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Oxidation of Industrially Important Alcohols by Ce(IV) in H_2SO_4–A Kinetic Approach

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The kinetics of oxidation of industrially important alcohols, geraniol, 1-phenyl ethanol and benzyl alcohol by Ce(IV) in H_2SO_4 has been studied in the micellar phase using sodium lauryl sulphate in the temperature range 30-50 ºC. The effect of concentrations of alcohol and Ce(IV) in H_2SO_4 ionic strength and temperature on the oxidation rate has been studied in details. Ni(II), Cu(II) and Zn(II) ions have been used to catalyze the oxidation of the alcohol to the corresponding carbonyl compounds. The oxidation rate increases with alcohol concentration but decreases with the concentration of the oxidation reagent due to the formation of unreactive $[Ce(IV)]_2$ species at higher concentrations of the oxidizing reagent. The thermodynamic activation parameters have been calculated. The negative values of ΔS^* indicate the reorientation of solvent molecules around the rigid activated complex formed during the course of the reaction. A suitable reactive mechanisim has been suggested for the oxidation process.

Key Words: Kinetics, Geraniol, 1-Phenyl ethanol, Benzyl alcohol, Ce(IV).

INTRODUCTION

The quantitative aspect of oxidation of the several alcohols has been extensively studied[1-6]. However, the kinetic and themodynamic studies of the oxidation of alcohols are few. This paper deals with the kinetics of oxidation of three alcohols extensively used in the perfumery industry, *i.e.*, geraniol, 1-phenyl ethanol and benzyl alcohol.

The effect of ionic strength on the oxidation rate has been studied using Na_2SO_4 . The kinetics of the metal ion catalyzed oxidation of the perfumery alcohols has been studied using the transition metal ions, Ni(II), Cu(II) and Zn(II). The themodynamic activation parameters have been evaluated from the effect of temperature on the oxidation rate. All the data collected has been collated and suitable reaction mechanisms have been suggested for the oxidation of alcohols in the presence and absence of metal ion catalysts.

EXPERIMENTAL

All the chemicals and regents used were of AR grade-geraniol and 1-phenyl ethanol (Ultra International Limited), benzyl alcohol (BDH), ceric ammonium sulphate (West Coast Laboratories) and sodium lauryl sulphate (Loba Chemie). AR Na_2SO_4 was used for the study of ionic strength on oxidation rate. The metal salts used for present studies were of AnalR grade (BDH).

The oxidation of the industrially important alcohols was studied under pseudo unimolecular conditions with respect to [Ce(IV)] and the progress of the reaction was monitored titrimetrically. The solutions of alcohol and oxidizing agent in required amounts were allowed to equilibrate in a previously adjusted thermostat (accuracy ± 0.1 ºC). After the temperature equilibrium was attained, the solutions were mixed to initiate 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 ammoniuim sulphate in H_2SO_4 using ferroin as an indicator.

The reaction was studied in the temperature range 30-50 ºC. The pseudo first order rate constants were evaluated from the linear plot of log (a-x) *vs.* time. From the Arrhenius plots of log k *vs.* 1/T, the energy of activation and other thermodynamic activation parameters were calculated.

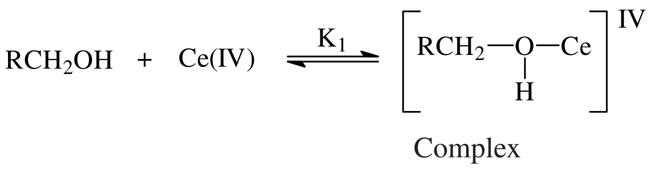
A similar procedure was used to study the effect of Ni(II), Cu(II) and Zn(II) on the reaction rate in the concentration range $[M(II)] = 0.5$ to 2.5×10^{-3} mol dm^{-3} at 30 ºC. The effect of ionic strength (μ) on the oxidation rate was studied in dilute solution in the range $\mu = 0.1$ to 0.5 mol dm^{-3} at 40 ºC using Na_2SO_4.

RESULTS AND DISCUSSION

Kinetics of oxidation of alcohols: [Ce(IV)] oxidises the primary alcohols, geraniol and benzyl alcohol to the corresponding aldehydes, geranial and benzaldehyde, respectively. 1-Phenyl ethanol is oxidized to methyl phenyl ketone.

The oxidation was monitored in the micellar phase using soduim lauryl sulphate (SLS). The rate constant increases with alcohol concentration but decreases with increase in Ce(IV) concerntration (Table-1).

Reaction mechanism of oxidation



$$RCH_2OH + Ce(IV) \overset{K_1}{\rightleftharpoons} \left[RCH_2-\underset{\substack{|\\H}}{O}-Ce \right]^{IV} \qquad (1)$$

Complex

TABLE-1
RATE CONSTANT DATA FOR THE OXIDATION OF ALCOHOLS BY Ce(IV) IN H_2SO_4
$[H_2SO_4]$ = 1 M, [SLS] = 0.05 m, Temp. = 303 K

$[Alc] \times 10^1$ (mol dm^{-3})	$[Ce(IV)] \times 10^2$ (mol dm^{-3})	$k \times 10^4$ (s^{-1})		
		Benzyl alcohol	1-Phenyl ethanol	Geraniol
1.000	0.25	6.91	1.49	15.30
1.000	0.50	1.22	0.78	6.50
1.000	1.00	0.75	0.54	2.14
1.000	1.50	0.42	0.48	0.99
1.000	2.00	0.17	0.19	0.85
1.000	2.50	0.12	0.12	0.84
0.250	0.50	0.18	0.48	1.22
0.500	0.50	0.31	0.61	2.07
0.625	0.50	0.47	0.69	3.07
0.750	0.50	1.01	0.77	4.06
0.875	0.50	1.06	0.86	4.24
1.000	0.50	1.15	0.95	4.31

$$\text{Complex} \xrightarrow[\text{slow}]{k} R\dot{C}HOH + Ce(III) + H^+ \qquad (2)$$

where, $R\dot{C}HOH$ is a free radical generated during the decomposition of the intermediate complex.

$$R\dot{C}HOH + Ce(IV) \xrightarrow{\text{fast}} R\overset{+}{C}HOH + Ce(III) \qquad (3)$$

$$R\overset{+}{C}HOH \xrightarrow{\text{fast}} \underset{\text{aldehyde}}{RCHO} + H^+ \qquad (4)$$

Net reaction, $RCH_2OH + 2Ce(IV) \longrightarrow RCHO + 2Ce(III) + 2H^+$
In case of a secondary alcohol, the corresponding ketone is produced.

The product of the oxidation reaction *i.e.* aldehyde or ketone was identified by 2,4-dinitro phenyl hydrazone test and confirmed by thin layer chrormatography.

In aqueous H_2SO_4 medium, Ce(IV) oxidizes alcohols through complexation followed by the generation of free radicals[7-9]. The decrease in rate constant with increase in Ce(IV) concentration is due to the formation of an unreactive dimeric Ce(IV) species[10-12] which increases with [Ce(IV)]

$$2Ce(IV) \rightleftharpoons [Ce(IV)]_2$$

The secondary alcohol, 1-phenyl ethanol is oxidized at a slower rate than the primary alcohols under study.

Effect of temperature on oxidation rate: The oxidation of the alcohols was studied in the temperature range 30-50 ºC. The energy of activation and other thermodynamic activation parameters were evaluated. The negative values of ΔS^* (-0.0502 kJ K^{-1} mol^{-1} for geraniol, -0.2423 kJ K^{-1} mol^{-1} for 1-phenyl ethanol and -0.2178 kJ K^{-1} mol^{-1} for benzyl alcohol) 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[13].

Effect of ionic strength on oxidation rate: Na_2SO_4 was used to study the effect of ionic strength (μ) on oxidation rate in dilute solution in the range $\mu = 0.1$ to 0.5 mol dm^{-3} at 40 ºC (Table-2). The graphs of log k *vs.* $\sqrt{\mu}$ were straight lines parallel to the $\sqrt{\mu}$ axis indicating that the oxidation rate was independent of ionic strength.

TABLE-2
EFFECT OF IONIC STRENGTH (M) ON THE RATE CONSTANT OF ALCOHOLS BY Ce(IV) IN H_2SO_4
[Alc] = 0.1 M, [SLS] = 0.05 M, [Ce(IV)] = 0.005 M, [H_2SO_4] = 0.5 M, Temp. = 313 K

μ (mol dm^{-3})	$k \times 10^4$ (s^{-1})		
	Benzyl alcohol	1-Phenyl ethanol	Geraniol
0.1	1.70	1.15	9.59
0.2	2.08	1.08	9.20
0.3	1.50	1.15	12.10
0.4	2.08	1.25	7.67
0.5	1.75	1.06	9.42

Kinetics of metal ion catalyzed oxidation of alcohols: The alcohols benzyl alcohol, 1-phenyl alcohol and geraniol were oxidized using Ce(IV) in H_2SO_4 in the micellar phase using sodium lauryl sulphate in the presence of the transition metal ions, Ni(II), Cu(II) and Zn(II) in the concentration range [M(II)] = 0.5 to 2.5 × 10 mol^{-3} dm^{-3} at 30 ºC. The rate constants are listed in Tables 3a-3c. For each of the alcohols under study, the reaction rate increases linearly with [M(II)].

Reaction mechanism of metal ion catalyzed oxidation of alcohols

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

$$RCH_2OH + M(II) \underset{}{\overset{K}{\rightleftharpoons}} \underset{\text{Complex } C_1}{M(II)\cdot R^{o}CH_2OH} \qquad (1)$$

TABLE-3a
EFFECT OF METAL IONS ON RATE OF OXIDATION OF BENZYL ALCOHOL BY Ce(IV) IN H_2SO_4
[Alc] = 0.1 M, [SLS] = 0.5 M, [Ce(IV)] = 0.025 M, [H_2SO_4] = 1 M, Temp. = 303 K

[M(II)] × 10^3 (mol dm^{-3})	k × 10^5 (s^{-1})		
	Ni(II)	Cu(II)	Zn(II)
In absence	4.31	4.31	4.31
0.50	5.65	9.21	4.60
1.00	6.90	9.59	6.00
1.50	8.45	10.00	7.50
2.00	9.21	11.00	8.90
2.50	10.60	11.51	10.30

TABLE-3b
EFFECT OF METAL IONS ON RATE OF OXIDATION OF 1-PHENYL ETHANOL BY Ce(IV) IN H_2SO_4
[Alc] = 0.1 M, [SLS] = 0.5 M, [Ce(IV)] = 0.025 M, [H_2SO_4] = 1 M, Temp. = 303 K

[M(II)] × 10^3 (mol dm^{-3})	k × 10^5 (s^{-1})		
	Ni(II)	Cu(II)	Zn(II)
In absence	0.86	0.86	0.86
0.50	1.42	1.20	1.15
1.00	1.70	1.34	1.34
1.50	1.88	1.61	1.60
2.00	2.25	2.05	1.84
2.50	2.50	2.30	2.10

TABLE-3c
EFFECT OF METAL IONS ON RATE OF OXIDATION OF GERANIOL BY Ce(IV) IN H_2SO_4
[Alc] = 0.1 M, [SLS] = 0.5 M, [Ce(IV)] = 0.025 M, [H_2SO_4] = 1 M, Temp. = 303 K

[M(II)] × 10^3 (mol dm^{-3})	k × 10^5 (s^{-1})		
	Ni(II)	Cu(II)	Zn(II)
In absence	0.98	0.98	0.98
0.50	1.41	1.49	2.79
1.00	1.53	1.84	3.76
1.50	2.13	2.76	8.06
2.00	2.90	3.45	9.46
2.50	3.45	4.10	13.10

$$\mathrm{M(II)\cdot RCH_2OH + Ce(IV)} \xrightarrow[\text{slow}]{k} \underset{\text{Complex } C_2}{\mathrm{M(III)RCH_2OH}} + \mathrm{Ce(III)} \tag{2}$$

The electron transfer reaction is slow[14].

$$\text{Complex } C_2 \xrightarrow{\text{fast}} \mathrm{R\dot{C}HOH + H^+ + M(II)} \tag{3}$$

where $\mathrm{R\dot{C}HOH}$ is a free radical generated during the course of the reaction.

$$\mathrm{R\dot{C}HOH + Ce(IV)} \xrightarrow{\text{fast}} \mathrm{R\overset{+}{C}HOH + Ce(III)} \tag{4}$$

$$\mathrm{R\overset{+}{C}HOH} \xrightarrow{\text{fast}} \mathrm{RCHO + H^+} \tag{5}$$

Net reaction: $\mathrm{RCH_2OH + 2Ce(IV) \longrightarrow RCHO + 2H^+ + 2Ce(III)}$

(In case of a secondary alcohols, the corresponding ketone is produced)

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

In presence of Zn(II) ions

$$\mathrm{RCH_2OH + M(II)} \xrightleftharpoons{K} \underset{\text{Complex}}{\mathrm{M(II)\cdot RCH_2OH}} \tag{1}$$

$$\text{Complex} + \mathrm{Ce(IV)} \xrightarrow[\text{slow}]{k} \mathrm{R\dot{C}HOH + H^+ + M(II) + Ce(III)} \tag{2}$$

where $\mathrm{R\dot{C}HOH}$ is a free radical generated during the reaction.

$$\mathrm{R\dot{C}HOH + Ce(IV)} \xrightarrow{\text{fast}} \mathrm{R\overset{+}{C}HOH + Ce(III)} \tag{3}$$

$$\mathrm{R\overset{+}{C}HOH} \xrightarrow{\text{fast}} \mathrm{RCHO + H^+} \tag{4}$$

Net reaction: $\mathrm{RCH_2OH + 2Ce(IV) \longrightarrow RCHO + 2H^+ + 2Ce(III)}$

(In case of a secondary alcohol, the corresponding ketone is produced)

Catalytic efficiency of transition 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 many other factors.

Thus the stabilty order of the complexes is expected to be Cu(II) > Zn(II) > Ni(II) and the catalytic efficiency of the metal ions is expected to be in the reverse order *viz.*, Ni(II) > Zn(II) > Cu(II). However such generalizations are only approximate guides and discrepancies are offen observed.

In the present study, the catalytic efficiency follows the sequences:

Benzyl alcohol	Cu(II) > Ni(II) > Zn(II)
1-Phenyl ethanol	Ni(II) > Cu(II) > Zn(II)
Geraniol	Zn(II) > Cu(II) > Ni(II)

The catalytic effect of metal ions on the secondary alcohol, 1-phenyl ethanol is much less than that on the primary alcohols under study.

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