



Kinetics of Controlled Oxidation of Some Aliphatic Alcohols Using Potassium Iodate

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The first-order oxidation kinetic, mechanistic and thermodynamic aspects of oxidation of several types of industrially important alcohols *viz.* 1-propanol, 1-butanol, 1-hexanol, isopropyl alcohol and isobutyl alcohol using an inorganic oxidant potassium iodate are reported in this article. Iodometric estimation of the unreacted oxidant at regular intervals during the reaction course was used to track reaction progress. The oxidation rate was directly and inversely related to alcohol concentration and $[KIO_3]$, respectively, in all the alcohols studied. The reaction mechanism suggested that oxidation rates were independent of ionic strength. The oxidation rate varied with temperature. The Arrhenius equation was used to determine thermodynamic activation parameters and interpreted on the basis of the molecular dynamics of oxidation process. The reaction mechanism has been explained on the basis of the formation of halic acid (HIO_3) and hypoiodite ion (IO^-) in an acidic medium. The oxidation rates follow the sequence: 1-propanol > 1-butanol > isopropyl alcohol > isobutyl alcohol > 1-hexanol, which has been explained on the basis of chain length and other structural features of the alcohols under investigation. Transition metal ions *viz.*, Mn(II), Co(II), Ni(II), Zn(II), Cu(II) and Cd(II) have been used to catalyze the oxidation of the aliphatic alcohols in acidic medium and the sequences of their catalytic efficiencies has also been determined.

Keywords: Aliphatic alcohols, Potassium Iodate, Kinetics.

INTRODUCTION

Oxidation of alcohols is an industrially useful reaction because it yields products with diverse applications. A literature survey revealed several reports of the quantitative conversion of alcohols to the corresponding carbonyl compounds [1-5]. However, only a few reports on the thermodynamic and kinetic aspects of alcohol oxidation by using inorganic oxidants are currently available. The oxidative kinetics of some industrially important alcohols and phenols mediated by organic and inorganic oxidizing agents are reported in the literature [6-11].

This study discusses the controlled oxidation kinetics of some primary and secondary aliphatic alcohols, which are used as diluents in the production of fragrances and perfumes. Potassium iodate, a rarely used oxidant, mediated the oxidation of the aliphatic alcohols in sulphuric acidic medium. The dependence of oxidation rates of alcohols on the concentrations of alcohols and oxidants, ionic strength (KIO_3) and temperature have been investigated. The effects of temperature on the oxidation rate provided data for the calculation and basis for interpretation of the thermodynamic activation parameters. The chain

length and other structural features of the aliphatic alcohols determined the sequence of oxidation rates. This study suggests a suitable reaction mechanism underlying aliphatic alcohol oxidation.

EXPERIMENTAL

The aliphatic alcohols were obtained from S.H. Kelkar & Co., Mumbai and Shaivi Industries, Lucknow, India and purified by distillation. All the metal salts used in the catalytic study were of Analar grade (S.D. Fine Chemical, Mumbai). All other chemicals used were also of Analar Grade.

Kinetics of oxidation of aliphatic alcohols: The first-order oxidation kinetics of aliphatic alcohols were examined with respect to inorganic oxidant (KIO_3). Iodometric estimation of unreacted oxidant was performed at regular intervals during the reaction course in order to track reaction progress. The slopes of the linear plots of $\log(a-x)$ versus time provided the values of first-order rate constants (k). The oxidation was carried out in the temperature range 303-318 K and the energy of activation and other thermodynamic activation parameters were deter-

mined from the Arrhenius plots of $\log k$ versus T^{-1} . The effect of ionic strength (μ) on the rate of oxidation was studied in dilute solution at 313 K using K_2SO_4 in the range $\mu = 5$ to $25 \times 10^{-2} \text{ mol dm}^{-3}$ in accordance with Bronsted-Bjerrum equation, $\log k = \log k_0 + 1.02 Z_A Z_B \mu^{1/2}$.

Kinetics of transition metal ion catalyzed oxidation of aliphatic alcohols: An identical procedure was followed to study the catalytic impact of transition metal ions on the oxidation rates of the aliphatic alcohols under study in the concentration range $[M(II)] = 2.5$ to $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ at 303 K.

RESULTS AND DISCUSSION

The primary alcohols, 1-propanol, 1-butanol, isopropyl alcohol and 1-hexanol were oxidized by KIO_3 in acidic medium to the corresponding aldehydes and secondary alcohol, while isobutyl alcohol was oxidized to ketone.

Kinetics of oxidation of aliphatic alcohols: For all the alcohols studied, the oxidation rate increased with alcohol concentration but decreased with oxidant concentration (Table-1).

Reaction mechanism of oxidation of 1° and 2° aliphatic alcohols: In acidic medium, KIO_3 rapidly forms the halic acid in the presence of iodic acid HIO_3 [12,13]. The oxidation of alcohols by KIO_3 in acidic medium results in the formation of hypoiodite ion (IO^-).



The unreacted oxidant was treated with ice cold 10 % KI in dilute H_2SO_4 and the liberated iodine was titrated with standard $Na_2S_2O_3$ using starch as indicator. The products of the reaction *i.e.* aldehyde and ketone were identified by 2,4-dinitrophenyl hydrozone test and confirmed by TLC.

The oxidation rates followed the sequence: 1-propanol > 1-butanol > isopropyl alcohol > isobutyl alcohol > 1-hexanol. All the primary aliphatic alcohols except 1-hexanol were oxidized faster than the secondary aliphatic alcohol *viz.*, isobutyl alcohol (Table-1). The oxidation rates were found to be inversely proportional to the chain lengths of the aliphatic alcohols in this study.

Effect of ionic strength on oxidation rates of aliphatic alcohols: KIO_3 was used in the range $\mu = 5$ to $25 \times 10^{-2} \text{ mol dm}^{-3}$ to study the effect of ionic strength on oxidation rates of alcohols (Table-2). The graph of $\log k$ versus $\mu^{1/2}$ were found to be straight lines parallel to $\mu^{1/2}$ axis confirming that ionic strength has no effect on the oxidation rates of alcohols due to the involvement of a non-ionic species in the oxidation process. This observation is supported by the reaction mechanism suggested for the oxidation of the aliphatic alcohols studied.

Effect of temperature on the oxidation rates of aliphatic alcohols: The oxidation of alcohols was studied at four different temperatures in the range 303-318 K and the thermodynamic activation parameters were determined from the Arrhenius plots of $\log k$ versus T^{-1} (Table-3).

The important inferences from the thermodynamic study are found as (a) oxidation rates of alcohols increase with temperature and are inversely proportional to energy of activation of the oxidation reaction; (b) for all the alcohols studied, entropy of activation (ΔS^\ddagger) is almost constant at all temperatures indicated that oxidation occurs at the same site *i.e.* OH bond; (c) negative values of ΔS^\ddagger indicate a decrease in entropy due to the formation of a rigid activated complex as a transient intermediate followed by reorientation of solvent molecules around the activated complex. Solvent molecules are tightly held to the -OH bond leading to decrease in disorder [14,15].

TABLE-1
RATE CONSTANT DATA FOR THE OXIDATION OF ALIPHATIC ALCOHOLS BY KIO_3 IN 0.1 M H_2SO_4 , TEMP. = 303 K

[Alc.] $\times 10^1$ (mol dm ⁻³)	[KIO ₃] $\times 10^3$ (mol dm ⁻³)	k $\times 10^4$ (s ⁻¹)				
		1-Propanol	1-Butanol	Isopropyl alcohol	Isobutyl alcohol	1-Hexanol
1.00	2.50	4.25	3.77	3.29	2.70	2.45
1.00	5.00	3.84	2.90	2.64	2.43	2.24
1.00	10.00	3.79	2.83	1.53	1.46	1.34
1.00	15.00	2.71	2.69	1.46	1.34	1.06
1.00	20.00	1.80	1.93	1.32	0.98	0.88
1.00	25.00	1.05	1.67	0.36	0.46	0.38
0.25	5.00	1.66	1.33	1.00	0.57	0.38
0.50	5.00	2.23	1.61	1.24	0.86	0.59
0.63	5.00	2.69	2.06	1.58	1.36	0.89
0.75	5.00	2.96	2.42	2.05	1.79	1.12
0.88	5.00	3.39	2.69	2.30	2.00	1.59
1.00	5.00	3.84	2.90	2.64	2.30	1.76

TABLE-2
EFFECT OF IONIC STRENGTH ON THE OXIDATION RATE OF ALIPHATIC ALCOHOLS
BY KIO_3 IN 0.1 M H_2SO_4 , [Alc.] = 0.1 M, [KIO₃] = 2.5×10^{-3} M, TEMP. = 313 K

$\mu \times 10^2$ (mol dm ⁻³)	k $\times 10^4$ s ⁻¹				
	1-Propanol	1-Butanol	Isopropyl alcohol	Isobutyl alcohol	1-Hexanol
Zero	4.25	3.77	3.39	2.60	2.35
5.00	4.36	3.96	3.45	2.70	2.45
10.00	4.25	3.51	3.28	2.66	2.33
15.00	4.18	3.95	3.39	2.71	2.42
20.00	4.36	3.69	3.26	2.81	2.33
25.00	4.25	3.72	3.49	2.75	2.54

TABLE-3
THERMODYNAMIC ACTIVATION PARAMETERS OF THE OXIDATION OF ALIPHATIC ALCOHOLS BY KIO_3 IN 0.1 M H_2SO_4

Temp. (K)	$k \times 10^4$ (s^{-1})	E (kJ mol^{-1})	$K^* \times 10^{15}$	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔS^* ($\text{kJ K}^{-1} \text{mol}^{-1}$)
1-Propanol						
303	3.48	7.28	4.76	1.60	97.45	-0.306
308	4.58	7.28	4.72	1.61	99.04	-0.306
313	5.98	7.28	4.67	1.74	100.44	-0.306
318	6.14	7.28	4.63	1.74	102.04	-0.306
1-Butanol						
303	2.90	8.65	6.14	1.11	98.36	-0.304
308	3.22	8.65	6.09	1.18	99.83	-0.304
313	4.05	8.65	6.06	1.18	101.46	-0.305
318	5.03	8.65	6.01	1.28	102.85	-0.305
Isopropyl alcohol						
303	2.64	22.97	20.46	3.34	95.59	-0.248
308	2.88	22.97	20.42	4.88	96.19	-0.246
313	3.04	22.97	20.37	5.09	97.65	-0.247
318	3.25	22.97	20.33	5.28	99.11	-0.248
Isobutyl alcohol						
303	2.43	24.89	22.37	1.05	98.50	-0.252
308	2.63	24.89	22.33	1.15	99.90	-0.251
313	2.89	24.89	22.28	1.22	101.37	-0.253
318	3.05	24.89	22.24	1.31	102.80	-0.253
1-Hexanol						
303	2.24	33.52	31.00	0.87	93.16	-0.205
308	2.35	33.52	30.95	1.11	94.09	-0.205
313	2.65	33.52	30.91	1.38	95.04	-0.205
318	2.85	33.52	30.87	1.54	96.28	-0.206

Kinetics of transition metal ion catalyzed oxidation of aliphatic alcohols: The aliphatic alcohols were oxidized using KIO_3 in acidic medium in the presence of transition metal ions in the range $[\text{M(II)}] = 2.5$ to $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ at 303 K. The rate constants were determined from the linear plots of $\log(a-x)$ versus time. For all the alcohols, the oxidation rates increased with $[\text{M(II)}]$ (Table-4).

Catalytic efficiencies of metal ions are inversely related to the stability of their complexes, which are short-lived intermediates formed during the reaction. Previous studies [16,17]

TABLE-4
CATALYTIC EFFECT OF TRANSITION METAL IONS ON THE OXIDATION OF ALIPHATIC ALCOHOLS
[Alc.] = 0.1 M, $[\text{KIO}_3] = 2.5 \times 10^{-3} \text{ M}$, Temperature = 303 K

$[\text{M(II)}] \times 10^4$ (mol dm^{-3})	$k \times 10^4$ (s^{-1})					
	Cu(II)	Zn(II)	Mn(II)	Co(II)	Ni(II)	Cd(II)
1-Propanol						
0.0	4.25	4.25	4.25	4.25	4.25	4.25
2.5	4.34	6.59	7.21	6.45	6.37	9.21
3.0	4.84	7.30	8.06	7.21	7.34	11.97
3.5	5.42	8.04	8.22	8.06	7.06	12.66
4.0	5.62	9.27	9.68	8.41	7.49	13.27
4.5	6.78	9.99	11.12	8.87	8.26	14.87
5.0	7.92	11.02	12.20	10.05	8.69	15.03
1-Butanol						
0.0	4.04	4.04	4.04	4.04	4.04	4.04
2.5	5.11	5.04	6.49	5.58	5.06	4.96
3.0	6.37	7.36	7.00	6.33	5.65	5.23
3.5	8.77	7.57	7.36	9.48	5.96	5.62
4.0	9.11	7.53	8.34	11.23	6.52	5.98
4.5	9.99	8.06	9.28	14.52	7.52	6.23
5.0	11.26	9.11	10.61	17.18	8.23	6.78

Isopropyl alcohol						
0.0	3.3	3.3	3.3	3.3	3.3	3.3
2.5	4.19	4.48	6.24	4.52	4.48	5.53
3.0	4.95	5.48	6.57	5.09	5.48	7.98
3.5	5.09	5.53	7.32	5.62	5.53	8.68
4.0	5.62	6.62	7.44	6.13	5.62	11.05
4.5	5.86	7.12	7.94	6.57	6.12	12.66
5.0	6.13	8.06	8.62	7.82	7.06	14.27
Isobutyl alcohol						
0.0	2.87	2.87	2.87	2.87	2.87	2.87
2.5	3.35	4.39	4.13	4.41	3.97	4.15
3.0	4.16	5.57	5.36	4.66	4.44	4.38
3.5	4.33	6.36	6.57	5.97	4.82	4.38
4.0	5.33	6.40	7.04	6.12	4.94	7.14
4.5	5.95	6.40	7.32	6.78	5.41	10.59
5.0	6.15	7.02	7.63	6.98	5.89	12.20
1-Hexanol						
0	2.69	2.69	2.69	2.69	2.69	2.69
2.5	3.59	3.50	3.65	4.14	2.69	3.58
3.0	5.21	3.86	4.57	5.37	2.99	3.60
3.5	7.52	4.25	7.67	7.67	3.12	3.68
4.0	8.52	5.21	8.13	9.13	3.30	3.86
4.5	9.29	7.13	8.82	10.59	3.46	3.97
5.0	10.98	8.29	10.66	12.20	3.59	4.52

have shown that order of stability of the metal ion complexes used in this study is $\text{Cu(II)} > \text{Zn(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Mn(II)} > \text{Cd(II)}$. Hence, the expected sequence of their catalytic efficiency is $\text{Cd(II)} > \text{Mn(II)} > \text{Co(II)} > \text{Ni(II)} > \text{Zn(II)} > \text{Cu(II)}$. Because generalizations of complex stability and catalytic efficiency can only enable an estimation the of behavior metal ions, discrepancies have been observed and reported in the literature [18,19].

In present study, various discrepancies have been observed as shown below:

(i) In 1-propanol: the rate of oxidation is follows: Cd(II) > Mn(II) > Zn(II) > Co(II) > Cu(II) > Ni(II) (Table-4).

(ii) In 1-butanol: Cd(II) > Ni(II) > Zn(II) > Cu(II) > Mn(II) > Co(II) (Table-4)

(iii) In isopropyl alcohol: Cd(II) > Mn(II) > Zn(II) > Co(II) > Ni(II) > Cu(II) (Table-4)

(iv) In isobutyl alcohol: Cd(II) > Mn(II) > Zn(II) > Co(II) > Cu(II) > Ni(II) (Table-4)

(v) In 1-hexanol: Cd(II) > Ni(II) > Zn(II) > Cu(II) > Co(II) > Mn(II) (Table-4).

Thus, Cd(II) ions appear to be the most effective catalyst for the oxidation of the aliphatic alcohols under study.

Conclusions

- The oxidation rates of aliphatic alcohols by KIO₃ in acidic medium follow the sequence: 1-propanol > 1-butanol > isopropyl alcohol > isobutyl alcohol > 1-hexanol.

- The oxidation of aliphatic alcohols is independent of ionic strength and accompanied by decrease in entropy of activation ΔS^* .

- Transition metal ions serve as effective catalysts for the oxidation of aliphatic alcohols with Cd(II) ions being the most effective.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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