

# Kinetics and Mechanism of Phosphotungstic acid Catalysed Oxidation of 2-hexanone by N-bromoisonicotinamide in Aqueous Acetic acid

Shahina Khan<sup>1\*</sup>, K. N. Sharma<sup>1</sup>

Department of Chemistry,  
Govt. Girls P.G. College Rewa (M.P.) India.

**Abstract:** The temperature dependence and catalysed rate coefficients for the reactions between 2-hexanone and N-bromoisonicotinamide have been determined. The stoichiometry correspondence to reaction in which one mole of enolic hexanone reacts with 2 moles of N-bromoisonicotinamide was assigned. The reaction shows the Michalis- Menten type of kinetics at the transition state which decomposes to form dione. A plausible reaction mechanism with derived rate law accounts for all experimental observations has been proposed. Various kinetic and activation parameters have been measured.

**Keywords:** 2-hexanone, Phosphotungstic acid, N-bromoisonicotinamide, oxidation, kinetics.

## 1. INTRODUCTION

Variety of N-halo reagents are utilized for the generation of hypohalous acids<sup>[1-7]</sup> in solution for their application in synthetic organic chemistry and analytical determinations of organic compound to assess the enolic impact in mechanistic aspects. The generated HOBr hypobromous acid<sup>[8]</sup> reacting species has been utilized as a protocol oxidations in amino acids,<sup>[9]</sup> alcohols,<sup>[10]</sup> and unsaturated acids.<sup>[11]</sup>

Phototungstic acid is a strong catalyst in Keggin type structure, being thermally stable has been used in wide range of oxidation reactions.<sup>[12-14]</sup>

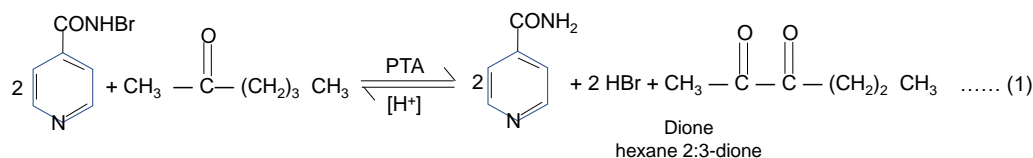
The few adjusting data available in the literature for kinetics of 2-hexanones<sup>[15-18]</sup> by different oxidants. The reaction has however not been studied catalysed by PTA with NBIN to examine the mechanistic step of the reaction rate. This has motivated us to investigate the oxidation of 2-hexanone and try to resolve some of the issue. This paper reports the PTA catalysed oxidation of 2-hexanone in aqueous acetic acid medium by using NBIN as an oxidant.

## 2. EXPERIMENTAL

The sample of PTA (synthesized) was used of analytical grade at pH 8 values. Its solution was prepared in doubly distilled water and mineral acid. 2-hexanone was of B.D.H. grade. All chemicals were used as received without further purification. The stock solution of NBIN (Across) was prepared in 80% acetic acid (B.D.H.) and kept in the dark to protect it from the exposure of the light. The purity of NBIN was checked by iodometric process. Various reagents used pertaining to study were of analytical grade.

## 3. Kinetic Study

The oxidation of 2-hexanone was investigated under first-order kinetic conditions with respect to NBIN i.e.  $[NBIN] \ll [2\text{-hexanone}]$ . The solutions of 2-hexanone and NBIN in required amounts were allowed to equilibrate in a previously adjusted thermostat (accuracy  $\pm 0.1^\circ\text{C}$ ) in separate flasks after the temperature equilibrium was attained, the solutions were mixed to start the reaction. 2 ml aliquot of the reaction mixture was withdrawn at regular time intervals and the unreacted NBIN was estimated iodometrically. The rate constants  $k_{\text{obs}}$  were determined from the linear plots of  $\log [\text{unreacted NBIN}]$  versus time, with reproducibility of within  $\pm 4\%$ . The estimated stoichiometry results showed that in the foregoing reaction, 1 mole of 2-hexanone is used up completely with 2 moles of oxidant (NBIN). For 2-hexanone, the PTA catalyzed oxidation reaction can be shown as :



The oxidation product hexane 2:3-dione was identified by spot test, and forming coloured inner complex as Nickel diketones and 2:4-DNP derivative, further, confirmed by TLC.

The oxidation of 2-hexanone by NBIN in nitrogen atmosphere did not initiate polymerization / precipitation by the addition of acryl amide monomer solution in the dark. The study indicated the absence of formation of free radicals species in the reaction sequence. 2-hexanone possesses  $>\text{C}=\text{O}$  group shows keto-enol equilibrium and its oxidation involves reaction at  $\alpha$ -position depending upon various operative physical factors.

#### 4. Results And Discussion

The effect of [NBIN] was investigated with the view to ascertaining the order of reaction with respect to [NBIN]. This was done, by five times more varying concentrations of NBIN as at fixed concentration of 2-hexanone an ionic strength of the medium. The values of first-order rate constant were obtained from the unit slopes of the plot  $\log [\text{NBIN}]$  vs. time.

The effect of concentration of 2-hexanone within the range  $1.25 \times 10^{-2}$  to  $6.25 \times 10^{-2}$  ( $\text{mol dm}^{-3}$ ) on the oxidation reaction was carried out at experimental conditions of the reaction and fixed ionic strength (Table 1). It was observed that reaction showed fractional-order kinetics confirming Michalis-Menten types of kinetics. (the double reciprocal plot  $\frac{1}{k_{\text{obs}}}$  vs.  $\frac{1}{[2\text{-hexanone}]}$ ) yielded non-zero intercept on ordinate axis (Fig.1) showing existence of complex formed between enolic substrate, PTA and HOBr at the transition state.

**Table 1: Dependence of rate on hexanone**

[NBIN] =  $3.33 \times 10^{-3}$  ( $\text{mol dm}^{-3}$ ) ;  $[\text{H}^+] = 0.002$  ( $\text{mol dm}^{-3}$ ) ;  
 [PTA] =  $2.50 \times 10^{-5}$  ( $\text{mol dm}^{-3}$ ) ;  $\text{CH}_3\text{COOH-H}_2\text{O} = 20 \%$ , (v/v) ;  
 Temperature = 308 K

$10^2 \times [2\text{-hexanone}]$ ( $\text{mol dm}^{-3}$ )	$10^4 k$ ( $\text{sec}^{-1}$ )	$\frac{10^2}{[2\text{-hexanone}]}$ ( $\text{mol}^{-1} \text{dm}^3$ )	$10^4 \times \frac{1}{k}$ (s)	$1000 k_2 = \frac{K}{[2\text{-hexanone}]}$ $\ell$ ( $\text{mol}^{-1} \text{s}^{-1}$ )
1.25	1.46	0.8000	0.6849	11.68
2.00	2.13	0.5000	0.4694	10.65
2.50	2.67	0.4000	0.3745	10.68
3.33	3.20	0.3003	0.3125	9.60
4.00	3.59	0.2500	0.2785	8.97
5.00	4.21	0.2000	0.2375	8.42
6.25	4.73	0.1600	0.2114	7.56

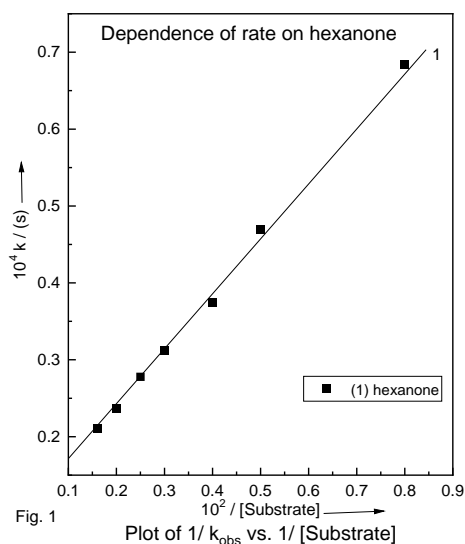


Fig. 1

[NBIN] =  $3.33 \times 10^{-3}$  (mol dm<sup>-3</sup>); [H<sup>+</sup>] = 0.002 (mol dm<sup>-3</sup>);  
 [PTA] =  $2.50 \times 10^{-5}$  (mol dm<sup>-3</sup>); CH<sub>3</sub>COOH-H<sub>2</sub>O = 20 %, (v/v);  
 Temperature = 308 K

The study reveals the pseudo first-order rate constant accelerated with rising concentration of H<sup>+</sup> ion (Table 2). The plots log k vs. log [H<sup>+</sup>] (Fig. 2) give rise slope values in fraction indicating that order with respect to [H<sup>+</sup>] falls from 1 to 0 at its higher concentration showing reaction is not acid catalysed.

**Table 2: Effect of Acidity on rate**

[2-hexanone] =  $2.50 \times 10^{-2}$  (mol dm<sup>-3</sup>); [NBIN] =  $3.33 \times 10^{-3}$  (mol dm<sup>-3</sup>);  
 [PTA] =  $2.50 \times 10^{-5}$  (mol dm<sup>-3</sup>); CH<sub>3</sub>COOH-H<sub>2</sub>O = 20 %, (v/v);  
 Temperature = 308 K

$10^3 [\text{H}^+]$ (mol dm <sup>-3</sup> )	$10^4 k$ (s <sup>-1</sup> )
1.00	1.68
1.50	2.08
2.00	2.67
2.50	2.92
3.33	3.46
4.00	3.69

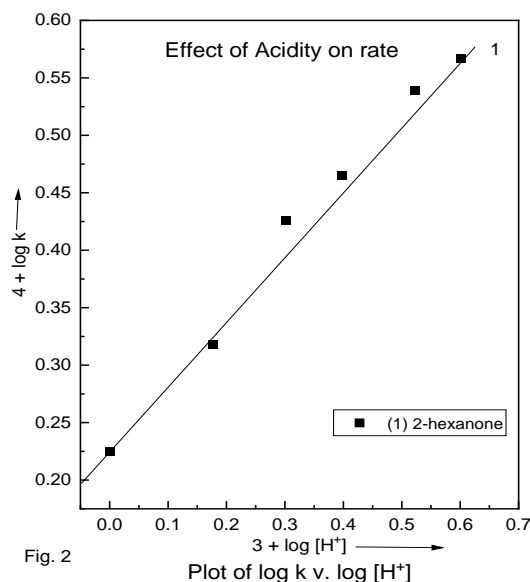


Fig. 2

[2-hexanone] =  $2.50 \times 10^{-2}$  (mol dm<sup>-3</sup>) ;  
 [NBIN] =  $3.33 \times 10^{-3}$  (mol dm<sup>-3</sup>) ;  
 [PTA] =  $2.50 \times 10^{-5}$  (mol dm<sup>-3</sup>) ;  
 CH<sub>3</sub>COOH-H<sub>2</sub>O = 20 %, (v/v) ;  
 Temperature = 308 K

The oxidation of 2-hexanone was studied in two different solvents which was not reacting with oxidant and hexanone. There was no reaction with the solvent chosen. The study shows that  $k_{obs}$  increases by decreasing dielectric constant of the medium (D). The Amis plot ( $\log k$  against  $\frac{1}{D}$ ) resulted positive slope intercept indicating involvement of ion-dipole in reaction mechanism.

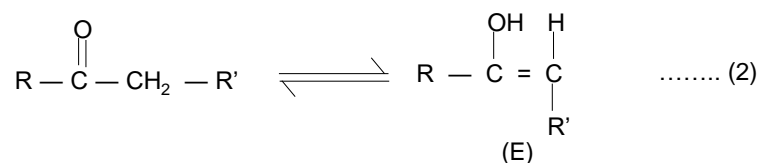
The neutral salts (NaCl and KCl) in 5X or excess when added in the oxidation reaction does not affect the reaction kinetics showing that primary salt effect is negligible.

Substantial addition of iso-nicotinamide a reductant product of oxidant gradually diminishes rate of oxidation indicating that iso-nicotinamide itself is not acting as a reacting species nor participating in the reaction mechanism.

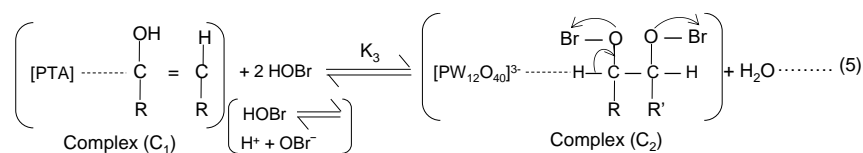
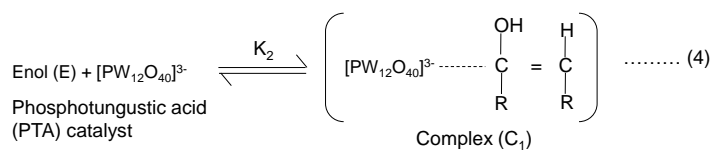
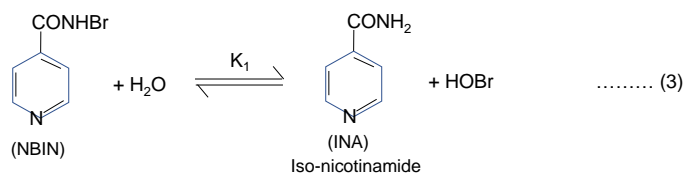
Heteropoly transition metal ion PTA (Keggin type) catalyst when used in five different concentrations in the NBIN mediated reaction of 2-hexanone at reaction conditions has shown capability to form a ternary complex between reacting species of oxidant and enolic substrate. Initially its presence in reaction, catalysed the reaction in low concentration but it shows fractional-order kinetics when used in higher concentration during the reaction PTA releases proton which does not alter sufficient reaction rate but are responsible for protonation of NBIN. It has been monitored in its literature that PTA acts as an outer sphere reagent causes oxidation of ketone with overlap enolization is an acid as well as base catalysed reaction proceed by push and pull mechanism. The enol content of the compound depends on the solvent hydrogen bonding and resonance in over investigation. The rate of enolization as determined by halogenation method was found much faster than the rate of oxidation. In light of above fact, enol form of 2-hexanone is probably participate in the rate determining step.

### Reaction mechanism

Based on the preceding discussion, the scheme given below is proposed, for the PTA catalysed reaction mechanism of oxidation of 2-hexanone by NBIN.

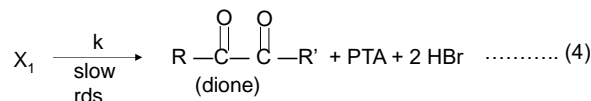
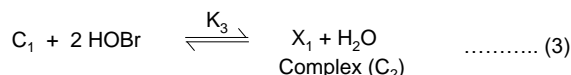
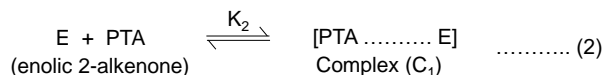
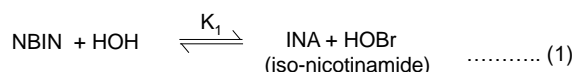


where, R = -CH<sub>3</sub> and R' = (CH<sub>2</sub>)<sub>2</sub> CH<sub>3</sub> for 2-hexanone respectively.



### Rate law

The rate law may be derived as :



$$\text{Rate} = k [\text{X}_1]$$

$$\text{Since, } [\text{X}_1] = \frac{K_3[\text{C}_1][\text{HOBr}]^2}{[\text{INA}]} \quad \dots\dots (5)$$

Substituting its value in above equation and execution of steady-state approach, we get final rate expression as :

$$k_{\text{obs}} = \frac{k K_1 K_2 K_3 [\text{E}][\text{PTA}]}{[\text{INA}] + K_1 + K_1 K_2 K_3 [\text{E}][\text{PTA}]} \quad \dots\dots (6)$$

Transforming equation (6) as equation (7)

$$\frac{1}{k_{\text{obs}}} \times [\text{PTA}] = \frac{1}{[\text{E}]} \left\{ \frac{[\text{INA}]}{k K_1 K_2 K_3} + \frac{1}{k K_2 K_3} \right\} + \frac{1}{k} \quad \dots\dots (7)$$

equation (7) is in good accordance with the kinetic findings. It justified Michalis-Menten mode of kinetics and other findings, showing many factors operative such as steric, hyperconjugative and inductive effects. In PTA catalysed study, dehydration of molecules occurs that affect the electron density on carbon atom. The enolic content together with +I effect creates electron deficient species at the transition state, which leads driving force towards the fission of α-C-H bond and expulsion of proton takes place.

The thermodynamic activation parameters ( $\Delta E_a = 61.72 \text{ kJ mol}^{-1}$ ,  $\Delta H^\ddagger = 60.80 \text{ kJ mol}^{-1}$ ,  $\Delta G^\ddagger = 87.40 \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = -85.69 \text{ JK}^{-1} \text{ mol}^{-1}$ ) for the foregoing catalysed reaction were measured.

The high negative value of  $\Delta S^\ddagger$  reduces the randomness of the molecule and indicates the ability of forming complexes with PTA and enolic hexanone at the top of the barrier. The high value of entropy is sufficient to cleavage  $\alpha$ -C-H bond to yield dione as the main product.

### Conclusion

In the present study, Keggin type of heteropoly phototungstic acid (PTA) participates in the formation of complex between enolic hexanone and HOBr reacting species of oxidant (NBIN) with stoichiometric ratio 1:2. The product identified was dione. The reaction exhibited first-order kinetics to [NBIN] and fractional-order kinetics each with 2-hexanone and  $\text{H}^+$  ions. The existence on Michales-Menten types kinetics was found in the system. Activation parameters were evaluated.

### Acknowledgement

We are thankful to principal and Head, Department of Chemistry, Govt. Girls P.G. College Rewa (M.P.) for encouragement and providing laboratory facilities.

### Conflict of Interest

The authors declare conflict of no interest whatsoever.

### REFERENCES

- [1]. Mahadevappa, D.S., Rangappa, K.S., Gowda, N.M.M., and Gowda, B.T. : *Int. J. Chem. Kinet.* 1982, 14, 1183.
- [2]. Meenakshi Sundaram, S., and Sockalingam, R.M. : *J. Mol. Catal. A. : Chem....*, 2000, 160, 269.
- [3]. Puttaswamy, Jagadeesh, R.V. : *Cent. Eur. J. Chem.*, 2005, 3(3), 482.
- [4]. Kondarasaiah, M.H., Ananda, S., Puttaswamy, Gowde, N.M. : *Synth. React. Inorg. Met. Org. Chem.*, 2003, 33(7), 1145.
- [5]. Puttaswamy, Jagadeesh, R.V. : *Int. J. Chem. Kinet.*, 2005, 37, 201.
- [6]. Puttaswamy, Jagadeesh, R.V. : *Ind. Engg. Chem. Res.*, 2006, 45, 1563.
- [7]. Vinod Kumar, C.H., Jagadeesh, R.V., Shivanand, K.N., Sree Sandhya, Y., and Naga Raju, C. : *Ind. Engg. Chem. Res.*, 2010, 49, 1550.
- [8]. Beckwith, R.C., and Margerum, D.W. : *Inorg. Chem.*, 1997, 36, 3754.
- [9]. Mathiyalagan, N. and Balasubramanian, M. : *Oriental J. Chem.*, 2014, 26, 1541.
- [10]. Singh, Nidhi, Parihar, Surendra Singh, and Singh, Santosh Kumar : *Int. J. Green and Herbal Chem.*, 2020, 9(4), Sec. A, 419-426.
- [11]. Prajapati, Aparna, Dwivedi, Arvind Prasad, and Parihar, Surendra Singh : *Int. J. Chem. Sci.*, 2019, 3(4), 09-11.
- [12]. Firouzabadi, H., Iranpoor, N. and Amani, K. : *Green Chem.*, 2003, 408-412.
- [13]. Singh, Sanjay K., Parihar, S.S. and Pandey, Deepti : *Int. J. Res. Engineering and Sciences*, 2021, 9(7), 32-39.
- [14]. Jain, N., Kumar, A., and Chauhan, S.N.S.: *Tetrahedron Lett.*, 2005, 46, 2599.
- [15]. Tiwari, S., Khan, M.U., Tiwari, B.M.L., Tiwari, K.S., and Valechha, N.D. : *Oxid. Commun.*, 1999, 22, No.3, 416-423.
- [16]. Singh, B., Singh, D., Chand, R., and Singh, A.K. : *J. Indian Chem. Soc.*, 1987, 64, 741.
- [17]. Khan, S., Khan, M.U., Singh, S.K., Gupta, H.D. and Singh, P.K. : *Asian J. Chem.*, 2007, Vol.15, No.2, 5267-5270.
- [18]. Prajapati, H.L., Khan, M.U., Singh, Santosh Kumar, Parihar, S.S., and Singh, P.K. : *Int. J. Green and Herbal Chem.*, 2013, Vol.2, No.3, 583-591.