



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 10, Issue, 06(B), pp. 32822-32825, June, 2019

**International Journal of
Recent Scientific
Research**

DOI: 10.24327/IJRSR

Research Article

KINETIC STUDY OF ETHYL ACETO ACETATE AND MALONIC ESTER BY ISOQUINOLINIUM BROMOCHROMATE IN ACETIC ACID MEDIUM

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DOI: <http://dx.doi.org/10.24327/ijrsr.2019.1006.3455>

ARTICLE INFO

Article History:

Received 06th March, 2019

Received in revised form 14th

April, 2019

Accepted 23rd May, 2019

Published online 28th June, 2019

ABSTRACT

The kinetic study of ethyl aceto acetate (EAA) and Malonic ester (ME) by Isoquinolinium bromochromate (IQBC) in aqueous acetic acid medium is presented. The reaction obeys a fractional-order with respect to substrates and first-order with respect to oxidant IQBC. The added H⁺ catalysed the reaction rate. The rise in percentage of acetic acid increased the rate of reaction. The redox reaction did not initiate polymerization with acrolonitrile and free-radical mechanism is ruled out. Based on the observations and determined activation parameters for the reactions a plausible mechanism and rate law were proposed.

Key Words:

polymerisation, activation,
conformity, stoichiometry, reactivity

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INTRODUCTION

Isoquinolinium bromochromate is a milder, more selective reagent than other chloro derivative of the isoquinoline. IQBC has been served as an oxidant for a number of transformations including alcohol¹, aniline² etc. Furthermore IQBC has emerged as the reagent of choice for the activations of aliphatic ketones³ and protonation of dialkyl acetone dicarboxylates⁴. Diketo esters (ethyl aceto acetate and diethyl melonate) belong to the active methylene compounds containing -CH₂- group interconnected by highly electrophilic two carbonyl system. Diketone esters are oxidized by different oxidizing agents and in all these reactions either > C=O or enolic substrate is attacked by the oxidant. The kinetics and oxidation of substrates by various oxidants like selenium dioxide,⁵ Nicotinium dichromate⁶, N-chlorosaccharin⁷, have been extensively carried out by many eminent workers. In recent years, the kinetic studies on the oxidation and halogenation of organic compounds by IQBC are gaining importance due to its applications in organic synthesis and also due to kinetic aspects. Since the IQBC exhibits, appreciable stability both in acid and alkaline medium, it is used as a redox titrant in analytical chemistry. It has found limited applications and only few reports are available of its uses in organic synthesis.

Literature survey reveals that no report was available on the kinetics of oxidation of diketo esters (ethyl aceto acetate, and malonic ester) by IQBC. Hence authors have chosen them for kinetic probe.

MATERIALS AND METHODS

All the chemicals and solvents used were of analytical grade. The solutions of ethyl aceto acetate (E. Merck) and malonic ester (GR grade) were prepared by dissolving their required amounts in CH₃COOH (B.D.H.). The solution of IQBC was prepared by taking its appropriate quantity in 100% acetic acid (B.D.H.), and its strength was judged iodometrically.⁸ The other important solutions required in experimental work such as oxalic acid, copper sulphate, potassium iodide, NaOH, and Na₂S₂O₃ were prepared as per procedure laid down in literature⁹. All the reactions were carried out in thermostat and the temperature was maintained ± 0.1^oC.

The kinetic studies were carried out in an aqueous acetic acid medium. The reactions were performed by maintaining a large excess of [diketo ester] over [IQBC]. The reaction mixture was homogeneous throughout the course of the reaction. The reaction rate was found by determining the amount of the consumed IQBC iodometrically upto 80% completion of the reaction. The rate constant k_{obs} were measured from the slopes

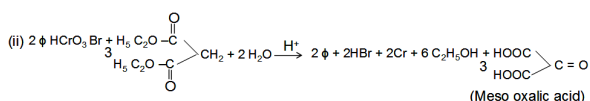
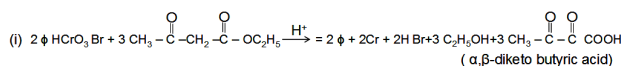
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of linear plots of \log [titre] versus time. The replicate runs showed that the k_{obs} for the oxidation reactions were reproducible within $\pm 3\%$.

RESULTS AND DISCUSSION

The stoichiometry of reaction was found out by installing several sets of experiment in duplicate by varying [IQBC]. The unconsumed IQBC remained after completion of the reaction realized that 3:2 (diketo ester: IQBC) seemed necessary. The fate of stoichiometric reactions can be represented as :



Where ϕ = isoquinoline.

α,β -diketo butyric acid and meso oxalic acid were isolated to be the major products of oxidation and were detected chromatographically, with those of the authentic samples and also by forming di-semicarboxone of α,β -diketo butyric acid and other existing chemical tests. The reactions completely fail to initiate polymerization on addition of monomers like acrylonitrile shows inertness for presence of free radicals.¹⁰

The factors affecting the rate of oxidation of EAA and ME by Isoquinolinium bromochromate such as [EAA], [ME], [IQBC], $[\text{H}^+]$ and dielectric constant have been studied. Rate of the reaction and activation parameters were evaluated.

At a constant [IQBC], $[\text{H}^+]$ and 40% of CH_3COOH , kinetic runs were carried out, with fixed various initial concentrations of EAA and ME, which yielded rate constant whose values depend on [substrates]. The pseudo first-order rate constants (k_{obs}) thus obtained were found to increase with [substrate]. The plot of $\log k_{\text{obs}}$ versus \log [substrate] at it higher concentration is liner with slope less than unity showing that the reaction is fraction-order in [substrate]. The plot of k_{obs}^{-1} versus [substrate]⁻¹ is linear with definite intercept on the rate ordinate, which indicates the operation of Michaelis-Menten mechanism.

The kinetics of oxidation of substrates have been examined at various initial concentrations of oxidant (IQBC) (1.25×10^{-3} - 5.0×10^{-3} mol dm^{-3}) and at fixed concentrations of other reactants and temperatures. The plot of \log [IQBC] versus time was found to be linear indicating first-order dependence on the reaction rate and from the slope of such plots pseudo first-order rate constant was evaluated.

The reaction rate constants measured with various $[\text{H}^+]$ (0.50×10^{-3} - 2.50×10^{-3} mol dm^{-3}) were found to increase with increase in H^+ ion concentration (Table 1). The order of reaction with respect $[\text{H}^+]$ is one (Plot of $\log k$ versus \log $[\text{H}^+]$) Fig. 1.

$$10^2 \times [\text{Ester}] (\text{mol dm}^{-3}) = 2.50 (1, 2);$$

$$10^3 \times [\text{IQBC}] (\text{mol dm}^{-3}) = 2.0 (1, 2);$$

$$\text{CH}_3\text{COOH-H}_2\text{O}, \%(v/v) = 40 (1, 2);$$

$$\text{Temperature } K = 313 (1, 2)$$

Table 1 Dependence of rate on concentration of Acid

S. No.	[Substrate] $\times 10^2$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$	
		Ethyl aceto acetate (1)	Malonic ester (2)
1.	0.50	1.13	0.81
2.	1.00	2.14	1.63
3.	1.50	3.59	1.94
4.	2.00	4.35	2.89
5.	2.50	5.71	3.37

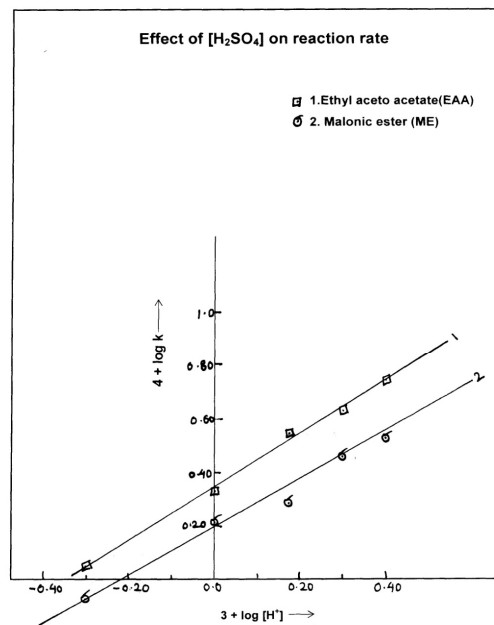


Fig. 1 $10^2 \times [\text{Substrate}] (\text{mol dm}^{-3}) = 2.50 (1, 2);$
 $10^3 \times [\text{IQBC}] (\text{mol dm}^{-3}) = 2.0 (1, 2);$
 $\text{CH}_3\text{COOH-H}_2\text{O}, \%(v/v) = 40 (1, 2);$
 Temp. $K = 313 (1, 2)$

The effect of dielectric constant (polarity) of the medium on rate of oxidation of EAA and ME by IQBC was analyzed in aqueous CH_3COOH mixtures of various compositions (Table 2). The data clearly revealed that the rate increases in the percentage of acetic acid (Fig. 2). The impact of ionic strength of the medium and neutral salt had in significant on rate whereas foreign added catalyst Cu^{++} ion indicates the increase in rate. The impact of temperature was observed in the range of 308-323 K and the results of several parameters calculated were shown in Table 3. It is obvious from the values that both the parameters ΔH^\ddagger and ΔS^\ddagger are important in controlling the rates of reactions though the enthalpy factor appears to be more predominating. The value of ΔS^\ddagger is negative indicating the loss of entropy during the formation of activated complex.

$$10^2 \times [\text{Ester}] (\text{mol dm}^{-3}) = 2.50 (1, 2);$$

$$10^3 \times [\text{IQBC}] (\text{mol dm}^{-3}) = 2.0 (1, 2);$$

$$10^3 \times [\text{H}^+] (\text{mol dm}^{-3}) = 1.50 (1), 2.0 (2);$$

$$\text{Temperature } K = 313 (1, 2)$$

Table 2 Effect of Dielectric constant of the medium on reaction rate

S. No.	HOAc-H ₂ O % (v/v)	10 ³ /D	$10^4 k (\text{s}^{-1})$	
			Ethyl aceto acetate (1)	Malonic Ester (2)
1.	30	19.15	2.88	2.42
2.	40	21.98	3.59	2.89
3.	50	25.64	4.36	3.45
4.	60	30.36	5.61	4.09

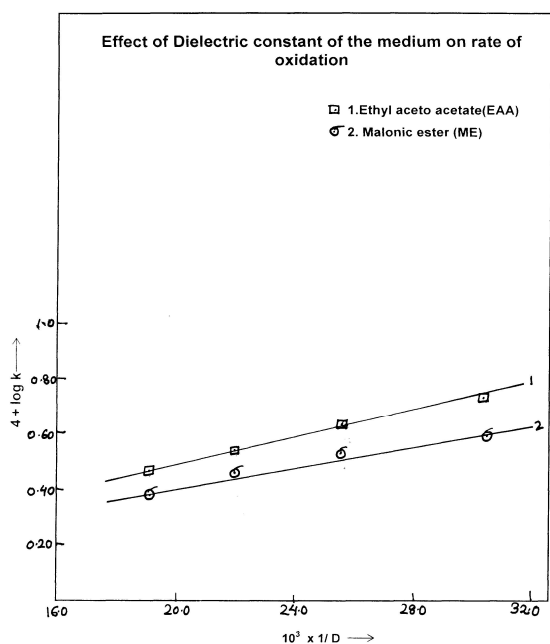


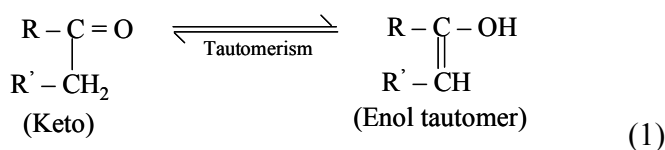
Fig. 2 $10^2 \times [\text{Substrate}] \text{ (mol dm}^{-3}\text{)} = 2.50 \text{ (1-2)}$;
 $10^3 \times [\text{IQBC}] \text{ (mol dm}^{-3}\text{)} = 2.0 \text{ (1, 2)}$;
 $10^3 \times [\text{H}_2\text{SO}_4] \text{ (mol dm}^{-3}\text{)} = 1.50 \text{ (1), 2.0 (2)}$;
 Temp. K = 313 (1,2)

Table 3 Thermodynamic parameters for the reactions between Ethyl aceto acetate, Malonic ester and IQBC

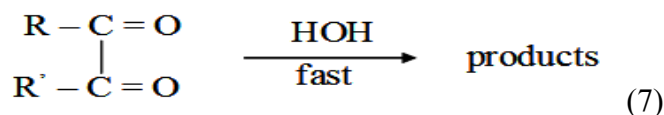
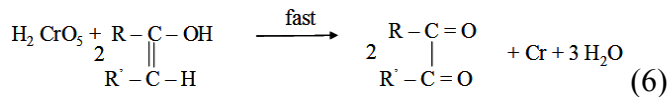
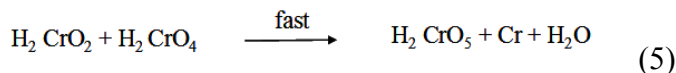
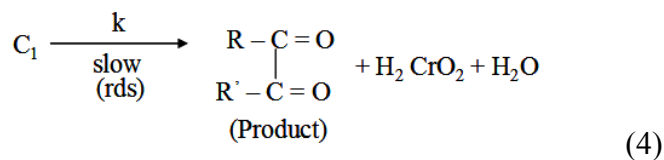
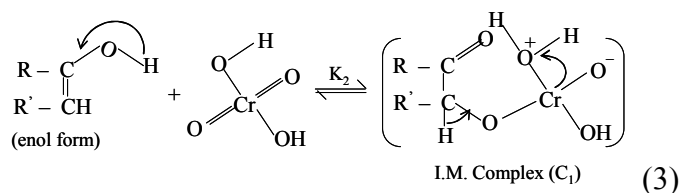
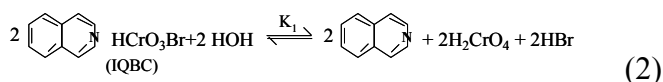
S. No.	Substrate	Thermodynamic parameters				
		Ea kJ (mol ⁻¹)	A (s ⁻¹)	ΔH [‡] kJ (mol ⁻¹)	ΔG [‡] kJ (mol ⁻¹)	-AS [‡] JK ⁻¹ (mol ⁻¹)
1.	Ethyl aceto acetate	62.21	7.40 10 ⁶	57.13	88.10	98.17
2.	Malonic ester	63.51	1.28 10 ⁷	50.31	88.77	121.90

Mechanism

In accordance with the kinetic observations and stoichiometry of the reactions the following reactions are involved to constitute the most probable mechanism of the reaction.



Where, R = CH₃ and R' = -OC₂H₅ for EAA
 R = -OC₂H₅ and R' = -CO-OC₂H₅ for DEM



The reacting species H₂CrO₄ of oxidant IQBC attacks on diketo ester in a slow step to produce complex on double bond of enol. The two carbonyl groups (>C=O) of diketo ester forms intermediate compound to lead oxidation.

Another equivalent of fresh H₂CrO₄ in continuation to form H₂CrO₅ may fast steps which further react with two fresh molecules of substrates. The mechanism is in conformity with the kinetic results, thermodynamic parameters and derived rate expression.

$$\therefore k_{\text{obs}} = \frac{k K_1 K_2 [E] [H^+]}{[IQ] K_1 + K_1 [H^+] + K_1 K_2 [E] + [H^+]} \quad (8)$$

The enol form of EAA is stabilized by intramolecular hydrogen bonding (Fig. 3).

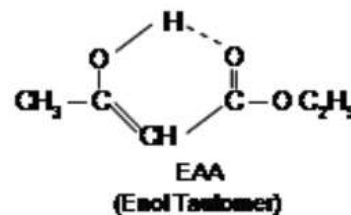


Fig 3

Enolisation is an acid as well as base catalyzed reaction and proceeds by a concerted or push-pull mechanism either by protonation of >C=O group or deprotonation of α-C of the conjugated acid. The low content in ME is due to the presence of two -OC₂H₅ group. The hindrance will be more prominent in ME as reported by Newman's Rule¹¹ of six ester group, hinders the rate of oxidation and follow above order of reactivity. However enols are acids of pka comparable to phenols (pka of Phenol □ 10, EAA □ 11, and ME □ 13) their esterification would be small. Hence attack of oxidant species at double bond seems more probable

Structure and Reactivity

The order of Reactivity was Observed as

Ethyl aceto acetate > Malonic ester

The enol content in EAA (8.0 %) is higher than Malonic ester (7.7 %) shows faster rate than ME. This is due to extra stability of chelate ring formation with intramolecular hydrogen bonding of enol form of EAA.

The reactivity is in accordance with the activation energy (E_a) measured. The reaction was found to enthalpy controlled exhibiting persistence of almost similar operative mechanism due to having close values of free energy (ΔG^\ddagger) for all. Similar pattern of mechanism has also been reported by eminent research workers with NDC¹² and authors have also been reported in their previous communication¹³ with IQBC.

CONCLUSION

Kinetic measurements of active methylene compounds explain the complex formation at transition state which decomposes in slow process to generate α,β -diketo p-butyric acid and meso oxalic acid as the oxidation products. The reactivity of EAA has been explained based on enolic content and hydrogen bonding.

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How to cite this article:

Ravendra Saket *et al.*, 2019, Kinetic Study of Ethyl Aceto Acetate and Malonic Ester by Isoquinolinium Bromochromate in Acetic Acid Medium. *Int J Recent Sci Res.* 10(06), pp. 32822-32825. DOI: <http://dx.doi.org/10.24327/ijrsr.2019.1006.3551>
