

A Green approach to the transition metal ion catalyzed oxidation of some industrially important alcohols using Ammonium metavanadate in acidic medium

Harichandra A Parbat* and Damodar V Prabhu

*Department of Chemistry, Wilson College (affiliated to University of Mumbai), Mumbai 400007. *Email: harishparbat@gmail.com*

Abstract

Environmentally hazardous metals like Os(VIII), Cr(VI) and Ru in different oxidation states have been used on a large scale to catalyze the oxidation of alcohols. As a green initiative, we have used relatively less harmful and less costly transition metal ions to study the kinetics of oxidation of different types of industrially useful alcohols using Ammonium metavanadate in acidic medium. The oxidation was studied under first order kinetic conditions with respect to the oxidant and the progress of the reaction was monitored iodometrically. The thermodynamic activation parameters were determined from the increase of oxidation rate with temperature. The oxidation rates of the transition metal on catalyzed oxidation of alcohols have been determined. The relative oxidation rates of the alcohols under study have been correlated with their structural and isomeric characteristics. The sequences of catalytic efficiencies of metal ions has been determined for each alcohol on the basis of Irving-Williams order of stability of the metal complexes formed during the course of the reaction. Suitable reaction mechanisms have been suggested for the oxidation of alcohols. Transition metal ions can effectively oxidize alcohols to the corresponding carbonyl compounds and thus the transition metal ion catalyzed oxidation promises to be an environmentally friendly process.

Keywords: Alcohols, Ammonium metavanadate, oxidation, kinetics, transition metal ions, catalytic efficiency.

1. Introduction

The quantitative aspects of oxidation of alcohols has been reported.^[2,6] In our laboratory, the kinetics of oxidation of alcohols and phenols using inorganic and organic oxidants has been studied.^[11,13] We report herein the first order kinetics of the transition metal ion catalyzed oxidation of the aliphatic alcohols, Propan-1-ol, Butan-1-ol, Propan-2-ol; cyclic alcohols, Isoborneol and Menthol and the unsaturated acyclic alcohol, cinnamyl alcohol using Ammonium metavanadate in acidic medium. All these alcohols are used in the manufacture of perfumes and fragrances. Menthol finds use in medicine as an anaesthetic.

The effects of alcohol and oxidant concentrations ionic strength and temperature on the oxidation rates of alcohols have also been reported

2. Experimental

2.1. Materials:

The alcohols were obtained from S H Kelkar & Co. Mumbai and were used after distillation. Analar Grade chemicals were used throughout the study.

2.2. Methods:

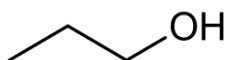
The oxidation was studied under first order kinetic conditions with respect to the inorganic oxidant. Aliquots of the reaction mixture were withdrawn at regular time intervals, the reaction was quenched using ice and the unreacted oxidant was estimated by titration against standard $\text{Na}_2\text{S}_2\text{O}_3$ using starch as indicator. The first order rate constants were determined from the linear plots of \log (unreacted oxidant) versus time.

Transition metal ions, Mn(II), Co(II) and Ni(II) were used in the concentration range $[\text{M(II)}] = 2.5 - 4.5 \times 10^{-4} \text{ mol dm}^{-3}$. The effect of ionic strength on the oxidation rate was determined using K_2SO_4 in the range $\mu = 0.05 - 0.25 \text{ mol dm}^{-3}$. The thermodynamic activation parameters were evaluated from the Arrhenius plots of $\log k$ versus T^{-1} .

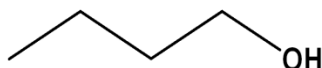
3. Results and Discussion

The primary alcohols (Propan-1-ol, Butan-1-ol and Cinnamyl alcohol) were oxidized to the corresponding aldehydes and the secondary alcohols (Propan-2-ol, Isoborneol and Menthol) were oxidized to the corresponding ketones.

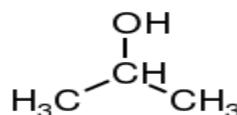
Propan-1-ol



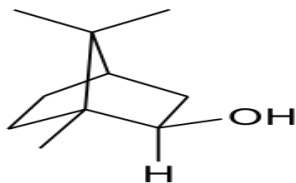
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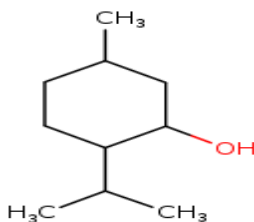
Propan-2-ol



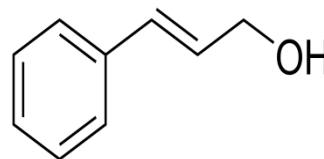
Isoborneol



Menthol

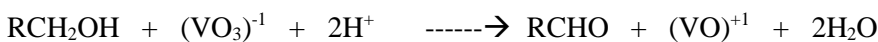


Cinnamyl alcohol

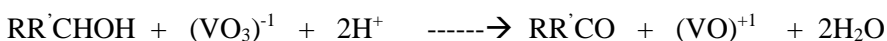


3.1. Reaction mechanism of oxidation of alcohols:

For a primary alcohol, the oxidation reaction can be represented as



For a secondary alcohol, the oxidation reaction can be represented as



The products of oxidation i.e. aldehyde and ketone were identified by 2,4-dinitrophenylhydrazone test and later confirmed by TLC.

For all alcohols under study, the oxidation rates increase with [alc.] but decrease with increasing NH_4VO_3 concentration [Table1].

The oxidation rates of the aliphatic alcohols follow the sequence:

Propan-2-ol > Propan-1-ol > Butan-1-ol [Table 1]

3.2. Effect of ionic strength on oxidation rates of alcohols:

K₂SO₄ was used to study the effect of ionic strength on the oxidation rates of alcohols in the range $\mu = 0.05-0.25 \text{ mol dm}^{-3}$ at 300K [Table 2]. The graphs of $\log k$ versus $\sqrt{\mu}$ were straight lines parallel to the $\sqrt{\mu}$ axis proving that the oxidation rates are independent of ionic strength due to the involvement of a neutral species in the reaction. This observation is borne out by the reaction mechanisms suggested for the oxidation processes.

3.3. Effect of temperature on oxidation rates of alcohols:

The oxidation was studied in the temperature range 300-315 K and the thermodynamic activation parameters were determined from the Arrhenius plots of

$\log k$ versus T^{-1} [Table 2].

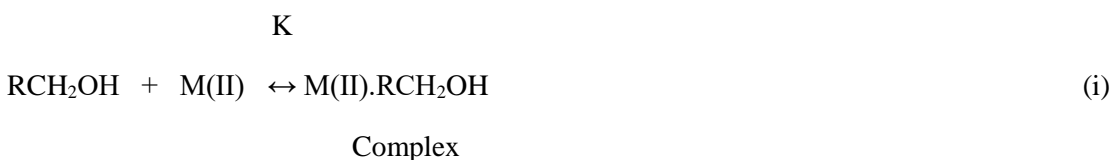
Negative values of ΔS^* indicate a decrease in entropy due to the formation of a rigid activated complex during the reaction, followed by reorientation of solvent molecules around the activated complex.^[1,7]

3.4. Kinetics of Transition metal ion catalyzed oxidation of alcohols:

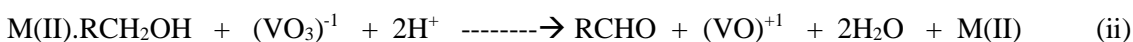
Mn(II), Co(II) and Ni(II) ions were used to catalyze the oxidation of alcohols in the concentration range $[M(II)] = 2.5-4.5 \times 10^{-4} \text{ mol dm}^{-3}$ at 303K. The rate constants were determined from the linear plots of \log (unreacted oxidant) versus time. In each case, the rate constant (k) increased with $[M(II)]$ [Table 4], [Figures 1a,1b,1c,1d,1e and 1f].

Reaction mechanism of transition metal ion catalyzed oxidation of alcohols

For a primary alcohol, the first step involves the formation of a short lived complex between the alcohol and metal ion



The complex then reacts with the vanadate ion in the presence of acid to give aldehyde. This slow step is represented as:



In the case of a secondary alcohol, the product obtained is a ketone, RR'CO.

The stability order of the transition metal ion complexes is expected to be

Ni(II) > Co(II) > Mn(II) and hence their catalytic efficiencies should follow the sequence, Mn(II) > Co(II) > Ni(II).^[8,9] But literature survey shows many discrepancies.^[14,15] We have also observed some deviations from the expected sequence of catalytic efficiencies:

Primary alcohols

Propan-1-ol	Ni(II) > Co(II) > Mn(II)	[Table 4], [Figure 1a]
Butan-1-ol	Mn(II) > Co(II) > Ni(II)	[Table 4], [Figure 1b]
Cinnamyl alcohol	Mn(II) > Co(II) > Ni(II)	[Table 4], [Figure 1f]

Secondary alcohols

Propan-2-ol	Co(II) > Ni(II) > Mn(II)	[Table 4], [Figure 1c]
Isoborneol	Mn(II) > Co(II) > Ni(II)	[Table 4], [Figure 1d]
Menthol	Mn(II) > Co(II) > Ni(II)	[Table 4], [Figure 1e]

4. Conclusion

Transition metal ions have been effectively used to catalyze the oxidation of a variety of alcohols. The oxidation reaction is independent of ionic strength and is accompanied by decrease in entropy of activation, ΔS^* .

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Table-1: Rate constant data for the oxidation of alcohols by Ammonium metavanadate in acidic medium $[H_2SO_4]= 0.1M$, Temperature=300K

[alc.]x10 ¹	[NH ₄ VO ₃]x10 ³	Propan-1-ol	Butan-1-ol	Propan-2-ol	Isoborneol	Menthol	Cinnamyl alcohol
mol dm ⁻³	mol dm ⁻³			k x10 ⁴ s ⁻¹			
0.25	5.00	3.75	2.21	4.75	2.07	1.64	2.73
0.50	5.00	4.58	3.02	5.60	2.69	2.51	2.99
0.63	5.00	4.79	3.33	5.67	3.09	2.76	3.45
0.75	5.00	5.48	4.32	6.03	4.38	3.15	4.46
0.88	5.00	6.36	5.03	7.25	4.77	4.06	4.84
1.00	5.00	6.68	7.75	8.01	5.07	4.61	4.69
1.00	2.50	7.53	5.85	6.77	5.52	5.53	6.86
1.00	5.00	6.03	5.46	3.96	4.84	4.48	4.94
1.00	10.00	4.10	4.44	3.45	3.68	3.45	4.15
1.00	15.00	2.63	4.31	1.50	2.76	2.53	4.03
1.00	20.00	2.46	4.21	1.47	2.08	1.96	3.51
1.00	25.00	2.07	3.20	1.08	1.38	1.61	2.07

Table -2: Effect of ionic strength on the oxidation rates of alcohols by Ammonium metavanadate in acidic medium.

[alc.]=0.1 M , [NH₄VO₃]= 2.5x10⁻³ M, [H₂SO₄]=2.5x10⁻²M, Temperature=313K

μ mol dm ⁻³	$\mu^{1/2}$	Propan-1-ol	Butan-1-ol	Propan-2-ol	Isoborneol	Menthol	Cinnamyl alcohol
0.00	0.00	4.95	2.50	2.08	2.51	2.01	4.96
0.05	0.22	5.13	2.51	2.07	2.52	2.03	5.15
0.10	0.32	4.90	2.49	2.10	2.50	2.02	4.91
0.15	0.39	5.10	2.53	2.11	2.53	2.05	5.00
0.20	0.45	4.97	2.47	2.05	2.49	2.04	5.08
0.25	0.50	5.10	2.52	2.02	2.47	2.06	4.95

Table-3: Thermodynamic activation parameters of the oxidation of alcohols by Ammonium metavanadate in acidic medium, $[H_2SO_4]= 0.1M$

Temp.(K)	kx10 ⁴ s ⁻¹	E kJ mol ⁻¹	K*x10 ¹³	ΔH^* kJ mol ⁻¹	ΔG^* kJ mol ⁻¹	ΔS^* kJ K ⁻¹ mol ⁻¹
Propan-1-ol						
300	1.05	20.85	1.69	18.36	73.37	-0.1833
305	1.08	20.85	1.70	18.32	74.57	-0.1844
310	1.40	20.85	2.17	18.27	75.16	-0.1836
315	2.97	20.85	4.53	18.23	74.45	-0.1784
Butan-1-ol						
300	3.01	21.21	4.81	18.71	70.76	-0.1734
305	3.20	21.21	5.04	18.67	71.82	-0.1742
310	4.30	21.21	6.66	18.43	72.27	-0.1730

315	5.00	21.21	7.62	18.59	73.09	-0.1730
Propan-2-ol						
300	1.92	21.51	3.07	19.02	71.87	-0.1761
305	2.00	21.51	3.15	18.96	73.01	-0.1771
310	2.33	21.51	3.50	18.93	73.85	-0.1771
315	2.83	21.51	4.22	18.90	74.58	-0.1767
Isoborneol						
300	2.40	20.73	3.80	18.21	72.05	-0.1777
305	2.72	20.73	4.24	18.16	72.96	-0.1779
310	3.29	20.73	5.05	18.12	73.69	-0.1775
315	3.92	20.73	5.92	18.08	74.45	-0.1772
Menthol						
300	0.23	26.76	0.36	24.24	77.96	-0.1773
305	0.25	26.76	0.39	24.19	79.07	-0.1781
310	0.30	26.76	0.46	24.15	79.93	-0.1781
315	0.39	26.76	0.59	24.11	80.55	-0.1774
Cinnamyl alcohol						
300	5.49	18.98	8.70	16.46	69.97	-0.1766
305	6.04	18.98	9.41	16.41	70.92	-0.1769
310	6.25	18.98	9.59	16.37	72.02	-0.1777
315	6.34	18.98	9.57	16.33	73.18	-0.1787

Table-4: Catalytic effect of transition metal ions on the oxidation of alcohols by Ammonium metavanadate in acidic medium

[alc.]=0.1M, $[\text{NH}_4\text{VO}_3]=2.5 \times 10^{-3}\text{M}$, $[\text{H}_2\text{SO}_4]=0.1\text{M}$, Temperature= 303K

$[\text{M(II)}] \times 10^4 \text{ mol dm}^{-3}$	$k \times 10^4 \text{ s}^{-1}$		
	Mn(II)	Co(II)	Ni(II)
Propan-1-ol			
0.00	2.46	2.46	2.46
2.50	4.17	4.56	5.78
3.50	5.25	5.23	6.24
4.50	6.48	6.59	6.77
Butan-1-ol			
0.00	3.20	3.20	3.20
2.50	4.24	4.57	3.68
3.50	6.61	5.96	4.61
4.50	7.45	6.15	6.55
Propan-2-ol			
0.00	3.45	3.45	3.45
2.50	3.52	4.24	3.66
3.50	3.66	5.96	4.35
4.50	5.04	7.12	6.37
Isoborneol			

0.00	2.07	2.07	2.07
2.50	2.76	2.36	2.30
3.50	4.38	3.45	4.15
4.50	5.53	5.52	4.38
Menthol			
0.00	1.53	1.53	1.53
2.50	3.22	2.82	2.12
3.50	4.36	4.01	2.53
4.50	5.31	4.61	2.99
Cinnamyl alcohol			
0.00	3.53	3.53	3.53
2.50	5.73	4.51	3.68
3.50	6.45	4.92	4.04
4.50	7.51	5.32	4.72

Fig.1a: Variation of rate constant of transition metal ion catalyzed oxidation of

Propan-1-ol with [M(II)]

Sequence of catalytic efficiencies: Ni(II) > Co(II) > Mn(II)

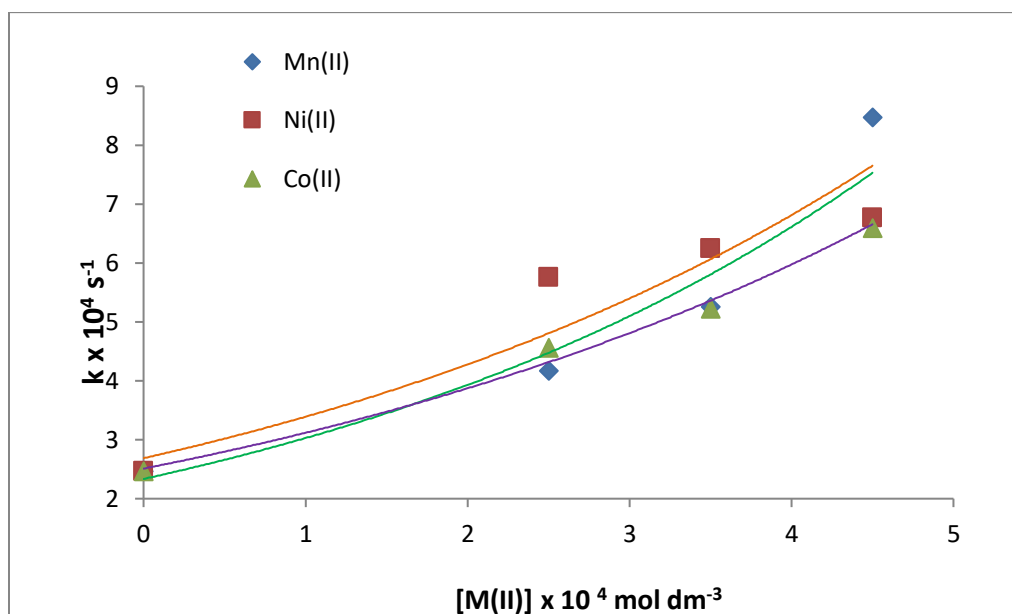


Fig.1b: Variation of rate constant of transition metal ion catalyzed oxidation of Butan-1-ol

with [M(II)]

Sequence of catalytic efficiencies :Mn(II) > Co(II) > Ni(II)

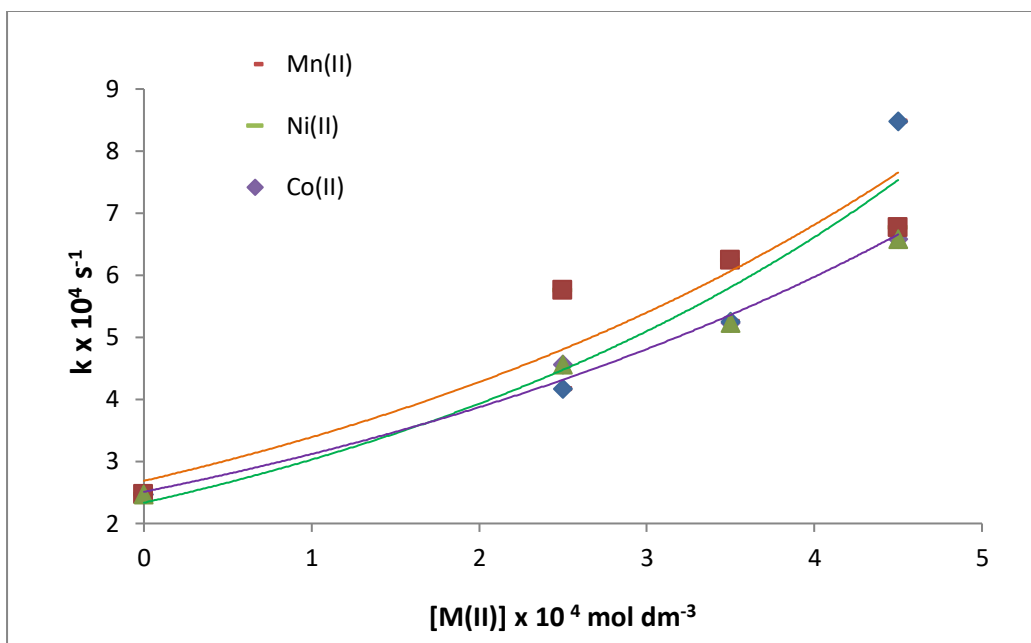


Fig.1c: Variation of rate constant of transition metal ion catalyzed oxidation of Propan-2-ol with [M(II)]

Sequence of catalytic efficiencies : Co(II) > Ni(II) > Mn(II)

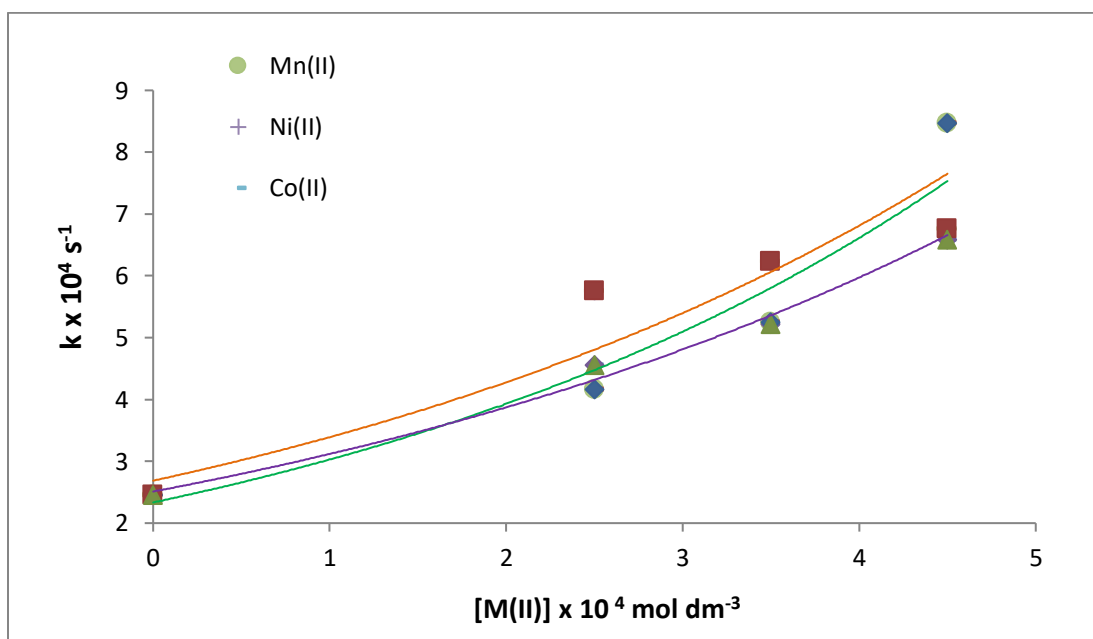


Fig.1d: Variation of rate constant of transition metal ion catalyzed oxidation of Isoborneol with [M(II)]

Sequence of catalytic efficiencies: Mn(II) > Co(II) > Ni(II)

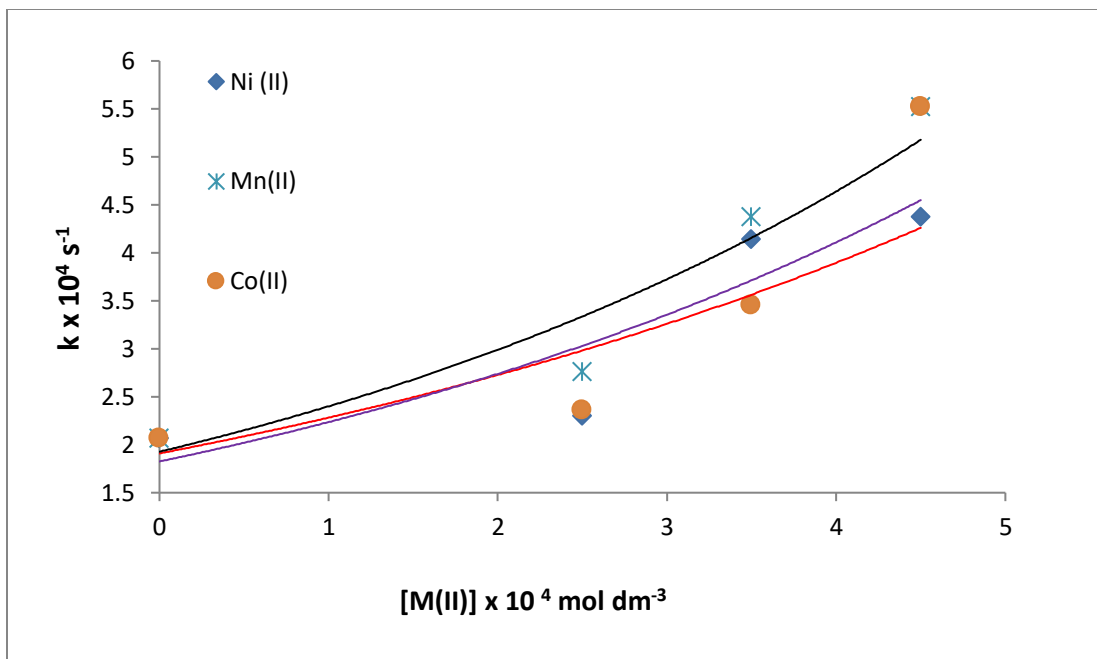


Fig.1e: Variation of rate constant of transition metal ion catalyzed oxidation of Menthol with {M(II)}

Sequence of catalytic efficiencies: Mn(II) > Co(II) > Ni (II)

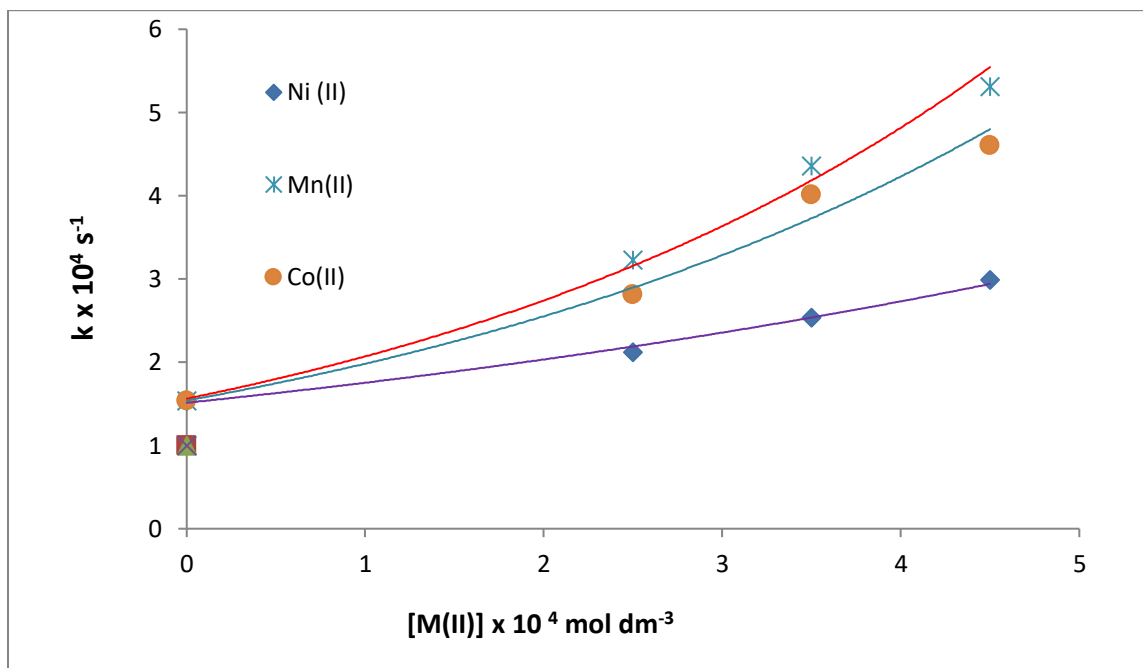


Fig.1f: Variation of rate constant of transition metal ion catalyzed oxidation of Cinnamyl alcohol with [M(II)]

Sequence of catalytic efficiencies: Mn(II) >Co(II) > Ni(II)

