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"TUNGSTOPHOSPHORIC ACID CATALYZED KINETICS OF OXIDATION OF SOME ALIPHATIC ALDEHYDES BY N-BROMOISONICOTINAMIDE (NBIN) IN ACETIC ACID-WATER MEDIUM"

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Abstract:-A new oxidant and also an N-halo compound, N-bromoisonicotinamide (NBIN) has been synthesized by the bromination of nicotinamide. N-bromoisonicotinamide was characterized by physical constant (melting point), elemental analysis and spectral studies including infra-red, proton, carbon NMR and mass. Its formal redox potential has been determined as 0.797V at 25ºC. The reaction is first order in [NBIN], zero order in [substrate] and inverse fractional order in [H+]. Increase in ionic strength increases the rate and addition of the reaction product isonicotinamide has a slight retarding effect on the reaction rate. Increase in the dielectric constant of the medium increases the rate. Activation parameters have been evaluated from Arrhenius plot by studying the reaction at different temperatures and oxidation products are identified. A most probable reaction mechanism is proposed and an appropriate rate law is deduced to account for the observed kinetic data.

Keywords: Tungstophosphoric acid, N-bromoisonicotinamide and Kinetics .

INTRODUCTION

Aliphatic aldehydes serve important functions in biological systems and play a significant role in metabolism. They are also employed in biochemical, microbiological and nutritional investigations. Some of them are employed as dietary supplements. Aliphatic aldehydes represent organism forerunners of essential biomolecules such as proteins, hormones, enzymes; also, they may serve as energy source, losing their amino group by two pathways: transamination and oxidative formination.[1]

The degradative metabolism of glutamic acid in animals involves oxidative deamination or transamination followed by oxidation of the resulting α-keto glutarate in the citric acid cycle.[2]

Chemically the majority of natural Aliphatic aldehydes are α-Aliphatic aldehydes, having the general formula $R(CH)NH_2COOH$. With the exception of glycine, the natural aliphatic aldehydes contain one or more asymmetric carbon atoms and all of them are of laevo configuration with respect to L-glyceraldehyde.

Aliphatic aldehydes are widely distributed in the plant and animal kingdoms. Microorganisms synthesize the aliphatic aldehydes from mineral and organic nitrogen sources. Their biosynthesis, however, requires one essential condition, viz., the structure and metabolism of an intact living cell.

N-halo compounds are known to be versatile oxidizing agents[1]. They are being used in kinetics, analytical[2], organic structural investigations and in synthesizing organic substrates[3]. N-halo compounds are referred to as positive halogen compounds. The kinetics of oxidation of alcohols by N-bromo succinimde[4,5], N-chlorosuccinimide[6], N-bromo acetamide[7], Bromamine-T[8], N-chloronicotinamide[9], Chloraamine-T[10], N-bromophthalimide[11], 1-Chloro - benzotriazole[12] is already known. The kinetics of oxidation of amino acids by N-bromonicotinamide[13]is already reported. N-bromoisonicotinamide$_{14}$ (NBIN) is a new, mild, stable, effective and efficient oxidant for organic substrates. NBIN is a biologically important oxidizing agent, due to its reported antimicrobial activity by disc diffusion method[15] against *Staphylococcus aureus, Kiebsiella agerogenoes, Proteus*

vulgaris, Salmonella typhi, Candida alebicans, and *Aspergillus niger* at different concentrations. However, the kinetics of oxidation of alcohols by NBIN in aqueous acetic acid medium is not reported so far and hence need for the title investigation.

MATERIALS AND METHODS

NBIN was prepared[16] in acetic acid (Merck) and the purity was checked iodometrically. All the other chemicals were of AnalaR grade. The alcohols were prepared in acetic acid. Kinetics runs were carried out under pseudo-first order conditions ([alcohols] >> [NBIN]). Requisite amounts of alcohols, per-chloric acid sodium sulphate and aqueous acetic acid were taken in a jena glass reaction vessel and placed in a water thermostat maintained at the desired temperature for 30 min. The reaction was initiated by a rapid addition of NBIN solution and progress was followed by estimating iodometrically the amount of unconsumed NBIN at regular intervals of time.

RESULTS AND DISCUSSION

A new oxidant and also an N-halo compound, N-bromoisonicotinamide (NBIN) has been synthesized by the bromination of nicotinamide. N-bromoisonicotinamide was characterized by physical constant (melting point), elemental analysis and spectral studies including infra-red, proton, carbon NMR and mass. Its formal redox potential has been determined as 0.797V at 25ºC.

Aliphatic aldehydes play a vital role in various chemical functions. They have been chosen as substrates. Four Aliphatic aldehydes namely, were subjected to oxidative decarboxylation by NBIN in aqueous acetic acid medium in the presence of hydrochloric acid.

Acetaldehyde	CH_3CHO
α- Chloroacetaldehyde	$Cl\text{-}CH_2CHO$
n-Propanaldehyde	$CH_3\text{-}CH_2\text{-}CHO$
n-Buatanaldehyde	$CH_3\text{-}CH_2CH_2CHO$

The stoichiometry and product analysis have been carried out. The stoichiometry for the oxidation of Aliphatic aldehydes by NBIN was found to be 1:1.The product analysis includes the checking of melting points of the DNP derivatives of corresponding aldehydes for other Aliphatic aldehydes and a-keto acids for aspartic and glutamic acids. The other products of oxidation, namely, carbon dioxide and ammonia were identified by lime water test and Nessler's reagent respectively.

The rates of oxidation of Aliphatic aldehydes by NBIN showed a first-order dependence on [NBIN] and fractional order dependence on [aliphatic aldehyde]. The rate of reaction decreased with increase in [NBIN] for all the amino acids. The reaction rate was found to decrease with increase in [HCl]. The rates were not affected by increase in concentration of [Cl-]. Solvent polarity influenced the rates of oxidation of Aliphatic aldehydes by NBIN. The rates increased with increase in amount of acetic acid in the acetic acid-water mixture. It was evident from the linear plot of log kobs Vs 1/D, the dielectric constant of the medium. It also revealed that the reaction belonged to ion-diploe type.

Retardation of rate was found when one of the products, nicotinamide was added to the reaction mixture. The addition of sodium perchlorate had no influence on rate. Its role was merely to keep the ionic strength constant. Mercuric acetate was added to the reaction mixture to suppress the formation of bromine which would vitiate the results. Added salts like $BaCl_2$, KCl, Na_2SO_4 and K_2SO_4 do not have any effect on the rate. No polymerization is observed when acrylonitrile is added to the reaction mixture.

Increase in temperature increased the rate of reaction. The effect of temperature has been studied from the plots of log k_{obs} Vs reciprocal of temperature. Arrehenius parameters and thermodynamic parameters have been evaluated. The entropy of activation is negative in all cases. The free energy of activation of all the Aliphatic aldehydes is nearly the same. The correlation coefficient for the Exner plot was found to be 0.9999.

A suitable mechanism consistent with the experimental results was proposed. Linearity of Exner's plot and constancy in ? G≠ values imply the operation of a similar type of mechanism in all amino acids. A rate law deciphering all the observed experimental facts was derived.

In vitro antimicrobial activity of N-bromoisonicotinamide (NBIN) was conducted with the view that the study might throw light for further identification and synthesis of similar organic compounds which can be used as new antimicrobial agents. The following are salient findings of the present study:

Antibacterial studies :

- The antibacterial activity of NBIN revealed different levels of inhibition of growth as well as different levels of optimum concentration of the compound for the various bacterial species tested.

- *Bacillus subtilis* and *Pseudomonas aeruginosa* have shown the maximum level of inhibition of growth 18.0 mm at optimum concentrations of 750 and 1000 ppm.
- *Clostridium butyricum* exhibited the maximum level of inhibition of growth 12.0 mm at optimum concentrations of 1250 and 1500 ppm.
- *Enterobacter aerogenes* has shown the maximum level of inhibition of growth 13.5 mm at an optimum concentration of 750 ppm.
- Escherichia coli exhibited two maximum inhibition zones of 13.5 mm and 13.0 mm at two extreme optimum concentration levels of 750 and 1500 ppm.
- *Staphylococcus aureus* has shown the maximum level of inhibition of growth 15.0 mm at optimum peak at the concentrations of 750, 1000 and 1250 ppm.
- The higher concentration of 1500 ppm tested for this work has shown decline in the inhibition rate for *B. subtilis E. aerogenes, P. aeruginosa* and *S. aureus.*

Antifungal Studies :

- The NBIN compound screened for antifungal activity showed a total inhibition of growth at 1000 ppm concentrations for all the fungi namely *Aspergillus restrictus, Candida albicans, Cladosporium herbarum, Fusarium oxysporum, Penicillium chrysogenum* and *Rhizoctonia solani* tested for this work.
- At 500 ppm concentration, 75% of growth inhibition was noticed for A. restrictus, C. herbarum, F. oxysporum, P. chrysogenum and R. solani and this concentration is found to be optimum.
- It is concluded that
- NBIN, as antibacterial agent, is comparable with commercial antibiotic Amikacin and utilized in new antibacterial formulations.
- NBIN, as antifungal agent, is comparable with commercial antifungal agent Bavistin, and utilized in new antifungal formulations.

NBIN has been found to possesses pharmacological activity. It had significant effect on locomotor activity. It did not show a significant enhancing effect on phenobarbital induced narcosis. It showed no antiepileptic activity.

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