Jan 2019 - Mar 2019, Vol 5, No. 1, 15-23 ISSN 2394 -9449

# Electronic Journal of Advanced Research

An International Peer review E-Journal of Advanced Research

## Research Articles

# "STUDY OF CATALYTIC EFFECT OF TUNGSTOPHOSPHORIC ACID ON THE OXIDATION OF PROPANAL AND BUTANAL BY N-BROMOSUCCINIMIDE IN AQUEOUS ACETIC ACID MEDIUM"

**S.K. Singh[1], Bharti Verma[*1], H.D.Gupta[2], Pawan Tiwari[1],**

**1.** Govt. T. R.S. (Auton.) College, Rewa (M.P.) **2**. Govt.Girls Degree College, Sidhi (M.P.)

| Received : 06-Feb-2019 | Revised : 17-Feb-2019 | Accepted : 23-Feb-2019 |
|---|---|---|

## ABSTRACT

In present paper explored kinetics and Mechanistic study of oxidation of aliphatic aldehydes (viz. propanal and butanal ) by *N*-bromosuccinimide which has been investigated in water-HOAc acid medium. The reaction is of pseudo first-order in [NBS], fractional order in [substrate] and first-order in TPA. 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. Corresponding carboxylic acids were identified as an end-product of oxidation.

*Key words:* aliphatic aldehydes; TPA catalyzed; fractional order; Dielectric constant of medium; thermodynamic parameters

[*] For correspondence

## INTRODUCTION

This study leads to work at stoichiometry, identification of intermediates and isolation of end products as an indirect support to reaction mechanism. The elucidation of reaction mechanism is still one of the most fascinating problems in inorganic and organic chemistry. A number of reports on the oxidation of organic compounds by different oxidants are available in the literature[5-10]. In the present work explored the kinetics and mechanistic path of oxidation of substrates by NBS, I have chosen NBS as an oxidant to oxidized aliphatic aldehydes (viz. propanal and butanal). NBS act an oxidant because >N-Br bonds are polar easily undergo heterolytic fission in polar medium[11].

## MATERIALS AND METHODS

The solution of NBS (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 aldehydes (viz. propanal and butanal) was prepared in requisite volume of glacial acetic acid. Other reagents are grade chemicals and doubly distilled water was used throughout the experiments.

## Method

The known volume of oxidant, acetic acid and TPA 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 ± $0.1^0$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 NBS 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 NBS. 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 [TPA] on the oxidation of aldehydes (viz. propanal and butanal) was determined by adding different

## 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 [substrate]. Plot of $k_1$ versus [substrate] 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 substrate and oxidant (NBS) and appeared before the slow step (Fig.1).

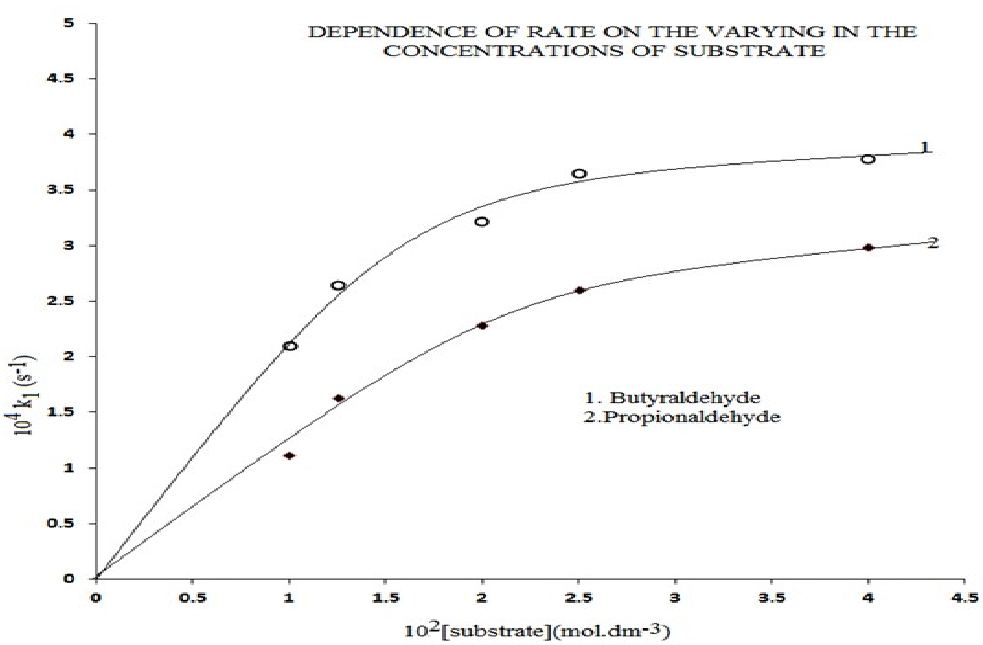



Fig.I

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

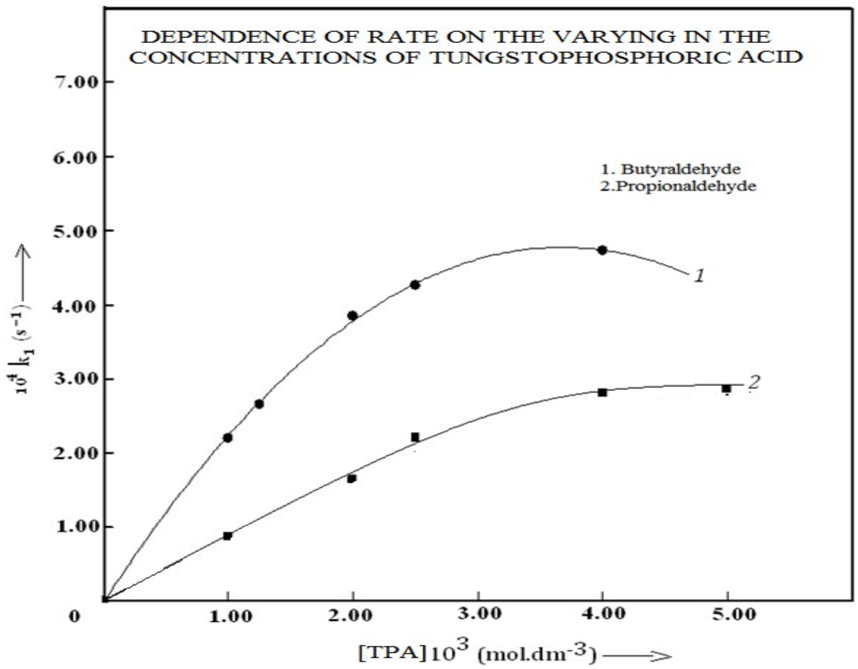



Fig.2: ***Effect* of [**TPA**)]**

***Effect of [H$^+$]: Reaction rate increases with increase the concentration of hydrochloric acid.*** The plot of $k_1$ vs. [H$^+$] ion is obtained linear with the positive unit slope, confirming that the reaction fully catalyzed.

***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: 3).

***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

Aldehydes – NBS system and according to the reaction mechanism, rate equation and order of reaction have been discussed(Table:3). Corresponding carboxylic acid were formed as the end-product of oxidation of substrates, which was identified by the determination of melting points of p-bromophenacyl ester derivatives of oxidation products and existing conventional methods. Identification of oxidation products by the compared observed melting points and reported melting points

| Substrate | Main oxidation Product | MELTING POINTS p-Bromophenacyl esters derivatives of oxidation products | |
|---|---|---|---|
| | | Observed melting point $^0C$ | reported melting point $^0c$ |
| Propinaldehyde | Propinoic acid | 59.2 | 59.0 |
| Butyraldehyde | Butyric acid | 63.4 | 63.1 |

**Table: 1**

[Substrates] $10^2$(mol.dm$^{-3}$) = 1.25(1, 2)
[TPA] $10^3$(mol.dm$^{-3}$) = 1.25(1), 2.00 (2)
HOAc-$H_2O$ % (v/V) = 20(1), 25(2),
Temperature K = 308((1), 313(2).

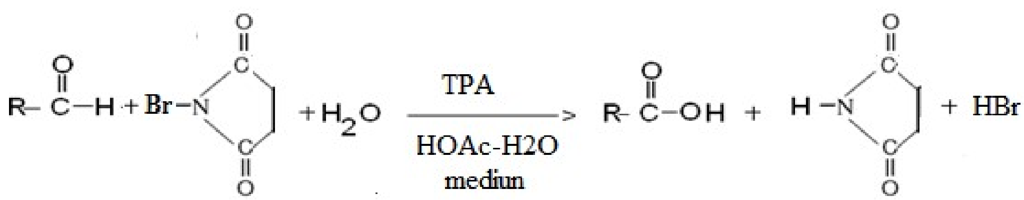
| [NBS]$10^3$ (mol.dm$^{-3}$) | | |
|---|---|---|
| | **1. Butyraldehyde** | **2. Propionaldehyde** |
| 1.00 | 2.68 | 1.68 |
| 2.00 | 2.67 | 1.66 |
| 2.50 | **2.65** | **1.64** |
| 4.00 | 2.65 | 1.65 |
| 5.00 | 2.65 | 1.64 |

**Table: 2**

[NBS] $10^3$ (mol.dm$^{-3}$) = 2.50(1,2);
[Substrate] $10^2$(mol.dm$^{-3}$) = 1.25(1,2);
[TPA] $10^3$ (mol.dm$^{-3}$) = 1.25(1); 2.00(2);
Temperature K = 308((1), 313(2).

| HOAc-$H_2O$ % (v/V) | $10^3$/D | 1.Butyraldehyde | 2.Propionaldehyde |
|---|---|---|---|
| | | ←— $10^4$ $k_1$ ($s^{-1}$) —→ | |
| 10 | 15.50 | 1.81 | - |
| 15 | 16.42 | 2.65 | 1.44 |
| 20 | 17.17 | 3.72 | 1.64 |
| 25 | 18.23 | 5.07 | 1.91 |
| 30 | 19.15 | 7.18 | 2.31 |
| 40 | 21.98 | - | 3.44 |
| 50 | 25.64 | - | - |

It is found that for complete oxidation of one mole of Substrate, one mole of NBS is required.




***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 Aldehydes – NBS system and according to the reaction mechanism, rate equation and order of reaction have been discussed (Table:3).

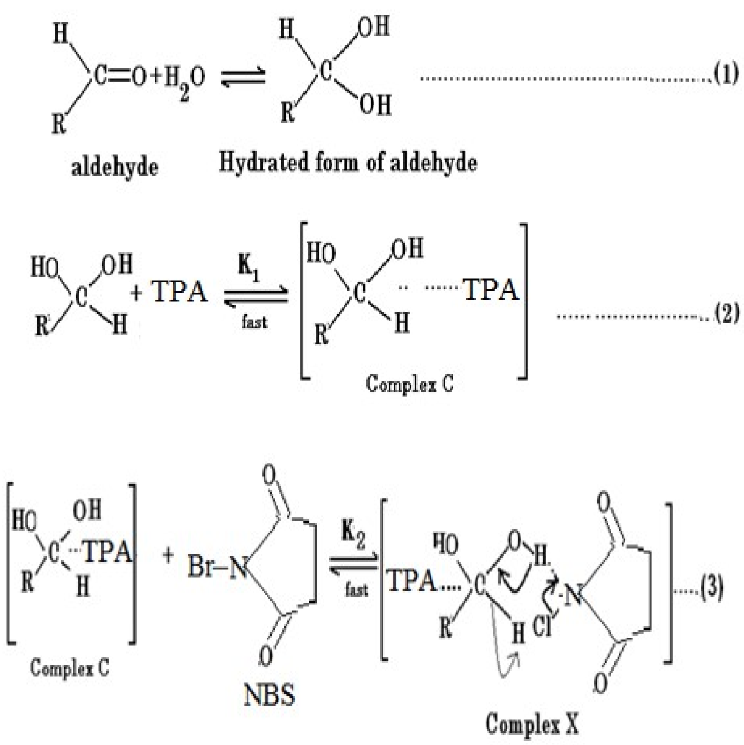
**Table: 3**

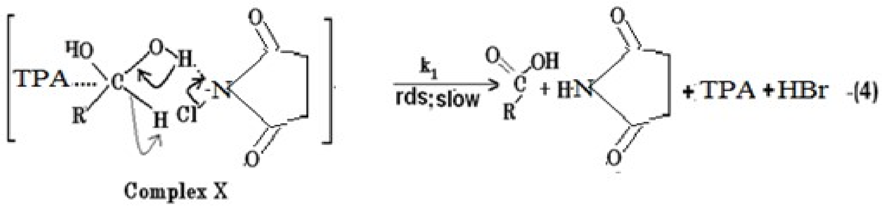
**Thermodynamics parameters**

| Substrate | Ea KJ mol$^{-1}$ | A s$^{-1}$ | ΔH$^{\#}$ KJ mol$^{-1}$ | ΔG$^{\#}$ KJ mol$^{-1}$ | ΔS$^{\#}$ JK mol$^{-1}$ |
|---|---|---|---|---|---|
| **PROPIONALDEHYDE** | **46.37 ±0.76** | **9. 815x10$^{3}$ ±0.22** | **45.471 ±0.64** | **-73.307 ±0.598** | **-92.57 ±0.79** |
| **BUTYRALDEHYDE** | **44.64 ±0. 63** | **5.134 x10$^{3}$ ±0.35** | **42.790 ±0.69** | **-72.26 ±0.621** | **-89.25 ±0.67** |

## MECHANISM

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






**where: R=C2H5 -, and C3H7 for standing for propionaldehyde and butyraldehyde respectively**

***Derived Rate law:***

$$k_{obs} = \frac{k_1 K_2 K_1 [TPA][Aldehyde]}{1+K_1\,[Aldehyde]+K_1 K_2\,[Aldehyde]}$$

Above rate Equation is in good agreement with the observed experimental data and results

**CONCLUSIONS**

Kinetic studies utilizing NBS 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 NBS 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[12-16].

## 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. Janibai, T.S. and Vasuki. M., *J. Indian Council of Chemists,* **21**, 60(2004).
4. Singh. A.K., *Asian J. Chem.,* **15,** 1313(2003).
5. Singh, A.K., *Asian J. Chem.,* **15**, 1307(2003).
6. Menakshisundaram S.P., Sathiyendrian V.; *J. Chem. Res. (S) 8 (2000) 458–468.*
7. Singh H.S., Singh R.K., Singh S.M., Sisodla A.K., *J. Phys. Chem. 81, 1044–1059,(1997).*
8. Puttaswamy, Jagadeesh R.V.; *Appl. Catal. A: Gen. 292, 259–270(2005).*
9. Morris J.C., Glyzar J.R., Winemann M.A., *J. Am. Chem. Soc. 70 2036–2047(1948).*
10. Kikkeri N. Mohana and Paanemangalore M. Ramdas Bhandarkar: *J. Chinese Chem. Soc.*, 2007, *54*, 1223-1232
11. Sanju Patel: M.Phil Dissertation(2012), central library, A.P.S. University, Rewa (M.P.)
12. Frederick George Mann and Bernard Charles Saunders: *"PRACTICAL ORGANIC CHEMISTRY" LONGMAN GROUP LIMITED London (1960) ,pp .245.*
13. Frederick George Mann and Bernard Charles Saunders: *"PRACTICAL INORGANIC CHEMISTRY" LONGMAN GROUP LIMITED London (1980), pp .179.*
14. Atkins P., Overton T., Rourke J., Weller M. & Armstrong F.: *Shriver and Atkins: Inorganic Chemistry*, Oxford University Press (2006).pp-436
15. Priya V., Balasubramaniyan M. and Mathiyalagan N.: *J. Chem. Pharm. Res., 2011, 3(1):522-528*
16. Patwari S.B., Khansole S.V. and Vibhute Y.B.: *J. Iran. Chem. Soc.,* Vol. 6, No. 2, 2009, pp. 399-404