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Kinetic Study of Oxidation of N-Methyl-2,6-Diphynyl–Piperidin-4-One Oxime [NMPO] - Effect of Varying the Substrate [NMPO]

V. Krishnasamy* and R. Kalpana Devi

Bharath University, Chennai – 600073, Tamil Nadu, India; ndippi@gmail.com, kalpsshankar@gmail.com

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 as Analar 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 (±0.10 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 Substrate [NMPO].

Keywords: Least Square Method, Kinetic study, N-methyl-2,6-diphynyl-piperidin-4-one Oxime, Oxidant, Rate Constant, Slope

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].

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[2]. The aqueous solution of PCC is more stable for a fairly long period. It liberates iodine quantitatively from acidified potassium iodide as shown below:

$$2PyHCrO_3Cl + 6KI + 3H_2SO_4 \longrightarrow$$

$$Cr_2O_3 + 3K_2SO_4 + 3I_2 + PyHCl + 3H_2O \text{ ----------[1]}$$

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 the reaction, added varying amounts of PCC to 1-octanol in methylene chloride. The progress of the reaction was followed by gas chromatography technique[3]. They predicted a two electron transfer, unlike in the case of chromic acid oxidation involving commonly a three electron transfer.

$$RCH_2OH + C_5H_5\overset{+}{N}HCrO_3\overset{-}{Cl} \longrightarrow RCHO + C_5H_5NHCl + CrO_2 + H_2O \text{ ------- [2]}$$

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

**Author for correspondence*

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[5]. The substituted mandelic acids gave an excellent fit into the Hammett equation, with a negative ρ - value. A suitable mechanism was also suggested.

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

Direct rate determining hydride – ion transfer from alcohol to protonated PCC and Prior formation of a chromate-ester between alcohol and PCC before the rate – determining hydride-ion transfer.

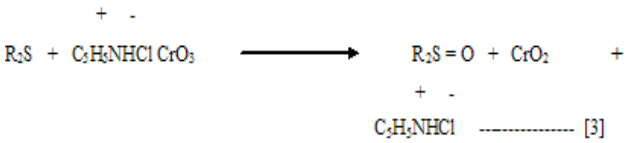
Chromate-ester formation is not likely to be susceptible to any considerable structural influence[6]. The large negative reaction constant can arise thus only from the differential effects of the substituents on the rate-determining step.

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)[7]. 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[8].

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 CrO_3 oxidation. The reaction in chlorobenzene-nitrobenzene mixture in the presence of large excess of the alkyl sulphide, showed first order dependence of the (oxidant)[9].

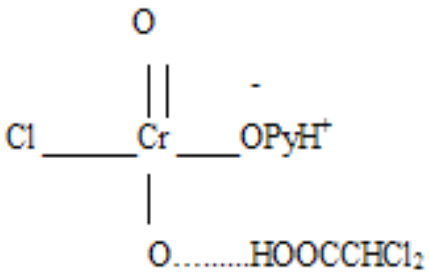
Variation of the substrate concentration at constant PCC concentrations, resulted in variation in k1 values, but k2 values (k2 = k1/sub.) were decreasing. So a double reciprocal plot of 1/k1 vs. 1/(substrate) showed an excellent linearity with an intercept, indicating that the reactions were of Michaelis – Menten type. Similar behavior was also shown by dipropyl and diphenyl sulphides[10].

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:



The stoichiometry was also not affected in acid catalyzed conditions[11]. 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[4–6].

Kinetics and substituent effects on the study of oxidation of differently substituted anilines in non-aqueous medium were reported by Panigrahi and Mahapatro[8,9,12]. 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).

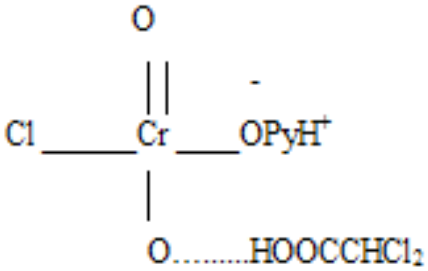


A novel oxidation of tetra substituted furan with PCC by Akbar et al.[9] has led to a covalent synthesis of 4-acetoxy-3-acetyl or methoxy–carbonyl-4-substituted phenylbut-3-en-2-one.

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).



2. Experimental Part

2.1 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[13].

2.2 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.

3. 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 (± 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[18]. 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 liter plots by least square method[14].

3.1 Substrate Effect

Piperidone oxime I: 1. Methyl-2,6-diphenyl-piperidin-4-oxime (NMPC)

Run – 6

Effect of Substrate

[NMPO] = 0.501 X 10^{-2} M [AcOH] = 100 %

[PCC] = 9.02 X 10^{-4} M Temperature = 35 ^{0}C

Time Secs.	Titre ml	log titre
63	10.6	1.0253
274	10.1	1.0043
650	9.1	0.9590
930	8.5	0.9294
1225	8.0	0.9031
1555	7.3	0.8633
1855	6.7	0.8261
2122	6.3	0.7993
2440	5.9	0.7708

r = 0.999

k = 2.50 X 10^{-4} .sec^{-1}

. = 3.13 X 10^{-3}

Run – 7

Effect of Substrate

[NMPO] = 1.002 X 10^{-2} M [AcOH] = 100 %

[PCC] = 9.02 X 10^{-4} M Temperature = 35 ^{0}C

Time Secs.	Titre ml	log titre
65	10.7	1.0294
313	9.8	0.9912
730	8.4	0.9242
990	7.6	0.8808
1293	6.8	0.8325

1565	6.2	0.7924
2155	4.9	0.6902
2378	4.6	0.6628

r = 0.999

$k = 3.71 \times 10^{-4}$. sec^{-1}

$Sd. = 2.92 \times 10^{-3}$

Run – 8

Effect of Substrate

[NMPO] = 1.253×10^{-2} M [AcOH] = 100 %

[PCC] = 9.02×10^{-4} M Temperature = $35\ ^0C$

Time Secs.	Titre ml	log titre
60	10.3	1.0130
309	9.4	0.9730
610	8.3	0.9191
928	7.2	0.8573
1216	6.5	0.8129
1436	5.8	0.7709
1695	5.4	0.7324
1970	4.8	0.6812

r = 0.999

$k = 4.03 \times 10^{-4}$. sec^{-1}

$Sd. = 3.30 \times 10^{-3}$

Run – 9

Effect of Substrate

[NMPO] = 1.00×10^{-2} M [AcOH] = 100%

[PCC] = 9.02×10^{-4} M Temperature = $35\ ^0C$

Time Secs.	Titre ml	log titre
63	10.4	1.0170
350	9.1	0.9590
647	8.1	0.9085
918	7.2	0.8573
1207	6.3	0.7993
1520	5.5	0.7403
1759	4.9	0.6902
1978	4.5	0.6532

r = 0.999

$k = 4.38 \times 10^{-4}$. sec^{-1}

$Sd. = 2.60 \times 10^{-3}$

Run – 10

Effect of Substrate

[NMPO] = 2.005×10^{-2} M [AcOH] = 100 %

[PCC] = 9.02×10^{-4} M Temperature = $35\ ^0C$

Time Secs.	Titre ml	log titre
75	9.8	0.9912
282	8.8	0.9445
598	7.4	0.8692
780	6.7	0.8261
954	6.0	0.7781
1170	5.5	0.7403
1358	4.9	0.6902
1548	4.5	0.6532

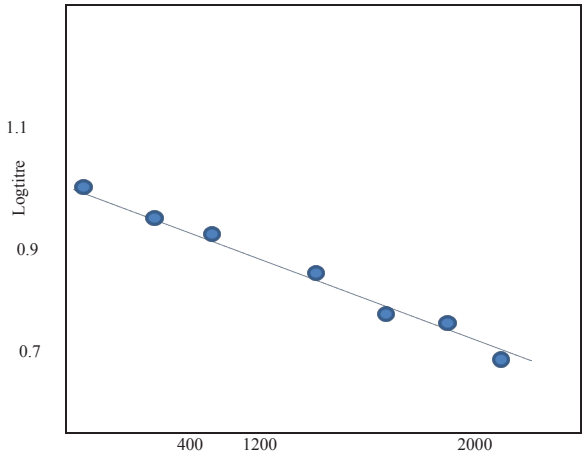
r = 0.999

$k = 5.33 \times 10^{-4}$. sec^{-1}

$Sd. = 4.11 \times 10^{-3}$

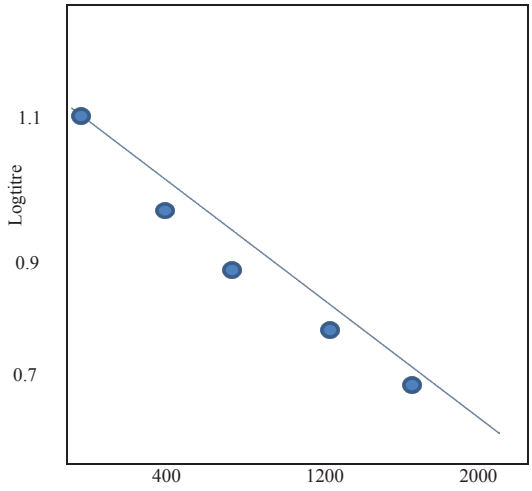
Effect of Substrate

Run - 6



time (sec)

Run - 7



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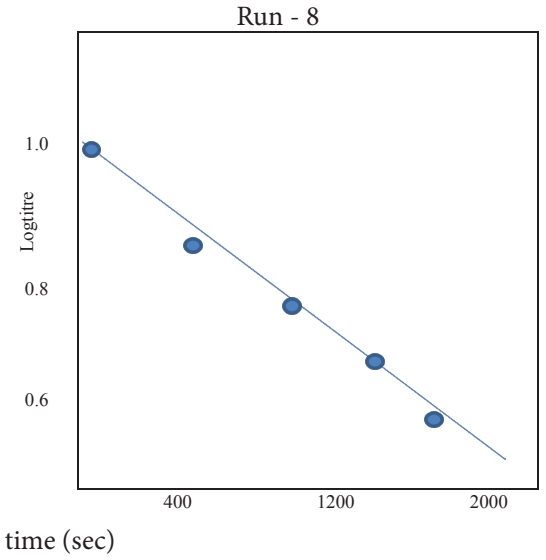

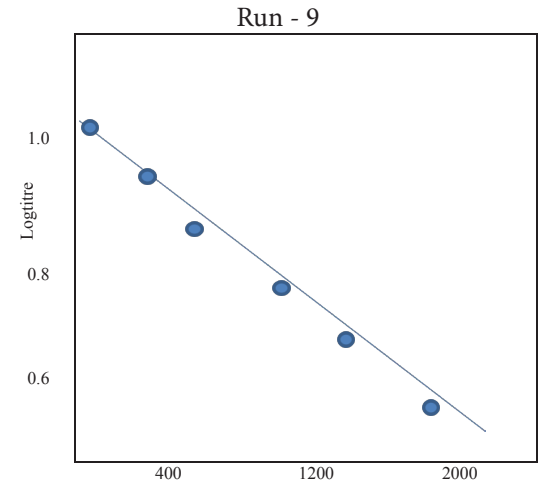

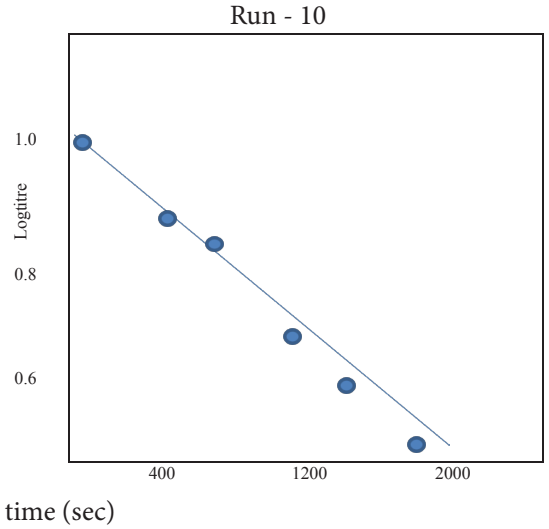

4. Discussion

4.1 Effect of Varying NMPO Concentration on the Reaction Rate

The reaction was investigated by varying the substitute concentration at constant PCC concentration[15]. With the increase in the concentration of the substrate the rate of the reaction was found to increase. The order with respect to NMPO was found to be fractional as evidenced by the linear plot of logk1 versus log (NMPO) with slope equal to 0.53[16,17].

[PCC] X 10^{-3} M	k X 10^{4} sec^{-1}	$K_{1.5} = K_1 / [\text{NMPO}]^{0.53}$
0.45	3.74	4.14
0.90	3.71	4.26
1.13	3.58	4.11
1.35	3.44	4.05
1.58	3.13	4.23

Table 2 a

3 + log [NMPO]	4 + log [NMPO]
0.70	0.40
1.00	0.57
1.10	0.61
1.18	0.64
1.30	0.73

r = 0.997

Slope = 0.53

Sd. = 1.03 x 10^{-2}

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