

# 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 n-BUTANOL BY TRICHLOROISOCYANURIC ACID IN AQUEOUS ACETIC ACID MEDIUM”

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Received : 24-Feb-2019	Revised : 26-Feb-2019	Accepted : 28-Feb-2019
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#### ABSTRACT

The kinetics of n-butanol by trichloroisocyanuric acid in aqueous acetic acid medium was investigated in presence of phosphotungstic acid at 303 and 308 K respectively. The velocity of the reaction was found to vary as first-order dependence of [TCICA], [H<sup>+</sup>] and [PTA], fractional-order dependence on [substrate]. The complex nature of kinetics was observed between oxidant's active species and substrate. The reaction velocity accelerated with decrease in dielectric constant of the medium. The mole ratio 3:1 involved in the reaction, was determined stoichiometrically. The n-butyraldehyde was identified as end-products by existing standard methods. The various thermodynamic parameters were evaluated. The plausible scheme of mechanism and reactivity was proposed in conformity with the kinetic findings.

**Key words:** Plausible, trend, phosphotungstic acid, trichloroisocyanuric acid, conformity.

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## INTRODUCTION

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems<sup>1-6</sup>. The kinetics of oxidation reactions and the investigation of the reaction mechanisms from the kinetic data have been always the most interesting subjects in chemistry. In any kinetic investigation, one may be interested to arrive at (i) the relationship between the rate and the various factors like concentrations of the reactants, temperature, reaction medium etc., and (ii) interpretation of the empirical rate laws in the light of the mechanism proposed<sup>7</sup>.

Present problem to explore the mechanistic path of the *oxidation* reaction between *n-butanol by trichloroisocyanuric acid in aqueous acid medium, in the presence of PTA as a catalyst first time.*

## MATERIALS AND METHODS

In the Present kinetic investigation of PTA catalyzed kinetics of oxidation of n-butanol by *Trichloroisocyanuric acid* in aqueous acetic acid medium, different chemicals were used in the form of solutions.

The solution of *Trichloroisocyanuric acid* (sigma-Aldrich sample) so obtained was prepared by dissolving its weighed quantity in 100% CH<sub>3</sub>COOH (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 standardization *Trichloroisocyanuric acid* was done by taking one ml of its solution in conical flask to which 10 ml of 2% KI solution followed by 5ml of 2N H<sub>2</sub>SO<sub>4</sub> added to it. The liberated iodine was titrated against standard sodium thiosulphate (hypo) solution using starch solution as an indicator<sup>8</sup>.

n-butanol (anal. grade)) was used as substrates for the preparation of solutions. The solution of n-butanol was prepared in requisite volume of glacial acetic acid. Other chemicals have been used analytical grade.

## Method

The known volume of oxidant, acetic acid and PTA 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  $\pm 0.1^{\circ}\text{C}$ . 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 -

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

Found fairly constant within the experimental error suggested that each reaction obeys first-order kinetics. The effect of [PTA] on the oxidation of n-butanol was determined by adding different concentrations.

## 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).

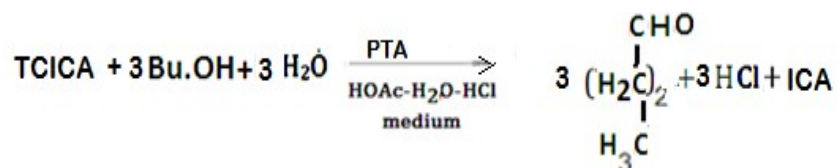
**Effect of substrate:** The reaction rate increased with increase in [n-butanol]. Plot of  $k_1$  versus [n-butanol] initially linear passing through origin at low concentrations but at higher concentrations of substrate it bent to x-axis tends 1 to 0 orders. This confirmed the existence of equilibrium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

**Effect of PTA:** Reaction is fully PTA catalyzed but velocity of the reaction increases with increase the concentration of PTA. The plot of  $k_1$  vs. [PTA] and plot of  $\log k_1$  vs.  $\log$  [PTA] is obtain linear with the positive unit slope, confirming that the reaction fully catalyzed.(Fig.3)

**Effect of dielectric constant of the medium:** The first-order rate constant increases with increase composition of acetic acid i.e. rate accelerated with increase in dielectric constant of the medium. The plot of  $\log k_1$  versus  $10^3/D$  were obtained linear with positive slope (Fig.4).

**Effect of [HCl]:** 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.

The reaction rate ebbs when the concentration of ICA added. 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. n-butanaldehyde was formed as the end-product of oxidation of n-Bu.OH, which was identified by the determination of melting points of 2,4-dinitrophenylhydrazone derivatives of oxidation products and existing conventional methods<sup>14</sup>. The stoichiometric determinations have been suggested that **3:1 mole** ratio for substrate and oxidant (TCICA).



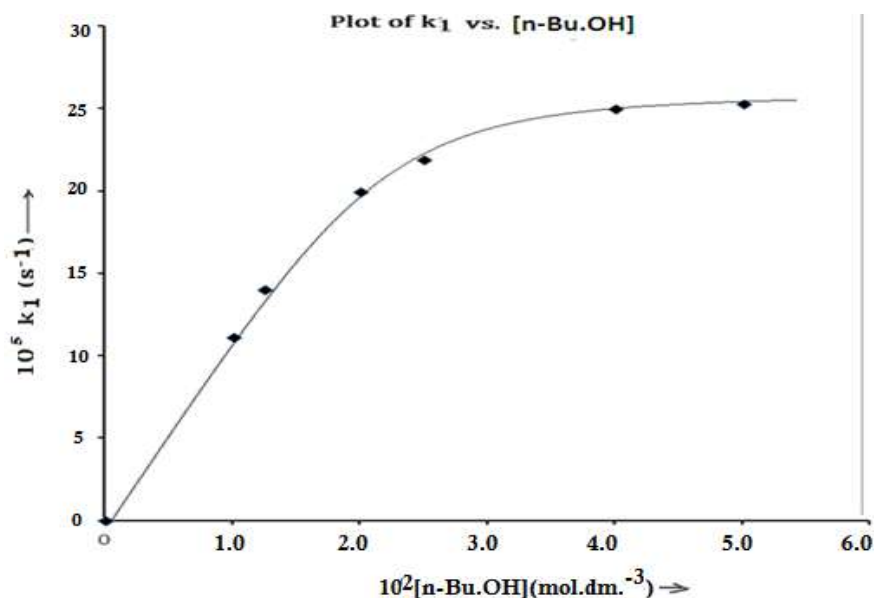
Various activation parameters namely temperature coefficient, energy of activation ( $E_a$ ), frequency factor (A), enthalpy of activation ( $\Delta H^\ddagger$ ), free energy of activation ( $\Delta G^\ddagger$ ), and entropy of activation ( $\Delta S^\ddagger$ ) for each reaction are calculated for n-Bu.OH –TCICA system and according to the reaction mechanism, rate equation and order of reaction have been discussed(Table:2).

**Table-1**

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

[n-Bu.OH]	=	$1.25 \times 10^{-2}$ (mol.dm. <sup>-3</sup> )
[PTA]	=	$1.25 \times 10^{-3}$ (mol.dm. <sup>-3</sup> )
[H <sup>+</sup> ]	=	$1.25 \times 10^{-3}$ (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> )	n-Bu.OH
	10 <sup>5</sup> k <sub>1</sub> (s <sup>-1</sup> )
1.00	13.89
2.00	13.97
2.50	13.99
4.00	14.04
5.00	14.01



**Fig.1 Effect of varying in the concentrations of n- Butanol**

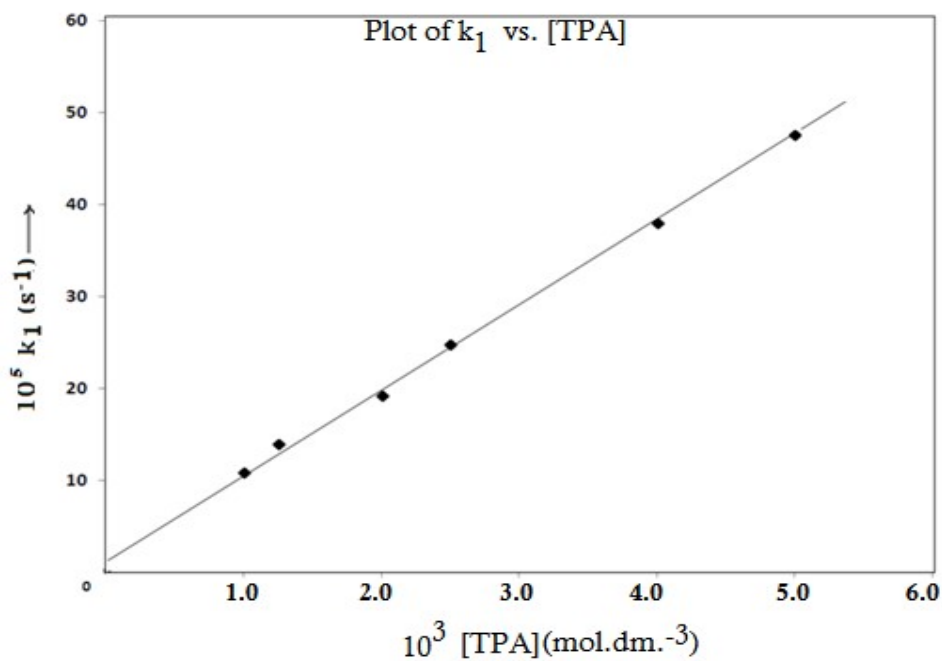


Fig.2:Effect of varying in the concentrations of tungstophosphoric acid

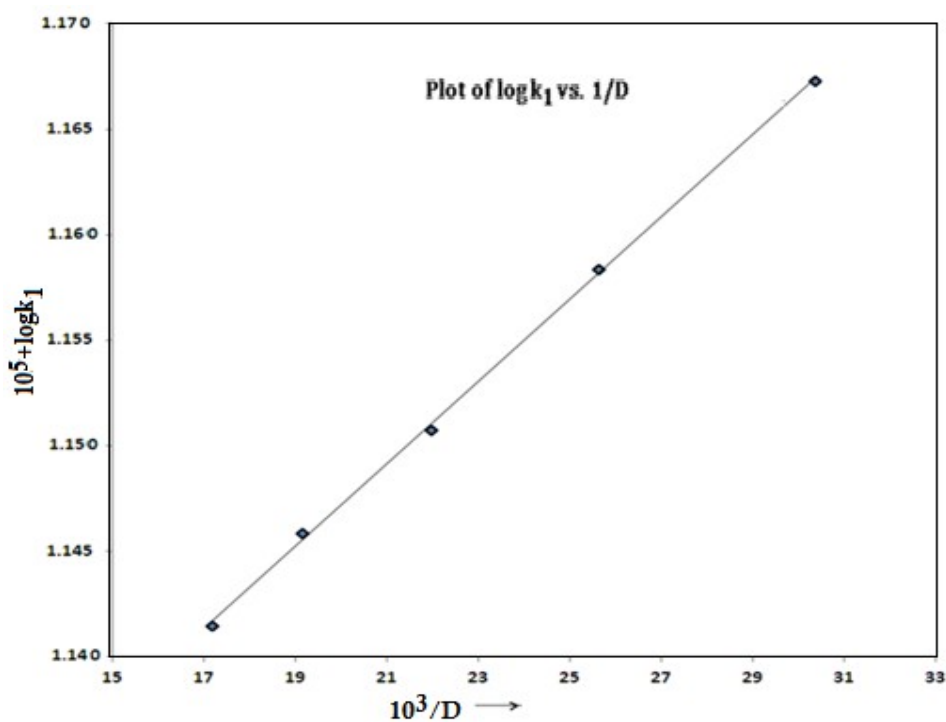


Fig. 3 Dependence of rate on the variations in the dielectric constant of the medium

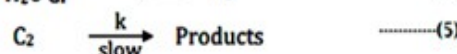
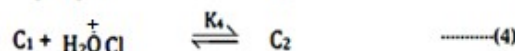
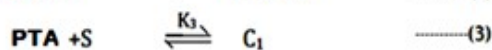
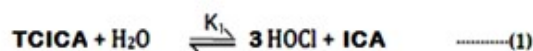
Table: 2

### Thermodynamic parameters

Substrate	$E_a$ kJ/mol.	$A$ ( $s^{-1}$ )	$\Delta H^\ddagger$ kJ/mol.	$-\Delta G^\ddagger$ kJ/mol.	$-\Delta S^\ddagger$ JK/mol.
n-Bu.OH	51.72 $\pm 0.64$	$4.21 \times 10^5$ $\pm 0.98$	54.30 $\pm 0.91$	78.23 $\pm 0.27$	101.84 $\pm 0.87$

### MECHANISM

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



Where

S stands for Substrate

$$\text{Rate} = k\text{C}_2 \quad \text{-----(6)}$$

$$= k_1 K_4 \text{C}_1 [\text{H}_2\text{O}^+\text{Cl}] \quad \text{-----(7)}$$

$$= k_1 K_3 K_4 [\text{S}] [\text{H}_2\text{O}^+\text{Cl}] [\text{PTA}] \quad \text{-----(8)}$$

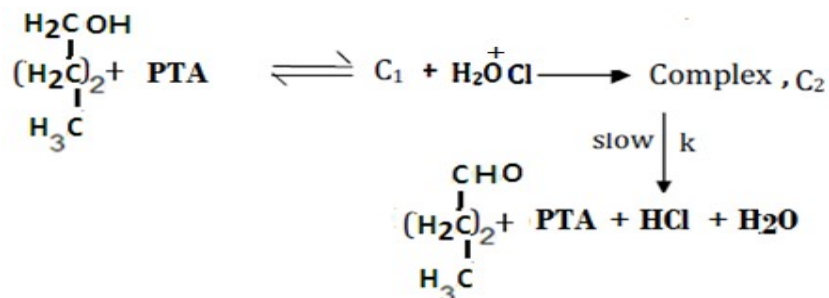
$$\text{Rate} = \frac{k_1 K_3 K_4 [\text{S}]_T [\text{H}_2\text{O}^+\text{Cl}] [\text{PTA}]}{[1 + K_3 [\text{PTA}]]} \quad \text{-----(9)}$$

$$= \frac{k_1 K_2 K_3 K_4 [\text{S}]_T [\text{H}^+] [\text{H}_2\text{O}^+\text{Cl}] [\text{PTA}]}{[1 + K_3 [\text{PTA}]]} \quad \text{-----(10)}$$

$$= \frac{k_1 K_2 K_3 K_4 [\text{S}]_T [\text{H}^+] [\text{H}_2\text{O}^+\text{Cl}] [\text{PTA}]}{[1 + K_3 [\text{PTA}]] [1 + K K_2 [\text{TCICA}]] [1 + K_2 [\text{H}^+]]} \quad \text{-----(11)}$$

$$\text{Rate} = k_{\text{obs.}} = \frac{k_1 K_2 K_3 K_4 [\text{S}]_T [\text{H}^+] [\text{H}_2\text{O}^+\text{Cl}] [\text{PTA}]}{[1 + K_3 [\text{PTA}]] [1 + K K_2 [\text{TCICA}]] [1 + K_2 [\text{H}^+]]} \quad \text{-----(12)}$$

Mechanistically, the reaction sequence can be depicted as follows under the kinetic conditions of [substrate] >> [oxidant]:



## CONCLUSIONS

The kinetics of the PTA catalyzed oxidation of n-Bu.OH, by TCICA in aqueous acid medium at 308 K, was discussed. A negative  $\Delta S^\ddagger$  value indicates the formation of transition state fair and rapid with lower degree of freedom. Further, the high value of free energy of activation suggests a solvated activated complex. n-butanaldehyde is the main product of the reaction.

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, Voglibose 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 largely 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>[9]</sup>.

TCICA is an important chemical product and has been widely applied in chemical, pharmaceutical and agricultural industries with various kinds of advantages including excellent stability, high content of bromine and high reactive activity<sup>10-14</sup>. Currently, the combined formulation between TCICA and other halogenated hydantoin



for application has become a hotspot in recent years such as the combined application of BCDMH and TCICA as well as the combined application of DCDMH and TCICA. For the combined formulation of TCICA and other halogenated imides/hydantoin, one critical factor is the ratio between effective chlorine and effective bromine. For example, at pH 7.1, compound formulation with the same dose of BCDMH and TCICA has a significantly higher bactericidal efficacy than TCICA alone or BCDMH alone. Many domestic and foreign experts believe that the most significant oxidizing biocide is the compound halogenated compound formulation combining BCDMH and TCICA. In agriculture, TCICA is mainly used for aquaculture including pond disinfection, prevention of water disinfection, disease treatment, etc., and is not affected by water quality, salinity, pH, temperature, and other organic compounds during usage. In addition, there has been already cases in which people has applied TCICA as high-efficiency and low-toxicity disinfectant for combined.

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