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Kinetics and mechanism of oxidation of benzyl alcohol and cyclohexanol by quinolinium fluorochromate

Suresh D. Dhage*[1], S. B. Patwari[2] and Swanand Mukhedkar[3]

[1]Department of Chemistry, SSJES, Arts, Comm. and Science College, Gangakhed, Parbhani (M.S.), India
[2]Department of Chemistry, Lalbahadur Shastri College, Dharmabad, Dist. Nanded. (M.S.) India
[3]Department of Chemistry, Shahir Annabhau Sathe College, Mukhed, Dist. Nanded (M.S.) India

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ABSTRACT

The kinetics of oxidation of cyclic alcohols like Benzyl alcohol and Cyclohexanol by Quinolinium Fluorochromate (QFC) has been studied in acetonitrile-nitrobenzene (1:1,v/v) medium. The reaction is first order with respect to oxidant and the rate is almost independent of the substrate concentration. The reactions are catalysed by an acid. The decrease in dielectric constant, increases the rate of reaction. The effect of temperature and solvent composition were studied and the various activation parameters are evaluated. Based on the experimental results, a probable reaction mechanism was proposed.

Keywords: Kinetics, Oxidation, Benzyl alcohol, Cyclohexanol, Quinolinium fluorochromate

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INTRODUCTION

The selective oxidation of alcohols to the corresponding aldehydes is a frequently used transformation in organic synthesis and hence variety of methods has been developed. Among them Chromium (VI) containing reagents have been extensively studied[1]. The most popular of them, the collins reagent, showed several difficulties. It should be used in large excess and it is unstable and it shows a poor selectivity in oxidation of alcohols to their aldehydes[2].

Quinolinium Flurochromate (QFC) has been used as a mild and selective oxidising agent in synthetic organic chemistry[3]. It oxidises secondary alcohols to corresponding ketones in dimethyl sulphoxide (DMSO)[4,5] and also oxidises atrolactic acid to ketones[6].

It has been reported that, this complex converts alcohols into aldehyde products at room temperature and it is a better oxidant than Pyridinium Chlorochromate, Pyridinium Fluorochromate [7].

In the present work, we report the kinetics of oxidation of Benzyl alcohol and cyclohexanol by Quinolinium Fluorochromate and evaluate the reaction rate constants at different temperature and discuss the probable mechanism.

EXPERIMENTAL SECTION

Materials:
All chemicals used were reagent grade materials from Merck. The solvents were purified and dried by distillation over P_2O_5. Quinolinium Fluorochromate (QFC) was prepared by the procedure described in literature[3] and its purity was checked by the melting point, TLC and iodometric method.

The reaction products Benzaldehyde and Cyclohexanone were characterized by spectral analysis and estimated as their 2,4-dinitrophenyl hydrazones.

Kinetic Measurements (Methods) :
For kinetic measurements, the reactions were performed under psudeo-first order conditions by maintaining a large excess (X 5 or greater) of alcohol over QFC. The reactions were carried out at constant temperature (+ 0.1K) and progress of reaction were followed by iodometric estimation of unreacted chromium (VI). The medium of reaction was always 1:1 (v/v) acetonitrile : nitrobenzene. This medium was chosen as a solvent, because acetonitrile did not react with QFC. The reaction mixture were homogeneous for the total period of kinetic investigation.

The rate constants were determined from the plot of log [oxidant] against time. Dielectric constant for the varying proportions of acetonitrile-nitrobenzene mixture were estimated from the dielectric constants of pure solvents[8] (Table 3). A constant ionic strength could not be maintained owing to the non-aqueous nature of the reaction medium.

The effect of temperatures on reaction rate were studied with varying temperatures of 303, 308, 313 and 318 K respectively for both alcohols. The activation parameters were evaluated by the standard procedure[9] (Table-4).

RESULTS AND DISCUSSION

Stoichimetry and Product analysis :
The stiochiometry of various oxidations studied and well estimated by the reaction of respective alcohol with an excess of oxidant (QFC) followed by estimating the unreacted Cr (VI). In some cases, however, an excess of alcohols were used and followed by the estimation of the carbonyl product. The stoichiometry of the reactions with Benzyl alcohol and cyclohexanol can be represented as follows

$$3RCH_2OH + 2Cr^{(VI)} \longrightarrow 3RCHO + 6H^+ + 2Cr^{(III)} \qquad ......\ (1)$$

$$2C_6H_{11}OH + 2Cr^{(VI)} \longrightarrow 3C_5H_{10}CO + 6H^+ + 2Cr^{III} \qquad ....(2)$$

The oxidation of benzene alcohol and cyclohexanol by QFC in 1:1 (v/v) acetonitrile-nitrobenzene leads to the formation of Benzaldehyde and Cyclohexanone respectively in very high yields showing no indication of further oxidation of carbonyls.

Effect of variation of [QFC] on reaction rate :
Like the analogous pyridinium chlorochromate[10-12], these two alcohols studied were found to be first order with respect to time, because the first order rates were constant at different times. The reactions were also first order with respect to oxidant (QFC) as the rate constants were found to be practically unchanged for most of the reaction times with varying concentration of oxidants as showing table 1.

Effect of variation of [Substrate] on reaction rate :
As the concentration of substrates (alcohols) increases, there is increase in the rate constants as shown in table 2.

The plot of log *k* v/s log [Substrate] shows that the rate of reaction increases with substrate concentration, indicating that, the complex formation takes place between substrate and oxidant.

Table 1 : Oxidant Dependence of the reaction rate :
T = 303 K

[QFC] × 10^{-3} mol dm^{-3}	$k_1 \times 10^4$ sec^{-1}	
	[Benzyl alcohol] 0.01 mol dm^{-3}	[Cyclohexanol] 0.01 mol dm^{-3}
1	7.52	8.34
2	8.06	8.60
3	7.52	8.45
4	7.38	8.68
5	7.32	8.71

Table 2 : Substrate Dependence of the reaction rate :
[QFC] = 0.001 mol dm^{-3};   T = 303 K

[Substrate] mol dm^{-3}	Rate constants $k_1 \times 10^4$ sec^{-1}	
	[Benzyl alcohol]	[Cyclohexanol]
0.01	7.52	8.34
0.02	8.93	12.90
0.03	9.20	14.89
0.04	9.63	16.34
0.05	10.65	18.17

Effect of solvent :

The reaction has been studied under various composition of solvent mixture as shown in table 3. It has been observed that, the reaction rate increases with decreases in dielectric constant of medium suggesting that, the more polar solvents may require larger reaction times for the oxidation reactions.

Table 3 : Dependence of Reaction Rate on Solvent Composition :
[Oxidant] = 0.002 mol dm^{-3}, T = 303 K

Nitrobenzene (%)	Acetonitrile (%)	Dielectric constant	[Benzyl alcohol] 0.02 mol dm^{-3} $k_1 \times 10^4$ sec^{-1}	[Cyclehexanol] 0.02 mol dm^{-3} $k_1 \times 10^4$ sec^{-1}
30	70	36.50	1.75	3.61
40	60	36.20	2.42	5.98
50	50	35.90	3.83	7.62
60	40	35.70	4.90	10.89
70	30	35.40	6.02	13.17

A plot of *log*k against the inverse of dielectric constants of the medium is a straight line with positive slope, which implies the occurrence of an interaction between a dipole and a positive ion [13], and also indicates the probable involvement of a protonated Cr^{VI} species, in presence of acid in the rate determining step.

Effect of temperature and determination of activation parameters :

The reaction rates at different temperatures were determined and the values of activation parameters were calculated as shown in table 4.

The data shows that, the rate of reaction increases with increase in temperature and these reactions were characterized by high negative values of entropy, suggests that the solvent molecules are strongly oriented around the ions, which results in the loss of entropy[14], the effect being larger in non-polar solvents. This confirms that, the decrease of polarity of medium results in increase of the entropy values and the number of unbound molecules in the solution increases[15].

Table 4 : Dependence of rate on temperature and activation parameters for the oxidation of alcohols by QFC :

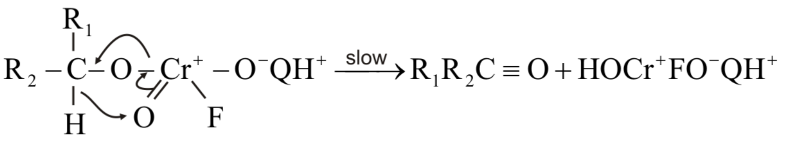
[QFC] = 0.001 mol dm^{-3}, [Substrate] = 0.01 mol dm^{-3}

Substrate	$k \times 10^4$ (sec^{-1})				ΔH* ($KJmol^{-1}$)	ΔS* ($JK^{-1}mol^{-1}$)	ΔG* ($KJmol^{-1}$)
	303 K	308 K	313K	318K			
Benzyl alcohol	7.52	7.60	7.92	8.12	2.99	-282.41	91.17
Cyclohexanol	8.34	8.72	9.12	9.55	5.22	-274.12	90.93

Further, the nearly constant values of free energies of activation suggests that, a similar mechanism is operative in both oxidations. Free energies of the acid catalysed reactions appear to be lower, as there has been pronounced increase in the rate of catalysed raction suggesting that a protonated Cr^{VI} species may be involved in the rate determining step in presence of an acid. This is in accord with the involvement of such species well established in Chromium(VI) Oxide oxidations[16].

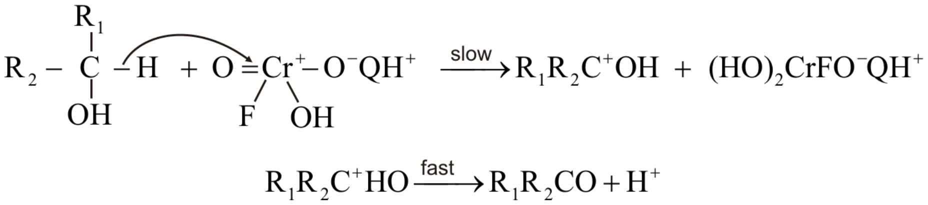
MECHANISM

In the view of the above results, the following reaction mechanism is proposed. The oxidation of alcohols proceeds via hydride-ion transfer involved in the rate determining step. The oxidation of alcohols results in the formation of corresponding carbonyl compounds.



$$R_2-\underset{H}{\overset{R_1}{C}}-O-\underset{O\;\;\;F}{Cr^+}-O^-QH^+ \xrightarrow{slow} R_1R_2C\equiv O+HOCr^+FO^-QH^+$$

(Scheme 1)



$$R_2-\underset{OH}{\overset{R_1}{C}}-H + O=\underset{F\;\;\;OH}{Cr^+}-O^-QH^+ \xrightarrow{slow} R_1R_2C^+OH + (HO)_2CrFO^-QH^+$$

$$R_1R_2C^+HO \xrightarrow{fast} R_1R_2CO+H^+$$

(Scheme 2)

It is possible that the hydride transfer may take place either through the prior formation of chromate (Scheme 1), or directly (Scheme 2). The present data also suggest, like the similar oxidations involving chromic acid[16], a chromate formation in the rate-determining step (Scheme 1).

CONCLUSION

At the end of this research work, we conclude that, in the kinetics of oxidation of Benzyl alcohol and Cyclohexanol by Quinolinium Fluorochromate (QFC), it has been found that the reaction was first order with respect to oxidant and rate is almost independent of substrate concentration. The reactions are catalyzed by an acid. The decrease in dielectric constant increases the rate of reaction significantly. The rate of reaction increases with temperature and the various activation parameters are evaluated. A suitable mechanism is proposed involving the hydride ion transfer in rate determining step.

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