ABSTRACT
The kinetics of oxidation of a cyclohexanol with quinoxalinium dichromate (QxDC) has been investigated in aqueous acetic acid 50% (v/v) solution in the presence of perchloric acid. The reaction is first order with respect to oxidant QxDC and exhibits Michaelis-Menten dependence on substrate concentration. The rate of reaction increased with increase in concentration of perchloric acid and the order with respect to [H+] was found to be fractional. From the kinetic data obtained, the activation parameters have been calculated and a plausible mechanism has been proposed.

Keywords: Oxidation, Cyclohexanol, Quinoxalinium dichromate, Kinetics.

INTRODUCTION
Quinoxalinium dichromate (QxDC), one of the Cr (VI) compounds in reported to be a neutral and mild oxidant for selective oxidation.

Kinetics and Mechanism of Oxidation of Cyclohexanol by Cr (VI)
KG. Sekar* and G. Manikandan
Department of Chemistry, National College, Tiruchirappalli, Tamil Nadu, India.

MATERIALS AND METHODS
Materials
The cyclohexanol purchased from Aldrich chemicals, QxDC was prepared by the literature method and its purity was checked by estimating Cr(VI) iodometrically. Acetic acid (AnalaR) was refluxed over CrO3 and distilled. All other chemicals used were AnalaR grade. The reaction mixture was homogeneous throughout the course of the reaction.
Kinetic Measurements
All the reactions were carried out in blackcoated vessels to avoid the possible photochemical reactions if any. The kinetic measurements were carried out using spectrophotometer (Systronics) at 470nm. All kinetic runs were made in aqueous acetic acid 50% (v/v) under pseudo-first order conditions by keeping the substrate always in excess over that of oxidant. The rate constants were evaluated from the linear plot of log absorbance against time by the least square method. The results were reproducible within ±3% error.

Product Analysis
The same experimental conditions were used for the kinetic determinations; solution of oxidant (0.10 mol), cyclohexanol (0.12 mol) and perchloric acid were mixed and kept under nitrogen atmosphere for 24h, for the completion of the reaction. The products were extracted with chloroform and the organic layer washed with water dried over anhydrous sodium sulphate and then concentrated, the products are separated by column chromatography using silica gel and eluting with varying proportions (100:0 to 70:30) (v/v) of hexane and chloroform, and were identified after concentrating the different fractions, the products were also detected by IR spectral studies and spot tests.

RESULTS AND DISCUSSION
Oxidation of cyclohexanol
The detailed kinetic data on the oxidation of cyclohexanol is given in Table 1.

Effect of oxidant
At fixed [H⁺] with [substrate] in excess, the plot of log absorbance against time was linear indicating first order in QxDC. But, the rate of the reaction decreased with increase in the concentration of oxidant. It is attributed to the decrease in effective concentration of Cr (VI) species in the reaction medium.

Effect of substrate
The rate of reaction is increased with increase the concentration of substrate. The order with respect to substrate was found to be fractional as evidenced by the linear plot of log k against log [s] with a double reciprocal plot of k against [s] gave a straight line indicating Michaelis-Menton type of kinetics in this reaction.

Effect of H⁺ion
The effect of added H⁺ion on the pseudo-first order rate constant was studied by adding HClO₄ in the region of 0.35-1.75 mol dm⁻³. The rate of reaction increased with increase the concentration of HClO₄. The plot of log k against log[H⁺] give a straight line with slope 0.503 (Fig. 1) indicating that the protonated species of the oxidant in the effective oxidant. It can be concluded that the reaction is simply an acid catalyzed one.

Effect of solvent and ionic strength
The effect of variation of solvent composition on the pseudo-first order rate constant was also studied. The rate was found to increase when the percent content of acetic acid increases. The data in Table 1 shows that the influence of ionic strength on rate constant is not significant. The reaction mixture showing the absence of any free radical in the reaction has ruled out the possibility of a one electron transfer during the addition of acrylonitrile. But a noticeable catalytic effect on the reaction rate on the addition of MnSO₄.

Effect of Temperature
The reactions were studied in the temperature range 303 K – 333 K for cyclohexanol (Table 2). An increase in temperature had resulted in an increase in the rate of the reaction. The activation parameters have been calculated using the Eyring’s plot and the least square analysis. From the kinetic data the following mechanism has been proposed.

### Table 1: Rate data on the oxidation of cyclohexanol by Quinoxalinium dichromate at 313 K

<table>
<thead>
<tr>
<th>[Cyclohexanol] (mol dm⁻³)</th>
<th>[QxDC] (mol dm⁻³)</th>
<th>[H⁺] (mol dm⁻³)</th>
<th>AcOH:H₂O (v/v)</th>
<th>[NaClO₄] (mol dm⁻³)</th>
<th>k x 10⁴ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 - 5.0</td>
<td>2.5</td>
<td>7.0</td>
<td>50:50</td>
<td>-</td>
<td>2.58 - 6.23</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0 - 4.0</td>
<td>7.0</td>
<td>50:50</td>
<td>-</td>
<td>3.85 - 2.03</td>
</tr>
<tr>
<td>2.0</td>
<td>2.5</td>
<td>3.5 - 17.5</td>
<td>50:50</td>
<td>-</td>
<td>2.53 - 5.82</td>
</tr>
<tr>
<td>2.0</td>
<td>2.5</td>
<td>7.0</td>
<td>40:60 - 60:40</td>
<td>-</td>
<td>1.98 - 4.98</td>
</tr>
</tbody>
</table>

### Table 2: Effect of temperature on the oxidation of cyclohexanol by quinoxalinium dichromate

<table>
<thead>
<tr>
<th>S.No</th>
<th>Temperature K</th>
<th>k x 10⁴ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>303</td>
<td>2.58</td>
</tr>
<tr>
<td>2</td>
<td>313</td>
<td>3.59</td>
</tr>
<tr>
<td>3</td>
<td>323</td>
<td>4.56</td>
</tr>
<tr>
<td>4</td>
<td>333</td>
<td>5.28</td>
</tr>
</tbody>
</table>

ΔH° = 10.98 kJmol⁻¹ \( \Delta S° = 197.38 JK^{-1} mol^{-1} \) \( \Delta G° = 72.76 kJmol^{-1} \)
Mechanism and Rate Law

\[ (C_{8}H_{8}N_{2})Cr_{2}O_{7}^{2-} + H_{2}O \xrightarrow{K_1} 2HCrO_{4}^{-} + C_{8}H_{8}N_{2}^{+} \]

\[ \begin{align*}
\text{O-H} & \quad \text{O} \quad \text{=Cr} \quad \text{OH} \\
\text{O-H} & \quad \text{O} \quad \text{=Cr} \quad \text{OH} \\
\text{O-H} & \quad \text{O} \quad \text{=Cr} \quad \text{OH} \\
\end{align*} \]

\[ \text{O-H} \quad \text{O} \quad \text{=Cr} \quad \text{OH} \quad \text{slow} \]

\[ \begin{align*}
\text{O-H} & \quad \text{O} \quad \text{=Cr} \quad \text{OH} \\
\text{O-H} & \quad \text{O} \quad \text{=Cr} \quad \text{OH} \\
\text{O-H} & \quad \text{O} \quad \text{=Cr} \quad \text{OH} \\
\end{align*} \]

\[ \begin{align*}
\text{Rate} & = k_{3}C_{1} \\
& = k_{3}K_{2} [\text{QxDC}] [S] \\
& = k_{3}K_{2}K_{1} [\text{QxDC}] [S] \\
-d [\text{QxDC}]/dt & = k_{obs}[\text{QxDC}][S] \\
\end{align*} \]

\[ r = 0.997 \quad B = 0.503 \]

Fig. 1: Plot of log k against log [H^+]


