# Kinetic Study of Ru(III) Catalyzed Oxidation of Active Methylene Compounds by Isoquinolinium Chlorochromate in Acetic Medium

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*Abstract*—**This paper envisages the results of Ru(III) catalyzed Michaelis-Menten kind kinetics of reaction, that proceeds by rupturing α-C-H bond of enolic acetyl acetone and benzoyl acetone by Isoquinolinium chlorochromate in acetic acid medium. The reaction rate is observed independent of the concentration of oxidant. The protonated species of oxidant is believed to be the reacting species involved in the proposed reaction mechanism corresponds to 2:3 stoichiometry.**

*Key words*—**Ruthenium(III), chloride, isoquinolinium chlorochromate, acetyl acetone, benzoyl acetone, stoichiometry.**

## I. INTRODUCTION

[The ruthenium(III) chloride is a non-toxic homogeneous catalyst, has been utilized in mechanistic oxidation of a few organic compounds with different oxidants. [1-3] Recently developed Isoquinolinium chlorochromate is complex of Cr(VI) acts as a versatile oxidant, and is very useful in conversion of organic compounds [4-8] through oxidation in synthetic organic chemistry. The active methylene compounds exhibit keto-enol tautomerism and become a site of reaction. Owing to presence of methylene group (-$CH_2$-) between two reactive carbonyl group (>C=O), the mechanism investigations with kinetic aspects of active methylene compounds by numerous oxidants have been published earlier. [9-12]

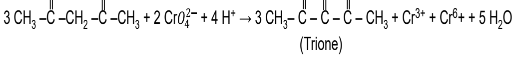
A study of literature appears that a little attention has been paid so far about the activity of ruthenium(III) chloride employed as catalyst in Cr(VI) oxidation. This prompted us to take the task of the present probe which constitute the oxidation kinetics of Ru(III) catalyzed oxidation of acetyl acetone and benzoyl acetone by IQCC.

## II. EXPERIMENTAL

The solution of oxidant (IQCC) was prepared by described procedure [13] and its standardization was carried out iodometrically. The solution of Ru(III) chloride (A.R. Johnson Matthey) was made in conc. HCl of known strength. The acetyl acetone (A.G. grade), benzoyl acetone's (E. Merck), solutions were prepared in distilled water and little acetic acid (B.D.H.). All other chemicals used in this experiments were of AnalaR quality. The reactions were commenced (in a thermostat, ± 0.1$^0$C) by addendum of appropriate IQCC solution and other participating reagents equilibrated at 308 K. The progress of the reaction (75% to 80%) was judged by measuring unconsumed [IQCC] at different time intervals, employing starch as an indicator by iodometric process. A graph drawn between log [IQCC], and time was found linear with $r^2 = 0.980$. The initial rates were enumerated using integration and graphical methods. For more than two runs replicability was ±3% was noticed.

## STOICHIOMETRY AND PRODUCT ANALYSIS

The stoichiometry of the reaction was determined by equilibrating the reaction mixture containing an excess of varying ratio [IQCC] over [active methylene compound] at 30$^0$ C for 36 h. Various observations showed that three moles of active methylene compound react with two moles of IQCC as formulated to overall equation (1)



$$3\,CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 + 2\,CrO_4^{2-} + 4\,H^+ \rightarrow 3\,CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3 + Cr^{3+} + Cr^{6}+ + 5\,H_2O \quad \ldots (1)$$

(Trione)

The oxidation product triones were confirmed by positive iodophenine test [14] and also by forming their 2,4-dinitro phenyl hydrazone (DNP derivatives) characterized by their melting point determination.

## III. RESULTS AND DISCUSSION

These oxidation reactions exhibited unit dependency with respect to IQCC, hence graphic was found linear between log [IQCC] and time. The rate constant do not vary appreciably on IQCC initial concentration.
The fractional-order (0 < 1) dependency was noticed for active methylene compounds (Table 1). The curvature of the plot drawn ($k_{obs}$ versus [substrate]) tending towards a lower level (Fig. 1), indicates the development of complex. The double reciprocal graphic between $k_{obs}^{-1}$ and [substrate]$^{-1}$ was noticed linear with positive intercept (Fig. 2) on ordinate axis, hence proving Michelis-Menten kind kinetics operative for each acetyl acetone and benzoyl acetone.

Table 1 : Rate data for active methylene compounds oxidation by IQCC at 308 K

$10^3 \times$ [IQCC] (mol dm$^{-3}$) = 4.0 (a, b) ;
[H$^+$] (mol dm$^{-3}$) = 0.15 (a), 0.166 (b) ;
$10^5 \times$ [Ru(III)] (mol dm$^{-3}$) = 1.66 (a, b) ;
AcOH-H$_2$O %, (v/v) = 20 (a), 30 (b)
Temp. K = 308 (a, b, c)

| | $10^4 \times k_{obs}$ (s$^{-1}$) | |
|---|---|---|
| $10^2 \times$ [AMC] (mol dm$^{-3}$) | Acetyl acetone (AA) (a) | Benzoyl acetone (BA) (b) |
| 0.50 | 2.23 | - |
| 0.80 | 3.20 | - |
| 0.88 | - | 1.91 |
| 1.00 | 3.84 | 2.23 |
| 1.50 | 4.73 | - |
| 1.66 | - | 3.16 |
| 2.00 | 5.26 | 3.61 |
| 2.50 | 5.52 | 4.15 |
| 3.33 | 5.54 | 4.53 |
| 4.00 | - | 5.27 |

AMC: active methylene compounds.

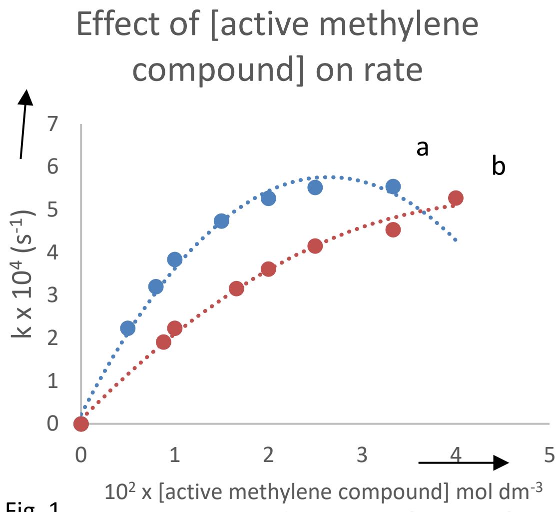


Fig. 1 Graphic plots of $k_{obs}$ against [substrate]

$10^3 \times$ [IQCC] (mol dm$^{-3}$) = 4.0 (a, b) ; [H$^+$] (mol dm$^{-3}$) = 0.15 (a), 0.166 (b) ;
$10^5 \times$ [Ru(III)] (mol dm$^{-3}$) = 1.66 (a, b); AcOH-H$_2$O %, (v/v) = 20 (a), 30 (b) :
Temp. K = 308 (a, b)

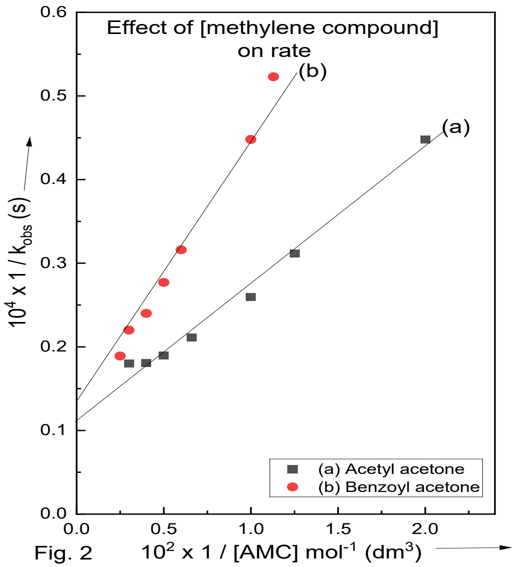


Fig. 2 Graphic plots of $k_{obs}^{-1}$ vs.[substrate]$^{-1}$
$10^3 \times$ [IQCC] (mol dm$^{-3}$) = 4.0 (a, b) ;
[H$^+$] (mol dm$^{-3}$) = 0.15 (a), 0.166 (b) ;
$10^5 \times$ [Ru(III)] (mol dm$^{-3}$) = 1.66 (a, b) ;
AcOH-H$_2$O %, (v/v) = 20 (a), 30 (b)
Temp. K = 308 (a, b)

The rates of oxidation of duo AA and BA are catalyzed by hydrogen ion concentration. The straight line with positive slope was obtained from the graphic between ln $k_{obs}$ and ln [H$^+$] (Fig. not given). This pours evidence for the acid catalyzed reaction. The kinetics was nearly the same with acetic acid solvent. The increment rate organization of acetic acid occurred with the decline in dielectric constant of the medium. This fact accounts that ion-dipole species participates in the reaction mechanism.

A plot of log k against 1/D represents relative permittivity of the solvent. The observed results of solvent effect revealed a perfect correlation as defined by Swain *et al.* [16]. Ruthenium trichloride exists in acidic solution as $[RuCl_6]^{3-}$ involved in the following equilibrium :

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [Ru\,Cl_5\,H_2O]^{2-} + Cl^- \ldots\ldots \quad (2)$$

We assume here Ruthenium trichloride in acidic medium as it's a real species explains negative effect of chloride ions. The oxidation reactions are catalyzed by Ru(III) in lower level of concentration (Table 2) and its order falls from one to zero at its optimum concentration. The graphic of ln $k_{obs}$ against ln [Ru(III)] (Fig. 3) with positive intercept on ordinate axis shows clearly that Ru(III) chloride has a capability to form complexes [17] with substrate. The neutral salt influence was found almost immaterial on the reaction rate.

Table 2 : Reliance of reaction rate on [Ru(III)]
$10^2 \times$ [AMC] (mol $dm^{-3}$) = 1.0 (a), 1.66 (b);
$10^3 \times$ [IQCC] (mol $dm^{-3}$) = 4.0 (a, b);
[$H^+$] (mol $dm^{-3}$) = 0.15 (a), 0.166 (b);
$CH_3COOH$-$H_2O$ %, (v/v) = 20 (a), 30 (b);
Temp. K = 308 (a, b)

| $10^5$x [Ru(III) (mol $dm^{-3}$) | 0.80 | 1.0 | 1.25 | 1.66 | 2.0 | 2.50 | 3.33 | 4.0 | 5.0 | 6.25 |
|---|---|---|---|---|---|---|---|---|---|---|
| $10^4$ $k_{obs}$ ($s^{-1}$) (AA) | 2.14 | 2.56 | 2.76 | 3.84 | 4.33 | 5.01 | - | 5.91 | 6.15 | 6.27 |
| $10^4$ $k_{obs}$ ($s^{-1}$) (BA) | - | 1.97 | 2.45 | 3.16 | 3.35 | 3.86 | 4.64 | 5.15 | 5.52 | 5.86 |

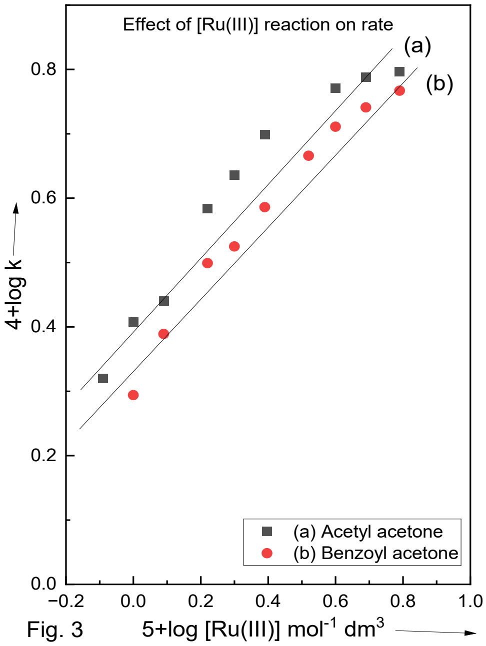


Fig. 3

Graphic of lg k against lg [Ru(III)]
$10^2 \times$ [AMC] (mol $dm^{-3}$) = 1.0 (a), 1.66 (b);
$10^3 \times$ [IQCC] (mol $dm^{-3}$) = 4.0 (a, b);
[$H^+$] (mol $dm^{-3}$) = 0.15 (a), 0.166 (b);
$CH_3COOH$-$H_2O$ %, (v/v) = 20 (a), 30 (b);
Temp. K = 308 (a, b)

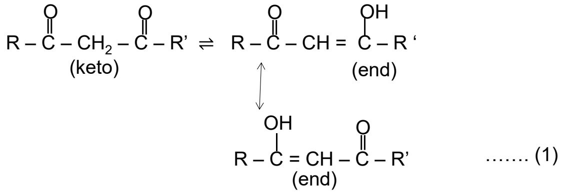
No impact of acrylonitrile and also trapping reagent BHT for free radicals [18] was noticed during the course of reaction.

Protonated oxidant (IQCC $H^+$) appears to be an iconic compound. It is observed after protonation of IQCC (Y) generate a protonated Cr(VI) species (Z) which is strong electrophile of oxidant IQCC as a result of which the oxidation process through IQCC depends on upon he proton concentration. The rate of enolization of active methylene compounds was conducted by bromination method [19] and rate was observed much faster than the rate of oxidation. In light of this fact, the enolic form of carbonyl group (active methylene compound) participates in the reaction. The enol ambience nature is supported by enhancement of rate by decreasing dielectric constant of the medium and $H^+$ ion catalyzed reaction.

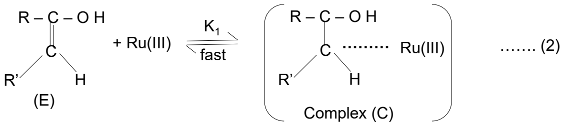
## IV. MECHANISM

Considering the protonated active species of IQCC, enolic substrate and he reacting species of ruthenium(III) chloride, the following mechanism may be proposed :

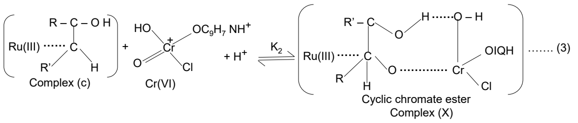
Acid-dependent paths (scheme-I)



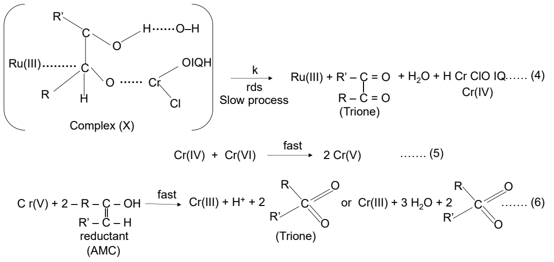
where, R = $CH_3$- for AA and BA and R'= $CH_3$-, and $C_6H_5$ for duo substrate.



where, R' = $CH_3CO$ for acetyl group.



Here IQ = $C_9H_7N$ (Isoquinolinium)



The acid-dependent mechanism (Scheme-I) is based on the experimental findings. The rate law can be determined on applying the equilibrium condition.

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

Since, $[complex\ (X)] = k_2[Cr(IV)][H^+] \times [C]$ ……(2)

More over, $[IQCC\ H^+] = K_1[IQCC][H^+]$ ….(3)

& $[C] = K_1[E][Ru(III)]$ ……(4)

$$\frac{-d}{dt}[Cr(VI)] = k\,k_1k_2\,[Ru(III)]\,[E][H^+] \times [IQCC]_t \ldots\ldots(5)$$

and $[Cr(IV)]_t = [Cr(VI)] + [X]$ …….(6)

At steady state condition with the reasonable approximation, rate law derived is :

$$k_{obs} = \frac{Rate}{[IQCC]_t} = \frac{k\,k_1k_2\ [E]\,[H^+]\,[Ru(III)]}{1+K_1\,K_2\ [E][H^+]} \ldots\ldots. (7)$$

On simplification and from eq. (5), eq. (6) and equation (8) we get

$$\frac{-d}{dt}[Cr(VI)] = \frac{k\,k_1k_2\ [H^+]\,[Ru(III)][E]}{1+K_1\,K_2\ [E][H^+]} \ldots\ldots(8)$$

The reciprocal of equation (8) gives equation (9)

$$[Ru(III)]\frac{1}{k_{obs}} = \frac{1}{k\,k_1k_2[E][H^+]} + \frac{1}{k} \quad \ldots\ldots(9)$$

The reaction system is well characterized by equation (9). The results also support the assumption of ruthenium(III) chloride as active species.

In the proposed mechanism, the oxidation state of Cr metal reduced from Cr(VI) to Cr(V) and expected further to react with another Cr(VI) to produce Cr(V). In a fast step this Cr(V) species at least yields Cr(III) species, such pattern of reactions in oxidations involving Cr(VI) is markedly established.[20]

The order of reactivity was assessed as :
*Acetyl acetone > benzoyl acetone.*

The presence of substituents gathering assume significant job and give the reasonable image of reactivity.

The stream electronegative character and polarity of > C=O group, the α-C-H bond goes under fission as the electrons are displaced towards electron atoms rendering the loss of α-H atom as the proton.
These compounds are enolized rapidly and stabilized by resonance due to formation of intramolecular hydrogen bonding.

The stream electronegative character of carbonyl of α-C-H bond, presence of high degree of enolic content, extra stability of forming chelating ring and exhibition of conjugate effect by presence of phenyl group in benzol acetone are the supportive factors leading to above order of reactivity.

The more responsible compound is relied upon to have lower energy of activation ($E_a$) which is as the reactivity pattern (Table 3). The curtailment of $-\Delta S^{\#}$ (entropy of activation) is negative restricts the degree of freedom of the solvated complex at transition state and account by loss of entropy. The estimation of

Gibbs free energy ($\Delta G^{\#}$) is around steady showing prevalence of operative mechanism over all assessment of reaction was found enthalpy controlled.

Table 3 : Ru(III) catalyzed activate methylene compound – IQCC complex decomposition rate constants and their parameters of activation

| **[AMC]** | **303 K** | **308 K** | **313 K** | **318 K** | **$E^a$ kJ $mol^{-1}$** | **$\Delta H^{\#}$ kJ $mol^{-1}$** | **$\Delta G^{\#}$ kJ $mol^{-1}$** | **$\Delta S^{\#}$ $JK^{-1}$ $mol^{-1}$** |
|---|---|---|---|---|---|---|---|---|
| $10^4$ $k_{obs}$ AA ($s^{-1}$) | 2.87 | 3.84 | 5.11 | 6.80 | 45.57 | 42.89 | 84.25 | -133.21 |
| $10^4$ $k_{obs}$ BA ($s^{-1}$) | 1.69 | 2.32 | 3.18 | 4.36 | 50.88 | 53.51 | 86.00 | -104.65 |

## V. CONCLUSION

Ru(III) catalyzed oxidation of enol active methylene compounds with protonated IQCC (oxidant) in fast dynamic equilibrium development of a 2:3 complex having cyclic chromate state transition recommended by Michaelis-Menten kind kinetics. The study indicated by the rate of decomposition of complex and suggests that in the rate controlling slowest path, the α-C-H bond is cleaved to produce corresponding triones as the main product.

## VI. ACKNOWLEDGEMENT

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## CONFLICT OF INTEREST

The authors declare conflict of no interest whatsoever.

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