Oxidation of α,β -unsaturated alcohols by Quinaldinium Fluorochromate

Krishnamoorthy Guna Sekar, Seplapatty Kalimuthu Periyasamy

Department of Chemistry, National College, Tiruchirappalli - 620 001, Tamilnadu, India

E-mail address: drkgsekar@yahoo.co.in , nctperiya85@gmail.com

ABSTRACT

The kinetics of oxidation of α,β -unsaturated alcohols (allyl alcohol, Crotyl alcohol, Cinnamyl alcohol) by quinaldinium fluorochromate has been studied in aqueous acid medium at 313 K. α,β -unsaturated alcohols were converted to the corresponding acrolein, crotonaldehyde and cinnamaldehyde. The reaction is first order each in oxidant, substrate and H^+ . The decrease in dielectric constant of the medium increases the rate of the reaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate constant. There is no polymerization with acrylonitrile. The reaction has been conducted at four different temperatures and activation parameters were calculated. From the observed kinetic results a suitable mechanism consistent with rate law has been proposed. The relative reactivity order was found to be Cinnamyl alcohol > Crotyl alcohol > Allyl alcohol.

Keywords:

Oxidation; Kinetics; α,β -unsaturated alcohols; Quinaldinium fluorochromate

1. INTRODUCTION

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds¹. Chromium especially Cr (VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidizable organic functional groups^{2,3}. Numerous reagents and experimental procedures have been developed to carry out this transformation⁴ in particular reagents containing chromium(VI) reactive species are widely used for the oxidation of alcohols to carbonyl compounds^{5,6}. Quinaldinium fluorochromate (QnFC) has been used in oxidation of many organic substrates. Quinaldinium fluorochromate is a mild, efficient and stable oxidizing agent. It is a bright yellow crystalline solid. The probable structure of quinaldinium fluorochromate (QnFC) is the following Scheme 1. Quinaldinium fluorochromate oxidises anthracene into anthraquinone in the presence of dichloromethane. α,β -unsaturated alcohols are used in many ways. Allyl alcohol finds a number of industrial applications in the preparation of resins, plasticisers, pharmaceuticals and many organic compounds. Crotyl alcohol was used in organic compound products, as pharmaceutical raw materials and dope. Cinnamyl alcohol was used in perfumery and as a deodorant. Kinetic studies on the oxidation of allyl alcohol with different oxidants such as Chloramine-T,^{7,8} potassium hexacyanoferrate(II)⁹, pyridinium fluorochromate¹⁰, potassium bromate¹¹, acid bromate¹², quinolinium dichromate¹³, and imidazolium dichromate¹⁴ have been reported.

The present study on the oxidation of α,β -unsaturated alcohols by quinaldinium fluorochromate is to ascertain the nature and the order of reactivity of these compounds under the given kinetic conditions.

2. EXPERIMENTAL METHODS

2. 1. Reagents

All the α,β -unsaturated alcohols such as allyl alcohol, crotyl alcohol and cinnamyl alcohol (Aldrich) were purified by distillation. This purity was checked from physical constants.

2. 2. Preparation of Quinaldinium fluorochromate [QnFC]¹⁵

Chromium trioxide (7 g) was dissolved in 8ml 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 added dropwise with stirring. The mixture was heated on a water bath for about 15 min, then cooled to room temperature, and allowed to stand for 1h. The bright yellow crystalline quinaldinium fluorochromate was isolated by filtration. It was recrystallized from water and dried vacuo for about 2 h. m.pt.146 – 148 °C.

2. 3. 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. 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.

2. 4. Kinetic measurements

The reactions were performed in aqueous acetic acid medium under pseudo-first order conditions by maintaining a large excess of substrate over quinaldinium fluorochromate. The kinetic measurements were carried out spectrophotometrically in a thermostated cell compartment of a spectrophotometer (Perkin Elmer-Lambda 35) at 470 nm. This wavelength of the maximum absorption due to quinaldinium fluorochromate has been observed and absorption due to other reaction species was negligible¹⁶. Oxidation reaction was studied only in the concentration range of quinaldinium fluorochromate where the Beer's law is obeyed. The reactions were followed upto 70% completion. The rate constants were evaluated from the linear plot of log (absorbance) *versus* time by the least square method and were reproducible within $\pm 3\%$.

2. 5. Stoichiometry and product analysis

Reaction mixtures containing an excess of the oxidant over α,β -unsaturated alcohols were kept at room temperature in 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 was dried over anhydrous sodium sulphate and then concentrated.

The products were acrolein (from allyl alcohol), Crotonaldehyde (from Crotyl alcohol), and Cinnamaldehyde (from Cinnamyl alcohol) identified by spot tests, the products were confirmed by its 2:4 DNP derivative (80% yield) and silver mirror test. The products were further characterised by IR spectra and GC-MS. The following stoichiometric reactions obtained from experimental results are given below.

3. RESULTS AND DISCUSSION

Oxidation of α,β -unsaturated alcohols by quinaldinium fluorochromate has been conducted in 40% acetic acid and 60% water medium at 313 K under pseudo - first order conditions and the observed results were discussed below. Effect of varying Oxidant concentration

The kinetic data reveals that the oxidation of α,β -unsaturated alcohols by quinaldinium fluorochromate is first order with respect to the oxidant. The plot of log absorbance *versus* time is linear indicating that the order with respect to quinaldinium fluorochromate is unity. The pseudo-first order rate constants were found to be independent of initial concentration of quinaldinium fluorochromate.

The concentration of quinaldinium fluorochromate was varied in the range 3.58×10^{-3} to $17.88 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The linear constancy in the value of k_1 irrespective of the concentration of the quinaldinium fluorochromate confirms the first order dependence on quinaldinium fluorochromate (QnFC).

3. 1. Effect of varying substrate concentration

The substrate α,β -unsaturated alcohols were varied in the range 2.0×10^{-2} to $10.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ at 313 K and keeping all other reactant concentration as constant and the rates were measured (Table 1).

The rate of oxidation increased progressively on increasing the concentration of α,β -unsaturated alcohols, indicating first order dependence with substrate. The plot of $\log k_1$ *versus* $\log [s]$ gave the slope of 1.02 ($r = 0.994$) (Figure 1) shows that the oxidation reaction was first order with respect to α,β -unsaturated alcohols.

Table 1. Rate constant for the oxidation of α,β -unsaturated alcohols and Quinaldinium Fluorochromate

[QnFC] 10^3 $\text{mol}\cdot\text{dm}^{-3}$	[Allyl alcohol] 10^2 $\text{mol}\cdot\text{dm}^{-3}$	[Crotyl alcohol] 10^2 $\text{mol}\cdot\text{dm}^{-3}$	[Cinnamyl alcohol] 10^2 $\text{mol}\cdot\text{dm}^{-3}$	$k_{\text{obs}} 10^4 \text{ s}^{-1}$		
				Allyl alcohol	Crotyl alcohol	Cinnamyl alcohol
3.58	4.00	4.00	4.00	7.86	14.40	19.90
7.15	4.00	4.00	4.00	7.89	14.43	19.92
10.72	4.00	4.00	4.00	7.69	14.38	19.88
14.30	4.00	4.00	4.00	7.67	14.35	19.91
17.88	4.00	4.00	4.00	7.77	14.42	19.89
7.15	2.00	2.00	2.00	3.86	7.06	9.74
7.15	4.00	4.00	4.00	7.89	14.43	19.92
7.15	6.00	6.00	6.00	11.88	21.92	30.26
7.15	8.00	8.00	8.00	15.25	27.89	38.50
7.15	10.00	10.00	10.00	19.21	35.14	48.51

Figure 1. Plot of $\log k_1$ versus $\log [S]$

3. 2. Effect of varying Perchloric acid concentration

The perchloric acid concentration was varied in the range of 0.5×10^{-1} to 2.5×10^{-1} $\text{mol} \cdot \text{dm}^{-3}$ and keeping the concentrations as constant and rate were measured (Table 2). The increase in perchloric acid in the oxidation reaction increases the rate of the reaction and shows a direct first order dependence on perchloric acid. A plot of $\log k_1$, against $\log [\text{H}^+]$ is linear. (Figure 2).

Table 2. Effect of varying Hydrogen ion concentration $[\text{QnFC}] = 7.15 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$
Temperature = 313 K $[\alpha, \beta\text{-unsaturated alcohols}] = 4.00 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

$[\text{H}^+] 10^2$ $\text{mol} \cdot \text{dm}^{-3}$	$k_{\text{obs}} 10^4 \text{ s}^{-1}$		
	Allyl alcohol	Crotyl alcohol	Cinnamyl alcohol
0.5	3.80	6.95	9.59
1.00	7.89	14.43	19.92
1.50	12.21	22.33	30.83
2.00	15.81	28.92	39.92
2.50	21.98	40.20	55.50

Figure 2. Plot of $\log k_1$ versus $\log [\text{H}^+]$

3. 3. Effect of varying ionic strength

There was no appreciable change in the rate with change of ionic strength indicating the involvement of neutral molecules in the rate-determining step.

3. 4. Effect of varying solvent composition

The reaction was carried out at five different percentage of acetic acid -water mixtures while all other factors were constant (Table 3). The reaction is facilitated by the medium of low dielectric constant (ϵ). The dielectric constant was decreased by the addition of water. The plot of $\log k_1$ versus inverse the dielectric constant gave a straight line with a positive slope (Figure 3). This might be probably due to ion-dipole interaction^{17, 18} in the rate determining step.

Table 3. Effect of varying solvent $[QnFC] = 7.15 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ $[H^+] = 1.02 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$
 $[\alpha, \beta\text{-unsaturated alcohols}] = 4.00 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ Temperature = 313 K

AcOH - H ₂ O (%v/v)	ϵ	$k_1 \cdot 10^4 \text{ s}^{-1}$		
		Allyl alcohol	Crotyl alcohol	Cinnamyl alcohol
30 - 70	57.85	6.92	12.65	17.47
35 - 65	54.15	7.41	13.48	18.19
40 - 60	50.46	7.89	14.43	19.92
45 - 55	46.93	8.31	15.48	20.89
50 - 50	43.08	8.98	16.42	22.67

Figure 3. Plot of $\log k_1$ versus D^{-1}

3. 5. Effect of acrylonitrile

The clear mixture containing alcohol and quinaldinium fluorochromate when allowed to stand with a drop of acrylonitrile no turbidity is formed suggesting the non involvement of free radical in this reaction.

3. 6. Effect of manganous sulphate

The reaction rate decreases with increasing the concentration of Mn^{2+} ion, (Table 4) confirming the involvement of two electron process in this reaction¹⁹.

Table 4. Effect of varying Manganous sulphate $[QnFC] = 7.15 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ $[H^+] = 1.02 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ $[\alpha, \beta\text{-unsaturated alcohols}] = 4.00 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ Temperature = 313 K

$[MnSO_4]$ $\text{mol} \cdot \text{dm}^{-3}$	$k_1 \cdot 10^4 \text{ s}^{-1}$		
	Allyl alcohol	Crotyl alcohol	Cinnamyl alcohol
0.00	7.89	14.43	19.92
0.50	7.61	14.40	19.50
1.00	6.88	14.00	19.28
1.50	6.77	13.90	18.76
2.00	6.53	13.75	18.53

3. 7. Effect of temperature

The oxidation reaction was conducted at four different temperatures viz., 303, 313, 323 and 333 K and the measured rate constant values were given in (Table 5).

Table 5. Activation parameters for the oxidation of α, β -Unsaturated alcohols by Quinaldinium Fluorochromate $[QnFC] = 7.15 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ $[H^+] = 1.02 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ $[\alpha, \beta\text{-Unsaturated alcohols}] = 4.00 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

S. No	α, β - Unsaturated alcohols	$k_{\text{obs}} \cdot 10^4$ (s^{-1})				$\Delta H^\ddagger$ (kJmol^{-1})	$-\Delta S^\ddagger$ ($\text{JK}^{-1}\text{mol}^{-1}$)	$\Delta G^\ddagger$ (kJmol^{-1}) at 313 K	Ea (kJmol^{-1}) at 313 K
		303 K	313 K	323 K	333 K				
1	Allyl alcohol	5.39	7.89	10.90	18.53	31.62 ± 0.20	176.88 ± 1	86.98 ± 0.20	34.22
2	Crotyl alcohol	9.63	14.43	20.68	29.36	28.46 ± 0.1	182.24 ± 1	86.50 ± 0.1	31.06
3	Cinnamyl alcohol	14.08	19.92	28.48	40.44	26.89 ± 0.1	184.38 ± 1	85.60 ± 0.1	29.49

Figure 4. Isokinetic plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$

Figure 5. Exner plot of $\log(k)_{303\text{K}}$ versus $\log(k)_{313\text{K}}$

An increase in temperature had resulted in an increase in the rate of reaction. The thermodynamic parameters were calculated by using the Eyring's²⁰ plot of $\ln k_2/T$ versus $1/T$. The negative values of the entropy of activation ($\Delta S^\ddagger$) suggested an extensive solvation of the transition state over the reactants. The values (Table 5) of the free energies of activation ($\Delta G^\ddagger$) were fairly constant indicating that a similar mechanism operated for the oxidation of all the α,β -unsaturated alcohols studied. A plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ (iso-kinetic plot) gives a straight line with excellent correlation coefficient ($r = 0.999$)^{21,22} (Figure 4). The Exner plot also gives a straight line with a very fine correlation coefficient of ($r = 0.999$) (Figure 5), indicating that all the three α,β -unsaturated alcohols are subjected by oxidation and their mechanism is common²³.

4. MECHANISM AND RATE LAW

As the reaction is showing first order dependence on the oxidant, H^+ ion and substrate. These two species should be involved in the slow step: The large increase in rate with acidity suggests the involvement of protonated Cr^{6+} species in the rate determining step. Thus a mechanism involving hydride ion transfer in the rate determining step can be postulated for the quinaldinium fluorochromate oxidation (Scheme 1).

The reactions were also carried out with some of the other structurally related alcohols as crotyl alcohol and cinnamyl alcohol. The rate of the reaction with respect to oxidant and substrate shows first order.

4. 1. Mechanism

(Here R = H, CH₃ and C₆H₅)

Scheme 1

4. 2. Rate law

The above mechanism leads to the following rate law:

$$- \frac{d[\text{QnFC}]}{dt} = Kk_2[\alpha, \beta\text{-Unsaturated alcohol}] [\text{QnFC}][\text{H}^+]$$

$$- \frac{d[\text{QnFC}]}{dt} = k_{\text{obs}}[\alpha, \beta\text{-Unsaturated alcohol}][\text{QnFC}][\text{H}^+]$$

The proposed mechanism and the derived rate law fit well to the experimental observation.

4. 3. Effect of structure and reactivity

The order of reactivity has been found to be **Cinnamyl alcohol (I) > Crotyl alcohol (II) > Allyl alcohol (III)**. When electron releasing groups were attached to, or were in close proximity to the site of the reaction, the rate was increased because of the increased electron density on the carbon atom. The phenyl group (cinnamyl alcohol) acted as an electron-releasing group to much larger extent than the methyl group (Crotyl alcohol), resulting in the rate of the oxidation being highest for cinnamyl alcohol.

5. CONCLUSION

The main products are found to be acrolein, crotonaldehyde and cinnamaldehyde. The reaction was first order each in [substrate] [oxidant] and $[H^+]$. The stoichiometry was found to be one mole of α,β -unsaturated alcohol consuming one mol of quinaldinum fluorochromate. The plots of $\log k$, versus $1/D$ were found to be linear, with positive slopes. The negative values of $\Delta S^\ddagger$ provided support for the formation of a rigid activated complex. A mechanism in terms of active species of oxidant and catalyst is proposed and the rate law is derived and verified.

Acknowledgement

The authors are thankful to the authorities of National College (Autonomous), Tiruchirappalli for providing facilities.

REFERENCES

- [1] J. Muzart, *Chem. Rev.* 92(1) (1992) 113-140.
- [2] A. Kothari, S. Kothari and K. K. Banerji, *Indian. J. Chem.* 44A (2005) 2039-2043.
- [3] S. A. Chimatadar, M. S. Salunke, S.T. Nandibewoor, *Indian. J. Chem.* 45A (2006) 388-393.
- [4] M. Hudlicky, *Oxidation inorganic chemistry/reductions in organic chemistry*, 1, 2nd Ed., Washington: ACS Monograph, ACS, (1990), 186.
- [5] L. Fieser and M. Fieser, *Reagents for organic synthesis*, New York, John Wiley and Sons, (1967), 144.
- [6] G. Cainelli and G. Cardillo, *Chromium oxidation in organic chemistry*, Springer-Verlag, New York, (1984).
- [7] Dandinasivara S. Mahadevappa, Hanumanthanaidu M. K. Naidu, *Aust. J. Chem.* 28 (1975) 899-901.
- [8] K. Ganapathy, B. Vijayan, *Proc. Indian Acad.Sci.* 87A (1978) 215-217.
- [9] Iftikhar Ahmad, C. Muhammad asraf, *Int. J. Chem. Kinet.* 11(8) (1979) 813-819.
- [10] AN. Palaniappan, K.G. Sekar, M. Ravishankar, *Oxid. Commun.* 18(1) (1995) 52-55.
- [11] S. M. Desai, N. N. Halligudi, S. T. Nandibewoor, *Int. J. Chem. Kinet.* 31(8) (1999) 583-589.
- [12] S. M. Desai, N. N. Halligudi, S. T. Nandibewoor, *Transition metal chemistry* 27(2) (2002) 207 – 212.
- [13] S. A. Chimatadar, S. B. Koujalagi, S. T. Nandibewoor, *Oxid. Commun.* 27(1) (2004) 81-89.
- [14] K. G. Sekar, M. Vellaisamy, *Der chemica sinica* 3(3) (2012) 703-707.
- [15] Nebahat Degirmenbasi, Beytiye Ozgun, *Monatshefte fur Chemie* (2004) 407-410.

-
- [16] B. Bhattacharjee, M. N. Bhattacharjee, M. Bhattacharjee, A. K. Bhattacharjee, *Int. J. Chem. Kin.* 17 (1985) 629-636.
- [17] J. E. Quinlan, E. S. Amis, *J. Am. Chem. Soc.* 77 (1955) 4187- 4191.
- [18] E. S. Amis : *Solvent effects on reaction rates and mechanism*, Academic press, New York, (1966) 42.
- [19] S. Banfi, M. Cavazzini, G. Pozzi, S. V. Barkanova, O. L. Kaliya, *J. Chem. Soc. Perkin Trans. 2* (2000) 871-877.
- [20] A. A. Frost, R.G.Pearson, *Kinetics and Mechanism*, Wiley Eastern NewDelhi,(1970).
- [21] R. C. Petersen, *J. Org. Chem.* 29 (1964) 3133-3135.
- [22] J. E. Leffler, *J. Chem. Phys.* 23 (1955) 2199-2205.
- [23] O. Exner, *Nature* 201 (1964) 488 - 490.