Jan 2020 - Mar 2020, Vol 6, No. 1, 23-31 ISSN : 2394 -9449

Electronic Journal of Advanced Research
An International Peer review E-Journal of Advanced Research

Research Articles

STUDY OF CATALYTIC EFFECT OF PHOSPHOTUNGSTIC ACID IN THE OXIDATION OF PROPAN-2-OL BY TRICHLOROISOCYANURIC ACID IN AQUEOUS ACETIC ACID MEDIUM"

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Received : 16-Feb-2020	Revised : 28-Feb-2020	Accepted : 15-Mar-2020

ABSTRACT

Kinetic investigations in Keggin-type phosphotungstic acid catalyzed oxidation of propan-2-ol by Trichloroisocyanuric acid in aqueous acetic acid medium have been carried out. The oxidation kinetics of propan-2-ol by TCICA in presence of PTA (Phosphotungstic acid) shows a first order dependence on [TCICA], [PTA] and fractional order on [propan-2-ol]. The variation of ionic strength, H^+ and phthalimide (reaction product) has insignificant effect on reaction rate. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperatures.

Keywords: ***Kinetics, Oxidation, isopropyl alcohol , Phosphotungstic Acid, Trichloroisocyanuric acid.***

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INTRODUCTION

In the recent years, studies of oxidation of various organic compounds by heteropoly acids and polyoxymetalates especially those with Keggin-type structure under homogeneous and heterogeneous reaction conditionshave attracted considerable attention of the researchers[1-5]. Literature survey reveals that phosphotungstic acid (PTA) due to its thermal stability and acidity makes it efficient and eco-friendly catalyst in oxidation of organic compounds[6-9].

In earlier literature, TCICA has been referred as a safe and efficient reagent for oxidation and chlorination process even on a large scale of organic compounds such as toluene and substituted toluenes[10,] benzhydrol[11], benzaldehyde and substituted benzaldehydes[12] aliphatic diols and cycloalkanols[13], ketones[14], hydroxy acids[15-17], unsaturated acids[18] benzyl alcohols and substituted benzyl alcohols[19], amino acids[20-21], amides[22-24] etc. It seems that there are no reports about the kinetics of oxidation of propan-2-ol by TCICA. The present work reports kinetics and mechanism of PTA catalyzed oxidation of propan-2-ol by trichloroisocyanuric acid in 30 % acetic acid medium.

EXPERIMENTAL

The oxidant TCICA (Aldrich sample) was used. Acetic acid (A. R. grade) was purified by the literature procedure. The standard solutions of propan-2-ol (isopropyl alcohol) (A. R. grade) were prepared in acetic acid. Double distilled water was employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of TCICA was stored in an amber colored bottle and its strength was checked iodometrically[25] 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 propan-2-ol over oxidant TCICA. Mixture containing requisite amount of solutions of TCICA, and PTA in 30 % acetic acid equilibrated at 308K. To this mixture added a measured amount of pre-equilibrated at 308 K., standard solution of TCICA. To maintain the desired temperature (within ± 0.1^{o}C) the reaction mixture was kept in a thermo stated water bath and the progress of the reaction was monitored iodometrically[25] by withdrawing aliquots of the reaction mixture at regular time of intervals.

RESULTS 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: 1

Summary: Dependence of rate of oxidation reaction on the initial concentration of oxidant

[IPA]	=	$1.25X10^{-2}$ (mol.dm.$^{-3}$)
[PTA]	=	$1.25X10^{-3}$ (mol.dm.$^{-3}$)
[H^+]	=	$1.25X10^{-3}$ (mol.dm.$^{-3}$)
HOAc-H_2O	=	30%(v/V),
Temperature	=	308 K.

[TCICA]10^3 (mol.dm.$^{-3}$)	Isopropyl alcohol(IPA) $10^5 k_1 (s^{-1})$
1.00	13.89
2.00	13.97
2.50	13.99
4.00	14.04
5.00	14.01

Effect of substrate: The reaction rate increased with increase in [Isopropyl alcohol]. Plot of k_1 versus [Isopropyl alcohol] 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 isopropyl alcohol and oxidant (trichloroisocynuric acid) and appeared before the slow step (Fig.1).

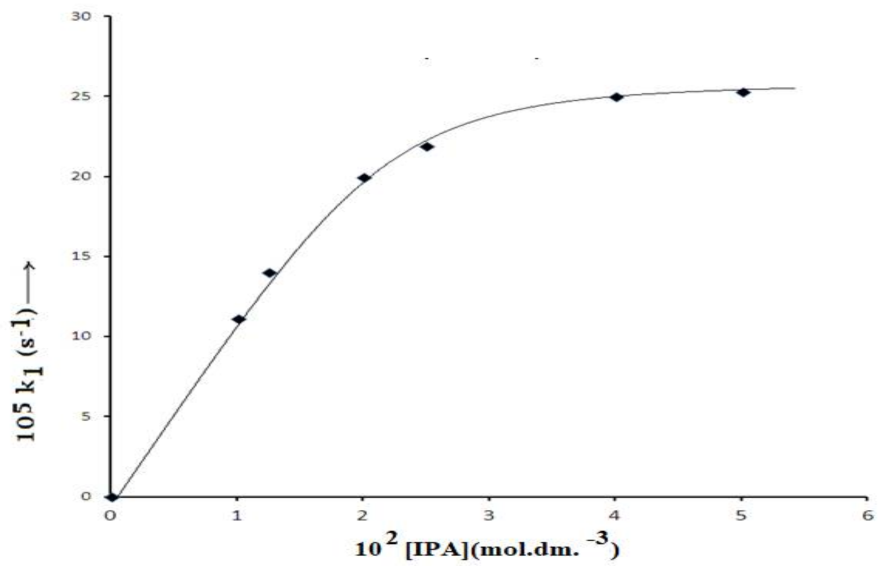


Fig.1: Dependence of rate on varying in the concentrations of isopropyl alcohol
Plot of k_1 vs. [IPA]

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

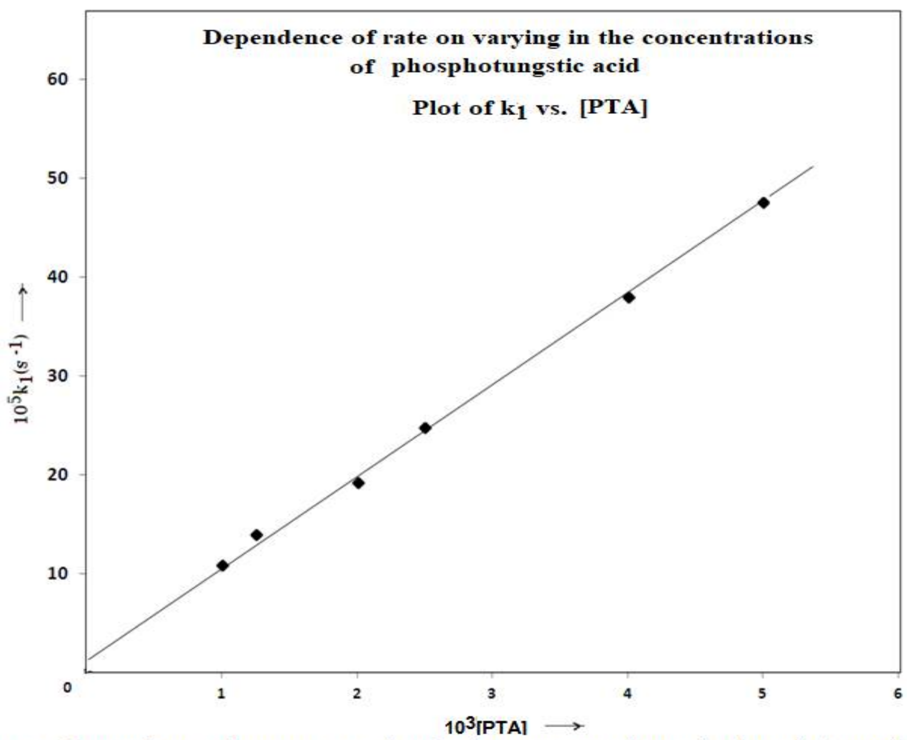


Fig 2 : Dependence of rate on varying in the concentrations of phosphotungstic acid

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).

Table: 2

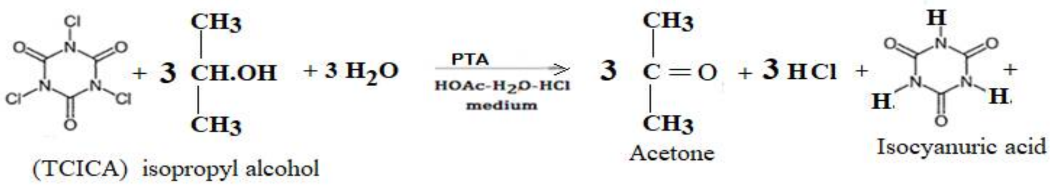
Summary: Dependence of rate on the variation of the composition of binary solvent polarity.

[TCICA]	=	$2.50X10^{-3}$ (mol.dm.$^{-3}$)
[IPA]	=	$1.25X10^{-3}$ (mol.dm.$^{-3}$)
[PTA]	=	$1.25X10^{-3}$ (mol.dm.$^{-3}$)
[H^+]	=	$1.25X10^{-3}$ (mol.dm.$^{-3}$)
Temperature	=	308 K.

HOAc-H_2O % (v/V)	$\frac{10^3}{D^\#}$	$10^5 k_1 (s^{-1})$
20	17.17	13.85
30	19.15	13.99
40	21.98	14.15
50	25.64	14.40
60	30.36	14.72

Effect of [H^+]ion : The velocity of the reaction increases with increase the concentration of HCl acid. The plot of k_1 vs. [HCl] and plot of log k_1 vs. log [HCl] is obtained linear with the positive unit slope, confirming that the reaction is fully acid catalyzed.

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. Acetone was formed as the end-product of oxidation of Acetone, which was identified by the determination of melting points of 2, 4-dinitrophenylhydrazone derivatives of oxidation products and existing conventional methods. The stoichiometric determinations have been suggested that **3:1 mole** ratio for substrate and oxidant (TCICA).



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 propan-2-ol(isopropyl alcohol)–TCICA system and according to the reaction mechanism, rate equation and order of reaction have been discussed. The iso-kinetic and Exner's have been explained.

MECHANISM

In view of the above experimental kinetic data, facts and finding, a suitable mechanism has been proposed for the oxidation of propan-2-ol(isopropyl alcohol)–TCICA system as:

$$TCICA + 3H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} 3HOCl + ICA \quad \text{.........................(1)}$$

$$HOCl + H^+ \overset{K_2}{\rightleftharpoons} H_2\overset{+}{O}Cl \quad \text{.........................(2)}$$

$$PTA + S \overset{K_3}{\rightleftharpoons} C_1 \quad \text{.........................(3)}$$

$$C_1 + H_2\overset{+}{O}Cl \overset{K_4}{\rightleftharpoons} C_2 \quad \text{.........................(4)}$$

$$C_2 \overset{k}{\longrightarrow} \text{products} \quad \text{.........................(5)}$$

The derived rate law is given as:

$$k_{obs.} = \frac{k\,K_1K_2K_3K_4\,[S][TCICA][\overset{+}{H}][PTA]}{\{1+K_3[PTA]\}\left[1+K_1K_2[TCICA]\right]\left[1+K_2[\overset{+}{H}]\right]} \quad \text{........(6)}$$

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, aliphatic ketones, amines and amino alcohols 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[26-27].

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