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Kinetic study of ethylacetoacetate with Isoquinolinium chlorochromate catalysed by Ru(III) in acetic medium

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Abstract : The Ru(III) catalysed oxidation kinetics of de-protonation from α-C-H bond of enol ethylacetoacetate by Isoquinolinium chlorochromate (IQCC) has been studied in aqueous acetic acid medium The Ru(III) chloride was not only catalyse the reaction but able to form complex with protonated species of IQCC and substrate in pre-equilibrium state. The reaction proceeds stoichiometrically (2:3) and followed by decomposition of a cyclic chromate ester complex in rate-determining slow process to α, β-diketo butyric acid as product. The rate was found proportional to [IQCC]. The reaction exhibited fractional-order kinetics each duo to acid and substrate. The derived rate law was strictly in conformity with postulated mechanism.

Key words - ethylacetoacetate, Isoquinolinium chlorochromate, Ru(III) chloride, oxidation, stoichiometry.

I. INTRODUCTION

The ethylacetoacetate ester belongs to active methylene compounds and contains, -CH_2- group flanked by two >C=O groups showing phenomenon of tautomerism. The dipolar character of carbonyl group and shifting of α-hydrogen atom to carbonyl oxygen produce enol form which is very prone site [1] for the attack of oxidant. By virtue of this character, it has a tendency to form complex with oxidant and is well stabilized by charge delocalisation in less polar medium.

Ruthenium(III) chloride is a non-harmful and homogeneous catalyst, its utility has not been not realized on large scale and left unnoticed for a decade in synthetic organic an inorganic chemistry. A very few report involving Ru(III) chloride as catalyst in the study of mechanistic oxidation of organic compounds [2-5] with variety of oxidants are available.

In recent year a new isoquinolinium halo chromate salt of Cr(VI) was synthesized as an oxidant which gives an excellent results in acidic medium. The widespread utilization of IQCC for the efficient oxidation of hydroxy acids,[6] aldehydes [7] sugarols,[8] diols [9] etc. has been testified for this trend.

The main aim of this piece of work in this communication to report mechanistic aspects of the reaction left unavailable for the Ru(III) catalyzed oxidation of ethyl acetoacetate by IQCC.

II. EXPERIMENTAL

The synthesized IQCC was prepared by the reported method [9] (Loc. cit.) and checked by an iodometric process. The solution ethyl acetoacetate (B.D.H.) was prepared in double distilled water. All other participating reagents and solvent pertaining to the study were employed of analytical grade (A.G.) in standard form. The solution of Ru(III) chloride (A.R. Johson-Matthey) was prepared in concentrated hydro chloric acid of known strength.

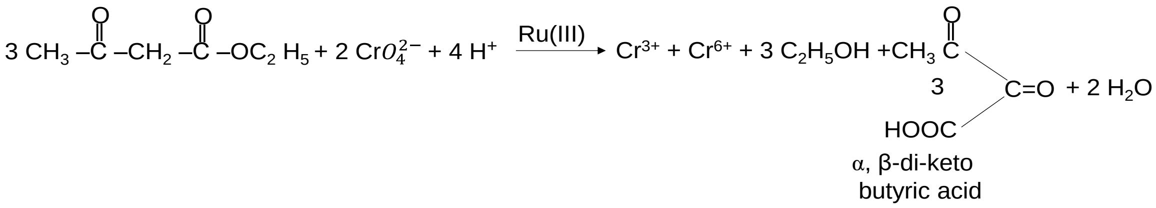
III. KINETIC STUDY

The reaction was studied under the condition [ethylacetoacetate] >> [IQCC] [H^+]. The appropriate volume of all the reagents inclusive of ethyl acetoacetate, were taken in reaction vessel and thermally equilibrated at 35^0 C. A definite volume of IQCC solution previously maintained at 35^0 C was gently poured into the content kept in reaction vessel. The oxidation kinetics was monitored by estimating the aliquots of the reaction mixture for residual IQCC concentration iodometrically, employing starch as an indicator.

IV. STOICHIOMETRY OF THE REACTION

The stoichiometry ratio $\frac{\Delta[IQCC]}{\Delta[EAA]}$ was measured under the experimental conditions [IQCC] >> [EAA]. The reaction mixture containing requisite all ingredients was kept in thermostat for 36 h at 35^0 C.

The regular estimation of [IQCC] left unconsumed iodometrically indicated two moles of IQCC consumed at the cost of three moles of ethyl acetoacetate as represented by equation.



$$3\,CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + 2\,CrO_4^{2-} + 4\,H^+ \xrightarrow{Ru(III)} Cr^{3+} + Cr^{6+} + 3\,C_2H_5OH + 3\,CH_3\overset{O}{\overset{\|}{C}}-C(=O)-COOH + 2\,H_2O$$

The products of oxidation were ethanol and α, β-diketo butyric acid, and identified by chemical tests and paper chromatography. [10]

V. RESULTS AND DISCUSSION

A progression of analysis was performed for the impact of 5X concentration of oxidant isoquinolinium chlorochromate (IQCC) on the rate constant. The direct plots of ln (a-x) against time (t) with derived slope value, unity confirms order with respect to oxidant is one i.e. dx/ dt ∝ [IQCC].

The graphic plot of k_{obs} versus [EAA] (Fig. 1) response straight line passing through origin and turning towards X-axis at higher conversion of substrate, where order changes 1 to 0. Thus, the reaction shows complex development behaviour between enol ethyl acetoacetate and protonated species of oxidant (IQCC) at transition state. The derived values of k_2 (second-order rate constant) are not fairly constant (Table 1).

Table 1 : Rate data for ethylacetoacetate oxidation by IQCC at 35^0 C
[IQCC] = 4.0×10^{-3} (mol dm^{-3}) ; [H$^+$] = 0.166 (mol dm^{-3}) ;
[Ru(III)] = 1.66×10^{-5} (mol dm^{-3}) ; AcOH-H$_2$O = 30 : 70%, (v/v)

[EAA] ×10^2 (mol dm^{-3})	10^4 k_{obs} (s^{-1})	$10^3 \times \frac{k}{[EAA]}$ $l\,mol^{-1}(s^{-1})$
0.80	1.34	16.75
1.00	1.63	16.30
1.25	1.89	15.12
2.00	2.57	12.85
2.50	3.08	12.32
3.33	3.52	10.57
4.00	3.78	9.45

EAA : ethyl acetoacetate

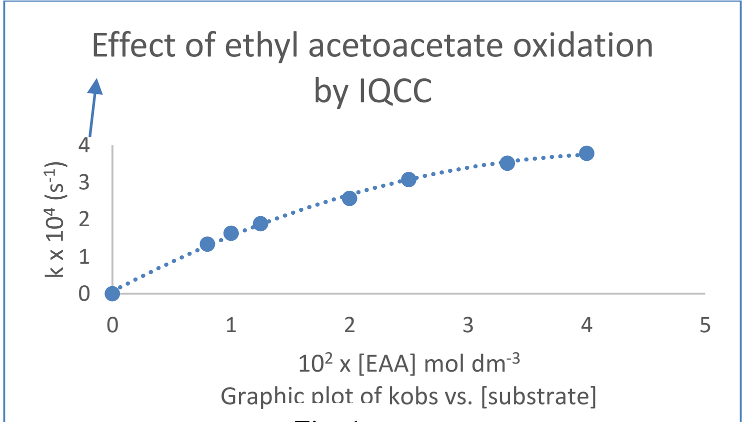


Fig. 1

The validation of two-fold proportional graphic between k_{obs} and [EAA] with positive slant on Y-axis, furnishes evidence for the existence of complex. An increase in [H$^+$] lead to a increase in pseudo- first-order rate constant (k) (Table 2) and the plot of k_{obs} versus [H$^+$] was found linear with unit slope (Fig. 2). The acceleration of rate by addition of acetic acid (-ve, dielectric constant D of the medium) accords dipole-dipole nature of the reaction satisfying Kirkwoo's theory. No significant impact of primary salt (NaCl) has been noticed in the rate of reaction under study nor and evidence was found for presence of free radicals when tested with acrylonitrile (monomer) for induced polymerization by trapping method.

Table 2 : Reliance of reaction rate on [H$^+$] at 35^0 C
[ethylacetoacetate] = 2.0×10^{-2} (mol dm^{-3}) ; [IQCC] = 4.0×10^{-3} (mol dm^{-3}) ;
[Ru(III)] = 1.66×10^{-5} (mol dm^{-3}) ; AcOH-H$_2$O = 30 : 70%, (v/v)

[H$^+$] (mol dm^{-3})	$10^4 \times$ (sec^{-1})	$10^3 \times \frac{k}{[H^+]}$

		$l\,mol^{-1}(s^{-1})$
0.066	1.13	1.71
0.100	1.71	1.71
0.125	2.26	1.80
0.166	2.57	1.54
0.200	3.41	1.70
0.250	4.45	1.78

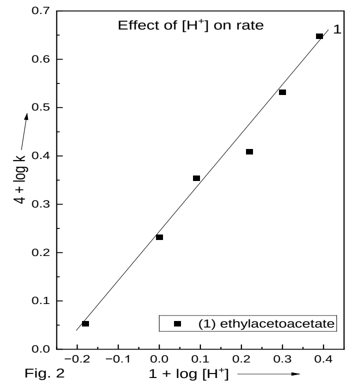


Fig. 2

Graphic plot of ln k_{obs} agaomst $[H^+]$

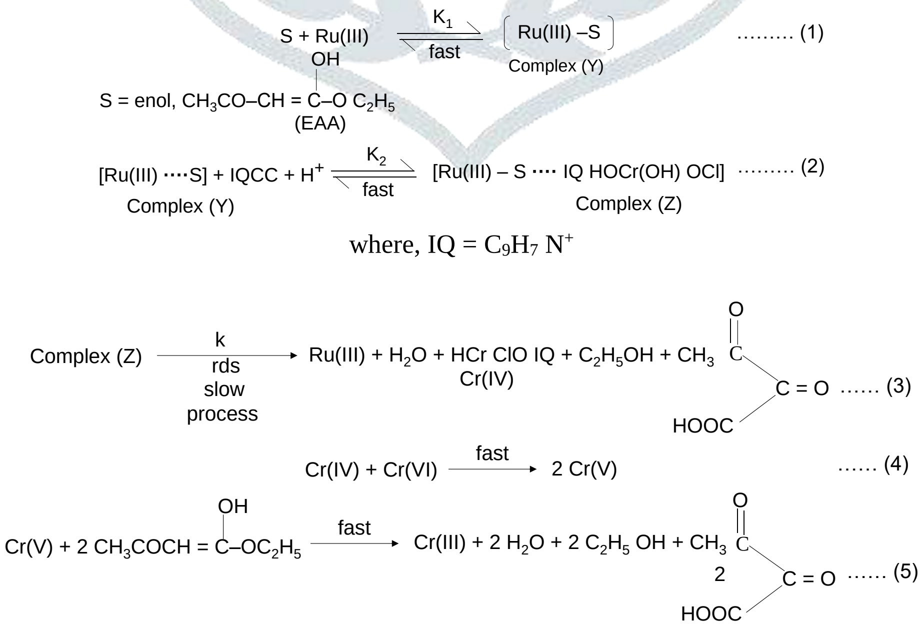
The Ru(III) belongs to platinum group metals and possesses to form complexes with organic substrates and exhibits high rates, owing to the formation of Ru(III) enol EAA complex which reacts with protonated species of IQCC in rate- controlling path to give products.

Ru(III) chloride acts as a prime reacting species in this investigation and catalyzed the reaction at its optimum concentration showing fractional-order kinetics. It pours ample of proof by the plot of $\frac{1}{k_{obs}}$ vs. $\frac{1}{Ru(III)}$, should be linear intercepting ordinate axis with positive slope. Moreover, chloride ions show negative impact on the reaction rate leads that equilibrium is favoured to right side in acidic solution of $RuCl_3$.

The rate of oxidation increase rapidly with increase in concentration of mineral acid also supports that protonated IQCC is the reactive entity in the present study. The enolization of ethyl acetoacetate under investigation was carried out by bromination method and rate was found much faster than the rate of oxidation. This facts concluded that enol form of the substrate participate in the reaction mechanism which favoured by increase in rate with increase in acetic acid content and catalyzed reaction with H^+ ions.

VI. MECHANISM

The Ru(III) catalysed and protonated species of IQCC (oxidant) based mechanism of enol substrate is suggested in Scheme-1.



$$S + Ru(III) \underset{fast}{\overset{K_1}{\rightleftharpoons}} \{Ru(III)–S\} \quad ……… (1)$$

Complex (Y)

$$S = enol,\ CH_3CO–CH = \overset{OH}{\overset{|}{C}}–O\ C_2H_5 \quad (EAA)$$

$$[Ru(III) \cdots\cdots S] + IQCC + H^+ \underset{fast}{\overset{K_2}{\rightleftharpoons}} [Ru(III) – S \cdots\cdots IQ\ HOCr(OH)\ OCl] \quad ……… (2)$$

Complex (Y) Complex (Z)

where, IQ = $C_9H_7\ N^+$

$$Complex\ (Z) \xrightarrow[\substack{rds\\ slow\\ process}]{k} \underset{Cr(IV)}{Ru(III) + H_2O + HCr\ ClO\ IQ} + C_2H_5OH + CH_3\overset{O}{\overset{\|}{C}}–\underset{HOOC}{C = O} \quad …… (3)$$

$$Cr(IV) + Cr(VI) \xrightarrow{fast} 2\ Cr(V) \quad …… (4)$$

$$Cr(V) + 2\ CH_3COCH = \overset{OH}{\overset{|}{C}}–OC_2H_5 \xrightarrow{fast} Cr(III) + 2\ H_2O + 2\ C_2H_5\ OH + 2\ CH_3\overset{O}{\overset{\|}{C}}–\underset{HOOC}{C = O} \quad …… (5)$$

The Scheme-I of the mechanism leads to the rate law :

$$\frac{-d}{dt}[Cr(VI)] = k\,[Complex\ (Z)] \quad .....(1)$$

Simplification of values of various steps involved in the mechanism and their substitution in equation (1) ultimately gives

$$\frac{-d}{dt}[Cr(VI)] = k\,K_1K_2[Ru(III)][S][IQCC] \,.....(2)$$

$$\text{Since, } [Cr(VI)]_t = [Cr(VI)] + [Complex\ (Z)] \quad ....(3)$$

$$\text{Here,} [Cr(VI]_t\ is\ [IQCC]_t$$

shows the total concentration of oxidant (IQCC)

$$\text{Therefore, } \frac{-d}{dt}[Cr(VI)] = k\,K_1K_2\frac{[Ru(III)][H^+][S][IQCC]_t}{1+K_1\,K_2\ [S][H^+]} \quad ....(4)$$

From equation (2), and equation (3) and imposing of steady state approximation as :
$k_{obs} = \frac{rate}{[IQCC]_t}$ we get, final rate expression as :

$$k_{obs} = \frac{k\,k_1k_2\ [S]\,[H^+]\,[Ru(III)]}{1+K_1\,K_2\ [S][H^+]} \,........\,(5)$$

The reciprocity of the equation, transform equation (4), lead as equation (5)

$$[Ru(III)] \times k_{obs}^{-1} = \frac{1}{k\,k_1k_2[S][H^+]} + \frac{1}{k} \qquad ....(6)$$

It is crystal clear from equation (6) that the graphic of $\frac{1}{k_{obs}}$ vs. $\frac{1}{[S]}$ at fixed (Ru(III)] is obtained linear with positive intercept on ordinate axis, proves the veracity of concept of Michaelis-Menten type kinetics for the reaction studied.

The $-CH_2-$ (methylene group) lies between two carbonyl group makes the molecule highly acidic, enolise rapidly and stabilized due to the ability to form chelation / complex and intramolecular hydrogen bonding. The enolic group paves the way to facilitate the formation of a cyclic chromate ester complex with some strain **[12]** in polar transition state which involve a process of α-C-H bond fission as a loss of proton. Similar mechanism has also been acclaimed by a number of recent researchers for oxidation of ethylacetoacetate by oxidants PDC**[13]** and IQBC**[14]** respectively. The derived rate law is in good agreement with mechanism. The various thermodynamics parameters were also assigned as temperature coefficient (T)=1.39 & 1.93 for respective temperature difference 5^0C & 10^0C, E^a = 54.00 kJ mol^{-1}, $\Delta H^\#$ = 49.97 kJ mol^{-1}, $\Delta G^\#$ = 86.99 kJ mol^{-1} and – $\Delta S^\#$ = -119.22 JK^{-1} mol^{-1} respectively. The cyclic nature of complex as per -ve value of entropy of activation ($\Delta S^\#$) was assessed.

VII. CONCLUSION

The proposed mechanism of the reaction proceeds through elimination of proton from α-C-H bond fission in rate-controlling step to yield product α, β-dibutyric keto acid with stoichiometric ratio (2:3). The protonated form of oxidant (IQCC) attacks at enol substrate to form complex in addition to catalysed reaction by Ru(III) and follow Michaelis-Menten type mechanism. The derived rate law is found in good agreement with the illustrated mechanism.

VIII. ACKNOWLEDGEMENT

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IX. CONFLICT OF INTEREST

The authors declare conflict of no interest whatsoever.

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