Cyclohexanol towards quinaldinium fluorochromate oxidation

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ABSTRACT

The kinetics of oxidation of cyclohexanol by Quinaldinium Fluorochromate (QnFC) has been studied in aqueous acetic acid medium. Cyclohexanol was converted to the corresponding cyclohexanone. The order of the reactions has been found to be one with respect to oxidant and fractional with respect to the substrate as well as hydrogen ion concentration. Increase in the percentage of acetic acid increases the rate of reaction. The reaction follows Michaelis-Menten type of reaction in a non free radical path way. Thermodynamic parameters has been calculated using Eyring's equation at four different temperatures. A suitable mechanism consistent with the observed kinetics has been proposed.

Keywords: Oxidation. Cyclohexanol , Quinaldinium Fluorochromate, Kinetics.
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INTRODUCTION

Quinaldinium Fluorochromate (QnFC) [1], one of the Cr (VI) compounds is reported to be a neutral and mild oxidant for selective oxidation. Kinetics of oxidation of some organic substrates by Quinaldinium Fluorochromate has already been reported. The kinetics of oxidation of cyclic alcohols with various oxidant shows that the reactivity varies with the type of oxidants [2-11]. The difference in the reactivity has been explained by the I-strain theory. The probable structure of quinaldinium fluorochromate (QnFC) is the following,

Quinaldinium Fluorochromate
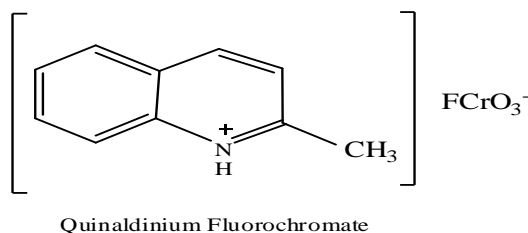
The present study on the oxidation of cyclohexanol by QnFC is to ascertain the nature and the order of reactivity of these compounds under the given kinetic conditions.

EXPERIMENTAL SECTION

Cyclohexanol
Cyclohexanol (Aldrich) are purified by fractional distillation. This purity was checked from physical constant.

Preparation of Quinaldinium fluorochromate [1]
Chromium trioxide (7 g) was dissolved in 8 ml of water in a polythene beaker and 11 ml of 40% hydrofluoric acid were added with stirring at room temperature. A clear orange red solution was formed, 9 ml of quinaldine were

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added drop-wise with stirring. The mixture was heated on a water bath for about 15 min, then cooled to room temperature, and allowed to stand for 1 h. The bright yellow crystalline quinaldinium fluorochromate was isolated by filtration. It was recrystallized from water and dried in vacuo for about 2 h. The compound melted at (147º C) [lit m.p 146-148º C] and further analysed through spectral data.

Acetic acid
Glacial acetic acid (AR) (2 litre) was partially frozen and about 1 litre of the liquid was removed. The residue was melted and refluxed with chromium trioxide (30 g) for 4 h and fractionally distilled [12]. The distilled portion was collected between 116-118°C, partially frozen and about half of the acid was discarded as liquid. The remaining residue was melted and fractioned again after treating with chromium trioxide (30 g). The boiled fraction was collected 116-118°C and kept in brown bottles.

All other chemicals were used as AR grade. Triply distilled water was used for the preparation of solutions.

Kinetic measurements:
The reactions were followed under pseudo-first order conditions by always maintaining the substrate concentration in excess of quinaldinium fluorochromate. The reactions were carried out at constant temperature ($\pm$0.1 K) and were followed spectrophotometer at 470 nm. The reactions were followed upto 70% completion. The rate constants were evaluated from the linear plot of log (absorbance) against time by the least square method and were reproducible to within $\pm$ 3%.

Stoichiometry and Product analysis:
Reaction mixtures containing an excess of the oxidant over cyclohexanol are kept at room temperature in the presence of perchloric acid for two hours. Estimation of the unreacted oxidant proved that one mole of oxidant consumes one mole of substrate. The same experimental conditions were used for kinetic determinations; a solution of the reaction mixture was kept under nitrogen for 24 h. The solution was extracted with ether, the organic layer washed with water dried over anhydrous sodium sulphate and then concentrated. The product obtained the corresponding cyclohexanone, whose boiling point agreed with those reported in the literature and IR Spectral studies and spot test [13].

RESULTS AND DISCUSSION

Effect of oxidant:
The reaction was found to be first order with respect to the oxidant as evidenced by a good linearity in the plot of log absorbance versus time (r = 0.996) (Table 1). The pseudo first order rate constants were found to be independent of initial concentration of quinaldinium fluorochromate

Effect of substrate:
The order with respect to substrate was found to be fractional as evidenced by the linear plot of log k versus log [substrate] with a positive slope of 0.48. It was further support by the fact that the plot of 1/k versus 1/[s] gives a straight line (Fig 1) with definite intercept indicating the Michaelis -Menten type of kinetics in the reaction (Table 1).

Table 1 Rate data on the oxidation of cyclohexanol by   Quinaldinium Fluomchromate at 313 K

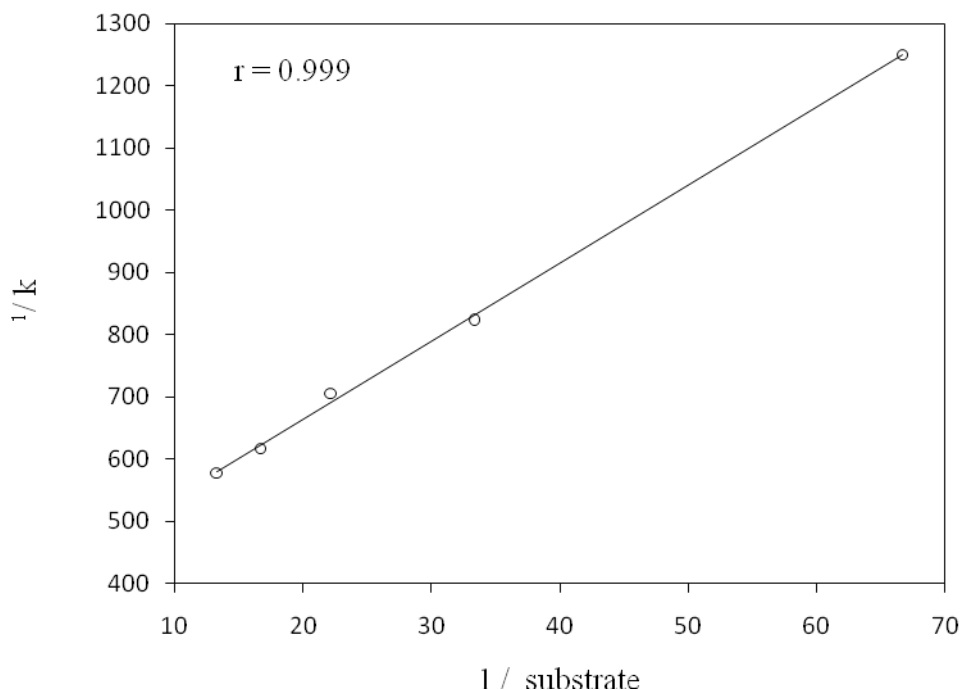| [CHOL] x 10^2 (mol dm^{-3})	[QnFC] x 10^4 (mol dm^{-3})	[H$^+$] x 10^2 (mol dim^{-3})	k_1 x 10^4 s^{-1}
1.5	10.5	3.0	8.00
3.0	10.5	3.0	12.17
4.5	10.5	3.0	14.18
6.0	10.5	3.0	16.20
7.5	10.5	3.0	17.32
3.0	7.0	3.0	12.22
3.0	14.0	3.0	12.26
3.0	17.5	3.0	12.23
3.0	21.0	3.0	12.27
3.0	10.5	1.5	10.11
3.0	10.5	4.5	14.31
3.0	10.5	6.0	14.95
3.0	10.5	7.5	15.95

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Fig 1. Plot of 1/k *versus* **1/substrate**

Effect of Perchloric acid:

At constant concentrations of the reactants and at constant ionic strength, the rate constants increased with increase in the concentration of perchloric acid (Table 1). It shows the participation of perchloric acid in the rate determining step and the order has been found to be 0.29 for the plot of log k versus log [H^+].

Effect of Ionic strength and Dielectric constant of the medium:

Increase in the ionic strength of medium by adding sodium perchlorate has no effect on the reaction rate indicating the involvement of molecule in the rate determining step [14]. The rates were found to increase with increase in the percentage of acetic acid. A plot of   log k versus D^{-1} is linear with a positive slope. This suggests an interaction between a positive ion and neutral molecule [15]. This is also confirms the involvement of protonated Cr (VI) species in the rate determining step (Table 2).

The reaction mixture when allowed to stand with acrylonitrile does not induce polymerization suggesting the absence of a free radical mechanism [16]. On the other hand the addition of Mn^{2+} ion retards the rate of the reaction. It suggest a two electron transfer process in the rate determining step [17] (Table 2)

Table 2 Dependence of rate constant on ionic strength, solvent composition, [MnSO₄] at 313 K

[CHOL] = 3.0×10^{-2} mol dm^{-3} [QnFC] = 10.5×10^{-4} mol dm^{-3} [H^+] = 3.0×10^{-1} mol dm^{-3}

[NaClO₄] x 10^2 (mol dm^{-3})	AcOH: H_2O (% v/v)	[MnSO₄] x 10^2 (mol dm^{-3})	k_1 x 10^4 s^{-1}
0.00	60-40	-	12.17
2.50	60-40	-	12.16
5.00	60-40	-	12.24
7.50	60-40	-	12.34
10.00	60-40	-	12.12
-	50-50	-	10.17
-	55-45	-	11.23
-	65-35	-	18.29
-	70-30	-	31.40
-	60-40	5.01	15.28
-	60-40	10.03	15.32
-	60-40	15.04	15.14
-	60-40	20.06	15.30

Effect of Temperature:
The reactions were studied in the temperature range 303-333 K for cyclohexanol by quinaldinium fluorochromate in aqueous acetic acid medium. An increase in temperature had resulted in an increase in the rate of reaction. The thermodynamic parameters have been calculated using Eyring's equation [18]. The negative values of the entropy of activation ($\Delta S^{\#}$) suggest an extensive solvation of the transition state over the reactants.
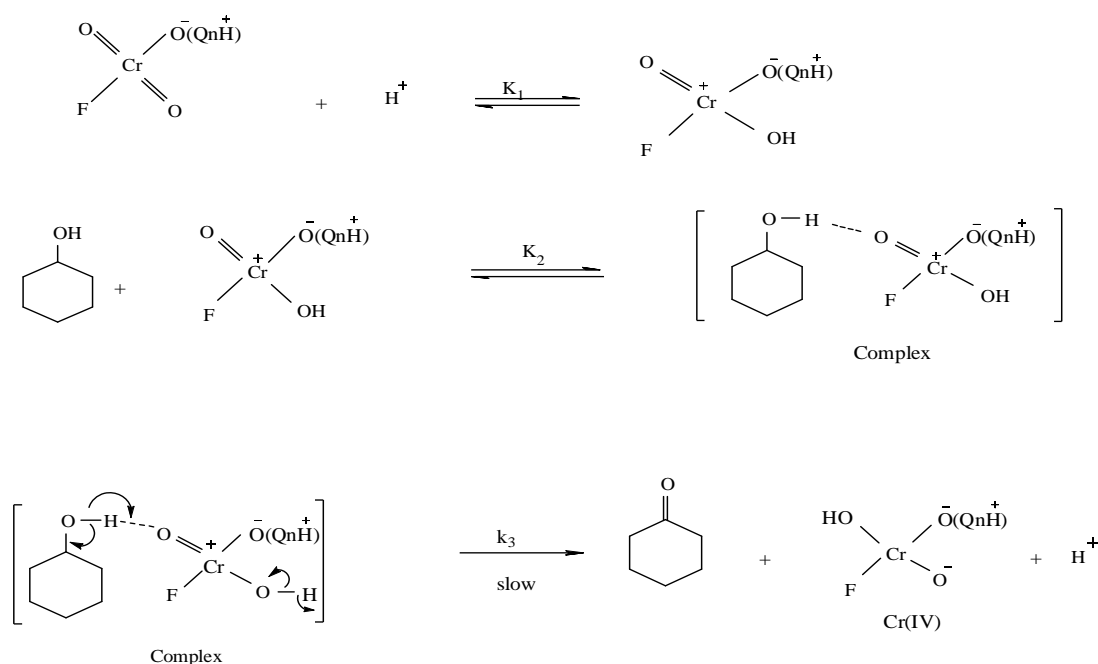
$\Delta H^{\#} = 26.56 \ k \ J \ mol^{-1}$
$\Delta S^{\#} = -186.94 \ J \ K^{-1} mol^{-1}$
$\Delta G^{\#} = 94.26 \ k \ J \ mol^{-1}$ at 313 K.
$Ea = 29.16 \ k \ J \ mol^{-1}$ at 313 K.

Mechanism and Rate Law
Considering all the above experimental facts the following mechanism (scheme 1) has been proposed.

Scheme 1

Complex

Complex

Cr(IV)

Rate Law :-
The above mehanism leads to the following rate law:

rate $= \dfrac{-d \ [QnFC]}{dt} = k_3$ [Complex]

Applying steady state approximation,

$$\text{rate} = \frac{k_3 K_2 K_1 \ [S] \ [O] \ [H^+]}{1 + K_2 \ [S] \ (1 + K_1 [H^+])}$$

Since, $K_1 K_2 \ [S] \ [H^+] \ll 1$:

$$k_{obs} = \frac{k_3 \ K_2 \ K_1 \ [S] \ [H^+]}{1 + K_2 \ [S] + K_1 \ [H^+]}$$

This rate law explains all the observed experimental facts.

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CONCLUSION

The oxidation of cyclohexanol by quinaldinium fluorochromate in aqueous acetic acid medium leads to the formation of complex and finally gives the product. The reaction follows simple order kinetics. The mechanism proposed for this oxidation reaction is in accordance with the observed kinetic facts.

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