Kinetic study of Oxidation of n-methyl - 2,6-diphynyl – piperidin-4-one Oxime [NMPO] - effect of varying sodium Per chlorate effect of ionic strength(NaClO$_4$) - 94 %

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ABSTRACT

PCC and N-methyl -2,6-diphynyl – piperidin-4-One Oxime were prepared , PCC by the method of Corey and Suggs. Then acetic acid was purified. Other reagents such asAnalar samples of Sodium Perchlorate and Trichloroacetic acid was used as such. Doubly distilled water was used throughout.

The purity of PCC was checked by estimating Cr(IV) iodometrically . The reaction was done at constant temperature ($\pm$ 0.1^0 C) and was followed iodometrically. The liberalized iodine was titrated against standardized sodium thiosulphate . The titration was repeated for the subsequent intervals of time The first order rate constant was found from the slope of the log litre plots by least square method.

First kinetic study of oxidation of N-methyl -2,6-diphynyl – piperidin-4-one oxime [NMPO] - by varying the concentration of the Sodium Perchlorate . (NaClO$_4$)

1. INTRODUCTION :

Pyridinium Chlorochromate (PCC) , an efficient reagent for the oxidation of primary and secondary alcohols to the carbonyl compounds was discovered by Corey and Suggs[1]. The structure of the complex could be either (XII) or (XIII).[1-4]
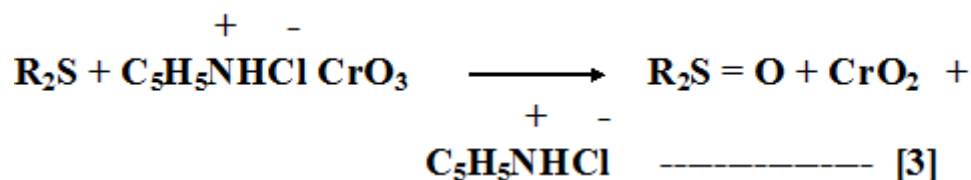
PCC exists as stable orange red crystalline solid (Molecular weight 215.45). it is freely soluble in cold water, benzene , acetic acid , glycerol, alcohols , chlorobenzene and nitrobenzene. The aqueous solution of PCC is more stable for a fairly long period. It liberates iodine quantitatively from acidified potassium iodide as shown below :[5-7]

$$2PyHCrO_3Cl + 6KI + 3H_2SO_4 \longrightarrow Cr_2O_3 + 3\ K2SO_4 + 3I_2 + PyHCl + 3H_20 \text{ ---------[1]}$$

Here two moles of PCC liberated six equivalents of iodine and hence the equivalent weight of PCC is equal to molecular weight /3 .

Brown , Gundu Rao and Kukerni [2] with a view to study the oxidation of Primary alcohols with PCC and in particular , to determine the stereochemistry of he reaction , added varying amounts of PCC to 1-octanol in methylene chloride. The progress of the reaction was followed by gas chromatography technique. They predicted a two electron transfer ,unlike in the case of chromic acid oxidation involving commonly a three electron transfer. [8-13]Thus ,

$$R_2S + C_5H_5\overset{+}{N}HCl\ \overset{-}{CrO_3} \longrightarrow R_2S = O + CrO_2 + C_5H_5\overset{+}{N}HCl\ \overset{-}{} \text{ ----------- [3]}$$

Even in the oxidation of 2-propanol with chromic acid , chromium(VI)species once formed is completely inert as an oxidant[3].

The kinetics and mechanism of the oxidation of substituted mandelic acid by PCC was reported by Banerji[4]. The reaction was followed under pseudo – first order conditions, uncatalysed as well as acid catalysed in 1:1 (v/v) methylene chloride – nitrobenzene mixture.

The order was found to be one each in (oxidant)(substrate), and (H$^+$) . Increase in the percentage of nitrobenzene decreased the rate in accordance with the suggestion that the rate – determining step , in the presence of an acid
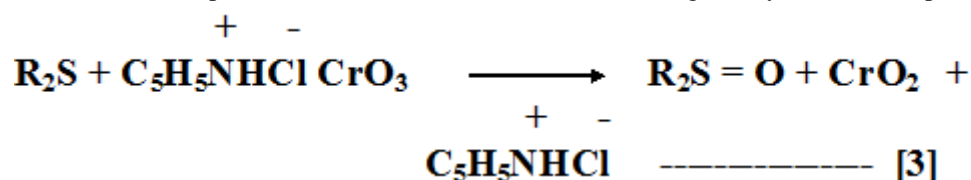
involved a protonated Cr(VI) species. No free radical was trapped. The substituted mandelic acids gave an excellent fit into the Hammett equation, with a negative ρ - value. A suitable mechanism was also suggested.[14-18]

Based on the experimental results , two types of rate – determining hydride – ion transfer mechanisms are proposed:

(i) Direct rate determining hydride – ion transfer from alcohol to protonated PCC and

(ii) Prior formation of a chromate-ester between alcohol and PCC before the rate – determining hydride- ion transfer.

Chromate –ester formation is not likely to be susceptible to any considerable structural influence 5,6. The large negative reaction constant can arise thus only from the differential effects of the substituents on the rate –determining step.[19-22]

The kinetics of oxidation of ten primary alcohols by PCC in dichloromethane – nitrobenzene mixture at 30^0C was studied under acid catalysed and uncatalysed conditions. In each primary alcohol the main product of the oxidation was the corresponding aldehyde. The reaction was first order each with respect to (alcohol) and the

(oxidant). The order with respect to (H+) was one , showing the involvement of the protonated PCC. The reaction did not induce polymerization of acrylonitrile. The values of the reaction constants , for the uncatalysed and acid catalysed oxidation were – 1.93 and – 1.75 respectively. Both the hydride – ion transfer and the chromate – ester formation mechanisms have been suggested.

Michaelis – Menten type of oxidation of dimethyl , dipropyl and diphenyl sulphides , in chlorobenzene - nitrobenzene mixture , studied by Panigrahi and Mahapatro[7], was not very fact as compared to $CrO3$ oxidation. The reaction in chlorobenzene - nitrobenzene mixture in the presence of large excess of the alkyl sulphide , showed first order dependence of the (oxidant).

Variation of the substrate concentration at constant PCC concentrations, resulted in variation in k1 values, but k2 values (k2= k1 / sub.) were decreasing. So a double reciprocal plot of 1/k1 vs 1/ (substrate) showed an excellent linearity with an intercept , indicating that the reactions were of Michaelis – Menten type. Similar behaviour was also shown by dipropyl and diphenyl sulphides.

The addition of acrylamide did not affect the rate and no plymerisation was observed. The order with respect to acid was one. The solvent effect showed an interaction between a positive – ion and a dipole. The stoichiometry was found to be 1:1 as given by two electron process :

$$R_2S + C_5H_5\overset{+}{N}HCl\ \overset{-}{C}rO_3 \longrightarrow R_2S = O + CrO_2 +$$

$$C_5H_5\overset{+}{N}HCl\ \overline{\ \ } \quad ----------- [3]$$

The stoichiometry was also not affected in acid catalysed conditions. Two schemes were proposed for the mechanism of the reaction and both envisaged an oxygen atom transfer from the oxidant in agreement with the earlier observations[4,5].

Kinetics and substituent effects on the study of oxidation of differently substituted anilines in non – aqueous medium were reported by Panigrahi and Mahapatro[8]. The reaction under pseudo – first order conditions in chlorobenzene - nitrobenzene mixture in the presence of dichloroacetic acid showed a first order dependent each on (aniline) ,(PCC) and (dichloroacetic acid) . The product of the reaction in each case was found to be azobenzene and p – benzoquinone. In one scheme the prior formation of an ester in a reversible step preceded by a hydride – ion shift was reported. In the other scheme , an equilibrium
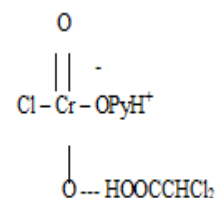
complex formation involving dichloroacetic acid , as a hydrogen bonded component of PCC was represented(XIV).

$$\begin{array}{c} O \\ \parallel \\ Cl - \overset{\displaystyle |}{Cr} - O\overset{-}{P}yH^+ \\ | \\ O --- HOOCCHCl_2 \end{array}$$

A novel oxidation of tetra substituted furan with PCC by Akbar et al[9] has led to a covalent synthesis of 4-acetoxy -3-acetyl or methoxy –carbonyl-4- substituted phenylbut-3-en-2-one.
The kinetics of oxidation of methylphenyl sulphide and several Para-substituted phenylmethyl sulphides by PCC was followed in binary solvent mixtures of 60% (v/v) aqueous acetic acid and 50%

(v/v) chlorobenzene – nitrobenzene by Rajasekaran et al[10].

Banerji , during the oxidation of benzhydrols[11] and diols[12] by PCC in dimethyl sulphoxide proposed the following cyclic hydride-ion transfer mechanism(XV).
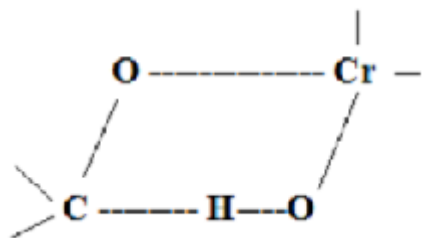
EXPERIMENTAL PART
General procedure for the N-methylation of piperidin-4-ones:
The piperidone(10g) was dissolved in 100ml of acetone and anhydrous potassium carbonate (10g) and methyl iodide(5ml) were added to the solution. The mixture was heated on a water bath for three hours. Acetone was removed and the residue was poured into water()150ml. The solid N-methypiperidone separated was filtered and recrystallised from ethanol.

General procedure for the N-methylation of piperidin-4-one oximes:

The piperidone (0.1mol)was dissolved in ethanol(50ml). saturated solutions of hydroxylamine hydrochloride and sodium acetate in water were added. The mixture was refluxed on a water bath for one hour. Then it was cooled , poured into water and the solidoxime obtained was filtered. All the oximes were recrystallised from ethanol.[23-27]

1.1.Kinetic Procedure:
The purity of PCC was checked by estimating Cr(IV) iodometrically .The present reaction was arranged to be under pseudo-first order conditions by keeping a large excess of oxime over PCC. The reaction was done at constant temperature ($\pm$ 0.1^0 C) and was followed iodometrically. The N-Methyl -2,6- diphenylpiperidin-4-one Oxime (NMPO) in acetic acid , Pyridinium Chlorochromate in acetic acid and acetic acid were thermally equilibrated . in a sample run the oxime solution , acetic acid were pipette out in to a flask kept in the thermostat. The oxidant was added lastly. Aliquots (2ml) were drawn and quenched into solution of 2 M sulphuric acid(10ml). to this were added potassium iodide (20ml ,20%) and starch s indicator. The liberalized iodine was titrated against standardized sodium thiosulphate . The titration was repeated for the subsequent intervals of time. The duplicate rate measurements were reproducible up to 3%. The first order rate constant was found from the slope of the log litre plots by least square method.

Effect of Ionic - strength
Run – 11
Effect of Substrate
[NMPO] = 0.501 X 10^{-2} M [AcOH] = 100 %
[PCC] = 9.02 X 10^{-4} M Temperature = 35 ^{0} c
[NaClO$_4$] = 0.531 X 10^{-2} M

Time Secs.	Titreml	Log titre
310	9.6	0.9823
720	7.9	0.8926
1100	6.8	0.8325
1300	6.2	0.7923
1570	5.6	0.7480
1860	5.0	0.6990
2160	4.4	0.6434
2400	4.0	0.6021

r = 0.999

k = 4.17 X 10^{-4} . sec^{-1}
Sd. = 4.15 X 10^{-3}

Effect of Ionic - strength
Run – 12
Effect of Substrate
[NMPO] = 0.501 X 10^{-2} M   [AcOH] = 100 %
[PCC] = 9.02 X 10^{-4} M   Temperature = 35 ^{0} c
[NaClO$_4$] = 1.062 X 10^{-2} M

Time Secs.	Titreml	Log titre
60	10.4	1.0170
315	9.2	0.9638
621	8.1	0.9085
908	7.2	0.8573
1165	6.5	0.8124
1392	5.8	0.7634
1709	5.1	0.7076
2200	4.1	0.6128

r = 0.999
k = 4.31 X 10^{-4} . sec^{-1}
Sd. = 2.92 X 10^{-3}

Effect of Ionic - strength
Run – 13
Effect of Substrate
[NMPO] = 0.501 X 10^{-2} M   [AcOH] = 100 %
[PCC] = 9.02 X 10^{-4} M   Temperature = 35 ^{0} c
[NaClO$_4$] = 1.590 X 10^{-2} M

Time Secs.	Titreml	Log titre
293	9.0	0.9542
530	8.0	0.9031
760	7.1	0.8512
940	6.5	0.8129
1125	6.0	0.7780
1310	5.4	0.7324
1454	5.0	0.6990
1614	4.7	0.6721

r = 0.999
k = 4.97 X 10^{-4} . sec^{-1}
Sd. = 2.9 X 10^{-3}

Effect of Ionic - strength
Run – 14
Effect of Substrate
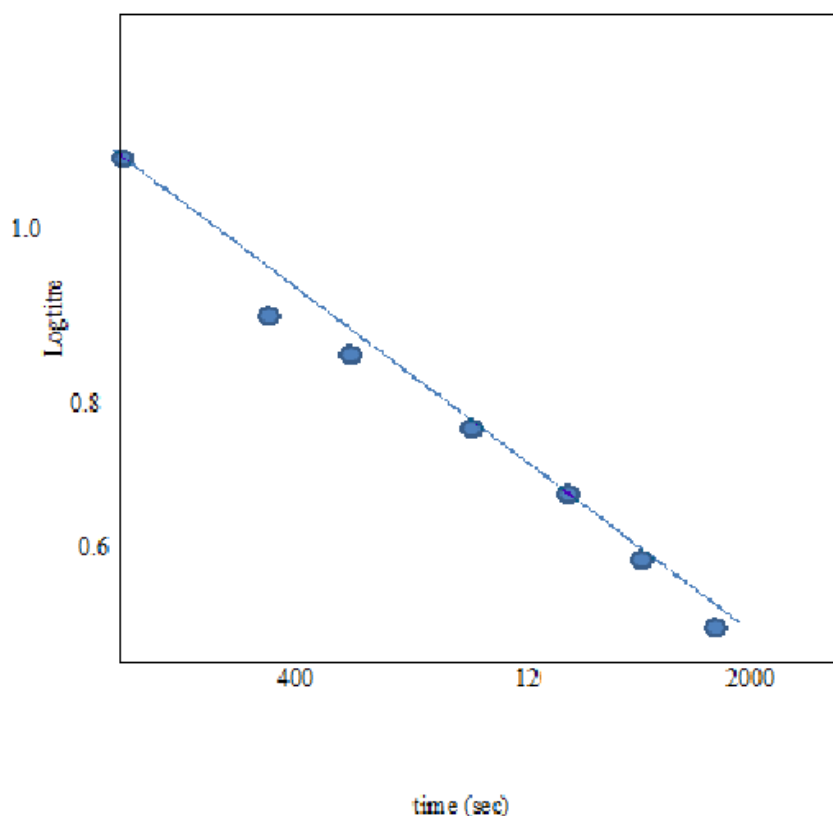[NMPO] = 0.501 X 10^{-2} M   [AcOH] = 100 %
[PCC] = 9.02 X 10^{-4} M   Temperature = 35 ^{0} c
[NaClO$_4$] = 1.328 X 10^{-2} M

Time Secs.	Titreml	Log titre
65	10.6	1.0250
307	9.5	0.9777
607	8.2	0.9130
795	7.3	0.8633
982	6.5	0.8124
1245	5.9	0.7708
1408	5.3	0.7242
1593	4.8	0.6812
1837	4.3	0.6335

r = 0.999
k = 5.22 X 10^{-4} . sec^{-1}
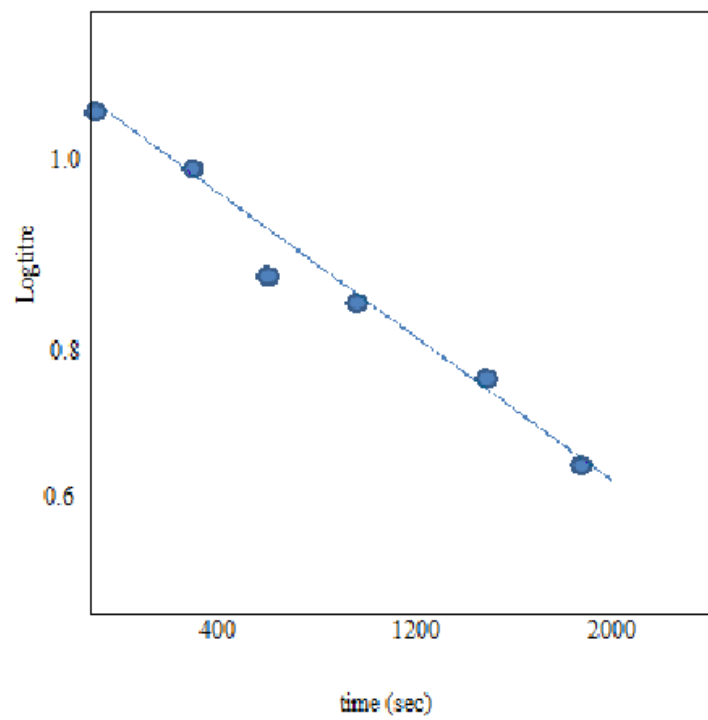Sd. = 1.13 X 10^{-3}

EFFECT OF IONIC - STRENGTH

Run - 11

Run - 12
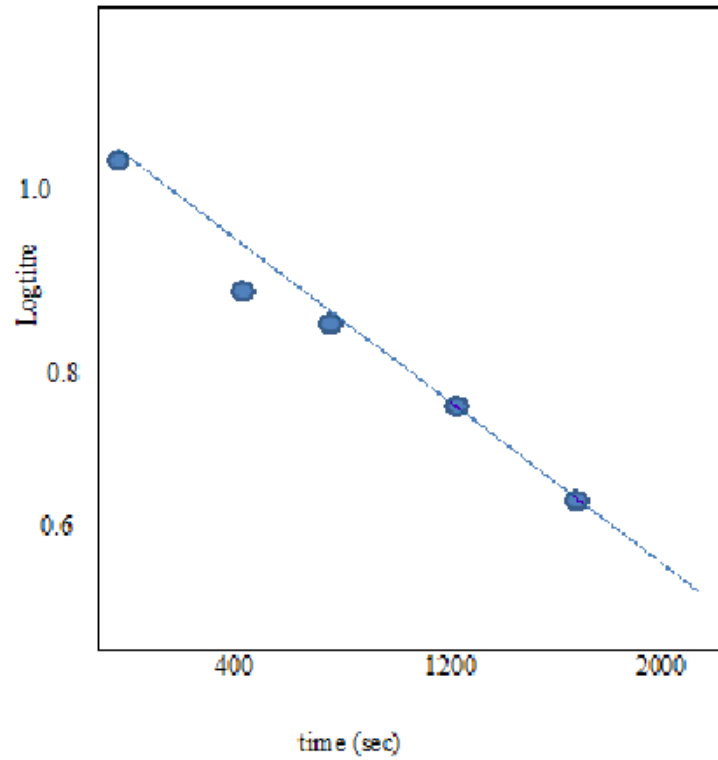
Run - 14

DISCUSSION :
Effect of Chemistry ionic strength on the reaction rate :
The reaction was studied with varying concentrations of Sodium perchlorate in order to know the Primary Salt effect. The rate increases with the increase in the Sodium perchlorate concentration.

Table III

[NMPO] : 1.00×10^{-2} M   [AcOH] : 100%
[PCC]   : 9.02×10^{-4} M   Temperature : 35^{0}c

[NaClO$_4$] X 10^2 M	k$_1$ X 10^4 sec^{-1}
0.00	3.71
0.53	4.17
1.06	4.31
1.33	4.97
1.59	5.22

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