RESEARCH ARTICLE   PEN ACCESS

A Comparative Study of Kinetics of Oxidation of Some acetophenones by Hexacyanoferrate [III] in alkaline medium.

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ABSTRACT
In this study the kinetics of oxidation of o- hydroxyacetophenone, p- hydroxyacetophenone & m-hydroxyacetophenone, p-methoxy acetophenone and p-bromo acetophenone by hexacyanoferrate (III) has been studied in alkaline medium and has been analysed. The order of reaction with respect of both acetophenone and hexacynoferrate (III) has been found to be unity. The rate of reaction increases with increase in the temperature. Various   activation parameters have been calculated. A negative entropy of activation due to solvation of activated complex has been studied in each case.
KEYWORDS: Acetophenone; Hexacyanoferrate; Oxidation; Mechanism; Kinetics
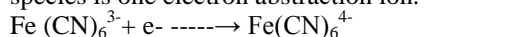

I.   INTRODUCTION

Aromatic ketones play a vital role and are being used for the synthesis of a large number of products such as, fragrances, colored dyes and pesticides [1-3]. Ketones are largely used for the synthesis of drugs in the pharmaceutical chemistry [4]. Aromatic ketones are mainly prepared by acylation of acyl chlorides, nitriles and also by dehydrogenation of alcohol. The Kinetics and mechanism of oxidation of acetophenone in acidic medium have been studied [5] due to high solubility in acids. But the study of oxidation of acetophenone in alkaline medium has not been researched enough by the researchers.

.Potassium   ferricyanides   also   known   as hexacyanoferrate (III), in which the oxidising species is one electron abstraction ion.
Fe $(CN)_6^{3-}$+ e- ----→ Fe$(CN)_6^{4-}$
The redox potential of the system is 0.45 volts. In alkaline medium the oxidation of aniline and substituted aniline has been studied by hexacyanoferrate (III) at constant ionic strength is reported by Radhakrishamurti & Panda. [6].

Hexacyanoferrate (III) has been proved to be an efficient oxidant for many reactions, because the CN^- ligands are resistant to substitution reactions and thereby outer-sphere electron transfer is the preferred oxidation pathway [7]. Kinetics of oxidation of ketones [8,9] has been studied in alkaline medium by hexacyanoferrate (III),which is an oxidising agent in which the oxidising species is a complex electron attracting ion and the reactions are brought to proceed by a radical formation [10,11]. In continuation of our earlier work[12, 13], the present paper deals with the comparative study of the kinetics and oxidation of o   –   hydroxyacetophenone,   p   –

hydroxyacetophenone, m-hydroxyacetophenone, p-methoxyacetophenone and p-bromo acetophenones by hexacyanoferrate (III) in alkaline medium. I am pursuing mainly the effect of temperature and will also evaluate various thermodynamic parameters like entropy, enthalpy etc and also compare rate of reaction of above mentioned acetophenones.

Aim of the Study

The kinetics of oxidation of ketones by hexacyanoferrate(III) has been done by many researchers. Singh et al [14] have studied the kinetics of oxidation of acetone and ethyl methyl ketone by different oxidants in alkaline medium .The mechanism of these reactions in solution can be determined by knowing the order of reaction with respect to each reactant. But evaluation of thermodynamic parameters are also important because it gives information about the rate of the reaction.

II.   EXPERIMENTAL
Materials and Methods

o, p & m-hydroxyacetophenone, p-methoxy acetophenone and p-bromo acetophenone (Fluka) and all other chemicals of A.R., B.D.H. grade were used. In a 50 ml flask freshly prepared standard solution of acetophenone in methanol-water (w/w) and in another flask desired solution of hexacyanoferrate(III) and NaOH were taken and placed in a thermostat maintained at ± 0.1° C accuracy.
After half an hour both the reactants were mixed. At different interval of time, 5 ml aliquot was taken out and poured in a flask containing 5 ml of 2N H_2SO_4 and 1 gm of KI. The

unreacted $K_3Fe(CN)_6$ was estimated by titrating the liberated iodine against standard sodium thiosulphate solution, using starch as an indicator.

$$2 \quad Fe(CN)_6^{3-} + 2I^- \longrightarrow 2Fe(CN)^{4--} + I_2$$
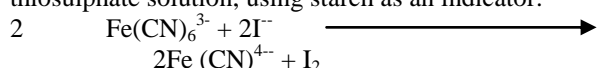
III. RESULT AND DISCUSSION

Under pseudo conditions [aceto]>>$[Fe(CN)_6]^{3-}$, the data collected at varying concentration of [acetophenones] at constant concenteration of $[Fe(CN)_6]^{3-}$ and at constant Ionic Strength show first order dependence .Under such conditions the reaction of all acetophenones are studied at 20°C, 25°C, 30°C, 40°C & 45°C. The summarized results in Table (1-5) show that the reaction rate increases with the increase in Temperature. Energy of activation has been calculated from the slopes of linear plots (Fig. 1-5) between log k_1 and 1/T. The values of the curves has been shown in Table (6) for each acetophenone.

Table 1
Effect of Temperature on o-hydroxy acetophenone oxidation

$[K_3Fe(CN)_6] = 2 \times 10^{-2}$ M, [NaOH]= 0.25 M, [Methanol] = 20% (v/V), μ=0.5 M,

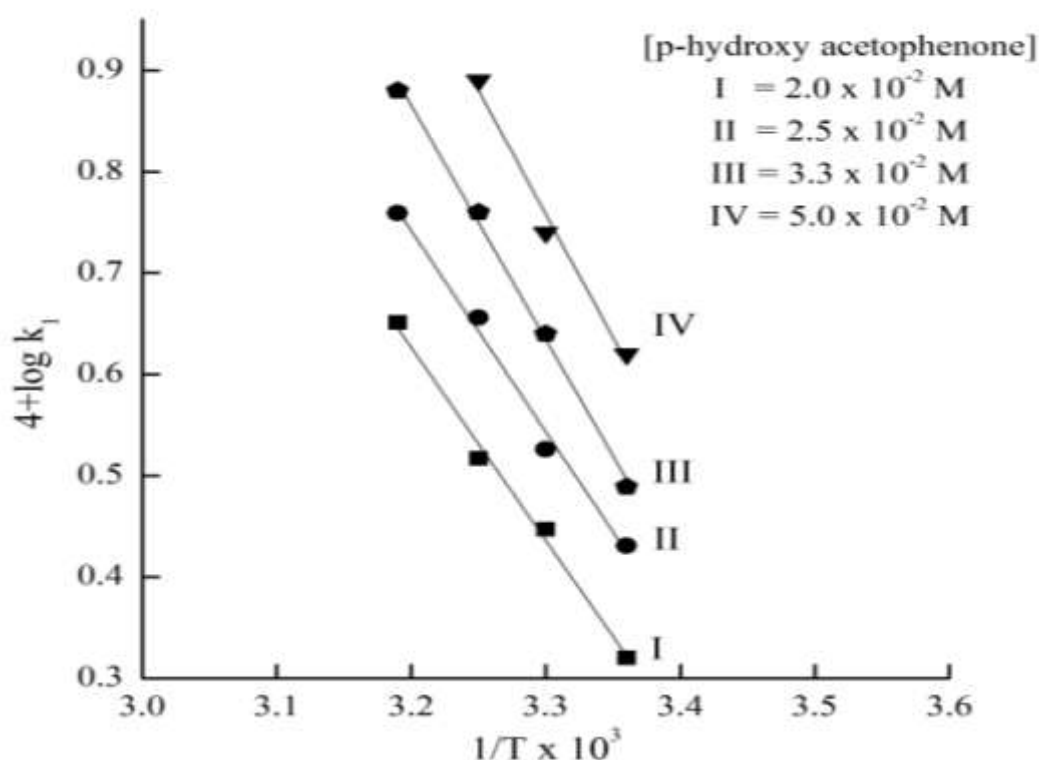| Temperature (°C)	$1/T \times 10^3$	$k_1 \times 10^4$	$4 + \log k_1$
[o-hydroxy acetophenone] = 2.0×10^{-2} M			
25	3.36	1.47	0.167
30	3.30	2.07	0.316
35	3.25	3.33	0.522
40	3.19	3.71	0.569
[o-hydroxy acetophenone] = 2.5×10^{-2} M			
25	3.36	1.70	0.230
30	3.30	2.80	0.447
35	3.25	3.86	0.587
40	3.19	5.63	0.751
[o-hydroxy acetophenone] = 3.3×10^{-2} M			
25	3.36	2.34	0.369
30	3.30	3.35	0.525
35	3.25	4.79	0.680
40	3.19	7.56	0.879
[o-hydroxy acetophenone] = 5.0×10^{-2} M			
25	3.36	3.54	0.549
30	3.30	5.31	0.725
35	3.25	7.63	0.883
40	3.19	14.0	1.150
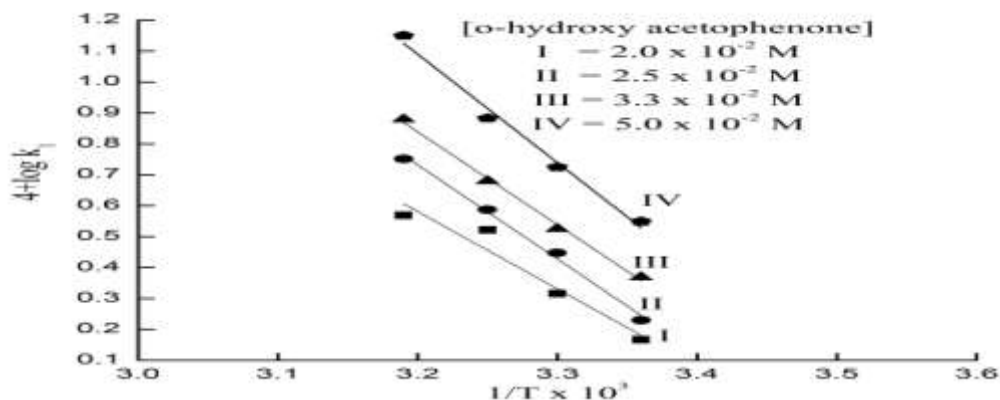
Fig.1: Effect of Temperature on o-hydroxy acetophenone oxidation at $[K_3Fe(CN)_6] = 2 \times 10^{-2}$ M, [NaOH]= 0.25 M, μ=0.5 M,

Table 2
Effect of Temperature on p- hydroxy acetophenone oxidation

$[K_3Fe(CN)_6]$ = 2.5 × 10^{-3} M, [NaOH]= 0.25 M, μ=0.5 M,

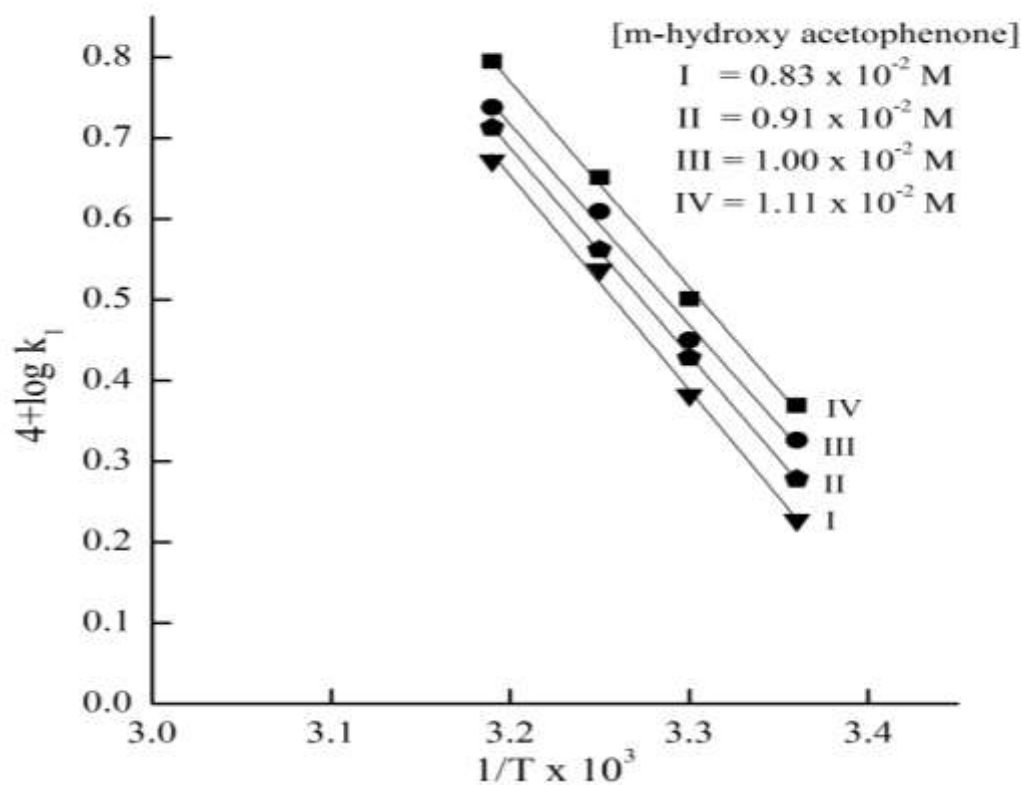| Temperature (°C)	1/T × 10^3	k_1 × 10^4	4 + logk_1
[p-hydroxy acetophenone] = 2.0 × 10^{-2} M			
25	3.36	2.10	0.320
30	3.30	2.80	0.447
35	3.25	3.29	0.517
40	3.19	4.48	0.651
[p-hydroxy acetophenone] = 2.5 × 10^{-2} M			
25	3.36	2.70	0.431
30	3.30	3.36	0.526
35	3.25	4.53	0.656
40	3.19	5.74	0.759
[p-hydroxy acetophenone] = 3.3 × 10^{-2} M			
25	3.36	3.09	0.489
30	3.30	4.40	0.640
35	3.25	5.79	0.760
40	3.19	7.72	0.880
[p-hydroxy acetophenone] = 5.0 × 10^{-2} M			
25	3.36	4.14	0.620
30	3.30	5.50	0.740
35	3.25	7.72	0.890
40	3.19	–	–

Fig.2: Effect of Temperature on p-hydroxy acetophenone oxidation at $[K_3Fe(CN)_6]$ = 2.5 × 10^{-3} M, [NaOH]= 0.25 M, μ=0.5 M,

Table 3
Effect of Temperature on m-hydroxy acetophenone oxidation
$[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M, [NaOH]= 0.1 M, μ=0.2 M

| Temperature (°C)	$1/T \times 10^3$	$k_1 \times 10^4$	$4 + \log k_1$
[m-hydroxy acetophenone] = 0.83×10^{-2} M			
25	3.36	1.69	0.227
30	3.30	2.41	0.382
35	3.25	3.44	0.537
40	3.19	4.69	0.672
[m-hydroxy acetophenone] = 0.91×10^{-2} M			
25	3.36	1.90	0.278
30	3.30	2.68	0.428
35	3.25	3.65	0.562
40	3.19	5.76	0.713
[m-hydroxy acetophenone] = 1.00×10^{-2} M			
25	3.36	2.12	0.326
30	3.30	2.82	0.45
35	3.25	4.07	0.609
40	3.19	5.47	0.738
[m-hydroxy acetophenone] = 1.11×10^{-2} M			
25	3.36	2.34	0.369
30	3.30	3.17	0.501
35	3.25	4.48	0.651
40	3.19	6.23	0.795

Fig.3: Effect of Temperature on m-hydroxy acetophenone oxidation at $[K_3Fe(CN)_6] = 1.0 \times 10^{-3}$ M, [NaOH]= 0.1 M, μ=0.2 M,

Table 4
Effect of Temperature on p-methoxy acetophenone oxidation

$[K_3Fe(CN)_6] = 2.5 \times 10^{-3}$ M, [NaOH]= 0.20 M, [Methanol] = 20% (v/V), μ=0.5 M

| Temperature (°C)	$1/T \times 10^3$	$k_1 \times 10^4$	$4 + \log k_1$
[p-methoxy acetophenone] = 2.00×10^{-2} M			
25	3.36	4.61	0.664
30	3.30	6.36	0.803
35	3.25	8.43	0.926
40	3.19	–	–
[p-methoxy acetophenone] = 1.66×10^{-2} M			
25	3.36	3.70	0.568
30	3.30	5.40	0.732
35	3.25	7.10	0.851
40	3.19	–	–
[p-methoxy acetophenone] = 1.43×10^{-2} M			
25	3.36	3.30	0.519
30	3.30	4.57	0.659
35	3.25	6.10	0.785
40	3.19	8.52	0.930
[p-methoxy acetophenone] = 1.25×10^{-2} M			
25	3.36	2.90	0.462
30	3.30	4.01	0.603
35	3.25	5.41	0.733
40	3.19	7.55	0.878
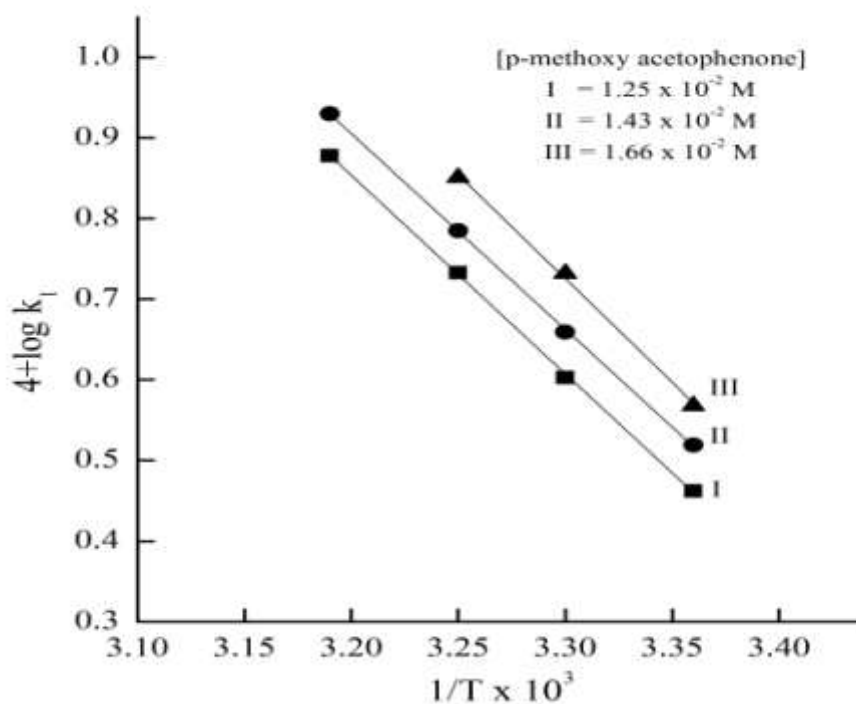
Fig.4: Effect of Temperature on p-methoxy acetophenone oxidation at $[K_3Fe(CN)_6] = 2.5 \times 10^{-3}$ M, [NaOH]= 0.2 M, [Methanol] = 20% (v/V), μ=0.5 M,

Table 5
Effect of Temperature on [p- bromo acetophenone] oxidation

$[K_3Fe(CN)_6] = 2.0 \times 10^{-3}$ M, [NaOH] = 0.167 M, [Methanol] = 30% (v/V), $\mu=0.4$ M

Temperature (°C)	$1/T \times 10^3$	$k_1 \times 10^4$	$4 + \log k_1$
[p-bromo acetophenone] = 1.67×10^{-2} M			
25	3.36	2.54	0.405
30	3.30	4.35	0.638
35	3.25	6.51	0.814
40	3.19	–	–
[p-bromo acetophenone] = 1.43×10^{-2} M			
25	3.36	2.17	0.336
30	3.30	3.68	0.566
35	3.25	5.55	0.744
40	3.19	–	–
[p-bromo acetophenone] = 1.25×10^{-2} M			
25	3.36	1.96	0.292
30	3.30	3.14	0.497
35	3.25	4.68	0.670
40	3.19	6.87	0.837
[p-bromo acetophenone] = 1.11×10^{-2} M			
25	3.36	1.64	0.215
30	3.30	2.78	0.444
35	3.25	4.26	0.629
40	3.19	6.47	0.811
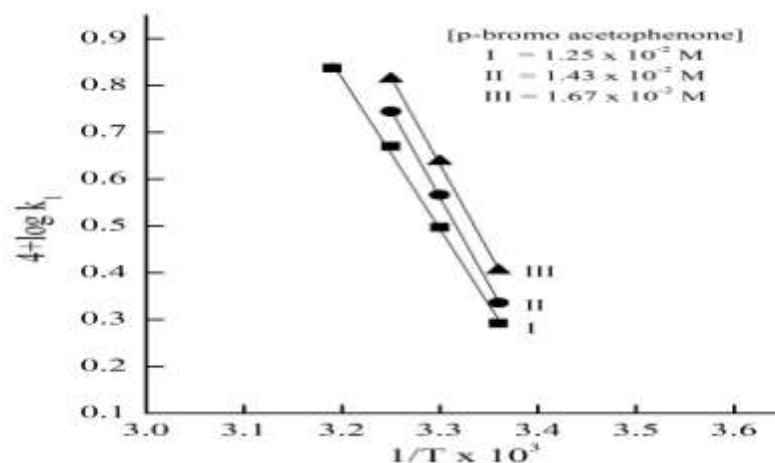
Fig.5: Effect of Temperature on p-bromo acetophenone oxidation at $[K_3Fe(CN)_6] = 2.0 \times 10^{-3}$ M, [NaOH]= 0.167 M, [Methanol] = 30% (v/V), $\mu=0.4$ M,

Table 6
Showing the Values of Energy of Activation

Acetophenones	Value of E_a obtained from curves				Mean E_a
	I	II	III	IV	
o-hydroxy	47.90	58.20	57.40	66.99	57.60
p-hydroxy	36.44	37.95	44.17	46.68	41.31
m-hydroxy	50.83	49.15	47.54	48.71	49.00
p-methoxy	47.06	48.40	49.34	–	48.26
p-bromo	61.74	71.06	71.27	–	68.02

Calculation of Activation Parameters-
Thermodynamically relationship between specific rate constant and entropy of activation is expressed as -

$$K_r = K_b \ T/h. \ e \ \Delta S^{\#}/R \ .e^{-} \ \Delta H^{\#}/RT$$

(Eyring Equation)

Where k is the Boltzman constant and h is the Planck's constant. From the above equation entropy of activation $\Delta S^{\#}$ can be calculated. $\Delta H^{\#}$ is calculated by the equation

$$\Delta H^{\#} = E_a - RT$$

The value of k_r in terms of $mole^{-2} \ lit^2 \ sec^{-1}$ in the present case are obtained by

$$K_r = k_1 / [Aceto] \ [O \ H^-]$$

With the help of the above equations the thermodynamic parameters have been evaluated and are listed below in Table (7, 8):

Table 7
Activation Parameters at 30°C

Activation Parameters (Units)	o-hydroxy acetophenone	p-hydroxy acetophenone	m-hydroxy acetophenone	p-methoxy acetophenone	p-bromo acetophenone
$k_r \times 10^2$ ($Mole^{-2}l^2s^{-1}$)	4.48	5.61	28.20	12.72	15.80
E_a (kJ $mole^{-1}$)	57.60	41.31	49.05	48.26	68.02
k" ($Mole^{-2}l^2s^{-1}$)	7.06×10^{-15}	8.80×10^{-15}	4.40×10^{-12}	2.00×10^{-14}	2.49×10^{-14}
$\Delta H^{\#}$ (kJ $mole^{-1}$)	55.08	38.79	46.53	45.74	65.50
$\Delta S^{\#}$ ($JK^{-1}mol^{-1}$)	−142.83	−141.08	−63.92	−111.34	−44.22
$\Delta F\#$ (kJ $mole^{-1}$)	98.36	81.54	65.90	79.48	78.90

Table 8
Activation Parameters At 35°C

Activation Parameters (Units)	o-hydroxy acetophenone	p-hydroxy acetophenone	m-hydroxy acetophenone	p-methoxy acetophenone	p-bromo acetophenone
$k_r \times 10^2$ ($Mole^{-2}l^2s^{-1}$)	6.10	6.58	40.70	16.86	23.44
E_a (kJ $mole^{-1}$)	57.60	41.31	49.05	48.26	68.02
k" ($Mole^{-2}l^2s^{-1}$)	9.0×10^{-16}	1.01×10^{-16}	6.1×10^{-14}	2.61×10^{-14}	3.6×10^{-14}
$\Delta H^{\#}$ (kJ $mole^{-1}$)	55.04	38.75	46.96	45.70	65.45
$\Delta S^{\#}$ ($JK^{-1}mol^{-1}$)	−109.44	−180.50	−102.17	−111.80	−44.96
$\Delta F\#$ (kJ $mole^{-1}$)	88.75	94.35	77.96	80.14	79.31

In the present case negative entropy of activation has been obtained which shows that activated complex becomes much more polarized and highly solvated in the later stage than earlier stage of complex formed by the interaction of reactants which leads to a decrease in entropy of activation for all five acetophenones.

IV. CONCLUSION

In comparing the rate of oxidation of these acetophenones (Table 6,7), it is observed that the rate of oxidation follow the order:

m-hydroxy acetophenone > p-bromo acetophenone > p-methoxy acetophenone > p- hydroxyl acetophenone > o-hydroxy acetophenone

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