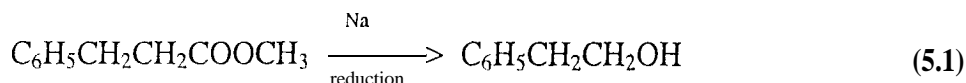


CHAPTER 5

KINETICS AND MECHANISM OF OXIDATION OF PHENETHYL ALCOHOLS BY MANGANESE(III) SULPHATE IN ACID MEDIUM.

5.1 GENERAL INTRODUCTION TO PHENETHYL ALCOHOLS

Phenethyl alcohol was first prepared²⁵¹ by the reduction of phenylethyl acetate with sodium in absence of alcohol.



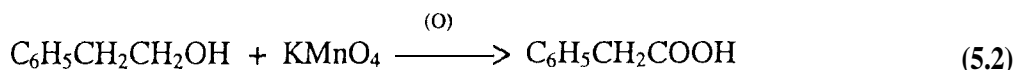
Phenethyl alcohol possesses a perfumery odour and is found in a number of natural essential oils such as rose, carnation, hyacinth, aleppopine, orange blossom, gernium bourbon, neroli and in the essential oil of champaca. Phenethyl alcohol is a colourless liquid, boiling at 219-221°C and melting at 27°C. It is isolated from the fungus, soluble in alcohol and ether but only 2ml of phenethyl alcohol dissolves in 100 ml water, after thorough shaking.

Phenethyl alcohol is used in manufacturing of perfumery products (particularly rose perfumes) and is used for synthesis of many organic compounds. A very relevant use could be for phenacetaldehyde synthesis. Phenethyl alcohol is also used as, antibacterial agent preservative in ophthalmic solutions, pharmaceutical aid (antimicrobial), in flavors, and is a strong local anesthetic. Experimentally it has been shown that phenethyl alcohol causes central nervous injury in mice.

Reaction of phenethyl alcohol (**PEA**) :

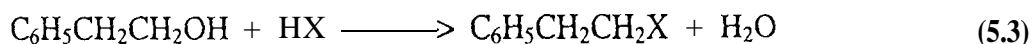
(i) oxidation of phenethyl alcohol :

oxidation of PEA with alkaline potassium permanganate gives phenyl acetic acid.



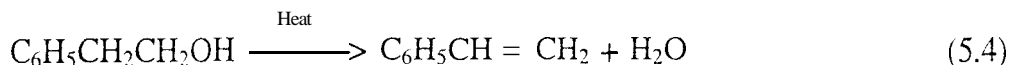
(ii) Reaction with hydrogen halide :

PEA reacts with halides (HX) gives phenethyl halides.



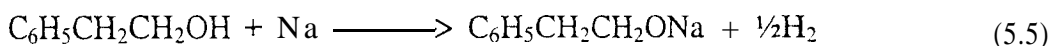
(iii) Dehydration of PEA with acid :

Dehydration of PEA with sulphuric acid gives phenyl ethene.



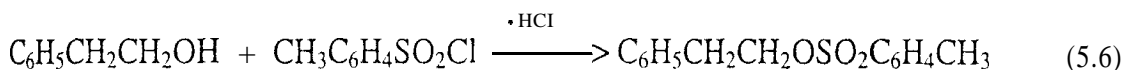
(iv) Reaction as acid :

PEA react with active metals like Na, K and Mg to liberate hydrogen gas and forms sodium phenethoxide.

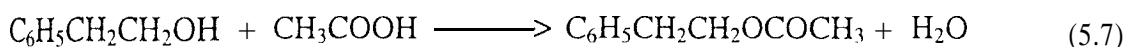


(v) Ester formation :

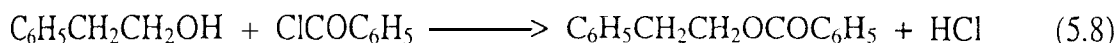
When PEA is treated with tosyl chloride it forms phenethyl tosylate.



PEA also reacts with acetic acid to form phenethyl acetate.

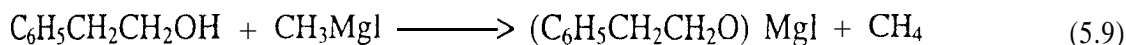


PEA reacts with benzoyl chloride gives phenethyl benzoate(benzoylation).



(vi) Reaction with Grignard reagent :

When PEA is treated with a Grignard reagent, the hydrogen atom of the OH group combines with the alkyl group of the Grignard reagent.



(vii) Phenethyl alcohol undergoes electrophilic aromatic substitutions like nitration, sulphonation, but it is usually better to protect the -OH group before affecting these substitutions.

5.2 OXIDATION OF PRIMARY ALCOHOLS : A REVIEW

A review of literature shows little information on the kinetics of oxidation of primary alcohols by N-haloamines. Mahadevappa and Naidu²⁵²⁻²⁵⁴ and Herlihy²⁵⁵ have reported on the oxidation of conjugated alcohols, allyl, cinnamyl and crotyl alcohols by CAT in

HCl medium. The rate is found to be first order each in [CAT], [H⁺] and [Cl⁻]. Similar results have been obtained²⁵⁶ with CAB. Mahadevappa and co-workers have also carried out the oxidation of primary alcohols by BAB²⁵⁷ and of allyl and crotyl alcohols by BAT catalysed by OsO₄²⁵⁸.

Mushran et al.²⁵⁹ have oxidised n-butanol, iso-butanol and iso-pentanol by CAT in acid medium. The rate is first order in each [CAT], and [H⁺] but shows a zero order dependence in [alcohol]. The proposed mechanism involves HOCl as the reactive species.

Uma and Mayanna²⁶⁵ have reported the oxidation of primary alcohols by CAT in alkaline medium, catalysed by OsO₄. The proposed mechanism indicates formation of an activated complex between the substrate and OsO₄ which slowly decomposes in a rate limiting step in to the aldehyde and Os(VI) formed is oxidised rapidly to Os (VIII) with the anion of CAT.

Mukherji and Banerji²⁶¹ have reported on the oxidation of nine primary alcohols by CAB in presence of HClO₄. The rate is first order each with respect to the [ox], [alcohol] and [H⁺] ions. The primary kinetic isotope effect using deuterated alcohol and the solvent isotope effect in D₂O medium have been studied. The reaction exhibits a reaction constant $\rho^* = 2.2$ at 298K. The probable oxidising species is PhSO₂NHCl. A mechanism involving transfer of hydride ion to the oxidant is suggested.

Singh et al²⁶² reported on the mechanism of Ru(III) catalysed oxidation of methanol and ethanol by BAT in acid medium. The rate shows a first-order each with respect to [BAT], [substrate], [H⁺] and [Ru(III)] and inverse first-order on [Cl⁻]. Kinetic results point to a mechanism involving interaction between a reactive species of BAT and a transient complex formed between the substrate and ruthenium(III) species. Similar results²⁶³ were obtained in the oxidation of n-propanol and n-butanol by BAT.

Mittal et al.²⁶⁴ reported on the kinetics and mechanism of the oxidation of primary alcohols by sodium N-chloro ethyl carbamate in acid medium. The reaction is first order each with respect to the $[ox]_o$ and $[alcohol]$. The rate increases with an increase in acidity (H_+) and the value of solvent isotope effect $k(H_2O) / k(D_2O) = 2.23$ at 298K. Plots of $(\log k_2 + H_+)$ vs $(H_+ + \log[H^+])$ are linear and a concerted mechanism involving transfer of a hydride ion from C-H bond of the alcohol to the oxidant and removal of a proton from the OH group by a water molecule has been proposed.

Negi et al.²⁶⁵ have reported on the kinetics and mechanism of the oxidation of aliphatic alcohols by sodium hypobromite in alkaline medium. The reaction is first order each with $[ox]$ and $[alcohol]$ and inverse order with respect to $[OH^-]$ ion. The primary kinetic isotope effect has been studied using deuterated alcohol.

Banerji²⁶⁶ has reported the oxidation of aliphatic alcohols by pyridinium fluoro chromate in dimethyl sulphoxide medium. The reaction is first order with respect of $[ox]$, but the order with respect to the $[alcohol]_o$ is less than one. The primary kinetic isotope effect and the formation constants of the alcohol-oxidant complex have been studied.

Mahadevappa et al.²⁶⁷ have oxidised substituted ethanols by BAB in the presence of HCl medium. The rate shows a first-order on $[BAB]$ and is fractional in $[alcohol]$, $[H^+]$ and $[Cl^-]$. The solvent isotope effect and the rates do not correlate satisfactorily with Taft's substituent constants is suggested.

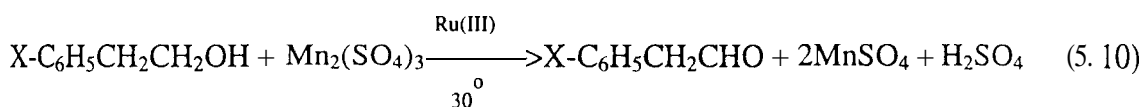
5.3 KINETICS OF OXIDATION OF PHENETHYL ALCOHOLS BY MANGANESE(III) SULPHATE IN ACID MEDIUM

This section deals with the results of oxidation of phenethyl alcohol (PEA) and its derivatives 4-chloro, 4-Bromo, 4-nitro, 4-methyl and 4-methoxy phenethyl alcohols by Mn(III) in H_2SO_4 medium at 30°C. The solution of phenethyl alcohol was prepared in

water but for substituted phenethyl alcohols, methanolic content of 5% (v/v) was maintained. Experiments have been designed to determine the kinetic order of reaction with respect to the oxidant and the substrate. The effects of, changes in hydrogen ion concentration, ionic strength (I), dielectric constant (D), addition of reaction product, Mn(II) and addition of neutral salts have been studied. Kinetic and thermodynamic parameters have been evaluated by determining the rate constant of the reaction at different temperature. A suitable mechanism has been proposed to account for the observed rate expression.

Stoichiometry :

The mixture containing PEA, H₂SO₄, Mn(II) and Ru(III) with excess of Mn(III) was kept for 24-48 hours at 30°C. Iodometric determination of the unconsumed Mn(III) indicated that one moles of oxidant was needed per mole of PEA to give the product. The stoichiometry of the reaction can be represented as follows :



Here X = -H, -Cl, -Br, -CH₃, -OCH₃ and -NO₂.

Product analysis :

The reaction product phenacetaldehyde was recrystallized from dichloromethane/petroleum ether, (m.p = 32-33°C), known m.p = 33-34°C (Merck index 11,7236). The aldehyde was further identified by its 2,4-dinitro phenylhydrazone (2,4-DNP) derivative. It was recrystallized from ethanol (recovery 67.8 %) and was found to be identical with the DNP derivative of an authentic sample.

RESULTS

The kinetics of oxidation of phenethyl alcohol and its derivatives with Mn(III) in presence of H₂SO₄ were investigated at several initial concentrations of reactants.

Effect of [Mn (III)] and [PEA]

With the substrate in excess, at constant [PEA], [H₂SO₄], [Ru(III)], [Mn(II)] and temperature, plots of log (O.D) Vs time were linear (Table 5.1 Fig. 5.1, $r > 0.998$ $s < 0.02$), indicating a first-order dependence of rate on [Mn(III)]₀. Further, variation in [Mn(III)]₀ had no effect on the rate. Values of the pseudo-first order rate constant (k_{obs}) are given in Table 5.2.

The rate increased initially with increase in [PEA]. A plot of log k_{obs} Vs [PEA], was linear (Table 5.2 Fig. 5.2. $r > 0.999$ $s < 0.01$) with a fractional slope (0.5). Michaelis – Menten kinetics was obeyed as plots of $1/k_{obs}$ Vs $1/[PEA]$ were linear (Fig. 5.3) with definite intercepts.

Effect of acidity

The rate decreased with increase in the concentration of sulphuric acid and the Zucker - Hammett plot of log k against acidity function ($-H_0$) was linear (Table 5.3 Fig. 5.4, $r > 0.997$ $s < 0.03$). The order with respect to $-H_0$ is inverse fractional (-0.07). The values of $-H_0$ at various acidities were taken from Paul and Long.

Effect of [Ru (III)]

At constant [Mn(III)], [PEA], [H₂SO₄], [Mn(II)] and temperature, the plots of log k_{obs} Vs log [Ru(III)] were linear (Table 5.2 Fig. 5.5, $r > 0.998$ $s < 0.02$), with a fractional slope (0.5), indicating a fractional-order dependence of [Ru(III)].

Effect of ionic strength and added salt:

Effect of varying ionic strength of the medium by the addition of NaClO₄ solution had no significant effect on the reaction rate. Similarly the effect of anions such as chloride, fluoride, sulphate and reaction product Mn(II) of the oxidant on the rate was insignificant (Table 5.5).

Effect of varying dielectric constant of medium

The dielectric constant of the medium was varied by adding methanol (0–12.5% v/v) to the reaction mixture, but the rates were not significantly altered (Table 5.4). Blank experiments with methanol indicated that oxidation of methanol was negligible during the period of the experiment.

Solvent isotope studies

Studies of the rate in D₂O medium for PEA revealed that, whereas $k(\text{H}_2\text{O})$ is $9.47 \times 10^{-4} \text{ s}^{-1}$, $k(\text{D}_2\text{O})$ is $6.85 \times 10^{-4} \text{ s}^{-1}$. The solvent isotope effect $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$ was thus 1.38. Proton inventory studies were made by carrying out the reaction in H₂O–D₂O mixtures with atom fractions 'n' of deuterium (Table 5.6 Fig. 5.6, $r > 0.996$ $s < 0.04$)

Effect of temperature on rate

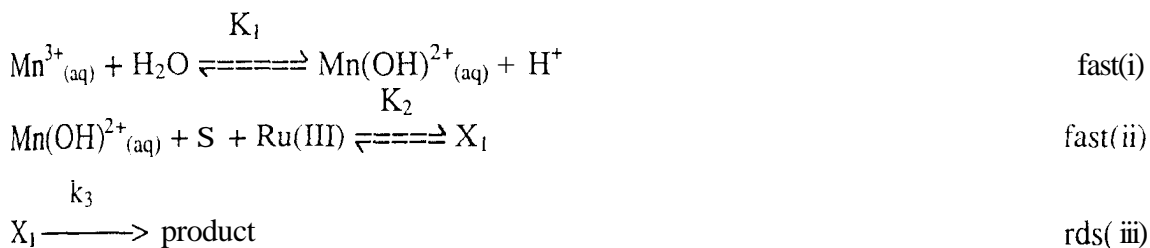
The reaction was studied at different temperatures (298–313K) and from the Arrhenius plots of $\log k_{\text{obs}}$ Vs $1/T$, values of the activation parameters for the composite reaction were calculated (Table 5.7 & 5.8 Fig. 5.7, $r > 0.969$ $s < 0.05$)

Test of free radical

Addition of aqueous acrylamide to the reaction mixture did not cause polymerisation suggesting the absence of free-radical involvement during the oxidation.

Discussion

It has been assumed that Mn(III) species present in aqueous sulphuric acid medium are $\text{Mn}^{3+}_{(\text{aq})}$, $\text{Mn}(\text{OH})^{2+}_{(\text{aq})}$ and $\text{MnSO}_4^{+}_{(\text{aq})}$ ⁷⁹. Since the effect of sulphate ion on the reaction is negligible, the $\text{Mn}(\text{OH})^{2+}_{(\text{aq})}$ species become important, in view of the fact that the rate is dependent of hydrogen ion concentration. In view of these facts, scheme 5.1 has been proposed for the oxidation of PEA by Mn(III) :



Scheme - 5.1

Scheme 5.1 assumes the formation of an intermediate, (X_1) and at the same time indicates simultaneous catalysis by Ru(III) ions. This is followed by the decomposition of X_1 in a rate limiting step to the products. Assuming $[\text{Mn}]_{(t)} = [\text{Mn}^{3+}] + [\text{Mn}(\text{OH})^{2+}] + [X_1]$, the following rate law can be derived for the oxidation of PEA by Mn(III) :

$$\text{rate} = \frac{K_1 K_2 k_3 [\text{Mn}]_{(t)} [\text{S}] [\text{H}_2\text{O}] [\text{Ru(III)}]}{[\text{H}^+] + K_1 [\text{H}_2\text{O}] \{ 1 + K_2 [\text{S}] [\text{Ru(III)}] \}} \quad (5.11)$$

Since $\text{rate} = k_{\text{obs}} [\text{Mn(III)}]$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_2 k_3 [\text{S}] [\text{Ru(III)}]} \left\{ \frac{[\text{H}^+]}{K_1 [\text{H}_2\text{O}]} + 1 \right\} \frac{1}{k_3} \quad (5.12)$$

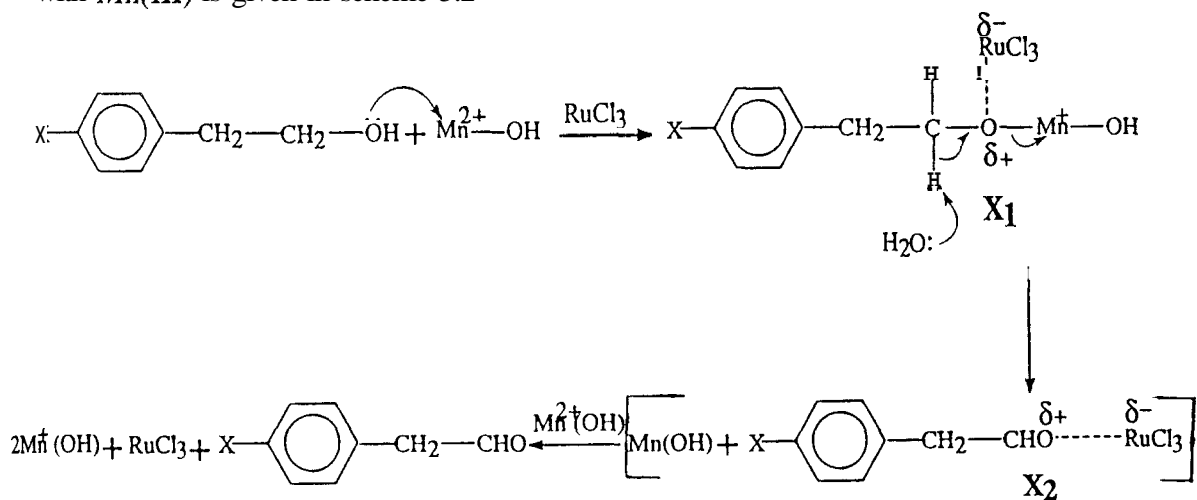
From double reciprocal plots (Fig. 5.3 & 5.8) of k_{obs} Vs [PEA]. and k_{obs} Vs $[\text{Ru(III)}]_0$, values of k_3 , K_1 and K_2 can be evaluated. In order to evaluate the activation parameters for the rate limiting step, the concentration of substrate was varied at several temperatures and values of k_3 were determined at each temperature (1.35×10^{-3} , 1.96×10^{-3} , 3.17×10^{-3} and $4.55 \times 10^{-3} \text{ sec}^{-1}$ at 298, 303, 308 and 313K respectively). The values of activation parameters for the rate limiting step determined from the Arrhenius plot of $\log k_3$ Vs $1/T$ are, $E_a = 64.1 \text{ kJ mol}^{-1}$, $A H^\ddagger = 61.5 \text{ kJ mol}^{-1}$, $A S^\ddagger = -94.7 \text{ JK}^{-1} \text{ mol}^{-1}$, $A G^\ddagger = 29.1 \text{ kJ mol}^{-1}$, and $\log A = 12.5$.

Spectral studies

The study of UV-visible spectra of pure Mn(III), Ru(III), PEA and mixture of (i) Mn(III) and Ru(III) (ii) Ru(III) and PEA (iii) Mn(III) and PEA and (iv) Mn(III), Ru(III) and PEA were studied. The following observed λ_{\max} were given as follows.

Component	λ_{\max} (nm)
Mn(III)	500
Ru(III)	460
Mn(III) + Ru(III)	460 & 500
Ru(III) + PEA	460
Mn(III) + PEA	480
Mn(III) + Ru(III) + PEA	480

It is observed from the above table that the complex formation takes place between Mn(III), Ru(III) and PEA but not between Mn(III) and Ru(III) or Ru(III) and PEA. It is however probable that the shift in λ_{\max} reflects the transient nature of the complex which breaks up into products. The measurement of λ_{\max} with time (for one hour) was also observed indicating the change in λ_{\max} from 480 to 420nm suggesting that a labile system (intermediate) is involved in the reaction sequence. A detailed mode of oxidation of PEA with Mn(III) is given in scheme 5.2



The hydroxyl oxygen of PEA transfers an electron to Mn^{2+} -OH forming an intermediate (Xi). The intermediate is further attacked by a molecule of water forming a transient free radical intermediate (X_2) and $Mn(OH)$. This $Mn(OH)$ further gives away an electron to another molecule Mn^{2+} -OH forming $2Mn^+$ -OH, while transient free radical intermediate (X_2) decomposes to give $RuCl_3$ and phenacetaldehyde.

The proposed mechanism is further supported by the fact that $k(H_2O) / k(D_2O) \approx 1.38$. Generally, for acid catalysed reactions, the ratio $k(H_2O) / k(D_2O) > 1$, since D_3O^+ is a stronger acid²⁷⁰ than H_3O^+ . But for H^+ retarded reactions, this ratio is less than unity as has been observed experimentally in the present study. Proton inventory studies in H_2O - D_2O mixture could throw light on the nature of the transition state. The dependence of the rate constant (k_{obs}) on 'n' the atom fraction of deuterium in a solvent mixture of D_2O and H_2O is given^{99.100(b)}, by a form of Gross Butler equation as in,

$$(k_{obs}^o)/(k_{obs}^n) = \frac{\prod_{TS} (1 - n + n\phi_i)}{\prod_{RS} (1 - n + n\phi_j)} \quad (5.13)$$

where ϕ_i and ϕ_j are the isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition states (TS) and reactant site (RS) respectively. Equation (5.13) allows the calculation of the fractionation factor of TS, if reactant fractionation factors are known. However the curvature of the proton inventory plot could reflect the number of exchangeable protons in the reaction.²⁷¹ A plot of k_{obs} Vs the deuterium atom fraction 'n' (Table 5.6 Fig. 5.6) in the present case is more or less a straight line ($r > 0.996$ $s < 0.04$) with the least curvature. Comparison with the standard curves²⁷¹ clearly indicates the involvement of a single proton or H-D exchange during the formation of the transition state.

The Bunnett plots²⁷² i.e $\log (k_{obs} + H_o)$ against $\log a_{H_2O}$ were linear (Table 5.3 Fig. 5.9, $r > 0.978$ $s < 0.05$) with negative slope $\omega = -1.62$ for the oxidation of PEA by $Mn(III)$.

The values of $\log a_{\text{H}_2\text{O}}$ at various acidities were taken from Bunnett.²⁷³ The values of ω indicates that no water molecule is participating in the rate controlling step.

Isokinetic relationship

The enthalpy of activation is low for the oxidation of phenethyl alcohol by Mn(III). The values of $A H^\ddagger$ and $A S^\ddagger$ for the oxidation of phenethyl alcohols are linearly related ($r > 0.008$ $s < 0.02$) and the isokinetic temperature $\beta = 330\text{K}$ was obtained. The genuine nature of the isokinetic relationship was verified by the Exner²⁷⁴ criterion by plotting $\log k_{\text{obs}}(298\text{K})$ Vs $\log k_{\text{obs}}(308\text{K})$. The value of β was calculated from the equation.

$$\beta = \frac{T_1 (1 - q)}{(T_1 / T_2) - q} \quad (5.14)$$

where q is the slope of the Exner plot and $T_1 > T_2$. The value of $\beta = 308\text{K}$. It is seen that the value of β is higher than the experimental temperature (303K) indicating enthalpy control on the reaction.

Structure – reactivity correlations

The following order of reactivity is observed with the substituents in para position : $-\text{OCH}_3 >$, $-\text{CH}_3 >$, $-\text{H} >$, $-\text{Cl} >$, $-\text{Br} >$, $-\text{NO}_2$ (Table 5.9). The order of reactivity shows that the oxidation rate is enhanced by electron donating substituents and retarded by electron withdrawing substituents.

Structure-reactivity correlations were made by attempting to fit the Hammett equation to the results. The Hammett plot²⁷⁵ shows two distinct lines (Fig. 5.10) for each of which, there is good correlation between the substituent constants and the logarithm of the rate constants, particularly when σ_p , the Okamoto-Brown¹¹⁴ constant is used. Of these, one has a large ρ of -0.48 ($r > 0.997$ $s < 0.03$) for electron releasing group while the other line has relatively low ρ of -0.16 ($r > 0.994$ $s < 0.05$) for electron withdrawing group at 30°C .

The reason for the break in the Hammett plot could be due to

- (1) a change in the reaction mechanism,
- (2) a change in the rate-determining step with change in the nature of the substituents,
and
- (3) a change in the transition state.

In this reaction, the non-linear Hammett plot is not due to the change in the reaction mechanism with respect to substituents, because the isokinetic plot of ΔH^\ddagger Vs ΔS^\ddagger ($r > 0.998$ $s < 0.02$) and Exner plot gave a very good correlation. These substrates follow Michaelis–Menten plot and yield definite intercept (Fig. 5.3). So the non-linear Hammett plot due to the nature of the substituents is also ruled out. In this case the rupture of C-H bond occurs after the O-H bond cleavage, creating a carbonium ion center or a positive character in the transition state which is stabilized by the electron donating groups, that is, the decrease in the rate with electron withdrawing groups is in agreement with this observation.

Finally, the observed non-linear Hammett plot is only due to the change in the transition state. A better correlation was observed by an Okamoto-Brown plot of $\log k_2$ Vs substituent constants σ^+ with slope = -0.16 (Fig. 5.11, $r > 0.998$ $s < 0.05$) is obtained. This suggests a cross conjugation between the substituent and the reaction centre.

Table 5.1 Fig. 5.1**Effect of [Mn(III)] on the rate of oxidation of PEA [Representative run]** $[\text{Mn(III)}]_0 = 5 \times 10^{-3} \text{ mol.dm}^{-3}$, $[\text{PEA}]_0 = 5 \times 10^{-2} \text{ mol.dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 2 \text{ mol.dm}^{-3}$, $[\text{Mn(II)}] = 0.12 \text{ mol.dm}^{-3}$, temp = 30°C.

Time (min)	% T	O.D	2+log (O.D)
1	39.0	0.4089	1.6117
3	43.0	0.3665	1.5641
5	46.0	0.3374	1.5279
7	50.0	0.3010	1.4786
9	54.0	0.2676	1.4275
11	57.0	0.244 1	1.3876
13	60.0	0.2218	1.346 1
15	63.0	0.2007	1.3025
17	66.0	0.1805	1.2564
19	69.0	0.1612	1.2072
21	71.5	0.1457	1.1634
23	72.5	0.1400	1.1451
25	76.0	0.1192	1.0762

$$k = 9.47 \times 10^{-4} \text{ s}^{-1}$$

Table 5.2**Effect of [Mn(III)], [PEA] and [Ru(III)] on the rate of oxidation of PEA.**[H₂SO₄]=2 mol.dm⁻³, [Mn(II)]=0.12 mol.dm⁻³, temp=30°C

[Mn(III)] ₀ x 10 ³ mol. dm ⁻³	[PEA] ₀ x 10 ² mol. dm ⁻³	[Ru(III)] x 10 ⁷ mol. dm ⁻³	k _{obs} x 10 ⁴ mol. dm ⁻³
1.0	5.0	1.0	9.43
2.0	5.0	1.0	9.37
3.0	5.0	1.0	9.73
4.0	5.0	1.0	9.64
5.0	5.0	1.0	9.47
6.0	5.0	1.0	9.32
7.0	5.0	1.0	9.52
8.0	5.0	1.0	9.17
5.0	1.0	1.0	4.38
5.0	2.0	1.0	6.14
5.0	3.0	1.0	7.28
5.0	4.0	1.0	8.54
5.0	6.0	1.0	10.25
5.0	7.0	1.0	11.26
5.0	8.0	1.0	12.09
5.0	9.0	1.0	12.66
5.0	5.0	0.8	8.41
5.0	5.0	1.2	10.59
5.0	5.0	1.6	12.06
5.0	5.0	1.8	12.75

Table 5.3**Effect of varying $[\text{H}_2\text{SO}_4]$ on the reaction rate.** $[\text{Mn(III)}]_0 = 5 \times 10^{-3} \text{ mol.dm}^{-3}$, $[\text{PEA}]_0 = 5 \times 10^{-2} \text{ mol.dm}^{-3}$, $[\text{Ru(III)}] = 1 \times 10^{-7} \text{ mol.dm}^{-3}$, $[\text{Mn(II)}] = 0.12 \text{ mol.dm}^{-3}$, $\text{temp} = 30^\circ\text{C}$

$[\text{H}_2\text{SO}_4] \text{ mol. dm}^{-3}$	$a_{\text{H}_2\text{O}}$	$-\text{H}_0$	$10^4 k_{\text{obs}} (\text{s}^{-1})$	$-\log(k_{\text{obs}} + \text{H}_0)$
0.5	0.993	0.02	10.84	2.95
1.0	0.963	0.28	10.63	2.69
1.5	0.933	0.73	9.96	2.27
2.0	0.896	1.10	9.47	1.92
2.5	0.869	1.47	8.96	1.58
3.0	0.832	1.96	8.33	1.13
3.5	0.801	2.34	7.71	0.77
4.0	0.768	2.54	7.34	0.59
4.5	0.737	2.95	6.86	0.22
5.0	0.699	3.41	6.44	0.21

Table 5.4**Effect of varying dielectric constant of medium on the rate.** $[\text{Mn(III)}]_0 = 5 \times 10^{-3} \text{ mol.dm}^{-3}$, $[\text{PEA}]_0 = 5 \times 10^{-2} \text{ mol.dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 2 \text{ mol.dm}^{-3}$, $[\text{Mn(II)}] = 0.12 \text{ mol.dm}^{-3}$, $\text{temp} = 30^\circ\text{C}$

% MeOH v/v	D	$10^3/D$	$10^4 k_{\text{obs}} (\text{s}^{-1})$
0.00	76.73	13.0	9.47
2.50	75.40	13.3	9.21
5.00	74.50	13.4	9.61
7.50	73.00	13.7	9.47
10.00	72.35	13.8	9.52
12.50	70.07	14.27	9.39

Table 5.5**Effect of varying ionic strength and added salt on the rate.**

$[\text{Mn(III)}]_0 = 5 \times 10^{-7} \text{ mol.dm}^{-3}$, $[\text{PEA}]_0 = 5 \times 10^{-2} \text{ mol.dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 2 \text{ mol.dm}^{-3}$, $[\text{Ru(III)}] = 1 \times 10^{-7} \text{ mol.dm}^{-3}$, $[\text{Mn(II)}] = 0.12 \text{ mol.dm}^{-3}$, temp = 30°C

$[\text{ClO}_4^-]$ mol.dm ⁻³	$10^4 k_{\text{obs}}$ (s ⁻¹)	$[\text{Cl}^-]$ mol.dm ⁻³	$10^4 k_{\text{obs}}$ (s ⁻¹)	$[\text{F}^-]$ mol.dm ⁻³	$10^4 k_{\text{obs}}$ (s ⁻¹)	$[\text{SO}_4^{2-}]$ mol.dm ⁻³	$10^4 k_{\text{obs}}$ (s ⁻¹)	$[\text{Mn(II)}]$ mol.dm ⁻³	$10^4 k_{\text{obs}}$ (s ⁻¹)
6.0	9.81	0.0	9.47	0.0	9.47	0.0	9.47	0.12	9.47
8.0	9.42	0.01	9.67	0.01	9.31	0.01	9.51	0.14	9.66
10.0	8.99	0.05	9.74	0.05	9.29	0.05	9.70	0.16	9.42
12.0	9.32	0.10	9.09	0.10	9.61	0.10	9.44	0.18	9.35

Table 5.6**Proton inventory studies for PEA in H₂O - D₂O mixture.**

$[\text{Mn(III)}]_0 = 5 \times 10^{-3} \text{ mol.dm}^{-3}$, $[\text{PEA}]_0 = 5 \times 10^{-2} \text{ mol.dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 2 \text{ mol.dm}^{-3}$, $[\text{Ru(III)}] = 1 \times 10^{-7} \text{ mol.dm}^{-3}$
 $[\text{Mn(II)}] = 0.12 \text{ mol.dm}^{-3}$, temp = 30°C

Atom fraction of deuterium (n)	$10^4 k_{\text{obs}}$ (s ⁻¹)
0.000	9.47
0.250	8.65
0.500	8.15
0.750	7.30
0.900	6.85

Table 5.7 Fig. 5.7**Effect of varying temperature on the reaction rate**

$[\text{Mn(III)}]_0 = 5 \times 10^{-7} \text{ mol.dm}^{-3}$, $[\text{PEA}]_0 = 5 \times 10^{-2} \text{ mol.dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 2 \text{ mol.dm}^{-3}$, $[\text{Ru(III)}] = 1 \times 10^{-7} \text{ mol.dm}^{-3}$, $[\text{Mn(II)}] = 0.12 \text{ mol.dm}^{-3}$, temp = 30°C

Temperature (K)	$10^4 k_{\text{obs}}$ (s ⁻¹)
298	6.82
303	9.47
308	12.91
313	17.78

Slope

 2.72×10^3

r

0.969

s

0.05

Table 5.8

Kinetic and thermodynamic parameters for the oxidation of PEA by Mn(III).

Ea kJmol ⁻¹	ΔH^\ddagger kJmol ⁻¹	ΔS^\ddagger JK ⁻¹ mol ⁻¹	ΔG^\ddagger kJmol ⁻¹	logA
52.3	49.7	140.1	92.5	10.1

Table 5.9

Second order rate constants for the oxidation of 4-substituted phenethyl alcohols by Mn(III)

Mn(III)₀=0.005 mol.dm⁻³, [PEA]=0.05 mol.dm⁻³, [H₂SO₄]=2 mol.dm⁻³,
 [Ru(III)]=1x10⁻⁷ mol.dm⁻³, [Mn(II)]=0.12 mol.dm⁻³, temp 30°C

substituents X	$10^2 k_2 = k_{obs} / [X-PEA]$ (dm ³ mol ⁻¹ s ⁻¹)	σ_p	σ^+
NO ₂	1.41	0.78	0.79
Cl	1.70	0.23	0.11
Br	1.79	0.23	0.15
H	1.89	0.00	0.00
CH ₃	2.21	-0.17	-0.3 1
OCH ₃	2.50	-0.27	-0.78

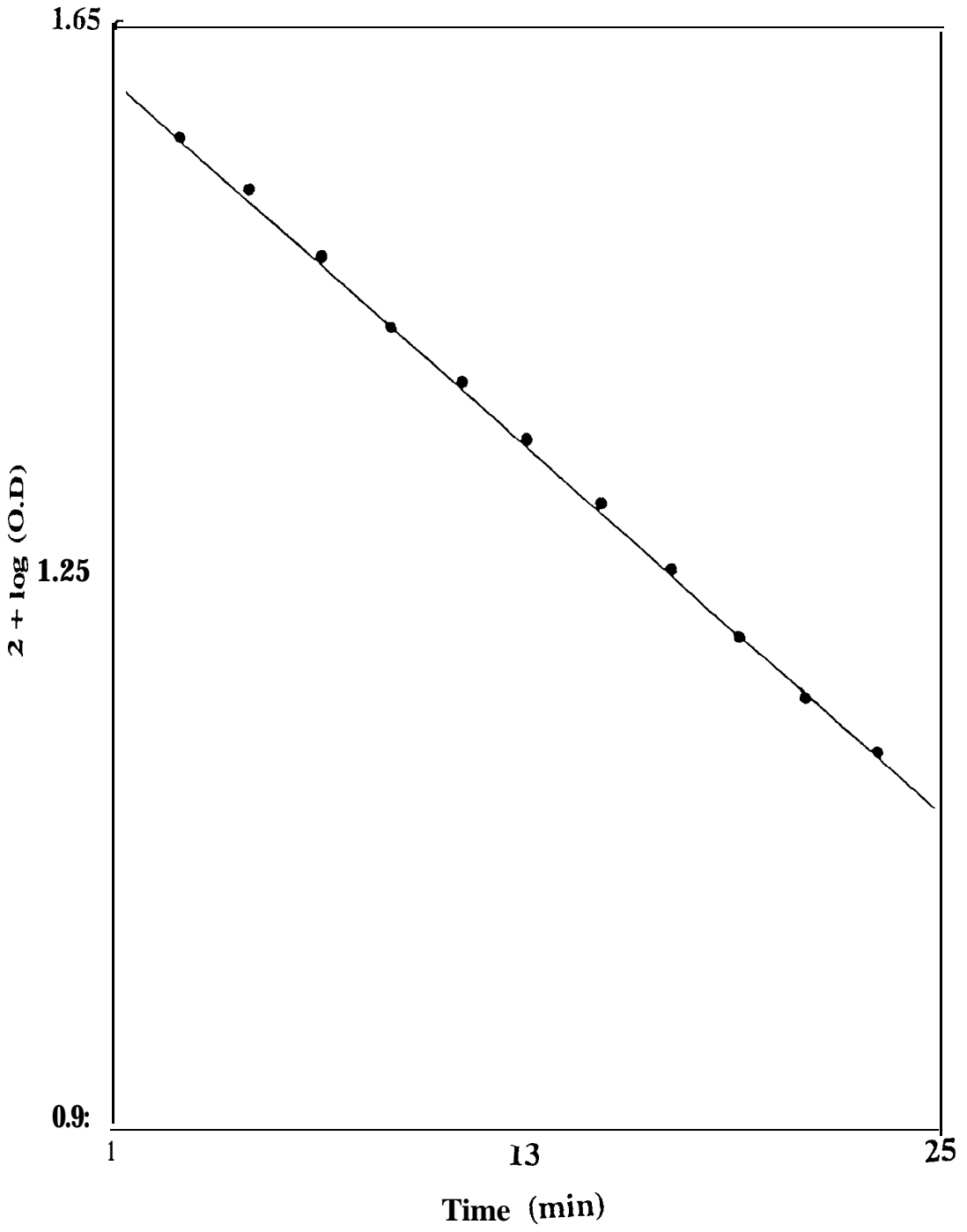
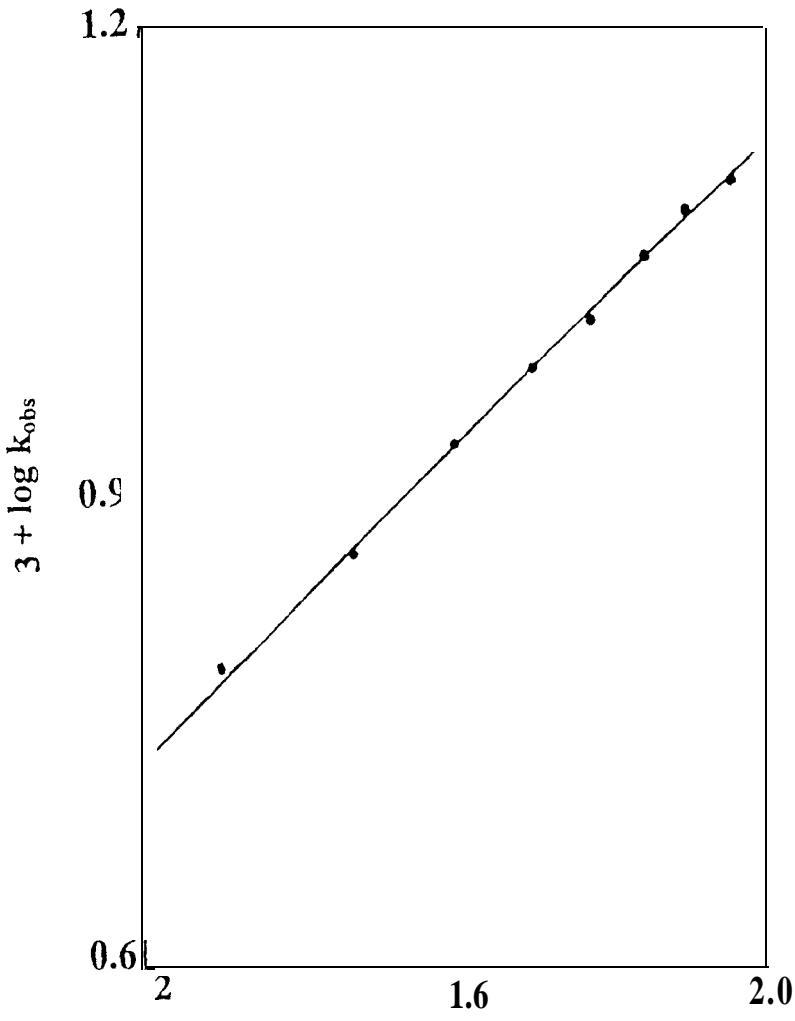


Fig. 5.1



$4 + \log [\text{PEA}]$,

Fig. 5.2

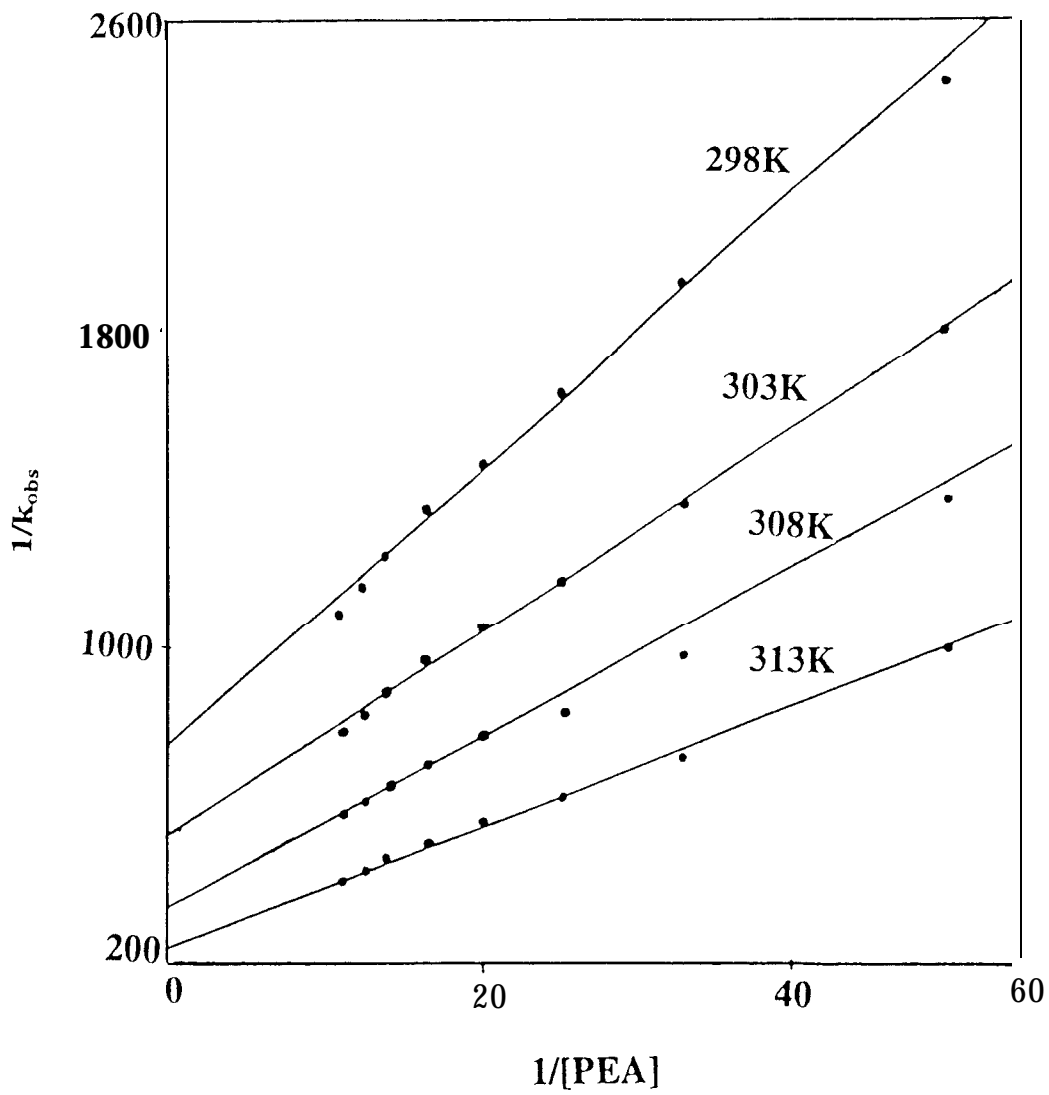


Fig. 5.3

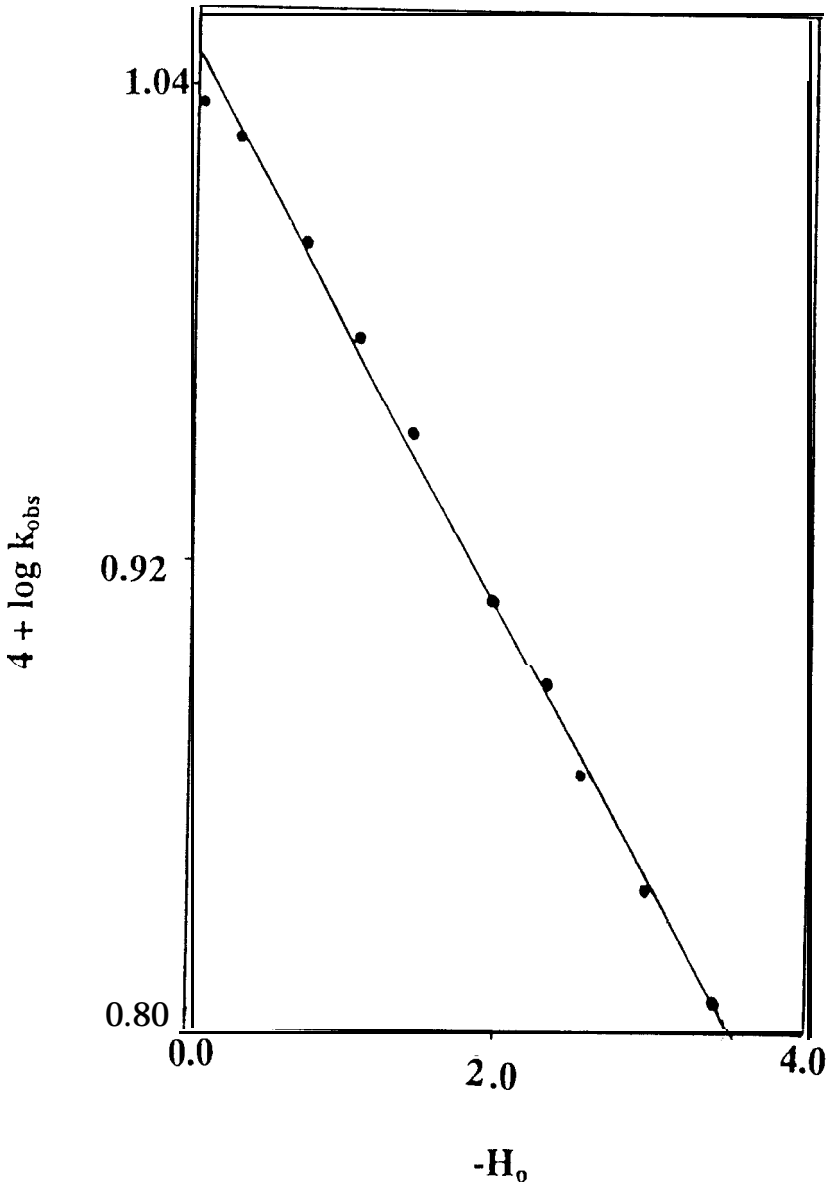


Fig. 5.4

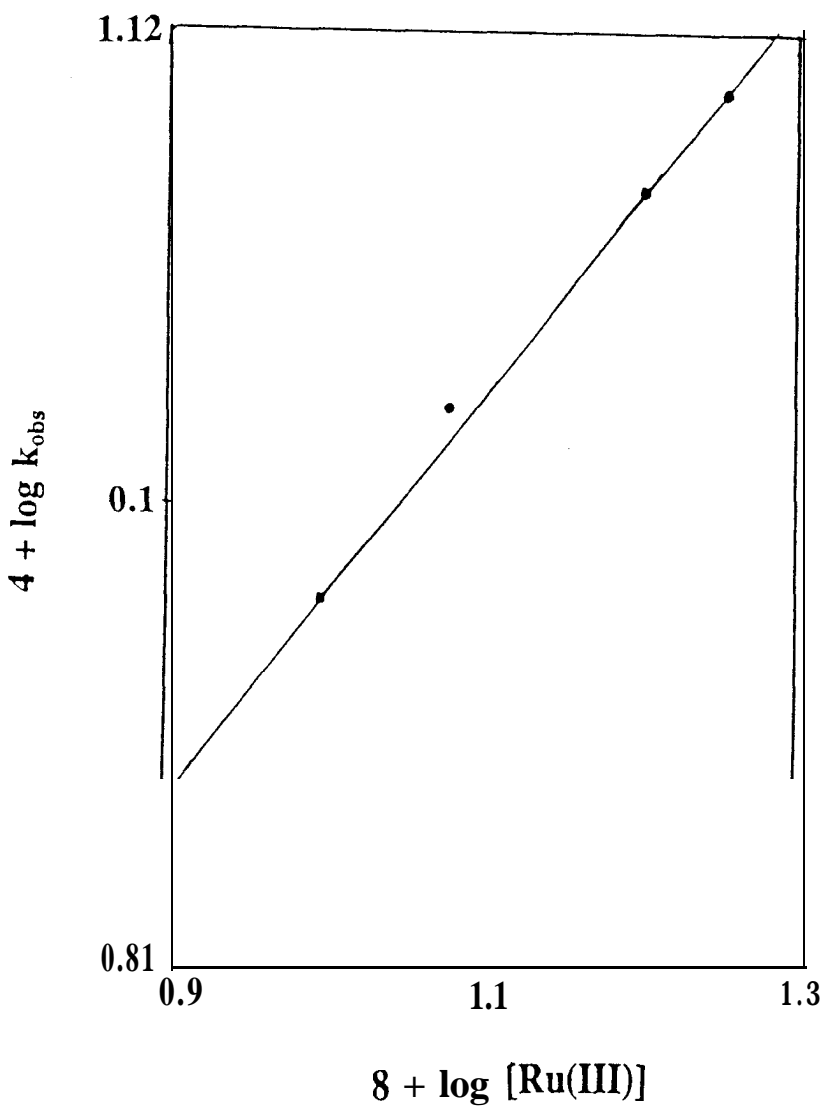


Fig. 5.5

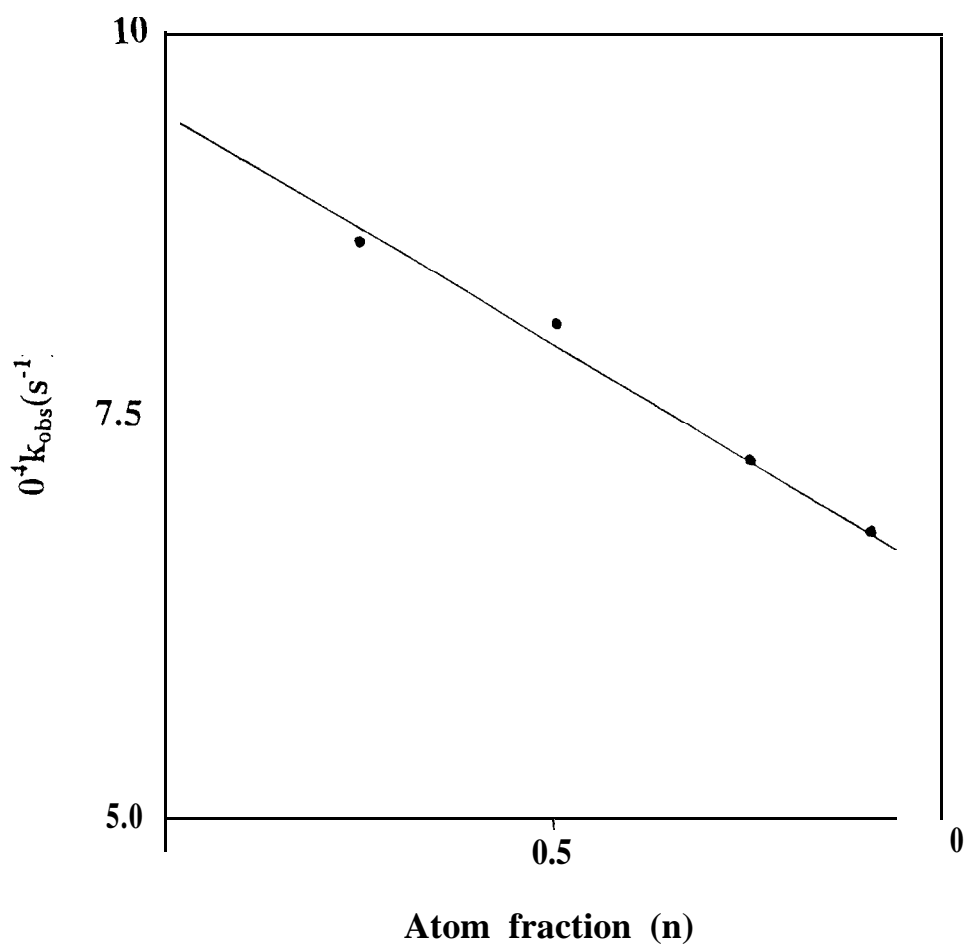


Fig. 5.6

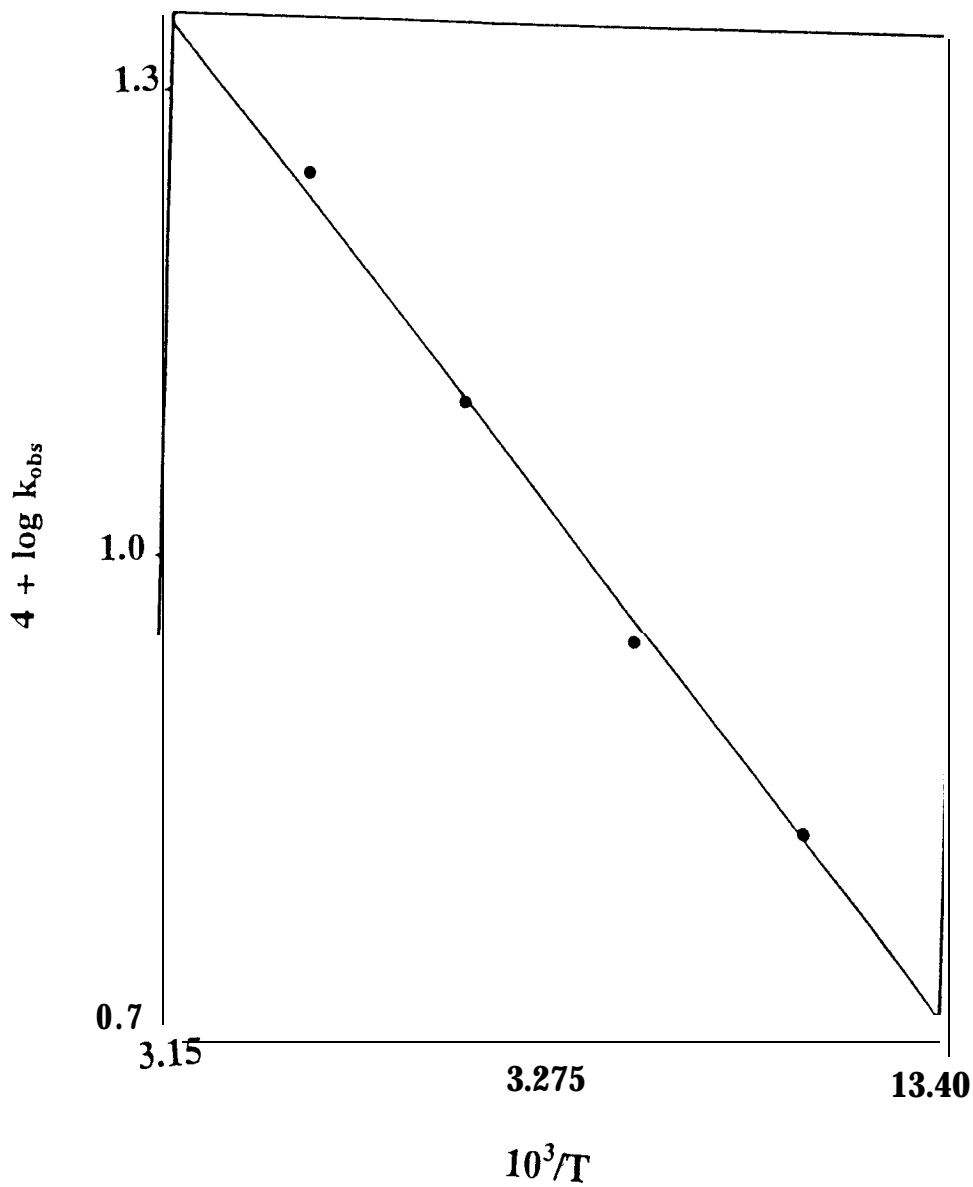


Fig. 5.7

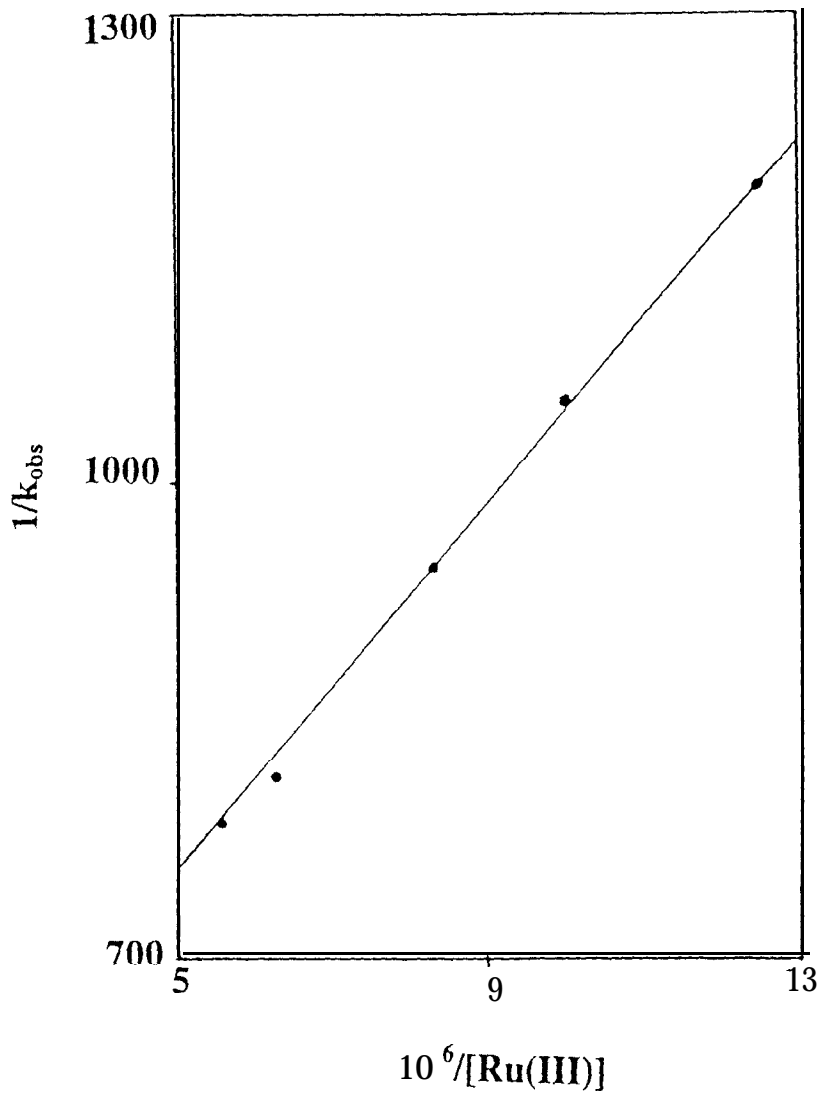


Fig. 5.8

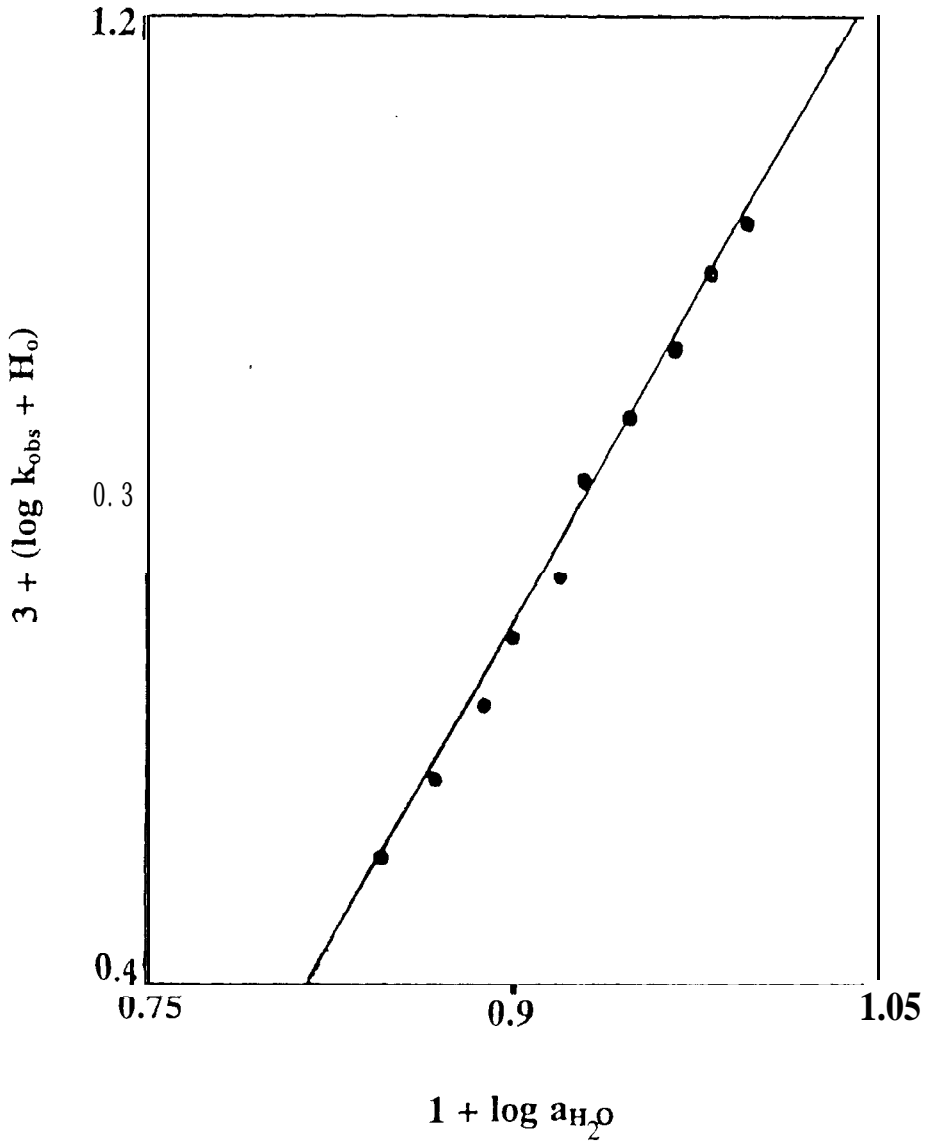


Fig. 5.9

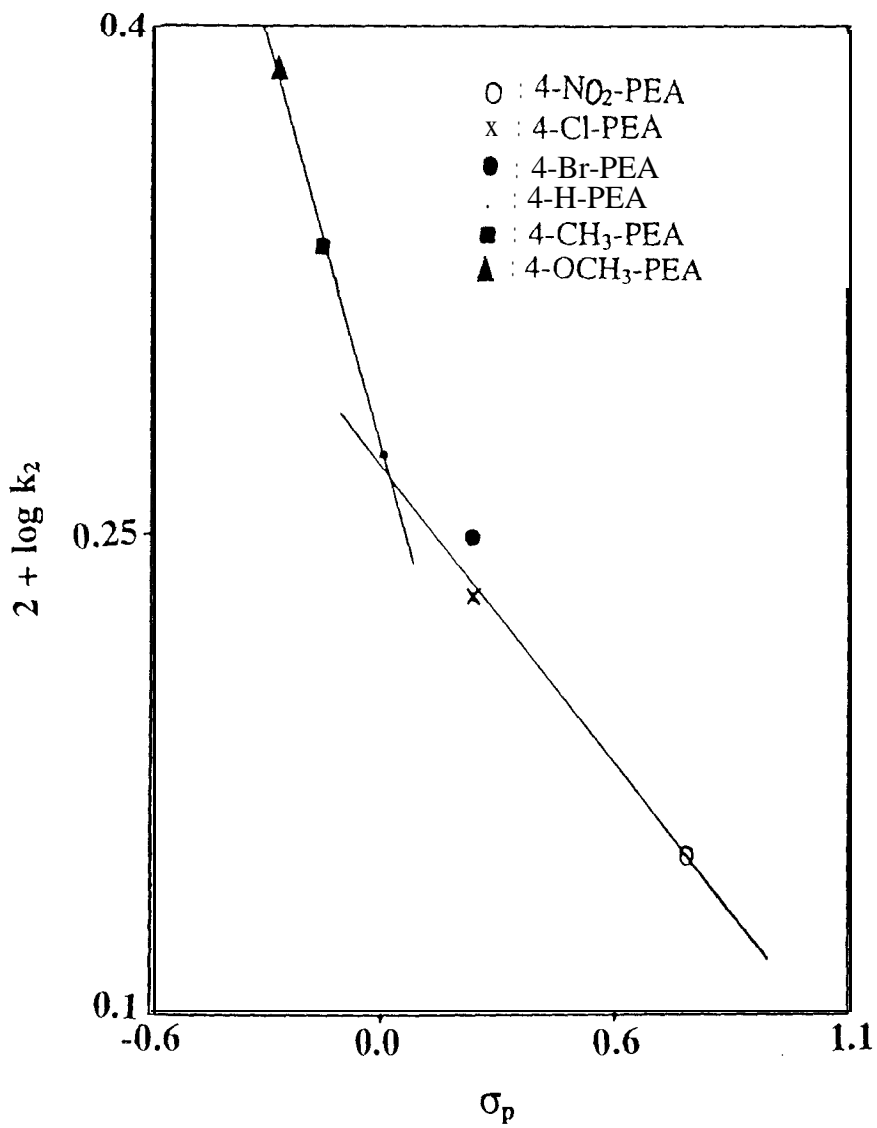


Fig. 5.10

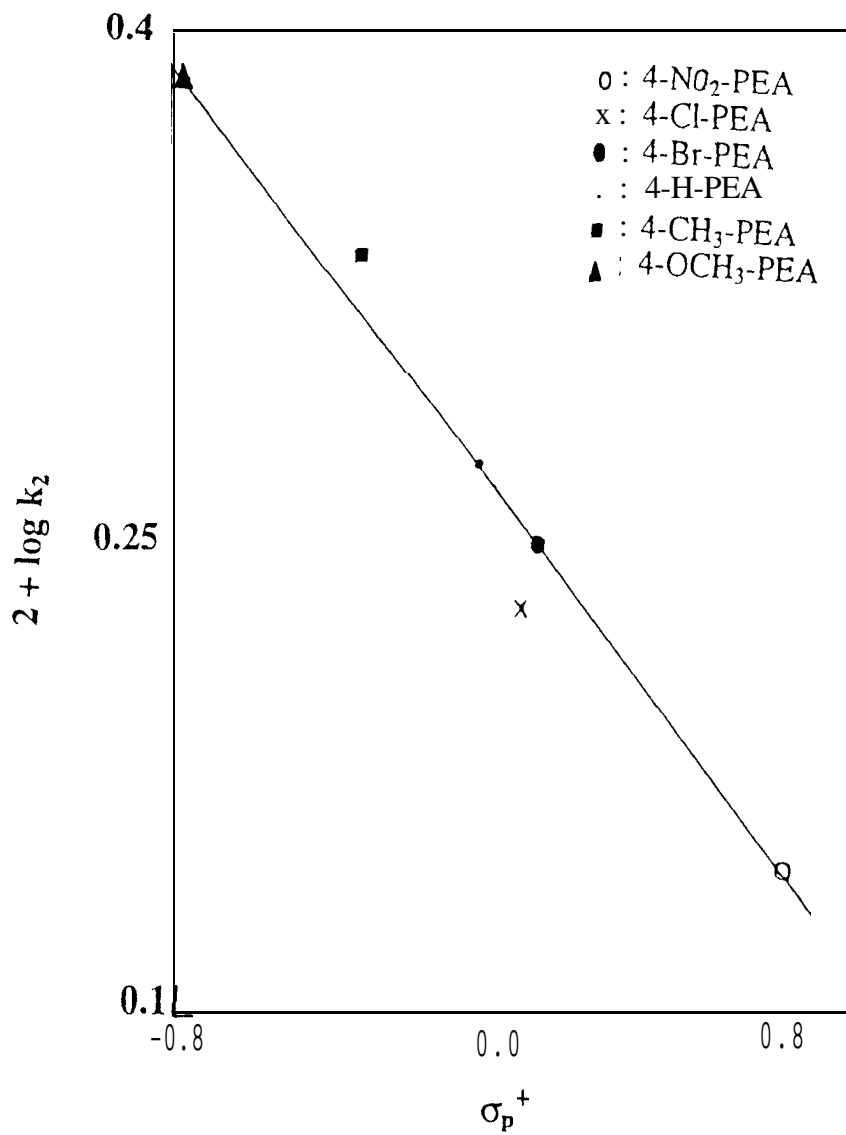


Fig. 5.11

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SUMMARY

Kinetic and mechanistic aspects of oxidation of some organic compounds such as D-glucose, D-fructose, D-mannose, L-sorbose (hexoses), D-xylose, L-arabinose, D-ribose (pentoses), D-glucuronic acid and D-galacturonic acid (uronic acids), L-fucose, L-rhamnose (6-deoxy hexoses) and aromatic primary alcohols by manganese(III) sulphate in sulphuric acid medium are presented in this thesis.

Four hexoses, viz. D-glucose, D-fructose, D-mannose and L-sorbose and three pentoses namely D-xylose, L-arabinose and D-ribose have been oxidized by Mn(III) in aqueous H₂SO₄ medium at 30°C. The rate shows first order dependence on Mn(III) and substrates, but independent of [H⁺]. The following rate law is obeyed

$$\text{Rate} = k_1 [\text{Mn}^{3+}] [\text{E}]$$

The effect of added anions such as Cl⁻, F⁻, SO₄⁻, ionic strength of medium, dielectric constant of medium and reaction product Mn(II) on the rate are studied. The products were analysed by paper chromatography using I-butanol; water; acetic acid (4:5:1) as solvent system and p-anisidine hydrochloride as detecting agent. A suitable mechanism has been proposed

The kinetics of oxidation of two uronic acids, D-glucuronic acid and D-galacturonic acid by Mn(III) in H₂SO₄ medium at 30°C has been studied. The observed rate law is of the form rate = k_{obs} [Mn³⁺] [E] i.e., rate shows a first order dependence on Mn(III) and substrate and it is independent of [H⁺]. Effect of added anions, ionic strength of medium, dielectric constant of medium and reaction product Mn(III) on the rate is studied. The products were analysed by paper chromatography using 1-butanol: acetic acid: water (4:1:5) as solvent system and p-anisidine hydrochloride as detecting agent. A suitable mechanism has been proposed from the above observed kinetics.

The kinetics of oxidation of 6-deoxyhexoses, L-fucose and L-rhamnose by Mn(III) in H₂SO₄ medium at 30°C has been studied. The rate shows first order dependence on Mn(III) and substrates, but independent of [H⁺]. The following rate law is obeyed

$$\text{rate} = k_1 [\text{Mn}^{3+}] [\text{E}]$$

The effect of added anions, ionic strength of medium, dielectric constant of medium and reaction product Mn(II) on the rate are studied. Products were analysed by paper chromatography using 1-butanol : water : acetic acid (4:5:1 v/v/v) as solvent system and p-anisidine hydrochloride as detecting agent.

Six aromatic primary alcohols - phenethyl alcohol, 4-chlorophenethyl alcohol, 4-bromo-phenethyl alcohol, 4-nitro-phenethyl alcohol, 4-methyl-phenethyl alcohol and 4-methoxy-phenethyl alcohol were oxidised by Mn(III) using Ru(III) as catalyst in H₂SO₄ medium at 30°C. The product phenacetaldehyde was identified by TLC and through its 2,4-dinitrophenylhydrazone derivative.

The rate shows first order with respect to Mn(III), fractional order in [PEA] and [Ru(III)] an inverse fractional order with respect to acidity function[H⁰]

Kinetics studies in D₂O medium shows that the rate is lower in D₂O leading to solvent isotope effect. Proton inventory studies have been made in H₂O-D₂O mixtures. Effects of substituents like -NO₂, -Cl, -Br, -CH₃ and -OCH₃ at position 4 in phenethyl alcohol on the rate has been studied at 30°C. The Hammett plot for various substrates, gives two distinct lines, but a better correlation was observed by Okamoto-Brown plot suggesting the cross conjugation between the substituent and the reaction center. An isokinetic relation is observed with $\beta = 330\text{K}$, which is higher than the experimental temperature (303K) indicating that the enthalpy of activation as rate controlling factor.

APPENDIX

Regression analysis of the experimental data

Regression coefficient 'r' is given by the formula',

$$r = \frac{\overline{XY} - \bar{x} \cdot \bar{Y}}{S_x \cdot s_Y}$$

Where $S_x = \sqrt{\frac{\Sigma X^2}{n} - \left(\frac{\Sigma X}{n}\right)^2}$

and $S_y = \sqrt{\frac{\Sigma Y^2}{n} - \left(\frac{\Sigma Y}{n}\right)^2}$

where n = Number of trials

Using the above equations for a given set of X and Y values, S_x and S_y can be calculated and 'r' the regression coefficient can be obtained.

Standard deviation 'S' of the points from the regression line can be calculated by the formula,

$$S = \sqrt{\frac{nS_y^2 - \frac{n(\overline{XY} - \bar{X} \cdot \bar{Y})^2}{S_x^2}}{n - 2}}$$

Also, 'r' can be calculated by the formula, $r = m \frac{\sigma_x}{\sigma_y}$

where the standard deviation in X, namely, $\sigma_x = \sqrt{\frac{\Sigma X^2}{n} - (\bar{X})^2}$,

the standard deviation in Y, namely, $\sigma_y = \sqrt{\frac{\Sigma Y^2}{n} - (\bar{Y})^2}$,

and 'm' is the slope for a given straight line for a set of X and Y values.

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