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Oxidation of Aliphatic Alcohols by Potassium Iodate: A Kinetic Approach

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ABSTRACT

The present study investigates the oxidation kinetics, mechanistic pathway, and thermodynamic behaviour of four alcohols—n-butanol, octanol, isopropyl alcohol, and 2-chloroethanol—oxidized by potassium iodate (KIO_3) in an acidic medium. Reaction progress was monitored via iodometric titration, and kinetic analysis revealed a first-order dependence on alcohol concentration and an inverse dependence on [KIO_3] for all substrates. The proposed mechanism involves the formation of reactive iodine species such as halic acid (HIO_3) and hypoiodite ion (IO^-). The rate of oxidation was found to be influenced by alcohol structure, particularly the presence of electron-withdrawing groups, chain length, and branching. Among the alcohols studied, 2-chloroethanol exhibited the highest oxidation rate, attributed to inductive activation by the chlorine substituent. n-Butanol followed due to its unbranched primary structure, while isopropyl alcohol showed moderate reactivity as a secondary alcohol. Octanol demonstrated the lowest rate, likely due to steric hindrance and reduced solubility in the aqueous medium. Activation energies (Ea) and related thermodynamic parameters were determined using the Arrhenius equation, supporting the structure–reactivity trends observed. The overall oxidation rate sequence was:

2-chloroethanol > n-butanol > isopropyl alcohol > octanol.

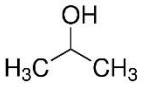
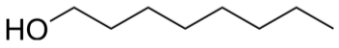
These findings highlight the role of molecular structure in modulating oxidation rates, offering practical insights for designing greener oxidation systems for industrial alcohols.

Keywords: *iodate, Alcohol oxidation, Kinetics, Thermodynamics, Reaction mechanism, 2-Chloroethanol, Aliphatic alcohols*

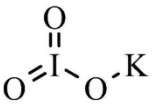
1. INTRODUCTION

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 [6-9]. 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 [10]. 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. length and other structural features of the aliphatic alcohols determined the sequence of oxidation rates.

An idea about alcohols used in this research:

Alcohol	Molecular formula	Molar mass	Structural formula
n-butanol	$C_4H_{10}O$	74.12	
2-chloroethanol	C_2H_5OCl	80.52	
Isopropyl alcohol	C_3H_8O	60.10	
octanol	$C_8H_{18}O$	130.2	

Oxidizing agent:

Name	Molecular formula	Molar mass	Structural formula
Potassium iodate	KIO_3	214.00	

2. MATERIALS AND METHODS

Under conditions governed by first-order kinetics concerning the inorganic oxidant, we conducted a thorough investigation into the oxidation of alcohol. At regular intervals, aliquots of the reaction mixture were withdrawn and promptly quenched with ice. Subsequently, the remaining unreacted oxidant was quantified via iodometric analysis [9].

To determine the first-order rate constants, we employed a graphical approach, constructing straight line plots of log (unreacted oxidant) against time. The oxidation was carried out in the temperature range 303-318 K and the energy of activation and other thermodynamic activation parameters were determined 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 Na_2SO_4 in the range μ = 5 to 25 × 10-2 mol dm-3 in accordance with Bronsted-Bjerrum equation, log k = log ko + 1.02 ZAZB $\mu^{1/2}$.

A large volume containing an excess of alcohol relative to the oxidant was allowed to react with 2, 4-dinitrophenylhydrazine. The formation of a yellow-orange precipitate ensued, which was then filtered, washed, dried, and weighed. The confirmation of the carbonyl compound (whether aldehyde or ketone) was performed by determining its melting point [10].

3. RESULTS AND DISCUSSION

1. Effect of KIO_3 Oxidizing agent

Aliphatic alcohols underwent oxidation [6, 7], resulting in corresponding aldehyde and ketone. Alcohol content enhanced the rate of oxidation, although oxidant concentration lowered it.

Table-1: Rate constant data for the oxidation of alcohols by KIO_4 in 0.2 M H_2SO_4 at temperature 303K

[alcohol] dm^{-3}	mol[KIO_3] mol dm^{-3}	k × 10^3 s^{-1}			
		n-butanol	2-chloroethanol	Isopropyl alcohol	octanol
1.0	2.5	3.95	6.26	2.55	1.35
1.0	5.0	3.21	4.94	1.85	0.65
1.0	10	2.91	4.67	1.68	0.45
1.0	15	2.52	4.34	1.52	0.34
1.0	20	2.48	3.80	1.40	0.26
1.0	25	2.38	3.76	1.15	0.05
0.25	5.0	2.34	3.86	1.32	0.20
0.5	5.0	2.54	4.67	1.56	0.24
0.63	5.0	3.21	5.94	1.75	0.35
0.75	5.0	4.42	6.26	1.88	0.58
0.88	5.0	4.78	6.84	2.45	1.25
1.0	5.0	5.08	7.08	2.73	1.40

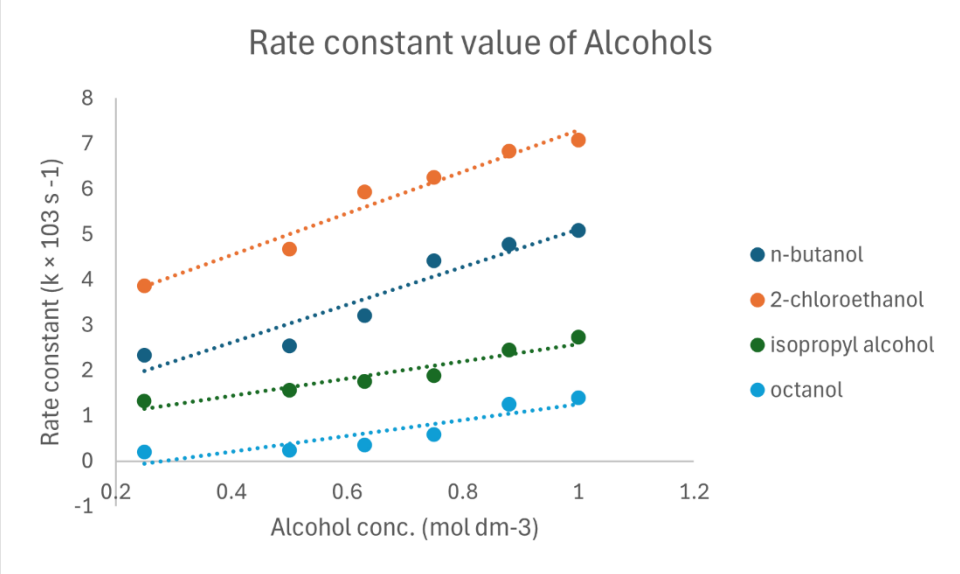


Fig.1 Rate constant data for aliphatic alcohols at various concentrations of alcohols

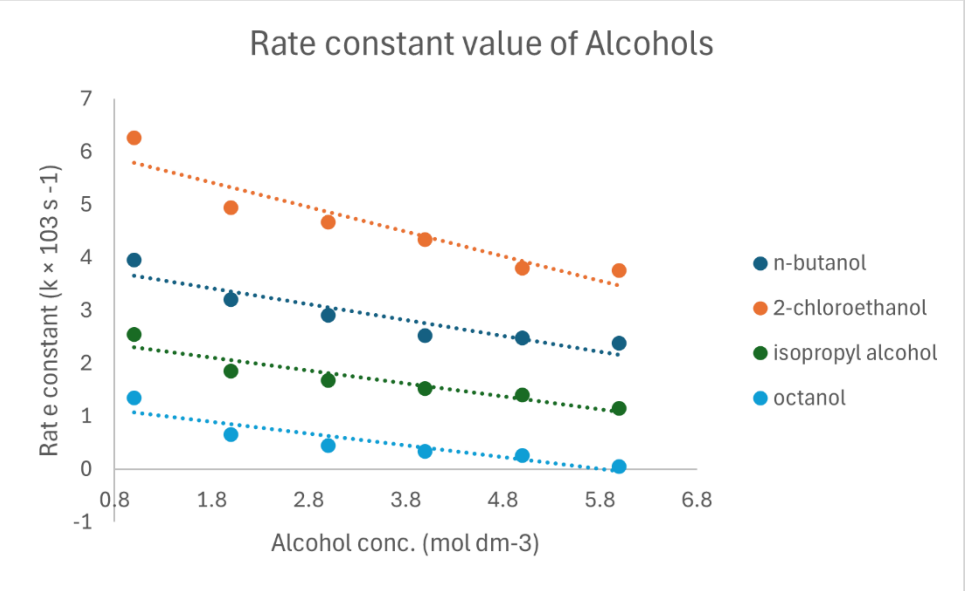


Fig.2 Rate constant data for aliphatic alcohols at various concentrations of KIO_3

Series of alcohol oxidation rates:

Aliphatic alcohols : 2-chloroethanol > n-butanol> isopropyl alcohol> octanol

2. Influence of ionic strength

The use of Na_2SO_4 was aimed to examine the impact of altering ionic strength within the range of $\mu = 5$ to 25 x 10^{-2} mol dm^{-3} at 313K on the oxidation rate[7,8]. The resulting graphs, depicting log k against $\sqrt{\mu}$, displayed linear trends running parallel to the $\sqrt{\mu}$ axis. These outcomes imply that fluctuations in ionic strength do not influence the oxidation rate. The Bronsted-Bjerrum equation was employed to ascertain the impact of ionic strength (μ) on the oxidation rate.

$\log k = \log k_0 + 1.02\ Z_A\ Z_B \sqrt{\mu}$

Table 2- Effect of ionic strength using Na_2SO_4

$\mu \times 10^2$ mol dm^{-3}	$k \times 10^3$ s^{-1}			
	n-butanol	2-chloroethanol	Isopropyl alcohol	octanol
5	3.18	5.69	2.06	1.07
10	3.18	5.65	1.92	1.06
15	3.16	5.66	1.96	1.07
20	3.18	5.61	1.88	1.07
25	3.14	5.65	1.92	1.07

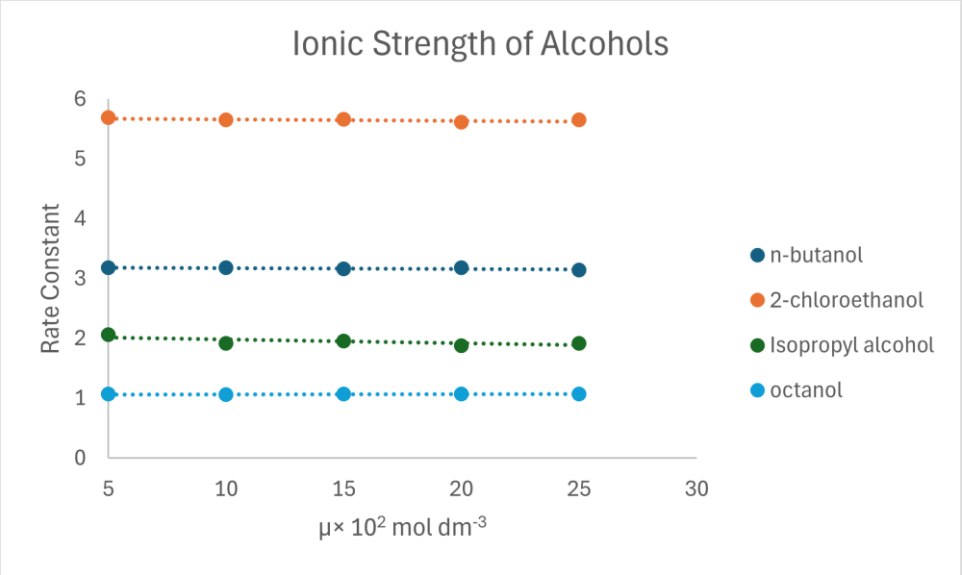


Fig.3 Effect of ionic strength on the oxidation rates of alcohols by KIO_3 in 0.2M H_2SO_4.[alc]=0.2 mol dm-3, [KIO_3] = 2.5 x 10-^{2} mol dm-^{3,} Temperature = 313K

Outcome of temperature effect

The oxidation process was investigated within the temperature range of 303-318K, and an assessment of the thermodynamic activation parameters was conducted. Across all the alcohols examined, the rate constants (k) exhibited an upward trend with increasing temperature, demonstrating an inverse relationship with the energy of activation (E).

Table 3- Effect of temperature

Alcohols	E_{act} kJmol^{-1}	ΔH* kJmol^{-1}	ΔG* kJmol^{-1}	ΔS* K^{-1} kJmol^{-1}
2-chloroethanol	10.1	7.800	-84.50	-0.256
n-butanol	13.9	11.40	-81.20	-0.228
Isopropyl alcohol	12.8	10.50	-83.10	-0.233
Octanol	16.5	13.60	-78.50	-0.2080

The observation of negative activation entropy (ΔS*) values indicates a decrease in the system's degrees of freedom, typically resulting from the formation of a highly ordered and rigid transition state. This structural rigidity necessitates the reorganization of surrounding solvent molecules, particularly water, thereby restricting the translational and rotational motions of the reactants and leading to an overall entropy reduction. For the alcohols examined, the activation entropy remained invariant with temperature, suggesting that the oxidation consistently occurs at a specific reactive site, independent of thermal conditions.

4. CONCLUSION

The oxidation of alcohols by potassium iodate (KIO_3) in an acidic medium demonstrates a clear dependence on the molecular structure of the alcohol substrate. The observed kinetics—first-order with respect to alcohol concentration and inverse with respect to KIO_3—along with mechanistic insights involving reactive iodine species, underline the role of electronic and steric factors in modulating reactivity. Among the four alcohols studied, 2-chloroethanol exhibited the highest oxidation rate due to the inductive effect of the chlorine atom, followed by n-butanol and isopropyl alcohol. Octanol showed the lowest reactivity, attributed to steric hindrance and reduced solubility. The determined activation energies and thermodynamic parameters align with these structure–reactivity trends. Overall, the findings highlight how variations in chain length,

branching, and substituent effects can be strategically leveraged to design more efficient and selective oxidation processes for alcohols, particularly in environmentally benign systems.

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