Kinetics and Mechanism of Oxidation of Ethyl acetoacetate by Pyridiniumbromochromate in Acetic Acid Medium

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Abstract-

The kinetics of oxidation of ethyl acetoacetate by þyridiniumbromochromate (PBC) in aqueous acetic acid medium yields α,-β-diketo acid as the main product. The stoichiometry corresponds to the reaction of two moles of PBC for 3 moles of substrate. The rate of reaction varies as a first power of concentration of oxidant. The reaction is being nearly first-order in acidity. The reaction does not induce polymerisation of acrylonitrile. The suggested rate law corresponds to the plausible reaction mechanism are discussed.

Key words: Pyridiniumbromochroamate, ethyl acetoacetate, oxidation, kinetics, stoichiometry.

1. INTRODUCTION

The kinetic studies employing þyridiniumbromochromate, a complex of chromium(VI) heterocyclic base pyridine and acid in acetic acid[1] medium are comparatively less known than the oxidation studies by its parent analogue PCC and PFC. There are only few reports available on the kinetics aspects of oxidation reactions involving PBC.[2-5] A perusal of literature showed that some oxidizing agents, oxidize active methylene compounds through α-C-H bond fission resulting in the formation of carbonyl compounds. The different Cr(VI)[6-10] complex showed different kinetic and mechanistic pathways of the oxidation of active methylene compounds. However, no such report was found in literature on the kinetics of oxidation of ethyl acetoacetate by PBC. The present study was aimed PBC oxidizes EAA in the redox system and its mechanistic aspects are discussed.

2. EXPERIMENTAL

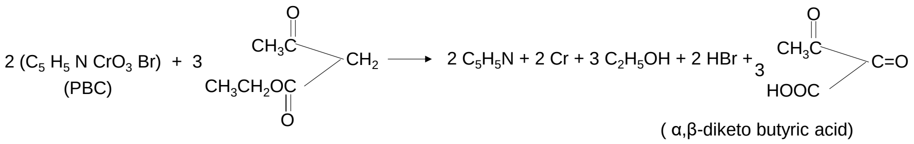
The PBC was prepared by the reported method and its purity was checked by estimating Cr(VI) iodometrically. The ethyl acetoacetate was obtained from B.D.H. and was used after distillation. Acetic acid (B.D.H.) used was distilled, at 115.8^0C.

Kinetic procedure

The kinetic study was initiated by allowing reaction in glass stoppered corning glass vessels. All ingredients of the reaction mixture except PBC were taken in a separate flasks kept in a thermostat ($\pm 0.1^0$C). The solution of temperature pre-equilibrated PBC of appropriate concentration was withdrawn and then time of initiation was recorded. An aliquot of the reaction mixture (2 cm^3) was withdrawn at different intervals of time and then discharged into (~10%) ice cold KI solution. The liberated iodine was titrated against sodium thiosulphate solution using starch as an indicator. The results in duplicate were reproducible to within ± 4%.

Initial rate (k_{obs} s^{-1}) were computed employing integration and graphical methods. Pseudo first-order plot (log [PBC] vs. time) was also made wherever reactions allowed.

The reaction was allowed to occur in a thermostated water-bath at 35^0C for 6 h under defined conditions $[PBC]_0$ > [ethyl acetoacetate]$_0$. The excess of PBC was determined iodometrically after completion of the reaction. The results indicate that two moles of the oxidant (PBC) require three moles of ethyl acetoacetate corresponding to stoichiometry represented by equation (1).



(where, Py = (C_6H_5N) is actually Pyridine)

Product analysis

The oxidation product α,β-diketo butyric acid was characterized and estimated by the isolation of its disemicarbazone[12] of α,β-diketo butyric acid. A one electron oxidation, giving rise to free radicals, is unlikely in view of the failure to induce polymerization of acrylonitrile[13].

3. Results and Discussion

The concentration of pyridiniumbromochromate was varied in the range (1.5 – 6.25 × 10^{-3} mol dm^{-3}) at constant concentrations of other reaction ingredient. A plot of initial rate against [PBC] yielded a straight line passing through origin. The slope value confirming first-order dependence with respect to PBC.

The concentration of ethyl acetoacetate (EAA) was varied nearly five times at pre-set conditions of the reaction. The study reveals to follow first-order kinetics at low concentration (EAA) and order falls from one to zero it its higher concentration. The study shows the existence of cyclic chromite ester complex at polar transition state (Table 1). The complex nature was confirmed by the double reciprocal plot 1/ k_{obs} vs. 1/[EAA] yielding non-zero intercept on ordinate [EAA] axis (Fig. 1). The rate coefficient k_{obs} increases with increase in hydrogen ion concentration and catalysed reaction has the form $k_{obs} = a + b [H^+]$, showing almost first-order reaction. The concentration of H_2SO_4 equinormally produces a large numbers of H^+ ions and thereby catalyses the reaction rate to a greater extent. The reaction was assessed by varying percentage composition (30-60%, (v/v) of acetic acid and enhancement in rate of oxidation of EAA was observed. The reaction follows Swain's equation[14]. It is reported that [11,12] extent of enolization is greatly affected by solvent concentration, that can be described in terms of multi para-metric.[15]

Table 1: Substrate Dependene of the Reaction rate
[PBC] = 3.33 ×10^{-3} (mol dm^{-3}) ; $[H^+]$ = 0.166 (mol dm^{-3}) ;
CH_3COOH : H_2O = 40 : 60% (v/v) ; Temp. = 308 K

[EAA]×10^2 mol dm^{-3}	**1.50**	**2.00**	**2.50**	**3.33**	**4.00**	**6.25**
10^4 k (s^{-1})	1.23	1.53	1.85	2.24	2.66	3.32

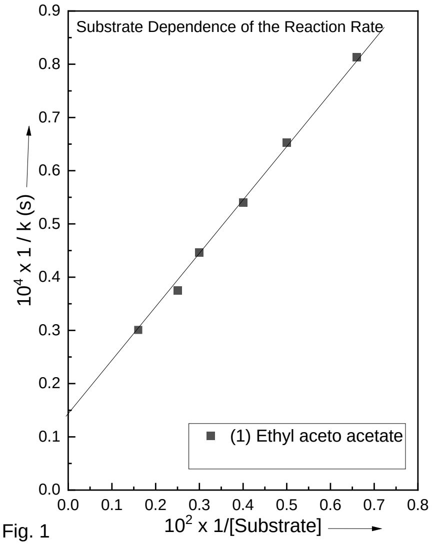
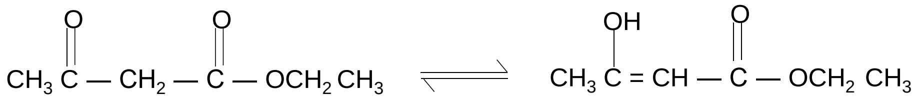


Fig. 1

Double reciprocal plots of 1/ k_{obs} vs. 1/[Substrate]
[PBC] = 3.33 x 10^{-3} (mol dm^{-3}) ;
[H^+] = 0.166 (mol dm^{-3}) ;
CH_3COOH-H_2O = 40 : 60 % (v/v) ;
Temp. = 308 K

The effect of ionic strength and employing neutral sodium chloride at fixed concentration, the pseudo first-order constant (k_{obs} s^{-1}) almost remains stationary.t

The result of enolization of EAA determined by bromination[5] method assigned enol form of reacting species. The two electron attracting> C=O groups, being highly acidic, enolize rapidly and stabilized by resonance.



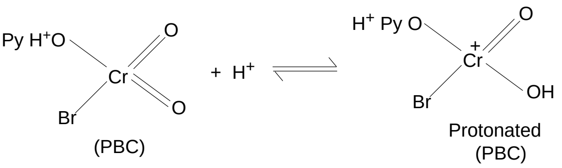
$$CH_3\overset{O}{\overset{\|}{C}} — CH_2 — \overset{O}{\overset{\|}{C}} — OCH_2CH_3 \rightleftharpoons CH_3\overset{OH}{\overset{|}{C}} = CH — \overset{O}{\overset{\|}{C}} — OCH_2\,CH_3$$

…… (2)

The Cr(VI) species are well speciated. The observed H^+ ion dependence suggests that reaction follows two mechanistic pathways one acid independent and another acid dependent. The acid catalysts may well attributed a protonation of either PBC to yield protonated Cr(VI) species which is a stronger oxidant and electrophile or the chromite ester with both the protonated and unprotonated forms being reactive.[16]

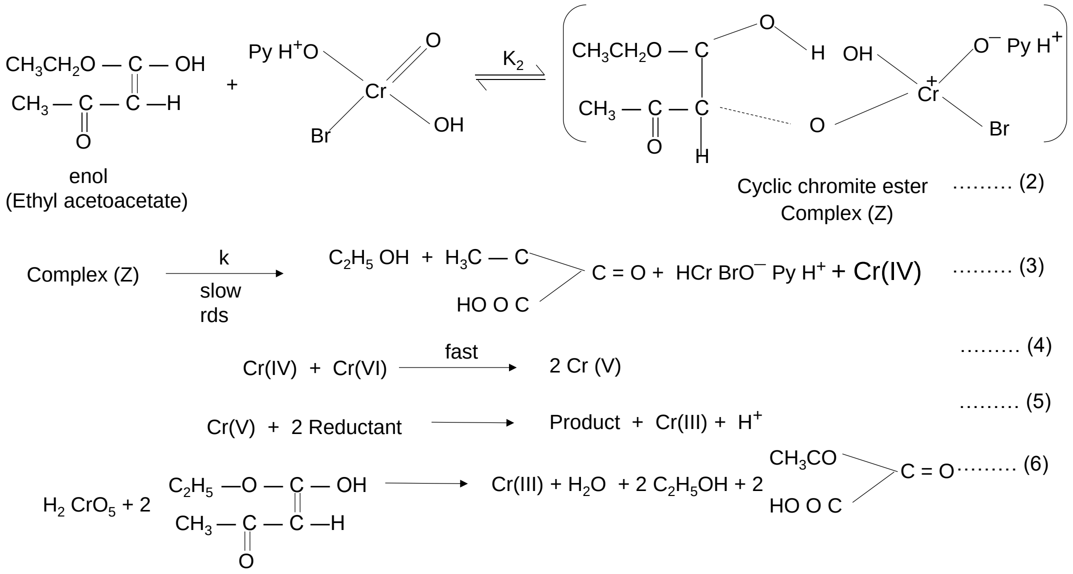
Mechanism

The protonated Cr(VI) species of the oxidant attacks at enolic ethyl acetoacetate to form intermediate complex prior to decomposition to product. The acid dependent path of the proposed mechanism is outlined.



………. (1)

where, Py = C_6



Rate Law

The rate expression for acid dependent path involved in mechanism can be deduced as :

$$\mathrm{PBC} + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} \underset{\text{Protonated oxidant}}{\mathrm{PBC\ H}^+} \qquad \text{......... (1)}$$

$$\text{Enol (substrate)} + \mathrm{PBC\ H}^+ \overset{K_2}{\rightleftharpoons} \text{Complex (Z)} \qquad \text{......... (2)}$$

$$\text{Complex (Z)} \xrightarrow[\text{slow}]{k} \text{Product} + \mathrm{Cr(IV)} \qquad \text{......... (3)}$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \xrightarrow{\text{fast}} 2\ \mathrm{Cr\ (V)} \qquad \text{......... (4)}$$

$$\mathrm{Cr(V)} + 2\ \text{Reductant} \longrightarrow \text{Product} + \mathrm{Cr(III)} + \mathrm{H}^+ \qquad \text{......... (5)}$$

The $Rate\ [Cr(VI)] \propto [Z]\ \ldots\ldots(6)$

$$Rate\ [Cr(VI)] = k\ [Z]\ \ldots\ldots(7)$$

Substituting the value of [Z] in equation.

$$r = k\ K_1 K_2\ [H^+][Enol]\quad \ldots\ldots(8)$$

or $r = k\ K_1 K_2\ [H^+][Enol] \times [Cr(VI)]\quad \ldots\ldots(9)$

On simplification of various steps involved in the mechanism.

$$Rate[Cr(VI)] = \frac{k\ K_1 K_2 [Enol][H^+][Cr(VI)]_t}{1 + K_1 K_2 [Enol][H^+]}\quad \ldots\ldots(10)$$

Since $Rate = k_{obs} \times [Cr(VI)]_t$ .... (11)

and $[Cr(VI)]_t = [Cr(VI) + [Z]$ ...... (12)

Applying the concept of steady-state approximation and employing the equations (10), (11) and equation (12) we get final rate law as :

$k_{obs} = \frac{k\ K_1 K_2 [E][H^+]}{1 + K_1 K_2 [E][H^+]}$ ..... (13)

This equation (13) apparently accounts all the kinetic results. The inverse of equation (13) so as to get equation.

$$\frac{1}{k_{obs}} = \frac{1}{k\ K_1 K_2 [E][H^+]} + \frac{1}{k}\quad \ldots\ldots\ (14)$$

This equation when brought in a graphical form with non-zero intercept on explains fraction-order kinetics with respect to EAA i.e. existence of complex at transition state, which is not to be much susceptible to structural influence.[17] The disproportionation of the complex facilitated due to de-protonation of α-C-H of the conjugate acid. The negative value of entropy of activation ($\Delta S^{\#}$) (Table 2) favours the proposed mechanism.

The substrate under investigation is stabilized by resonance as it forms intra molecular hydrogen bonding showing simultaneously conjugate effect and steric hinderance.[16] The thermodynamic parameters were determined and plots of ln k vs. 1/T was made of Ea for perusal (Fig. 2).

Table 2: Temperature dependence of the reaction constant and activation parameters

[PBC] = 3.33 ×10^{-3} (mol dm^{-3}) ; [H^+] = 0.166 (mol dm^{-3}) ;
CH_3COOH : H_2O = 40 : 60% (v/v)

Temp. = ± 0.1 K	10^4 k (s^{-1}) ←	→
	[Ethyl acetoacetate] = 2.50 ×10^{-2} (mol dm^{-3}) (s)	[Ethyl acetoacetate] = 3.33 ×10^{-2} (mol dm^{-3}) (s)
303	1.28	1.55
308	1.85	2.24
313	2.67	3.23
318	3.84	4.65
Ea (kJ mol^{-1})	57.55	
$\Delta H^{\#}$ (kJ mol^{-1})	55.27	
-$\Delta S^{\#}$ (JK^{-1} mol^{-1})	-105.82	
$\Delta F^{\#}$ (kJ mol^{-1})	88.63	

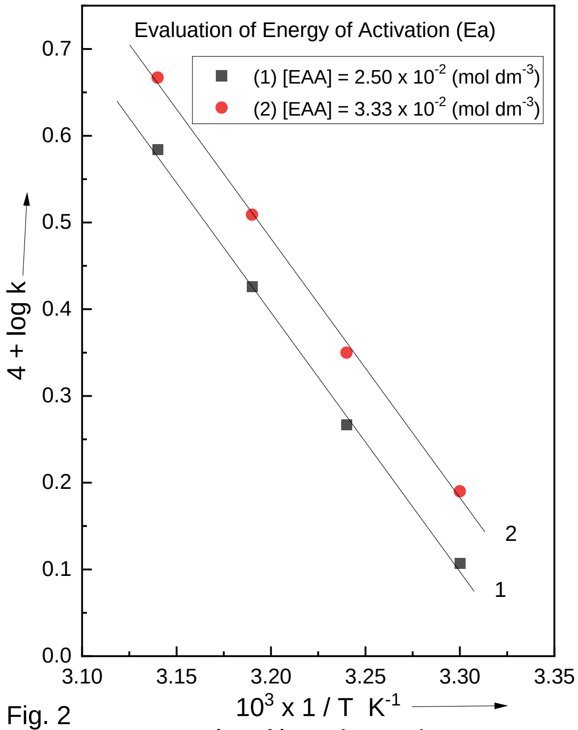


Fig. 2

Plot of $\log_{10}$ k vs. 1/T

[PBC] = 3.33 x 10^{-3} (mol dm^{-3}) ;
[H^+] = 0.166 (mol dm^{-3}) ;
CH_3COOH-H_2O = 40% (v/v)

Conclusion

The oxidation of ethylacetoacetate (EAA) by þyridiniumbromochromate (PBC) in aqueous acetic acid is first-order with respect to PBC and reaction exhibited Michaelis-Menten type kinetics for EAA. The reaction is catalysed by hydrogen ions, has the form $k_{obs} = a + b [H^+]$. The stoichiometry was assigned 2:3. The enolic form of substrate takes part in reaction. The oxidation leads to the formation of corresponding α-β-diketo butyric acid as the product.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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