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Research Article

Transition Metal Ions as Catalysts for Oxidation of Cinnamyl Alcohol - A Green Initiative

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Abstract

One of the 12 principles of Green Chemistry is the use of catalysts in preference to stoichiometric reagents to enhance the atom economy and yield of chemical reactions. Oxidation of alcohols to the corresponding carbonyl compounds is an industrially important reaction as it yields useful by products.

Environmentally hazardous metal ions like Cr(VI), Os(VIII) and Ru in different oxidation states have been routinely used to catalyse the oxidation of alcohols. As a green initiative, we have used the relatively inexpensive and less harmful transition metal ions to catalyse the oxidation of alcohols used in the manufacture of perfumes and fragrances.

This paper reports the kinetic study of the oxidation of the unsaturated primary perfumery alcohol, Cinnamyl alcohol by Ce(IV) in acidic medium. The oxidation was carried out under first order kinetic conditions with respect to Ce(IV) at different temperatures. From the variation of oxidation rate with temperature, the thermodynamic activation parameters of the reaction were evaluated and correlated with the proposed reaction mechanism. The effect of ionic strength on the oxidation was studied in dilute solution using Analar Grade K_2SO_4.

Transition metal ions Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) in the concentration range [M(II)]=2.5 -5.0 x 10^{-4}mol dm^{-3} were used to catalyse the oxidation of Cinnamyl alcohol by Ce(IV) in acidic medium and the sequence of their catalytic efficiencies was determined as Mn(II)>Co(II)>Ni(II)>Cu(II)>Zn(II).Mn(II) ions seem to be the best catalysts among the transition metal ions studied. Suitable reaction mechanisms have been proposed for the oxidation of Cinnamyl alcohol in the presence and absence of transition metal ion catalysts.

Keywords: Cinnamyl alcohol; Oxidation; Ce (IV); Kinetics; Transition metal ion catalysts; Catalytic efficiency; Hyper valent ions; Ionic strength; Thermodynamic activation parameters; Reaction mechanism

Introduction

Organic oxidants have been widely used for the oxidation of alcohols, but inorganic oxidants have been sparingly used [1-6]. Also, there are few reports of the kinetic studies of the oxidation of alcohols [7-10]. We have investigated the oxidation of some perfumery alcohols using organic and inorganic oxidants [11-14].

Herein, we report the transition metal ion catalysed oxidation of the perfumery primary alcohol, Cinnamyl alcohol (Molar mass 134.17g mol^{-1}, Mol. formula $C_9H_{10}O$, C_6H_5 CH=CH CH_2OH) using Ce (IV) in acidic medium. The oxidation was studied under first order kinetic conditions with respect to the inorganic oxidant i.e. [Ce(IV)] << [alc.] and the progress of the oxidation was monitored titrimetrically. The thermodynamic activation parameters were determined from the variation of oxidation rate with temperature (308-318K). K_2SO_4 was used to study the influence of ionic strength on the oxidation rate in dilute solution. The effects of alcohol and oxidant concentrations, ionic strength and temperature on the oxidation rate of alcohol were studied in depth.

Inexpensive and less hazardous transition metal ions, Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) were used to catalyse the oxidation of Cinnamyl alcohol and the sequence of their catalytic efficiencies determined on the basis of Irving - Williams order of stability constants of the transient metal complexes formed during the oxidation process. Suitable reaction mechanisms have been suggested for the uncatalyzed and catalysed oxidation of the alcohol under investigation.

Materials and Methods

Cinnamyl alcohol was obtained from S.H. Kelkar and Co., Mumbai, India and used as received. Metal salts of required purity were procured from E. Merck, Germany. All other chemicals and reagents used were of Analar Grade.

The oxidation was studied under first order kinetic conditions with respect to the inorganic oxidant. The solutions of alcohol and oxidant in requisite amounts were allowed to equilibrate in a previously adjusted thermostat with accuracy +/- 0.1°C. When the temperature equilibrium was attained, the solutions were quickly mixed to start the reaction. Aliquots of the reaction mixture were withdrawn at regular time intervals during the course of the reaction, the reaction was quenched using ice and the unreacted oxidant was titrated against standard Ferrous ammonium sulphate in sulphuric acid medium using Ferroin as an indicator. From the linear plots of log (unreacted Ce(IV)) vs. time ,the first order rate constants (k) were determined.

The thermodynamic activation parameters were determined from the Arrhenius plots of logkvs T^{-1} in the temperature range 308-318K. K_2SO_4 was used to study the effect of ionic strength on the oxidation rate of alcohol in the range μ=0.05-0.25mol dm^{-3}.

An identical procedure was followed to study the catalytic effect of transition metal ions on the oxidation rate of alcohol in the range [M(II)]=2.5-5.0 x 10^{-4}mol dm^{-3}. It was found that the oxidation rate increased with [M(II)].

Results and Discussion

Oxidation of primary alcohol, Cinnamyl alcohol by Ce(IV) in acidic medium

Effect of alcohol and oxidant concentrations on rate of oxidation: The rate constant data for the oxidation of Cinnamyl alcohol by Ce(IV) in acidic medium is given in Table1.The rate of oxidation increases with [alc.] but decreases with concentration of Ce(IV).

Table 1: Rate constant data for oxidation of Cinnamyl alcohol by Ce(IV) in acidic medium[alc.]=0.2mol dm^{-3} [Ce(IV)]=0.05mol dm^{-3} [H_2SO_4]=1.0mol dm^{-3} Temperature=303K

[alc.] x10^1mol dm^{-3}	[Ce(IV)]x10^3mol dm^{-3}	kx10^2s^{-1}
0.25	5.00	1.84
0.50	5.00	3.22
0.63	5.00	4.37
0.75	5.00	5.29
0.88	5.00	6.21
1.00	5.00	7.13
1.00	2.50	9.67
1.00	5.00	8.75
1.00	10.00	7.59
1.00	15.00	6.67
1.00	20.00	5.70
1.00	25.00	4.83

Reaction mechanism of oxidation:

$RCH_2OH + Ce(IV) \overset{K}{\leftrightarrow} [RCH_2OH\text{-}Ce]^{IV}$……………………………..(i)

Primary alcohol Complex

$[RCH_2OH\text{-}Ce]^{IV} \xrightarrow{k,\ slow} RC^*HOH + Ce(III) + H^+$ ……………………..(ii)

where RC*HOH is a free radical produced during the course of the reaction.

$RC^*HOH + Ce(IV) \xrightarrow{fast} RC + HOH + Ce(III)$ ……………………(iii)

$RC + HOH \xrightarrow{fast} RCHO + H^+$ ………………………………..(iv)

aldehyde

Net Reaction: $RCH_2OH + 2Ce(IV) \longrightarrow RCHO + 2Ce(III) + 2H^+$

The product of the oxidation i.e. aldehyde was identified by 2,4dinitrophenylhydrazone test and later confirmed by TLC.

In aqueous acidic medium, Ce(IV) oxidizes alcohols through complexation followed by free radical generation [15-17].

The rate constant increases with [alc.] but deceases with [Ce(IV)] (Table 1).This decrease in oxidation rate is due to the formation of an unreactive dimeric $[Ce(IV)]_2$ species which increases with [Ce(IV)][18-20] as per the reaction, $2Ce(IV) \leftrightarrow [Ce(IV)]_2$.

Effect of ionic strength on oxidation rate: Table 2 shows the effect of ionic strength (μ) on the oxidation rate of Cinnamyl alcohol.

Table 2: Effect of ionic strength on the oxidation rate of Cinnamyl alcohol by Ce(IV) in acidic medium [alc.]=0.1mol dm^{-3} $[H_2SO_4]$=0.3 mol dm^{-3} [Ce(IV)]=$5x10^{-3}$ mol dm^{-3} Temperature=308K

μ mol dm^{-3} (K_2SO_4)	$kx10^2s^{-1}$
0.05	1.66
0.10	1.59
0.15	1.68
0.20	1.64
0.25	1.65

The graphs of logk vs.$\mu^{1/2}$ were found to be straight lines parallel to the $\mu^{1/2}$ axis indicating that in dilute solution, the oxidation rate is independent of ionic strength. This confirms the involvement of a non-ionic species viz. alcohol in the oxidation in accordance with the Bronsted-Bjerrum equation, $\log k = \log k_0 + 1.02 Z_A Z_B\ \mu^{1/2}$ and justifies the reaction mechanism suggested for the oxidation process.

Effect of temperature on oxidation rate: The oxidation was studied at different temperatures (308-318K). The rate constants were determined from the straight-line graphs of logk vs. time. The energy of activation (E) and other thermodynamic activation parameters were determined from the Arrhenius plots of logk vs. T^{-1} and are recorded in Table 3.

Table 3: Thermodynamic activation parameters of the Oxidation of Cinnamyl alcohol by Ce(IV) in acidic medium [alc.]=0.1 mol dm^{-3} [Ce(IV)]=$5x10^{-3}$mol dm^{-3} $[H_2SO_4]$=1.0mol dm^{-3}

Temp. (K)	$kx102s^{-1}$	E kJ mol^{-1}	K^*x10^{15}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
308	2.00	27.37	3.17	24.85	84.17	-0.1958
311	2.31	27.37	3.55	24.78	86.09	-0.1970
313	2.52	27.37	3.83	24.76	86.44	-0.1970
318	2.90	27.37	4.38	24.72	87.72	-0.1972

The important inferences from the thermodynamic study are:

1. The rate constant of oxidation k increases with temperature as expected.
2. K*, the equilibrium constant for the formation of the activated complex from the reactants increases with temperature hence K* is a function of temperature.
3. The constant values of energy of activation E at all temperatures indicate that the site of oxidation ie -OH bond is the same at all temperatures.
4. The negative values of entropy of activation, ΔS* indicate the orientation of solvent molecules around a rigid activation complex [21]. The water molecules are tightly held to the -OH bond which is the site of oxidation resulting in the curtailment of the vibrational and rotational motions of the reacting system and consequently a decrease in entropy.

Catalytic effect of transition metal ions on the oxidation rate of cinnamyl alcohol by Ce(IV) in acidic medium

Transition metal ions Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) were used to catalyse the oxidation of Cinnamyl alcohol in the concentration range

[M(II)]=2.5-5.0 x 10^{-4} mol dm^{-3}(Table 4; Figure 1).

The oxidation rate of Cinnamyl alcohol increased linearly with [M(II)] and the sequence of catalytic efficiencies of the transition metal ions under study was found to be Mn(II)>Co(II)>Ni(II)>Cu(II)>Zn(II) (Table 4; Figure 1).

Table 4: Catalytic effect of transition metal ions on the oxidation rate of Cinnamyl alcohol by Ce(IV) in acidic medium [alc.]=0.1mol dm^{-3} [Ce (IV)]=$2.5x10^{-3}$mol dm^{-3} $[H_2SO_4]$=1.0 mol dm^{-3} Temperature=308K

[M(II)] $x10^4$ mol dm^{-3}	Mn(II) $kx10^2s^{-1}$	Co(II) $kx10^2s^{-1}$	Ni(II) $kx10^2s^{-1}$	Cu(II) $kx10^2s^{-1}$	Zn(II) $kx10^2s^{-1}$
0.00	2.00	2.00	2.00	2.00	2.00
2.50	4.60	4.14	3.68	2.99	2.30
3.00	5.98	5.52	5.06	4.14	3.68
3.50	7.36	6.44	5.98	5.52	4.83
4.00	8.75	8.29	6.90	6.21	5.75
4.50	9.67	8.75	8.06	7.36	6.67
5.00	10.36	9.67	8.98	8.06	7.59

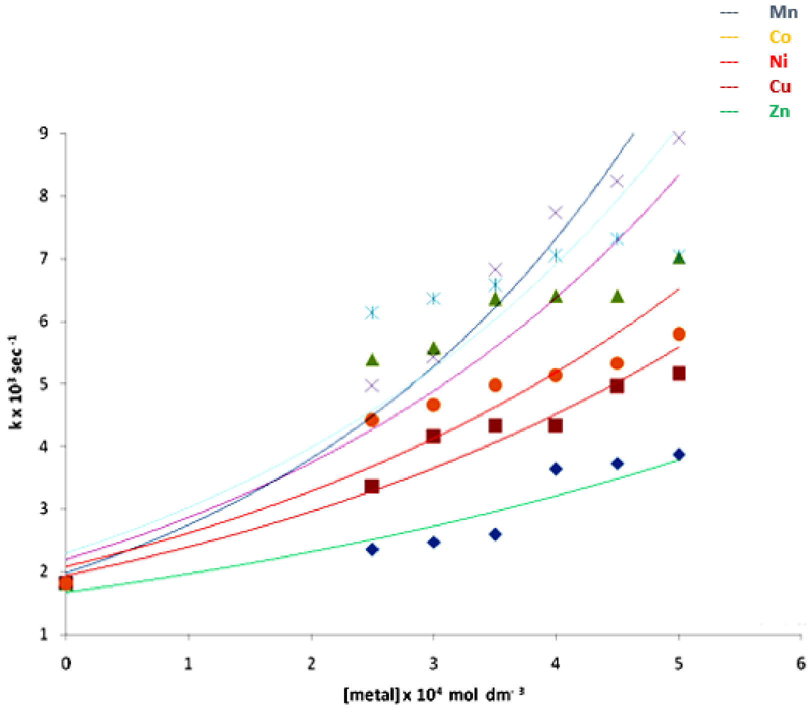

Figure 1: Catalytic effect of transition metal ions on the oxidation rate of Cinnamyl alcohol by Ce(IV) in acidic.

Reaction mechanism of transition metal ion catalysed oxidation of cinnamyl alcohol

Mn, Co, Ni and Cu form the hypervalent ions Mn(III), Co(III), Ni(III) and Cu(III) respectively due to their low third ionization enthalpies unlike Zn which has a relatively high third ionization enthalpy (3829kJ mol^{-1}) and its energy of solvation is not sufficient to make the 3^+ 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 unstable intermediate complex between hypervalent M(III) ions and alcohol.

K

RCH_2OH + M(II) ↔ M(II)(RCH_2OH) ....(i)

Primary alcohol Complex C_1

k, slow

M(II)(RCH_2OH) + Ce(IV) --------> M(III)(RCH_2OH) + Ce(III) .....(ii)

Complex C_1 Complex C_2

The electron transfer reaction is slow [10].

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

fast

Complex C_2 ---------> RC*HOH + H^+ + M(II) ....(iii)

where RC*HOH is a free radical produced during the course of the reaction.

fast

RC*HOH + Ce(IV) ---------> RC+HOH + Ce(III) ....(iv)

fast

RC+ HOH ---------> RCHO + H^+ ....(v)

aldehyde

Net reaction: RCH_2OH 2Ce(IV) -------> RCHO + $2H^+$ + 2Ce(III)

In presence of Zn(II) ions:

K

RCH_2OH + M(II) ↔ M(II)(RCH_2OH) ....(i)

Primary alcohol Complex

k, slow

M(II) (RCH_2OH) + Ce(IV) ---> RC*HOH + H^+ + M(II) + Ce(III).....(ii)

Complex

where RC*HOH is a free radical produced during the reaction.

fast

RC*HOH + Ce(IV) ------> RC+HOH + Ce(III) ....(iii)

fast

RC+HOH -------> RCHO + H^+ ....(iv)

aldehyde

Net Reaction: RCH_2OH + 2 Ce(IV) -------> RCHO + $2H^+$ + 2Ce(III)

Sequence of catalytic efficiencies of transition metal ions:

The catalytic efficiency of a metal ion is inversely proportional to the stability of its complex formed as a transient short lived intermediate during the reaction. The stability of such unstable complexes depends mainly on the charged density of the metal ions involved. Therefore, the stability order for the complexes of the transition metal ions under study is expected to be

Cu(II)>Zn(II)>Ni(II)>Co(II)>Mn(II) [22,23] and the expected sequence of catalytic efficiencies of the metal ions is

Mn(II)>Co(II)>Ni(II)>Zn(II)>Cu(II).This is a general guide to metal ion behavior but several discrepancies have been observed and reported in literature [24-28]. In the present investigation, we have observed differences between the experimentally observed sequence of catalytic efficiencies of the transition metal ions and the theoretically expected sequence viz. Mn(II)>Co(II)>Ni(II)>Cu(II)>Zn(II) (Table 4; Figure1).

Conclusion

Transition metal ions have been effectively used to catalyse the oxidation of Cinnamyl alcohol to Cinnamaldehyde under first order kinetic conditions with respect to the oxidant Ce(IV) in acidic medium. The reaction mechanism has been explained on the basis of the formation of intermediate complexes involving hypervalent ions, Mn(III),Co(III),Ni(III) and Cu(III). Certain discrepancies have been found between the observed sequence of catalytic efficiencies of the metal ions and the theoretically expected sequence. Among the transition metal ions studied, Mn(II) appears to be the most effective catalyst for the oxidation of Cinnamyl alcohol.

The thermodynamic activation parameters of the oxidation have been determined and correlated with the molecular dynamics of the oxidation reaction. Ionic strength has no effect on the oxidation of Cinnamyl alcohol.

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