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## Research Articles

### *“Ir (III) CHLORIDE-CATALYZED OXIDATION OF SORBITOL BY TRICHLOROISOCYANURIC ACID IN ACID MEDIUM”*

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## ABSTRACT

Kinetic study of Trichloroisocyanuric acid oxidation of sorbitol in aqueous acetic acid medium in the presence Ir(III)chloride has been investigated. The reaction follows first order kinetics in oxidant and Ir(III)chloride and fractional order to sorbitol . The oxidation exhibits first order dependency at lower concentration of substrate while at higher concentration the reaction follows zero order kinetics. Binding parameters have been calculated by analyzing the data. The effect of temperature on the reaction has been investigated in the temperature range 30<sup>0</sup>C to 45<sup>0</sup>C. Mechanism proposed and derived rate law is in agreement with the observe kinetics.

## INTRODUCTION

Sugar alcohols (also called polyhydric alcohols, polyalcohols, alditols or glycitols) are organic compounds, typically derived from sugars, comprising a class of polyols. Sorbitol, less commonly known as glucitol, is a sugar alcohol with a sweet taste which the

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\* For correspondence

human body metabolizes slowly. It also occurs naturally in many stone fruits and berries from trees of the genus *Sorbus*. It can be used as a laxative via an oral suspension or enema. It can be obtained by reduction of glucose, changing the aldehyde group to a hydroxyl group. Most sorbitol is made from corn syrup, but it is also found in apples, pears, peaches, and prunes etc. In the Present kinetic investigation of Ir (III) chloride catalyzed kinetics of oxidation of Sorbitol by *Trichloroisocyanuric acid* (TCICA) in aqueous acetic acid medium. The aim of the present work is to probe the unreported results on the mechanistic rate of *Trichloroisocyanuric acid* oxidation of sorbitol in the presence of Ir(III)chloride. The literature survey reveals that there is no report on the mechanistic studies to investigate the catalytic effect of Ir(III) chloride on the *Trichloroisocyanuric acid* (TCICA) oxidation of sorbitol in aqueous acetic acid medium.

## EXPERIMENTAL

The oxidant *Trichloroisocyanuric acid* (TCICA) (Aldrich sample), Sorbitol (anal. grade) were used and purified by the literature procedure<sup>9</sup>. The standard solution of Sorbitol (sigma chemicals sample) was prepared in acetic acid. Double distilled water employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of *Trichloroisocyanuric acid* (TCICA) was stored in an amber colored bottle and its strength was checked iodometrically<sup>33</sup> using 1 % solution of freshly prepared starch as an indicator.

**Kinetic measurements:** All kinetic measurements made under pseudo first-order conditions, by keeping large excess of Sorbitol over oxidant *Trichloroisocyanuric acid*. Mixture containing requisite amount of solutions of *Trichloroisocyanuric acid* , and Ir(III)chloride in 40 % acetic acid equilibrated at 308 K. To this mixture added a measured amount of pre-equilibrated at 308 K., standard solution of *Trichloroisocyanuric acid*. To maintain the desired temperature (within  $\pm 0.1^\circ\text{C}$ ) the reaction mixture was kept in a thermo stated water bath and the progress of the reaction was monitored iodometrically by withdrawing aliquots of the reaction mixture at regular time of intervals.

## RESULT AND DISCUSSION

**Effect 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: III B-1**

**Summary: Dependence of rate of oxidation reaction on the initial concentration of oxidant (TCICA)**

[Sorbital]	=	$1.25 \times 10^{-2}$ (mol.dm. <sup>-3</sup> )
[Ir (III)]	=	$1.25 \times 10^{-3}$ (mol.dm. <sup>-3</sup> )
HOAc-H <sub>2</sub> O	=	30%(v/V),
Temperature	=	308 K.

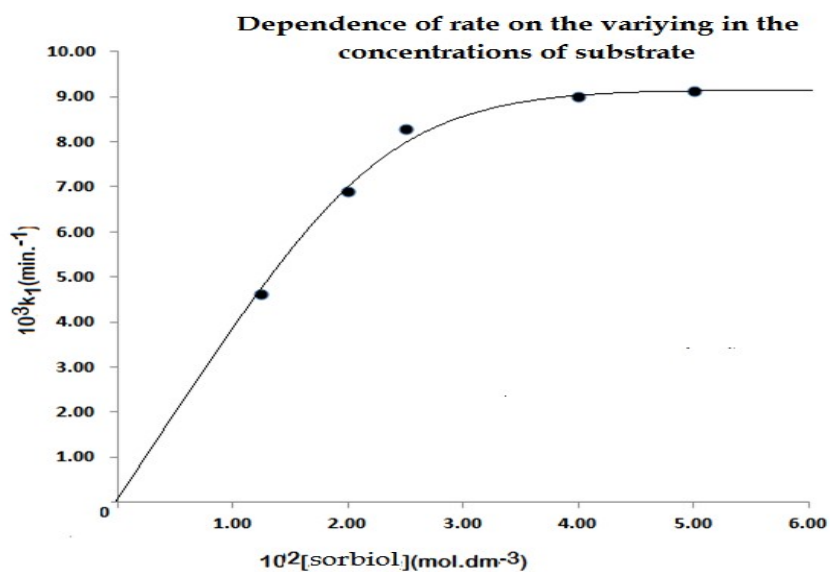
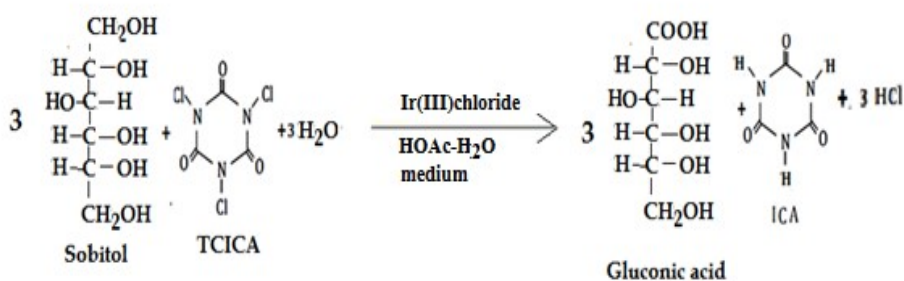
[TCICA ]10 <sup>3</sup> (mol.dm. <sup>-3</sup> )	Sorbital
	10 <sup>3</sup> k <sub>1</sub> (min. <sup>-1</sup> )
1.00	4.61
2.00	4.63
2.50	4.61
4.00	4.64
5.00	4.64

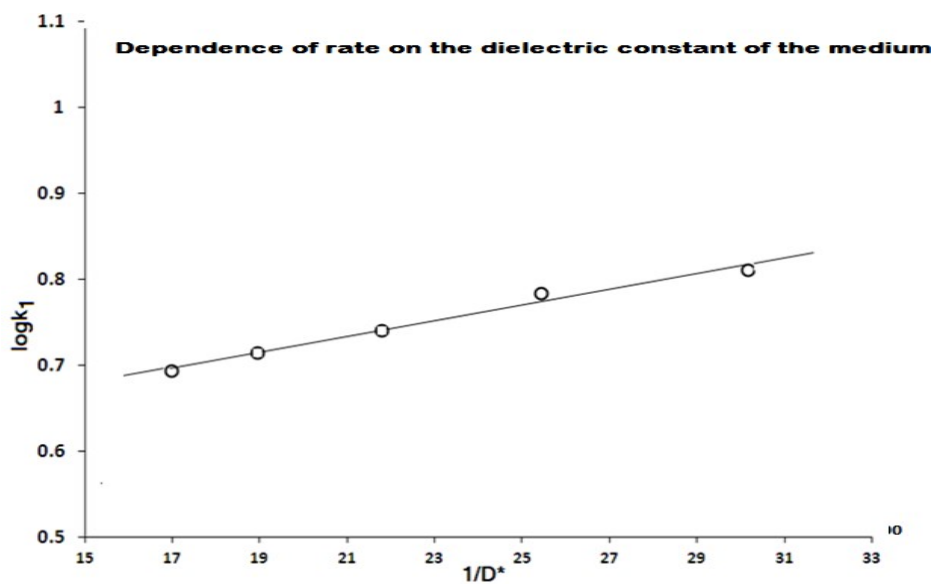
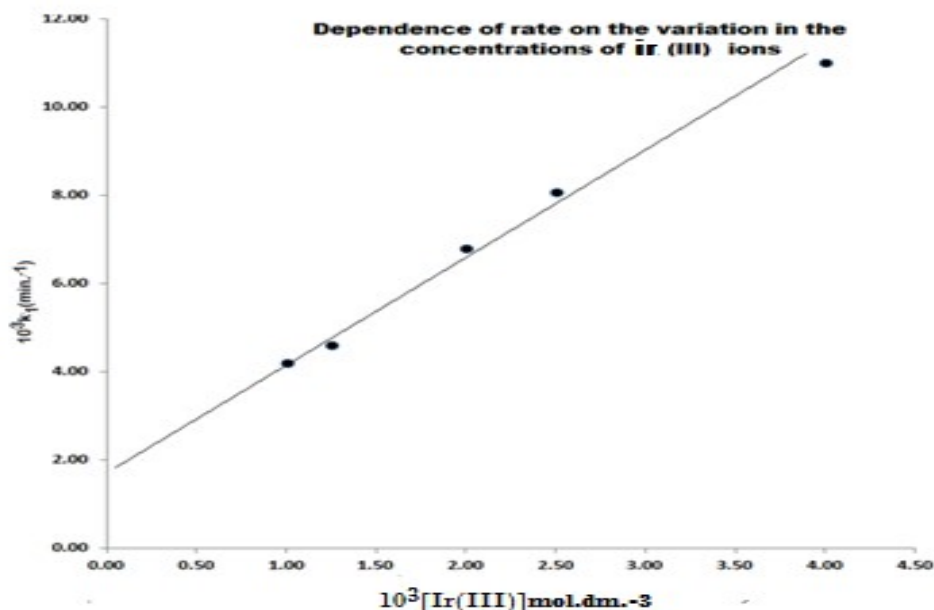
**Effect of substrate:** The reaction rate increased with increase in [Sorbital]. Plot of  $k_1$  versus [Sorbital] initially linear passing through origin at low concentrations but at higher concentrations of substrate it bent to x-axis tends 1 to 0 orders. This confirmed the existence of equilibrium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

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

**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 (fig: 3).

Gluconic acid was formed as the end-product of oxidation of sorbitol, which was identified by the determination of melting points of amide derivatives (mp.90°C) of oxidation products and existing conventional methods. It is found that for complete oxidation of one mole of Substrate, one mole of TCICA is required. The stoichiometric equations empirically can therefore, be represented as:



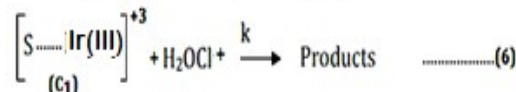
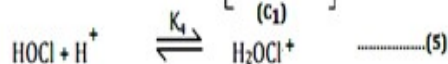
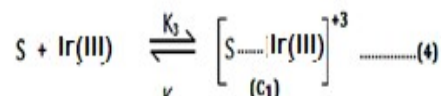
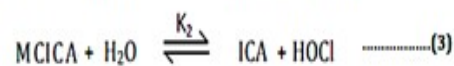
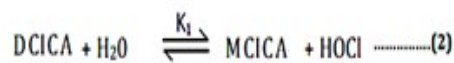
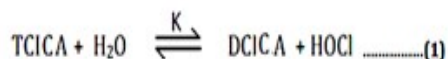


**Absence of free radical in the system:** The presence of free radicals in the system under study was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and white precipitate clearly indicates the absence of free radicals in the system.

Various activation parameters namely temperature coefficient, energy of activation (E<sub>a</sub>) , frequency factor (A), enthalpy of activation (ΔH<sup>#</sup>), free energy of activation (ΔG<sup>#</sup>), and entropy of activation (ΔS<sup>#</sup>) for each reaction are calculated for Sorbitol –TCICA system and according to the reaction mechanism, rate equation and order of reaction have been discussed.

## MECHANISM

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



Where, S is standing for sorbitol(substrate)

### *Derived Rate law:*

$$\begin{aligned} \text{Rate} &= - \frac{d[\text{TCICA}]}{dt} = k [\text{C}_1] [\text{H}_2\text{OCl}^+] \\ &= \frac{k K K_1 K_2 [\text{C}_1]_{\text{T}} [\text{H}_2\text{OCl}^+]}{1 + K_4 [\text{H}^+]} \\ &= \frac{k K K_1 K_2 K_3 K_4 [\text{S}] [\text{Ir(III)}] [\text{TCICA}]}{1 + K_3 [\text{Ir(III)}]} \quad \because 1 \ll K_3 [\text{Ir(III)}] \end{aligned}$$

$$\mathbf{k_{obs}} = k K K_1 K_2 K_4 [\text{S}] [\text{Ir(III)}] [\text{TCICA}]$$

Above rate Equation is in good agreement with the observed experimental data and 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<sup>34-37</sup>.

## REFERENCES

1. Filler R.; *Chem Rev.* 60, 21 (1965).
2. Fieser L & Fieser M.; *Reagents for organic synthesis, 11* (Jhon Wiley, NY) 426 (1969)
3. Ot Siji Y. Kurida T. & Imoto N; *Bull Chem.Soc Perkin II* , 949 (1963).
4. Vasudevan K.S., Venkat Subramanian N.; *Indian J. Chem.* 24 A: 304 (1985)
5. Bhavani N., Lily K.; *Current Science* 20, No.18 (1983)
6. Tiwari S.; Dwivedi H.P.; Saket S.S, Chauhan D.B.S; Singh Brijendra; *Int. J. Chem., Sci., Secrets. No. 1, Vol.1, 33-39(2014)*
7. Singh S. K. , Singh Santosh K. , Khan N., Soni P., Gupta H.D. *Elect. Journal of advance research, Vol 1, No. 1, 16 – 24(2015)*
8. Singh H.S., Singh R.K., Singh S.M., Sisodla A.K., *J. Phys. Chem.* 81, 1044–1059,(1997).
9. Puttaswamy, Jagadeesh R.V.; *Appl. Catal. A: Gen.* 292, 259–270(2005).
10. Morris J.C., SGlyzar J.R., Winemann M.A., *J. Am. Chem. Soc.* 70 2036–2047(1948).
11. Kikkeri N. Mohana and Paanemangalore M. Ramdas Bhandarkar: *J. Chinese Chem. Soc.*, 2007, 54, 1223-1232
12. Patel Sanju: M.Phil Dissertation(2012), central library, A.P.S. University, Rewa (M.P.)
13. Verma R.S, Reddy M.J. and Shastry V.R., *J. Chem. Soc. Perkin 2*, 1976.
14. Mucientes A., Pobleto F.J.; J. Casado, *React. Kinet. Catal. Lett.*, 2005,43(1),249.
15. Khan J.A., Chandraiah U. and Kandlikar S., *J. Ind. Coun. Chem. IV*, 1988,3.
16. Land H. and Waters W.A., *J. Chem. Soc.*, 1955, 4312.
17. Vardarajan R. and Hussaini M.A.. *Ind. Chem. Manu.*, 1980, 18(8), 14.
18. Sathuram B. and Navneeth R.I.; *Ind. J. Chem.*, 1977, 15, 528.
19. Moodithaya B.S. and Gowda B.T., *Ind. Coun. Chem.*, XI annual conf.,India, 1983.



20. Kumar A. and Mathur S., *J Ind. Coun. Chem.*, 1998,15,75.
21. Malik W.W. and Aslam M., *Ind. J Chem.*, 1970,8,736.
22. Upadhyayand S.K. Agrawal M.E., *Ind. J Chem.*, 1977, 15,416.
23. Kumar A., Kumar P. and Ramamurthy P., *Polyhedron*, 1999,18,773.
24. Shan I.H., Li, S.Y S.M.. Huo, Shen S.G. and. Sun H.W, *J. Iranian Chem., Soc.*, 2005, 2(3), 226.
25. V. Seregar, T.M. Veeresh and S.T. Nandibewoor, *J. Mol. Catal. A:Chem.*, 2007,271,253.
26. H. Shi, S. Shen, H. Sun, Z. Liu and L. Li, *J. Inorg. Biochem.*, 2007, 101,
27. Bakore G. V. and Shankar R., *Ind. J. Chem.*, 1963, I, 331.
28. Sheikh R.A. and Water W.A., *J. Chem. Soc.*, 1970,988.
29. Sthapak J.K. and S. Ghosh, *J. Ind. Chem. Soc.*, 1970, 47,347.
30. Rajagopala, Vardarajan and M. Joseph, *Ind. J. Chem.*, 1980, 19A,977.
31. Kataria A.K. and Hiran B.L., *Asian J. Chem.*, 2000, 12(3), 816.
32. Chandraju, Mahadevappa and Rangappa K.S., *Ind. J. Chem.*, 1997, 36A, 974.
33. M.Z. Barakat, A.M.P. Wahab, *Anal. Chem.* 26 (1954) 1973–1984.
34. Frederick George Mann and Bernard Charles Saunders: “*PRACTICAL INORGANIC CHEMISTRY*” LONGMAN GROUP LIMITED London (1980) ,pp .179.
35. Atkins P., Overton T., Rourke J., Weller M. & Armstrong F.: *Shriver and Atkins: Inorganic Chemistry*, Oxford University Press (2006).pp-436
36. Priya V., Balasubramaniyan M. and Mathiyalagan N.: *J. Chem. Pharm. Res.*, 2011, 3(1):522-528
37. Patwari S.B., Khansole S.V. and Vibhute Y.B.: *J. Iran. Chem. Soc.*, Vol. 6, No. 2, 2009, pp. 399-404.