Kinetic Study of oxidation of 2, 6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one by Manganese (IV) Ion

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Abstract- **Kinetic study of oxidation of 2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one by Mn (IV) in acidic medium represents that the reaction are of first order. In present work it was found that rate of reaction is directly proportional to the acid concentration. The presence of 3-alkyl substituent decrease the rate of oxidation with Mn(IV). The order of reactivity of oxidations is observed as 2,6-Diphenyl-Piperidine-4-one > 3-Methyl 2,6-Diphenyl-Piperidine-4-one.**

Keywords- **Kinetic study, Oxidation, 2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one, Mn (IV), Acidic medium**

I. INTRODUCTION

Kinetic investigations of redox reactions in aqueous organic solvents and the subsequent correlation of the reaction rates with various solvent parameters provide important information regarding the mechanism of such reactions [1]. Kinetic studies on the oxidation of acids, cyclohexnol, allylalcohol, dimethyl sulpoxide and substituted aniline by N-chloro-3-methyl-2, 6- diphenylpiperidine-4-one have been reported [2]. The kinetics of oxidation of diphenylmethane by permanganate was studied by Gopalan *et. al* and they pointed out that more than one manganese species are involved in the oxidation [3]. Manganese (III) has been extensively used for the oxidation of several classes of compounds including hydrocarbons, hydroxyl compounds and carboxylic acids [4]. Among the transition elements such as *d* and *f* orbital involving various oxidation states [5, 6] partially form metal complexes. These transition metal ions by virtue of their d-orbital are capable of coordinating with a number of ligands depending on their electronic configuration [7]. The tetravalent manganese dioxide is known as an oxidizing agent, there has not been any reports on the use of Mn(IV) solution as an oxidizing agent[8]. The kinitics of oxidation of cyclohexanone by two electron oxidants like Mn(VII) and one electron oxidants like Mn (III) has been reported by Littler [9-12)]. The studies of soluble Mn(IV) species in the oxidation of 2,4 pyrimidine diones has been reported by Fillmore Freeman et.al [13]. Mn(IV) has been used as an analytical reagent in the titrimatric determination of Fe, V, Ur, Mo, As, Oxalate and Iodide [14].

II. MATERIAL AND METHOD

2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one, BDH(AR) were prepared in double distilled water according to Balaish and Noller and used [15]. Potassium permanganate -BDH (AR) was used without further purification. Sulphuric acid -BDH (AR) was used without further purification. Sodium sulphate -BDH (AR) was used without further purification. All other chemicals, acids and solvents used in the present work were of analytical reagent grade. In order to prepare 0.05 M solution of manganese (IV) about 7.9 g of potassium permanganate was dissolved in 9 M sulphuric acid with vigorous stirring by a magnetic stirrer for a period of 8 hours. The solution was kept overnight and made up to 1 litre with 9 M sulphuric acid. Manganese (IV) solution was also determined titrimetrically [16] by using Iron (II) sulphate solution. Ferrion indicator was used to detect the end point.

Determination of Stoichiomety

Stoichiometry was determined by estimating the concentration of Mn(IV) in reaction samples by titration. The concentration of Mn(IV) was determined after known intervels of time in order to find out the stoichiometry as a function of time. The initial concentration of Mn(IV) was always determined before running into the stoichiometric samples. The stoichiometry was found to be 2:1 (oxidant ratio substrate) as given in the Table 1.

Temp. 35^0C,   I = 1.8M,   [piperiodone] $= 6\times10^{-5}$M
[Mn (IV)] $= 6\times10^{-4}$M,   [H$^+$] = 0.5M

TABLE-1

Time	$\dfrac{\Delta[\mathbf{Mn(IV)}]}{\Delta[\mathbf{Piperidine}]}$
4 hrs.30 min.	0.955
20 hrs. 30 min.	1.250
24 hrs. 30 min.	2.062

Products of oxidation

An acidic solution of piperidone was mixed with an excess of Mn(IV) solution and neutralized by adding Na2CO3 solution drop by drop. On cooling alcohol was added and the product was isolated by etherification and GC/MS analysis. The oxidation product was found to an acid.

Kinetic Measurements

Kinetic Measurements [17] were performed spectrophotometrically at 525 nm, 420nm and 380nm using an S.P 700/500 spectrophotometer. The rate of disappearance of Mn (IV) in the presence of excess [Piperidone] was found to be first order. Concentration of piperdine varied from 0.01 M - 0.02M these measurements were carried out at three different acidities ranging from 0.3M - 0.5M keeping the ionic strength constant at 1.8 M by the addition of Sodium sulphate solution.

III. RESULT AND DISCUSSION

Kinetics and mechanism of oxidation of 2,6-diphenyl piperidine-4-one and 3- methyl 2,6-diphenyl pipridine- 4-one by Mn(IV) in acidic medium have been investigated. The plots of 1+ log O.D against time are linear (fig.1). The value of K_0 at various acidities is collected in Table 2(a, b).
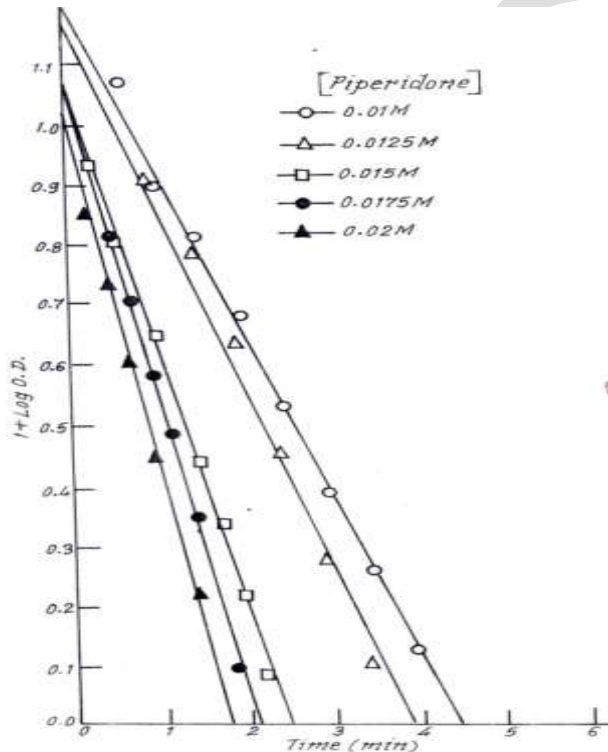

Fig.1: Plots of 1+ Log O.D. against time for 2, 6-diphenyl piperidine-4-one oxidation by Mn (IV) at 55℃, I = 1.8M, [H⁺] = 0.5M

The plots of K_0 against [Piperidone] at constant acidity and constant ionic strength were found to be linear (fig. 2a, 2b)

and the bimolecular rate constant K_2 have been calculated from the slops of these lines.
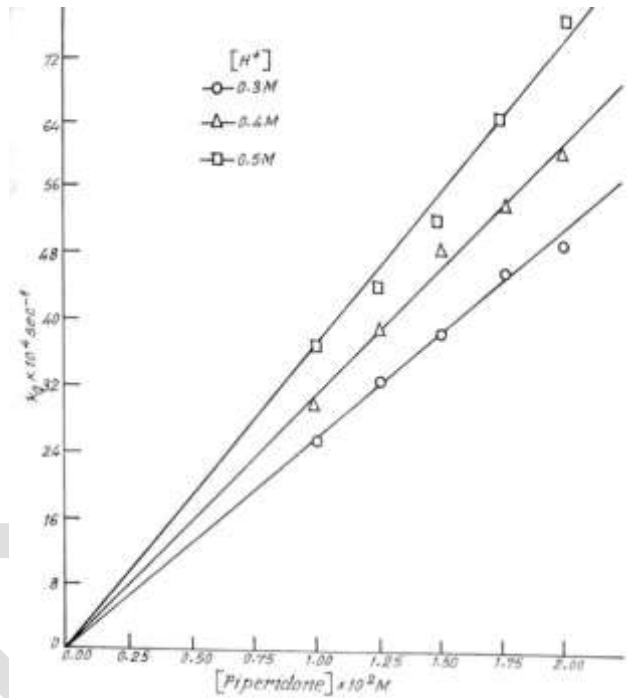

Fig.2 a: Plots of K_{obs} against [2, 6-diphenyl piperidine-4-one] M at 45˚C.
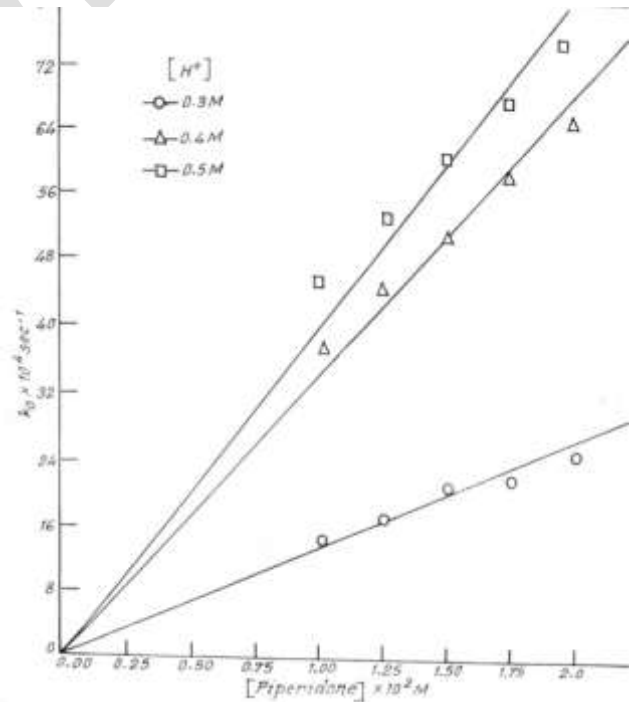

Fig.2 b: Plots of K_{obs} against [3-methyl-2, 6 diphenyl piperidine-4-one] M at 45˚C

Table-2a

Value of rate constants $k_o \times 10^4$ sec^{-1} for the oxidation of 2, 6-diphenyl piperidine-4-one at I= 1.8 M and [Mn(IV)] = 6×10^{-4} M

Temp. °C	[piperidone] $\times 10^2$ M	[H$_2$SO$_4$] M		
		0.3	0.4	0.5
25	1.00	3.93	2.98	4.39
	1.25	4.26	3.74	5.08
	1.50	4.61	4.54	5.76
	1.75	4.93	5.31	6.46
	2.00	5.24	6.08	7.21
35	1.00	-	14.17	18.21
	1.25	-	16.57	24.52
	1.50	16.47	18.97	30.40
	1.75	17.63	21.37	34.24
	2.00	18.81	28.30	38.19
45	1.00	14.58	39.11	48.31
	1.25	17.08	45.45	54.80
	1.50	19.54	51.77	61.29
	1.75	22.01	58.07	67.79
	2.00	24.49	64.39	74.29
55	1.00	73.72	80.97	108.49
	1.25	81.63	90.79	126.14
	1.50	89.50	100.49	143.77
	1.75	97.49	110.39	161.38
	2.00	105.29	120.21	178.90

Table-2b

Value of rate constants $k_o \times 10^4$ sec^{-1} for the oxidation of 3-methyl-2, 6-diphenyl piperidine-4-one at I= 1.8 M and [Mn(IV)] = 6×10^{-4} M

Temp. °C	[piperidone] $\times 10^2$ M	[H$_2$SO$_4$] M		
		0.3	0.4	0.5
25	1.00	3.61	2.99	4.96
	1.25	4.20	3.81	5.75
	1.50	4.96	4.68	6.51
	1.75	5.36	5.50	7.28
	2.00	5.97	6.35	8.05
35	1.00	12.85	11.81	14.40
	1.25	15.09	14.99	19.20
	1.50	17.31	18.20	23.93
	1.75	19.49	21.35	28.70
	2.00	21.72	24.55	33.57
45	1.00	26.37	28.80	37.85
	1.25	32.89	40.94	43.34
	1.50	39.41	48.83	53.07
	1.75	45.95	54.31	65.23
	2.00	52.45	59.81	77.37
55	1.00	52.59	71.15	68.61
	1.25	64.98	85.54	86.35
	1.50	77.34	100.00	104.12
	1.75	89.74	114.21	121.83
	2.00	102.12	128.67	139.57

Effect of varying concentration of oxidant on reaction rate:

With respect to oxidant, the reaction is formed to be first order. The first order nature with respect to oxidant is confirmed from the constancy in the rate constant at different initial concentration of oxidant.

2,6-diphenyl piperidine-4-one and 3-methyl- 2,6-diphenyl piperidine-4-one Effect of different concentration of piperidones:

The piperidone concentration was varied from 0.01 -0.02 M, keeping the Mn(IV) concentration constant. The values of K_0 at various acidities are collected in Tables (2a, 2b). The plots of K_0 against [piperidones] at constant acidity and constant ionic strength were found to be linear (fig. 2a, 2b).

The bimolecular rate constants K_2 have been calculated from the slops of these lines (Table 3a, 3b).

TABLE-3A

Bimolecular rate constants $K_0 \times 10^2$ L M^{-1} sec^{-1} for the oxidation of 2,6-diphenyl piperidine-4-one

Temp. °C	[H$_2$SO$_4$] M		
	0.3	0.4	0.5
25	2.30	3.05	3.35
35	8.85	12.76	19.01
45	21.90	26.05	48.53
55	49.55	57.54	70.99

TABLE-3B

Bimolecular rate constants $K_0 \times 10^2$ L M^{-1} sec^{-1} for the oxidation of 3-methyl- 2,6-diphenyl piperidine-4-one

Temp. °C	[H$_2$SO$_4$] M		
	0.3	0.4	0.5
25	1.37	2.78	3.09
35	4.63	9.53	10.32
45	9.93	25.24	25.97
55	31.64	39.25	60.47

Effect of varying concentration of acid on reaction rate

The kinetics of oxidation of the substituted piperidones have been studied in various acidity range 0.3- 0.5 M (Table 3a and 3b). The rate of reaction was found to increase with acid concentration.

Effect of varying temperature on reaction rate

The oxidation rate of 2,6-diphenyl piperedine-4-one and 3 methyl 2,6-diphenyl piperedine-4-one have been measured at four temperatures in the range 25- 55℃. The rate of reaction was found to increase with increasing temperature. The activation parameters have been calculated from the linear Arrhenius plot (fig. 3a, 3b) of log K_2 vs T-1.
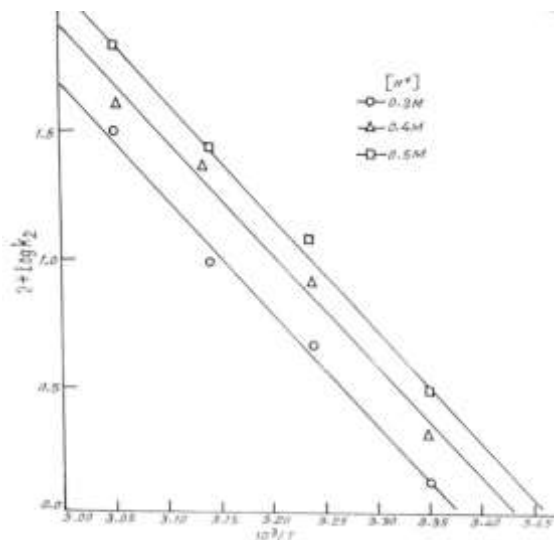
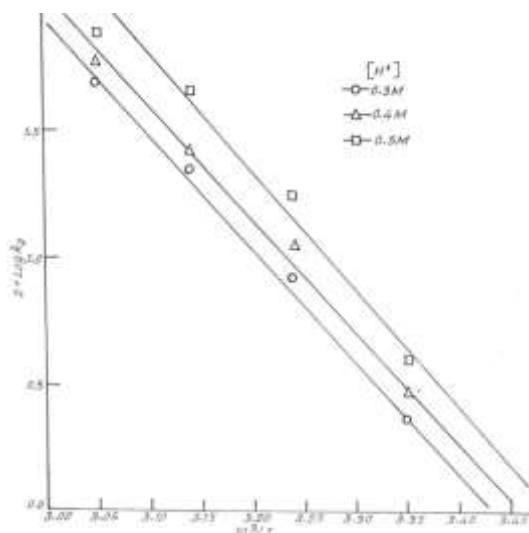Fig.3a: Arrhenius plots for 2,6-diphenyl piperidine-4-one oxidation

Fig.3b: Arrhenius plots for 3-methyl-2,6 diphenyl piperidine-4-one oxidation

Activation parameters

Linear plot is obtained for log K2 against 1/T °K. The values of ΔEa, ΔH*, ΔS* and ΔG* were calculated in Table (4a, 4b).

TABLE-4A
Values of activation parameters for the oxidation of 2,6-diphenyl piperidine-4-one

| [H₂SO₄] M	ΔEₐ kJ mole⁻¹	ΔH* kJ mole⁻¹	ΔS* JK⁻¹ mole⁻¹	ΔG* kJ mole⁻¹
0.3	67.55 ± 0.72	67.39 ± 0.72	−14.24 ± 3.73	81.59 ± 1.36
0.4	78.92 ± 1.13	81.41 ± 1.13	−0.83 ± 2.25	81.65 ± 2.35
0.5	89.90 ± 2.45	81.41 ± 2.45	6.63 ± 7.82	82.06 ± 4.89

TABLE-4B
Values of activation parameters for the oxidation of 3-methyl-2,6-diphenyl piperidine-4-one

[H₂SO₄] M	ΔEₐ kJ mole⁻¹	ΔH* kJ mole⁻¹	ΔS* JK⁻¹ mole⁻¹	ΔG* kJ mole⁻¹
0.3	85.64 ± 0.95	79.51 ± 0.95	−10.15 ± 6.25	83.25 ± 1.86
0.4	82.10 ± 1.89	83.11 ± 1.89	−1.74 ± 3.03	81.59 ± 3.64
0.5	85.52 ± 2.23	82.97 ± 0.95	4.75 ± 8.15	81.41 ± 1.81

Rate law

On the basis of the above experimental data the rate expression can be represented as:

$$[Mn(OH)_3^+] \rightarrow MnO_2 + H2O + H$$
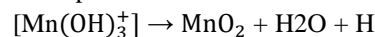
$$-\frac{d[Mn(IV)]}{dt} = k \, [\text{piperidone}] \, [\, Mn(IV)] \, [H^+]$$

Mechanism of oxidation

It is difficult to dissolve MNO_2 (Mn in oxidation state IV) in acids, the best method suggested for prepration of Mn(IV) solution is by reduction of $KMnO_4$ in acid medium. Further an aged solution of Mn(IV) in sulphuric acid prepared by above method gives a precipitate of MnO_2. This means in a freshly reduced solution of KMnO4, Mn(IV) as $Mn(OH)_3^+$ are the dominant species. Hence we have assumed that $Mn(OH)_3^+$ as the attacking species. So the following mechanism could be proposed for Mn(IV) oxidation.
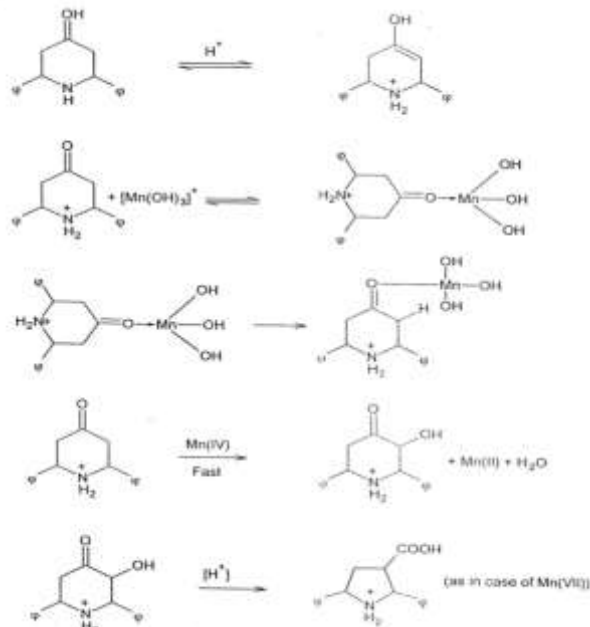
Mechanistic pathway of oxidation

Both proton transfer and hydride ion transfer can be envisaged. Proton transfer will give rise to the intermediate radical which is in agreement with the observed kinetic results. Mn(IV) and Mn(II) oxidations of piperidones are similar. Such observation is expected because of similar redox potentials.

Comparison of the oxidation rate of 2,6-diphenyl piperidine-4-one and 3-methyl-2,6-diphenyl piperidine-4-one

A comparative study of the oxidation state of 2,6-diphenyl piperidine with or without 3-alkyl substituent was done, the oxidation with Mn(IV) reveals that the rate of oxidation of the former is higher than that of the 3-alkyl substituent (Table 5).

TABLE-5
Rate constants for the oxidation of 2, 6-diphenyl piperidine-4-one and 3-methyl-2, 6-diphenyl piperidine-4-one by Mn(IV)

[piperidone]	H_2SO_4	Oxidant Mn(IV)
2,6-diphenyl piperidine-4-one	0.3	49.6
	0.4	57.7
	0.5	71.1
3-methyl-2,6-diphenyl piperidine-4-one	0.3	32.1
	0.4	39.1
	0.5	60.2

In the present study the rate constant value is decreased by the introduction of methyl group at 3 positions in the piperidine ring system (Table6).

TABLE-6
Comparison of the bimolecular rate constants $K_0 \times 10^2$ L M-1 sec-1 for the oxidation of 2,6-diphenyl piperidine-4-one and 3-methyl- 2,6-diphenyl piperidine-4-one by Mn(IV) at 55°C

[Piperidone]	H_2SO_4		
	0.3	0.4	0.5
2,6-diphenyl piperidine-4-one	50.0	58.0	71.0
3-methyl-2,6-diphenyl piperidine-4-one	32.0	40.0	60.0

IV. CONCLUSION

The present work has been successful in the determining the mechanism of oxidation of substituted piperidones by Mn(IV) in acid medium. The reaction shows variations in acidity dependence. For Mn(IV) $Mn(OH)_3^+$ has been proposed as the active species. The rate of oxidation for the substituted piperidones the order: 2,6-di phenylpiperidinne-4-one > 3-methyl 2, 6-diphenyl piperidine - 4-one.

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