

# Oxidation of Ester by Quinolinium Dichromate

Sarita Kushwaha<sup>1\*</sup>, Manisha Pradhan<sup>1</sup>

<sup>1</sup>Department of Chemistry, Government Girls P.G. College, Rewa-486001 (M.P.) India.

**Abstract:** Here we describe the kinetics of ethyl acetoacetate oxidation mediated by Quinolinium dichromate in aqueous acetic acid and mineral acid medium which yields to the formation of  $\alpha,\beta$ -diketo butyric acid. The uncatalyzed reaction is shown to proceed by complex mechanism involving a pre-equilibrium of its adducts. The reaction is first-order in [QDC] that follows protonated and non-protonated dependency showing occurrence of  $\alpha$ -C-H cleavage. The activation parameters have also been determined, which could be applied to explain all experimental phenomenon.

**Key words:** ethyl acetoacetate, Quinolinium dichromate, kinetics, oxidation, rate constant.

## 1. INTRODUCTION

Transition metal like chromium in a higher oxidation state acts as a good oxidant in a definite pH value medium. The oxidation of a few of organic compounds in higher oxidation state by Cr(VI)<sup>[1-4]</sup> has also been performed. It has been established that  $\text{HCrO}_4^-$  reacts with different ways to form complexes of different stabilities. Consequently, the rates and mechanism of oxidation of ester by QDC in different acids and ligand environments would be different.<sup>[5]</sup> Organic compounds of Quinolinium dichromate have long been known, subsequently, several papers have appeared on the oxidations of ethylene glycol cyclohexanediol, 2-furaldehydes,<sup>[6]</sup> and arsenic(II).<sup>[7]</sup>

Recently extensive studies of oxidation of active methylene compounds (ethyl acetoacetate) have been made with several oxidants, e.g. with thallium(III)<sup>[8]</sup> nicotinium dichromate,<sup>[8]</sup> isoquinolinium bromochromate,<sup>[10]</sup> halo-oxidant,<sup>[11]</sup> (N-chlorosaccharin) and rare earth oxide  $\text{SeO}_2$ ,<sup>[12]</sup> etc. Nevertheless, a systematic kinetic study of the oxidation of ester by QDC has not been made. It is with this aim that we undertook study on the oxidation of ethyl acetoacetate by QDC.

## EXPERIMENTAL

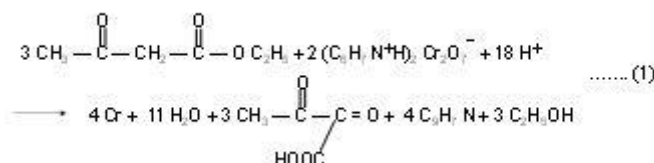
Materials-Quinolinium dichromate<sup>[13]</sup> solution was prepared by dissolving its appropriate weighed quantity in distilled water in a mineral acid. Its purity was checked iodometrically. Ethyl acetoacetate (B.D.H.) was used for kinetic oxidation first distilled under reduced pressure with a trace of Zn dust with immaculateness before setting experiments. Its solution was freshly prepared in water and little acetic acid. Various other required solutions of reagents were prepared which were chemically pure.

### Kinetic study

The required volume of oxidant (QDC) was taken in a pyrex flask and ester solution with acetic acid and  $\text{H}^+$  in another flask and immersed in the same water bath at 313 K. The kinetic study was followed under pseudo first-order condition  $[\text{EAA}] \gg [\text{QDC}]$   $[\text{H}^+]$ .

The reaction was initiated by mixing definite quantity of QDC with substrate's content and progress of the reaction was followed by estimation iodometrically for disappearance of QDC upto 80 to 85% completion of reaction. The rate constant  $k_{\text{obs}}$  was calculated by integration method.

The stoichiometric ratio  $\frac{\Delta[\text{QDC}]}{\Delta[\text{EAA}]}$  was observed as 2:3 as depicted in equation.



The products,  $\alpha,\beta$ -diketobutyric acid and ethanol were determined by their characteristics spot test,<sup>[14]</sup> and transforming into 2,4-dinitrophenylhydrazone derivative.

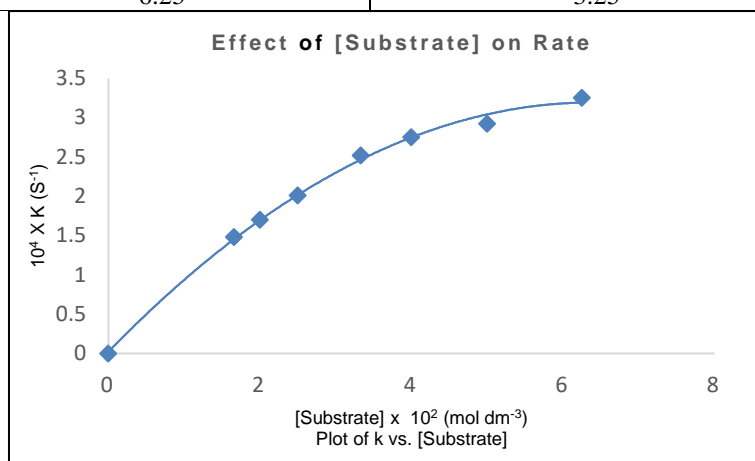
## Results and Discussion

In all kinetic runs, ethyl acetoacetic ester (EAA) concentration was kept in excess to oxidant. In QDC oxidant, variation rate values were calculated. The order with respect to [QDC] was confirmed by plotting  $\log(a-x)$  versus time (oxidant variation) which were dublicately averaged with reproducibility within  $\pm 4\%$  and order was found unity with respect to oxidant. Under fixed earlier conditions of the reaction, the  $\frac{-dc}{dt}$  values increase proportionately with rising [EAA] at low concentrations, but this increase is not much prominent at higher [EAA]. On graphic plotting, rate values against [EAA], a straight line passing through the origin is obtained in the beginning but its higher concentrations trend of the line becomes parallel to the X-axis (Table 1) apparent. Further, the double reciprocal plot of  $\frac{1}{k_{\text{obs}}}$  versus  $\frac{1}{[\text{EAA}]}$  confirms the facts of fraction-order of EAA and reaction tends to become independent (Fig. 1).

### Table 1: Dependence of rate on ethyl acetoacetate ester

$[\text{QDC}] = 3.33 \times 10^{-3}$  (mol  $\text{dm}^{-3}$ );  $[\text{H}^+] = 0.20$  (mol  $\text{dm}^{-3}$ );  
 $\text{CH}_3\text{COOH}-\text{H}_2\text{O} = 40 : 60$  % (v/v); Temperature = 313 K

$10^2 \times [EAA]$ (mol dm <sup>-3</sup> )	$10^4 k$ (sec <sup>-1</sup> )
1.66	1.48
2.00	1.70
2.50	2.01
3.33	2.52
4.00	2.75
5.00	2.92
6.25	3.25



To confirm removal of H<sup>+</sup> ions and reduction of ODC before rate determining step, the effect of these ions on the rate was studied by ch Fig. 1 [QDC]= 3.33×10<sup>-3</sup>(mol dm<sup>-3</sup>) ; [H<sup>+</sup>] = 0.20 (mol dm<sup>-3</sup>) ; reaction increases with increasing [H<sup>+</sup>] (Table 2). On plotting lg k v CH<sub>3</sub>COOH-H<sub>2</sub>O = 40:60%, (v/v) ; Temperature = 313 K hus, reaction was found acid catalyzed.

**Table 2: Effect of Acidity on Rate**

[QDC] = 3.33 × 10<sup>-3</sup> (mol dm<sup>-3</sup>) ; [EAA] = 2.50 × 10<sup>-2</sup> (mol dm<sup>-3</sup>) ;  
CH<sub>3</sub>COOH-H<sub>2</sub>O = 40 : 60 %, (v/v) ; Temperature = 313 K

[H <sup>+</sup> ] (mol dm <sup>-3</sup> )	$10^4 k$ (sec <sup>-1</sup> )
0.100	1.15
0.166	1.73
0.200	2.01
0.250	2.62
0.333	3.34
0.400	4.05
0.500	4.99

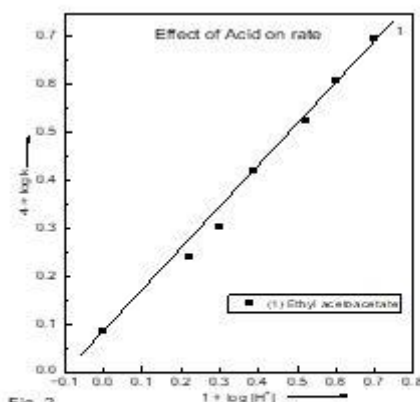


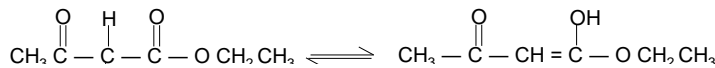
Fig. 2  
Plot of log k vs. log [H<sup>+</sup>]  
[QDC] = 3.33 × 10<sup>-3</sup> (mol dm<sup>-3</sup>) ;  
[Ethyl acetoacetate] = 2.50 × 10<sup>-2</sup> (mol dm<sup>-3</sup>) ;  
CH<sub>3</sub>COOH-H<sub>2</sub>O = 40 : 60 %, (v/v) ;  
Temperature = 313 K

The rate of reaction velocity was found positive within percentage composition of CH<sub>3</sub>COOH ranging from 30% to 60% (v/v). The selection of the solvent was restricted to acetic acid and water. It was observed that k<sub>obs</sub> accelerates by decrease in dielectric constant of the medium, follows. Amis concept of solvent employed indicating ion-dipole involved in the reaction mixture. The ionic strength of the medium (μ) and primary salt had shown inert effect towards rate. The added acrylonitrile (monomer) to the reaction did not induce polymerization clearly, rules out the involvement of initiation of free radicals based mechanism.

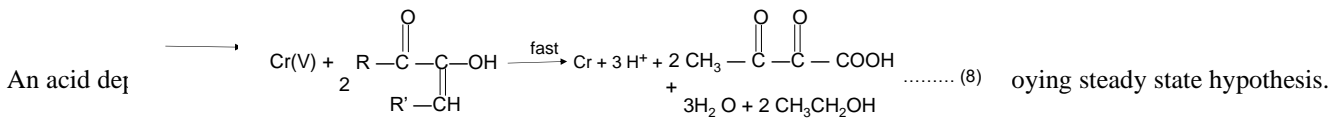
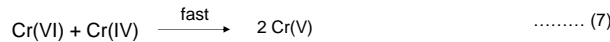
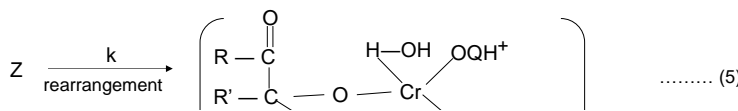
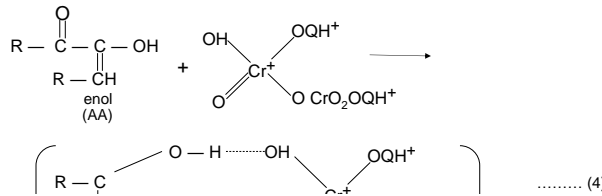
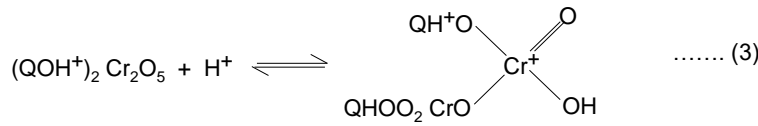
**Reaction Mechanism**

Based on foregoing work, stoichiometry results and involving enolic content of the ester, QDC- ethyl acetoacetate reaction mechanism was proposed as a mode :

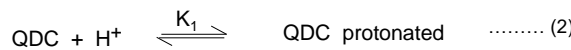
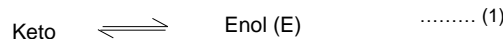
The converts  
**Scheme-I**



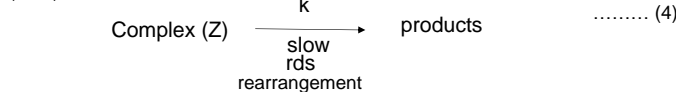
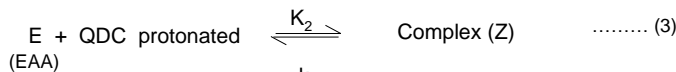
where, Q refer  
and R= -CH<sub>3</sub> an



Using steady state hypothesis.



**Rate law**



The values of [E] and [QDC] are derived and substituted in equation (1) to get

$$Rate = \frac{k K_1 K_2 [QDC]_t [H^+] [E]}{1 + K_1 K_2 [H^+] [E]} \dots\dots (8)$$

$$[QDC]_t = [QDC] + \text{Complex [Z]} \dots\dots (9)$$

$$k_{obs} = \frac{Rate}{[QDC]_t} \dots\dots (10)$$

From equation (8) and with collaboration of equation (10), we get final expression of rate law as :

$$k_{obs} = \frac{k K_1 K_2 [H^+] [E]}{1 + K_1 K_2 [H^+] [E]} \dots\dots (11)$$

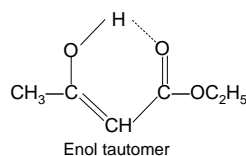
Rewriting equation (11) in inverse form, we get

$$\frac{1}{k_{obs}} = \frac{1}{k K_1 K_2 [H^+] [E]} + \frac{1}{k} \dots\dots (12)$$

Equation (12) explains the complex behaviour of the reaction verifying Michaelis-Menten type kinetic equation at its higher concentration and explains all the kinetic features.

The stream electronegative character of the α-C-H bond is weekend and fission takes place by loss of α-H atom.

The enol form of EAA is stabilized by intramolecular hydrogen bonding.



The values of thermodynamic parameters  $E_a$  (57.76 kJ mol<sup>-1</sup>),  $\Delta H^\ddagger$  (55.48 kJ mol<sup>-1</sup>),  $\Delta G^\ddagger$  (89.63 kJ mol<sup>-1</sup>) and  $\Delta S^\ddagger$  (-108.23 JK<sup>-1</sup> mol<sup>-1</sup>) were determined. Effect of solvation formation of transition state takes place when charge segregation occurs. The large negative value of  $\Delta S^\ddagger$  suppresses the translational and rotational degree of freedom, shows steric hindrance. Similar mechanism has also been earlier reported by many authors in oxidation of EAA by NDC<sup>[15]</sup> and IQBC<sup>[10]</sup> (Loc. cit.) respectively.

#### Conclusions

The QDC initiated oxidation of ethyl acetoacetic ester (EAA) exhibits first-order kinetics with respect to oxidant and fraction-order to enolic EAA. The reaction was fully catalyzed by H<sup>+</sup> ions. The observed molar ratio of reductant to QDC was 2:3. The corresponding products were  $\alpha,\beta$ -diketo acid and ethanol identified by forming 2:4-DNP derivatives. The protonated form of QDC participate in reaction with elimination of  $\alpha$ -H atom. It could be concluded that rate should be changed with position of several additives to molecules.

#### Acknowledgement

Authors are thankful to Principal and Head Govt. Girls P.G. College, Rewa (M.P.) for providing facilities (Laboratory and library) related to research work.

#### Conflict of Interest

None declared.

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