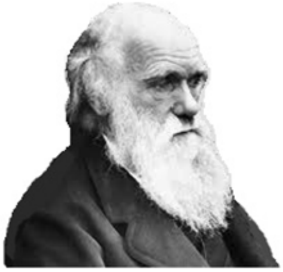
Available online at www.worldnewsnaturalsciences.com



World News of Natural Sciences

WNOFNS 13 (2017) 113-121 EISSN 2543-5426

Oxidation of Distyryl Ketone by Quinaldinium Chlorochromate – A Kinetic Study

Seplappatty Kalimuthu Periyasamy* and **K. Saravanakumar**

Department of Chemistry, Jamal Mohamed College (Autonomous),
Tiruchirappalli – 620 020, Tamil Nadu, India

*E-mail address: nctperiya85@gmail.com

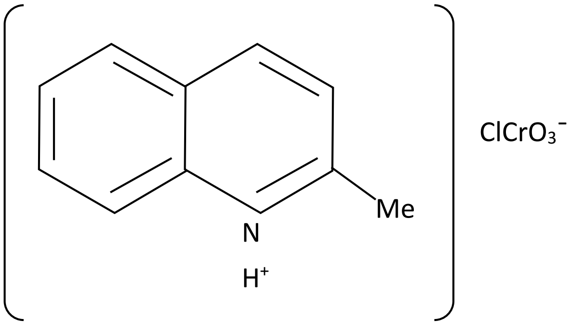
ABSTRACT

Oxidation of distyryl ketone by quinaldinium chlorochromate [QnCC] in water and acetic acid medium has been studied under pseudo-first order condition. The reaction shows unit order dependence, each with respect to oxidant and hydrogen ion. The reaction with respect to substrate is found to be fractional order. The reaction rate decreases with increasing the concentration of Mn^{2+} ions. The reaction does not induce the polymerization of acrylonitrile. A possible mechanism has been proposed in the formation of cinnamic acid and Phenyl acetaldehyde.

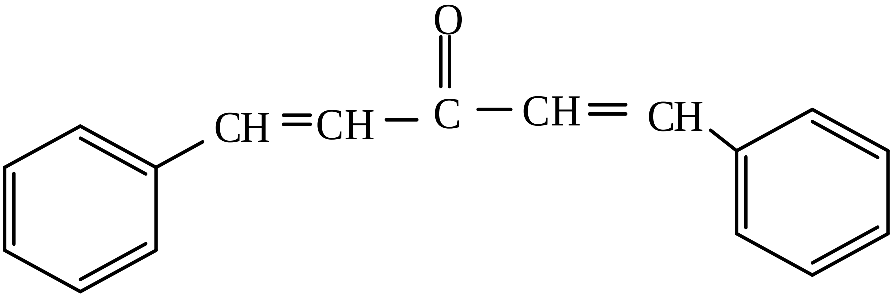
***Keywords*: Oxidation, distyryl ketone, Quinaldinium chlorochromate, Kinetics

1. INTRODUCTION

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. A number of new chromium-containing compounds like quinolinium fluorochromates (Sheila Srivastava *et al*., 2010), quinolinium chlorochromate(Sangita Sharma *et al*., 2011), nicotinum dichromates (Karunukaran *et al*., 2001), quinolinium dichromates (Hauzachin Saunte *et al*., 2010), morpholinium chlorochromates (Malani *et al*., 2008), benzimidazolium fluorochromates (Sivamurugan *et al*., 2005), imadazolium dichromates (Sheik Mansoor *et al*., 2009) have been used to study the kinetics and mechanism of oxidation of various organic compounds. However most of these reagents have been 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 excess of reagent. To overcome these disadvantages, we synthesized new reagent QnCC which is mild, efficient, stable reagent in synthetic organic chemistry, which acts as an oxidizing agent. Literature survey reveals that no report is available on the kinetics of oxidation of distyryl ketone by QnCC. Hence, we have considered it worthwhile to study the kinetics and mechanism of oxidation of distyryl ketone by QnCC. The possible structure of QnCC is given below:



Dibenzylideneacetone or dibenzalacetone is a type of chalcone and is often abbreviated as DBA. It is an organic compound with the formula $C_{17}H_{14}O$. It is a bright yellow solid, insoluble in water, but soluble in ethanol, and its structure is given below



Dibenzylideneacetone or Dibenzalacetone or Distyrylketone

The kinetics of oxidation of chalcone by quinolinium dichromate in aqueous acetic acid medium in the presence of sulphuric acid has been reported (Manikyamba *et al*., 2002). The kinetics and mechanism of oxidation of styryl biphenyl and styryl fluorenyl ketones by pyridinium chlorochromate (Ananthakrishnanadar *et al*., 1999), and the kinetics of the oxidation of distyryl ketone by quinaldinium fluorochromate (65%, v/v) acetic acid medium (K.G. Sekar *et al*., 2012) have also been reported. The main products are cinnamic acid and phenyl acetaldehyde. We report here on the kinetics of the oxidation of distyryl ketone by quinaldinium chlorochromate in acetic acid as solvent. The mechanistic aspects are also discussed.

2. EXPERIMENTAL

2. 1. Material and Methods

The solutions of the distyryl ketones were freshly prepared in acetic acid and standardized by titrating it against a standard solution of iodine. Quinaldinium chlorochromate was prepared by the reported method (Nebahat Degirmenbasi *et al*., 2003) and its purity was checked by an iodometric method. The solvents were purified by usual methods (Perrin *et al*., 1966).

2. 2. Stoichiometry

The kinetics of reaction was to establish the stoichiometry of the reaction and identify any side reactions. The stoichiometry of the reaction [QnCC]:[distyryl ketone] was determined by taking excess of [QnCC] over [distyryl ketone] and allowing the reaction to go for completion.

After a sufficient length of time, all the substrate has completely reacted to quinaldinium chlorochromate, leaving behind the unreacted quinaldinium chlorochromate. The unreacted quinaldinium chlorochromate was estimated iodometrically. The estimation of unreacted quinaldinium chlorochromate showed that one mole of substrate was consumed by one mole of oxidant. The stoichiometry between distyryl ketone and QnCC was found to be 1:1.

2. 3. Product analysis

The reaction mixture containing distyryl ketone (0.1 M) in acetic acid, and QnCC (0.1 M) in acetic acid was added, and the medium was maintained using perchloric acid. Then the reaction mixture was slightly warmed and was kept aside for about 48 h for the completion of reaction.

After 48 h, the reaction mixture was extracted with ether and dried over anhydrous sodium sulfate. The ethereal layer was washed with water several times and kept on a water bath for ether evaporation and cooled to get the product. Cinnamic acid and phenyl acetaldehyde were identified as products.

2. 4. Kinetic measurements

The reaction was performed under pseudo-first order conditions by keeping the distyrylketone in quinaldinium chlorochromate and acetic acid – water as a solvent. The reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions and were followed up to Ca 80% conversion by monitoring the decrease in the [QnCC] at 376 nm on the spectrophotometer (Elico Scanning mini Spectrophotometer -Model SL177).

The pseudo-first order rate constants, k_{obs}, were evaluated from the linear plot ($r = 0.994$-0.999). The rate constants were obtained from the slope of the plot of log absorbance versus time by the linear least square method. The results were reproducible within ±3%. The second-order rate constants were evaluated from the relation $k_2 = k_{\mathrm{obs}}$ /[reductant].

3. RESULTS AND DISCUSSION

3. 1. Effect of varying [QnCC]

The reaction was investigated with varying concentrations of quinaldinium chlorochromate at constant distyryl ketone and perchloric acid concentrations. The reaction was found to be first-order with respect to [QnCC], as evidenced by the linear plot of log absorbance versus time and also from the constancy of the pseudo-first order rate constant.

3. 2. Effect of varying [distyryl ketone]

The rate of the reaction increases with increase in [substrate]. A plot of log k_1 *versus* log [substrate] gives a straight line with a fractional slope, the correlation coefficient being 0.999. The rate of the oxidation is fractional order with respect to substrate. It was further well demonstrated by Michaelis-Menten's plot which gives a definite intercept at the rate axis (**Table 1**).

Table 1. Effect of varying the distyryl ketone concentration on the oxidation of Quinaldinium fluorochromate

$[QnCC] = 1.00 \times 10^{-3}$ mol·dm^{-3} Temperature = 313 K

$[H^+] = 3.00 \times 10^{-2}$ mol·dm^{-3} AcOH-H_2O = 50 :50 (%)

[distyryl ketone] 10^2 mol·dm^{-3}	**K_1 10^4 s^{-1}**
1.50	4.36
2.00	5.07
2.50	5.57
3.00	6.21
3.50	6.73

3. 3. Effect of acidity

The reaction was carried out at different initial concentrations of perchloric acid. The effect of acidity was studied by varying the concentrations of perchloric acid, and rate constants were found to increase with increase in the concentration of perchloric acid. The reaction was found to be first order in $[H^+]$, as evidenced by the slope of the plot of log k_1 *versus* log $[H^+]$, while the other variables were kept constant. Plot of log k_1 *versus* log$[H^+]$ gave a straight line, with acid catalyzed on the reaction rate.

3. 4. Effect of varying ionic strength

There was no appreciable change in the rate with the change of ionic strength indicating the involvement of neutral molecules in the rate-determining step (**Table 2**).

Table 2. Effect of ionic strength on the oxidation of distyryl ketone by Quinaldinium chlorochromate

[QnCC] = 1.00×10^{-3} mol·dm^{-3} [H$^+$] = 3.00×10^{-2} mol·dm^{-3}
[distyryl ketone] = 1.50×10^{-2} mol·dm^{-3} Temperature = 313 K
AcOH-H$_2$O = 50 :50 (%)

[NaClO$_4$] **10^3 mol·dm^{-3}**	**k$_1$ 10^4 s^{-1}**
0.00	4.36
0.50	4.44
0.75	4.49
1.00	4.08
1.25	4.22
1.50	4.68

3. 5. Effect of solvent

The reaction was carried out at five different percentage of acetic acid-water mixtures while all other factors were constant. 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. This indicates that the presence of ion-dipole interaction, (Quinlan *et al.*, 1955; Amis, 1966) was in consonance with the observation that in the presence of acid, the rate determining step involved a protonated Cr(VI) species (Wiberg, 1965).

3. 6. Induced polymerization of acrylonitrile

The oxidation of distyryl ketone by quinaldinium chlorochromate, was done in an atmosphere of nitrogen. The reaction does not induce polymerization of acrylonitrile. Further, the addition of acrylonitrile has no effect on the reaction mixture, indicating the absence of free radical mechanism (Littler and Waters, 1959). This indicates a one-electron oxidation giving rise to free radicals is unlikely in the present reaction.

3. 7. Effect of manganous sulfate

The reaction was followed with varying concentrations of Mn^{2+} ions, keeping all the other factors constant (**Table 3**). There was an appreciable decrease in the rate with increasing concentrations of Mn^{2+} ions confirming the involvement of two-electron transfer process in the reaction (Banfi *et al.*, 2000).

3. 8. Effect of temperature

The reaction has been carried out at four different temperatures keeping all other factors constant (Table 3). The thermodynamic parameters have been computed from the linear plot of $\ln(k_2/T)$ *versus* 1/T of Eyring's equation. The entropy of activation ($\Delta S^{\#}$) and the free energy of activation ($\Delta G^{\#}$) were calculated using the Eyring's equation respectively (Frost et al., 1970; Peterson et al., 1961)

Table 3. Effect of varying temperature on the oxidation of distyryl ketone by Quinaldinium chlorochromate

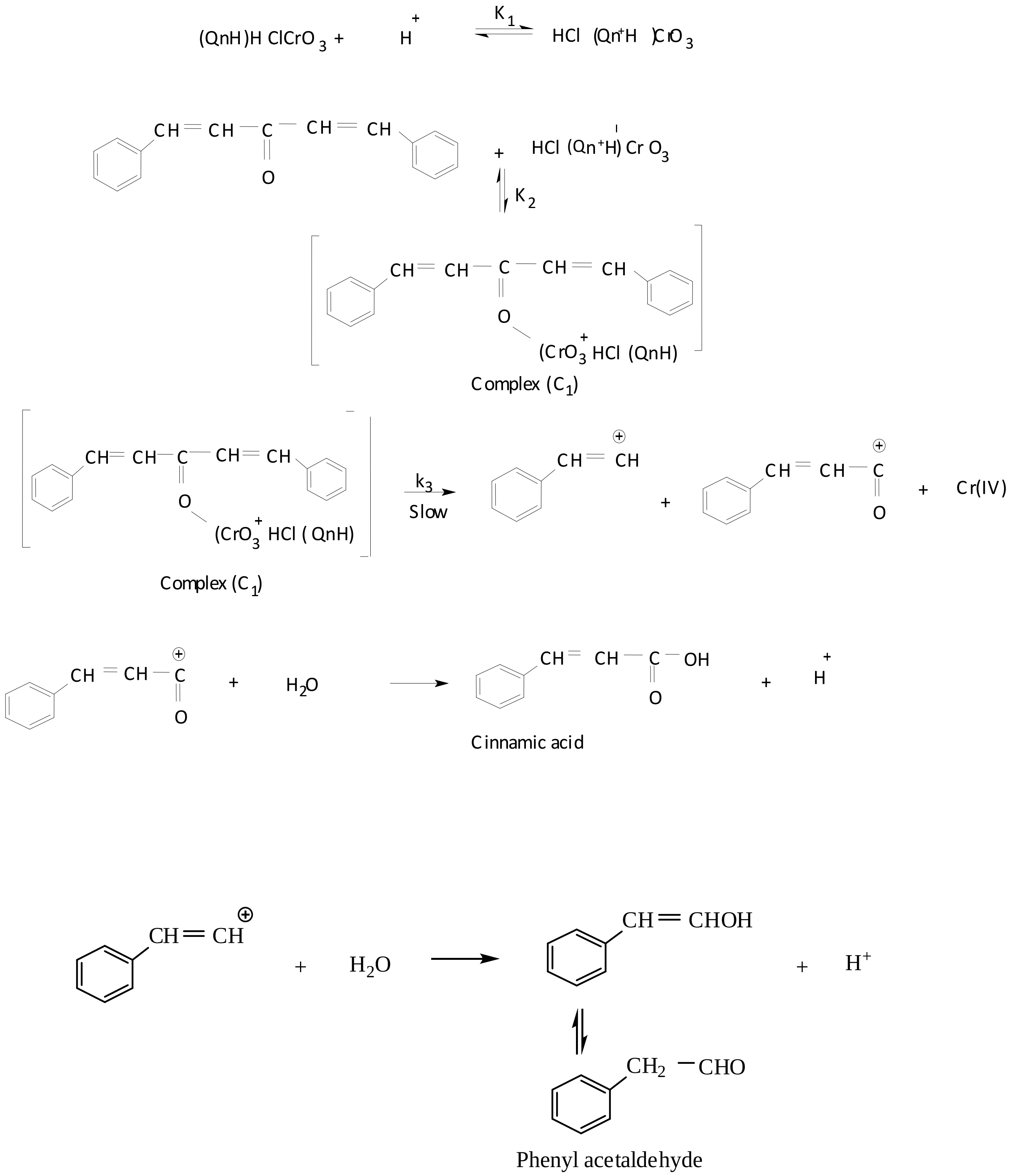
$[QnCC] = 1.00\times10^{-3}$ mol·dm^{-3} $[H^+] = 3.00\times10^{-2}$ mol·dm^{-3}

[distyryl ketone] $= 1.50\times10^{-2}$ mol·dm^{-3} $AcOH\text{-}H_2O$ = 50:50 (%)

Temperature, K	**$k_1\,10^4$ s^{-1}**
303	2.45
313	4.36
323	6.48
333	9.26

3. 9. Mechanism and Rate Law

From the above observations it is clear that the reaction is showing unit order dependence with respect to the oxidant and perchloric acid, and fractional order with respect to substrate. It obeys Michaelis-Menten type kinetics. The reaction is facilitated by the medium of low dielectric constant. The reaction does not induce polymerization of acrylonitrile, indicating the absence of free radical pathway. The added Mn^{2+} ions, having a retardation on the reaction rate, confirms the two-electron transfer process involved in the reaction. In this case, the concentration of chromium(VI) is very much lower under this condition with the active oxidizing species of $HCrO_4^-$. Based on the above facts, the following mechanism is proposed for the oxidation of distyryl ketone by quinaldinium chlorochromate (**Scheme 1**).


(QnH)H ClCrO3 + H+ K1 HCl (Qn+H)CrO3
CH=CH—C—CH=CH
O
+ HCl (Qn+H) Cr O3
K2
(CrO3+ HCl (QnH)
Complex (C1)
k3
Slow
Cr(IV)
H2O
CH—C—OH
H+
Cinnamic acid
CH=CHOH
CH2 —CHO
Phenyl acetaldehyde

Scheme - 1

3. 10. Rate Law

The above mechanism leads to the following rate law

$$-\frac{d[QnCC]}{dt} = k_3\,C_1$$

$$= \frac{k_3K_2[OxH^+]\,[S]}{1 + K_2[S]}$$

$$= \frac{k_3K_1K_2\,[Ox]\,[H^+]\,[S]}{1 + K_2\,[S]}$$

This rate law explains all the experimental facts.

4. CONCLUSIONS

The oxidation of distyryl ketone by quinaldinium chlorochromate in aqueous acetic acid medium leads to the formation of cinnamic acid and phenyl acetaldehyde as the products. The reaction follows simple order kinetics. The mechanism proposed for this oxidation reaction is in accordance with the observed kinetic facts.

Acknowledgement

The authors thank the Principal and Management, Jamall Mohamed College (Autonomous), Tiruchirappalli, Tamil Nadu, India, for providing necessary facilities and encouragement.

References

[1] Sheila Srivastava, Parul Srivastava. *Bull. Chem. Soc. Jpn.* 57 (2010) 258-260.

[2] Sangita Sharma, Jayesh Ramani, Jasmin Bhalodia, Falguni Thakkar. *Derchemica Sinica* 2(4) (2011) 140-151.

[3] Chockalingam Karunakaran, Vaithiyalingam Chidambaranathan. *Croatia Chemica Acta* 74(1) (2001) 51-59.

[4] Hauzachin Saunte, Girija S., Chaubey M.K., Mahanti. *Croatia Chemica Acta*, 83(3) (2010) 291-298.

[5] Malani N., Pohani S., Baghmar M., Sharma P.K, *Indian Journal of Chemistry*, 47 (A), (2008) 1373-1376.

[6] Sivamurugan V., Abraham Rajkumar, Banumathi Arabindoo, Murugesan, V., *Indian Journal of Chemistry* 44(B) (2005) 144-147.

[7] Sheik Mansoor, S., Syed Shafi, S.E. *Journal of Chemistry*, 6(S1) (2009) S522-S528.

[8] Manikyamba, P., Aruna, K., *Ultra sciences*, 14 (3) (2002) 483-486.

[9] Dae Dong Sung, Ananthakrishna Nadar P., *Bull. Korean Chem. Soc.* Vol. 20 (1999) No. 12 1487.

[10] Sekar, K.G., Periyasamy, S.K., *Journal of Chemical and Pharmaceutical Research*, 4(4) (2002) 2153-2161.

[11] Nebahat Degirmenbasi, Beytiye Ozgun. *Monatshefte furchemie*. 135 (2004) 407.

[12] Perrin, D.D., Armarego, W.L., Perin, D.R., Purification of Organic Compounds. Pergamon Press Oxford, (1966).

[13] Quinlan, J.E., Amis, ES. *J. Am. Chem. Soc.* 77 (1955) 4187-4191.

[14] Amis E.S., Solvent effects on reaction rates and mechanism, Academic Press, New York, 42, (1966)

[15] Wiberg, K.B., Oxidation in Organic Chemistry Part A, Academic Press New York **(**1965)

[16] Littler, J.S., Waters, W.A., Oxidations of Organic compounds with quinquevalent Vanadium, Part 1. General Survey and the Oxidation of Pinaco. *J. Chem. Soc.* 1299 (1959)

[17] Banfi, S., Cavazzini, M., Pozzi, G., Barkanova, S.V., Kaliya, O.L., *J. Chem. Soc. Perkin Trans*. 2 (2000) 879.

[18] Frost A.A., Pearson R.G., Kinetics and Mechanism. Wiley Eastern New Delhi, (1970)

[19] Peterson R.C., Markgraf J.H., Ross S.D., *J. Am. Chem. Soc*. 83 (1961) 3819-3823.

(Received 23 August 2017; accepted 08 September 2017)