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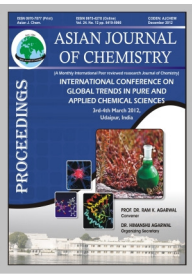

Catalytic Impact of Transition Metal Ions on the Oxidation of Fragrance and Cosmetic Alcohols†

D.V. PRABHU*, HARICHANDRA A. PARBAT and M.A. TANDEL

Department of Chemistry, Wilson College (University of Mumbai), Mumbai-400 007, India

*Corresponding author: E-mail: dvprabhu48@gmail.com

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The controlled oxidation of secondary cyclic alcohols, borneol, isoborneol and menthol 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 cyclic enantiomers borneol and isoborneol are used in the manufacture of fragrances, flavours and cosmetics. Menthol also has medicinal uses. The oxidation reaction was monitored under pseudo unimolecular conditions with respect to [Ce(IV)] in the temperature range 303-318 K. The effect of alcohol and oxidant concentrations, ionic strength and temperature on the oxidation rate have been studied. Expensive Ru(VIII), Os(VIII) and Cr(VI) ions have been exhaustively used to catalyse a variety of organic reactions. In the present study, relatively inexpensive metal ions of the first transition series have been used as effective catalysts for the oxidation of the fragrance and cosmetic alcohols under study. We have observed that the observed 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 absence of metal ions, the oxidation rates follow the sequence: borneol > isoborneol > menthol. The relative oxidation rates have been discussed and explained on the basis of structures, steric factors and isomeric characteristics of the fragrance and cosmetic alcohols under study.

Key Words: Oxidation, Cyclic secondary 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 cyclic secondary alcohols borneol, isoborneol and menthol 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 catalyzed oxidation of the above cyclic secondary 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 cyclic secondary alcohols in the presence and absence of metal ions.

EXPERIMENTAL

All the chemicals and reagents used were of AR Grade: Secondary cyclic alcohols borneol, isoborneol, menthol (S.H. 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 AnalR Grade (B.D.H.).

The oxidation of the secondary cyclic 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 ºC). 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.

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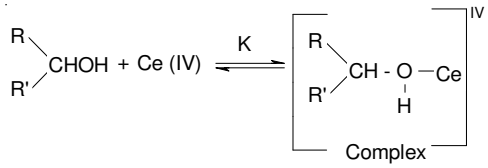
An identical procedure was used to study the oxidation rate in presence of metal ions in the concentration range [M(II)] = 2.5 to 5 × 10^{-4} mol dm^{-3} in the range 303-318 K. The pseudo first order rate constants for the metal ion catalyzed reaction were determined from the linear plots of log(a-x) *vs.* time.

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

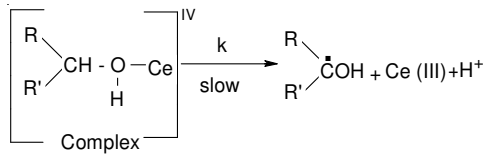
RESULTS AND DISCUSSION

Kinetics of oxidation of alcohols: The secondary cyclic alcohols borneol (A), isoborneol (B) and menthol (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:

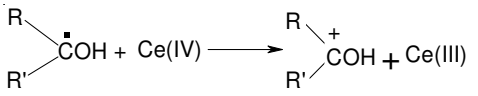


(1)

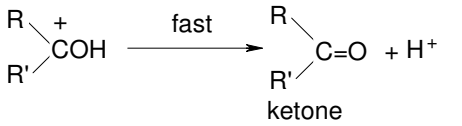


(2)

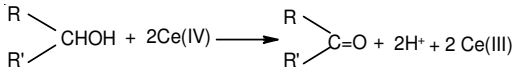
where,  is a free radical generated during the course of the reaction.



(3)



(4)

Net reaction: 

The product of the oxidation *i.e.* ketone was identified by 2,4-dinitrophenyl hydrazone 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: borneol > isoborneol > menthol (Table-1, Fig. 1).

The relative rates of oxidation of secondary cyclic alcohols are consistent with respect to their steric effects on the oxidation Borneol has the least hindered α-hydrogen hence its oxidation is the fastest. Menthol has most hindered α-hydrogen hence it is least susceptible to oxidation.

TABLE-1
RATE CONSTANT DATA FOR THE OXIDATION OF SECONDARY CYCLIC ALCOHOLS BY Ce(IV) IN 0.1 M H_2SO_4 at 303 K

[Alc] × 10^1 mol dm^{-3}	Ce(IV) × 10^3 mol dm^{-3}	k × 10^3 s^{-1}		
		Borneol	Isoborneol	Menthol
1.00	2.50	28.90	10.91	10.17
1.00	5.00	10.24	9.58	9.35
1.00	10.00	9.64	9.46	7.62
1.00	15.00	9.02	8.94	7.72
1.00	20.00	8.38	8.34	6.91
1.00	25.00	7.27	7.66	6.08
0.25	5.00	7.62	6.54	5.76
0.50	5.00	8.85	7.62	6.45
0.625	5.00	9.26	8.68	7.62
0.75	5.00	9.92	9.12	8.23
0.875	5.00	9.99	9.36	8.86
1.00	5.00	12.24	10.24	9.12

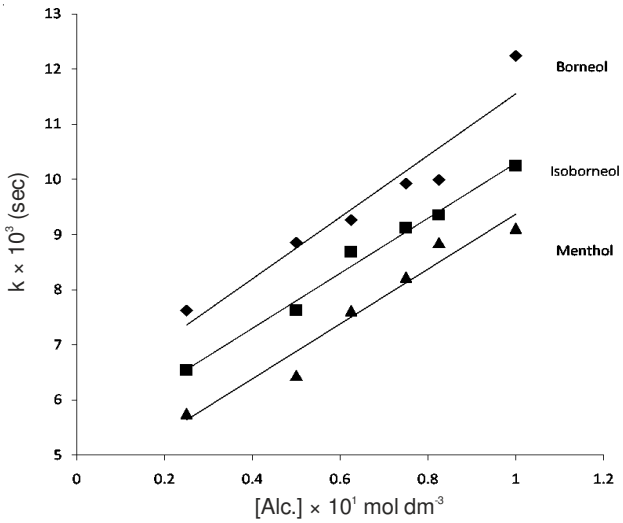


Fig. 1. Variation of rate constant of oxidation of secondary cyclic alcohols with [Alc.]

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 μ = 5 to 25 × 10^{-2} mol dm^{-3} at 313 K (Table-2). The graphs of log k *vs.* √μ were found to be straight lines parallel to the √μ axis indicating that the oxidation rate was independent of ionic strength.

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 at 313 K

μ × 10^2 (mol dm^{-3})	k × 10^3 s^{-1}		
	Borneol	Isoborneol	Menthol
0.00	10.20	9.26	6.91
05.00	10.24	9.24	6.58
10.00	10.14	9.26	6.59
15.00	10.12	9.24	6.91
20.00	10.32	9.24	6.08
25.00	10.24	9.42	6.08

Effect of temperature: The oxidation was studied in the temperature range 303-318 K. From the effect of temperature

on the oxidation rate of alcohols, the energy of activation and other thermodynamic parameters were evaluated (Table-3).

TABLE-3
THERMODYNAMIC ACTIVATION PARAMETERS FOR OXIDATION OF ALCOHOLS BY Ce(IV) IN H_2SO_4 AT 303 K

Thermodynamic parameters	Borneol	Isoborneol	Menthol
Ea (kJ mol^{-1})	11.30	11.27	12.14
ΔH* (kJ mol^{-1})	8.78	1.46	1.04
ΔG* (kJ mol^{-1}	85.80	86.06	86.91
ΔS* (kJ K^{-1} mol^{-1})	-0.2542	-0.2537	-0.2551

The negative values of ΔS* 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 catalyzed oxidation of alcohols: The secondary cyclic alcohols borneol (A), isoborneol (B), menthol (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) ions in the concentration range, M(II) = 2.5 to 5.0 × 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-4(a-c). For each of the metal ion catalysts, the oxidation rate increases linearly with [M(II)] [Fig. 2(a-c)]. The thermodynamic activation parameters for the metal ion catalyzed oxidation of alcohols are given in Table-5.

Reaction mechanism of metal ion-catalyzed 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.

TABLE-4a
CATALYTIC EFFECT OF METAL IONS ON OXIDATION OF BORNEOL, [Alc.] = 0.1 M [Ce(IV)] = 2.5 × 10^{-3} M at 303 K

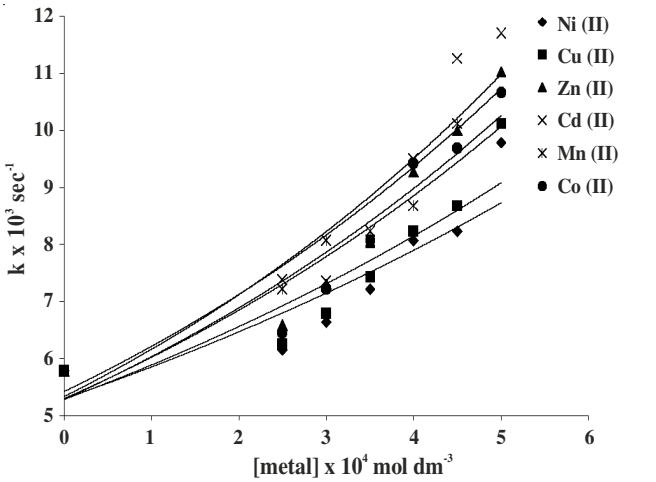
[M(II)] × 10^4 (mol dm^{-3})	k × 10^3 s^{-1}					
	Ni (II)	Cu(II)	Zn(II)	Mn(II)	Co(II)	Cd(II)
0.0	5.78	5.78	5.78	5.78	5.78	5.78
2.5	6.15	6.14	6.59	7.21	6.45	7.37
3.0	6.63	6.24	7.30	8.06	7.21	7.34
3.5	7.21	7.42	8.04	8.22	8.06	8.06
4.0	8.06	8.22	9.27	8.68	9.41	9.49
4.5	8.22	8.68	9.99	10.12	9.67	11.26
5.0	9.78	10.12	11.02	12.20	10.65	11.69

TABLE-4b
CATALYTIC EFFECT OF METAL IONS ON OXIDATION OF ISOBORNEOL, [Alc.] = 0.1 M [Ce (IV)] = 2.5 × 10^{-3} M at 303 K

[M(II)] × 10^4 (mol dm^{-3})	k × 10^3 s^{-1}					
	Ni (II)	Cu(II)	Zn(II)	Mn(II)	Co(II)	Cd(II)
0.0	2.84	2.84	2.84	2.84	2.84	2.84
2.5	3.64	4.19	4.48	6.24	4.52	4.48
3.0	3.73	4.95	5.48	6.57	5.09	5.48
3.5	3.82	5.09	5.53	7.32	5.62	5.53
4.0	3.87	5.62	6.62	7.44	6.13	6.62
4.5	4.33	5.86	7.12	7.94	6.57	7.12
5.0	5.20	6.13	8.06	8.62	6.82	8.06

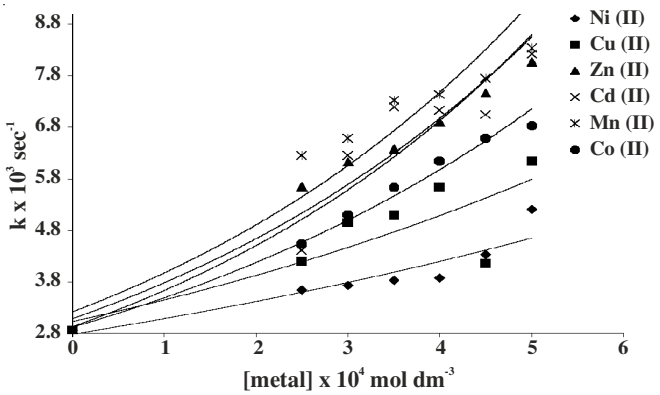
TABLE-4c
CATALYTIC EFFECT OF METAL IONS ON OXIDATION OF MENTHOL, [Alc.] = 0.1 M [Ce (IV)] = 2.5 × 10^{-3} M at 303 K

[M(II)] × 10^4 (mol dm^{-3})	k × 10^3 s^{-1}					
	Ni (II)	Cu(II)	Zn(II)	Mn(II)	Co(II)	Cd(II)
0.0	1.80	1.80	1.80	1.80	1.80	1.80
2.5	2.35	3.35	5.39	6.13	4.41	4.97
3.0	2.47	4.16	5.57	6.36	4.66	5.44
3.5	2.59	4.33	6.36	6.57	4.97	6.82
4.0	3.64	4.33	6.40	7.04	5.12	7.74
4.5	3.73	4.95	6.40	7.32	4.78	5.41
5.0	3.87	5.15	7.02	7.03	4.56	7.89



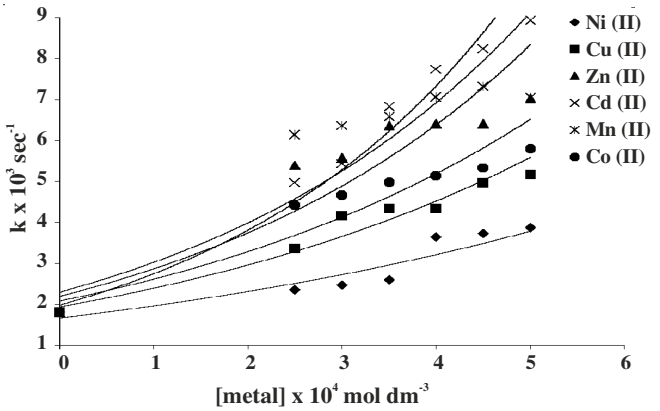
Cd(II) > Mn(II) > Zn(II) > Co(II) > Cu(II) > Ni(II)

Fig. 2a. Variation of rate constant of oxidation of borneol with [M(II)]



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

Fig. 2b. Variation of rate constant of oxidation of isoborneol with [M(II)]



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

Fig. 2c. Variation of rate constant of oxidation of menthol with [M(II)]

TABLE-5
THERMODYNAMIC ACTIVATION PARAMETERS OF THE METAL ION CATALYZED OXIDATION OF ALCOHOLS AT 303 K

Metal ion	Ea (kJ mol^{-1})	ΔH* (kJ mol^{-1})	ΔG* (kJmol^{-1})	ΔS* (kJ K^{-1} mol^{-1})
		Borneol		
Ni(II)	14.72	0.97	87.09	-0.2472
Cu(II)	11.81	0.97	87.09	-0.2568
Zn(II)	11.74	1.04	86.91	-0.2564
Mn(II)	12.17	1.30	81.36	-0.2531
Co(II)	12.12	1.18	86.41	-0.2535
Cd(II)	11.44	1.17	86.63	-0.2565
		Isoborneol		
Ni(II)	13.88	5.85	88.37	-0.2542
Cu(II)	13.18	6.64	88.06	-0.2554
Zn(II)	12.71	8.94	87.31	-0.2545
Mn(II)	12.12	11.60	86.65	-0.2543
Co(II)	12.07	8.90	87.32	-0.2547
Cd(II)	12.41	9.89	87.05	-0.2547
		Menthol		
Ni(II)	14.85	3.91	95.19	-0.2735
Cu(II)	14.00	5.31	94.94	-0.2737
Zn(II)	13.07	8.54	93.22	-0.2729
Mn(II)	12.33	11.20	92.55	-0.2731
Co(II)	12.94	8.12	93.35	-0.2737
Cd(II)	13.26	7.88	93.43	-0.2729

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.

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

$$M(II)\cdot(R)_2CHOH + Ce(IV) \xrightarrow[\text{slow}]{K} \underset{\text{Complex } C_2}{M(III).(R)_2CHOH} + Ce(III) \quad (ii)$$

The electron transfer reaction is slow[16]

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

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

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

$$(R)_2{}^+COH \xrightarrow{\text{fast}} \underset{\text{Ketone}}{(R)_2CO} + H^+ \quad (v)$$

Net reaction: $(R)_2CHOH + 2Ce(IV) \rightarrow (R)_2CO + 2H^+ + 2Ce(III)$

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:

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

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

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

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

$$(R)_2COH \xrightarrow{\text{fast}} \underset{\text{Ketone}}{(R)_2CO} + H^+ \quad (iv)$$

Net reaction: $(R)_2CHOH + 2Ce(IV) \rightarrow (R)_2CO + 2H^+ + 2Ce(III)$

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(III) > Zn(II) > Ni(III) > Co(III) > 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 to metal line behaviour only approximate guides[19] and discrepancies are often observed and reported in literature. In the present study, the sequence, of the catalytic efficiency is as follows:

Borneol (Fig. 2a): Cd(II) > Mn(II) > Zn(II) > Co(II) > Cu(II) > Ni(II); Isoborneol (Fig. 2b): Mn(II) > Cd(II) > Zn(II) > Co(II)> Cu(II) > Ni(II); Menthol (Fig. 2c): Cd(II) > Mn(II) > Zn(II) > Co(II) > Cu(II) > Ni(II)

Conclusion

The oxidation rates of the secondary cyclic alcohols using Ce(IV) in H_2SO_4 follow the sequence, borneol > isoborneol > menthol. 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 catalyzed oxidation reaction has been explained on the basis of the formation of an intermediate complex involving hypervalent Mn(III) and Co(III) ions. Cd(II) appears to be the most effective catalyst for the oxidation of the secondary cyclic alcohols under study.

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