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Kinetics and Mechanistic Study of Ru (III) Catalyst Oxidation of Crotonic Acid by Chloramine-T

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Abstract
Catalysed oxidation of Crotonic acid by Ru (III) in acidic medium ofChloramine-T in the presence of Hg(OAc)$_2$ has been investigated. The order with respect to Ru (III)and [Crotonic acid] is one andzero order is found with respect to Chloramine-T.[KCl] shows Positive effect on the reaction rate. The Negligible effect [H$^+$] and ionic strength of medium have been observed. The activation parameters have been computed at different temperatures.Mechanistic steps, consistent with kinetic results, reaction stoichiometry andproduct analysis has been done.

Keywords: kinetics, Ru (III) chloride, Crotonic acid, Chloramine-T Hg(OAc)$_2$

Introduction

Ru (III) has been proved as an efficient catalyst in many redox reactions hence ruthenium (III) with [CAT], which is mild oxidizing agents, has been extensively used of a variety of organic compounds[1-2]. These oxidant contain strongly N linked halogen. They undergo two electron exchange form halide ion and corresponding sulphonamides [3]. Crotonic acid is widely used as cosmetic polymer intermediate, pesticide and pharmaceuticals[4-5]. Objectives of the present study are, to elucidate a plausible mechanism, to identify the oxidation products, to deduce the rate law, to ascertain the various reactive species of catalyst and oxidant andto calculate the activation parameters, because since now no work has been done with crotonic acid and chloramine-T catalysed by Ru (III)
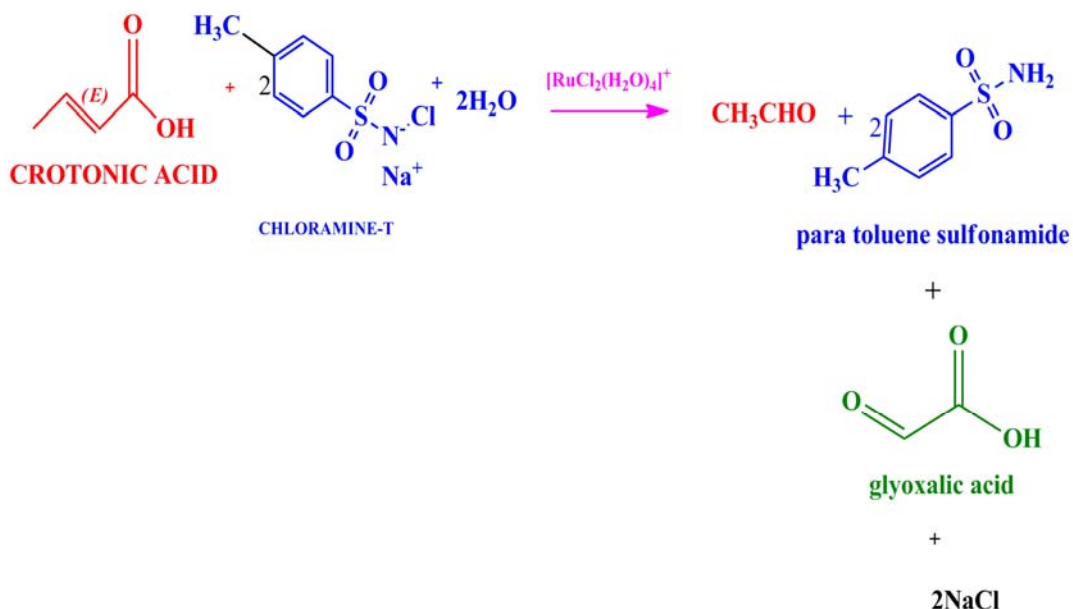
Material and Method

Crotonic acid, Ru (III) Chloride, HClO$_4$, KCl, NaClO$_4$, Hg (OAc)$_2$, Chloramine-Twere of A.R grade. All solutions were prepared in double distilled water. The stock solution of Ru (III) Chloride was prepared by dissolving the 1 gm of sample in HCl of known strength (.018N) and total volume of solution was made up 100 ml in black- coated flask to prevent photochemical decompositions. The stock solutions of Chloramine-T and Ruthenium chloride were stored in black coated bottles to prevent photochemical decompositions. The reaction vessel were also coatedfrom outside with black paint to avoid any photochemical effect NaClO$_4$ and HClO$_4$ were used to maintain the required ionic strength and acidity, respectively. Crotonic acid, Perchloric acid, Mercuric acetate Ruthenium chloride, expects Chloramines-T were taken in the reaction vessel and kept in thermostatic water bath maintained at 40 ^{0}C temperature (±1 ^{0}C). Chloramine-T was also thermostated at the same temperature and required amount of oxidant was added into the reaction mixture to start the reaction.5ml aliquot were pipette out at regular intervals of time and poured into a black-coated flask containing 5ml of 4 percent KI and 5ml of 1N H$_2$SO$_4$ and few drops of starch. The liberated iodine then titrated against standard sodium thiosulphate (hypo) solution to a starch end point.Measuring unconsumed amount of CAT iodometrically monitored the progress of rate of reaction. The order of reaction in each reactant is measured with the help of plot drawn between concentration of reactant and time. The rate of reaction (-dc/dt) was determined by slope tangent drawn using the plane mirror method.

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Stoichiometry

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of oxidant [CAT] over [crotonic acid] in different ratio at room temperature for two days and estimation of unconsumed oxidant [CAT] in different sets showed that one mole of crotonic acid consumes one mole of [CAT].

Product analyzed has been mentioned in several reports. The Product analyzed by NUCON gas Chromatography using prorapok-Q 101 column reaction and programmedhaving F.I.D detector oven temperaturethe product were identified as the glyoxalin acid and acetaldehyde[6]The Ruthenium catalyst oxidation of crotonic acid by comparison ofthe retention time with the standard solution

Product Analysis

The set of reaction mixtures such as, reducing Crotonic acid, Perchloric acid, Mercuric acetate, KCl, Ruthenium chloride, and excess of Chloramines -T were taken into the reaction vessel and kept for two days at room temperature, and UV spectral analysis was done which showedabsorbance band at 245 nm. This indicates that the complex formation has taken place between Ru (III) and substrate.
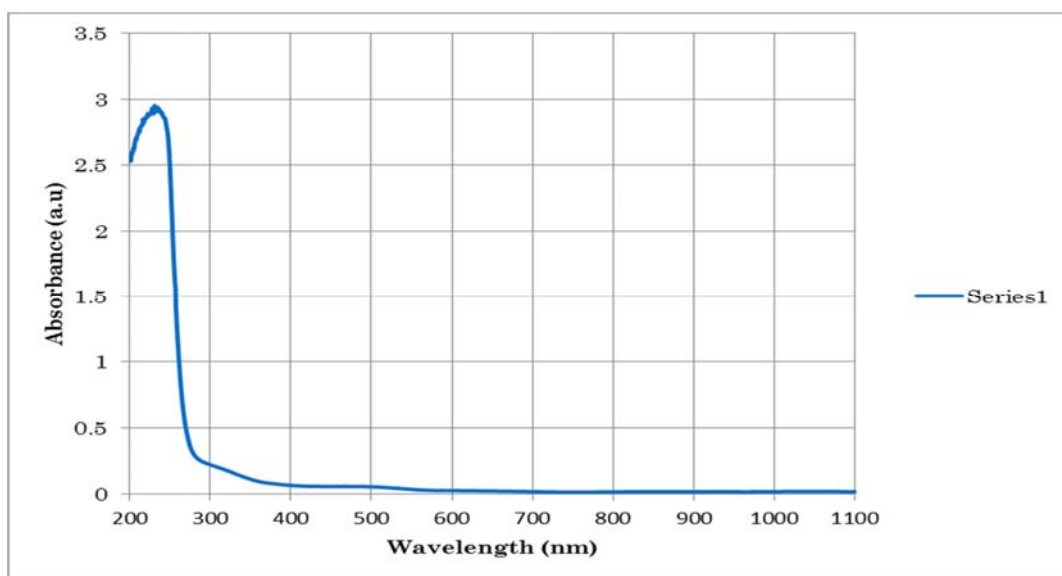
Kinetic Result and Discussion

Kinetics of Ru (III) chloride oxidation of cotonic acid by Chloramine-T was investigated at constant temp- 313K. The Kinetic investigations were carried out by varying the concentration of different reactant such as substrate (crotonic acid), catalyst Ru (III), oxidant(chloramine–T), $HClO_4$ and mercuric acetate. Kinetic results are reported in table-1 first order dependence on substrate and catalyst, zero order dependence on CAT was observed This was confirmed byplotting the graph between (-dc/dt) vs conc of substrate in fig -1 and (-dc/dt) vs. catalyst in fig-2 which gave the straight line.

Successive addition of mercuric acetate showed negligible effect H^+ ions also indicate negligible effect by variation of concentration of hydrogen ion (table-2)

Table1: Effect the variation of oxidant, Ru (III) and Crotonic acid at Temp 40⁰C

| CAT x10^3 moldm^{-3}	Ru(III) Catalyst x 10^6Mol dm^{-3} s^{-1}	Crotonic acid [Substrate] X 10^3 mol dm^{-3}	(-dc/dt) x 10^{-7}	K_1 x 10 Mol^{-1} S^{-1}
.83	3.35	1.00	.40	-
1.00	3.35	1.00	.43	-
1.25	3.35	1.00	.43	-
1.67	3.35	1.00	.46	-
2.5	3.35	1.00	.47	-
5.0	3.35	1.00	.45	-
1.00	1.67	1.00	.30	.17
1.00	3.35	1.00	.36	.10
1.00	5.02	1.00	.48	.095
1.00	6.67	1.00	.65	.097
1.00	8.34	1.00	.67	.08
1.00	10.05	1.00	1.3	.13
1.00	3.35	.83	.31	.37
1.00	3.35	1.00	.35	.35
1.00	3.35	1.25	.40	.32
1.00	3.35	1.67	.51	.30
1.00	3.35	2.50	.68	.30
1.00	3.35	5.00	1.3	.30
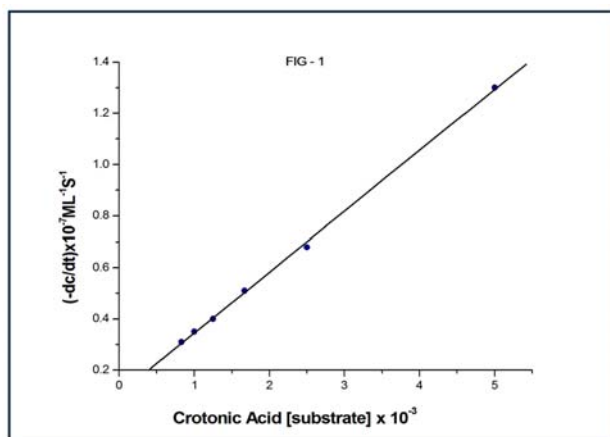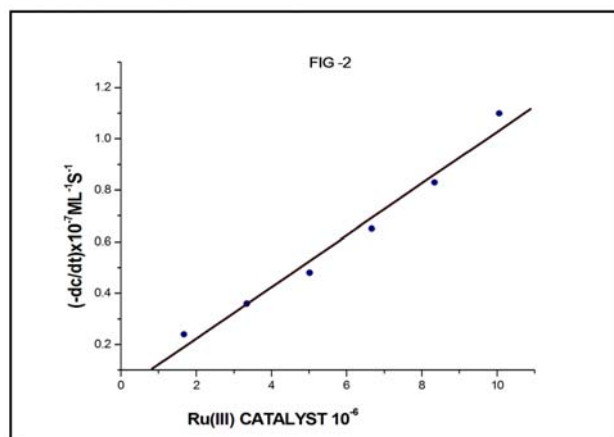
Successive addition of mercuric acetate show (table 2), and the rate of reaction followed Positive effect with respect to Chloride ion.Experimental data showed negligible effect of ionic strength of medium on the rate. Reaction showed no effect of [H$^+$] ion Concentration. Successive addition of acetic acid increased the reaction rate showing a negative dielectric effect on the rate.
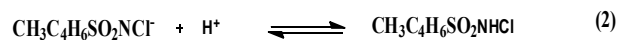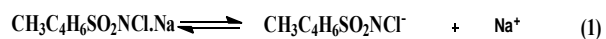
Effect of Temperature
The increase in temperature increased the rate of reaction. The plot of log k_1 versus (1/T) (Fig-3) is straight line. The proposed mechanisms are also supported by the moderate value of energyofactivation and thermodynamic parameters (Table –4) ΔE entropy of activation indicates transition state is highlysolvated andnegative values of theΔS, high positive value free energy of activation ΔF are calculated from the rate measurements at 303, 308, 313 and 318 K. The number of possible chloro species of Ru (III) present in the solution can be represented by the general formula [Ru (III) (6 – x) (H$_2$O) Cln]$^{3-x}$ where n = 1- 6. All these species are highly pH dependent. The species present in the pH range studied is however [RuCl$_2$(H$_2$O)$_4$]$^+$ This was confirmed by the reported absorption spectra of Ru (III) solution from 1 x 10^{-3} M to1x10^{-5} M in the pH range 1.00 to 3.00 at constant ionic strength (μ=0.1 M KNO$_3$). These studies have been shown that octahedral complex species such as [RuCl$_5$(H$_2$O)]$^{2-}$

[RuCl$_4$(H$_2$O)$_2$]$^-$,[RuCl$_3$(H$_2$O)$_3$], [RuCl$_2$(H$_2$O)$_4$]$^+$ and [RuCl(H$_2$O)$_5$]$^+$ do not exist inan the aqueous solution RuCl$_3$ [7-8]. The study on oxidation state Ru(III) exist in acidic medium.

$$[RuCl_3(H_2O)_3] + H_2O \rightleftharpoons [RuCl_2(H_2O)_4]^+ + Cl^- \quad (1)$$
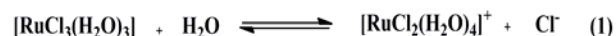
Discussion and Mechanism
Chloramine-T behaves as a strong electrolyte and ionization may be represented by, equation (2) and (3).In acidic medium the anion Chloramine-T readily accept a proton and form free acid N-chloro-p- toulenesulphonamide. N-chloro-p- toulenesulphonamide on hydrolysis give p-toulenesulphonamide.

$$CH_3C_4H_6SO_2NCl.Na \rightleftharpoons CH_3C_4H_6SO_2NCl^- + Na^+ \quad (1)$$

$$CH_3C_4H_6SO_2NCl^- + H^+ \rightleftharpoons CH_3C_4H_6SO_2NHCl \quad (2)$$

On the basis the above reaction and taking [RuCl$_2$ (H$_2$O)$_4$]$^+$ andCH$_3$C$_6$H$_4$SO$_2$NHCl as the most reactive speciesof CAT and Ruthenium Chloride respectively.Proposed the mechanism Ru (III) Catalyzed oxidation of crotonic acid in acidic medium[9-10]

$$CH_3CH=CHCOOH + [RuCl_2(H_2O)_4]^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [RuCl_2(H_2O)_4.CH_3CH=CHCOOH]^+ \quad \text{(III)}$$

[S]   [X]   [Y]

$$[RuCl_2(H_2O)_4.CH_3CH=CHCOOH]^+ + 2H_2O \xrightarrow{\text{Slow}}^{K} [RuCl_2(H_2O)_4]^+ + \underset{\underset{\text{OH OH}}{|\quad|}}{CH_2CH-CHCOOH} \quad —\text{(IV)}$$

[Y]   [X]   Intermediate [C]

$$+ 2H^+$$

Intermediate [C] $CH_2C-CHCOOH$ (OH OH)

$$+ 2 \quad \text{(H}_3\text{C—C}_6\text{H}_4\text{—SO}_2\text{—N(H)—Cl)} \xrightarrow[\text{Fast}]{[2Na^+]} CH_3CHO + \underset{HOOC}{\overset{CHO}{\diagdown}}$$

$$+ \quad\quad\quad —\text{(V)}$$

$H_3C—C_6H_4—SO_2—NH_2$ (2)

para toluene sulfonamide

2NaCl

Step (4) is slow and rate determine step rate of reaction. The rate of reaction is term of consumption of concentration of [RNCl⁻] ions may be written as eq (1)

$$\frac{-d[RNCl^-]}{dt} = K_2[Y] \quad\quad\quad (1)$$

Whenapplying steady state treatment to the concentration of [Y] we can determine the concentration of Yas given below. Hence,

$$\frac{d[Y]}{dt} = K_1[X][S] - K_{-1}[Y] - K_2[Y] \quad\quad = 0$$

or $[Y](K_{-1}+K_2) = K_1[X][S]$

or $[Y] = \dfrac{K_1[X][S]}{(K_{-1}+K_2)} \quad\quad\quad (2)$

On subsututing the value of [Y] in eq(1) we get

$$\frac{-d[RNCl^-]}{dt} = \frac{K_2K_1[X][S]}{(K_{-1}+K_2)} \quad\quad\quad (3)$$

The total concentration of Ru (III) chloride, i.e. [Ru (III)]$_T$ may be written by eq (4)

$$[Ru\,(III)]_T = [X] + [Y] \quad\quad\quad (4)$$

Putting value from eq (2) to eq (4) we get

$$[Ru\,(III)]_T = [X] + \frac{K_1[X][S]}{(K_{-1}+K_2)}$$

$$[Ru\,(III)]_T = [X]\left(1 + \frac{K_1[S]}{(K_{-1}+K_2)}\right)$$

$$[Ru\,(III)]_T = [X]\left(\frac{(K_{-1}+K_2)+K_1[S]}{(K_{-1}+K_2)}\right)$$

$$[X] = \frac{[Ru\,(III)]_T(K_{-1}+K_2)}{(K_{-1}+K_2)+K_1[S]} \quad\quad\quad (5)$$

On comparing ion equation (3) and (5)

$$\frac{-d[RNCl^-]}{dt} = \frac{K_2K_1[Ru\,(III)]_T\{K_{-1}+K_2\}[S]}{\{K_{-1}+K_2\}(K_{-1}+K_2)+K_1[S]} \quad (7)$$

$$\frac{-d[RNCl^-]}{dt} = \frac{K_2K_1[Ru\,(III)]_T[S]}{(K_{-1}+K_2)+K_1[S]} \quad\quad\quad (8)$$

On assuming, $K_2 \gg K_{-1}+K_1[S]$ on neglecting the second term in the denomination of eq (8) we get

$$\frac{-d[RNCl^-]}{dt} = k_1[Ru\,(III)]_T[S]$$

Table 2: Effect of variation HClO$_4$, KCl, Hg(OAc)$_2$ NaClO$_4$ at 40 ^{0}C

[HClO$_4$] x 10^3 mol	[KCl] x 10^{3}Mol^1	[Hg(OAc)$_2$] x 10^3 mol	[NaClO$_4$] x 10^3 mol	-(dc/dt) x 10^{-7}
.83	1.00	1.00	1.00	.47
1.00	1.00	1.00	1.00	.42
1.25	1.00	1.00	1.00	.42
1.67	1.00	1.00	1.00	.40
2.50	1.00	1.00	1.00	.41
5.00	1.00	1.00	1.00	.38
1.00	.83	1.00	1.00	.40
1.00	1.00	1.00	1.00	.42
1.00	1.25	1.00	1.00	.45
1.00	1.67	1.00	1.00	.35
1.00	2.50	1.00	1.00	.34
1.00	5.00	1.00	1.00	.44
1.00	1.00	.83	1.00	.47
1.00	1.00	1.00	1.00	.40
1.00	1.00	1.25	1.00	.46
1.00	1.00	1.67	1.00	.46
1.00	1.00	2.50	1.00	.41
1.00	1.00	5.00	1.00	.43
1.00	1.00	1.00	.83	.46
1.00	1.00	1.00	1.00	.48
1.00	1.00	1.00	1.25	.42
1.00	1.00	1.00	1.67	.42
1.00	1.00	1.00	2.50	.37
1.00	1.00	1.00	5.00	.44

Table 3: Temperature Variation

Temperature^{0}C	dc/dt	(kr) 10^2
30	2.6	9.2
35	3.7	13.02
40	5.0	17.60
45	6.3	22.18

Fig-3
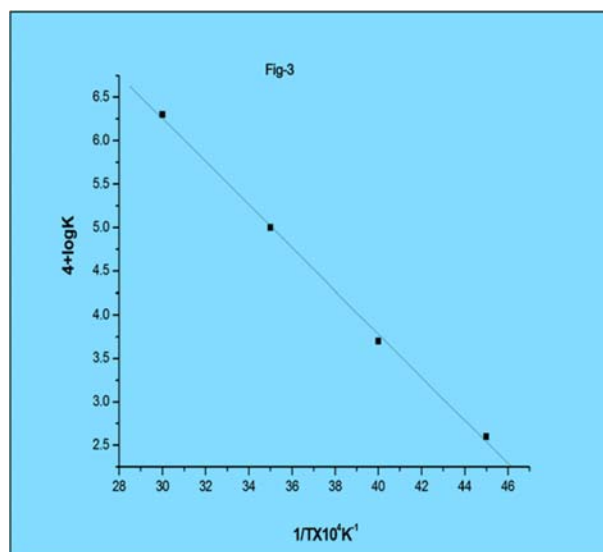
Table4: Values of Activation Parameter

Substrate	ΔE*(KJmol^{-1})	log A	ΔS*(K^{-1}Jmol^{-1})	ΔF*(KJmol^{-1})
Crotonicacid	73.69	4.92	-9.85	29.77

Conclusion

It is concluded from the present investigation that RNCl$^-$ and [RuCl$_2$ (H$_2$O)$_4$]$^+$ are the reactive species of Chloramine-T and Ru (III) Chloride in an Acidic medium respectively**.**

Acknowledgment

References

1. Sheila Srivastava, Singh Oxid. Comm P. **(**Mechanistic investigation of Pd(II) catalyzed oxidation of maltose by chloramines-T in acidic medium: A kinetic study", Oxid. Comm 2010; 33(2):408-415.
2. Srivastava S, Singh Pushpanjali, Jaiswal Arti, Chemtrack J. (Palladium (II) catalyzed oxidation of glycine by Chloramine-T: A kinetic study, J Chemtracks. 2011; 13(1):173-178.
3. Rajesh Shukla, Sushma Rani, Tewari IC. International journal of Chemical Research, Oxidation of Crotonic acid with CE (IV) Perchlorate).2012; 4:122-125.
4. Sarasan Geetha, Pathak Namrata. Research Journal of Chemical Science (Effect of Acetic Acid on Chlorination of Some phenols by Chloramine –T: A Kinetic Approach).2014; 4(3):86-89.
5. SinghAjaya K, Singh Ashok K, Singh Vineeta, Surya Ashish, Singh Prakash, Singh B. The Open Catalysis Journal (Kinetic and Mechanism of aquochlororuthenium (III) Catalysed oxidation Tartaric Acid by potassium promate) 2013, 6, 8, 16.
6. Ashish, Singh Ajaya K, Ashok K, Singh B.The Indian Journal Chemistry (Kinetic of Oxidation crotonic acid by CAT in presence of Pd (ii) and Os as homogenous).2004;43A:16451653.
7. Sudha RaniKB, AnandaS, Made Gowda NM. American Journal of Chemistry, Kineticand Mechanism of L-Trytophan oxidation by CAT I Basic Medium: A Spectroflurofluorometric study).2013; 3(1):1-53.
8. Babasaheb Bhosale D, Gavisidappa Gokavi S. Advances in Applied Science ResearchKineticand mechanism ruthenium catalysed oxidation of d-glucose by 12 tungstocobaltate(III) in aqueous hydrochloric acid mesium)2012; 3(2):785-792.
9. Salem Et. Ashoor, Fatima Ansoor M, Noori Y, Salman Rasayan. J ChemKinetic and Mechanism of oxidation of (E)-1, 5 Diphenyl carbazone (Co ^{ii}ArNNCONNAr) by CAT2013, 6(1-6).
10. Mehrotra RM. Asian J Chem (Kinetic and Mechanism of Oxidation of Isopropanal by Chloramine-T) 1992; 4(3):438-443.