

Kinetics and Mechanistic Study of Ru (III) Catalysed Oxidation of oxalic Acid by Chloramine-T: in Acidic Medium

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ABSTRACT – The Kinetics of Ru (III) Catalyzed oxidation of Oxalic acid by Chloramine-T in acidic medium, in the presence of mercuric acetate as an Scavenge, exhibit zero order with respect to Oxalic acid and First order with Ru (III) and Chloramine-T. Potassium Chloride and acetic acid have a positive effect while variation of $\text{Hg}(\text{OAc})_2$ and NaClO_4 do not bring any significant change. Various activation parameters have been calculated. On the basis of experimental findings, a suitable mechanism consistent with observed kinetic results is proposed. The rate law has been derived on the basis of obtained data.

Key Words: Oxidation, kinetics, Ru (III) chloride, *oxalic acid*, *Chloramine-T*

I INTRODUCTION

Ruthenium (III) Chloride has been widely used as a homogenous catalyst in the various redox reactions. The Ru (III) acts as a Catalyst with number of oxidants like Chloramine-T, N-Bromosuccinimide³⁻⁴, N-Bromoacetamide⁵⁻⁶ and potassium bromate⁷⁻⁸, sodium Periodate⁹⁻¹⁰ have been earlier used in oxidation of various organic compounds. Ru (III) catalyse mechanism is complicated due to formation of different intermediate products. The mechanism of catalyst depends on the nature of the substrate, oxidant and on the experimental conditions. Chloramine-T [CAT] is most important member of organic halo amine family and behaves as an oxidizing agent in acidic and alkaline medium¹¹⁻¹². Oxidizing nature of [CAT] is also due to halonium cation and Nitrogen anion in their structure, which can act both as a base and

Nucleophile. Oxalic acid has toxic effects. Main applications of oxalic acid include cleaning or bleaching, especially for the removal of rust. Rhubarb leaves contain about 0.5% oxalic acid. Oxalic acid is also used to clean iron and manganese deposits from quartz crystals. Only few kinetic studies of oxalic acid oxidation have been reported.

II EXPERIMENTAL

All chemical were of the highest purity and double distilled water was used. All reagents e.g. Oxalic acid, Ru (III) Chloride, HClO_4 , KCl, NaClO_4 , $\text{Hg}(\text{OAc})_2$, Chloramine-T were 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. Solution of Chloramine-T was prepared by double distilled water and its concentration was estimated iodometrically. All reaction vessel were also black coated from outside to avoid any photochemical effect. NaClO_4 was used to maintain the required ionic strength of the medium.

III KINETIC STUDY

Calculated amount of reactants, i.e. Oxalic acid, Perchloric acid, Mercuric acetate Ruthenium chloride, expects Chloramines-T were taken in the reaction vessel and kept in thermostatic water bath maintained at 40⁰c temperature ($\pm 1^0\text{C}$). After allowing sufficient time for reaction mixture to attain the temperature of 40⁰C, requisite amount of Chloramines -T, solution also thermo-stated at the same temperature was rapidly pipette out and added into the reaction vessel. The volume of reaction mixture was 50 ml. At suitable interval of time the amount of unconsumed Chloramine-T was estimated iodometrically. 5ml aliquot was pipette out at regular intervals of time and poured into a

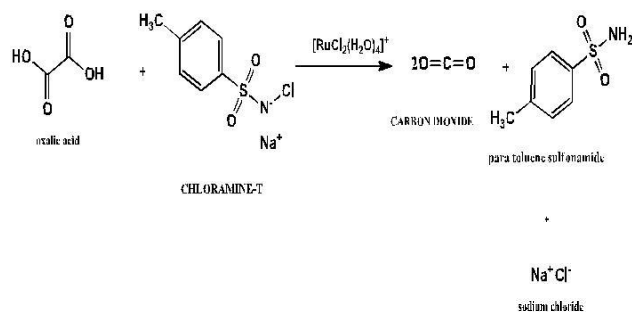
black-coated flask containing 5ml of 4 percent KI and 5ml of 1N H₂SO₄ and few drops of starch. The liberated iodine was then titrated against standard sodium thiosulphate (hypo) solution to a starch end point. Measuring unconsumed amount of CAT iodometrically monitored the progress of rate. The rate of reaction (-dc/dt) was determined by slope tangent drawn using the plane mirror method at fixed [CAT] for each kinetic run. The order of reaction in each reactant was measured with the help of plot (-dc/dt) versus concentration of reactant.

IV STOICHIOMETRY OF Ru (III) CATALYZED OXIDATION OF OXALIC ACID BY CHLORAMINE-T

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of oxidant [CAT] over substrate [oxalic acid] in different ratio at room temperature for two days and estimation of unconsumed oxidant [CAT] in different sets showed that one mole of oxalic acid consume one mole of [CAT]. This result showed 1:1 stoichiometry. After the reaction was complete the end product was confirmed by spot test, TLC analysis and also through dinitrophenylhydrazine (DNP) derivative.

Structure: - Para Toluene sulfonamide (TsNH₂)

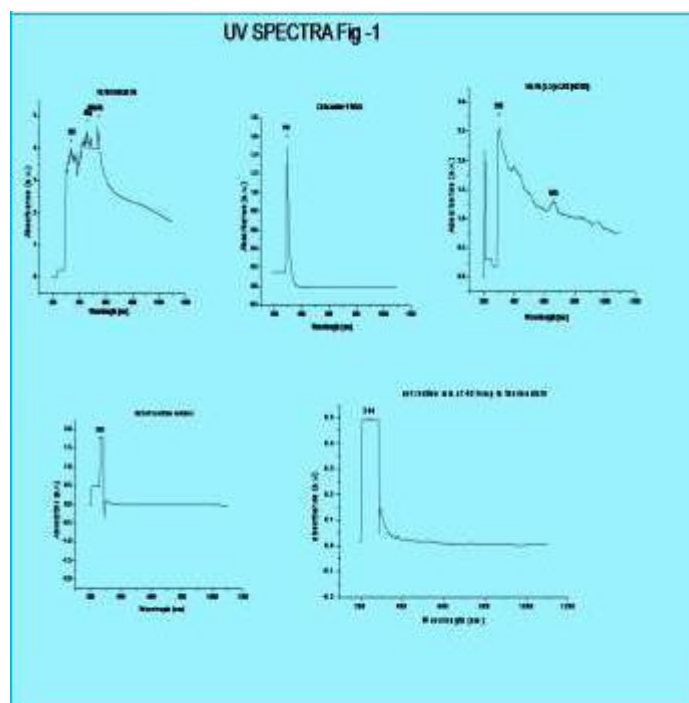
Here (Ts = p-CH₃C₆H₄SO₂)



V Product Analysis

Ultraviolet spectral measurements showed that the sharp absorption band was notice at 342 nm for Ru(III) of 1N

Solution in presence HCl, and 291 nm for CAT N/50 solution and a mixture of oxidant (CAT) and Ru(III) catalyst in the presence of HCl showed the absorption band 299 nm while the set of reaction mixture such as, reducing Oxalic acid, Perchloric acid, Mercuric acetate Ruthenium chloride, excess of Chloramines -T were taken the reaction vessel and kept for two day at room temperature showed absorbance band 263 nm and set of reaction mixtures kept two day at 40⁰C thermostat was absorbance band 244 nm. Indicate the complex formation take place between Ru (III) and oxidant.



VI RESULT AND DISCUSSION

Kinetics of the oxidation of oxalic acid by Chloramine-T in the presence of Ru (III) chloride as a homogenous catalyst has been studied at constant temp of 40⁰ C. The kinetic data are reported in (table-1). The reaction followed first order dependence in Chloramine-T at all concentration of the reactant. The reaction followed first order kinetics with respect to Chloramine-T. This was confirmed by plotting a graph between (-dc/dt) vs [CAT]. Fig (2) First order kinetics was also found in the case Ru (III) and graph plotted

between $(-dc/dt)$ and $[Ru(III)]$ gave straight line (fig 3).
Oxalic acid variation showed zero order.

TABLE No.01
EFFECT OF VARIATION OF OXIDANT, RU (III)
AND OXALIC ACID
AT TEMP 40°C

[CAT] $\times 10^3$ mol dm^{-3}	Ru(III) Catalyst 10^4 Mol $dm^{-3} s^{-1}$	OA [Substrate] $\times 10^3$ mol dm^{-3}	(dc/dt) $\times 10^{-1}$	$K_1 \times 10^3$ s^{-1}
.83	3.35	1.00	.42	.50
1.00	3.35	1.00	.50	.50
1.25	3.35	1.00	.60	.50
1.67	3.35	1.00	.75	.45
2.50	3.35	1.00	1.1	.44
5.00	3.35	1.00	2.0	.40
1.00	1.67	1.00	.26	.10
1.00	3.35	1.00	.36	.10
1.00	5.02	1.00	.46	.10
1.00	6.67	1.00	.56	.10
1.00	8.34	1.00	.66	.10
1.00	10.05	1.00	.76	.10
1.00	3.35	.83	.37	-
1.00	3.35	1.00	.40	-
1.00	3.35	1.25	.43	-
1.00	3.35	1.67	.48	-
1.00	3.35	2.50	.51	-
1.00	3.35	5.00	.56	-

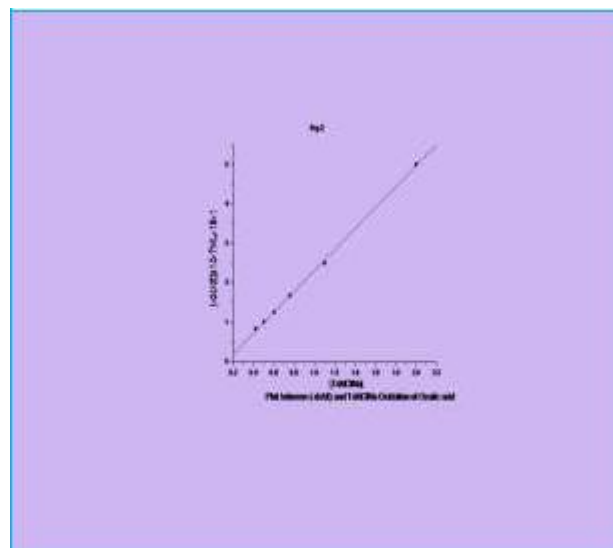
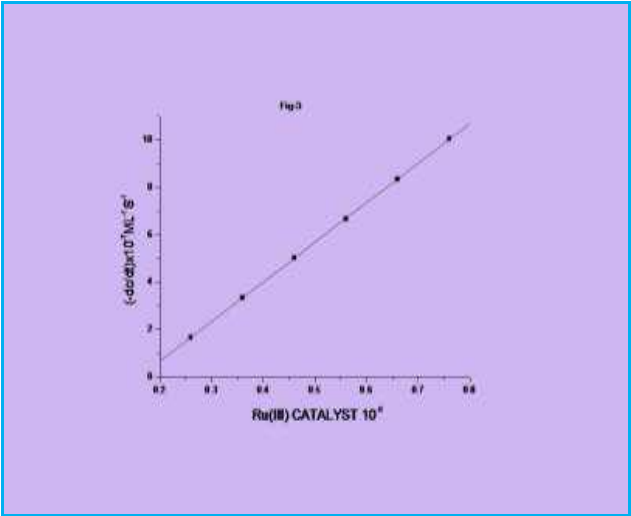


Fig 2:- Effect of Variation of rate constant with the Oxidant of Table-01

Fig 3:- Effect of Variation of rate constant with the Oxidant of Table-01

[HClO ₄] X 10 ³ mol	[KCl] x 10 ³ Mol l	[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	.36
1.00	1.00	1.00	1.00	.36
1.25	1.00	1.00	1.00	.42
1.67	1.00	1.00	1.00	.46
2.50	1.00	1.00	1.00	.45
5.00	1.00	1.00	1.00	.46
1.00	.83	1.00	1.00	.36
1.00	1.00	1.00	1.00	.45
1.00	1.25	1.00	1.00	.46
1.00	1.67	1.00	1.00	.46
1.00	2.50	1.00	1.00	.50
1.00	5.00	1.00	1.00	.53
1.00	1.00	.83	1.00	.45
1.00	1.00	1.00	1.00	.46
1.00	1.00	1.25	1.00	.35
1.00	1.00	1.67	1.00	.46
1.00	1.00	2.50	1.00	.35
1.00	1.00	5.00	1.00	.51
1.00	1.00	1.00	.83	.42
1.00	1.00	1.00	1.00	.46
1.00	1.00	1.00	1.25	.40
1.00	1.00	1.00	1.67	.46
1.00	1.00	1.00	2.50	.46
1.00	1.00	1.00	5.00	.45



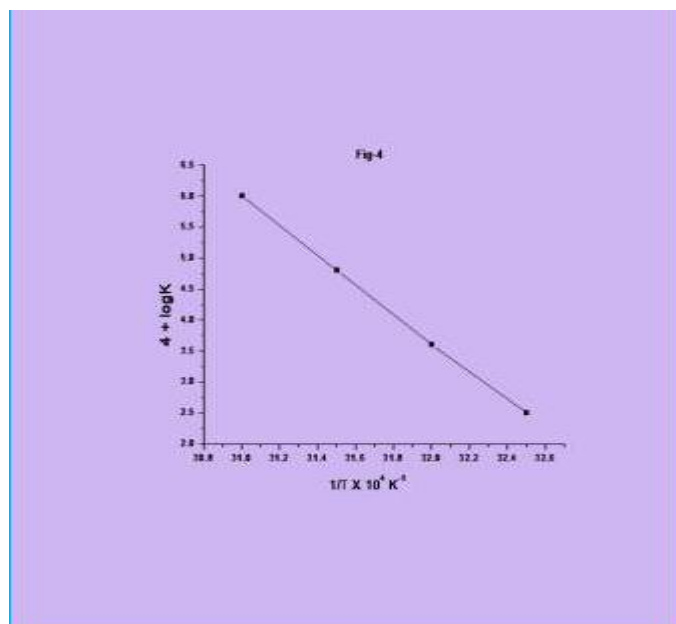
The negligible effect of Hg(OAc)₂ excluded the possibility of its involvement either as a catalyst or as an oxidant. Experimental data showed negligible effect of ionic strength of medium on the rate. Reaction showed no effect of [H⁺]

ion Concentration. Effect of variation of [KCl] concentration showed positive effect on the rate of reaction in (table-2). Successive addition of acetic acid increased the reaction rate showing a negative dielectric effect on the rate. The experiments were also done on the temperature 30⁰C, 35⁰C & 45⁰C . Specific rate constants were calculated and a plot was drawn between log k versus 1/T (Fig-3) which was linear. Calculated value of activation parameter for various sets of reaction is shown in the table-3. The activation energy (ΔE*) is calculated. With help of rate of constant kr, value of the other activation parameters such as log A where (A) is Arrhenius factor, entropy of activation (ΔS*), Free energy of activation (ΔF*) were calculated. The number of possible chloro species of Ru (III) present in the solution can be represented by the general formula [Ru (III) (6 – x) (H₂O) Cl_n]^{3-x} where n = 1- 6. All these species are highly pH dependent. The species present in the pH range 1³, 1⁴ studied is however (RuCl₂(H₂O)₄)⁺ This was confirmed by the reported absorption spectra of Ru (III) solution from 1 x 10⁻³ M to 1x10⁻⁵ M in the pH range 1.00 to 3.00 at constant ionic strength (μ=0.1 M KNO₃)

TABLE No.02
EFFECT OF VARIATION HClO₄, KCl, Hg(OAc)₂
NaClO₄ at 40⁰C

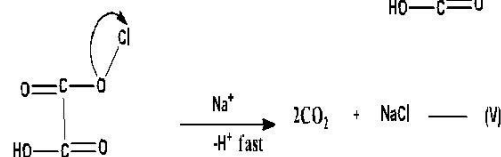
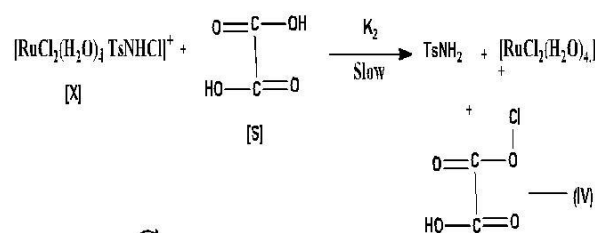
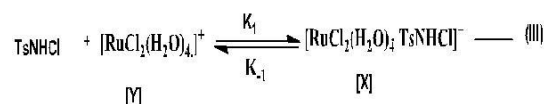
TABLE NO. 03
ACTIVATION PARAMETER AT 40⁰C

Activation Parameter	Temperatu re °C	Oxalic acid
K ₁ x10 ⁴ s ⁻¹	30	2.5
K ₁ x10 ⁴ s ⁻¹	35	3.6
K ₁ x10 ⁴ s ⁻¹	40	4.8
K ₁ x10 ⁴ s ⁻¹	45	6.0
ΔE*(KJmol ⁻¹)	40	58.18
log A	40	5.14
ΔS*(K ⁻¹ Jmol ⁻¹)	40	-10.28
ΔF*(KJmol ⁻¹)	40	30.56



In acidic medium, the probable oxidizing species are the free acid (TsNCINa), as in the present study contain TsNCl⁻, TsNHCl may react of Oxalic Acid to give product. TsNCl⁻ is easily protonated in acidic medium in yield TsNHCl Sopre et al. Showed direct interaction of N chloro-p-toulenesulphonamide, with the substrate could be slow, it is therefore reasonable to neglect to direct interaction of TsNHCl with Oxalic acid.

On the basis the above fact and observed the kinetic mechanism of oxidation of Oxalic acid may be represent follow.



VII DISCUSSION AND MECHANISM-

Pryde and Soper¹⁵, Morries et al¹⁶, Bishop and Jennings¹⁷ have been shown the existence of similar equilibrium in acid and alkaline solute ion of N- Metallo- N halo - arly sulphonamides. Chloramine-T behaves as a strong electrolyte and ionization may be represented by, equation (1) and (2). 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 and hypochlorous acid.



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

$$-\frac{d[\text{TsNCl}^-]}{dt} = K_2 [\text{X}] [\text{S}] \quad \text{--- (1)}$$

Concentration of the complex i.e. [x] May be determined by applying steady state treatment to [x]

Hence,

$$\begin{aligned} \frac{d}{dt} &= \frac{K_1[\text{TsNHCl}][Y] - K_{-1}[X] - K_2[X][S]}{K_{-1} + K_2[S]} = 0 \\ K_1[\text{TsNHCl}][Y] &= K_{-1}[X] + K_2[X][S] \\ &= [X] \{ K_{-1} + K_2[S] \} \\ [X] &= \frac{K_1[\text{TsNHCl}][Y]}{K_{-1} + K_2[S]} \quad (2) \end{aligned}$$

On substituting the value of [X] from (2) to (1) we get

$$\frac{-d[\text{TsNCl}]}{dt} = \frac{K_2 K_1 [\text{TsNHCl}][Y][S]}{K_{-1} + K_2[S]} \quad (3)$$

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

$$[\text{Ru (III)}]_T = [Y] + [S] \quad (4)$$

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

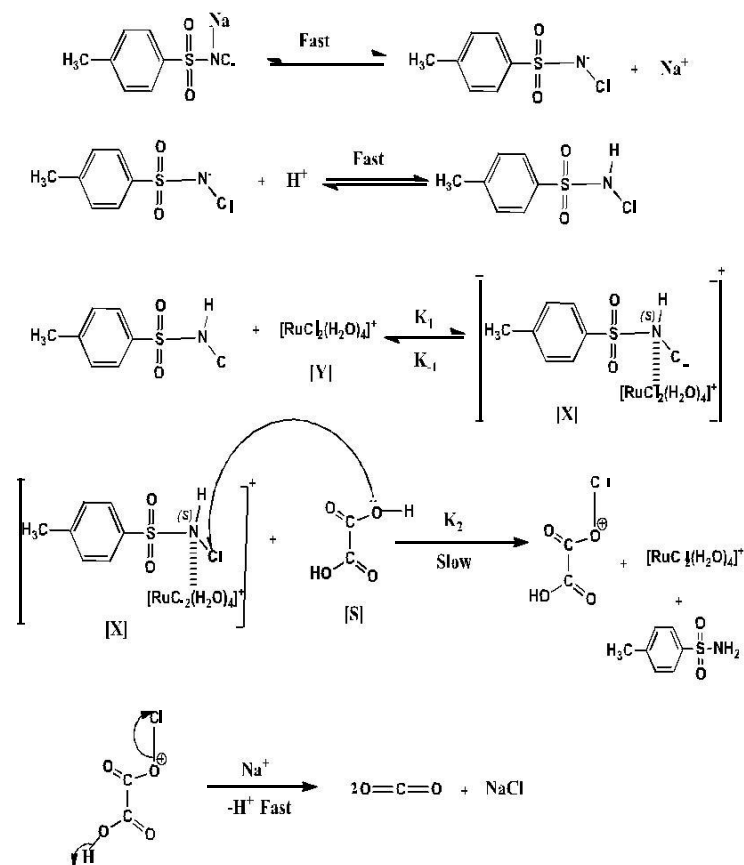
$$\begin{aligned} [\text{Ru (III)}]_T &= [Y] + \frac{K_1[\text{TsNHCl}][Y]}{K_{-1} + K_2[S]} \\ &= [Y] \left\{ 1 + \frac{K_1[\text{TsNHCl}]}{K_{-1} + K_2[S]} \right\} \\ &= [Y] \left\{ \frac{K_{-1} + K_2[S] + K_1[\text{TsNHCl}]}{K_{-1} + K_2[S]} \right\} \\ [Y] &= [\text{Ru (III)}]_T \left\{ \frac{K_{-1} + K_2[S]}{K_{-1} + K_2[S] + K_1[\text{TsNHCl}]} \right\} \quad (5) \end{aligned}$$

On comparing ion equation (3) and (4)

$$\begin{aligned} \frac{-d[\text{TsNCl}]}{dt} &= \frac{K_2 K_1 [\text{TsNHCl}][\text{Ru (III)}]_T \{ K_{-1} + K_2[S] \} [S]}{\{ K_{-1} + K_2[S] \} \{ K_{-1} + K_1[\text{TsNHCl}] + K_2[S] \}} \\ &= \left\{ \frac{K_2 K_1 [\text{TsNHCl}][\text{Ru (III)}]_T [S]}{K_{-1} + K_2[S] + K_1[\text{TsNHCl}] + K_2[S]} \right\} \quad (6) \end{aligned}$$

On assuming, $K_2[S] \gg K_{-1} + K_1[\text{TsNHCl}]$ and on neglecting the second term in the denomination of eq (6) we get

$$\begin{aligned} \frac{-d[\text{TsNCl}]}{dt} &= \frac{K_2 K_1 [\text{TsNHCl}][\text{Ru (III)}]_T [S]}{K_2[S]} \\ &= K_1 [\text{TsNHCl}][\text{Ru (III)}]_T \end{aligned}$$



VIII CONCLUSION

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

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