Kinetic Studies of Transition Metal Ion Catalyzed Oxidation of Some Fragrance Alcohols

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The controlled oxidation of the aliphatic alcohols 2-propanol, 2-butanol and 3-methyl-1-butanol to the corresponding carbonyl compounds has been carried out using Ce (IV) in acidic medium in the absence and presence of transition metal ions of the first series. The aliphatic alcohols are widely used as diluents in the perfumery industry. The oxidation reaction was monitored under pseudo unimolecular conditions with respect to [Ce (IV)] in the temperature range 303-318 K. Aliquots of the reaction were withdrawn at regular time intervals, quenched using ice and the unreacted oxidant was estimated titrimetrically using standard ferrous ammonium sulphate with ferroin as indicator. The pseudo first order rate constants were determined from the linear plots of log (a-x) *versus* time. It was observed that the rate increases with alcohol concentration but decreases with Ce(IV) concentration. This has been attributed to the formation of unreactive dimeric $[Ce(IV)]_2$ at higher concentration of Ce(IV). Potassium sulfate was used to study the effect of ionic strength on the oxidation rate. The thermodynamic activation parameters were determined from the effect of temperature on the oxidation rate. The Ru(VIII), Os(VIII) and Cr(VI) ions have been exhaustively used to catalyse a variety of organic reactions. In the present study, relatively low-cost metal ions of the first transition series have been used as effective catalysts for the oxidation of the fragrance alcohols under study. The reaction mechanism suggested for the oxidation process involves intermediates with hypervalent ions *i.e.*, M(III). The catalytic efficiency of the metal ions is based on the stability of the complexes formed as reaction intermediates which in turn depends on the charge density of the metal ions involved. We have observed some discrepancies as the experimentally determined sequence of catalytic efficiency of metal ions does not follow the theoretically expected sequence. Suitable reaction mechanisms have been suggested for the oxidation of the alcohols in the absence and presence of transition metal ions. In the absence of metal ions, the oxidation rates of aliphatic alcohols the sequence: 2-propanol > 2-butanol > 3-methyl-1-butanol. The relative rates of oxidation of alcohols have been discussed and explained on the basis of structures, steric factors and isomeric characteristics of the perfumery alcohols under study.

Keywords: Oxidation, Aliphatic alcohols, Entropy of activation, Metal ion catalysis, Hypervalent ions.

INTRODUCTION

The quantitative conversion of alcohols to carbonyl compounds has been studied by several workers[1-7]. However, there are few reports available in literature on the kinetic study of oxidation of fragrance and cosmetic alcohols[8].

This paper deals with (i) the kinetics of oxidation of the aliphatic alcohols 2-propanol, 2-butanol and 3-methyl-1-butanol by Ce(IV) in H_2SO_4 in the temperature range 303-318 K (ii) the effect of ionic strength on the oxidation rate of the above alcohols using K_2SO_4 (iii) the kinetics of the metal ion catalysed oxidation of the above aliphatic alcohols using Ni(II), Cu(II), Zn(II), Mn(II), Co(II) as well as Cd(II) ions in order to study their relative catalytic efficiency.

All the data collected has been collated and suitable reaction mechanisms have been suggested for the oxidation of the aliphatic alcohols in the presence and absence of metal ions.

EXPERIMENTAL

All the chemicals and reagents used were of AR Grade: aliphatic alcohols 2-propanol, 2-butanol and 3-methyl-1-butanol (SH Kelkar and Co., Mumbai and Ultra International), cerric ammonium sulphate (West Coast Laboratories). A.R.K_2SO_4 was used to study the effect of ionic strength on reaction rate. All the metal salts used for the catalytic study were of AnalaR grade (B.D.H.).

Methods: The oxidation of the aliphatic alcohols was studied under pseudo unimolecular conditions with respect to the oxidizing agent and the progress of the reaction was monitored titrimetrically. The solutions of alcohol and oxidizing agent in requisite amounts were allowed to equilibrate in a previously adjusted thermostat (accuracy ±0.1 °C). After the temperature equilibrium was reached, the solutions were mixed to start the reaction. Aliquots of the reaction mixture were

withdrawn at regular intervals and the reaction was arrested using ice. The unreacted Ce(IV) was estimated by titration against standard ferrous ammonium sulphate in H_2SO_4 using ferroin as an indicator.

The reaction was studied in the temperature range 303-318 K. The plots of log (a-x) *vs.* time were found to be straight lines and the pseudo first order rate constants were evaluated from the slopes of the linear plots. From the Arrhenius plots of log k *vs.* T^{-1}, the energy of activation and other thermodynamic activation parameters were calculated.
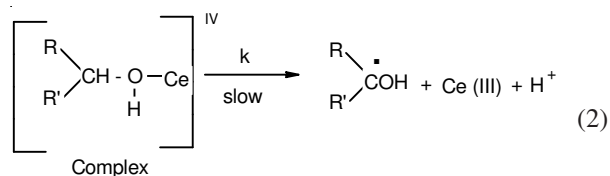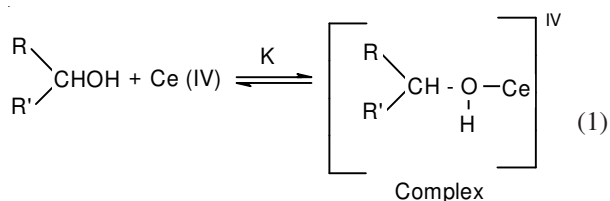
An identical procedure was used to study the oxidation rate in presence of metal ions in the concentration range [M (II)] = 2.5 to 5×10^{-4} mol dm^{-3} in the range 303-318 K. The pseudo first order rate constants for the metal ion catalysed reaction were determined from the linear plots of log (a-x) *vs.* time.

The effect of ionic strength (μ) on oxidation rate was studied in dilute solution in the range, $\mu = 5$ to 25×10^{-2} mol dm^{-3} at 313 K using K_2SO_4.
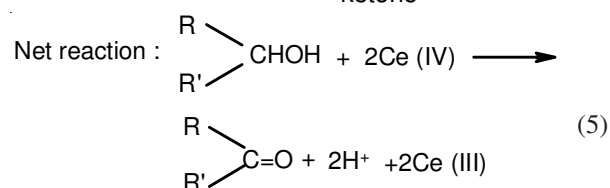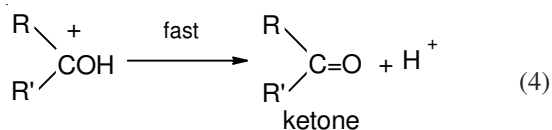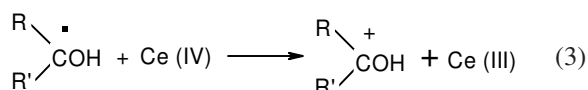
RESULTS AND DISCUSSION

Kinetics of oxidation of alcohols: The aliphatic alcohols 2-propanol (A), 2-butanol (B) and 3-methyl-1-butanol (C) were oxidized using Ce(IV) in H_2SO_4. The values of the rate constant of oxidation are listed in Table-1. The rate constant increases with alcohol concentration as expected but decreases with increase in Ce(IV) concentration.

Reaction mechanism of oxidation:

$$R\!\!-\!\!CHOH + Ce(IV) \overset{K}{\rightleftharpoons} \left[R\!\!-\!\!CH-O-Ce \atop H \right]^{IV} \quad (1)$$

Complex

$$\left[R\!\!-\!\!CH-O-Ce \atop H \right]^{IV} \overset{k}{\underset{slow}{\longrightarrow}} R\!\!-\!\!\dot{C}OH + Ce(III) + H^+ \quad (2)$$

Complex

where $R\!\!-\!\!\dot{C}OH$ is a free radical generated during the course of the reaction.

$$R\!\!-\!\!\dot{C}OH + Ce(IV) \longrightarrow R\!\!-\!\!\overset{+}{C}OH + Ce(III) \quad (3)$$

$$R\!\!-\!\!\overset{+}{C}OH \overset{fast}{\longrightarrow} R\!\!-\!\!C=O + H^+ \quad (4)$$

ketone

Net reaction :

$$R\!\!-\!\!CHOH + 2Ce(IV) \longrightarrow R\!\!-\!\!C=O + 2H^+ + 2Ce(III) \quad (5)$$

The product of the oxidation *i.e.*, ketone was identified by 2,4-dinitrophenyl hydrozone test and confirmed by TLC. In aqueous H_2SO_4 medium, Ce(IV) has been found to oxidize alcohols through complexation followed by free radical generation[9-11]. The rate constant decreases with increase in Ce(IV) concentration (Table-1). This decrease in oxidation rate is due to the formation of an unreactive dimeric $[Ce(IV)]_2$ species[12-14] which increases with [Ce(IV)]

$$2Ce(IV) \rightleftharpoons [Ce(IV)]_2$$
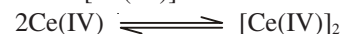
The oxidation rates of the alcohols understudy followed the sequence:

2-propanol > 2-butanol > 3-methyl-1-butanol

TABLE-1
RATE CONSTANT DATA FOR THE OXIDATION OF ALIPHATIC ALCOHOLS BY Ce(IV) IN 0.1M H_2SO_4, TEMPERATURE = 303 K

[Alc.] $\times 10^1$ mol dm^{-3}	Ce(IV) $\times 10^3$ mol dm^{-3}	$k \times 10^3$ (s^{-1})		
		2-Propanol	2-Butanol	3-Methyl-1-butanol
1.00	2.50	10.17	9.67	5.14
1.00	5.00	9.12	5.76	3.68
1.00	10.00	5.76	2.76	2.49
1.00	15.00	5.14	2.53	0.37
1.00	20.00	4.93	2.07	0.30
1.00	25.00	2.74	1.52	0.29
0.25	5.00	3.68	3.22	1.22
0.50	5.00	4.93	3.69	1.36
0.625	5.00	5.76	4.15	1.68
0.75	5.00	7.14	4.84	2.63
0.875	5.00	8.68	7.37	3.45
1.00	5.00	9.12	5.76	3.68
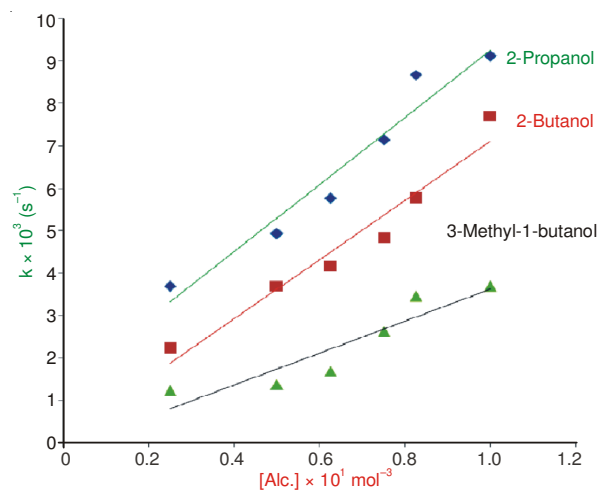
Fig. 1. Variation of rate constant of oxidation of aliphatic alcohols with [Alc]

Effect of ionic strength: K_2SO_4 was used to study the effect of ionic strength (μ) on oxidation rate in dilute solution in the range $\mu = 5$ to 25×10^{-2} mol dm^{-3} at 313 K (Table-2, Fig. 2). The graphs of log k *vs.* $\sqrt{\mu}$ were found to be straight lines parallel to the $\sqrt{\mu}$ axis indicating that the oxidation rate was independent of ionic strength.

Effect of temperature: The oxidation was studied in the temperature range 303-318 K. From the effect of temperature on reaction rate, the energy of activation and other thermodynamic parameters were evaluated (Table-3).

TABLE-2
EFFECT OF IONIC STRENGTH ON THE OXIDATION RATES OF ALCOHOLS BY Ce(IV) IN 0.1M H_2SO_4 [ALC.] = 0.1 M, [Ce(IV)] = 2.5×10^{-3} M, Temperature = 313 K

$\mu \times 10^2$ (mol dm^{-3})	$k \times 10^3$ (s^{-1})		
	2-Propanol	2-Butanol	3-Methyl-1-butanol
0.00	9.02	5.51	5.25
05.00	9.12	5.76	5.30
10.00	9.26	5.70	5.30
15.00	9.02	5.51	5.07
20.00	9.24	5.88	5.30
25.00	9.24	5.14	5.75

TABLE-3
THERMODYNAMIC ACTIVATION PARAMETERS FOR OXIDATION OF ALCOHOLS BY Ce(IV) IN H_2SO_4 [Alc.] = 0.1 M [Ce(IV)] = 2.5×10^{-3} M temperature = 303 K

| Temp. (K)	$k \times 10^3$ s^{-1}	E_a (kJ mol^{-1})	$K^* \times 10^{15}$	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔS^* (kJ K^{-1} mol^{-1})
			2-Propanol			
303	9.12	13.24	1.44	10.72	86.09	-0.2487
308	10.70	13.24	1.67	10.67	87.15	-0.2482
313	26.81	13.24	4.11	10.64	86.22	-0.2414
318	57.57	13.24	8.69	10.60	85.61	-0.2359
			2-Butanol			
303	5.75	11.05	0.91	8.53	87.25	-0.2598
308	6.91	11.05	1.08	8.49	88.27	-0.2590
313	23.05	11.05	3.54	8.45	86.60	-0.2497
318	41.45	11.05	6.26	8.40	86.48	-0.2455
			3-Methyl-1-butanol			
303	3.68	14.41	0.59	11.89	88.38	-0.2524
308	4.73	14.41	0.23	11.85	92.23	-0.2609
313	9.11	14.41	0.29	11.81	93.09	-0.2597
318	13.78	14.41	0.30	11.77	88.44	-0.2411
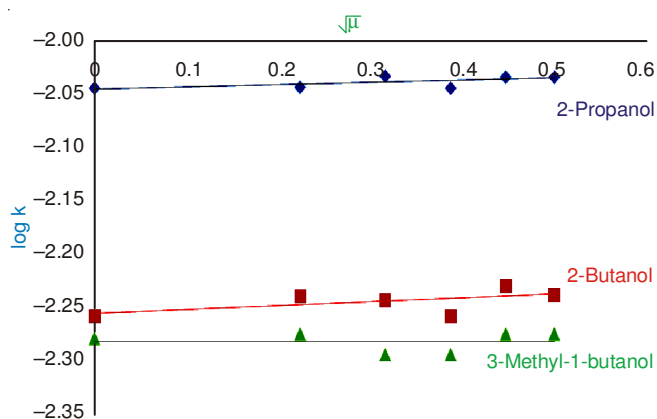
Fig. 2.   Variation of rate constant of oxidation of aliphatic alcohols with ionic strength

The negative values of ΔS^* (-0.2570 kJ K^{-1} mol^{-1} for A, -0.2601 kJ K^{-1} mol^{-1} for B and -0.2603 kJ K^{-1} mol^{-1} for C) indicate a decrease in the degrees of freedom due to the formation of a rigid activation complex resulting in an extensive reorientation of solvent molecules. The negative values of ΔS^* can be explained by a model in which the water molecules are tightly held to the -OH bond which is the site of oxidation[15].

Kinetics of metal ion catalysed oxidation of aliphatic alcohols: The aliphatic alcohols 2-propanol (A), 2-butanol (B), 3-methyl-1-butanol (C) were oxidized using Ce(IV) in H_2SO_4 in the presence of Ni(II), Cu(II), Zn(II), Mn(II), Co(II) and

Cd(II) in the concentration range, M(II) = 2.5 to 5×10^{-4} mol dm^{-3} at 303-318 K. The values of the rate constants of the metal ion-catalyzed oxidation are given in Table-4a-c. For each of the metal ion catalysts, the oxidation rate increases linearly with [M(II)]. The thermodynamic activation parameters for the metal ion catalyzed oxidation of alcohols are given in Table-5a-c.
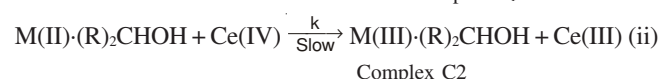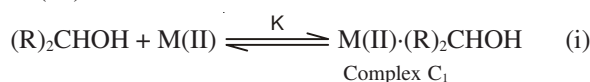
TABLE-4
CATALYTIC EFFECT OF METAL IONS ON OXIDATION OF SOME FRAGRANCE ALCOHOLS
[ALC.] = 0.1M; [Ce(IV)] = 2.5×10^{-3} M; TEMPERATURE = 303 K

[M(II)] $\times 10^4$ (mol dm^{-3})	$k \times 10^4$ (s^{-1})					
			2-Propanol			
	Ni(II)	Cu(II)	Zn(II)	Mn(II)	Co(II)	Cd(II)
0.0	3.68	3.68	3.68	3.68	3.68	3.68
2.5	4.15	4.61	4.38	4.15	4.26	7.21
3.0	5.57	2.76	4.84	6.45	5.32	8.97
3.5	3.68	6.45	4.84	2.07	5.55	9.66
4.0	5.53	8.52	5.99	8.29	6.67	10.27
4.5	9.21	8.98	9.67	9.44	7.59	11.87
5.0	9.67	11.28	10.13	9.99	8.29	13.03
			2-Butanol			
0.0	2.97	2.97	2.97	2.97	2.97	2.97
2.5	2.30	5.29	4.96	2.76	3.68	3.92
3.0	3.68	5.99	6.22	4.15	4.61	4.38
3.5	6.22	6.91	8.52	5.99	6.22	6.68
4.0	7.83	7.60	10.36	7.37	6.91	11.05
4.5	9.21	8.52	11.74	7.60	8.75	12.66
5.0	12.66	11.97	13.81	8.52	2.30	14.27
			3-Methyl-1-butanol			
0	2.69	2.69	2.69	2.69	2.69	2.69
2.5	3.60	3.50	2.30	2.69	3.27	4.15
3.0	4.21	3.86	4.65	2.99	3.56	4.38
3.5	4.53	4.26	6.45	3.02	3.68	4.38
4.0	5.53	5.21	8.13	3.30	3.86	7.14
4.5	8.29	7.14	10.82	3.47	4.26	10.59
5.0	8.98	8.29	12.66	3.60	4.53	12.20

Reaction mechanism of metal ion-catalysed oxidation of alcohols: Mn, Co, Ni and Cu form the hypervalent ions Mn(III), Co(III), Ni(III) and Cu(III), respectively as their third ionization enthalpies (third ionization potentials) are comparatively small unlike Zn and Cd. In Zn and Cd, the energies of solvation or lattice solvation cannot suffice to make the 3+ chemical state chemically stable.

In presence of Mn (II), Co (II), Ni (II) and Cu (II) ions: The reaction mechanism has been explained on the basis of the formation of an intermediate complex involving hypervalent M(III) ions and alcohol.

$$(R)_2CHOH + M(II) \xrightleftharpoons{K} M(II) \cdot (R)_2CHOH \quad (i)$$
$$\text{Complex } C_1$$

$$M(II) \cdot (R)_2CHOH + Ce(IV) \xrightarrow[\text{Slow}]{k} M(III) \cdot (R)_2CHOH + Ce(III) \quad (ii)$$
$$\text{Complex } C2$$

The electron transfer reaction is slow[16].

$$\text{Complex } C_2 \xrightarrow{\text{fast}} (R)_2\overset{\bullet}{C}OH + H^+ + M(II) \quad (iii)$$

where $(R)_2\overset{\bullet}{C}OH$ is a free radical generated during the course of the reaction.

$$(R)_2\overset{\bullet}{C}OH + Ce(IV) \xrightarrow{\text{fast}} (R)_2{}^+COH + Ce(III) \quad (iv)$$

$$(R)_2{}^+COH \xrightarrow{\text{fast}} (R)_2C{=}O + H^+ \quad (v)$$
$$\text{ketone}$$

Net Reaction: $(R)_2CHOH + 2Ce(IV) \longrightarrow$
$$(R)_2C{=}O + 2H^+ + 2Ce(III)$$
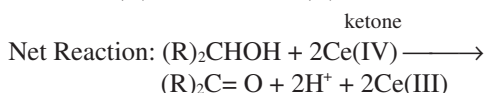
TABLE-5
THERMODYNAMIC ACTIVATION PARAMETERS OF METAL ION CATALYSED OXIDATION OF SOME FRAGRANCE ALCOHOLS AT DIFFERENT TEMPERATURES

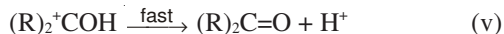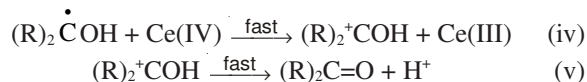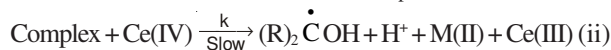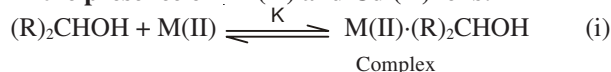| Temp. (K)	$k \times 10^4$ (s^{-1})	E_a (kJ mol^{-1})	$K^* \times 10^{17}$	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔS^* (kJ K^{-1} mol^{-1})
2-Propanol						
Ni(II)						
303	4.140	21.19	18.67	6.56	93.89	-0.2482
308	4.560	21.19	18.63	7.11	95.23	-0.2487
313	5.750	21.19	18.59	8.82	96.22	-0.2480
318	6.750	21.19	18.55	10.20	97.37	-0.2478
Cu(II)						
303	4.609	19.14	16.62	7.30	93.62	-0.2541
308	5.290	19.14	16.58	8.115	94.85	-0.2541
313	5.291	19.14	16.54	8.25	96.43	-0.2553
318	6.491	19.14	16.50	9.80	97.47	-0.2547
Zn(II)						
303	1.010	19.84	17.32	1.60	97.44	-0.2644
308	1.380	19.84	17.28	2.50	98.29	-0.2630
313	4.139	19.84	17.24	6.35	97.07	-0.2551
318	8.750	19.84	17.20	13.20	96.68	-0.2499
Mn(II)						
303	4.141	19.14	16.58	6.56	93.89	-0.2551
308	4.370	19.14	16.54	6.81	95.34	-0.2559
313	5.750	19.14	16.50	8.82	96.22	-0.2547
318	7.598	19.14	16.46	11.50	97.06	-0.2435
Co(II)						
303	5.560	18.34	16.62	8.81	93.14	-0.2526
308	6.669	18.34	15.77	10.40	94.26	-0.2548
313	7.830	18.34	15.74	12.00	95.41	-0.2546
318	8.980	18.34	15.70	13.60	96.61	-0.2545
Cd(II)						
303	3.450	19.28	16.76	5.47	94.35	-0.2561
308	3.680	19.28	16.72	5.74	95.78	-0.2567
313	6.450	19.28	16.68	9.89	95.92	-0.2532
318	6.900	19.28	16.64	10.40	97.31	-0.2537
2-Butanol						
Ni(II)						
303	2.994	20.64	18.12	3.65	95.37	-0.2549
308	3.380	20.64	18.08	5.27	96.00	-0.2530
313	4.375	20.64	18.04	6.71	96.93	-0.2520
318	5.296	20.64	18.00	8.00	98.08	-0.2516
Cu(II)						
303	2.993	19.26	16.74	4.24	94.71	-0.2573
308	2.993	19.26	16.70	4.67	96.31	-0.2585
313	5.527	19.26	16.66	8.48	96.32	-0.2545
318	9.669	19.26	16.62	14.60	96.42	-0.2510
Zn(II)						
303	4.957	19.17	16.65	7.85	93.43	-0.2534
308	5.066	19.17	16.61	7.90	94.96	-0.2544
313	5.527	19.17	16.56	8.48	96.32	-0.2548
318	6.219	19.17	16.52	9.39	97.59	-0.2550
Mn(II)						
303	2.763	13.24	10.72	4.38	94.91	-0.2778
308	2.992	13.24	10.68	4.67	96.31	-0.2786
313	3.684	13.24	10.64	5.65	97.37	-0.2771
318	5.527	13.24	10.60	8.34	97.90	-0.2745
Co(II)						
303	2.303	11.04	8.52	3.65	95.36	-0.2866
308	2.565	11.04	8.48	4.00	96.70	-0.2865
313	2.763	11.04	8.44	4.24	98.12	-0.2865
318	3.455	11.04	8.40	5.21	99.14	-0.2854
Cd(II)						
303	3.915	11.04	16.28	6.20	94.02	-0.2566
308	4.146	11.04	16.24	6.46	95.47	-0.2573
313	7.140	11.04	16.20	10.90	95.65	-0.2538
318	9.213	11.04	16.16	13.90	96.54	-0.2528
3-methyl-1-butanol						
Ni(II)						
303	1.599	20.64	9.72	2.51	94.24	-0.2790
308	1.612	20.64	9.67	4.24	97.89	-0.2864
313	2.763	20.64	9.63	5.70	98.12	-0.2827
318	3.915	20.64	9.59	5.91	98.81	-0.2806
Cu(II)						
303	1.612	19.26	20.05	3.21	94.31	-0.2451
308	2.763	19.26	20.00	4.24	97.89	-0.2529
313	3.499	19.26	19.97	5.55	98.12	-0.2497
318	3.915	19.26	19.93	5.91	98.81	-0.2481
Zn(II)						
303	2.303	19.16	32.79	3.65	95.37	-0.2065
308	2.992	19.16	32.75	4.67	96.31	-0.2064
313	3.915	19.16	32.71	6.00	97.22	-0.2061
318	4.372	19.16	32.67	6.60	98.52	-0.2071
Mn(II)						
303	0.921	13.24	47.05	1.46	97.67	-0.1670
308	1.151	13.24	47.00	1.79	98.76	-0.1680
313	1.612	13.24	47.97	2.47	99.53	-0.1679
318	2.303	13.24	46.93	3.48	100.21	-0.1676
Co(II)						
303	3.684	11.04	20.94	5.84	94.18	-0.2417
308	3.965	11.04	20.89	6.18	95.60	-0.2425
313	5.066	11.04	20.85	7.77	96.55	-0.2418
318	5.551	11.04	20.81	8.38	97.88	-0.2424
Cd(II)						
303	1.145	18.80	20.96	2.15	93.88	-0.2407
308	1.381	18.80	20.91	2.47	98.29	-0.2512
313	1.612	18.80	20.86	2.78	99.53	-0.2513
318	1.842	18.80	20.83	6.57	100.80	-0.2515

At any given time, the steady state concentrations of the intermediate complexes C_1 and C_2 are very small.

In the presence of Zn (II) and Cd (II) ions:

$$(R)_2CHOH + M(II) \underset{}{\overset{K}{\rightleftharpoons}} \underset{\text{Complex}}{M(II){\cdot}(R)_2CHOH} \quad (i)$$

$$\text{Complex} + Ce(IV) \xrightarrow[\text{Slow}]{k} (R)_2\overset{\bullet}{C}OH + H^+ + M(II) + Ce(III) \quad (ii)$$

where $(R)_2\overset{\bullet}{C}OH$ is a free radical generated during the reaction.

$$(R)_2\overset{\bullet}{C}HOH + Ce(IV) \xrightarrow{\text{fast}} (R)_2C^+OH + Ce(III) \quad (iii)$$

$$(R)_2\overset{+}{C}OH \xrightarrow{\text{fast}} (R)_2C{=}O + H^+ \quad (iv)$$
$$\text{ketone}$$

Net reaction: $(R)_2CHOH + 2Ce(IV) \longrightarrow$
$$(R)_2C{=}O + 2H^+ + 2Ce(III)$$
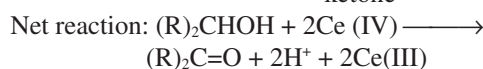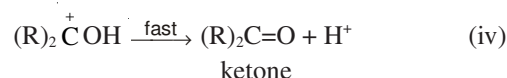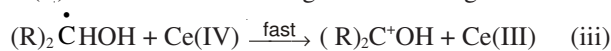
Comparative study of the catalytic efficiency of metal ions: The catalytic efficiency of metal ions is inversely proportional to the stability of their complexes which may be formed as short lived intermediates during the course of reaction. The stability of the complexes generally depends on the charge density of the metal ions involved in addition to several other factors. Thus, 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)[17,18] and their catalytic efficiency is expected to follow the sequence, Cd(II) > Mn(II) > Co(II) > Ni(II) > Zn(II) > Cu(II). However such generalizations are only approximate guides[19] to metal ion behavior and discrepancies are often observed and reported in literature.

In the present study, the sequence, of the catalytic efficiency is as follows:

2-Propanol (Fig. 3a):

Cd (II) > Cu (II) > Zn (II) > Ni (II) > Mn (II) > Co (II)

2-Butanol (Fig. 3b):

Cd (II) >Zn (II) > Cu (II) > Ni (II) > Co (II) > Mn (II)

3-Methy-l-butanol (Fig. 3c):
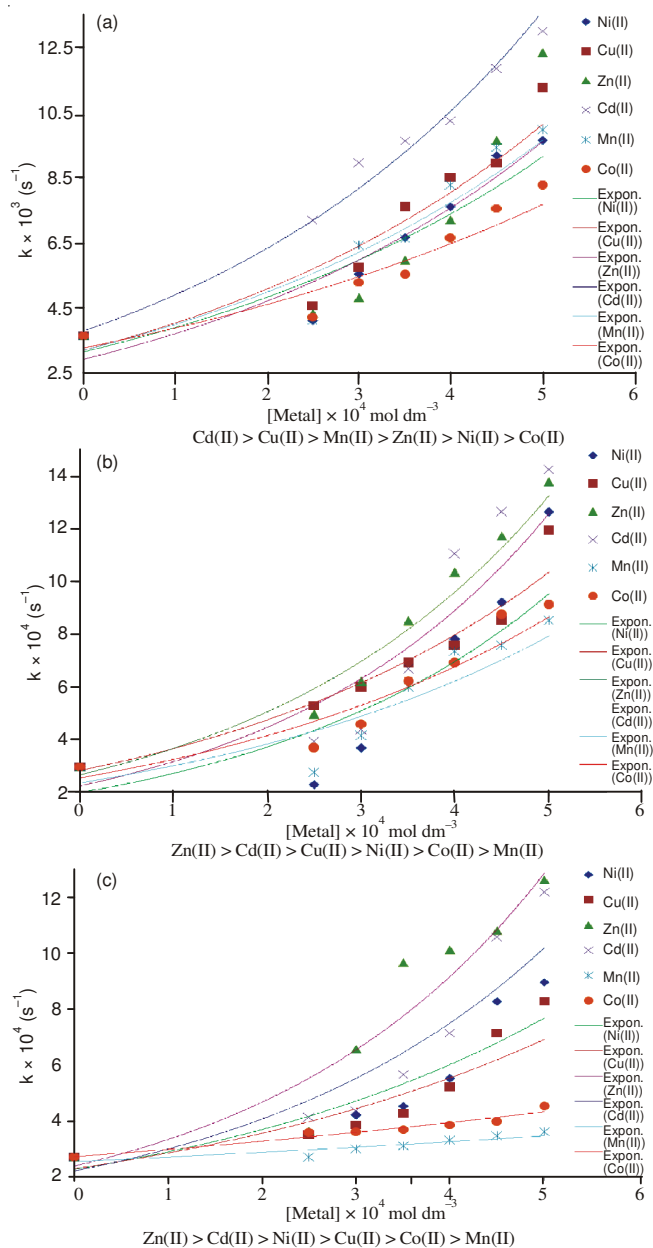
Zn (II) > Cd (II) > Ni (II) > Cu (II) Co (II) > Mn (II)

Fig. 3.   (a) Variation of rate constant of oxidation of 2-propanol with [M(II)]
(b) Variation of rate constant of oxidation of 2-butanol with [M(II)]
(c) Variation of rate constant of oxidation of 3-methyl-1-butanol with [M(II)]

Conclusion

The oxidation rates of the aliphatic alcohols using Ce(IV) in H_2SO_4 follow the sequence, 2-propanol > 2-butanol > 3-methyl-1-butanol. The oxidation rates are found to be independent of ionic strength.

Metal ions Ni(II), Zn(II), Cu(II), Mn(II), Co(II) and Cd(II) serve as effective catalysts for the oxidation of the alcohols though, certain discrepancies are observed in their relative catalytic efficiencies and hence in the oxidation rates of alcohols. The reaction mechanism of the metal ion catalysed oxidation reaction has been explained on the basis of the formation of an intermediate complex involving hypervalent Mn(III), Co(III), Ni(III) and Cu(III) ions. Cd (II) appears to be the most effective catalyst for the oxidation of the aliphatic alcohols under study.

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