

Comparative Study of Kinetics for Oxidation of 3-Methyl 2,6-Diphenylpiperidine-4-one and 2,6-Diphenylpiperidine-4-one by Mn(III) and Mn(IV) 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 (IV) and Mn (III) in acidic medium shows that reactions are of first order reaction. In present study it was observed that rate of reaction and acid concentration is directly proportional to each other. The presence of 3-methyl substituent decreases the rate of oxidation with Mn(IV) and Mn(III). The results are rational by a mechanism involving intermediate products. On the basis of result is clear that the rate of oxidation is higher by Mn(IV) than Mn(III) in case of 2,6-Diphenylpiperidine-4-one then 3-Methyl-2,6-Diphenylpiperidine-4-one.

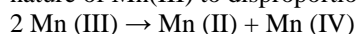
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I. Introduction

Transition metal ions are easily and inexpensively prepared and stored and their reactions can be suitably controlled by the right choice of oxidants and reaction conditions¹. Electronic configurations of unpaired electrons are said to be paramagnetic and respond to the proximity of magnets. Fully paired electrons are diamagnetic and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state² is? Mn(III) is viewed as a potentially strong oxidant due to its high reduction potential³, but it is very unstable in aqueous solution because of its fast disproportionate to Mn₂O and MnO₂. These Mn(III) ligand complexes are often directly used as oxidants for oxidation purposes, such as oxidative degradation of contaminants in wastewater⁴. The variety of an oxidant is resolute by the nature of the substrate, the preferred products and condition of medium and temperature. There was little information on the nature of the strongly oxidizing Mn(III) and the possible reason for this neglect lies in the nature of Mn(III) to disproportionate.



This directs to retardation of oxidation by Mn (II) ions in the oxidation of formaldehyde. Manganese(III) has been widely used for the oxidation of some classes of compounds with hydrocarbons, carboxylic acids and hydroxyl compounds⁵. The highest oxidation state of manganese corresponds to the total number of 3d and 4s electrons. The (VII) state occurs only in the oxo-compounds MnO₄⁻¹, Mn₂O₇, MnO₃Cl and MnO₃F. Mn(VII) is powerfully oxidizing usually being reduced to Mn(II). The intermediate oxidation states are known but only a few compounds of Mn(V) have been characterized, Mn(V) species are frequently postulated as intermediates in the reduction of permanganates. In Mn(III) and Mn(IV) the most common geometry is octahedral⁶. Square pyramidal structures are possible in the case of Mn(III) as in [Et₄N]₂MnCl₅. The mechanism and kinetics for the oxidation of cyclohexanone by Mn(IV) and Mn(III) has been explained by J.S Littler⁷. Here, comparison for mechanism in acidic medium for the oxidation of 2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one by Mn(III) and Mn (IV) has been represented.

II. Material and Method

All solutions were prepared with double distilled water and as per the requirements. We use the following reagents during this research work Sulphuric Acid, Sodium Sulphate, Potassium Permanganate, Manganese(II) Sulphate, Ferrous Ammonium Sulphate, Iron(II) Sulphate Solution, Sodium Thiosulphate, Potassium Dichromate, Sodium Carbonate, Oxalic Acid, 2,6-Diphenylpiperidine-4-one, 3-Methyl-2,6-Diphenylpiperidine-4-one, Raney Nickel Catalyst, o-Phenylenediamine, Purification of Acetic Acid⁸.

Preparation of Manganese (III) Sulphate: 0.05 M solution of manganese(III) sulphate was prepared⁹ using the standard anodic oxidation of 0.2 M solution of manganese(II) sulphate in 5 M sulphuric acid performed in an undivided cell with a platinum foil anode and a thin platinum spiral cathode. The manganese(III) sulphate solution contained an excess but known concentration of manganese (II) sulphate to suppress the disproportionation reaction. Though the solution appeared to be stable for more than a month at $[H^+] > 5.0$ M, solution of manganese(III) sulphate prepared a fresh daily was used in the experiments. Triply distilled water was used for preparing aqueous solutions.

Manganese (IV) Solution: 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.

Determination of Manganese (III) and Manganese (IV): Manganese (III) sulphate was determined titrimetrically by using standard sodium thiosulphate¹⁰. Manganese (IV) solution was also determined titrimetrically^{11,12} by using Iron (II) sulphate solution. Ferrion indicator was used to detect the end point.

Stoichiometry determination: It was determined by calculating the concentration of Mn(IV) and Mn(III) in samples by titration. The concentration of Mn(IV) and Mn(III) was calculated after different time intervals to get the stoichiometry as a function of time. Before running samples into the stoichiometric, the initial concentration of Mn(IV) and Mn(III) was always determined. Table no 1 shows that the stoichiometry ratio for oxidant and substrate was noticed approx 2:1 for Mn(IV) and Mn(III) both.

$$\begin{aligned} &\text{Temperature } 35^{\circ}\text{C, } I = 1.8\text{M,} \\ &\text{Conc. of piperidone} = 6 \times 10^{-5}\text{M, } [H^+] = 0.5\text{M} \\ &[Mn(IV)] = 6 \times 10^{-4}\text{M, } [Mn(III)] = 6 \times 10^{-4} \end{aligned}$$

Table no 1: Stoichiometry ratio

Time	$\frac{\Delta[Mn(IV)]}{\Delta[Piperidine]}$
5 hrs	0.951
20 hrs	1.257
25 hrs	2.068
Time	$\frac{\Delta[Mn(III)]}{\Delta[Piperidine]}$
2 hrs.	1.40
8 hrs.	1.89
20 hrs.	2.39
24 hrs.	2.59

Kinetic Measurements: All kinetic measurements^{13, 14} were performed spectrophotometrically at 525nm, 420 nm and 380 nm using either an SP 700 spectrophotometer or an SP 500 spectrophotometer.

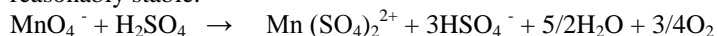
Calculation of Thermodynamic Parameter: The energy of activation ΔE_a is correlated¹⁵ with the rate constant by the Arrhenius equation

$$\begin{aligned} k &= A e^{-\Delta E_a/RT} \\ \text{Or, } \log k &= \log A - \Delta E_a/2.303 RT \end{aligned}$$

Where, k is the rate constant of any order, log A is the combined effect of frequency of collision and steric factor, R is the universal gas constant = 1.987 cal. Deg⁻¹ mole⁻¹ and T is the absolute temperature.

III. Results and Discussion

Oxidation of piperidones by Mn (IV) and Mn(III): 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. The use of Mn (IV) as an oxidimetric reagent is not known till recently due to difficulties in preparation of a fairly stable solution. Mn (IV) is formed due to decomposition of $KMnO_4$ in 8-11 M sulphuric acid according to equation given in reasonably stable.



The redox potential of Mn (IV) has been found to be 1.577 V. Kinetic studies regarding such powerful oxidizing agent is rather scanty. The UV-visible spectra of Mn (IV) in 0.5 M H_2SO_4 was scanned in the entire wavelength of 200 to 800nm. Similar spectra were scanned in the following substrates:

1. Mn (IV) in 0.5 M H_2SO_4 + 0.01 M solution of 2,6-diphenyl piperidine-4-one
2. Mn (IV) in 0.5 M H_2SO_4 + 0.01 M solution of 3-methyl-2,6-diphenyl piperidine-4-one

Kinetics: The rate of disappearance of both Mn(IV) and Mn(III) in the presence of [piperidone] excess (30 times) of piperidone was found to be first order (Tables no 3). Different Concentration of piperidine from 0.01 M - 0.02M was used, and the measurements were carried out at three different acidic ranges between 0.3M and 0.5M, at constant ionic strength 1.8 M after the addition of Na₂SO₄ solution. The piperidone concentration was varied from 0.01 to 0.02 M, keeping the Mn(IV) and Mn(III) concentration constant. Under these conditions reproducible pseudo first order plots were obtained. The plots of 1 + log O.D. against time are linear (Figures1 (a) and (b)). The pseudo first order rate constants k_{obs} were determined over a range of [H₂SO₄] (0.3 to 0.5M) keeping the ionic strength constant at 1.8 M. The values of k_o at various acidities are collected in tables no. 2 (a) and (b). The plots of k_o against [piperidone] at constant acidity and constant ionic strength were found to be linear (Figures2(a) and (b)) and the bimolecular rate constants k_2 have been calculated from the slopes of these lines are collected in tables no. 3 (a) and (b).

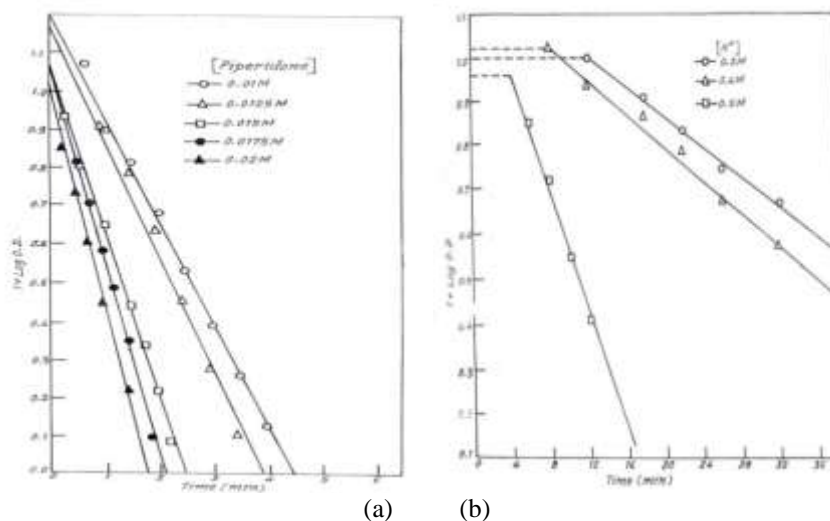


Figure 1a & b: Plots of 1+ Log O.D. against time for 2, 6-diphenyl piperidine-4-one oxidation by Mn (IV) and Mn(III) at 55 °C, I = 1.8M, [H⁺] = 0.5M

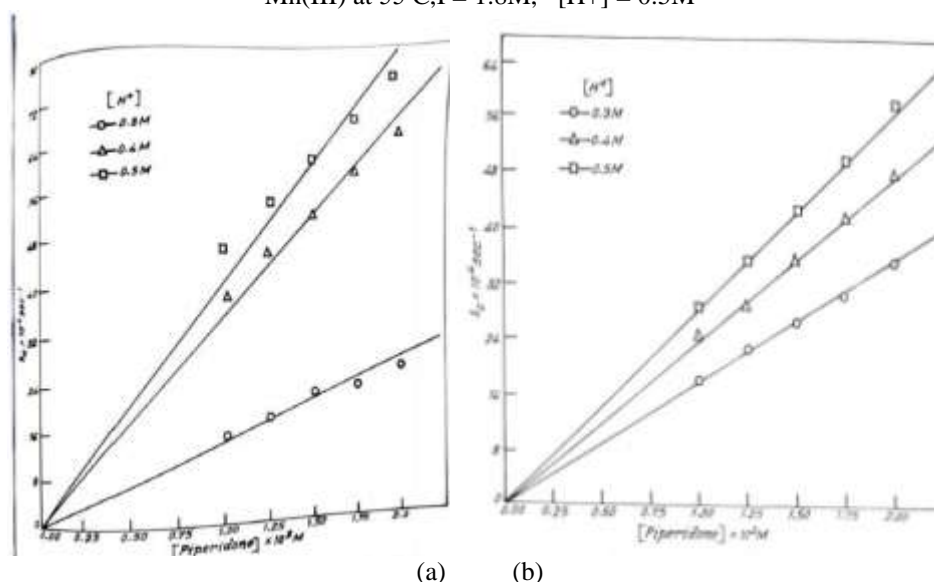


Figure 2 a & b: Plots of k_{obs} against [3-methyl-2,6-diphenyl piperidine-4-one] by Mn (IV) and Mn(III)M at 45 °C

Study of rate constant indicates that the K_0 values increased noticeable with increasing concentration of piperidones. Table no 2a and 2b show values of K_0 at various acidities are composed for both Mn(IV) and Mn(III). The graph of K_0 against concentration of piperidone at constant acidity and ionic strength were found to be linear (Figure 2a and b), hence the reaction is 1st order in piperidone.

Table no 2a: Value of rate constants $k_0 \times 10^4 \text{ sec}^{-1}$ for the oxidation of 2, 6-diphenylpiperidine-4-one at $I= 1.8 \text{ M}$ and $[\text{Mn(IV)}] = [\text{Mn(III)}] = 6 \times 10^{-4} \text{ M}$

Temp. °C	[piperidone] $\times 10^2 \text{ M}$	[H ₂ SO ₄] M for Mn(IV)			[H ₂ SO ₄] M for Mn(III)		
		0.3	0.4	0.5	0.3	0.4	0.5
35	1.00	-	14.16	18.20	12.24	9.62	10.45
	1.25	-	16.56	24.51	13.47	12.92	15.66
	1.50	16.46	18.96	30.39	14.68	16.21	20.86
	1.75	17.62	21.36	34.23	15.93	19.54	-
	2.00	18.80	28.29	38.18	17.17	22.82	31.26
45	1.00	14.57	39.10	48.30	24.93	25.69	39.07
	1.25	17.07	45.44	54.79	28.54	32.17	45.25
	1.50	19.53	51.76	61.28	32.16	38.64	51.44
	1.75	22.00	58.06	67.78	-	45.12	57.62
	2.00	24.48	64.38	74.28	39.39	51.61	63.81
55	1.00	73.71	80.96	108.48	26.89	29.38	85.05
	1.25	81.62	90.78	126.13	34.98	52.23	105.01
	1.50	89.49	100.48	143.77	43.08	75.05	124.96
	1.75	97.48	110.38	161.37	51.16	97.89	145.01
	2.00	105.28	120.20	178.89	59.27	120.71	164.88

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

Temp. °C	[piperidone] $\times 10^2 \text{ M}$	[H ₂ SO ₄] M for Mn(IV)			[H ₂ SO ₄] M for Mn(III)		
		0.3	0.4	0.5	0.3	0.4	0.5
35	1.00	12.84	11.80	14.39	10.95	16.11	15.56
	1.25	15.08	14.98	19.19	13.19	17.03	17.46
	1.50	17.30	18.19	23.92	15.44	17.95	19.37
	1.75	19.48	21.34	28.69	17.68	18.85	21.27
	2.00	21.71	24.54	33.56	19.92	19.77	23.18
45	1.00	26.36	28.79	37.84	18.51	25.51	29.29
	1.25	32.88	40.93	43.33	22.88	31.06	36.51
	1.50	39.40	48.82	53.06	27.26	36.63	43.72
	1.75	45.94	54.30	65.22	31.64	42.19	50.93
	2.00	52.44	59.80	77.36	36.01	47.75	58.15
55	1.00	52.58	71.14	68.60	33.95	24.23	28.53
	1.25	64.97	85.53	86.34	38.61	42.18	38.81
	1.50	77.33	99.00	104.11	43.28	-	49.08
	1.75	89.73	114.20	121.82	47.95	58.17	59.36
	2.00	102.11	128.66	139.56	52.62	66.08	69.64

Table no 3a: Bimolecular rate constants $K_0 \times 10^2 \text{ L}^{-1} \text{ sec}^{-1}$ for the oxidation of 2,6-diphenyl piperidine-4-one

Temp. °C	[H ₂ SO ₄] M for Mn(IV)			[H ₂ SO ₄] M for Mn(III)		
	0.3	0.4	0.5	0.3	0.4	0.5
25	2.29	3.04	3.34	2.00	3.00	5.90
35	8.84	12.75	19.00	4.29	13.23	20.82
45	21.89	26.04	48.52	14.46	25.90	24.74
55	49.54	57.53	70.98	32.37	49.82	61.33

Table no 3b: Bimolecular rate constants $K_0 \times 10^2 \text{ L}^{-1} \text{ sec}^{-1}$ for the oxidation of 3-methyl- 2,6-diphenyl piperidine-4-one

Temp. °C	[H ₂ SO ₄] M for Mn(IV)			[H ₂ SO ₄] M for Mn(III)		
	0.3	0.4	0.5	0.3	0.4	0.5
25	1.36	2.77	3.08	4.95	-	4.95
35	4.62	9.52	10.31	7.62	8.90	7.62
45	9.92	25.23	25.96	22.25	28.85	22.25
55	31.63	39.24	60.46	31.86	41.11	31.86

Effect of Temperature: The oxidation rates of 2,6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one with Mn(IV) and Mn(III) have been measured at four temperatures in the range 25-55 °C and the rate constants are recorded in tables 3(a) and (b). 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 (Figures 3 and 4) of $\log k_2$ vs T^{-1} (Tables 5 (a) and (b)).

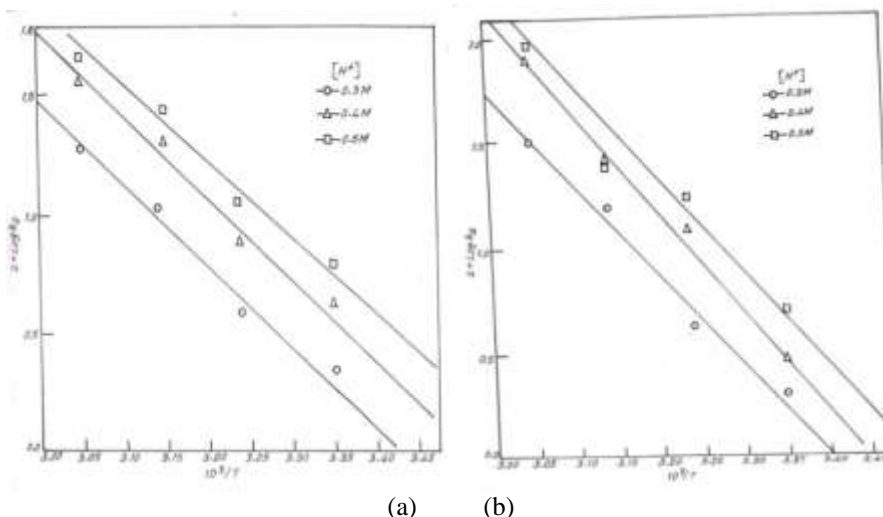


Figure 3 a & b: Arrhenius plot for 3-methyl-2,6-diphenylpiperidine-4-one and 2,6-diphenylpiperidine-4-one oxidation by Mn(III)

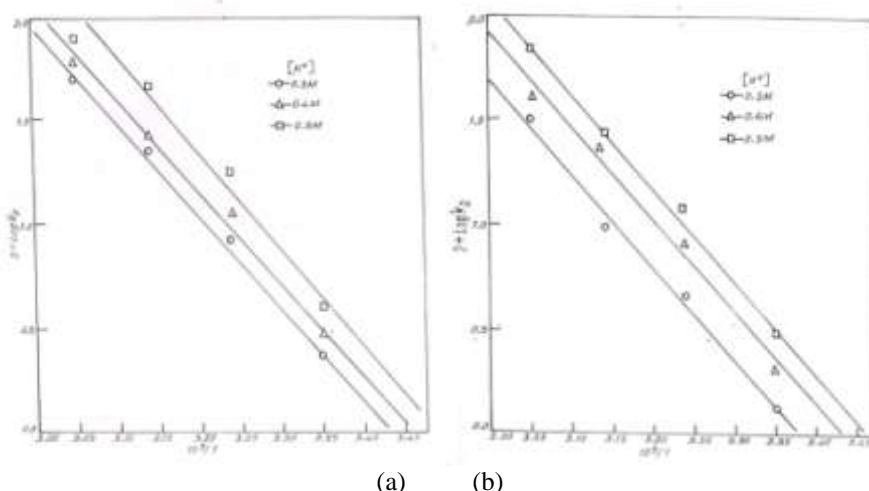


Figure 3 a & b: Arrhenius plot for 3-methyl-2,6-diphenyl piperidine-4-one and 2,6-diphenyl piperidine-4-one oxidation by Mn(IV)

Acidity Dependence: The kinetics of oxidation of the substituted piperidones has been studied in the acidity range 0.3 to 0.5 M (Figures 3a and b) and the data are collected in tables 3 (a) and (b). The rate of reaction was found to increase with acid concentration in both the cases and 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.

Rate Law: On the basis of the above experimental data the rate expression is given by

$$-\frac{d[Mn(IV)]}{dt} = k [piperidone][Mn(IV)][H^+]$$

Activation Parameters: A linear plot is obtained for $\log k_2$ against $1/T$ °K (Figures 3 a and 3b). The values of ΔE_a , ΔS^* , ΔH^* and ΔG^* are collected in tables 4 (a) and (b).

Table no 4a: Values of activation parameters for the oxidation of 2,6-diphenyl piperidine-4-one

[H ₂ SO ₄] M	ΔE_a kJ mole-1	ΔH^* kJ mole-1	ΔS^* JK-1 mole-1	ΔG^* kJ mole-1
Mn(IV)				
0.3	67.54 ± 0.71	67.38 ± 0.71	-14.23 ± 3.72	81.58 ± 1.35
0.4	78.91 ± 1.12	81.40 ± 1.12	-0.82 ± 2.24	81.64 ± 2.34
0.5	89.89 ± 2.44	81.40 ± 2.44	6.62 ± 7.81	82.05 ± 4.88
Mn(III)				
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 no 4b: Values of activation parameters for the oxidation of 3-methyl-2,6-diphenyl piperidine-4-one

[H ₂ SO ₄] M	ΔE_a kJ mole ⁻¹	ΔH^* kJ mole ⁻¹	ΔS^* JK ⁻¹ mole ⁻¹	ΔG^* kJ mole ⁻¹
Mn(IV)				
0.3	85.63 ± 0.94	79.50 ± 0.94	-10.14 ± 6.24	83.24 ± 1.85
0.4	82.09 ± 1.88	83.10 ± 1.88	-1.73 ± 3.02	81.58 ± 3.63
0.5	85.51 ± 2.22	82.96 ± 0.94	4.74 ± 8.16	81.40 ± 1.80
Mn(III)				
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

The low entropies of activation in the present study clearly suggest that there was no complex formation between the interacting species. The values of ΔH^* and ΔG^* show that the reaction in the possible scheme proposed is endothermic in nature; the reactions are thus expected to be more facilitated at higher temperatures. In such cases the transition state resembles the products more closely and hence changes which will increase the stability of the products will increase the rate of the reaction. Further the nature of product formation is in accordance with the enthalpy change and the available free energy as experimentally found.

Oxidation rate of 2,6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one: An evaluation of oxidation state of 2,6-diphenylpiperidine with or without 3-alkyl substituent during the basis of oxidation with Mn(IV) and Mn(III) expose that the rate of oxidation of the former is higher than that of the 3-alkyl substituent, table no 5.

Table no 5: Rate constants for the oxidation of 2,6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one by Mn(IV) and Mn(III)

piperidone	H ₂ SO ₄	Oxidant	
		Mn(IV)	Mn(III)
2,6- diphenyl piperidine-4-one	0.3	49.4	32.5
	0.4	57.4	50.0
	0.5	70.9	61.3
3-methyl-2,6- diphenyl piperidine-4-one	0.3	31.9	19.0
	0.4	38.9	32.0
	0.5	59.9	41.0

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

IV. Conclusions

The present investigations have been successful in determining the mechanisms of oxidation of substituted piperidones by Mn (IV) and Mn (III) in sulphuric acid media. The reaction shows variations in acidity dependence. The rate of oxidation for the substituted piperidones follow the order 2,6-diphenylpiperidine-4-one > 3-methyl-2,6-diphenylpiperidine-4-one, and the oxidizing capacity of oxidants in the expected order of Mn (IV) > Mn (III).

References

- [1]. Ambedkar Dr. M. R., Kumar Dr. K. and Kumari Dr. R., 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]. Oxtoby D., Gillis H. P., Campion, A. Principles Of Modern Chemistry, 6th Ed. Thomson Brooks/Cole, Belmont, 313-318, 2008.
- [3]. Shifa Z., Huichun Z., New Insight Into The Reactivity Of Mn(III) In Bisulfite/Permanganate For Organic Compounds Oxidation: The Catalytic Role Of Bisulfite and Oxygen, *Water Research*, 148, 198-207, 2019..
- [4]. Gao, Y., Jiang, J., Zhou, Y., Pang, S., Technology, J.C., Does Soluble Mn (III) Oxidant Formed In Situ Account For Enhanced Transformation Of Triclosan by Mn (VII) In The Presence Of Ligands? *Environ. Sci. Technol.* 52, 4785-4793, 2018.
- [5]. Kemp T.J., Waters W.A. *J Chem. Soc.*, 339, 1964.
- [6]. Vinod K., Soni R. and Monika C., Kinetic Study Of Oxidation Of 2,6-Diphenylpiperidine-4-One And 3-Methyl-2,6-Diphenylpiperidine-4-One By Manganese (III) Ion, *IOSR Journal Of Applied Chemistry*, Vol. 17, (3), Pp 01-07, 2024.
- [7]. Rafael O. C. Et.Al, A New Mixed-Valence Mn(II), Mn(III) Compound With Catalase And Superoxide Dismutase Activities, *Front Chem*, 6: 491, 2018.
- [8]. Vogel A.I. A Text Book Of Practical Organic Chemistry, 3rd, Edn., Elbs., 640, 1971.
- [9]. Kumara M. N., Channe G D, Thimme G A and Rangappa K S, Anodically Generated Manganese (III) Sulphate For The Oxidation Of Dipeptides In Aqueous Sulphuric Acid Medium: A Kinetic Study, *J. Chem. Sci.*, Vol. 116 (1), 49-53, 2004.
- [10]. Diebler H., Sutin N., *J Phys. Chem.*, 68 (1), 174, 1964.