MINOR RESEARCH PROJECT
ON
Kinetics and oxidation reactions of trichloro isocyanuricacid and Dichloroisocyanuricacid with differentdi carboxylic acid series –A comparative study

SUMMARY

Submitted to

ज्ञान-विज्ञान विमुक्तये
UGC
University Grants Commission

The Joint secretary
South Eastern Regional Office
University Grants Commission
A.P.SF.C Building 4th floor , Chirag- Ali- lane
Hyderabad-500001

Submitted by

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S.R.R & C.V.R
ESTD : 1937

SRR & CVR GOVERNMENT COLLEGE(A)
NAAC: B+ (III Cycle with CGPA :2.60
ISO 9001-2015 certified
VIJAYAWADA ANDHRAPRADESH

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DEPARTMENT OF BIOCHEMISTRY

BY Dr.NEERAJA.VALLURU

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SUMMARY

1.Kinetics of Oxidation of oxalic acid by DCICA :

oxidation ofoxalic acidby DCICA in AcOH – $HClO_4$ medium is reported. The reaction orders are first order in oxidant, first order in substrate, independent with H^+ ion concentration, insensitive with increase of percentage of acetic acid the rate is increased with addition of Mn(II) ,rate increased with increase of temperature. The insensitivity of the reaction rate with increase of percentage of acetic acid is due to the change in solvent composition as observed in present investigation with oxalic acid has to be traced to specific solvent effects. The following rate law explains all the kinetic observations.

$$\text{Rate} = \frac{kx_2Kc2\ KpKh1[S]_T\ [DCICA][H^+]}{\{1+Kc_2\ [S]\}\{1+K_{h1}\}\{1+K_1[H^+]+K_1K_2[H^+]^2+Kc_2KpKh_1\ [DCICA][H^+]\}}$$

2.KINETICS OF OXIDATION OF MALONIC ACID BY DCICA

The investigation deals with oxidation of malonic acid with dichloroisocyanuric acid. The reaction have been carried out in acetic acid and perchloric acid mixtures . The reaction orders are first order in DCICA, fractional order in substrate, unaffected with H^+ ion concentration, insensitive with increase of percentage of acetic acid the rate is increased with addition of Mn(II) ,rate increased with increase of temperature. The insensitivity of the reaction rate with increase of percentage of acetic acid is due to the change in solvent composition as observed in present investigation with oxalic acid has to be traced to specific solvent effects. The following rate law explains all the kinetic observations.

$$\text{Rate} = \frac{kx_2Kc2\ KpKh1[S]\ T\ [DCICA][H^+]}{\{1+Kc_2[S]\}\{1+K_{h1}\}\{1+K1[H^+]+Kc_2KpKh_1[DCH][H^+]\ K_1K_2[H^+]^2\}}$$

3.Kinetics of Oxidation of oxalic acid by TCICA

The investigation deals with oxidation of oxalic acid with Trichloroisocyanuric acid. The reaction have been carried out in acetic acid and perchloric acid mixtures The reaction orders are first order in TCICA,first order in substrate, unaffected with H^+ ion concentration,rate decreased with increase of percentage of acetic acid the rate is unaffected with addition of Mn(II) ,rate increased with increase of temperature. The reaction rate is unaffected by the addition of Mn(II) despite the face that Mn(II) catalyses all the oxidations reported so far by all metallic and non metallic oxidants This confirms the above point that the absence of catalysis dependant upon the nature of the system as well as that of the oxidant. The reaction rate is unaffected by the addition of Mn(II) despite the face that Mn(II) catalyses all the oxidations reported so far by all metallic and non metallic oxidants The following rate law explains all the kinetic observations.

$$\text{Rate} = \frac{K_P\ K_{C2}\ K_{h1}\ k_{x2}\ [S]_T\ [H^+]\ [TCICA]_T}{([H^{+2}] + K_1[H^+] + K_1K_2 + K_{c2}\ [S]_T)}$$

4.Kinetics of oxidation of malonic acid byTCICA.

It was of interest to study the kinetics of oxidation of malonic acid by TCICA in aqueous acetic acid – perchloric acid mixtures are malonic acid system has reactive methylene group.The investigation deals with oxidation of malonic acid with Trichloroisocyanuric acid. The reaction have been carried out in acetic acid and perchloric acid mixtures The reaction orders are first order in TCICA,first order in

substrate, unaffected with H^+ ion concentration, rate decreased with increase of percentage of acetic acid, rate increased with increase of temperature. Addition of Mn(II) resulted in an increase of the reaction rate. In these reactions addition of halide ions like Cl^- and I-results increase the rate its because of the formation of molecular chlorine and an interhalogen compound like ICl which act as better oxidising agent than $H_2O\ Cl^+$ in the system involving C-H bond fission.

5.Ru(III) catalysrd oxidation of maleic acid and fumaric acid by TCICA and DCICA

Kinetics of oxidation of maleic and fumaric acids by trichloroisocyanuric acid (TCICA)and (DCICA)catalysed by Ru(III) in AcOH - $HClO_4$ medium reveals that the reaction is first order in TCICAand DCICA, first order in Ru(III) and zero order in H^+ with both geometrical isomers with TCICA and DCICA. With maleic acid dependence on substrate is zero where as it is first order with fumaric acid. The rate law is as follows:

$$\text{Rate} = \frac{k.K_4K_5K_6[Ru(III)][S][H^+][TCICA]_T}{\{1+K_6[S]\}\{1+K_1+K_1K_4H^+\}}$$

A complex between substrate and intermediate active Ru(V) species is envisaged which yields products in a rate determining step. The reactivity pattern is fumaric acid > maleic acid.

5.Comparision of reactivity of Trichloroisocyanuric Acid and Dichloroisocyanuric acid:

It is observed that the rate constants and the similar conditions of experimentation the oxidation of Oxalic and Malonic acids by Dichloro isocyanuric acid are $4.64x10^1min^{-1}$ and $1.16x10^1min^{-1}$.The rate costants observed in case of Trichloro

isocyanuricacid are 9.30×10^{3} min^{-1} and $7.89 \times 10^{3} min^{-1}$.By observing the above result it is crystal clear that the rate of the trichloro isocyanuricacid is two times faster than dichloro isocyanuricacid.

The order of reaction is :

TCICA > DCICA

The rate difference in these N-Halo compounds is mainly due to first step hydrolysis in TCICA are very faster when compared to the DCICA.It is explained in the below rate law. The data observed in various experiments in carboxylic acid series is TCICA > DCICA.The difference in these compounds is mainly due to difference in their first step hydrolysis .The higher reactivity of TCICA is mainly due to first stp hydrolysis in these species very faster in comparison with DCICA

Report of Workdone for Minor Research project

First year

In the first two months of the first year I collected triple distilled water and procured required chemicals and processed recrystallistaion of all carboxylic acid i.e oxalic acid ,malonic acid ,maleic acid .fumaric acid.

After that

I selected two dicarboxylic acids one is oxalic acid second is malonic acid with **Dichloroisocyanuric acid** in acetic and perchloric acid mixture In this we studied

a.oxidant variation (With both oxalic and malonic acid)

b.substrate variation (With both oxalic and malonic acid)

c.perchloric acid variation (With both oxalic and malonic acid)

d.temperature variation (With both oxalic and malonic acid)

e. Efeect of Mn(II)ions on reaction (With both oxalic and malonic acid)

f.Effect of chloride and iodide ion effect(With both oxalic and malonic acid)

.The addition of Mn(II) results increasing the rate of reaction. Briefly In both Dichloroisocyanuric acid and Trichloroisocyanuric acidswith oxalic and malonic acids

After completion of Oxalic acid and malonic acid work I proposed rate laws and mechanisms and determination of order of reactions to oxalic acid and malonic acids separately with DCICA.

After completion of oxidation of oxalic acid and malonic acid by DCICA

Oxidation of oxalic acid and malonic acid by TCICA : It is very interesting to compare the rate of DCICA and TCICA.In this study we did oxalic acid second is malonic acid with **Trichloroisocyanuric acid** in acetic and perchloric acid mixture In this we studied

a.oxidant variation (TCICA)

b.substrate variation (With both oxalic and malonic acid)

c.perchloric acid variation (With both oxalic and malonic acid)

d.temperature variation (With both oxalic and malonic acid)

e. Efeect of Mn(II)ions on reaction(With both oxalic and malonic acid)

f.Effect of chloride and iodide ion effect(With both oxalic and malonic acid)

After completion of Oxalic acid and malonic acid work I proposed rate laws and mechanisms and determination of order of reactions to oxalic acid and malonic acids separately with TCICA.

Second year

This work is the out come of a desire for projecting new mechanistic aspects of some reactions in systems more or less earlier investigated but not well understood. A few systems have been newly investigated under catalytic conditions using N-halo compounds drichloroisocyanuricacid (DCICA) and trichloroisocyanuricacid (TCICA) and a series of carboxylic acid.The work attempts to bring out

mechanistic generalization wherever possible involved in each of the reaction systems investigated.

Ru(III) catalysis in the oxidation of maleic and fumaric acids by trichloroisocyanuric acid (TCICA)and Dichloroisocyanuric acid (DCICA):

It is interesting to study stereo isomers fumaric acid and maleic acid by both the oxidising agents TCICA and DCICA. Oxidation of fumaric acid and maleic acid by both the oxidising agents TCICA and DCICA are studied catalysed by Ru(III).

DCICA work

a.oxidant variation (With both fumaric acid and maleic acid)

b.substrate variation (With both fumaric acid and maleic acid)

c.perchloric acid variation (With both fumaric acid and maleic acid)

d.temperature variation (With both fumaric acid and maleic acid)

e.proposed rate laws and mechanisms and determination of order of reactions to oxalic acid and malonic acids separately with both DCICA.

TCICA work

a.oxidant variation (With both fumaric acid and maleic acid)

b.substrate variation (With both fumaric acid and maleic acid)

c.perchloric acid variation (With both fumaric acid and maleic acid)

d.temperature variation (With both fumaric acid and maleic acid)

e.proposed rate laws and mechanisms and determination of order of reactions to oxalic acid and malonic acids separately with both DCICA.

Kinetics of oxidation of maleic and fumaric acids by trichloroisocyanuric acid (TCICA) catalysed by Ru(III) in AcOH - $HClO_4$ medium reveals that the reaction is first order in TCICA, first order in Ru(III) and zero order in H^+ with both geometrical isomers. With maleic acid dependence on substrate is zero where as it is first order with fumaric acid. The rate law is as follows:

$$\text{Rate} = \frac{k.K_4K_5K_6[Ru(III)][S][H^+][TCICA]_T}{\{1+K_6[S]\}\{1+K1+K_1K_4H^+\}}$$

FINAL REPORT

This work is the out come of a desire for projecting new mechanistic aspects of some reactions in systems more or less earlier investigated but not well understood. A few systems have been newly investigated under catalytic conditions using N-halo compounds drichloroisocyanuricacid (DCICA) and trichloroisocyanuricacid (TCICA) and a series of carboxylic acid.The work attempts to bring out mechanistic generalization wherever possible involved in each of the reaction systems investigated.

Ru(III) catalysis in the oxidation of maleic and fumaric acids by trichloroisocyanuric acid (TCICA):

Kinetics of oxidation of maleic and fumaric acids by trichloroisocyanuric acid (TCICA) catalysed by Ru(III) in AcOH - $HClO_4$ medium reveals that the reaction is first order in TCICA, first order in Ru(III) and zero order in H^+ with both geometrical isomers. With maleic acid dependence on substrate is zero where as it is first order with fumaric acid. The rate law is as follows:

$$\text{Rate} = \frac{k.K_4K_5K_6[Ru(III)][S][H^+][TCICA]_T}{\{1+K_6[S]\}\{1+K1+K_1K_4H^+\}}$$

A complex between substrate and intermediate active Ru(V) species is envisaged which yields products in a rate determining step. The reactivity pattern is fumaric acid > maleic acid.

After completion of work one paper is published and presented in the proceedings of 4th International conference on Advances in humanities science and management with ISBN No 978-81-939386-3-8. Title of the paper is Kinetics of Ru(III) catalysed oxidation of Maleic and fumaric acid by Trichloroisocyanuric acid and dichloroisocyanuric acid .

Two more papers are in pipeline.

Work done so far and results achieved and publications if any ,resulting from the work :

Initially I selected two dicarboxylic acids one is oxalic acid second is malonic acid with Dichloroisocyanuric acid and Trichloroisocyanuric acid in acetic and perchloric acid mixture .In this we studied manganous chloride effect on reaction rate.The addition of Mn(II) results increasing the rate of reaction. Briefly In both Dichloroisocyanuric acid and Trichloroisocyanuric acidswith oxalic and malonic acids in oxidant variation first order ,in substarte variation it is fractional order , in perchloric acid variation both the substrates with both the oxidants exhibits independent nature ,in case of acetic acid variation oxalic acid exhibits inverse action in case of malonic acid exhibits insensitive nature .The rate is increased with increase of temperature , Arrhenius parameters are calculated for every substarte.

The independence to acidity can be traced to the following reason. In the oxidation of oxalic acid by DCICA there monoprotonation of oxalic acid due to $[H^+]$ leading to inverse first order dependence to acidity .

Insensitive reaction rate is due to decrease in dielectric constants of the medium .normally one would have expected a decrease in dielectric constant in system like present case where both the reactants are positive ion - positive ion reactions as per the theories of Laidler and Amis. The insensitivity of the reaction rate to the

change in solvent composition as observed in present investigation with oxalic acid has to be traced to specific solvent effects.

In our present study we report the rate of reaction of oxalic acid is more than malonic acid .This is due to the more acidic nature of oxalic acid with less Pka value i.e.,1.27 than malonic acid with high pka value i.e.,2.85.

$$\text{Rate} = \frac{k x_2 Kc2\ KpKh1[S]_T\ [DCICA][H^+]}{\{1+Kc_2[S]\}\{1+K_{h1}\}\{1+K_1[H^+]+K_1K_2[H^+]^2+Kc_2KpKh_1[DCICA][H^+]\}}$$

After completion of two more substrates we are going to publish our work.

Brief objectives of the project : Trichloroisocyanuric Acid (TCICA) and Dichloroisocyanuric Acid(DCICA) are member of N-halogen compounds both are well known synthetic reagents.The present investigation deals with the oxidation of dicarboxylic acid series like oxalic acid ,malonic acid by Trichloroisocyanuric Acid (TCICA) and Dichloroisocyanuric Acid (DCICA) for the purpose of comparision and to establish the differential reactivity of the two oxidizing agents.The kinetics of oxidation of Dicarboxylic acids has been investigated variety of oxidizing agents .A perusal of literature shown that kinetics of dicarboxylic acids by N-halo derivatives has not received much attention. The present investigation deals with kinetics of oxidation of a series of Dicarboxylic acids by Trichloroisocyanuric Acid (TCICA) and Dichloroisocyanuric Acid (DCICA) in aqueous acetic acid –perchloric acid mixtures .

1.

UNIVERSITY GRANTS COMMISSION
SERO ,CHIRAG ALI LANE ,ABIDS
HYDERABAD

ANNUAL REPORT OF THE WORK DONE ON MINOR RESEARCH PROJECT

1. Project Report No : 1
2. UGC Reference No : **MRP-5512/15(SERO/UGC)**
3. Period of Time : From Jan 2015 -2016
4. Title of the research work :Kinetics and oxidation reactions of TCICA & DCICA with different Carboxylic acid series –A Comparitive study

5. Name of the Principal Investigator : Dr.Neeraja.Valluru

6. Department and college where work has progressed: Dept. of chemistry and Biochemistry

7. Effective Date of starting of the project : 1/3/2015

8. Grant approved and expenditure incurred during the period of the report :

   a. Total amount approved for the project :Rs 4.7 lakh
   b. Total amount received in the first year :Rs 3,55,000
   c. Total expenditure Incurred in the first year :Rs 3,49.501.