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Kinetics and Mechanism of Ruthenium (III) Catalyzed Oxidation of Inositol by Trichloroisocyanuric Acid in Aqueous Acetic Acid Medium

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ABSTRACT

The Inositol has much biological significance associated with it and plays an essential role in the pharmaceutical chemistry. Inositol plays different vital roles in synthesis of oligosaccharides, gene expression, and signal transduction membrane tethering and auxin perception. In present paper explored kinetics and Mechanistic study of oxidation of Inositol by trichloroisocyanuric acid which has been investigated in water-HOAc-water medium. The reaction is of pseudo first-order in [TCICA], fractional order in [inositol] and first-order in [Ru^{3+}] ion. The velocity of the reaction increases with increase the Dielectric constant of medium and solvent polarity. Effect of temperature has been studied and thermodynamic parameters are calculated and a suitable mechanism has been suggested. Acetaldehyde was identified as an end-product of oxidation.

Key words: Inositol, fractional order, Dielectric constant of medium, thermodynamic parameters

INTRODUCTION

The elucidation of reaction mechanism is still one of the most fascinating problems in inorganic and organic chemistry. The chemical kinetics remains one of the most important tools even this day in finding out the undetermined mechanism of the reaction. The above study leads to work at stoichiometry, identification of intermediates and isolation of end products as an indirect support to reaction mechanism. A number of reports on the oxidation of organic compounds by TCICA are available in the literature[5-10]. In the present work explored the kinetics and mechanistic path of oxidation of Inositol by TCICA. Therefore, I have chosen TCICA as an oxidant to oxidized Inositol in presence perchloric acid as catalyst. TCICA act an oxidant because >N-Cl bonds are polar easily undergo heterolytic fission in polar medium[11].

MATERIALS AND METHODS

The solution of TCICA(sigma-Aldrich china sample) so obtained was prepared by dissolving its weighed quantity in 100% CH_3COOH (B.D.H.) and kept either amber colored flask or black paper wrapped around it to save it from the action of diffused day light which alters appreciably its

concentrations. The solution of Inositol was prepared in requisite volume of glacial acetic acid. Other reagents are grade chemicals and doubly distilled water was used throughout the experiments[13].

METHOD

The known volume of oxidant, acetic acid and Ru(III) solutions were taken in a conical flask while substrate and rest amount of water were in another conical flask. These two-stopper flasks were placed at experimental temperature in a thermostat of sensitivity $\pm 0.1^0$C. After the equilibrium of the temperature, the both solutions were mixed and aliquot was withdrawn immediately and was quenched. The amount of un-reacted TCICA was estimated iodometrically with the help of standard solution of sodium thiosulphate using starch as an indicator. The titre value at zero time was taken as "a". The aliquots were withdrawn at regular intervals and were estimated for un-reacted TCICA. These readings are the values of (a-x) at time "t". The experimental data were fed into the integrated form of equation for first-order reactions. The values of pseudo first-order rate constant obtained from the rate equation –

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

RESULT AND DISCUSSION

Effect of concentrations of oxidant: The linear plots of log (a-x) vs. Time, suggested that the first-order rate dependency with respect to oxidant. The value of first-order rate constant evaluated from the plot is excellently in good agreement with those calculated from first-order rate equation, (Table: 1).

Table: 1

[Inositol]	=	1.25×10^{-2} (mol.dm.$^{-3}$)
[Ru(III)]	=	1.25×10^{-3} (mol.dm.$^{-3}$)
HOAc-H_2O	=	30%(v/V),
Temperature	=	308 K.

[TCICA]10^3 (mol.dm.$^{-3}$)	Inositol
	$10^3 k_1$(min.$^{-1}$)
1.00	4.61
2.00	4.63
2.50	4.61
4.00	4.64
5.00	4.64

Effect of concentrations of Inositol: The reaction rate increased with increase in [Inositol]. Plot of k_1 versus [Inositol] initially linear passing through origin at low concentrations but at higher concentrations of substrate it bent to x-axis tends 1 to 0 orders. This confirmed the existence of equilibrium between Inositol and oxidant (TCICA) and appeared before the slow step (Fig.1).
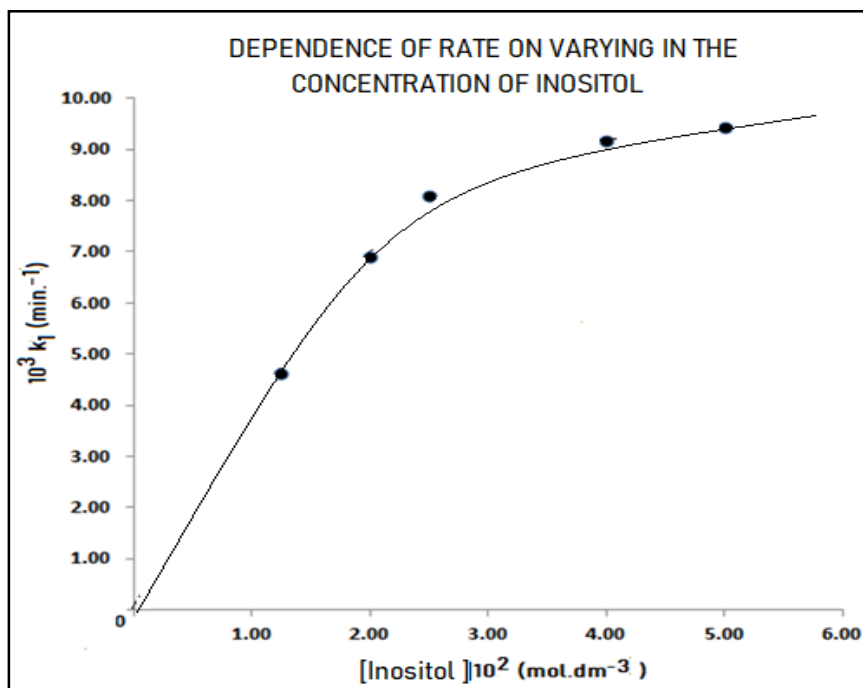

Fig.1

[TCICA]	=	2.50×10^{-3} (mol.dm.$^{-3}$)
[Ru(III)]	=	1.25×10^{-3} (mol.dm.$^{-3}$)
HOAc-H_2O	=	30%(v/V),
Temperature	=	308 K.

Effect of Ru[III] ion: Reaction is fully *Ru[III]* ion catalyzed and velocity of the reaction increases with increase the concentration of *Ru[III]* ion. The plot of k_1 vs. *Ru[III]* ion is obtained linear with the positive unit slope, confirming that the reaction fully *Ru[III] ion* catalyzed (Fig.2).
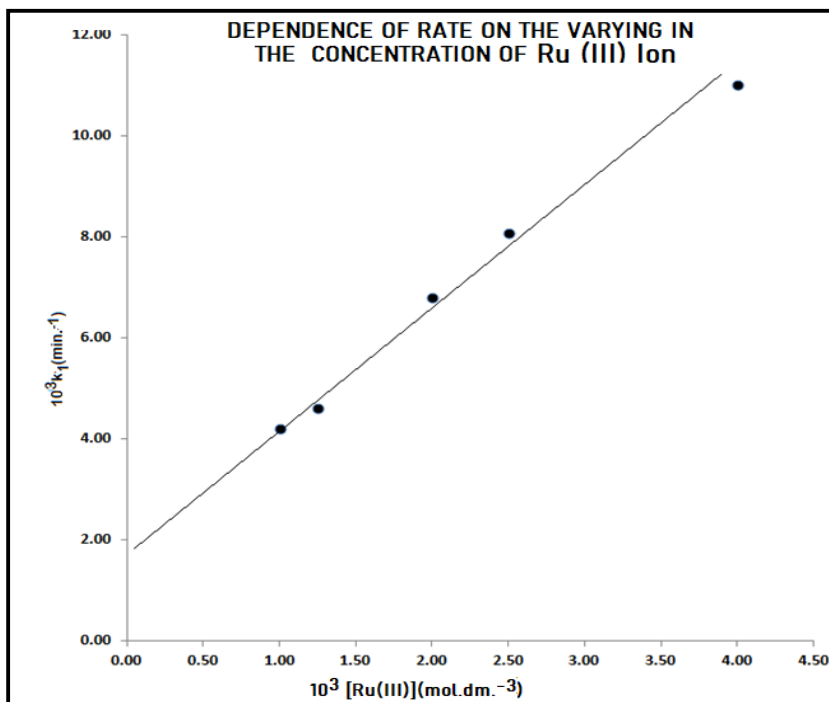
Fig.2

[TCICA]	=	2.50×10^{-3} (mol.dm.$^{-3}$)
[Inositol]	=	1.25×10^{-2} (mol.dm.$^{-3}$)
Temperature	=	308 K.

Effect of dielectric constant of the medium: first-order rate constant slightly increases with increase composition of acetic acid *i.e.* rate slightly accelerated with increase in dielectric constant of the medium (Table: 2).

[TCICA]	=	2.50×10^{-3} (mol.dm.$^{-3}$)
[Inositol]	=	1.25×10^{-2} (mol.dm.$^{-3}$)
[Ru(III)]	=	1.25×10^{-3} (mol.dm.$^{-3}$)
Temperature	=	308 K.

HOAc-H$_2$O % (v/V)	$\dfrac{10^3}{D^\#}$	$10^3 k_1 (\text{min.}^{-1})$
20	17.17	4.42
30	19.15	**4.61**
40	21.98	4.79
50	25.64	4.95
60	30.36	5.19

Absence of free radical in the system: The presence of free radicals in the system understudy was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and white precipitate clearly indicates the absence of free radicals in the system. Various activation parameters namely temperature
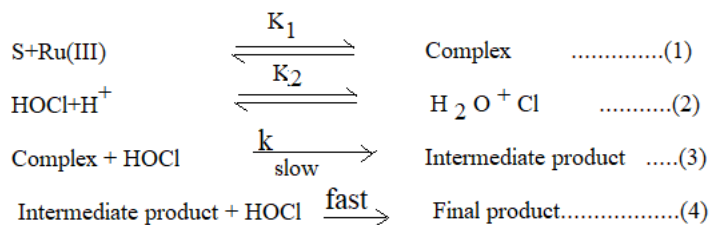
coefficient, energy of activation (Ea) , frequency factor (A), enthalpy of activation ($\Delta H\#$), free energy of activation ($\Delta G\#$), and entropy of activation ($\Delta S\#$) for each reaction are calculated for inositol– TCICA system and according to the reaction mechanism, rate equation and order of reaction have been discussed (Table:3).

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Table:3
Thermodynamics parameters

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[TCICA] $=$ 2.50×10^{-3} (mol.dm.$^{-3}$)
[Inositol] $=$ 1.25×10^{-2} (mol.dm.$^{-3}$)
[Ru(III)] $=$ 2.00×10^{-3} (mol.dm.$^{-3}$)

Substrate	Ea KJ/ mol	A Min^{-1}	$\Delta H^{\#}$ KJ/ mol	$-\Delta G^{\#}$ KJ/ mol	$-\Delta S^{\#}$ KJ/ mol
Inositol	53.98 ±0.61	8.99×10^{4} ±0.92	59.69 ±0.35	87.96 ±0.39	101.98 ±0.97

MECHANISM: In view of the above experimental kinetic data, facts and finding, a suitable mechanism has been proposed for the oxidation of Inositol – TCICA system as:

$$S + Ru(III) \underset{K_2}{\overset{K_1}{\rightleftharpoons}} Complex \quad \dots\dots\dots(1)$$

$$HOCl + H^{+} \rightleftharpoons H_2O^{+}Cl \quad \dots\dots(2)$$

$$Complex + HOCl \xrightarrow[slow]{k} Intermediate\ product \ \dots(3)$$

$$Intermediate\ product + HOCl \xrightarrow{fast} Final\ product \dots\dots\dots(4)$$

Where,   S stands for Inositol (substrate)

Rate law: The rate derived for above mechanism is given as:

$$\text{Rate} = \frac{k K_1 [S][Ru(III)]_T [HOCl]_T}{\{1 + K_1[S]\}\{1 + K_2[H^+]\}} \quad \dots\dots(5)$$

Where,   S stands for Inositol (substrate)

Thus, the above equation explains all the experimental kinetics results**.**

CONCLUSIONS

Kinetic studies utilizing TCICA as an oxidant in series of reaction lead us to conclude that the activity of it is much limited and needs to be explored in a Broadway. It possesses vital potentiality with two-electron system and displays interesting behaviors at moderate condition of temperature. The study will act as a milestone and will pave the way for future researcher to enlighten the mechanism utilizing TCICA as an oxidant for some other organic compounds like disulphide, acetophenone and substituted acetophenones, aliphatic ketones, amines and amino acids in the similar manners and also can be catalyzed by micelles like CTAB and phosphotungstic acid etc. The contribution and

information through kinetic study will enrich chemical literature to a great extent in journals. Its applied aspects may be judged in lather industries, analytical, chemical separation, and identification of organic compounds and paper and pulp industries[12-15] .

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References

1. Chattaway,F.D.: J. Chem. Soc.**1905**,87,1884.
2. Bacchawat, J.M.: Indian J. Chem., 9, 1335. **(1971)**
3. Bacchawat,J.M.: Indian J. Chem., 11,609. **(1973)**
4. Vijay Mohan,K; Raghunath Rao; P, Sundaram,E.V.: Proc.N. Acad .Sc, Indian **1988;** 58A,37.
5. Singh V.P.; Khan M.U.;Tiwari R.K.;Verma J.K;Gupta H.D.: Oxid. Commun.**1997**,20No1,117-123
6. Venketasubramanian;N: J. Indian Chem., Soc.,**1980**,19A,569.
7. Khan M.U.; Sharma V.K, Sharma K , Dwivedi H.P.: Oxid. Commun.**1991**,14 No1,60-65.
8. Khan M.U.; Verma J.K; Singh V.R, Dwivedi H.P.: Oxid. Commun.**1993**,16No3,235-239.
9. Khan M.U.; Nigam S.K.,Chauhan R.P.S.,Verma J.K: Oxid. Commun.**1995**,18No3,304-311
10. Singh V.P.;Khan M.U.; Chauhan D.B.S.,: Oxid. Commun.**1997,**20 , No1,124-131.
11. Khan M.U.; Nigam S.K., Verma J.K, Parihar S.S.; Dwivedi H.P.: Oxid. Commun.1998, 21No3, 362-368.
12. Singh Niharika: Ph.D. thesis A.P.S. Universitry,Rewa(M.P.)India,(**2005**)
13. Mohamed N. A. Farook, Seyed Dameem G. A., Murugesan A. and Kanagaraj M. : E-Journal of Chemistry,Vol. 1, No. 2, pp 132-136, April **2004.**
14. Kaur Raman Deep, Arora Monika, Gujral Harjeet, Kaur Gurpreet, Nayak S.N. and Singh S.K. : Int. J. Chem Tech Res.**2010**,2(3)
15. Alhaji N.M.I. , Uduman Mohideen A.M. and Sofia Lawrence Mary S. : E-Journal of Chemistry,**2011**, 8(**1),** 159-166

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