^{-1})
1.	40	21.98	2.26
2.	50	25.64	2.35
3.	60	30.36	2.79
4.	70	38.04	3.23

(e) The addition of primary salt such as sodium chloride (NaCl), almost shows negligible salt effect on the reaction rate.

(f) The addition of metal cation i.e. Cu^{++} and Mn^{++} ions to the system show variation in rates. The effect of increasing concentration of Cu^{++} ions show an acceleration in the reaction velocity while Mn^{++} ions retard the rate of oxidation.

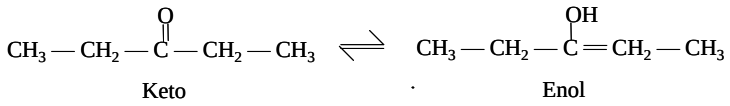
(g) The presence of free radicals in the system understudy was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and white precipitate clearly indicate the absence of free-radicals in the system.

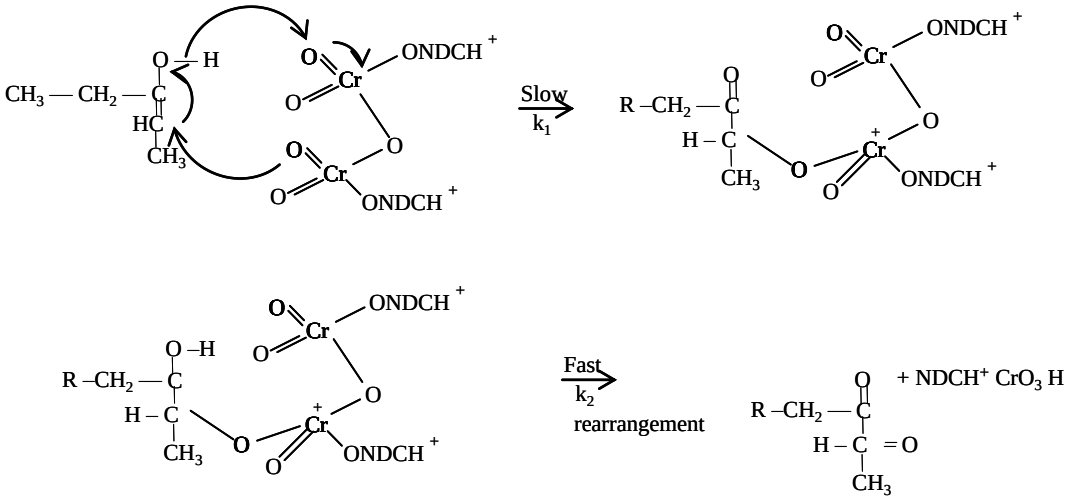
(h) Corresponding diones were formed as the end-products of oxidation of 2-pentanone-NDC system which were identified by their melting points and also with existing conventional methods.

(i) The stoichiometric determination have been found 1:1 mole ratio for substrate and oxidant (NDC).

Proposed mechanism for 2-pentanone -NDC system

The kinetic data as briefed in the beginning of the various sections of chapter-III reveal that the reaction velocity follows nearly first-order kinetics at low concentration of 2-pentanone. Considering these facts a probable mechanism for the oxidation of 2-pentanone with NDC could be proposed as per following scheme:





The rate expression leads the law

$$\frac{-d\,[NDCH^+]}{dt} = k_1 k_2\,[2\text{-pent.}]\,[NDC]\,[H^+]$$

$$\frac{-d\,[NDCH^+]}{dt} = k_1\,[2\text{-pent.}]\,[NDC]\,[H^+]$$

It is relatively more sterically hindered because of bigger -C_2H_5 group than -CH_3 group and thus increase in content of enol occurs due to exhibiting of probably tautomerism, consequently rate of reaction increse in 2-pentanone

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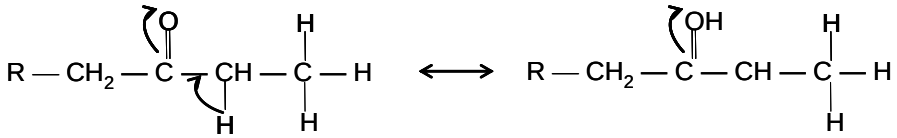
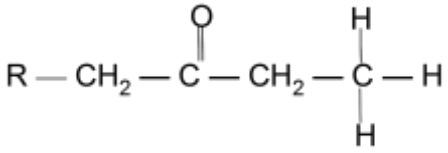


Where R = –CH_3

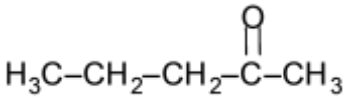
In pentanone, the -CH_3 group, with three hydrogen atoms is linked to the α-carbon atom in comparison to the other ketones with methylene group, with two hydrogen atom attached to the α-carbon atom.

Therefore, 2-pentanone experiences greater other 2-pentanone tautomersim oscillation of protons in compared to the .



where R = $-CH_3$

The order of reactivity were found as :



(2–pentanone)

The existed dominancy of steric, inductive and hyper conjugative effects among the molecules are the main reasons of above order of reactivity.

(j) Various activation parameters namely temperature coefficient, energy of activation (Ea), frequency factor (A), enthalpy of activation ($\Delta H^{\#}$), free energy of activation ($\Delta G^{\#}$), and entropy of activation ($\Delta S^{\#}$) for each reaction have been calculated for 2-pentanone-NDC system. On the basis of experimental findings the reaction mechanism[24-26], rate expression and order of reactivity have been discussed accordingly. The isokinetic plot has also been explained.

CONCLUSION

Kinetic studies employing NDC as an oxidant and allied aspects of its reactions lead us to conclude that the activity of NDC is much limited and needs to be explored in a broad way. It possesses vital potentiality and displays interesting behaviours at moderate condition of temperature. It use can be extended in analytical, applied chemistry and in separation/ identification of organic compound.

Fruitful outcome of the kinetic studies can suitably be applied in the field of pharmacology, Hi-tech, bio-chemistry, in finding the rate of growth192-197 of tissues and malignancy. The study will certainly enlighten the future workers in carrying out researches of great value contribution and information's through kinetic study will enrich chemical literature to a great extents.

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