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To find out the methodology of oxidation of substituted piperidones by Mn (IV) in sulphuric acid medium

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Abstract
Transition metal ions are widely used as oxidants both in synthetic organic chemistry and analytical chemistry. In the present work we have undertaken the kinetic and mechanistic studies of the oxidation of 2,6–Diphenyl piperidine–4–one and 3–methyl–2,6–Diphenyl piperidine–4–one by Manganese (IV) in sulphuric acid media.The kinetic studies with Mn (IV) have been carried out in aqueous sulphuric acid in the range of 0.3 to 0.5 M, in the temperature range of 25 to 55 °C. The reaction show variations in acidity dependence. The acid permanganate seems to be the active species in the case of Mn (VII) oxidations whereas in the case of Mn (III) the aquo species seems to be the active species. As for Mn (IV), Mn $(OH)_3^+$ has been proposed as the active species. Further in all these cases it has been assumed that the monomeric form of Mn (IV) or Mn (III) predominantes in the oxidation process and all the rate equations have been derived on the basis of this concept. Kinetic studies have been carried out spectrophotometrically using Unicam SP 700 oran SP 500 spectrophotometer (Series 2) at 520, 380 and 420nm. Electrolysis was carried out at a current density of 12 mA/cm² at 0 °C.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) > Mn (VII).

Keywords: Oxidation by Transition Metal Mn, The oxidation of 2,6–Diphenyl piperidine–4–one by Mn (IV), The oxidation of 3–methyl–2,6–Diphenyl piperidine–4–one by Mn (IV)

1. Introduction

Transition metal ions are widely used as oxidants both in synthetic organic chemistry and analytical chemistry. 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 conditions. Stemming from the pioneering work of Westheimer and later studies made by Waters, Wells and McAuley, there has been much interest shown in kinetic and mechanistic features of the oxidation reactions of organic substrates with transition metal ions. This subject has been reviewed several times and articles have appeared in the books of Waters [1], Turney[2], Wiberg[3], Stewart[4], Bamford[5] and Benson [6].

1.1 Types of Oxidants

In electron transfer steps, metal ion oxidants function as one–equivalent or two–equivalent reagents. One–equivalent oxidants are those which accept a single electron by direct electon transfer or by interaction with a hydrogen atom. Two equivalent oxidants accept two electrons from a substrate or alternatively, they accept two hydrogen ions or loose an oxygen atom.Some metal ions react only by one–equivalent steps, some by two–equivalent steps and some metal ions oxidize substrates by either one– equivalent or two–equivalent steps. A classification of some metal ions in this respect [7] is given in (Table 1).

Table 1: Oxidizing Metal Ions

| One–equivalent	Two–equivalent	One– or Two–equivalent
Ce (IV)	Tl (III)	Cr (VI)
Co (III)	Pb (IV)	Mn (VII)
Fe (III)		Pt (IV)
Mn (III)		V (V)

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1.2 Types of Mechanisms

1.2.1 Mechanism of Oxidation: The simplest mode of explaining the common features in the oxidation of organic compounds such as aldehydes or ketones assumes either the direct transfer of hydrogen from the organic compound to the oxidizing agent or of oxygen from oxidizing agent to the organic compound. Electron transfer reactions of metal ions are of two basic types. These have been known as outer−sphere and inner−sphere processes. In principle, an outer sphere process occurs with substitution−inert oxidants whose co−ordiantion shall remain unchanged in forming the activated complex. On the other hand, in an inner−sphere process substitution takes place prior to electron transfer [8].The selection of an oxidant is determined by the nature of the substrate, the desired products and conditions of medium and temperature.Recently, there was little information on the nature of the strongly oxidizing Mn (III). The probable reason for this neglect lies in the tendency of Mn (III) to disproportionate.

$$2 \text{ Mn (III)} \rightleftharpoons \text{Mn (II)} + \text{Mn (IV)}$$
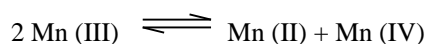
This leads to the retardation of oxidation by Mn (II) ions in the oxidation of formaldehyde[9]. Manganese (III) has been extensively used for the oxidation of several classes of compounds including hydrocarbons, hydroxyl compounds and carboxylic acids.
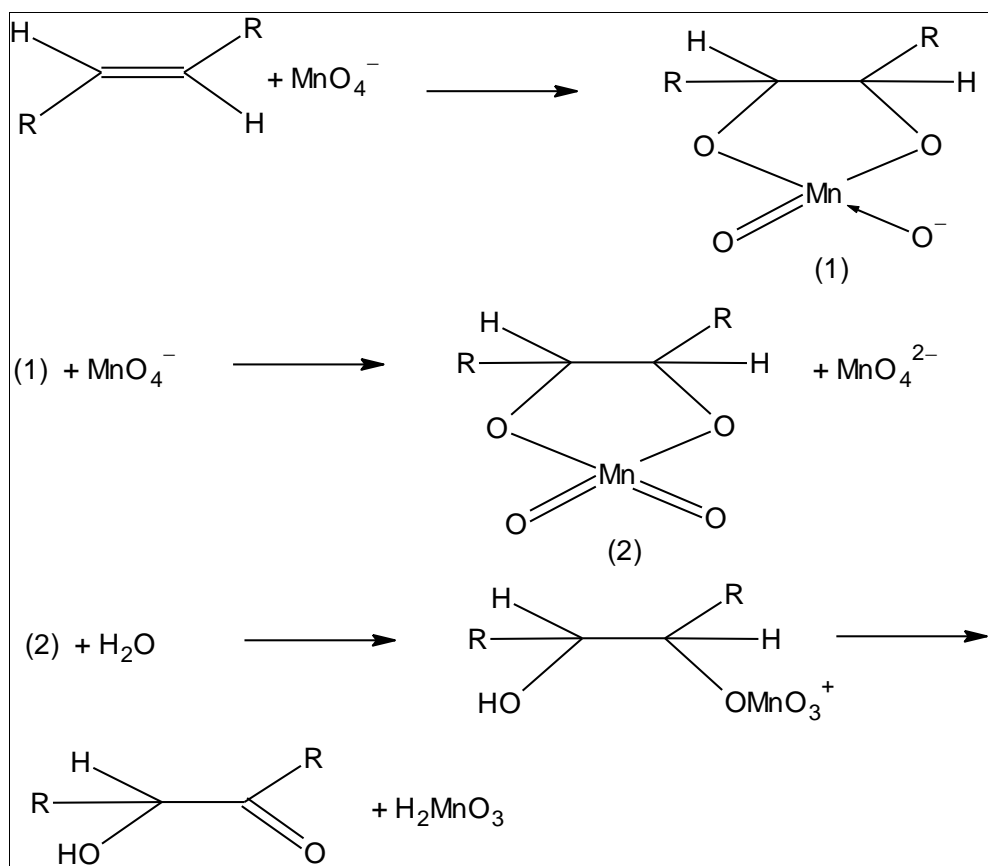
Scheme I
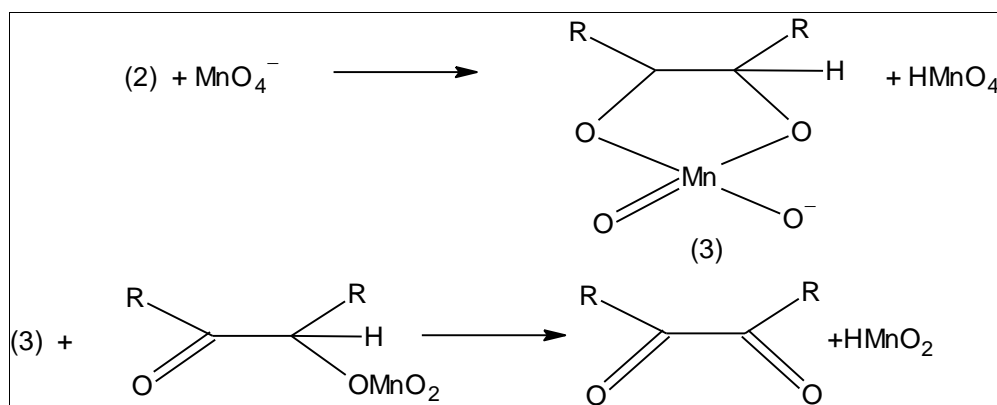
Scheme II

Lee *et al*. [10] studied the mechanism of oxidation of alkenes with potassium permanganate. The products obtained from the oxidation of terminal alkenes were found to be corresponding carboxylic acids, with less carbon, while non−terminal alkenes gave diones, diols and ketols as well as carboxylic acids.The oxidation of alkenes in aqueous solutions have indicated that ketols are formed by the reaction sequence depicted in Scheme I [3, 11].
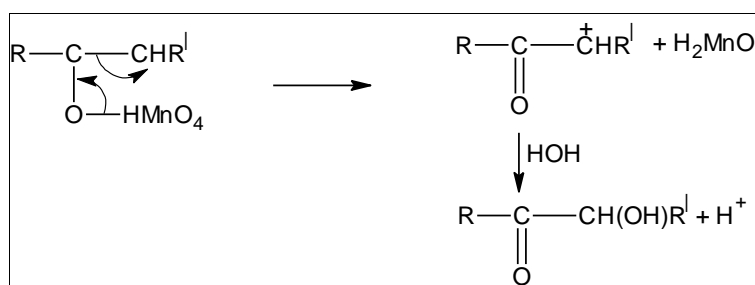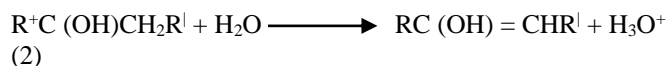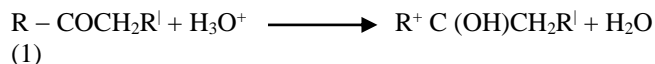
In the absence of water, the hydrolysis of (1) was prevented and further reaction with oxidant gave the dione as suggested in Scheme II. The oxidation of (2) has been depicted as a hydrogen atom abstraction in analogy with the oxidation of alcohols [3].
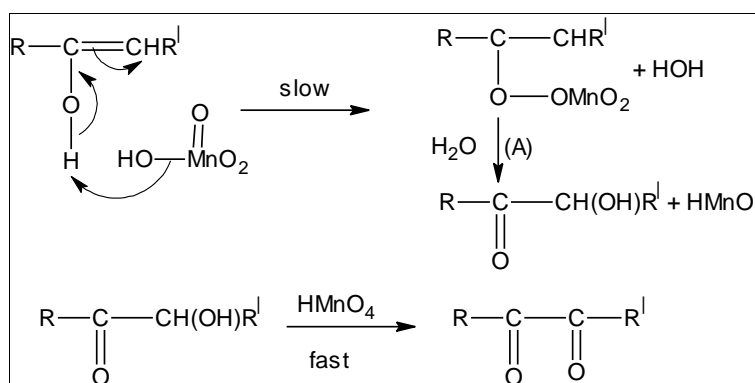
1.3 Oxidation States

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 MnO_4^-, Mn_2O_7, MnO_3Cl and MnO_3F. 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, nevertheless, Mn (V) species are frequently postulated as intermediates in the reduction of permanganates. In Mn (II), Mn (III) and Mn (IV) the most common geometry is octahedral. Square pyramidal structures are possible in the

case of Mn (III) as in $[Et_4N]_2MnCl_5$. Mn (II) forms tetrahedral and square planar complexes although co−ordination number of 7 is also possible as in $[Mn (ETDA) (H_2O)]^{2-}$ which has a structure similar to NbF_7^{2-}.

The first order rate constant was found to be independent of the initial concentration of the permanganate. The reaction rate was linearly dependent on the $[H^+]$ in solutions of constant ionic strength. In confirmty with the kinetic data the following two mechanistic schemes have been proposed.
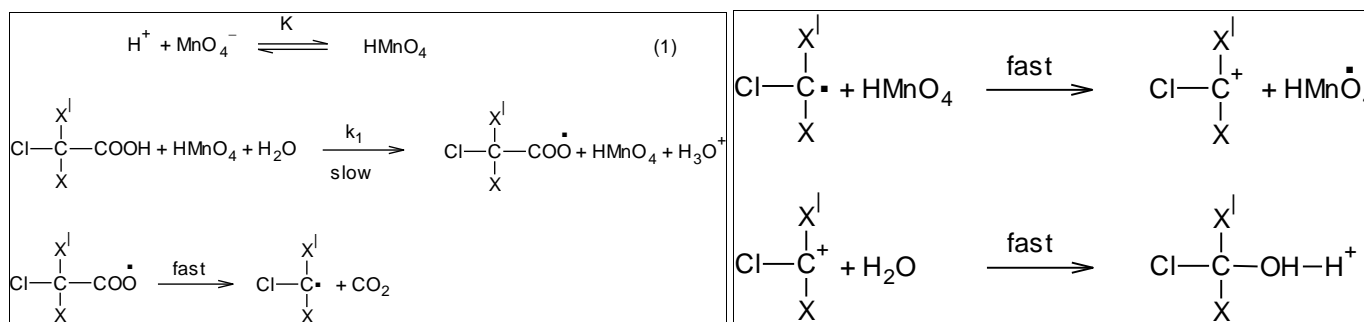
$$R - COCH_2R^| + H_3O^+ \longrightarrow R^+C (OH)CH_2R^| + H_2O$$
(1)

$$R^+C (OH)CH_2R^| + H_2O \longrightarrow RC (OH) = CHR^| + H_3O^+$$
(2)

Mechanism 1

Mechanism 2

According to Bunnett's empirical observations these values in both the acid media indicated that the molecule should act as a proton absorbing agent in the rate determining step. Based

on these facts, the mechanism shown in the following scheme was proposed.

Where $X = X^| = H$, $X = H$ and $X^| = Cl$ and $X = X^| = Cl$ for monochloro, dichloro and trichloroacetic acids respectively.
The following rate law was proposed according to the above mechanism.

$$-\frac{d}{dt}[MnO_4^-] = \frac{K\,k_1[MnO_4^-][substrate][H^+]}{1 + K[H^+]}$$

Or

$$\frac{1}{k} = \frac{A}{[H^+]} + \beta$$

Where

$$A = \frac{1}{k_1 . K} \quad \text{and} \quad \beta = \frac{1}{k_1}$$

The kinetics of oxidation of esters by potassium permanganate in sulphuric acid medium has been studied [12]. The reaction was found to be first order with respect to both [oxidant] and [ester]. The rate was found to increase with increasing sulphuric acid concentration.

2. Material and Methods
2.1 Materials
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 [13], 3–Methyl–2,6–Diphenylpiperidine–4–one [14], Raney–Nickel Catalyst [15], o–Phenylinediamine, Purification of Acetic Acid [16].

2.2 Methods
2.2.1 Electrolytic Preparation of Manganese (III) Sulphate
Manganese (III) sulphate solution was prepared by standard method [17].

2.2.2 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.

2.2.3 Determination of Manganese (III) and Manganese (IV)
Manganese (III) sulphate was determined titrimetrically by using standard sodium thiosulphate [18].
Manganese (IV) solution was also determined titrimetrically[19] by using Iron (II) sulphate solution. Ferrion indicator was used to detect the end point.

2.2.4 Spectral Studies of Samples
The spectra of manganese (VII), manganese (IV) and manganese (III) sulphate and of typical samples of kinetic mixture containing manganese (VII), manganese (IV) and manganese (III), substrate, sulphuric acid were taken respectively (Figs. 1 and 2. These spectra were recorded using an SP 700 spectrophotometer in the wave–length range of 200 nm to 700 nm with moderately fast scanning to avoid excessive reduction of manganese (VII), manganese (IV) and manganese (III) sulphate.
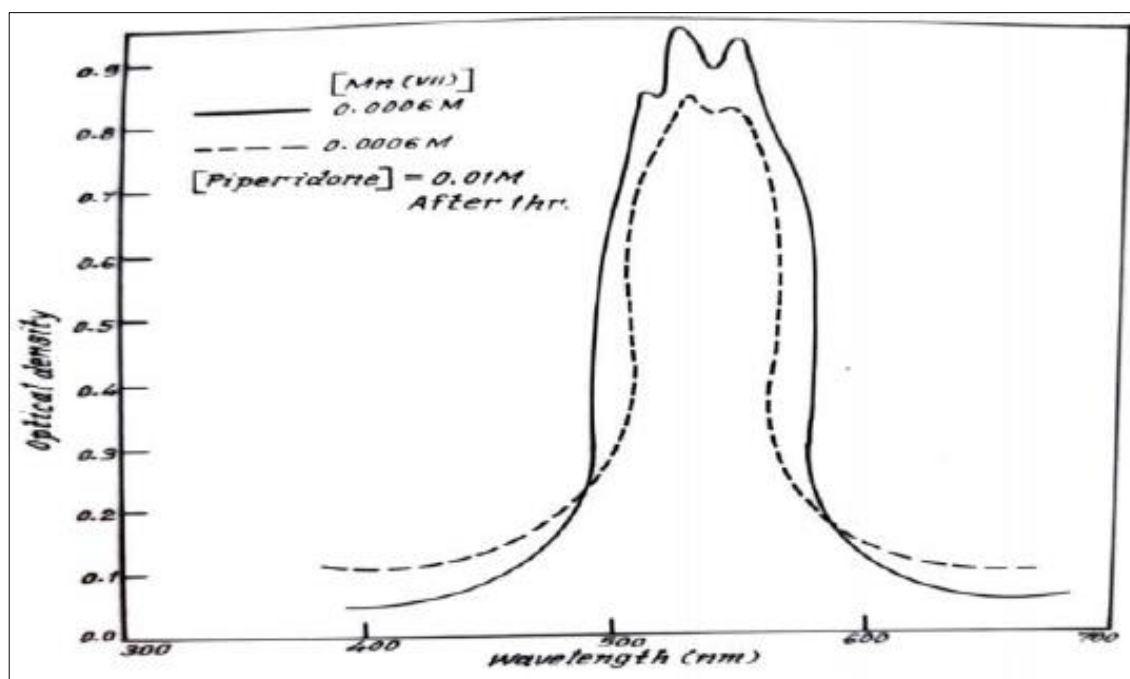

Fig 1: UV-visible spectrum of manganese (VII) and manganese (VII) – piperidone reaction mixture in 0.5 M Sulphuric acid at 25 °C
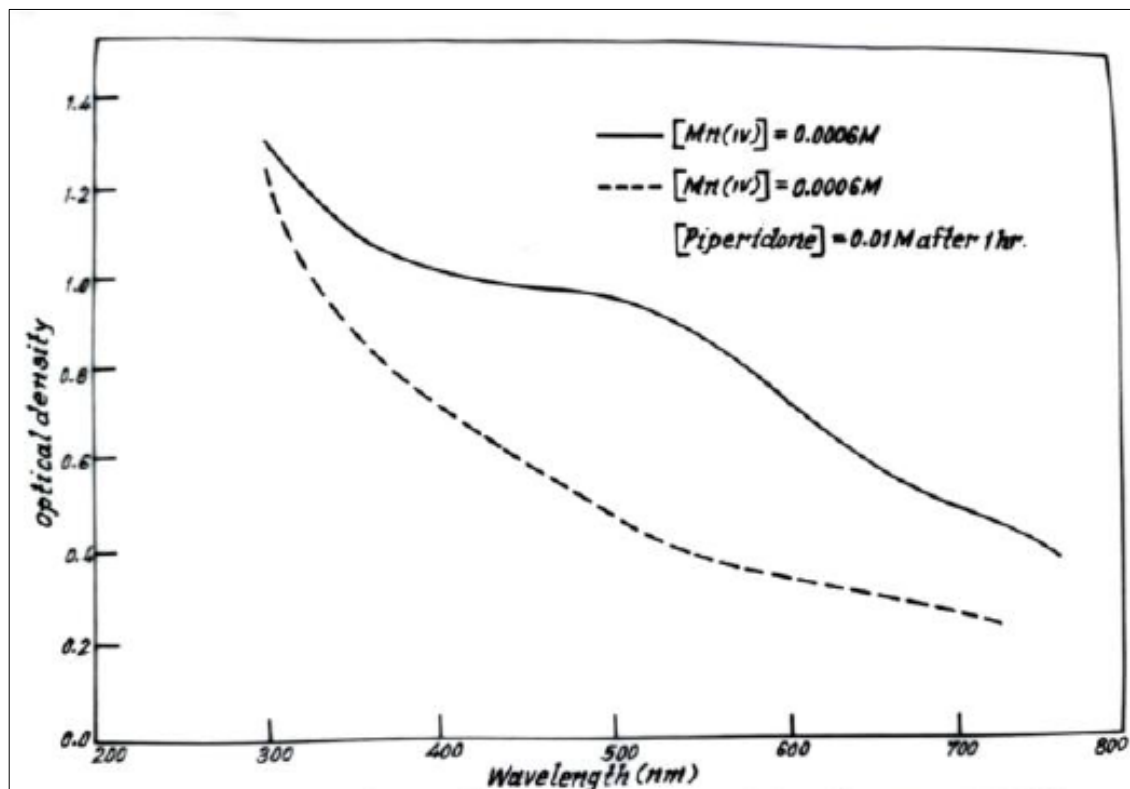
Fig 2: UV-visible spectra of manganese (IV) and manganese (IV) – piperidone reaction mixture in 0.5 M Sulphuric acid at 25 °C

2.2.5 Kinetic Measurements [20, 21]

Allkinetic measurements were performed spectrophotometricallyat 525nm, 420 nm and 380 nm using either an SP 700 spectrophotometer or an SP 500 spectrophotometer (series 2).

2.2.6 Product Investigations

The products of the oxidation reactions were identified by qualitative tests and GC/ MS analysis.The GC/MS instrument used for the product analysis is JEOL, JMS−D 300 with JMA−200 Data Analysis system. The conditions under which the product analysis has been done are:

GC
Column: SE−30, 3 mm × 3 m
Helium carrier: 1.4 kg / cm^2
Injection temperature: 200 °C
Column temperature: 190–250 °C, 10 °C / min.

MS
Resolution (10% valley): 1000
Ionization current   : 100 μA
A.C. Voltage: 3 kV
Ion source temperature: 200 °C

2.2.7 Calculation of Thermodynamic Parameter [22]

The energy of activation ΔE^a is correlated with the rate constant by the Arrhenium equation

$$k = Ae^{-\Delta E_a/RT}$$

orlog k = log A $-\Delta E_a/2.303$ RT
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.

2.2.8 Best Fitting Plot by Linear Regression[23−26]

For a series of data having two variables y and x conforming to an equation of the form

y = a + bx

where y is the dependent and x the independent variable, a and b are the coefficients,

3. Results and Discussion
### 3.1 Oxidation of substituted piperidones by Mn (IV)
3.3.1 The Oxidation of Ketones

The kinetics of oxidation of cyclohexanone by two electron oxidants like Iodine, Bromine, Mercury (II), Thallium (III), Manganese (VII), Chromium (VI) and one electron oxidants like Cobalt (III), Cerium (IV), Manganese (III) and Vanadium (V), has been reported by Littler[27−30]. Though 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 till recently [31]. FillmanFreemore *et al.* [32] have reported the studies of soluble manganese (IV) species in the oxidation of 2,4 (1H, 3H)−pyrimidine diones. Manganese (IV) has been used as an analytical reagent in the titrimetric determination of Iron, Vanadium, Uranium, Molybdenum, Arsenic, Oxalate and Iodide [33].

3.2 Oxidation of Substituted Piperidones

Active manganese dioxide in its tetravalent form is known for a long time for its oxidation properties. It oxidizes Fe (II) to Fe (III), oxalic acid to CO_2 and H_2O. Even though MnO_2 itself does not dissolve in sulphuric acid, it can be brought into solution in presence of reductant. The use of Mn (IV) as an oximetric reagent is not known till recently due to difficulties in preparation of a fairly stable solution. Mn (IV) is formed due to decompositioin of $KMnO_4$ in 8−11 M

sulphuric acid according to equation given in reasonably stable.

$$MnO_4^- + H_2SO_4 \rightleftharpoons Mn(SO_4)_2^{2+} + 3HSO_4^- + 5/2H_2O + 3/4O_2$$
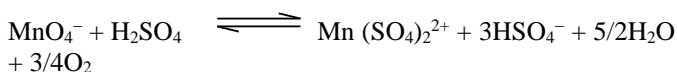
The redox potential of Mn (IV) has been found to be 1.577 V. Kinetic studies regarding such powerful oxidixing agent is rather scanty. The UV−visible spectra of Mn (IV) in 0.5 M H_2SO_4 was scanned in the entire wavelength of 200 to 800nm. A similar spectra were scanned in the following substrates:

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

After keeping for 24 hours the resulting solution was also scanned. A wavelength has been chosen to monitor kinetics after a thorough investigation of all those so that no other species absorbs in this wavelength.

The present investigations have been carried out in sulphuric acid media with Manganese (IV) in order to get some insight into the mechanisms involved as compared to the oxidation of similar ketones with Mn (VII) and Mn (III). Due to the limited solubility of these ketones in perchloric acid the oxidative studies have been carried out in sulphuric acid medium, under constant ionic strength kept by the addition of sodium sulphate.

3.2.1 Stoichiometry

The stoichiometries of these reactions were determined by keeping excess of Mn (IV) with piperidone for several hours and estimating the remaining Mn (IV) by titrimetry. The stoichiometry was found to be 2:1 (oxidant: substrate) as given in Table 2.

Table 2: Stoichiometries of piperidone oxidationTemp. 35 °CI = 1.8 M[piperidone] = 6×10^{-5}[Mn (IV)]=6×10^{-4} M[H$^+$] = 0.5 M

Time	$\dfrac{\Delta[Mn(IV)]}{\Delta[piperidone]}$
4 hrs.	0.953
20 hrs. 30 min.	1.26
24 hrs. 30 min	2.06

3.2.2 Products of Oxidation

An acidic solution of piperidone was mixed with an excess of Manganese (IV) solution and was neutralized by adding sodium carbonate solution drop by drop. The solution was cooled well and alcohol was added. The product was isolated by esterification and GC/MS analysis. The oxidation product was found to an acid as in the case of permanganate oxidation.

3.2.3 Kinetics

The rate of disappearance of Mn (IV) in the presence of excess [piperidone] was found to be first order (Tables 3 (a) and (b)).

The piperidone concentration was varied from 0.01 to 0.02 M, keeping the Mn (IV) concentration constant. Under these conditions reproducible pseudo− first order plots were obtained. The plots of 1 + log O.D. against time are linear (Figs. 2 (a) and 2(b)). The pseudo−first order rate constants k_{obs} were determined over a range of [H_2SO_4] (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 3 (a) and (b). The plots of k_o against [piperidone] at constant acidity and constant ionic strength were found to be linear (Figs. 3(a) and 3(b)) and the bimolecular rate constants k_2 have been calculated from the slopes of these lines (Tables 4 (a) and (b)).
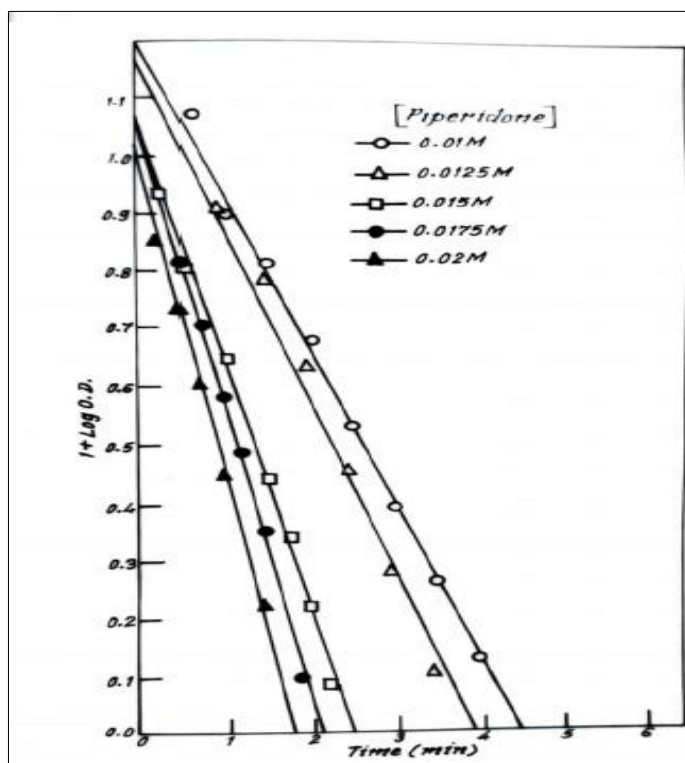

Fig 2 (a): Plots of 1 + log 0.D against time for 2,6-diphenylpiperidine-4-one oxidation by Mn (IV) at 55 °C, [H$^+$] = 0.5 M, I = 1.8 M
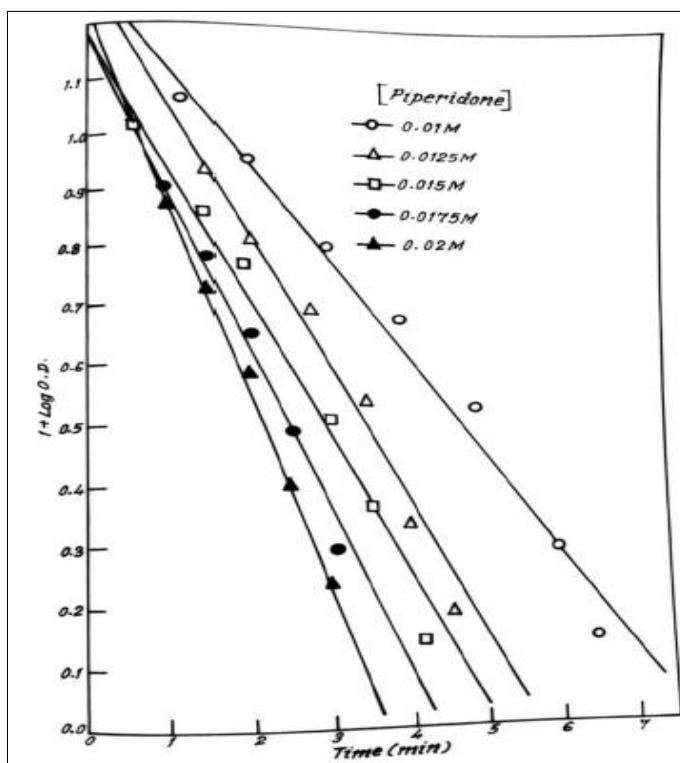

Fig 2 (b): Plots of 1 + log 0.D against time for 3-methyl-2,6-diphenylpiperidine-4-one oxidation by Mn (IV) at 55 °C, [H$^+$] = 0.5 M, I = 1.8 M
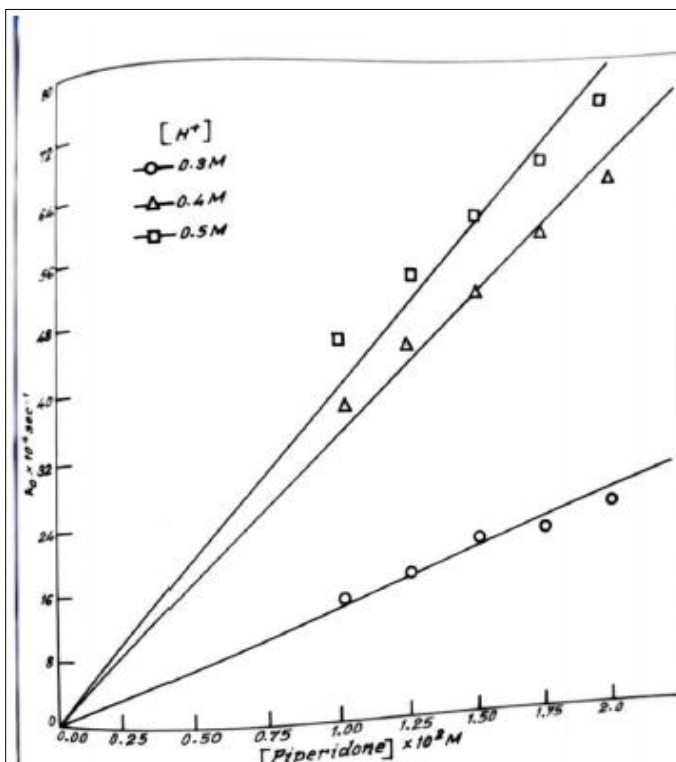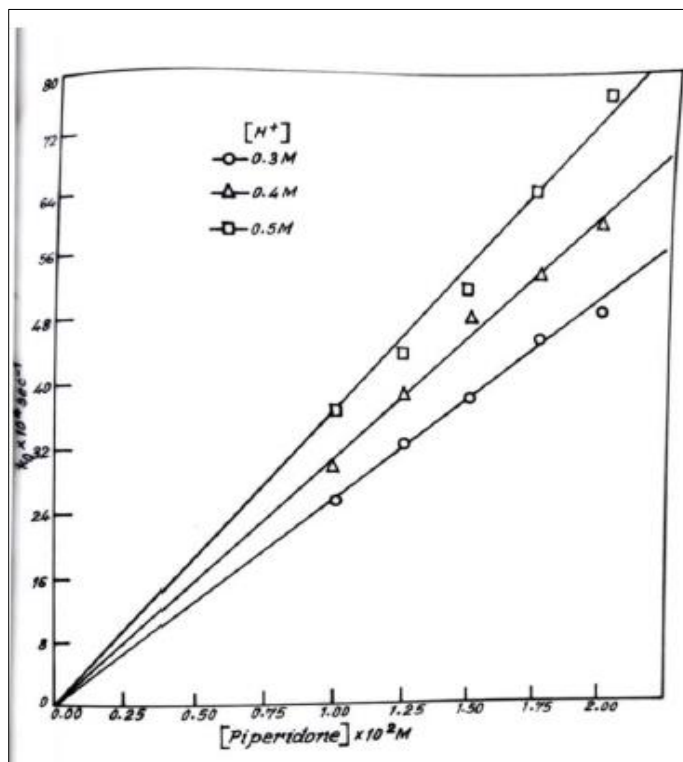
Fig 3(a): Plots of K_0bs against [2, 6-diphenylpiperidine-4-one] at 45°C

Fig 3(b): Plots of K_0bs against [3-methyl-2, 6-diphenylpiperidine-4-one] at 45°C

Table 3. (a): 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 (IV)] = 6 × 10^{-4} M

Temp. °C	[piperidone] × 10² M	[H₂SO₄] M		
		0.3	0.4	0.5
25	1.00	3.94	2.97	4.40
	1.25	4.27	3.75	5.09
	1.50	4.60	4.53	5.78
	1.75	4.92	5.30	6.47
	2.00	5.25	6.09	7.20
35	1.00	–	14.18	18.20
	1.25	–	16.57	24.53
	1.50	16.48	18.96	30.41
	1.75	17.64	21.36	34.25
	2.00	18.80	28.32	38.20
45	1.00	14.59	39.12	48.32
	1.25	17.07	45.44	54.81
	1.50	19.55	51.76	61.30
	1.75	22.03	58.08	67.80
	2.00	24.50	64.40	74.28
55	1.00	73.73	80.98	108.50
	1.25	81.64	90.80	126.15
	1.50	89.50	100.50	143.76
	1.75	97.48	110.40	161.37
	2.00	105.30	120.20	179.00

Table 3 (b): Values of observed rate constants $k_o \times 10^4$ sec^{-1} for the oxidation of 3–methyl–2,6–diphenylpiperidine–4–one at I = 1.8 M[Mn (IV)] = 6 × 10^{-4} M

Temp. °C	[piperidone] × 10² M	[H₂SO₄] M		
		0.3	0.4	0.5
25	1.00	3.62	2.98	4.97
	1.25	4.21	3.82	5.74
	1.50	4.97	4.67	6.51
	1.75	5.38	5.52	7.28
	2.00	5.96	6.36	8.06
35	1.00	12.86	11.82	14.41
	1.25	15.08	15.00	19.18

	1.50	17.30	18.19	23.95
	1.75	19.50	21.37	28.72
	2.00	21.73	24.56	33.56
	1.00	26.38	28.81	37.86
	1.25	32.90	40.95	43.35
45	1.50	39.42	48.84	53.09
	1.75	45.94	54.33	65.22
	2.00	52.46	59.82	77.36
	1.00	52.60	71.14	68.62
	1.25	64.97	85.52	86.36
55	1.50	77.35	99.90	104.10
	1.75	89.73	114.20	121.83
	2.00	102.11	128.66	139.57

Table 4 (a): Biomolecular rate constants $k_o \times 10^2$ litre mole^{-1} sec^{-1} for the oxidation of 2,6–diphenylpiperidine–4–one

Temp. °C	[H$_2$SO$_4$] M		
	0.3	0.4	0.5
25	2.34	3.08	3.38
35	8.87	12.73	19.08
45	21.95	26.07	48.54
55	49.50	57.51	70.95

Table 4 (b): Biomolecular rate constants $k_o \times 10^2$ litre mole^{-1} sec^{-1} for the oxidation of 3–methyl–2,6–diphenylpiperidine–4–one

Temp. °C	[H$_2$SO$_4$] M		
	0.3	0.4	0.5
25	1.31	2.76	3.11
35	4.69	9.57	–
45	9.91	25.28	26.00
55	31.66	39.21	60.43

3.2.4 Effect of Temperature

The oxidation rates of 2,6–diphenylpiperidine–4–one and 3–methyl–2,6–diphenylpiperidine–4–one have been measured at four temperatures in the range 25-55 °C and the rate constants are recorded in Tables 4 (a) and (b). The activation parameters have been calculated from the linear Arrhenius plots (Figs. 4 (a) and 4(b)) of log k_2 vs. T^{-1} (Tables 5 (a) and (b)).

3.2.5 Acidity Dependence

The kinetics of oxidation of the substituted piperidones have been studied in the acidity range 0.3 to 0.5 M (Figs. 4(a) and 4(b)) and the data are collected in Tables 4 (a) and (b). The rate of reaction was found to increase with acid concentration.
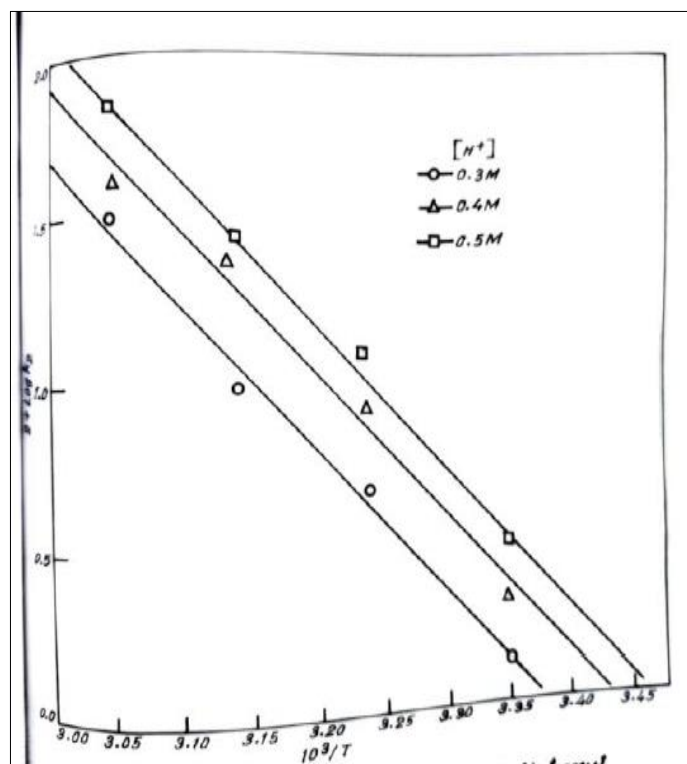

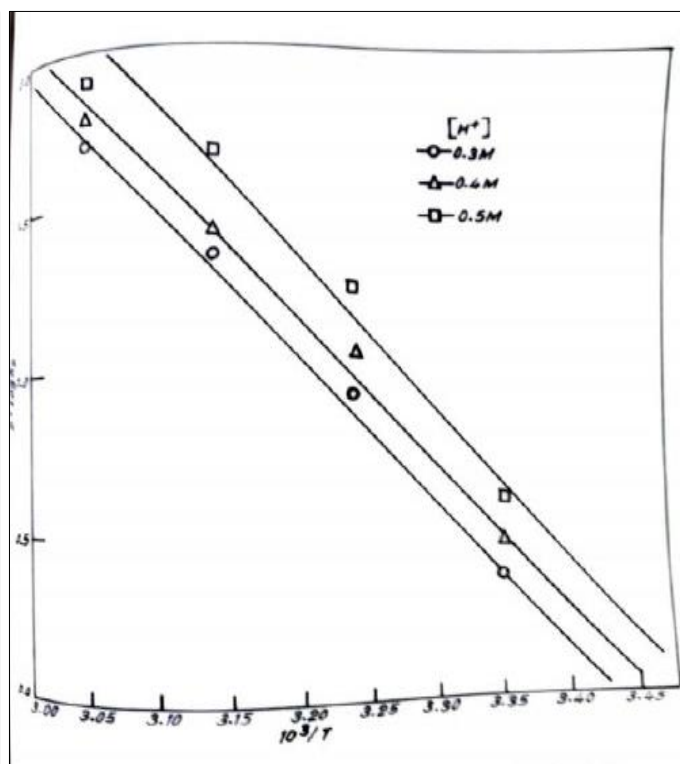Fig 4(a): Arrhenius plots for 2,6-diphenylpiperidine-4-one oxidation

Fig 4(b): Arrhenius plots for 3-methyl-2,6-diphenylpiperidine-4-one oxidation

3.2.6 Rate Law

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

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

3.2.7 Activation Parameters

A linear plot is obtained for log k_2 against 1/T °K (Figs. 3.2.3 (a) and (b)). The values of ΔE_a, ΔS^*, ΔH^* and ΔG^* are collected in Tables 5 (a) and (b).

Table 5 (a): Values of the activation parameters for the oxidation of 2,6–diphenylpiperidine–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}
0.3	67.60 ± 0.70	76.41 ± 0.70	–14.21 ± 3.76	81.55 ± 1.40
0.4	78.96 ± 1.16	81.38 ± 1.16	–0.80 ± 2.30	81.60 ± 2.32
0.5	83.93 ± 2.42	81.38 ± 2.42	5.64 ± 7.86	82.01 ± 4.84

Table 5 (b): Values of the activation parameters for the oxidation of 3–methyl–2,6–diphenylpiperidine–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}
0.3	85.69 ± 0.92	79.46 ± 0.92	–10.18 ± 6.20	83.27 ± 1.84
0.4	82.05 ± 1.84	83.09 ± 1.84	–1.76 ± 3.05	81.55 ± 3.68
0.5	85.48 ± 2.20	82.93 ± 0.92	4.77 ± 8.11	81.48 ± 1.84

The low entropies of activation in the present case clearly suggests that there was no complex formation between the interacting species. The activatioin energy having a magnitude of 85 kJ mole^{-1} at all the acidities (0.3 to 0.5 M) lie in the order of oxidation of cyclohexanone and cyclohexanol by Co (III) stearate (ΔE_a = 92 kJ mol^{-1} and 82.44 kJ mole^{-1} respectively). 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 increases the stability of the products will increase the rate of the reaction. This is a case for reaction were the rate determining step is the formulation of reactive intermediates such as free radicals, carbonium ions and unstable carbanons.The absence of formation of an intermediate free radical indicated in its failure to initiate acrylonitrile polymer in nitrogen atmosphere in the present case demonstrates that the reaction may be of 2 electron transfer reaction involving aquo–species. Further the nature of product formation is in accordance with the enthalpy change and the available free energy as experimentally found.
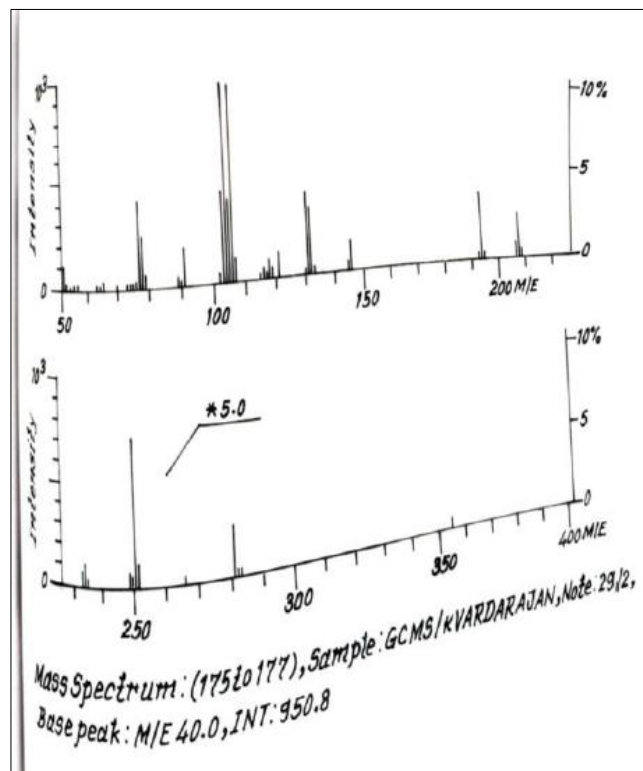

Fig 5: Mass spectrum: (175 to 177), Sample: GCMS/kVARDARAJAN, Note: 29/2, Base peak: M/E 40.0, INT: 950.8
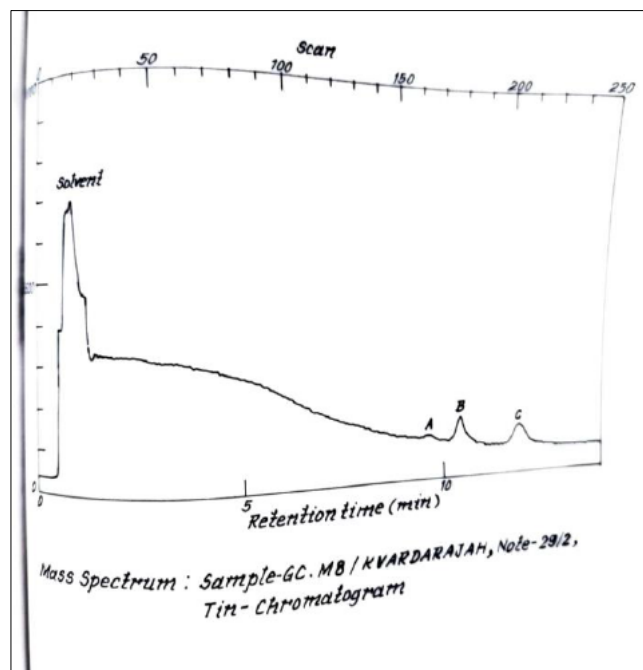

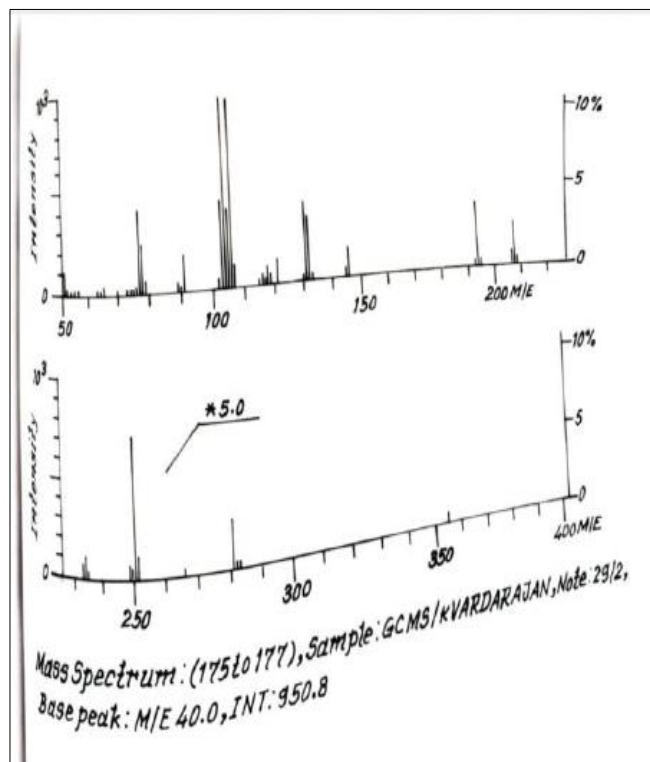**Fig 6:** Mass Spectrum: Sample-GC.MB/kVARDARAJAN, Note: 29/2, Tim - chromatogram

Fig 7: Mass Spectrum: (175 to 177), Sample: GCMS/kVARDARAJAN, Note: 29/2, Base peak: M/E 40.0, INT: 950.8

4. Conclusions

The present investigations have been successful in determining the mechanisms of oxidation of substituted piperidonesbyMn (IV) in sulphuric acid media.

The reaction show 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) > Mn (VII).

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