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A KINETIC APPROACH TO THE OXIDATION OF ALIPHATIC ALCOHOLS BY $KBrO_3$ IN ACIDIC MEDIUM USING TRANSITION METAL ION CATALYSTS

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ABSTRACT

This paper discusses the kinetic and thermodynamic investigations of the oxidation of the aliphatic alcohols, 1-propanol, 1-butanol, 1-hexanol, Isoamyl alcohol and Isobutyl alcohol by $KBrO_3$ in acidic medium using transition metal ion catalysts. The oxidation was studied under first-order kinetic conditions [$KBrO_3$]<< [alc.].For all the alcohols studied ,the oxidation rate increased with alcohol concentration but decreased with increasing [KB rO_3]. The oxidation rates of alcohols were found to be independent of ionic strength. The oxidation was carried out at different temperatures and the thermodynamic activation parameters were calculated.The oxidation rates follow the sequence 1-propanol > 1-butanol > Isoamyl alcohol > Isobutyl alcohol > 1-hexanol, which has been explained on the basis of chain length .Transition metal ions of the first series were effectively used to catalyze the oxidation of the aliphatic alcohols by $KBrO_3$ in acidic medium and the sequences of their catalytic efficiencies have been determined.

Keywords: aliphatic alcohols, $KBrO_3$, kinetics, ionic strength, Arrhenius equation, transition metal ion catalysts.

INTRODUCTION

The quantitative conversion of alcohols to carbonyl compounds has been reported[1-5]. We have earlier reported the kinetics of oxidation of some industrially important alcohols and phenols using different types of organic and inorganic oxidizing agents[6-11]

This paper reports the kinetics of the controlled oxidation of some primary and secondary aliphatic alcohols by $KBrO_3$ in acidic medium.

The effects of alcohol and oxidant concentrations, ionic strength (K_2SO_4) and temperature on the oxidation rates of alcohols have been studied. From the variation of oxidation rate with temperature, the energy of activation and other thermodynamic activation parameters have been evaluated. The sequence of oxidation rates of the aliphatic alcohols has been explained on the basis of their chain lengths and other structural features. Transition metal ions of the first series and Cd(II) have been used to catalyze the oxidation of aliphatic alcohols and the sequence of their catalytic efficiencies has been determined for each alcohol.

EXPERIMENTAL

The aliphatic alcohols were obtained from S. H. Kelkar & Co.Mumbai and Shaivi Industries,Lucknow and purified by distillation. All other chemicals used were of AR Analar Grade.

Kinetics of Oxidation of Aliphatic Alcohols

The oxidation was studied under first-order kinetic conditions [$KBrO_3$] << [alc]. The reaction was monitored by iodometric estimation of the unreacted oxidant at regular time intervals. The first order rate constants (k) were determined from the first order plots of log (a-x) versus time. The oxidation was carried out in the temperature range 303-318K and the energy of activation and other thermodynamic activation parameters were determined from the Arrhenius plots of log k versus T^{-1}. The effect of ionic

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strength (μ) on the rate of oxidation was studied in dilute solution at 313K using K_2SO_4 in the range, μ = 5 to 25 x 10^{-2} mol dm^{-3}.

Kinetics of Transition Metal Ion Catalyzed Oxidation of Aliphatic Alcohols

An identical procedure was followed to study the catalytic impact of transition metal ions on the oxidation rates of the aliphatic alcohols under study in the concentration range [M(II)]= 2.5 to 5.0 x 10^{-4} mol dm^{-3} at 303K.

RESULTS AND DISCUSSION

The primary alcohols, 1-propanol,1-butanol,Isoamyl alcohol(3-methyl-1-butanol) and 1-hexanol were oxidized by $KBrO_3$ in acidic medium to the corresponding aldehydes and the secondary alcohol ,Isobutyl alcohol (2-butanol) was oxidized to a ketone.

Kinetics of Oxidation of Aliphatic Alcohols

For all the alcohols studied, the oxidation rate increased with alcohol concentration but decreased with oxidant concentration (Table-1, Fig.-1).

Table-1: Rate constant data for the oxidation of aliphatic alcohols by $KBrO_3$ in 0.1 M H_2SO_4.Temp. = 303K

		k x 10^4 s^{-1}				
[Alc.] x 10^1 mol dm^{-3}	[$KBrO_3$] x 10^3 mol dm^{-3}	1-propanol	1-butanol	Isoamyl alcohol	Isobutyl alcohol	1-hexanol
1.00	2.50	6.25	5.77	5.29	4.70	4.45
1.00	5.00	5.84	4.90	4.64	4.43	4.24
1.00	10.00	4.89	4.75	3.73	3.46	3.34
1.00	15.00	4.41	4.09	3.49	3.34	3.06
1.00	20.00	3.80	3.53	3.32	2.98	2.88
1.00	25.00	3.08	2.67	2.30	2.46	2.38
0.25	5.00	3.66	3.33	3.00	2.57	2.18
0.50	5.00	4.22	3.61	3.24	2.86	2.59
0.63	5.00	4.69	4.06	3.58	3.36	2.89
0.75	5.00	4.95	4.42	4.05	3.79	3.12
0.88	5.00	5.49	5.09	4.35	4.00	3.59
1.00	5.00	5.84	5.30	4.74	4.30	3.76

Reaction Mechanism of Oxidation of Primary and Secondary Aliphatic Alcohols

In acidic medium ,$KBrO_3$ rapidly forms the halic acid, Bromic acid $HBrO_3$ which is a strong acid and strong oxidizing agent[12,13].The oxidation of alcohols by $KBrO_3$ in acidic medium results in the formation of hypohalite ions OBr^-.

$$RCH_2OH + BrO_3^- + 2H^+ \rightarrow RCHO + OBr^- + 2H_2O$$
$$RR'CHOH + BrO_3^- + 2H^+ \rightarrow RR'C{=}O + OBr^- + 2H_2O$$

The products of the reaction i.e. aldehyde/ ketone were identified by 2.4-dinitrophenyl hydrazone test and confirmed by TLC.

The oxidation rates followed the sequence:

1-propanol > 1-butanol > Isoamyl alcohol > Isobutyl alcohol > 1-hexanol
All the primary aliphatic alcohols except 1-hexanol were oxidized faster than the secondary aliphatic alcohol, Isobutyl alcohol (Table-1,Fig.-1).
The oxidation rates were found to be inversely proportional to the chain lengths of the aliphatic alcohols under study.

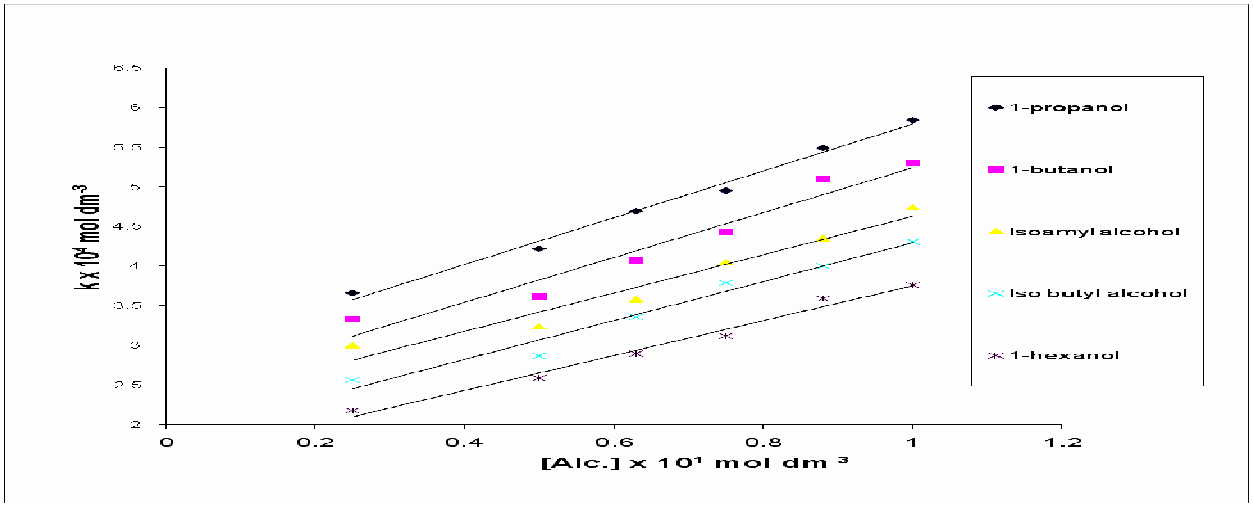

Fig.-1: Variation of the Rate Constant of Oxidation of Aliphatic Alcohols by $KBrO_3$ with [Alc.]

Effect of Ionic Strength on Oxidation Rates of Aliphatic Alcohols
K_2SO_4 was used in the range μ = 5 to 25 x10^{-2} mol dm^{-3} to study the effect of ionic strength on oxidation rates of alcohols (Table-2).The graphs of log k versus $\mu^{1/2}$ were found to be straight lines parallel to the $\mu^{1/2}$ axis confirming that ionic strength has no effect on the oxidation rates of alcohols due to the involvement of a non-ionic species in the oxidation process (Fig.-2).

Table-2: Effect of Ionic Strength on the Oxidation Rate of Aliphatic Alcohols by $KBrO_3$ in 0.1M H_2SO_4,[Alc.]= 0.1M , [$KBrO_3$]= 2.5 x10^{-3} M, Temp.=313K

μ x 10^2 mol dm^{-3}	k x $10^4 s^{-1}$				
	1- propanol	1- butanol	Isoamyl alcohol	Isobutyl alcohol	1-hexanol
00.00	6.25	5.77	5.29	4.70	4.45
05.00	6.36	5.96	5.45	4.70	4.45
10.00	6.25	5.51	5.28	4.66	4.33
15.00	6.18	5.95	5.39	4.71	4.42
20.00	6.36	5.69	5.26	4.81	4.33
25.00	6.25	5.72	5.49	4.75	4.54

Effect of Temperature on the Oxidation Rates of Aliphatic Alcohols
The oxidation of alcohols was studied in the range 303-318K and the thermodynamic activation parameters were determined from the Arrhenius plots of log k versus 1/T(Table-3). Negative values of ΔS^* indicate a decrease in entropy due to the formation of a transient activated complex followed by reorientation of solvent molecules near the –OH bond[14, 15].

Table-3: Thermodynamic Activation Parameters of the Oxidation of Aliphatic Alcohols by $KBrO_3$ In 0.1M H_2SO_4

Temperature (K)	k x 10^4 s^{-1}	E kJ mol^{-1}	K* x 10^{17}	ΔH^* kJ mol^{-1}	ΔG^* kJ mol^{-1}	ΔS^* kJ K^{-1} mol^{-1}
1-Propanol						
303	6.25	6.30	9.9	3.78	92.85	-0.2971

308	6.58	6.30	10.3	3.72	94.29	-0.2962
313	6.98	6.30	10.7	3.69	95.71	-0.2952
318	7.14	6.30	10.6	3.65	97.26	-0.2944
1-Butanol						
303	5.77	10.74	9.14	8.22	93.05	-0.2800
308	6.22	10.74	9.70	8.17	94.44	-0.2801
313	6.68	10.74	10.20	8.13	95.83	-0.2800
318	7.03	10.74	10.60	8.10	97.26	-0.2805
Isoamyl Alcohol						
303	5.29	11.67	7.45	9.15	93.57	-0.2781
308	5.88	11.67	7.62	9.10	95.05	-0.2784
313	6.14	11.67	8.04	9.07	96.46	-0.2784
318	6.65	11.67	9.42	9.02	97.57	-0.2783
Isobutyl Alcohol						
303	4.70	14.71	7.45	12.19	93.57	-0.2692
308	4.89	14.71	7.68	12.14	95.05	-0.2696
313	5.24	14.71	8.04	12.10	96.64	-0.2697
318	6.24	14.71	9.42	12.06	97.57	-0.2691
1-Hexanol						
303	4.45	19.05	7.05	16.53	93.56	-0.2555
308	4.68	19.05	7.31	16.48	95.09	-0.2554
313	4.98	19.05	7.64	16.44	96.04	-0.2567
318	5.65	19.05	9.91	16.40	97.44	-0.2568

Kinetics of the Transition Metal Ion Catalyzed Oxidation of Aliphatic Alcohols

The aliphatic alcohols were oxidized using $KBrO_3$ in an acidic medium in the presence of transition metal ions in the range [M(II)] = 2.5 to 5.0 x 10^{-4} mol dm^{-3} at 303K.The rate constants were determined from the linear plots of log (a-x) versus time. For all the alcohols, the oxidation rates increased with [M(II)] (Tables-4 to 8,Figs.-3 to7).The stability order for the complexes of the metal ions under study is expected to be Cu(II) >Zn(II) >Ni(II) >Co(II) >Mn (II) > Cd(II)[16,17]. Hence their catalytic efficiency is expected to follow the sequence, Cd(II) >Mn(II) >Co(II) >Ni(II) >Zn(II) >Cu(II). Since such generalizations are only approximate guides to metal ion behavior, discrepancies have been observed and reported in literature.[18,19]

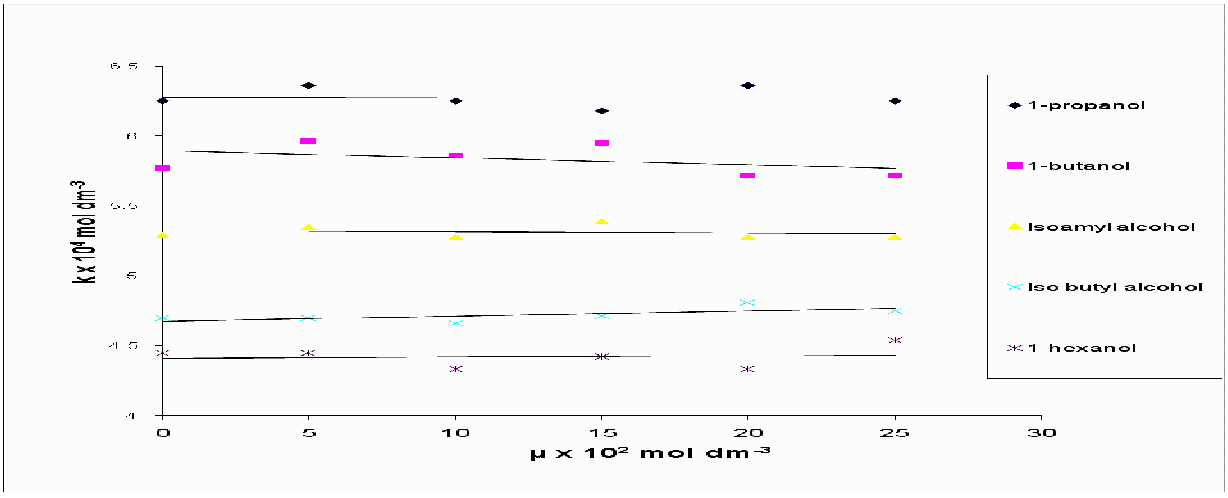

Fig.-2: Effect of Ionic Strength on the Rate Constant of Oxidation of Aliphatic Alcohols by $KBrO_3$

In our study, we have also observed discrepancies as shown below (Table-4,Fig.-3):

1-propanol Cd(II) >Mn(II) >Zn(II) >Co(II) >Cu(II) >Ni(II)

Table-4 : Catalytic Effect of Transition Metal Ions on the Oxidation of 1-propanol
[Alc.] = 0.1M, [$KBrO_3$]=2.5x 10^{-3}M,Temperature=303K

[M(II)] x 10^4mol dm^{-3}	k x 10^4s^{-1}					
	Cu(II)	Zn(II)	Mn(II)	Co(II)	Ni(II)	Cd(II)
0.0	6.25	6.25	6.25	6.25	6.25	6.25
2.5	6.34	7.59	8.21	6.45	7.37	9.89
3.0	6.84	7.3	9.06	7.21	8.34	10.97
3.5	7.42	8.04	9.22	7.86	9.06	11.36
4.0	7.62	9.27	10.68	8.41	9.68	12.27
4.5	8.78	9.99	12.12	8.87	10.08	13.66
5.0	9.92	11.02	13.2	10.05	11.02	14.98

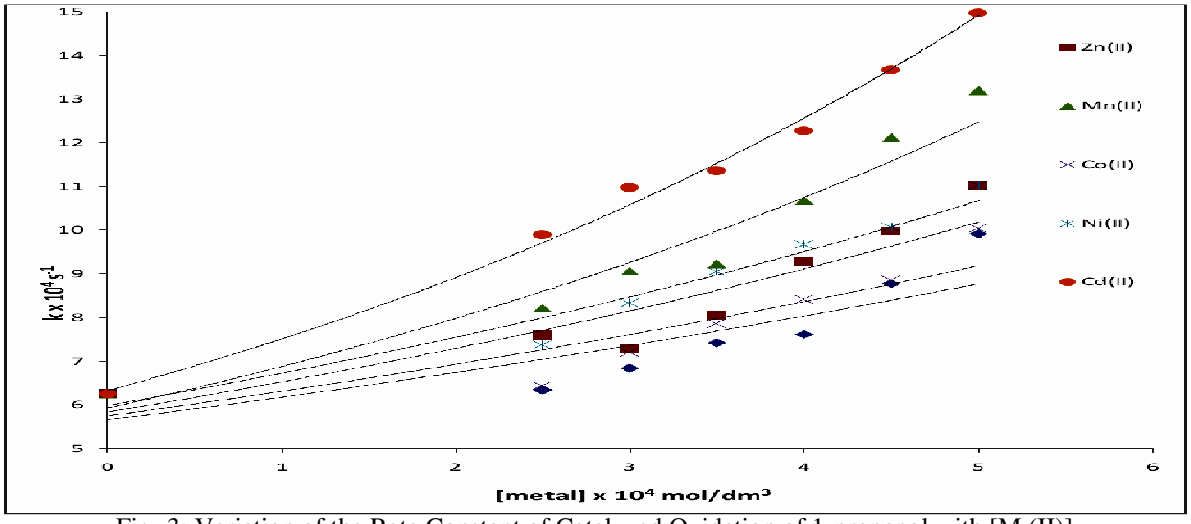

Fig.-3: Variation of the Rate Constant of Catalyzed Oxidation of 1-propanol with [M (II)]

1-butanol Cd(II) >Ni(II) >Zn(II) >Cu(II) >Mn(II) >Co(II) (Table-5,Fig.-4)

Table-5 : Catalytic Effect of Transition Metal Ions on the Oxidation of 1-butanol
[Alc.]= 0.1M, [$KBrO_3$]=2.5x 10^{-3}M,Temperature=303K

[M(II)] x 10^4 mol dm^{-3}	k x 10^4s^{-1}					
	Ni (II)	Cu(II)	Zn(II)	Cd(II)	Mn(II)	Co(II)
0.0	5.77	5.77	5.77	5.77	5.77	5.77
2.5	6.65	6.04	6.49	7.58	6.06	5.96
3.0	7.37	7.36	7.00	8.33	5.65	5.23
3.5	8.77	7.57	7.36	9.48	5.96	5.62
4.0	9.11	7.53	8.34	10.23	6.52	5.98
4.5	9.99	8.06	9.28	11.52	7.52	6.23
5.0	11.26	9.11	10.61	12.18	8.23	6.78

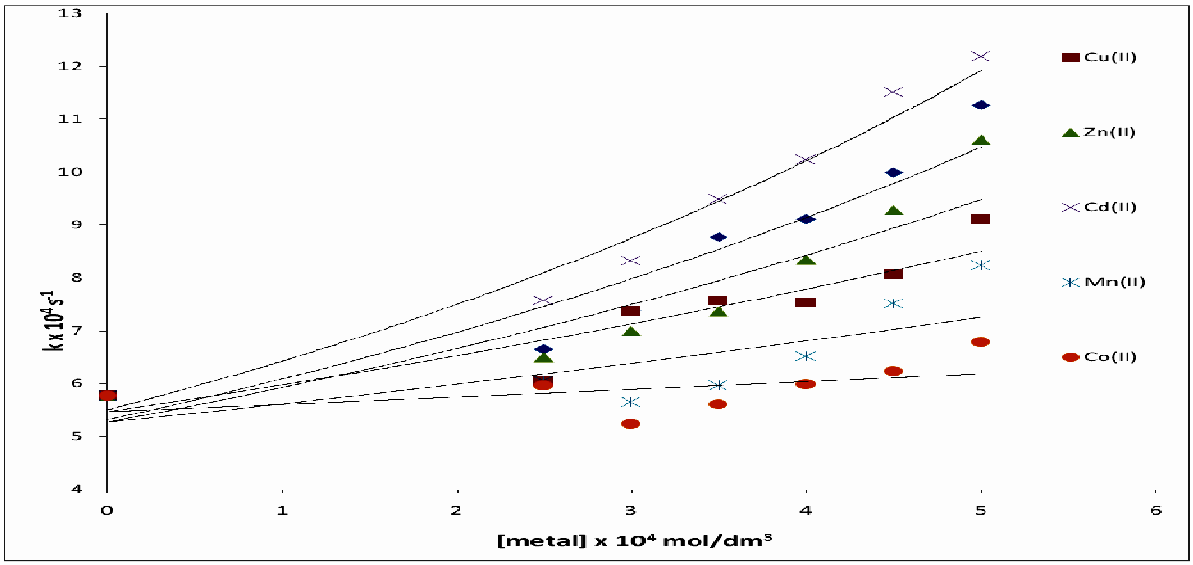

Fig.-4: Variation of the Rate Constant of Catalyzed Oxidation of 1-butanol with [M(II)]

Isoamyl alcohol Cd(II) > Mn(II) >Zn(II) >Co (II) > Ni(II) >Cu(II) (Table-6.Fig.-5)

Table-6 : Catalytic Effect of Transition Metal Ions on the Oxidation of Isoamyl Alcohol
[Alc.] = 0.1M, [$KBrO_3$] =2.5x 10^{-3}M, Temperature= 303K

[M(II)] x 10^4 mol dm^{-3}	k x $10^4 s^{-1}$					
	Cu(II)	Zn(II)	Mn(II)	Co(II)	Ni(II)	Cd(II)
0.0	5.29	5.29	5.29	5.29	5.29	5.29
2.5	5.39	5.48	6.24	5.52	5.48	6.53
3.0	5.95	6.28	6.57	6.09	5.78	7.98
3.5	6.09	6.83	7.32	6.62	6.23	8.68
4.0	6.62	7.62	8.44	7.13	6.62	9.95
4.5	6.86	8.12	9.94	8.57	7.12	10.66
5.0	7.13	9.06	10.62	8.82	8.06	11.27

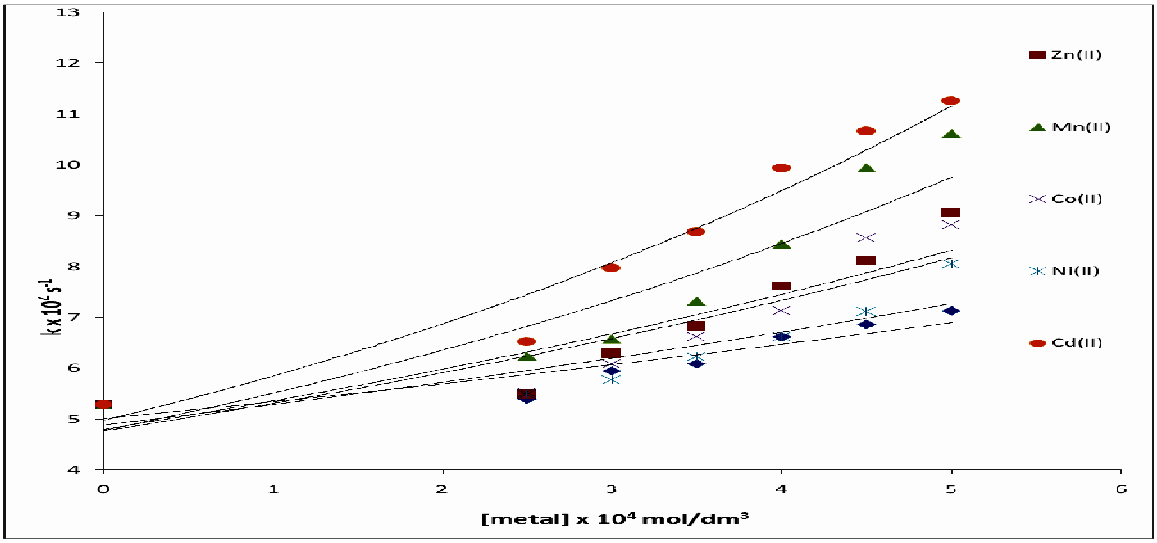

Fig.-5: Variation of the Rate Constant of Catalyzed Oxidation of Isoamyl Alcohol with [M(II)]

Isobutyl alcohol Cd(II)>Mn(II)>Zn(II)>Co(II)>Cu(II) >Ni(II) (Table-7,Fig.-6)

Table-7 : Catalytic Effect of Transition Metal Ions on the Oxidation of Isobutyl Alcohol
[Alc.]= 0.1M, [$KBrO_3$]=2.5x 10^{-3}M, Temperature=303K

[M(II)] x 10^4 mol dm^{-3}	k x 10^4 s^{-1}					
	Cu(II)	Zn(II)	Mn(II)	Co(II)	Ni(II)	Cd(II)
0.0	4.70	4.70	4.70	4.70	4.70	4.70
2.5	4.78	4.86	5.13	4.86	4.70	5.15
3.0	5.16	5.27	5.36	5.24	4.98	6.33
3.5	5.33	6.36	6.89	5.97	5.26	7.38
4.0	5.66	6.40	7.04	6.12	5.34	7.88
4.5	5.95	7.40	8.32	6.78	5.41	9.59
5.0	6.15	8.02	9.63	6.98	5.89	10.20

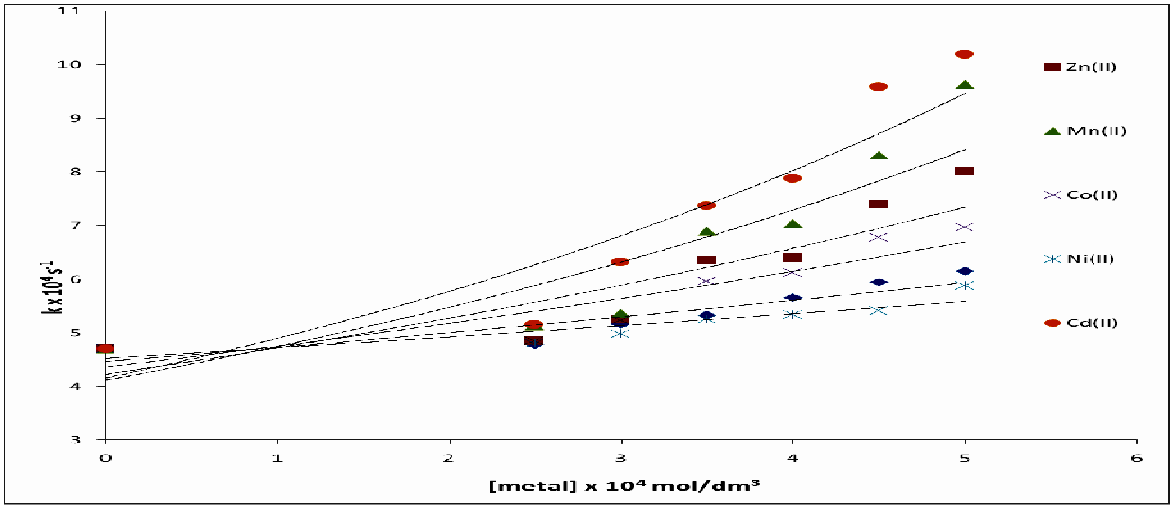

Fig.-6: Variation of the Rate Constant of Catalyzed Oxidation of Isobutyl Alcohol with [M(II)

1-hxanol Cd(II) >Ni(II) >Zn(II) >Cu(II) >Co(II) >Mn(II) (Table-8.Fig.-7)

Table-8: Catalytic Effect of Transition Metal Ions on the Oxidation of 1-Hexanol
[Alc.] = 0.1M, [$KBrO_3$] =2.5x 10^{-3}M, Temperature=303K

[M(II)] x 10^4 mol dm^{-3}	k x 10^4 s^{-1}					
	Ni (II)	Cu(II)	Zn(II)	Cd(II)	Mn(II)	Co(II)
0.0	4.45	4.45	4.45	4.45	4.45	4.45
2.5	4.59	4.50	4.65	5.14	4.65	4.49
3.0	5.21	4.86	5.00	6.37	4.55	4.60
3.5	6.82	5.25	5.67	7.67	4.69	4.78
4.0	7.52	5.61	6.13	8.13	5.30	5.86
4.5	8.29	6.13	6.82	8.59	5.46	5.97
5.0	8.56	7.29	7.66	8.98	6.29	6.52

CONCLUSION

1. The oxidation rates of aliphatic alcohols by $KBrO_3$ in acidic medium follow the sequence: 1-propanol > 1-butanol > Isoamyl alcohol > Isobutyl alcohol > 1-hexanol.

2. The oxidation of aliphatic alcohols is independent of ionic strength in accordance with Bronsted-Bjerrum equation, $\log k = \log k_0 + 1.02\ Z_A Z_B\ \mu^{1/2}$ and is accompanied by a decrease in entropy of activation ΔS^*.
3. Transition metal ions effectively catalyze the oxidation of aliphatic alcohols with Cd(II) and Mn(II) ions being the most effective catalysts.

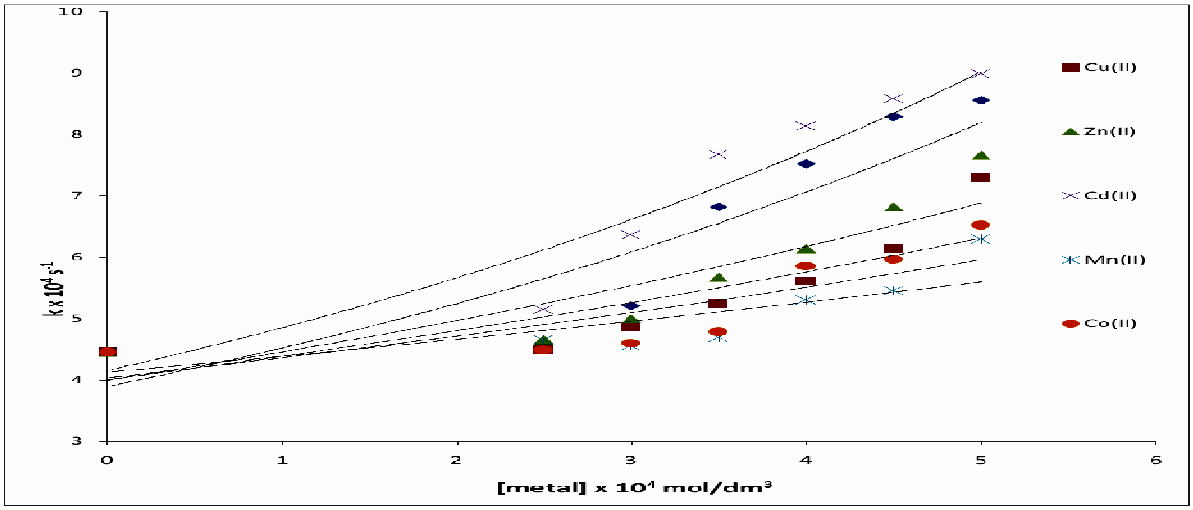

Fig.-7: Variation of the rate constant of catalyzed oxidation of 1-hexanol with [M(II)]

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