

# Pyridinium Dichromate Oxidation of Ethyl Acetoacetate - A Kinetic Approach

Umakant Sahu<sup>1\*</sup>, Nagmani Manikpuri<sup>2</sup>

1. Department of Chemistry, S.G.S. Govt. P.G. College Sidhi (M.P.) India.

2. Department of Chemistry, Govt. Nehru P.G. College Burhar, Distt. Shahdol (M.P.) India.

**Abstract:** Pyridinium dichromate (PDC) oxidative study of active methylene compound ethyl acetoacetate (EAA) in acetic acid produces product  $\alpha$ - $\beta$ -diketobutyric acid. A Michaelis-Menten type kinetics was observed for substrate ester while dependency on rate was noticed unity with respect to oxidant PDC. The oxidation kinetics accelerates with increase in proton concentration. The solvent polarity showed that the reaction was of ion-ion dipole type. A mechanism based on measured activation parameters in which rate controlling decomposition of the complex is suggested with a cyclic transition state.

**Keywords:** Pyridinium dichromate, ethyl acetoacetate, oxidation, kinetics, solvent polarity.

## 1. INTRODUCTION

Pyridinium dichromate (PDC) is principally related to Collins reagent<sup>1</sup> and is the pyridinium salt of dichromate  $[\text{Cr}_2\text{O}_7]^{2-}$ . The advantages of this salt is less reactive, more easily handled, more exotic adducts of nitrogen hetero cycles with Cr(VI), facilitate a number of oxidative transformation of organic compounds. When employed, it eliminates many of the operational hurdles associated with chromium-mediated oxidations. Methods employing in aqueous acetic acid for oxidations of substrates with hetero atom functionality that may co-ordinate to chromium.<sup>2</sup> The PDC seems to be behaved similar to newly synthesized Corye's reagents i.e. pyridinium halochromates used widely in oxidation kinetics of diols<sup>3-7</sup> etc. in different solvents. The survey of literature reveals that only few kinetic studies on esters are documented<sup>8,9</sup> with different oxidants. However, no study on PDC led oxidation of ethyl acetoacetate (EAA) in aqueous acetic acid medium so far available as an information in literature.

## 2. EXPERIMENTAL

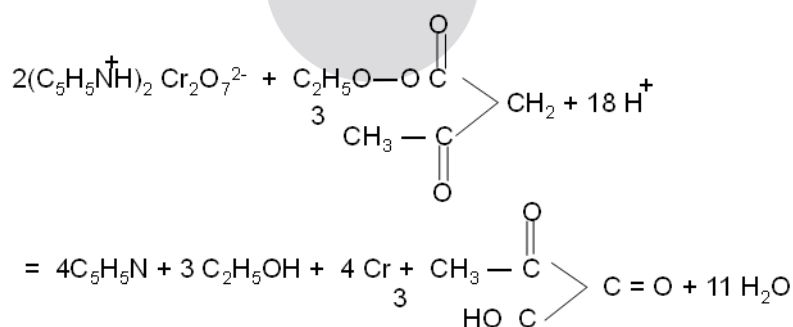
The ester ethyl acetate (B.D.H.) was distilled under reduced pressure before use and its solution was prepared by dissolving its requisite volume in acetic acid-water. PDC was prepared by the laid down procedure as mentioned in literature.<sup>10,11</sup> Its estimation was carried out by iodometric process. Other solvent and reagents were purified by the usual methods<sup>12</sup> and their solutions of desired concentrations were made in double distilled water.

### Kinetic Measurement

The pseudo first-order condition was attained by maintaining an excess ( $\times 10$  or greater) of the EAA over the [PDC]. The reaction was studied at constant temperature ( $\pm 0.1\text{K}$ ). The solvent was unless stated otherwise and was followed by the determining the disappearance of [PDC] iodometrically for up to 75-80% completion of the reaction. The pseudo first-order rate constant, was evaluated from the linear graphical plots of  $\log [\text{PDC}]$  against time. The duplicate kinetic run indicated that the  $k_{\text{obs}}$  were reproducible to within  $\pm 3\%$ .

## 3. Results and Discussions:

The oxidation of active methylene compound (ethyl acetoacetate) by pyridinium dichromate resulted in the formation of  $\alpha$ , $\beta$ -diketobutyric acid under the existing experimental conditions, no further oxidation of the product was observed. The stoichiometric experiment was performed under the condition of  $[\text{PDC}] > [\text{EAA}]$  at 308K under nitrogen atmosphere. The stoichiometric ratio  $\Delta[\text{PDC}] / \Delta[\text{EAA}]$  was determined 2/3 i.e. 3 moles of EAA are consumed by 2 moles of oxidant, which leads to the reaction.



Under pre-set conditions of the reaction, the reaction product was extracted with ether, that was removed and finally product was recrystallized with yield 85%. The isolated product  $\alpha,\beta$ -diketobutyric acid was also confirmed by forming its disemiacarbazone<sup>13</sup> after recrystallized from ethanol.

The added acrylonitrile did not affect the rate, rules out the involvement of one electron oxidation obscure to free radicals, is unlikely in the present task of reaction.

The reaction was initiated at constant temperature and was monitored by decrease in the concentration of PDC at 303K for upto 80% of the reaction. The rate constants did not vary with initial [PDC]. The individual kinetic runs was first-order with respect to [PDC].

The kinetic order rate with respect to the [EAA] was determined as less than one at its higher concentration showing complex kinetics between protonated PDC and enol form of EAA.

The reaction under investigation was catalysed by acid and  $-d/dt$  [PDC] varies as a first-power of  $[H^+]$  (Table 1). The reaction showed first-order, the study pours an ample of evidence in support of above fact graphically. The lg-lg plot of  $k_{obs}$  vs.  $[H^+]$  with slope  $> 0.971$  and  $r^2 > 0.98$  (Fig.1).

**Table. 1: Dependence of the reaction rate on hydrogen ion concentration**

[Ethyl acetoacetate] =  $1.66 \times 10^{-1}$  (mol dm<sup>-3</sup>); [PDC] =  $3.33 \times 10^{-3}$  (mol dm<sup>-3</sup>);  
HOAc-H<sub>2</sub>O = 20 %, (v/v); Temperature = 308 K

$[H^+]$ (mol dm <sup>-3</sup> )	0.08	1.25	2.0	0.25	0.333	0.40
$10^4 k$ (s <sup>-1</sup> ) for EAA	1.03	1.55	2.22	2.91	3.75	4.74

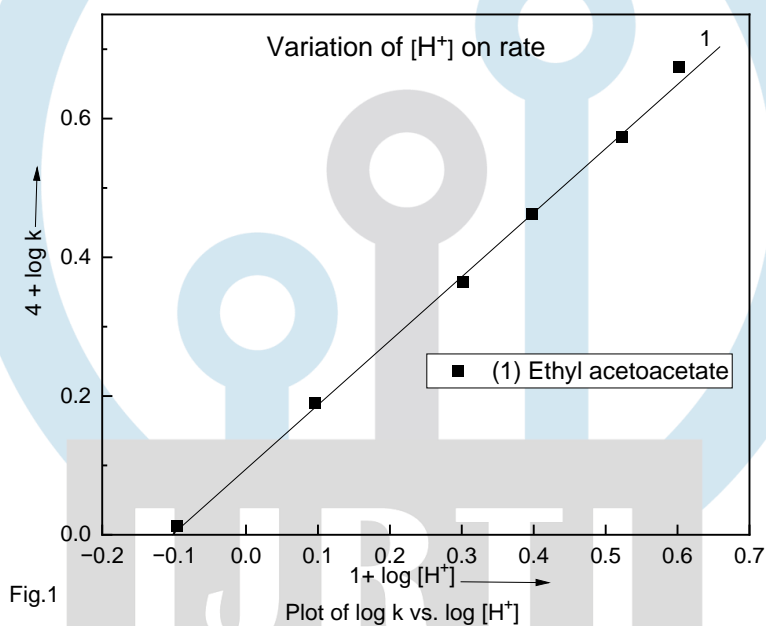


Fig.1

Plot of  $\log k$  vs.  $\log [H^+]$   
[Ethyl acetoacetate] =  $1.66 \times 10^{-1}$  (mol dm<sup>-3</sup>); [PDC] =  $3.33 \times 10^{-3}$  (mol dm<sup>-3</sup>);  
HOAc-H<sub>2</sub>O = 20 %, (v/v); Temperature = 308 K

The rate constant  $k$  was determined by considering a complete range in solutions containing varying proportions (10-50%) of CH<sub>3</sub>COOH and H<sub>2</sub>O. A decrease in the dielectric constant ( $D$ ) of the medium increased the rate of oxidation (Table 2). The positive slope evaluated from the plot of  $\lg k$  vs.  $1/D$  reaction covered evidence for the fact that is of the ion-dipole type (Fig.2).

**Table.2: Dependence of rate constants on Solvent composition**

[Ethyl acetoacetate] =  $1.66 \times 10^{-1}$  (mol dm<sup>-3</sup>); [PDC] =  $3.33 \times 10^{-3}$  (mol dm<sup>-3</sup>);  
[H<sub>2</sub>SO<sub>4</sub>] = 0.20 (mol dm<sup>-3</sup>); Temperature = 308 K

H <sub>2</sub> O-Ac OH (%,(v/v))	90-10	80-20	70-30	60-40
$10^3/D$	15.15	17.17	19.15	21.98
$10^4 k$ (s <sup>-1</sup> ) for ethyl acetoacetate	1.38	2.22	2.69	4.26

The primary salt effect was found negligible on rate of oxidation.

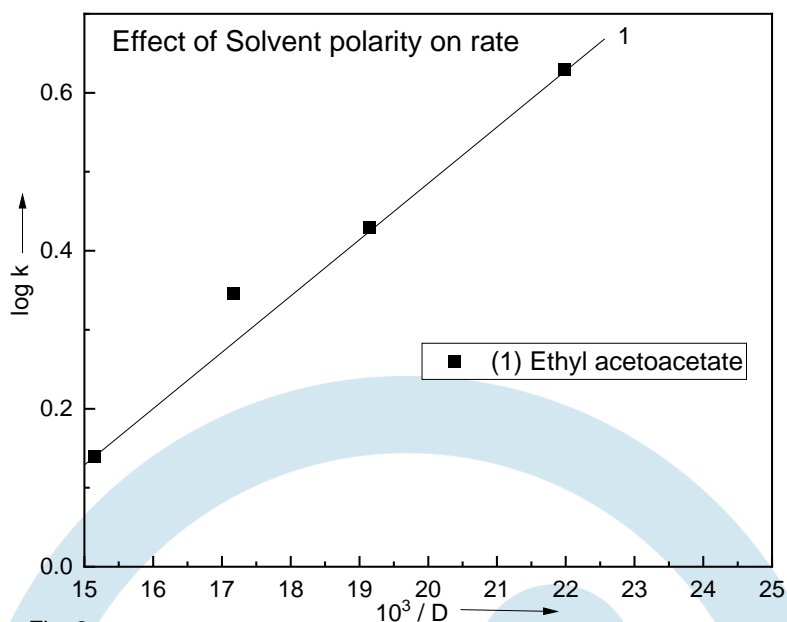
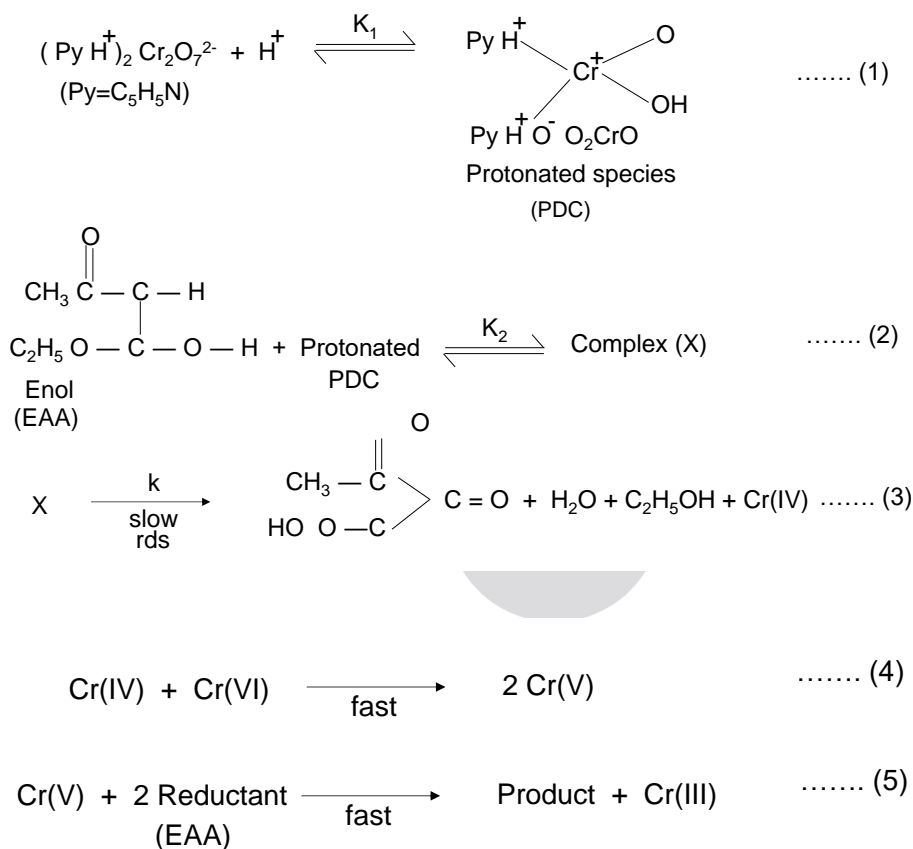


Fig. 2 Amis plot of  $\log k$  against  $1/D$   
 Ethyl acetoacetate] =  $1.66 \times 10^{-1}$  (mol  $\text{dm}^{-3}$ ); [PDC] =  $3.33 \times 10^{-3}$  (mol  $\text{dm}^{-3}$ );  
 [H<sub>2</sub>SO<sub>4</sub>] = 0.20 (mol  $\text{dm}^{-3}$ ) ; Temperature = 308 K

**Mechanism**

**Scheme-I**

The prevalent mechanism based on attack of protonated species of PDC on the enolic ester in the oxidation reaction is proposed.



**Rate law**

The mechanism suggests the following rate law

$$-\frac{d}{dt}[\text{PDC}] = k[\text{X}] \dots \dots \dots (1)$$

$$\text{whereas, } [\text{X}] = K_2 [\text{EAA}][\text{PDC}] \dots \dots \dots (2)$$

Its value is, derived and substituted in equation (1) to get rate as :

$$\text{Rate (R)} = \frac{k K_1 K_2 [\text{Cr(VI)}]_t [\text{H}^+] [\text{EAA}]}{1 + K_1 K_2 [\text{H}^+] [\text{EAA}]} \dots \dots \dots (3)$$

$$\text{Total concentration of } [\text{Cr(VI)}]_t \text{ i. e. } [\text{PDC}] = \text{Cr(VI)} + [\text{complex (X)}] \dots (4)$$

Here  $K_1$  is small and protonated species of PDC commences the reaction with ethyl acetoacetate

$$\therefore \text{Rate} = k_{\text{obs}} \times [\text{Cr(VI)}]_t \dots \dots (5)$$

From equation (3) and equation (4) in collaboration with equation (5) give rise the final expression for rate law

$$k_{\text{obs}} = \frac{k K_1 K_2 [\text{EAA}][\text{H}^+]}{1 + K_1 K_2 [\text{EAA}][\text{H}^+]} \dots \dots \dots (6)$$


The reciprocal of  $k_{\text{obs}}$  equation (6) yields as equation (7)

$$k_{\text{obs}}^{-1} = \frac{1}{k K_1 K_2 [\text{H}^+] [\text{EAA}]} + \frac{1}{k_2} \dots \dots \dots (7)$$

explains all the kinetic facts.

There was ample of kinetic evidence for the formation of chromite ester intermediate<sup>14</sup> in any appreciable concentration between the EAA and PDC as verified by the double reciprocal plot of  $k_{\text{obs}}^{-1}$  vs.  $[\text{EAA}]^{-1}$  with positive intercept on rate axis. The decomposition of the chromate ester would be facilitated/ feasible only when there is no rate enhancing steric hindrance in the transition state.

The mechanism supports the view that the oxidation of EAA would involve the protonation of carbonyl group or de-protonation of  $\alpha$ -CH of the conjugated acid. However, enol (EAA) is acid with 18.0 % content and  $\text{p}K_a = 11$  comparable to phenol  $\text{p}K_a = 10$ . Therefore, esterification would be small, hence attack of protonated species at double bond seems to be more probable. The proposed mechanism is also supported by the observed negative value of entropy activation ( $-89.68 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $E_a$  ( $55.42 \text{ kJ mol}^{-1}$ ). The

two ends become extremely, solvated when charge egression occurs. The  group is stabilized by resonance due to formation of intramolecular hydrogen bonding showing conjugate effect and steric hindrance. Similar mechanism has also been reported earlier by the eminent kinetists, in the oxidation of EAA by oxidants- NDC<sup>15</sup> and IQBC<sup>16</sup> respectively.

**Conclusions**

The oxidation of ethyl acetoacetate by pyridinium dichromate in aqueous acetic acid medium yields  $\alpha$ - $\beta$ -diketobutyric acid and ethanol as the corresponding products. The stoichiometric ratio  $\frac{\Delta[\text{PDC}]}{\Delta[\text{EAA}]}$  was determined as 2/3. A  $\alpha$ -C-H bond is cleaved in the rate determining step. The observed acid dependence of the reaction points to a reversible protonation of the enolic EAA to form intermediate complex prior to its disproportionation, A mechanism depicted in Scheme-1 accounts for the experimental results. The rate law based on postulated mechanism was derived.

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**Conflict of Interest**

The authors declare conflict of no interest whatsoever.

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