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KINETIC STUDY OF RUTHENIUM (III) CATALYZED OXIDATION OF SUCCINIC ACID BY *N*-CHLORO 4-METHYLBENZENESULFONAMIDE, SODIUM SALT

Amrita Srivastava*[1] **and Neelam**[2]

Chemistry Department, Lucknow University, Lucknow-226007, U.P., India.

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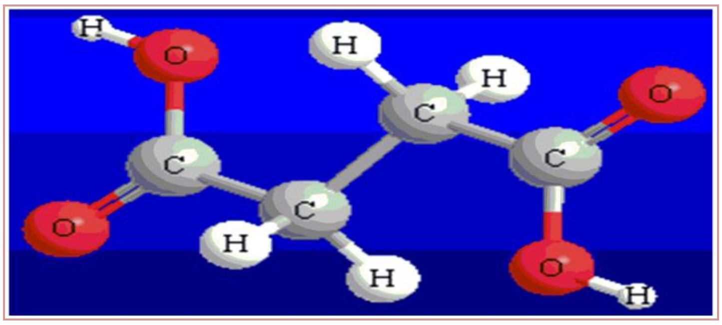
***Correspondence for Author**
Dr. Amrita Srivastava
Chemistry Department,
Lucknow University,
Lucknow-226007, U.P.,
India.

ABSTRACT

The Ruthenium catalysed oxidation of succinic acid by Chloramine-T as an Oxidant has been done in acidic medium, in presence of mercuric acetate as scavenger. The result obtained shows that reaction follows the First order kinetic with respect to Ru(III) and substrate while zero order with respect to oxidant [CAT]. Effect of variations of KCl on the rate of reaction is in positive direction. The Negligible effect of [Hg $(OAC)_2$] and ionic strength of the medium have been observed. The activation parameters have been computed at different temperatures. Product analysis has been done.

KEYWORDS: kinetics, Ru (III) chloride, Succinic acid, Chloramine-T, $Hg(OAc)_2$.



Butanedioic acid or ethane-1,2-dicarboxylic acid (3D Structure)

INTRODUCTION

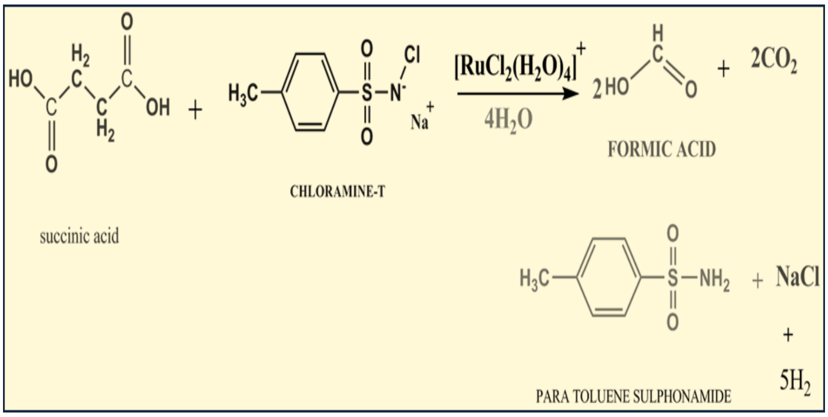
Succinic acid is externally used for rheumatic aches and pain. The acid is combustible, corrosive and causing burns. Eyes contact may cause serious damage. Many transition metal ions such as ruthenium, and iridium[2-3] used as a catalyst in various redox processes. Ruthenium (III) Catalyst acts with many organic and inorganic substrate (D-fructose, thiamine, ornidazole and vanillin).[4-5] The mechanism of reaction can be quite complicated due to formation of intermediate complex. The mechanism of reaction depends on the nature of the substrate, oxidant and on the experimental conditions. [CAT], which is oxidizing agents, has been extensively used in variety of organic compounds.

MATERIAL AND METHOD

All the reagents used are of AR grade. Succinic acid, Ru (III) Chloride, $HClO_4$, KCl, $NaClO_4$, $Hg(OAc)_2$, Chloramine-T. All solutions were prepared in double distilled water. The stock solution of Ru (III) Chloride was prepared by dissolving 1 gm of sample in HCl of known strength (.018N) and total volume of solution was made up to 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 coated from 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. Measured amount of Succinic acid, Perchloric acid, Mercuric acetate and Ruthenium chloride, expcets Chloramines-T were taken in the reaction vessel and kept in thermostatic water bath maintained at 40^0c temperature ($\pm 1^0$C). Chloramine-T was also thermostated at the same time in separate flask. At the desired temperature, 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_2SO_4 and few drops of starch. The unreacted chloramines-t react with KI liberated iodine that was titrated against standard sodium thiosulphate (hypo) solution using starch as an indicator. Measuring unconsumed amount of CAT iodometrically monitored the progress of rate of reaction. A graph is plotted between concentration of reactant and time. The rate of reaction (-dc/dt) was determined by slope tangent drawn using the plane mirror method.

Stoichiometry

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



Carbon dioxide has been detected by usual lime water test and carboxylic acid group has been detected by sodium bicarbonate test. The formation of formic acid confirmed following test.

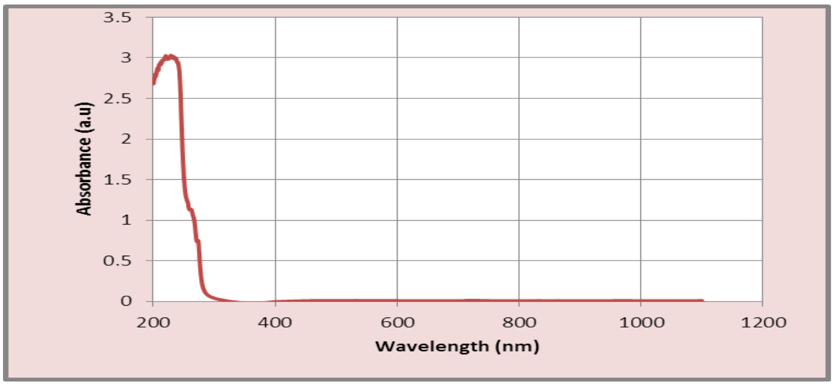
(1) In the sample of Solution added 1ml of tollen reagent and warmed A grey precipitate with silver mirror was obtained.

(2) Dcolourised alkaline $KMnO_4$ solution.

On Warming with Cons H_2SO_4 . Carbon dioxide was evolved which burns with blue flame. Finally product was confirmed by TLC analysis.[6-7]

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. The set of reaction mixtures such as, reducing Succinic 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 showed absorbance band at 300 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 Succinic 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 (Succinic 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,as zero order dependence on [CAT] was observed, this was confirmed by plotting 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)

Table:1. Effect the variation of oxidant, Ru (III) and Succinic acid at Temp 40^0C

CAT x10^3 mol dm^{-3}	Ru(III) Catalyst x 10^6Mol dm^{-3} s^{-1}	Succinic acid [Substrate] X 10^3 mol dm^{-3}	(-dc/dt) x 10^{-7}	K_1 x 10 Mol^{-1} S^{-1}
.91	3.35	1.00	.52	-
1.11	3.35	1.00	.52	-
1.42	3.35	1.00	.50	-
2.0	3.35	1.00	.50	-
3.33	3.35	1.00	.58	-
10.0	3.35	1.00	.50	-
1.00	1.67	1.00	.22	.13
1.00	3.35	1.00	.32	.09
1.00	5.02	1.00	.51	.10
1.00	6.67	1.00	.60	.08
1.00	8.34	1.00	.77	.09
1.00	10.05	1.00	.84	.08
1.00	3.35	.83	.30	.37
1.00	3.35	1.00	.35	.35
1.00	3.35	1.25	.51	.38
1.00	3.35	1.67	.65	.38
1.00	3.35	2.50	.84	.34
1.00	3.35	5.00	1.5	.30

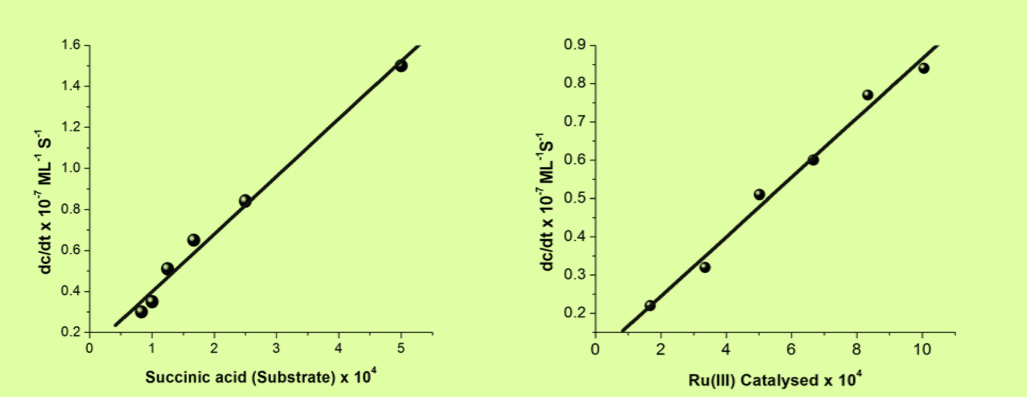
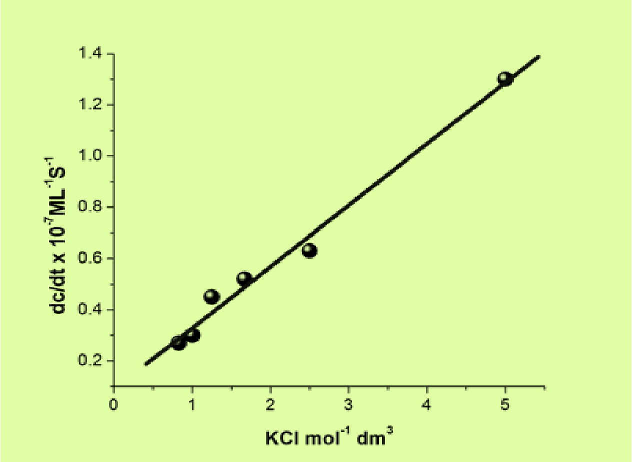


Table-2. Effect of variation $HClO_4$, KCl, $Hg(OAc)_2$ $NaClO_4$ at 40^0C

$[HClO_4]$ x 10^3 mol	[KCl] x 10^3Mol ^{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	.38
1.00	1.00	1.00	1.00	.38
1.25	1.00	1.00	1.00	.38
1.67	1.00	1.00	1.00	.36
2.50	1.00	1.00	1.00	.33
5.00	1.00	1.00	1.00	.38
1.00	.83	1.00	1.00	.27
1.00	1.00	1.00	1.00	.30
1.00	1.25	1.00	1.00	.45
1.00	1.67	1.00	1.00	.52
1.00	2.50	1.00	1.00	.63
1.00	5.00	1.00	1.00	1.3
1.00	1.00	.83	1.00	.24
1.00	1.00	1.00	1.00	.29
1.00	1.00	1.25	1.00	.23
1.00	1.00	1.67	1.00	.23
1.00	1.00	2.50	1.00	.27
1.00	1.00	5.00	1.00	.20
1.00	1.00	1.00	.83	.33
1.00	1.00	1.00	1.00	.30
1.00	1.00	1.00	1.25	.31
1.00	1.00	1.00	1.67	.35
1.00	1.00	1.00	2.50	.38
1.00	1.00	1.00	5.00	.36



Kinetics and Activation parameter

The increase in temperature increased the rate of reaction. The plot of log k_1 versus (1/T) (Fig-3) is straight line. Presented table-3.According to Arrhenius equation the specific rate constant log A, Energy activation ΔE, entropy of activation of the ΔS, free energy of activation Δ*F* are calculated from the rate measurements at 303, 308, 313 and 318 K (Table –

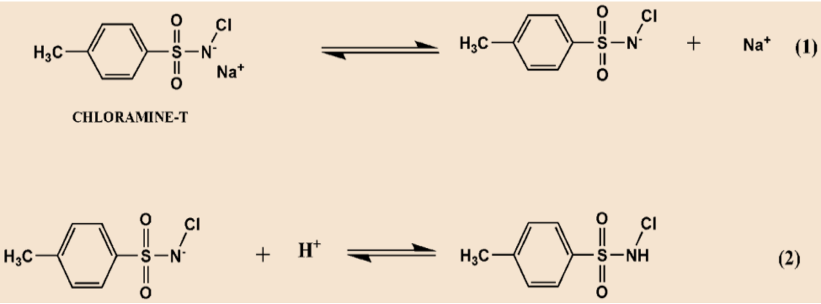
4). The number of possible chloro species of Ru (III) present in the solution can be represented by the general formula [Ru (III) (6 – x) (H_2O) Cln] $^{3-x}$ where n = 1- 6. All these species are highly pH dependent. The species present in the pH range' studied is however $[RuCl_2(H_2O)_4]^+$ This was 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).

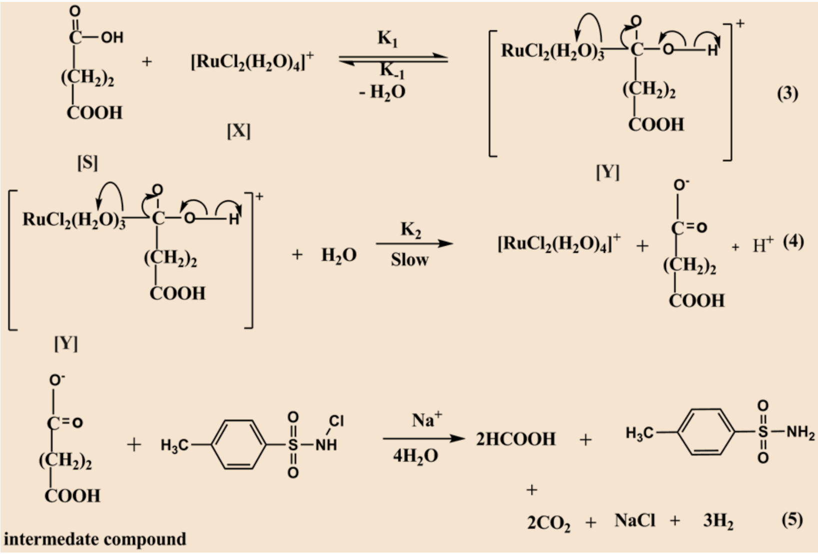
The octahedral complex species such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^+$ do not exist in an the aqueous solution $RuCl_3$.[8-9] The study on oxidation state Ru(III) exist in acidic medium.

$$[RuCl_3(H_2O)_3] + H_2O \rightleftharpoons [RuCl_2(H_2O)_4]^+ + Cl^- \qquad (1)$$

7 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. on hydrolysis give p- toulenesulphonamide.[9-10]





The rate determines step (4) is slow. The rate of reaction is term of consumption of concentration of [TsNCl$^-$] ions may be written as eq (1)

$CH_3C_6H_4SO_2$=Ts

$$\frac{-d[TsNCl^-]}{dt} = K_2Y \qquad (1)$$

Applying steady state treatment to the concentration of [Y] we can determine the concentration of Y as given below.

Hence,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Comparing ion equation (3) and (5)

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

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

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

$$\frac{-d[\mathrm{TsNCl}^-]}{dt} = K_1\ [\mathrm{Ru\ (III)}]_T\ \ [S]$$

Table -3 Temperature Variation

Temperature K	dc/dt	(kr) 10^2
303	2.8	11.80
308	4.3	18.13
313	5.6	23.61
318	6.6	22.83

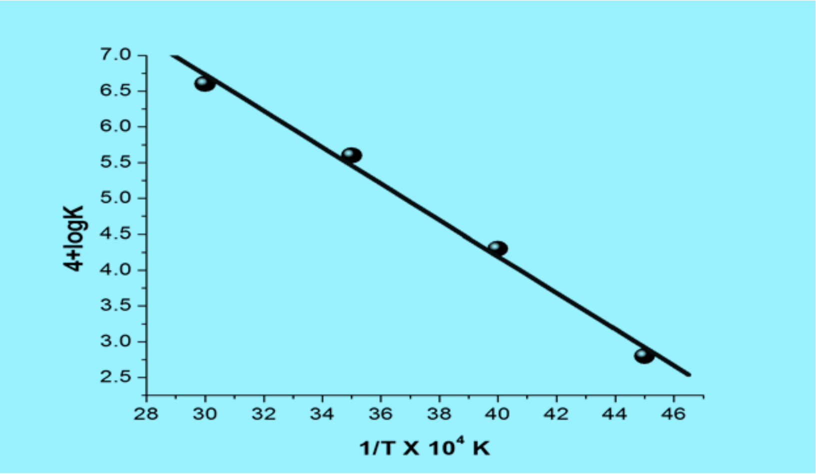


Table-4 VALUES OF ACTIVATION PARAMETER

Substrate	**ΔE*(KJmol^{-1})**	**log A**	**ΔS*(K^{-1}Jmol^{-1})**	**ΔF*(KJmol^{-1})**
Suucinic acid	59.21	3.99	-7.98	24.12

CONCLUSION

First order kinetics with respect to Ru(III) Catalyst.

First order kinetics with respect to succinic acid (substrate).

The reaction shows zero order kinetics with respect to oxidant (CAT).

The first order kinetics with respect to Chloride ion.

The value of activation parameters ΔE , log A *ΔF* were positive , ΔS was negative**,**. The reaction was spontaneous. The product of oxidation of succinic acid by CAT,catalysed by Ru(iii) in acidic medium was found as formic acid and p-toulenesulphonamide and carbon dioxide.

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