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## Kinetics and mechanism of oxidation of primary alcohols by acidic solution of quinolinium fluorochromate in the presence of Ru(III) as homogeneous catalyst

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### ABSTRACT

The mechanistic study of ruthenium(III)-catalyzed oxidation of n-hexanol and n-heptanol (primary alcohols) has been studied by quinolinium fluorochromate (QFC) in aqueous perchloric acid medium at 308 K. The reaction followed zero order kinetics with respect to [primary alcohols]. First-order kinetics with respect to [QFC] and [Ru(III)] were observed for the oxidation of primary alcohols. The variation of [H<sup>+</sup>], [Cl<sup>-</sup>] and ionic strength of the medium had no significant effect on the rate of the reaction. The values of rate constants observed at four different temperatures were utilized to calculate the activation parameters. The reaction between QFC and primary alcohols, in acidic medium, exhibits 1:1 stoichiometry. A plausible mechanism conforming to the kinetic results has been proposed.

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### KEYWORDS

Mechanistic;  
Oxidation;  
Ru(III) catalyst;  
Acidic quinolinium  
fluorochromate;  
Primary alcohols.

### INTRODUCTION

n-Hexanol is an organic alcohol with a six carbon chain and a condensed structural formula of CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>OH. This colorless liquid is slightly soluble in water, but miscible with ether and ethanol. Many isomeric alcohols have the formula C<sub>6</sub>H<sub>13</sub>OH. n-Hexanol is believed to be a component of the odour of freshly mowed grass. It is used in the perfume industry. Heptanol is commonly used in cardiac electrophysiology experiments to block gap junctions and increase axial resistance between myocytes. Increasing axial resistance will decrease conduction velocity and increase the heart's susceptibility to reentrant excitation and sustained arrhythmias. n-Heptanol has a pleasant smell and is used

in cosmetics for its fragrance. Halochromates have been used as mild and selective oxidizing reagent in synthetic organic chemistry. A variety of compounds containing chromium(VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group. The kinetics and mechanism of oxidation of Cr(VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with diverse substrates. The development of chromium(VI) reagents for the oxidation of organic substrates continues to be of interest.

A number of new chromium containing compounds like pyridinium bromochromate<sup>[1]</sup>, quinolinium chlorochromate<sup>[2]</sup>, 2,2'-bipyridinium chlorochromate<sup>[3]</sup>, pyridinium fluorochromate<sup>[4]</sup>, Isoquinolinium

Bromochromate<sup>[5]</sup>, quinolinium bromochromate<sup>[6]</sup>, quinolinium dichromate<sup>[7]</sup>, pyridinium fluorochromate<sup>[8]</sup>, imadazolium fluorochromate<sup>[9]</sup> have been used to study the kinetics and mechanism of oxidation of various organic compounds. However, most of the reagents developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, hygroscopicity, low selectivity, long reaction time and need for large excess of reagent. To overcome these disadvantages, we have synthesized quinolinium fluorochromate, as a mild, efficient and stable reagent which is able to work as both an oxidizing agent and a fluorinating reagent.

## EXPERIMENTAL

### Reagents

All the chemicals and reagents were of analytical grade. All the solutions used in the study were made by using doubly distilled water.

Quinolinium fluorochromate was prepared by the following method: Chromium(VI) oxide (15g., 0.15 mole) was dissolved in water (25ml) in a polythene beaker and 40% hydrofluoric acid (11.3ml, 0.23 mole) added to it with stirring at room temp. Within 5 min, a clear solution resulted in. To this solution, quinoline (17.7ml, 0.15 moles) was added slowly with stirring. The mixture was heated on a steam-bath for half an hour, and then cooled at room temp. and allowed to stand for 1 hr. The bright red-orange crystalline quinolinium fluorochromate was isolated by filtration and dried in vacuo for 1 hr, m.p. 162-163°C.

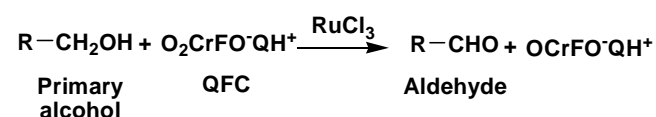
### Kinetics measurements

A thermo-stated water bath was used to maintain the desired temperature within  $\pm 0.1^\circ\text{C}$ . The appropriate strength of the QFC,  $\text{HClO}_4$ ,  $\text{KCl}$ ,  $\text{Ru(III)}$  chloride and water were taken in a reaction vessel which was kept in a thermostatic water bath. After allowing sufficient time to attain the temperature of the experiment, requisite volume of primary alcohols solution, also thermo-stated at the same temperature was rapidly pipette out and poured into the reaction vessel. The total volume of the reaction mixture was 100 ml in each case. 5ml aliquots of reaction mixture was pipette out at different intervals of time and quenched with 4% acidified

potassium iodide solution. The progress of the reaction was monitored by iodometric estimation of QFC by titration against a standard solution of sodium thiosulphate using starch as an indicator to determine unconsumed QFC at regular time intervals. Each kinetic run was studied for 75% reaction. The initial rate of reaction ( $-dc/dt$ ) was determined by the slope of the tangent drawn at a fixed [QFC] in each kinetic run. The order of reaction in each reactant was calculated with the help of plot of ( $-dc/dt$ ) versus concentration of the reactants.

### Stoichiometry and product analysis

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of QFC largely in excess over n-hexanol and n-heptanol (primary alcohols). The estimation of unreacted QFC showed that 1 mol of primary alcohols reacts with mol of QFC.



Where R =  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$  for n-hexanol

=  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$  for n-heptanol

The oxidation products are hexanal and heptanal for n-hexanol and n-heptanol respectively.

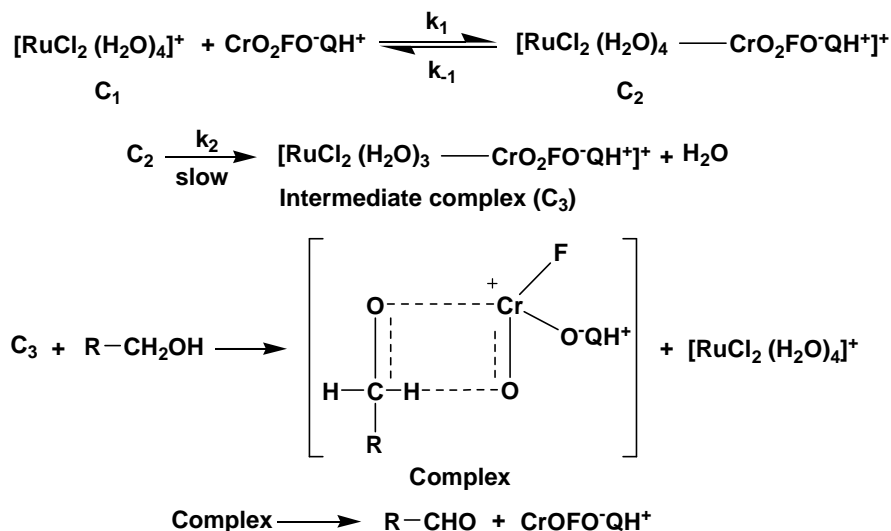
Product analysis was carried out under kinetic conditions i.e. with an excess of the reductant over QFC. In this experiment, the primary alcohols (0.2 mol) and QFC (6.18g, 0.02 mol) were dissolved in 100 ml of acetone and allowed to stand for 24 h to ensure completion of the reaction. The solution was then treated with an excess of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 M HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitrophenylhydrazine (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yields of DNP before and after recrystallization were 2.52 g (88%) and 2.26 g (79%) respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of hexanal and heptanal in the oxidation of n-hexanol and n-heptanol respectively.

## RESULTS AND DISCUSSION

### Effect of catalyst

The kinetics recorded at various  $[\text{Ru}^{\text{III}}]$ , ionic

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Where R = -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> (n-hexanol) and  
 = -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> (n-heptanol)

## Scheme

strengths of the medium along with kinetics effects of potassium chloride and substrate are given in TABLE 2. First order dependence on [Ru<sup>III</sup>] is evident from close resemblance between the slope values ( $2.04 \times 10^{-1} \text{ s}^{-1}$  &  $4.25 \times 10^{-1} \text{ s}^{-1}$  (for n-hexanol) and  $3.14 \times 10^{-1} \text{ s}^{-1}$  &  $5.20 \times 10^{-1} \text{ s}^{-1}$  (for n-heptanol) at 35°C & 45°C respectively) of (-dc/dt) vs. [Ru(III)] plot (Figure 2) and average  $k_1$  values ( $2.20 \times 10^{-1} \text{ s}^{-1}$  &  $4.30 \times 10^{-1} \text{ s}^{-1}$  (for n-hexanol) and  $3.05 \times 10^{-1} \text{ s}^{-1}$  &  $5.26 \times 10^{-1} \text{ s}^{-1}$  (for n-heptanol) at 35°C & 45°C respectively).

Ruthenium(III) chloride has been reported to give a number of possible chloro species dependent pH of the solution. Under the experimental range in the present investigation,  $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$  has been proposed and confirmed<sup>[10]</sup> as reactive species dominant in the pH range 1.00-3.00. The dissociation or association possibility of chloride ions seems to be remote due to insignificant effect of chloride ions.

## Effect of variation of substrate concentration

At constant concentrations of QFC and HClO<sub>4</sub>, the increase in amount of substrate did not affect the rate of reaction (TABLE 1).

## Effect of variation of QFC concentration

At constant concentrations of substrate and HClO<sub>4</sub>, the increase in concentration of QFC enhances the re-

action rate (TABLE 1). Plots of log (-dc/dt) against log[QFC] gave a straight line with slope nearly 1 confirming thus first order with respect to n-hexanol and n-heptanol (Figure 1).

Effect of variation of H<sup>+</sup> and Cl<sup>-</sup> concentration

Variation of concentration of hydrogen ions and chloride ion did not influence the value of (-dc/dt) appreciably, showing thus zero order kinetics in both H<sup>+</sup> ions and Cl<sup>-</sup> ions (TABLE 1).

## Effect of ionic strength

NaClO<sub>4</sub> was used for the study of ionic strength of the medium. Variation of ionic strength of the medium did not bring about any significant change on the rate of reaction under the constant experimental conditions (TABLE 1). According to the rate determining step in reaction scheme that involves ion-dipole interaction, negligible effect of variation of ionic strength of the medium on the rate of oxidation of Primary alcohols is well explained.

## Effect of solvent composition

The oxidation of primary alcohols was studied in 10 different organic solvents. The choice of solvents was limited due to solubility of QFC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics was simi-

TABLE 1 : Effect of variation of reactants on the reaction rates n-hexanol and n-heptanol at 35°C. Conditions: [QFC] = 1.00 × 10<sup>-3</sup>M

[Ru(III)] × 10 <sup>6</sup> M	[Substrate] × 10 <sup>2</sup> M	[KCl] × 10 <sup>3</sup> M	[HClO <sub>4</sub> ] × 10 <sup>3</sup> M	[NaClO <sub>4</sub> ] × 10 <sup>3</sup> M	(-dc/dt) × 10 <sup>7</sup> ML <sup>-1</sup> s <sup>-1</sup> n-hex n-hept
2.40	2.00	1.00	0.20	-	1.64 0.94
4.80	2.00	1.00	0.20	-	3.24 1.85
7.20	2.00	1.00	0.20	-	4.90 2.80
9.60	2.00	1.00	0.20	-	6.54 3.75
12.00	2.00	1.00	0.20	-	8.16 4.70
14.40	2.00	1.00	0.20	-	11.95 5.65
1.00	0.33	1.00	0.20	-	3.00 2.30
1.00	0.40	1.00	0.20	-	3.28 2.85
1.00	0.50	1.00	0.20	-	3.25 2.60
1.00	0.66	1.00	0.20	-	3.20 2.58
1.00	1.00	1.00	0.20	-	3.20 2.65
1.00	2.00	1.00	0.20	-	3.24 2.80
1.00	2.00	0.83	0.20	-	2.62 2.70
1.00	2.00	1.00	0.20	-	3.24 2.80
1.00	2.00	1.25	0.20	-	2.70 2.54
1.00	2.00	1.67	0.20	-	2.00 2.84
1.00	2.00	2.50	0.20	-	3.76 2.79
1.00	2.00	5.00	0.20	-	2.40 2.68
1.00	2.00	1.00	0.04	-	2.72 2.82
1.00	2.00	1.00	0.08	-	3.20 2.80
1.00	2.00	1.00	0.12	-	3.55 2.64
1.00	2.00	1.00	0.16	-	3.00 2.84
1.00	2.00	1.00	0.20	-	3.20 2.80
1.00	2.00	1.00	0.24	-	3.36 2.76
1.00	2.00	1.00	0.20	0.83	3.35 2.85
1.00	2.00	1.00	0.20	1.00	3.20 2.80
1.00	2.00	1.00	0.20	1.25	2.62 2.92
1.00	2.00	1.00	0.20	1.67	3.49 2.75
1.00	2.00	1.00	0.20	2.50	3.20 2.88
1.00	2.00	1.00	0.20	5.00	3.56 2.74

lar in all the solvents. The values of  $k_1$  at 35°C are recorded in TABLE 2.

### Effect of temperature

The reaction was studied at different temperatures (303-323 K) (TABLE 3). From the linear Arrhenius plot of  $\log k$  versus  $1/T$ , the activation energy ( $E_a$ ) was calculated (Figure 3). With the help of the energy of activation, values of the other activation parameters such as enthalpy of activation ( $H^*$ ), entropy of activation ( $S^*$ ), Gibbs free energy of activation ( $G^*$ ) and Arrhenius factor ( $A$ ), were calculated and these values are given in TABLE 3.

Entropy of activation plays an important role in the case of reaction between ions or between an ion and a neutral molecule or a neutral molecule forming ions. When reaction takes place between two similarly charged species, the transition state will be a more highly charged ion, and due to this, more solvent molecules will be required than for the separate ions, leading to a decrease in entropy. On the other hand, when reaction takes place between two ions of opposite charges, their union will result in a lowering of the net charge and due to this some frozen solvent molecules will be released with an increase of entropy. On the basis of this information, observed negative entropy

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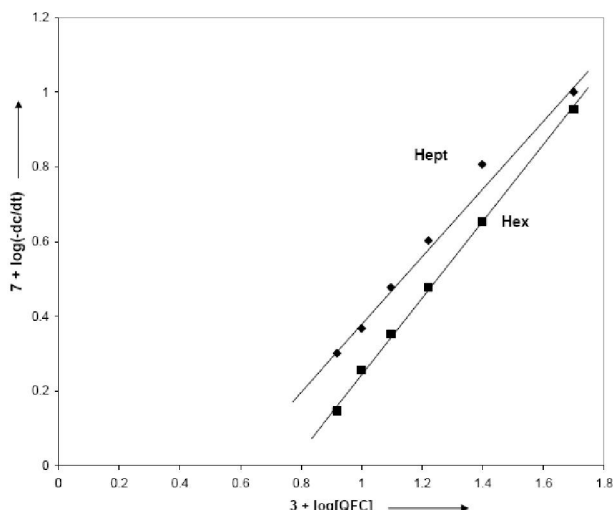


Figure 1 : Plot between  $\log[\text{QFC}]$  and  $\log(-dc/dt)$  for oxidation of hexanol (Hex) and heptanol (Hept) at  $35^\circ\text{C}$

TABLE 2 : Effect of solvents on the oxidation of primary alcohols by QFC, Conditions:  $[\text{Ru(III)}] = 4.80 \times 10^{-6} \text{ M}$ ,  $[\text{QFC}] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{Substrate}] = 2.00 \times 10^{-2} \text{ M}$ ,  $[\text{KCl}] = 1.00 \times 10^{-3} \text{ M}$ ,  $[\text{HClO}_4] = 1.00 \times 10^{-3} \text{ M}$

Solvents	$10^4 k_1 \text{ s}^{-1}$	
	n-hex	n-hept
Acetone	3.24	2.80
Butanone	2.75	2.85
Benzene	3.50	2.95
Ethyl acetate	2.95	2.84
Nitrobenzene	3.58	3.02
Acetic acid	1.74	2.50
t-butyl alco.	3.38	3.90
Acetophenone	5.91	2.78
Choloroform	3.61	6.05
Toluene	3.50	2.70

of activation supports the rate limiting step of the proposed reaction scheme. The proposed mechanism is also supported by moderate value of energy of activation and other activation parameters. The high positive values of  $\Delta H^*$  and  $\Delta G^*$  indicate that the transition state is highly solvated.

From the above statements lead us to suggest the following reaction scheme which gives the details of various steps in the title reaction.

The oxidation product of n-hexanol and n-heptanol are  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHO}$  (hexanaldehyde) and  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHO}$  (heptanaldehyde) respectively.

On applying steady state approximation and con-

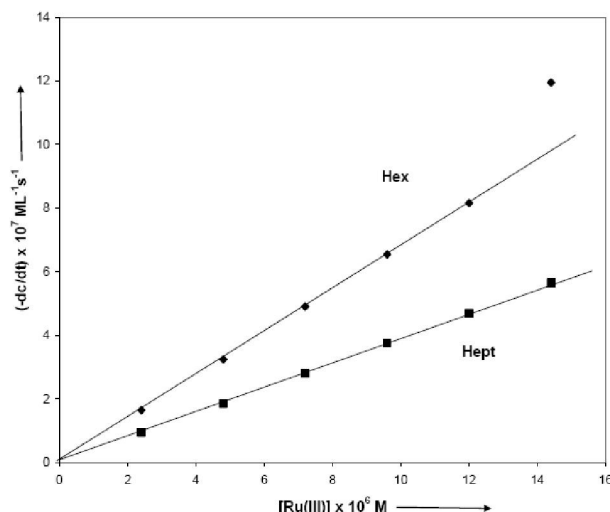


Figure 2 : Plot between  $(-dc/dt)$  and  $[\text{Ru(III)}]$  for oxidation of hexanol (Hex) and heptanol (Hept) at  $35^\circ\text{C}$

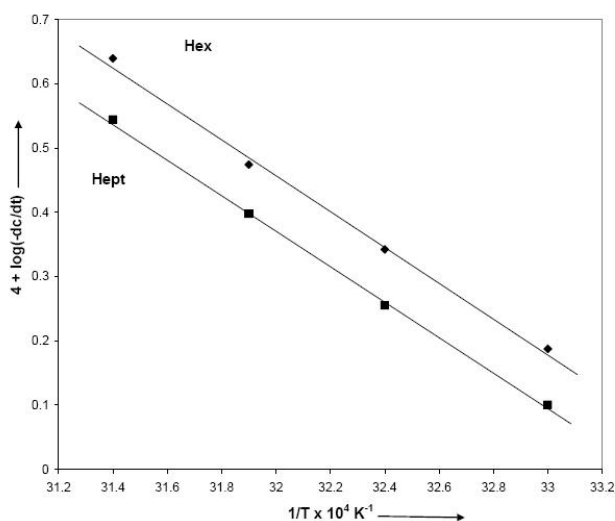


Figure 3 : Plot between  $\log(-dc/dt)$  and  $1/T$  for oxidation of hexanol (Hex) and heptanol (Hept) at  $35^\circ\text{C}$

sidering steps (i) and (ii), the rate law may be derived as:

$$\frac{-d[\text{QFC}]}{dt} = k_2[\text{C}_2] \quad (1)$$

Total concentration of Ru(III) i.e.  $[\text{Ru(III)}]_T$  may be written as equation (2)

$$[\text{Ru(III)}]_T = [\text{C}_1] + [\text{C}_2] \quad (2)$$

$$\text{Rate} = \frac{K_1 [\text{QFC}][\text{Ru(III)}]_T}{1 + K_1 [\text{QFC}]} \quad (3)$$

When the complex is unstable  $K_1$  is small or  $1 \gg K_1 [\text{QFC}]$ , then we have

$$\frac{-d[\text{QFC}]}{dt} = K_1 [\text{QFC}][\text{Ru(III)}]_T \quad (4)$$

The rate law accords well to the kinetic results.

**TABLE 3 : Rate constants and activation parameters of oxidation of primary alcohols by QFC. Conditions: [Ru(III)] =  $4.80 \times 10^{-6}$  M, [QFC] =  $1.00 \times 10^{-3}$  M, [Substrate] =  $2.00 \times 10^{-2}$  M, [KCl] =  $1.00 \times 10^{-3}$  M, [HClO<sub>4</sub>] =  $1.00 \times 10^{-3}$  M**

Substrate	$10^4 k_r (s^{-1})$ at (°C)				$\Delta E^* (kJ mol^{-1})$	$\Delta G^* (kJ mol^{-1})$	$\Delta H^* (kJ mol^{-1})$	$\Delta S^* (kJ mol^{-1})$	log A
	30	35	40	45					
n-hex	2.27	3.24	4.56	6.50	52.60	76.30	53.34	-15.75	10.35
n-hept	1.94	2.80	3.86	5.58	53.05	74.04	69.04	-16.23	9.44

## CONCLUSION

The Ru(III) catalyzed oxidation of primary alcohols by QFC was studied in the acidic medium at 35°C. The oxidation of primary alcohols by QFC in perchloric acid become facile in the presence of micro-quantity of Ru(III) ( $10^{-9}$  M). Among the various species of Ru(III) in acidic medium,  $[RuCl_2(H_2O)_4]^+$  is considered as the reactive species while QFC is considered as the reactive species of oxidant. Oxidation products have been identified and activation parameters were evaluated for the catalyzed reaction. A plausible reaction mechanism and related rate law has been worked out. In conclusion, it can be said that Ru(III) is a most efficient catalyst in the oxidation of the primary alcohols by QFC in acidic medium.

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