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# Kinetics of Oxidation of  Allyl Alcohol by Cr(VI)

## K. G. SEKAR[1] and V. PALANIVEL[2]

[1]Department of Chemistry, National College (Autonomous),Tiruchirappalli - 620 001 (India).
[2]Department of Chemistry, Periyar EVR College, (Autonomous), Tiruchirappalli - 620 023 (India).
*Corresponding  author:  E-mail:drkgsekar@yahoo.co.in,  palanievr@gmail.com

## ABSTRACT

The kinetics of  oxidation of allyl alcohol by quinaldinium chlorochromate is  investigated in 40 % acetic acid – water (v/v) medium. The order with  respect to oxidant and hydrogen ion concentration is found to be one and fractional with respect to substrate. The rate of the reaction is decreases  with the decrease in the  dielectric constant of the medium. The rate of the reaction has negligible effect with  the increase of  ionic strength. The reaction does not induce the polymerization of acrylonitrile. From the kinetic data obtained, the activation parameters have been calculated and a plausible mechanism has been proposed.

**Keywords :** Kinetics, Mechanism, Oxidation, Allyl alcohol, Quinaldinium Chlorochromate.

## INTRODUCTION

Quinaldinium chlorochromate (QnCC) has been used as a mild and stable oxidizing agent in synthetic organic chemistry[1]. The structure of QnCC is given below,
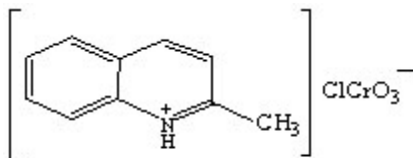


Quinaldinium Chlorochromate

Allyl alcohol (prop-2-en-1-ol) is an with the $CH_2$=$CHCH_2OH$. It is a water soluble and colourless liquid. Allyl alcohol is used as a raw material for the production of glycerol and also used as a precursor to many specialized compounds. The kinetics and mechanism of oxidation of  allyl  alcohol by various oxidants have been reported[2-12]. The kinetics of oxidation of allyl alcohol by QnCC has not been reported by investigation. The kinetics of oxidation of allyl alcohol by QnCC in aqueous acetic acid medium  has been  investigated and also the mechanism  and rate law has been derived.

## EXPERIMENTAL

**Materials and methods**
**Preparation of quinaldinium chlorochromate**

Chromium trioxide (10.0 g) was dissolved in 6 M hydrochloric acid (18.4 ml) and then it was cooled to 0° C (ice-water bath). Quinaldine (13.9 ml) was added to chromium trioxide solution drop-

wise during 30 minutes. The reaction mixture was cooled for 2 h. The resulting product was filtered off and washed with ether (4´50 ml) affording Quinaldinium chlorochromate (10 g) as yellow solid m.p. 139° C, yield 72%. From the IR spectral data, it was confirmed.

### Allyl alcohol

Allyl alcohol was distilled and the fraction collected at 97ºC was used.

### 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 116-118æ%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 reaction was carried out under pseudo – first order conditions [Allyl] k" [QnCC] in 40 % (v/v) aqueous acetic acid medium containing perchloric acid. The course of the reaction was followed spectrophotometically at 470 nm for upto 80% of the reaction and the pseudo – first order rate constants $k_1$ were computed from the linear plots of log absorbance *versus* time by the least square method, and reproducible within ±1%

### Stoichiometry and Product analysis

Reaction mixture containing an excess of the oxidant over allyl alcohol were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unchanged oxidant showed that one mole of allyl alcohol consumed one mole of the oxidant. The product acrolein , was identified by IR spectra and the reaction proceeds quantitatively according to the equation,
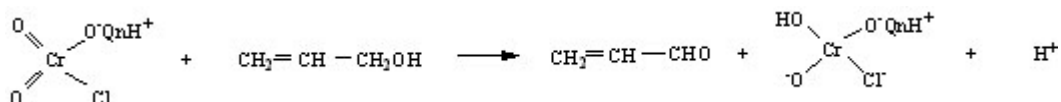


**Table 1: Rate constants for the oxidation of Allyl alcohol by QnCC at 40°C**

| [Allyl]×$10^2$ (M) | [QnCC]×$10^3$ (M) | [HClO$_4$]×$10^1$ (M) | [NaClO$_4$]×$10^3$ (M) | AcOH-H$_2$O (%v/v) | $k_{obs}$×$10^4$ (s$^{-1}$) |
|---|---|---|---|---|---|
| 2.0 - 10.0 | 7.2 | 1.0 | —— | 40 | 4.87-6.25 |
| 4.0 | 3.6-18.0 | 1.0 | —— | 40 | 5.47-5.99 |
| 4.0 | 7.2 | 0.5-2.5 | —— | 40 | 3.39-12.88 |
| 4.0 | 7.2 | 1.0 | 0.0-7.2 | 40 | 5.47-5.70 |
| 4.0 | 7.2 | 1.0 | —— | 30-50 | 5.01-6.17 |

### RESULTS AND DISCUSSION

### Effect of varying quinaldinium chlorochromate

The kinetic data reveals that the rate of oxidation of allyl alcohol by quinaldinium chlorochromate is found to be first. The plot of log absorbance *versus* time is linear indicating that the order with respect to quinaldinium chlorochromate

is unity. The pseudo-first order rate constants were found to be independent of initial concentrations of quinaldinium chlorochromate**.**(Table 1)

### Effect of varying allyl alcohol

At constant [QnCC], the rate constants are increased with the increase in the concentrations of the allyl alcohol( Table 1). A plot of log $k_1$ *versus*
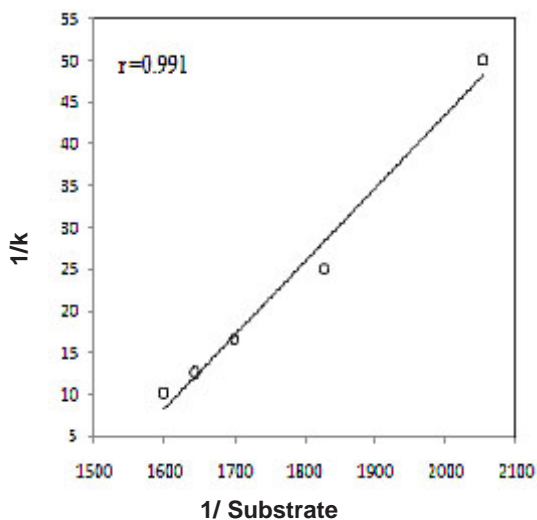
**Fig 1. Plot of 1/k *versus* 1/substrate**



**Fig 2. Plot of log $k_1$ *versus* log [H⁺]**
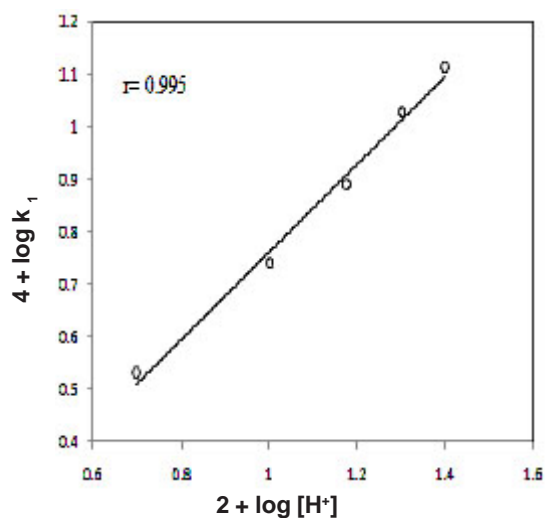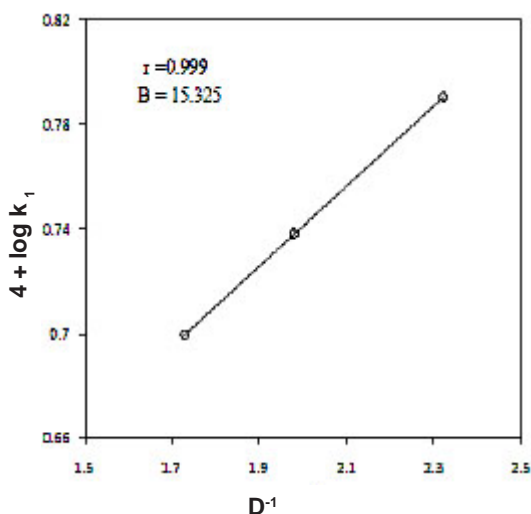


**Fig 3. Plot of log $k_1$ *versus* D⁻¹**
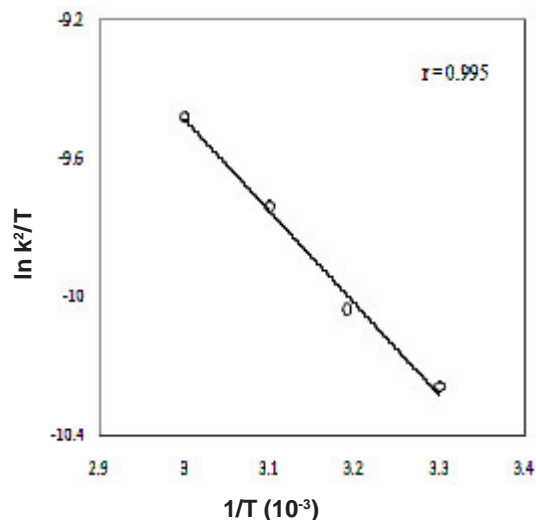


**Fig 4. Plot of ln $k_2$/T versus 1/T**

log [substrate] with a slope was 0.15. It was further supported by the fact that the double reciprocal plot of $k_{obs}$ *versus* [substrate] gave a straight line with a definite intercept indicating the Michaeli's-Menten type of this reaction (Fig. 1).

**Effect of varying Hydrogen ion concentration**

The effect of acidity was studied by varying the concentrations of perchloric acid and the rate constants were increased with the increase in the concentrations of perchloric acid (Table 1). The reaction was found to be first order in hydrogen ion

as evidenced by the unit slope of the plot of log $k_1$ *versus* log [H⁺]. (Fig 2)

**Effect of varying solvent composition**

Increase in the percentage of acetic acid of the medium increases the rate of the oxidation process (Table 1). This is normally observed in the oxidation reactions of Cr(VI). Further correlation of log $k_{obs}$ with the reciprocal of the dielectric constant of the medium give linear plot (Fig 3) suggesting an ion-dipole interaction [13-15] between allyl alcohol and quinaldinium chlorochromate.

**Table.2: Effect of varying manganous sulphate**

[QnCC] = $7.20 \times 10^{-3}$ *mol dm$^{-3}$*
[H$^+$] = $10.00 \times 10^{-2}$ *mol dm$^{-3}$*
[Allyl alcohol] = $4.00 \times 10^{-2}$ *mol dm$^{-3}$*
AcOH-H$_2$O = 40: 60 (%)
Temperature = 313 K

| [MnSO$_4$] $\times 10^4$ ( M ) | $k_1 \times 10^4$ $s^{-1}$ |
|---|---|
| 0.00 | 5.48 |
| 1.80 | 5.00 |
| 3.60 | 4.96 |
| 5.40 | 4.55 |
| 7.20 | 4.00 |

**Table.3: Effect of varying temperature**

[QnCC]=$7.20 \times 10^{-3}$ *mol dm$^{-3}$*
[H$^+$] =$10.00 \times 10^{-2}$ *mol dm$^{-3}$*
[Allyl alcohol] = $4.00 \times 10^{-2}$ *mol dm$^{-3}$*
AcOH-H$_2$O = 40:60 (%)

| Temperature (K) | $k_1 \times 10^4$ $s^{-1}$ |
|---|---|
| 303 | 4.24 |
| 313 | 5.47 |
| 323 | 7.60 |
| 333 | 10.17 |

**Effect of varying ionic strength**

The rate constants were constant when the concentrations of the sodium perchlorate increases. There was no appreciable change in the rate with the change of ionic strength (Table 1) indicating the involvement of neutral molecules in the rate determining step[16].

**Effect of added acrylonitrile**

The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway[17].

**Effect of varying manganous sulphate**

The reaction was followed with the varying concentrations of Mn$^{2+}$ ions keeping all the other factors constant. There was an appreciable decrease[18 – 19] in the rate with the increase of the concentrations of Mn$^{2+}$ ions confirms the involvement of two electron transfer process in the reaction (Table 2).

**Effect of varying temperature**

The reaction has been carried out at four different temperatures 303 K, 313 K, 323 K and 333 K respectively, 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 (20) (Fig 4)

$\Delta H^{\#}$ = 22.09 *k J mol$^{-1}$*
$\Delta S^{\#}$ = -210.29 *J K$^{-1}$mol$^{-1}$*
$\Delta G^{\#}$ = 96.33 *k J mol$^{-1}$* at 313 K
Ea = 24.69 *k J mol$^{-1}$*    at 313 K

**Mechanism and rate law**

From the above observations, it is clear that the reaction is showing unit order with respect to oxidant and [H$^+$] ion and fractional order with respect to substrate. And the following mechanism is proposed for the oxidation of allyl alcohol by quinaldinium chlorochromate.
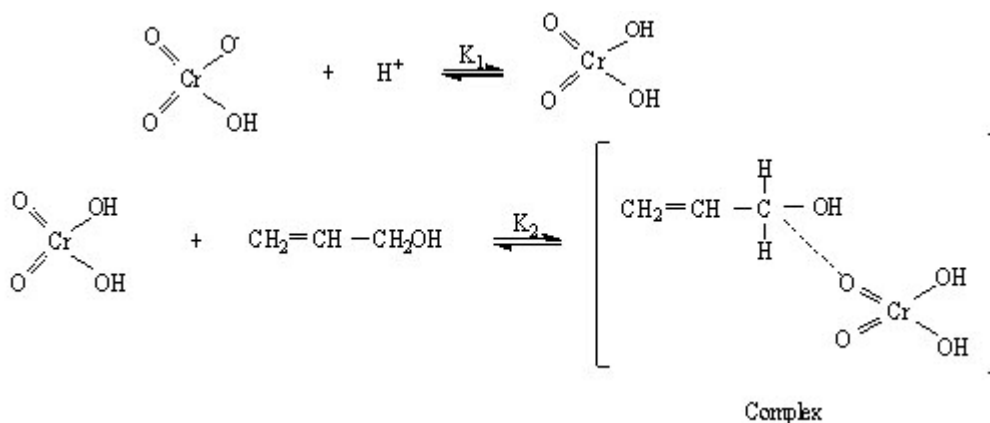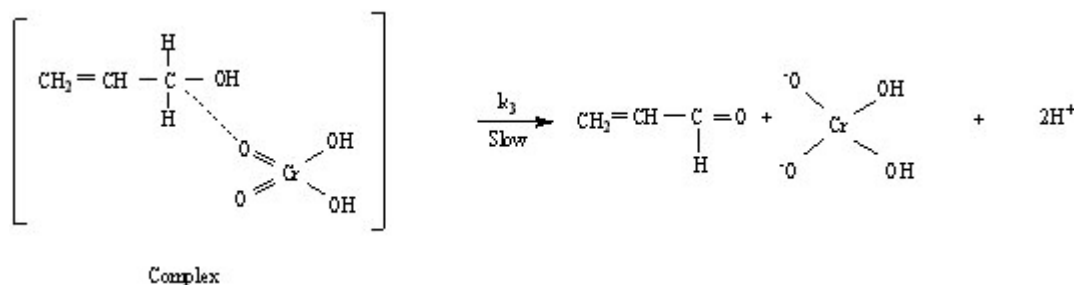


Complex

Complex

**Rate law**

These above observations suggest that the rate law can be shown as

Rate = $k_3$ Complex

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

**CONCLUSION**

The oxidation of allyl alcohol by quinaldinium chlorochromate in aqueous acetic acid medium leads to the formation of complex and finally gives the product. The reaction follows simple order kinetics.

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