

Catalytic Oxidation of Cyclopentanol with N-Bromophthalimide

Ankita Saraf^{1*}, S.P. Singh², Arvind Prasad Dwivedi³

¹Department of Chemistry, Pt. S.N.S. Govt. P.G. College (NAAC) Shahdol (M.P.) India

²Department of Chemistry, Govt. I.G. H. Sc. P.G. College Shahdol (M.P.) India

³Department of Chemistry, Govt. Sanjay Gandhi Smrati Auto., P.G., College Sidhi M.P

***Corresponding Author:** Ankita Saraf, Department of Chemistry, Pt. S.N.S. Govt. P.G. College (NAAC) Shahdol (M.P.) India

Abstract: The tungstophosphoric acid catalysed oxidation of cyclic alcohol (Cyclopentanol) by N-bromophthalimide (NBP) in 50% aqueous acetic acid medium in absence of mercuric (II) acetate and in presence of mineral acid was reported spectrophotometrically. The available spectral data was used for the verification of Beer-Lambert Law. The study reveals first-order kinetics for oxidant whereas fractional-order for substrate and catalyst PTA. The presence of mineral acid had insignificant effect whereas phthalimide shows retarding trends while increase in solvent polarity shows increase in rate of oxidation. A reasonable complex mechanism with mole ratio 1:1 was proposed consistent with the kinetic findings supported by thermodynamic parameters.

Key words: Consistent, versatile, investigation, suppression, retardation.

1. INTRODUCTION

NBP is a potential oxidizing agent, versatile in nature on hydrolysis produces HOBr reacting species extensively used in the oxidation of alcohols,1 benzhydrols,2 amino acids,3 hydroxy acids4 etc., whereas PTA a Keggin type anionic catalyst due to its thermal stability and acidity finds commendable position in Inorganic chemistry and is of academic importance in national and international laboratories. The kinetic oxidative studies of several organic compounds viz. aromatic alcohols,5 benzyl alcohols,6 involving PTA have been investigated. Cyclopentanol is a monohydric cyclic alcohol, shows a variety of reactions with different number of oxidants KBrO₃,7 NCP,8 QDC,9 NBA,10 CAT11, Ce(IV)12, Ru(III)13. However, there is no report available on the possible reaction mechanism or its selectivity under special condition with NBP spectrophotometrically. Hence this has prompted authors to undertake the task of kinetic investigation.

2. MATERIALS AND METHODS

All chemicals were reagent grade (B.D.H., C.D.H., Analar LOBA) and were used without further purification. All the required solutions used in this investigation, are freshly prepared and after kept in dry & cool places. The stability of the solution was tested under same operating conditions. A UV-visible double beam spectrophotometer of standard model fitted with cells was used in the experiments. The catalytic oxidation reactions were carried out in a 500 ml glass reaction vessel with variable speed stirrer, a condenser and a jacket for the circulation of the thermo regulating fluid. The temperature of the water or solution was regulated with a precision of $\pm 0.1^{\circ}\text{C}$ by an external thermostat. The concentration of the NBP species was determined spectrophotometrically at their respective absorption maxima.

2.1. Kinetic Measurement

The kinetic study of the PTA catalysed reaction was approached by the method of initial velocities, carrying the concentration of one reagent at a time. The calculated amount of NBP solution was added

to the cyclopentanol with different reagents in appropriate concentrations.

The progress of reaction kinetics was monitored spectrophotometrically followed by the reduction reaction and measuring its decrease in absorption/optical activity for unreacted NBP at wave length = 238.6 nm. The observed data was fed in equation $k = 1/t \ln D_0 - D_e / D_t - D_e$ to calculate rate constants.

3. RESULTS AND DISCUSSION

The PTA catalytic reaction was studied under $[\text{Cyclopentanol}] > [\text{NBP}]$ at experimental temperature in aqueous acetic acid medium in presence of mineral acid H_2SO_4 at temperature 308 K using UV-vis. Spectrometer at peak $\lambda_{\text{max}} = 238.6 \text{ nm}$. The spectral data follow the Beer-Lambert law from the veracity of the plot drawn between optical density/ absorbance and $[\text{NBP}]$ (Table 1, Fig.1). The unit slope of linear plot suggested that the order with respect to halooxidant $[\text{NBP}]$ is one. The spectral data of kinetics for cyclopentanol within concentration range 1.50×10^{-2} to $5.0 \times 10^{-2} \text{ (mol dm}^{-3}\text{)}$ have been collected. The spectrophotometric study shows fractional-order with respect to substrate. The study provides an evidence for complex kinetics between reacting species HOBr of oxidant (NBP) and substrate which is supported by double reciprocal linear plot of k^{-1} vs. $1/[\text{S}]$ with yielding positive intercept on Y-axis.

Table1. Effect of concentration of oxidant (NBP) on rate of oxidation

$[\text{Cyclopentanol}] = 2.50 \times 10^{-2} \text{ (mol dm}^{-3}\text{)}$; $[\text{PTA}] = 2.50 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$;

$[\text{H}^+] = 0.80 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$; $\text{HOAc-H}_2\text{O} = 30 \% \text{ (v/v)}$;

Temperature = 308 K; $\lambda_{\text{max}} = 238.6 \text{ nm}$

| S. No. | Time(min.) | Optical Density | $[\text{NBP}] \times 10^3 \text{ (mol dm}^{-3}\text{)}$ |
|--------|------------|-----------------|---|
| 1. | 0.00 | 0.650 | 7.00 |
| 2. | 0.60 | 0.551 | 6.00 |
| 3. | 1.20 | 0.436 | 5.00 |
| 4. | 1.50 | 0.414 | 4.50 |
| 5. | 2.00 | 0.380 | 4.00 |
| 6. | 3.00 | 0.270 | 3.00 |
| 7. | 4.00 | 0.251 | 2.50 |
| 8. | 5.00 | 0.173 | 2.00 |
| 9. | 5.50 | 0.123 | 1.25 |
| 10. | 6.00 | 0.101 | 1.00 |

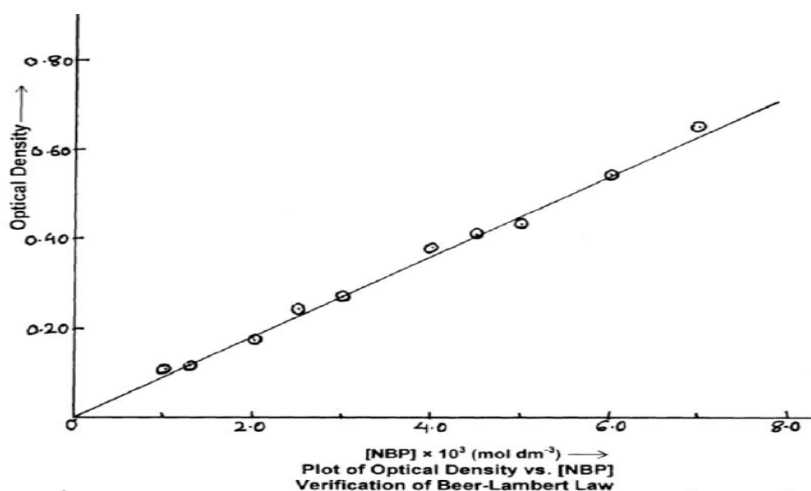


Figure1. $[\text{Cyclopentanol}] = 2.50 \times 10^{-2} \text{ (Mol Dm}^{-3}\text{)}$; $[\text{PTA}] = 2.5 \times 10^{-4} \text{ (Mol Dm}^{-3}\text{)}$; $[\text{H}^+] = 0.80 \times 10^{-3} \text{ (Mol Dm}^{-3}\text{)}$; $\text{Hoac-H}_2\text{O} = 30 \% \text{ (V/V)}$; Temperature = 308 K; $\lambda_{\text{max}} = 238.6 \text{ Nm}$

In the next series of experiments, the spectral kinetic data have been obtained for almost five times variation of H_2SO_4 at fixed concentration of other reagents, temperature and wavelengths. The study shows that H_2SO_4 had no appreciable effect on spectral absorption or rate of oxidation.

Though phosphotungstic acid (PTA) is anion of Keggin type $[\text{PW}_{12}\text{O}_{40}]^{3-}$ catalyst, employed in the investigation exhibits fractional-order kinetics at its higher concentration and forms complex with

substrate by loosing one molecule of water and release protons during the course of study. In presence of mineral acid it causes suppression and forms the complex. The wavelength of PTA has been found, to reduce during study of the substrate. It is possible to show that variation in the binary composition of solvent polarity, acetic acid and water (20 to 50%) increases the rate of oxidation with increasing percentage composition of acetic acid (Table 2). The Amis¹⁴ plot of log k vs. 1/D gives positive slope (Fig.2).

The addition of varying concentration of NaCl neutral salt had a nominal effect on the rate of oxidation indicating that one of the neutral species of the reagent is involved in the reaction kinetics. The added reaction product phthalimide indicates slightly retardation trends in the rate of oxidation. Activation parameter for the reactions have been determined for the catalytic reactions at four different temperatures (30⁰, 35⁰, 40⁰ and 45⁰C) and two concentrations [2.0 × 10⁻² and 2.50 × 10⁻² (mol dm⁻³)]. The values have been demonstrated in (Table 3). The study rules out the presence of free radicals when tested with polyacrylonitrile. The stoichiometry of the reaction was ascertained which revealed 1:1 mole ratio of cyclopentanol and oxidant NBP. The cyclopentanone was obtained as a reaction product which was identified by determining its melting point, and also forming its 2,4-DNP derivatives.¹⁵ The cyclopentanone was also confirmed by chromatographic and IR methods.

Table2. Effect of Dielectric Constant of the Medium on Rate of Oxidation

[Cyclopentanol] = 2.50 × 10⁻² (mol dm⁻³); [NBP] = 5.0 × 10⁻³ (mol dm⁻³);

[PTA] = 2.50 × 10⁻⁴ (mol dm⁻³); [H⁺] = 0.80 × 10⁻³ (mol dm⁻³);

Temperature = 308 K; λ_{max} = 238.6 nm

| S. No. | CH ₃ COOH-H ₂ O % (v/v) | 10 ³ / D | 10 ⁴ k (s ⁻¹) |
|--------|---|---------------------|--------------------------------------|
| 1. | 20 | 17.17 | 35.65 |
| 2. | 30 | 19.15 | 38.17 |
| 3. | 40 | 21.98 | 42.28 |
| 4. | 50 | 25.64 | 46.90 |

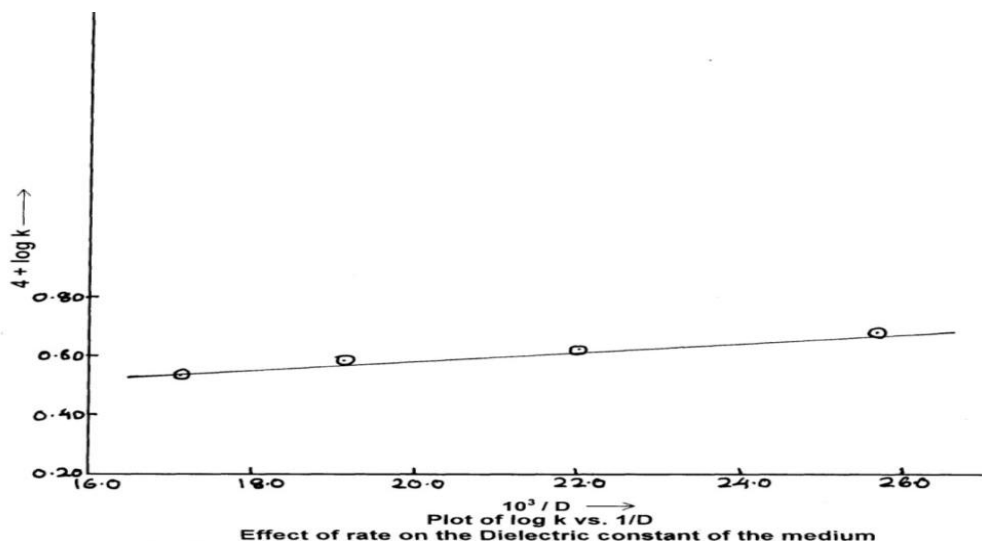


Figure2. [Cyclopentanol] = 2.50 × 10⁻² (mol dm⁻³); [NBP] = 5.0 × 10⁻³ (mol dm⁻³); [PTA] = 2.50 × 10⁻⁴ (mol dm⁻³); [H⁺] = 0.80 × 10⁻³ (mol dm⁻³);

Temperature = 308 K; λ_{Max} = 238.6 nm

Table3. Activation Parameters for Catalysed PTA Oxidation of Cyclopentanol- NBP System

| S.No. | Substrate | Ea kJ (mol ⁻¹) | A (s ⁻¹) | ΔH [#] kJ (mol ⁻¹) | ΔG [#] kJ(mol ⁻¹) | ΔS [#] JK ⁻¹ (mol ⁻¹) |
|-------|---------------|----------------------------|------------------------|---|--|---|
| 1. | Cyclopentanol | 38.09 | 9.62 × 10 ² | 35.53 | 86.46 | -163.99 |

3.1. Reaction Mechanism and Rate Law

On the basis of kinetic results and considering HOBr a prime oxidizing species, the probable mechanism is proposed:

- [7] Sewanee, J.P., Valechha, Anita, Singh, Alka, and Valechha, N.D., J. Indian Chem. Soc., 1980, 70-76.
- [8] Bharad, Jagdish, Balaji Madje, Fulchand Charan, Mazahar, Farooqui and Milind Ubale, J. Phy. Chem., 2008, Vol.3, issue 2-3.
- [9] Nongkynrih, I., and Mohanti, M.K., Bull. Chem. Soc., Japan, 1996, **69**, 1403-1407.
- [10] Shrivastava, A., Awasthi, and Singh, K., Int. J. Chem. Kinet., 2005, **37**, 275.
- [11] Prabhu, D.V., Oriented J. of Chem. 2008, Vol. **24**(1), 163-166.
- [12] Herold, L., Hintz, L. and Johnson, D.C., Am. Chem. Soc., Phoenix Art Jan. 1966.
- [13] Shrivastava, S., Singh, K., Shukla, M. and Pandey, N., Oxid. Commun, 2001, **24**, 558.
- [14] Amis, E.S., Solvent Effect on Reaction Rates and Mechanism, Academic Press, Newyork, 1962, pp. 733.
- [15] Vogel, I., Elementary Practical Organic Chemistry, Pearson, Education Publication, 2010.
- [16] Tiwari, S.N., Dwivedi, H.P., Khan, Khushbo, Nusrat Babey and Chauhan, R.P.S., Intl. J. Creative Res. Thoughts, 2015, Vol. **3** (6) 1-4.

Citation: Saraf, A. et.al. (2019). "Catalytic Oxidation of Cyclopentanol with N-Bromophthalimide". *International Journal of Advanced Research in Chemical Science (IJARCS)*, 6(2), pp.19-23. DOI: <http://dx.doi.org/10.20431/2349-0403.0602001>

Copyright: © 2019 Authors. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.