Kinetic study of oxidation of 2,6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one by Manganese (III) ion

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Abstract:
Kinetics of oxidation of 2,6-diphenylpiperidine-4-one and 3-Methyl-2,6-diphenylpiperidine-4-one by Mn (III) in acidic medium reveals that the kinetic orders are first order. The rate of reaction was formed to increase with increase acid concentration. The rate of oxidation of piperidone in aqueous sulphuric acid media is independent of added Mn(II).The results are rational by a mechanism involving intermediate products. The fallowing order of reactivity is observed: 2, 6-diphenylpiperidine-4-one > 3-Methyl-2,6-diphenylpiperidine-4-one.

Keywords: *Kinetics, Oxidation, 2, 6-diphenylpiperidine-4-one and 3-Methyl-2,6-diphenylpiperidine-4-one, Mn (III), Acid medium*

I.   Introduction

Transition metal ions are widely used as oxidants both in synthetic organic chemistry and analytical chemistry and have many industrial and research applications[1]. Also, many biological systems have transition metal ions as cofactors. Transition metals also can acquire high number of oxidation states which increases their tendency to form complexes[2]. Partial filled d-orbitals in transition metals participate in the electron withdrawing or donating process with reagents which activate their catalytic properties[3].One of the most extensively studied transition metals is Manganese. Under acidic conditions Mn^{2+} state is very stable; however, under alkaline condition Mn^{2+}state are readily oxidized to Mn^{3+} state. In solution, Mn^{3+} state disproportionate to Mn^{2+} state and Mn^{4+} state. Oxidation of Mn^{2+} state to Mn^{3+} state is faster in the oxygen rich environment than in inert environment suggesting different reaction kinetics are involved[4]. The kinetics of oxidation of diphenylmethane was explained and they determined that more than one manganese ions are concerned in the oxidation[5].Manganese (III) has been usually used for oxidation of many compounds collectively with carboxylic acids hydrocarbons, and hydroxyl compounds[6]. The transition and inner-transition metals of d and f orbital illustrate different oxidation states and form metal complexes[7]. Because of the existence of vacant d-orbital, these transition metal forms many coordination compound with ligands along with their electronic configuration[8]. The mechanism and kinetics for the oxidation of cyclohexanone by Mn (VII) and Mn (III) has been reported[9]. The study of reaction kinetics in chemical reactions is significant in deciding the reaction mechanisms. The kinetic study of change in concentrations of components of the reaction system with the change in time and outcomes are summarized in the form of rate expressions[10].

II.   Material and Method

2,6-Diphenylpiperidine-4-one and 3-Methyl 2,6-diphenylpiperidine-4-one, BDH(AR) were prepared in double distilled water according to Balaish and Noller and used[11,12].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. A solution of manganese (II) sulphate of 0.2 M concentration was prepared in 3 M sulphuric acid with suitable dilutions. A sufficient amount of this solution was taken in the vessels forming the anode and cathode compartments. The anode compartment, which had a sintered silica base was of 50 ml capacity while the cathode compartment was of about 200 ml. Electrolysis was carried out at a current density of about 12 mA cm^{-2} at a temperature of about 0°C. A milliampere relay was used to maintain the current density at this value. Manganese (III) sulphate solution cherry red in colour, obtained after electrolysis and stored in stoppered conical flasks at 0°C in the freezing compartment of the refrigerator.

Determination of Stoichiometry: Stoichiometry was determined by estimating the concentration of Mn(III) in reaction samples by titration. The concentration of Mn(III) was determined [13] after known intervals of time in order to find out the stoichiometry as a function of time. The initial concentration of Mn(III) was always determined before running into the stoichiometric samples. The stoichiometry was found to be 2:1 (oxidant ratio substrate) given in table 1. Stoichiometry of piperiodone oxidation temperature, at 35^0C.

$$I = 1.8M \qquad [piperiodone] = 6 \times 10^{-5} M$$
$$[Mn (III)] = 6 \times 10^{-4} M \qquad [H^+] = 0.5M$$

Table no. 1: Stoichiometrics of piperiodone oxidation

Time	$\dfrac{\Delta[Mn(III)]}{\Delta[piperidone]}$
2 hrs.	1.40
8 hrs.	1.89
20 hrs.	2.39
24 hrs.	2.59

Products of Oxidation: An acidic solution of piperidone was mixed with excess of manganese (III) solution. After 24 hours the reaction mixture was neutralized by adding sodium carbonate solution drop by drop. The solution as cooled well and alcohol was added. The product was isolated by filtration. The product was identified by esterification and GC/MS analysis.

Kinetics: It has been found that the rate of disappearance of Mn(III) in presence of excess of piperidone is always first order rate constants k_o were determined for varying order (Tables no 2 and 3). The values for the pseudo amounts of Mn(III) show that the rate of oxidation of piperidone in aqueous sulphuric acid media is independent of added Mn(II). The concentration of piperidones was varied from 0.01 to 0.02 M, keeping the Mn(III) concentration constant, first order plots were obtained. The plots of 1 + log O.D. against time are under these conditions, reproducible pseudo first order rate constants k_o were determined over a range of [H_2SO_4] 0.3 to linear. The pseudo 0.5 M keeping the ionic strength fixed at 1.8 M.

III.   Result and Discussion

Kinetics and mechanism of oxidation of 2,6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpipridine-4-one by Mn(III) in acidic medium have been investigated. The plot of 1+ log O.D against time shows (figure-1) a typical autocatalysed reaction with a conduction period. This has been formed to decrease with increasing temperature as well as acid concentration. This is indicative of coupled reaction where the intermediate has more reducing properties. Taking into account of the induction time for this autocatalysis, the 1+ log OD has redrawn for these observations which give a straight line.

Effect of varying concentration of oxidant on reaction rate: The reaction is formed to be first order with respect to oxidant. 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-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one

Effect of varying concentration of piperidones: Inspection of the rate constant shows that the K_o value rise markedly with increasing concentration of piperidones. The plot of K_o against (piperidones) yield straight line (Fig. 2 & 3) and hence the reaction is first order in (piperidones).

The bimolecular rate constant has been calculated from the slopes of these lines and is calculated in (Table no 4 & 5). The values for the pseudo-first order rate constants k_0 were determined for varying amounts of Mn(III) show that the rate of oxidation of piperidone in aqueous sulphuric acid media is independent of added Mn(II).

Effect of addition of Mn (II): The values for the pseudo-first order rate constants k_0 were determined for varying amounts of Mn(III) show that the rate of oxidation of piperidone in aqueous sulphuric acid media is independent of added Mn(II), (Table no 6).

Effect of varying concentration of acid on reaction rate: The kinetics of oxidation of the substituted piperidones has been studied at various acidities i.e 0.3, 0.4 and 0.5 M (Figure2 and 3) (Tables no 2 and 3). The rate of reaction was formed to increase with increase acid concentration the plot of overall bimolecular rate constant log K_2 against log [H^+] which gives a linear plot suggests that the aquo-manganese (III) ions are more reactive than the hydrolyzed species.

Table no 2: Values of observed rate constants $k_0 \times 10^4$ sec^{-1} for the oxidation of 3-methyl-2,6-diphenylpiperidine-4-one at I = 1.8 M, [Mn(III)] = 6 × 10^{-4} M

Temp. °C	[piperidone] × 10²M	[H₂SO₄] M		
		0.3	0.4	0.5
25	1.00	3.68	5.26	6.71
	1.25	4.18	6.51	7.33
	1.50	4.68	7.74	9.57
	1.75	5.18	8.98	11.14
	2.00	5.68	10.22	14.53
35	1.00	10.95	16.11	15.56
	1.25	13.19	17.03	17.46
	1.50	15.44	17.95	19.37
	1.75	17.68	18.85	21.27
	2.00	19.92	19.77	23.18
45	1.00	18.51	25.51	29.29
	1.25	22.88	31.06	36.51
	1.50	27.26	36.63	43.72
	1.75	31.64	42.19	50.93
	2.00	36.01	47.75	58.15
55	1.00	33.95	24.23	28.53
	1.25	38.61	42.18	38.81
	1.50	43.28	-	49.08
	1.75	47.95	58.17	59.36
	2.00	52.62	66.08	69.64

Table no3: Values of observed rate constants $k_o \times 10^4$ sec^{-1} for the oxidation of 2,6-diphenylpiperidine-4-one at I = 1.8 M(Mn(III)) = 6 × 10^{-4} M

| Temp. °C	[piperidone] × 10²M	[H₂SO₄] M		
		0.3	0.4	0.5
25	1.00	5.68	6.38	5.22
	1.25	6.21	7.14	6.72
	1.50	6.72	7.91	8.22
	1.75	7.22	8.68	9.71
	2.00	7.71	9.44	11.21
35	1.00	12.24	9.62	10.45
	1.25	13.47	12.92	15.66
	1.50	14.68	16.21	20.86
	1.75	15.93	19.54	-
	2.00	17.17	22.82	31.26
45	1.00	24.93	25.69	39.07
	1.25	28.54	32.17	45.25
	1.50	32.16	38.64	51.44
	1.75	-	45.12	57.62
	2.00	39.39	51.61	63.81
55	1.00	26.89	29.38	85.05
	1.25	34.98	52.23	105.01
	1.50	43.08	75.05	124.96
	1.75	51.16	97.89	145.01
	2.00	59.27	120.71	164.88
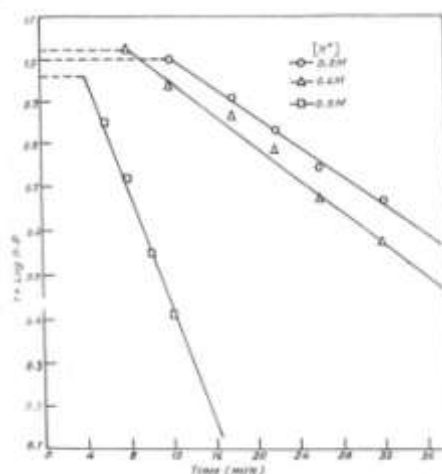
Figure 1: Plots of 1+ Log O.D. against time for the oxidation of 2, 6 diphenyl piperidine-4-one with Mn (III)
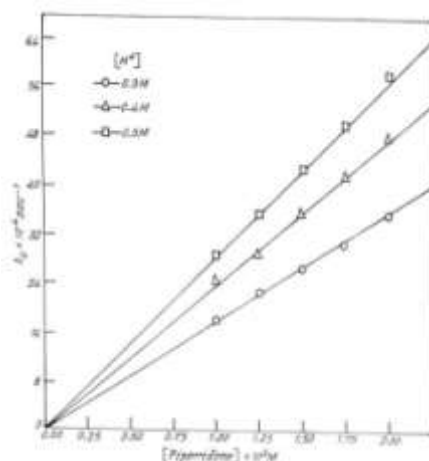

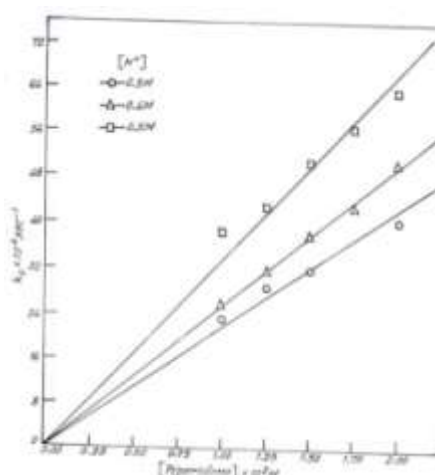**Figure2:** Plots of k_{obs} against [3-methyl-2,6-diphenyl piperidine-4-one] M at45^{0}C

Figure 3: Plots of k_{obs} against [2,6-diphenyl piperidine-4-one] M at45^{0}C

Table no4: Bimolecular rate constants k_o x 10^2 litre mole^{-1} sec^{-1} for the oxidation of 2,6-diphenylpiperidine-4-one

Temp. °C	[H₂SO₄] M		
	0.3	**0.4**	**0.5**
25	2.00	3.00	5.90
35	4.29	13.23	20.82
45	14.46	25.90	24.74
55	32.37	49.82	61.33

Table no 5: Bimolecular rate constants k_0 x 10^2 litre mole^{-1} sec^{-1} for the oxidation of 3-methyl-2,6-diphenylpiperidine-4-one

Temp. °C	[H₂SO₄]M		
	0.3	**0.4**	**0.5**
25	3.60	4.95	—
35	3.68	7.62	8.90
45	17.51	22.25	28.85
55	18.70	31.86	41.11

Table no 6: Effect of added Mn(II) on pseudo-first order rate constants [piperidone] =0.01 M; Temp. 55°C; [H+] = 0.5 M [Mn(III)] = 6 x 10^{-4}M; I = 1.8 M

[Mn(II)]M	k_o x 10^3 sec^{-1}
0.001	6.00
0.003	6.09
0.005	6.32
0.008	6.17

0.01	6.39

Effect of varying temperature on reaction rate: The oxidation rate of both 2,6-diphenylpiperedine-4-one and 3-methyl-2,6-diphenylpiperedine-4-one have been observed at various temperature i.e 25, 35, 45 and 55°C with increasing .The rate of reaction even found to increase temperature for all the substrate concentration at all acidities. The activation parameters have been calculated from the linear Arrhenius plots (Figure 4and 5), of log k_2 vs. T^{-1} (Tables no7 and 8).

The high negative entropies of activation for this oxidation resemble that of permanganate oxidation as mentioned in the earlier section. The fact that it is almost same entropies of activation in either case suggests that the oxidation proceeds by a similar mechanism even though in both the oxidations it was not possible to get either spectrophotometrically or kinetically any complex formation between the interacting species. It has been observed that the oxidation rate is directly proportional to the $[H^+]$ and the slope obtained from the plot of log k2 vs. log $[H^+]$ is almost equal to one. As the rate of oxidation is proportional to $[H^+]$ it is likely that the Mn(III) ion attacks the enolised ketone rather than the ketone itself unlike the oxidation of Mn(III) sulphate of cyclohexanone. It is apparent here that the ketone does not provide the easiest route for the one electron oxidation of enolised ketone. Perhaps the protonated NH^+ facilitates the enolisation unlike a simple cyclohexanone. Attack on the ketone or enol would give the same radical.

Table no 7: Values of the activation parameters for the oxidation of 2,6-diphenylpiperidine-4-one

$[H_2SO_4]M$	ΔE_a kJ mole^{-1}	ΔH^* kJ mole^{-1}	ΔS^* JK^{-1} mole^{-1}	ΔG^* kJ mole^{-1}
0.3	79.38 ± 1.40	64.37 ± 1.04	-49.40 ±3.68	79.55 ±2.08
0.4	86.06 ±1.20	76.83 - 1.21	-21.95 ±3.93	79.80 ±2.42
0.5	66.90 ±2.14	83.51 ±2.14	9.07 ±6.94	80.72 ±4.28

Table no8: Values of the activation parameters for the oxidation of 3-methyl-2,6-diphenylpiperidine-4-one

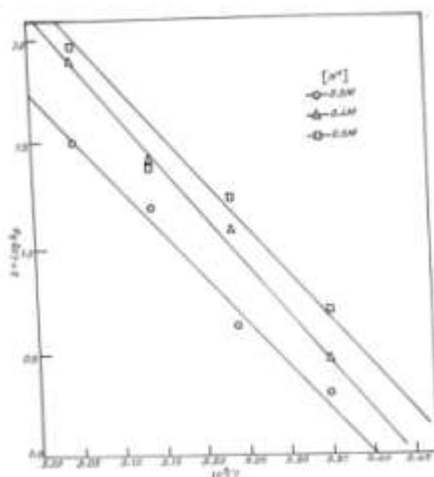| $[H_2SO_4]M$	ΔE_a kJ mole^{-1}	ΔH^* kJ mole^{-1}	ΔS^* JK^{-1} mole^{-1}	ΔG^* kJ mole^{-1}
0.3	54.13 ±2.78	51.58 ± 2.78	-105.08 ±9.02	84.00 ±5.56
0.4	54.13 ±1.20	51.58 ± 1.20	-98.98 ±3.88	82.05 ±2.40
0.5	67.88 ±2.45	65.33 ±2.45	-50.58 ±7.70	80.88 ±5.90

Figure 4: Arrhenius plot for 2,6-diphenylpiperidine-4-one oxidation

Collisions between reacting molecules occur while suitably oriented solvent molecules are clustered around the body collision, where polar solvent reactive molecules so that collision remains a two body collision but amounts to molecules take approximate positions and coordinately saturate the oxidant and the substrate at the transition state.

H* are found to very in the acidity range 0.3 to 0.5 M. But the values for free energies are seen to be constant (~ 80 kJ/mole). Values of enthalpies or free energies are all positive and show that these reactions in the possible schemes postulated are endothermic in nature as in the permanganate oxidation. In all the above oxidation processes there has been found little difference among the free energy changes, and a mutual compensation of free energies have been maintained by changes in enthalpies of activation[14].
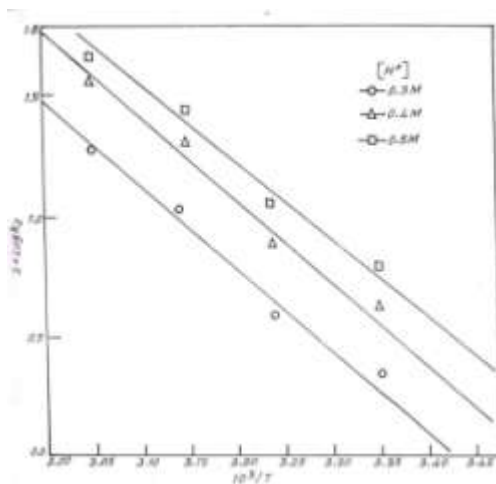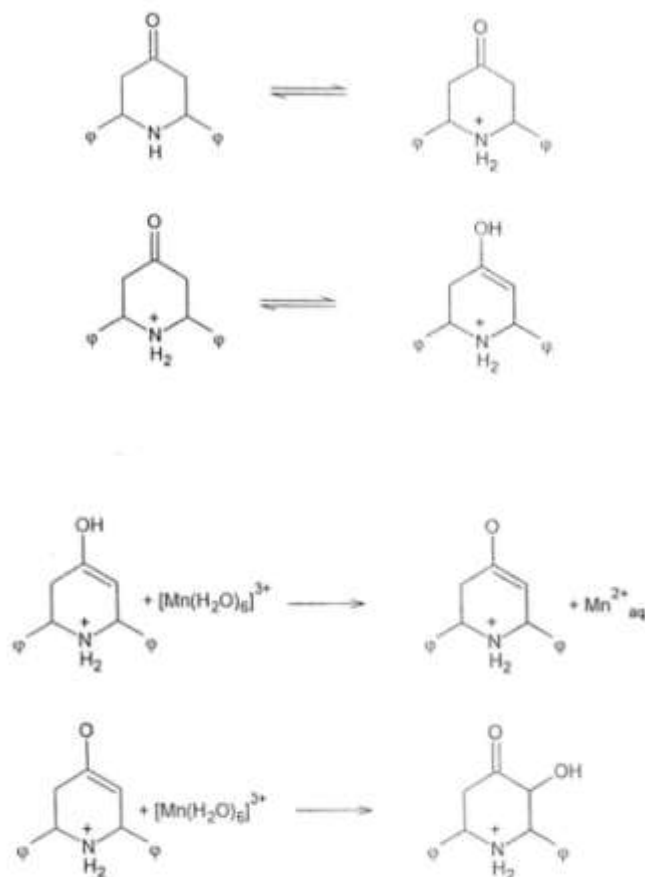
Figure 5: Arrhenius plot for 3-methyl-2,6-diphenyl piperidine-4-one oxidation

Mechanistic Pathway of oxidation: Mn(III) oxidations are similar to that of cobalt (III) like many one-equivalent oxidants. This mechanism can be given as:

The redox potentials of Mn(III)/ Mn(II) is 1.511 V and that of MnO_4^- as Mn(II)/Mn(III) is 1.52 V[15].

Oxidation rate of 2, 6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one: The oxidation state of 2,6- diphenyl piperidine-4-one and3-methyl-2,6- diphenyl piperidine-4-one with Mn(III) reveals that the rate of oxidation of the former is higher than that of 3-methyl-2,6- diphenyl piperidine-4-one (Table 9).

Table no 9: Oxidation rate of 2,6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one by Mn(III)

[piperidone]	H₂SO₄	Oxidant Mn(III)
2,6-diphenylpiperidine-4-one	0.3	32.5
	0.4	50.0
	0.5	61.3
3-methyl-2,6-diphenylpiperidine-4-one	0.3	19.0
	0.4	32.0
	0.5	41.0

IV.   Conclusion

This research work has been successfully conclude the mechanisms of oxidation of substituted piperidones by Mn(III) in acid media. The reaction represents variations in acidity dependence. The rate of oxidation for the substituted piperidones shows that 2,6-diphenylpiperidine-4-one is reactive than 3-methyl-2,6-diphenylpiperidine-4-one.

References

[1].   Dr. M. R. Ambedkar, Dr. K. Kumar and Dr. R. Kumari, To Find out The Methodology of Oxidation of Substituted Piperidones by Mn (Iv) In Sulphuric Acid Medium, *International Journal of Chemical Studies*, 11 (3): 27-36, 2023.
[2].   S. Patra Et.Al, Role of Transition Metal Nanocomposites In Organic Reactions: A State of Art As An Alternative to Conventional Catalysts, *Results In Chemistry*, Volume 6, 2023.
[3].   S. Yadav, N. Rani, K. Saini, A Review on Transition Metal Oxides Based Nanocomposites, Their Synthesis Techniques, Different Morphologies and Potential Applications, *Mater. Sci. Eng.*, 1225, 2022.
[4].   M. Wekesa, Md. Jamaluddin, and H. F. Sobhi, An Insight Into Mn (Ii) Chemistry: A Study of Reaction Kinetics Under Alkaline Conditions, *Int J. Chem Res*, Vol 2, Issue 4, 2011, 34-37.
[5].   A. Jain, G. Tazwar, V. Devra, Kinetics and Mechanism of Permanganate Oxidation of Nalidixic Acid In Aqueous Alkaline Medium, *Journal of Applied Pharmaceutical Science*, Vol. 7 (01),135-143, 2017.
[6].   D. Singh And S. Rani, Solvent Effects on The Oxidation Rates of 2,6-Diphenylpiperidine-4- One And 3-Methyl-2,6-Diphenylpiperidine-4-One By Mn(VII) In Acetic Acid Media, *IOSR Journal of Applied Chemistry*, Volume 13, Issue 8 Ser. I, Pp 64-67, 2020.
[7].   K. Martin, Highest Oxidation States of The Transition Metal Elements, Coordination Chemistry Reviews, 253(5):606-624, 2009.
[8].   A. K. Singhal, A Complete Resource Book For Jee Main: Chemistry, Ch-5, 2018.
[9].   O. C. Rafael Et.Al, A New Mixed-Valence Mn(II)Mn(III) Compound With Catalase And Superoxide Dismutase Activities, *Front Chem*, 6: 491, 2018.
[10].   S. Rani and B. K. Sharma, Kinetic Study of Oxidation of 2, 6-Diphenyl-Piperidine-4-One And 3-Methyl 2,6-Diphenyl-Piperidine-4-One By Manganese (IV) Ion, *International Journal of Latest Technology In Engineering, Management & Applied Science* , Volume VI, Issue I, 2017.
[11].   V. Balaiah and C. Noller; *J. Am. Chem. Soc.*, 3853, 1948.
[12].   A.I. Vogel, A Text Book of Practical Organic Chemistry, 3rd Edn., Elbs, P. 640, 1971.
[13].   H. Diebler and N. Sutin; *J. Phys. Chem.*, 68, 174, 1964.
[14].   R. Devarajan, P. Elayaperumal, T. Balakrishnan and M. Santappa; *Indian J. Chem.*, 18a, 488, 1979.
[15].   G. Milazzo And S. Caroli, "Tables of Standard Electrode Potentials", *John Wiley And Sons Inc*, P. 302, 1978.