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Kinetic Study of Phosphotungustic Acid Catalyzed Oxidation of Cyclopentanol

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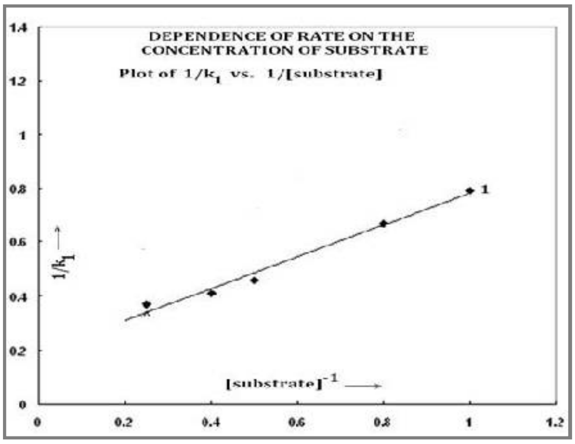
ABSTRACT

A kinetic and mechanistic study of phosphotungustic acid catalyzed oxidation of cyclopentanol by N-bromosaccharin was carried out in acidic medium. The reaction is first order each in N-bromosaccharin. The reaction constant is positive and increase with increase in temperature. Hydrogen ion shows positive effect on reaction rate. Activation parameters were calculated at different temperature. The main oxidizing product of the reaction has been identified as corresponding ketone. The proposed mechanism is well supported by kinetic data.

Graphical Abstract



Dependence of rate on the concentration of substrates.

Keywords: Halonium ion, N-bromosuccinimide, N- bromosaccharin, Cycloheptanone.

INTRODUCTION

Several oxidizing agents, specific and selective to varying degree, have been added to the literature of oxidation of organic and inorganic compounds. In addition to metal cation oxidants, the other group that has received much attention, now days is N-halo compounds. Originally, these compounds were known for their halogenating properties but now the diverse nature because of their ability to produced halonium ion, hapohalite species or N-anions etc. These compounds include N-halo amides, imides and N-halogeno-metallo compounds. N-halo imides are stronger oxidizing agents, as compared to N-halo amides, the former being more acidic loose halogen atom as halonium ion which is an electrophile and further the resulting anion is stabilized by resonance. Hence, such compounds under heterolytic fission to produced halonium ion rather than halogen free radicals. Owing to this reason, these compounds are not good allytic halogenating reagents but are good oxidants. Saccharin is an imide of orthosulphobezenoic acid and is a stronger acid as compared to other imides of dicarboxylic acid such as succinic acid. The anion of saccharin gets extra stabilization as the acyl and sulphonyl group provides larger orbital for the electron delocalization. Saccharin form stable bromo and chloro derivatives, the former being successfully applied as oxidizing reagent and Bacchawat and Mathur [1] synthesized N-Bromo saccharin by the bromination of saccharin and utilized it for both allylicbromination as well as quantitative oxidation of different organic substrates. It was observed that it bring about C-C and C-N bond fission in the oxidation of hydroxy acid, glycol and α-amino acids. A titrant potential of NBSa for the oxidimetric determination of some typical reductant in aqueous acetic acid medium. The formal potential of the couple was determined to +1.201, which indicates that is a moderately strong oxidant. NBSa oxidations are carried out in acetic acid medium in the presence of $HBrO_4$. In aqueous acetic acid, it may exist as molecular NBSA or its hydrolytic product HOBr or as halonium ion. In the presence of H+, protonation of NBSa and HOBr yields protonated NBSa (NBSaH+) and H_2O+Br one cannot ignore the existence of acetate complexes in acetic acid medium as $CH_3CO.OBr$ and $CH_3CO.O$+HBr. The choice of active species depends on kinetic results specially dependence of reaction rate on [H+] and [saccharin].

Sunderam *et al.*, investigated the oxidation kinetics of secondary alcohols including cyclic alcohols by N-bromosaccharin in the presence of added saccharin and Hg(II)acetate [2]. The reactions exhibit first order dependence in oxidant and substrate except for propan-2-ol and butan-2-ol where the order is the less than unity. The rate law given as the observed order of reactivity is propan-2-ol < butan-2-ol, pentan-2-ol, octan-2-ol, *i.e.* rate of oxidation increases with increase in the lengh of carbon chain. For the cyclic alcohols the observed order of reactivity is cyclopentanol,<cyclo-heptanol<cyclo-octanol. Ketones were reported as product of oxidation. Ganesan *et al.*, Reported the oxidation kinetics of cyclohexanol and tert-butyl cyclohexanols by NCSA in perchloric acid and aqueous acetic acid [3]. The reactions are first order each in oxidant and substrate. The equatorial alcohol is oxidized at a faster rate than axial alcohol. Venkatsubramanian *et al.*, reported the oxidation of secondary alcohols taking propan-2-ol as parent substrate and in the absence of added saccharin [4]. In binary solvent mixture of the acetic acid and water, in the presence of Hg (II) acetate. The reaction is acid catalyzed but no specific dependence on [H+] could be seen. The value of ρ= -2.3 suggested the formation of electron deficient transition state. Mechanistic steps of oxidation of primary alcohols were explored kinetically [5]. The reaction was acid catalyzed and exhibit michaelis- menten‟s kinetics in substrate. C-H fission in mechanistic step was suggested on the basis of non-reactiveness of tert-butyl alcohol under similar experimental conditions. The value of ǿ and w suggested the involvement of water molecule as proton abstracting agent. On the basis of kinetic results a mechanism analogous to E-2 elimination was proposed. The observed reactivity amyl>n-butyl>n-propyl>ethyl>methyl alcohols are also accordance with mechanism. Kinetic study of phosphotungustic acid catalyzed oxidation of cyclic alcohols by n-bromophthalimide. Kinetic investigations in keggin-type Phosphotungustic acid catalyzed oxidation of some cyclic alcohols (cyclopentanol, cyclohexanol and cycloheptanol) by N-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric (II) acetate as a scavenger have been studied [6]. The reaction exhibits a first order rate dependence with respect to oxidant, while it is fractional order in cyclic alcohols and PTA. The variation of ionic strength, $Hg(OAC)_2$, H+ and phthalimide (reaction product) have insignificant effect on reaction rate. Effect of varying dielectric constant of medium on the rate has been studied. Activation parameters have been evaluated from Arrhenius plot by studying the reaction at different temperature. Cycloheptanone in perchloric acid media is oxidized to 1, 2-cycloheptanedione by N-bromosuccinimide. The oxidation process has been monitored in presence of mercuric acetate. Zero order dependence in NBS and first order dependence in cycloheptanone and [H+] are observed [7]. Addition of mercuric acetate, succinimide and sodium perchlorate have negligible effect on the rate of oxidation. Methanol addition showed a positive effect. Various Thermodynamic parameters have been computed. A rate law deduced as: $-d/dt[NBS]=2k_1\ k_2/(\ k_{-1}+k_2)$ [cyclo-Hp] [H+] explains all the kinetic results.

MATERIALS AND METHODS

In the kinetic investigation of cyclic alcohols by N-bromosaccharin in aqueous acetic acid medium in presence of phosphotungstic acid, different chemicals were used in the form of solutions. The procedure employed for the preparation of these solutions and for the kinetic study is mentioned in the following sections:

Preparation of N-bromosaccharin solution and its standardization: The solution of N-bromosaccharin (NBSa) (sigma-Aldrich)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 standardization of NBSa 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_2SO_4 added to it. The liberated iodine was titrated against standard sodium thiosulphate (hypo) solution using starch solution as an indicator.

Preparation of substrate's solution: Cyclic alcohol cyclopentanol, (sigma chemicals India) was used as substrates for the preparation of solution. The solution of cyclic alcohol was prepared in requisite volume of glacial acetic acid.

Preparation of Phosphotungstic acid solution: The solution of Phosphotungstic acid was prepared by dissolving the weighed amount of sigma Aldrich sample in doubly distilled water carefully because it is slightly dangerous to dangerous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.

Preparation of $K_2Cr_2O_7$ and hypo solution: The standard solution of $K_2Cr_2O_7$ was prepared by dissolving the weighed amount of B.D.H. sample in distilled water. However, it was essential to prepare a fresh solution as it is reported that the spectra of this solution do not alter appreciably for over a period of days or weeks even in diffused day of light. The solution on of sodium thiosulphate was prepared by taking a (B.D.H. grade) sample in distilled water and standardized against standard $K_2Cr_2O_7$ solution iodometrically. Preparation of sulphuric acid solution Stock solution of H_2SO_4 (Analar E. Merck) of appropriate strength was prepared by diluting the calculated volume (from specific gravity) of acid with distilled water and finally its concentration was determined by titrating it against standard NaOH solution using phenolphthalein as an indicator. Preparation of other solutions (a) Saccharin is sparingly soluble in H_2O; hence 0.016 M solution of saccharin was used. (b) Binary solvent mixtures of acetic acid-water were prepared by mixing known volume of these solvents. (c) The solution of acrylonitrile was prepared by standard method for the identification of free radical formed during the course of oxidation. Kinetic studies Preliminary experiments for the oxidation of cyclic alcohol (cyclopentanol) with NBSa (N-bromosaccharin) was conducted to choose the appropriate conditions of concentration of the reactants and temperature under which these oxidation proceeds with measurable rate. It has been observed that in the presence of H3PW12O40 [PTA], the oxidation of these substrates proceeds at a measurable rate. The kinetic study of each system undertaken was carried out by integration and Ostwald‟s isolation methods. In each set of reaction, concentration of substrate was taken in large excess over the concentration of oxidant.

Procedure: The known volume of oxidant, acetic acid and $H_3PW_{12}O_{40}$ acid were taken in a conical flask while substrate and rest amount of water were in another conical flask. These two-stoppered flasks were placed at experimental temperature in a thermostat of sensitivity $\underline{+}$ 0.10°C. After the equilibrium of the temperature, the both solutions were mixed and aliquot was withdrawn immediately and was quenched. The amount of unreacted NBSa was estimated iodometrically 7 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 unreacted NBSa. 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.

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

Were found fairly constant within the experimental error suggested that each reaction obeys first-order kinetics. The effect of [PTA] on the oxidation of cyclic alcohols was determined by adding different concentrations of PTA (five-fold). The effect of saccharin was also investigated. Different compositions of binary solvent mixtures of acetic acid-water were used to study the effect of variation of dielectric constant of the medium.

Effect of temperature: The rate of reaction was studied at different temperatures to evaluate various activation parameters such as temperature coefficient, frequency factors and energy of activation, free energy of activation and enthalpy of activation and entropy of activation.

Temperature coefficient: The temperature coefficient of the reaction for 5° and 10°C rises in temperature was calculated by following expression:

$$\text{Temperature coefficient} = \frac{k_2}{k_1}$$

Where, k_1 is rate constant at temperature t and k_2 is rate constant at 5° or 10°C higher than “t” Energy of activation the effect of temperature on the rate of reaction given by Arrhenius equation – Where, k is rate constant at absolute temperature T, A is frequency factor, Ea is the energy of activation, and R is the gas constant. From equation (2) we obtain

$$K = Ae^{-Ea/RT} \qquad \dots (2)$$

$$\text{Log } k = \log A \quad \frac{Ea}{2.303\ RT} \qquad \dots (3)$$

Therefore, a plot of log k against inverse of T should be straight line having a

$$\text{Slope} = -\frac{Ea}{2.303\ R}$$

The energy of activation was determined graphically and also by calculating from equation:

$$Ea = \frac{2.303\ RT_1T_2}{(T_2 - T_1)} \log \frac{k_2}{k_1} \qquad \dots (4)$$

Where k_1 and k_2 are constant at temperature T_1 and T_2 respectively. Frequency factor by rearranging equation (3) frequency factor “A” can be obtained as

$$\text{Log } A = \log k + \frac{Ea}{2.303\ RT} \qquad \dots (5)$$

Free energy of activation ($\Delta G^{\#}$)

The free energy of activation ($\Delta G^{\#}$) is obtained using equation

$$-\Delta G^{\#} = 2.303\ RT\ Log\ k^{\#}$$

Where $k^{\#} = krh/KaT$

Therefore, $$-\Delta G^{\#} = 2.0303\ RT\ Log\ krh = KaT \quad \ldots(6)$$

Enthalpy of activation ($\Delta G^{\#}$)
The enthalpy of activation ($\Delta G^{\#}$) of the reaction was obtained from the Eyring‟s equation by plotting log $k_r h/K_B T$ vs. 1/T graphically. The slope of the plot is $\Delta G^{\#}/2.303R$. Entropy of activation ($\Delta G^{\#}$) the entropy of activation ($\Delta G^{\#}$) is calculated from the equation

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad \ldots(7)$$

Thus the values of the activation parameters viz. Ea, A, $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$ are calculated for each reaction.

Stoichiometry and product analysis: The stoichiometry of each reaction understudy was determined under experimental conditions. The oxidation products of the reaction were identified chromatographically and by spot test qualitatively. Test for free radicals the formation of free radicals during the course of reaction was tested using the solution of acrylonitrile (monomer) by trapping method.

Dependence of rate of oxidation reactions on the initial concentration of oxidant (NBSa): The dependence of rate on the initial concentration of oxidant was investigated by the five-fold varying concentration of oxidant i.e. N-bromosaccharin, while the concentrations of other reactants are kept constant at their respective temperature.

RESULTS AND DISCUSSION

Perusal of table 1 shows that the substrate understudy, obey first-order kinetic and the value of pseudo first order rate constant is nearly constant. The plots of log (a-x) vs. time are linear with nearly uniform slope (Figure 1) in each substrate. Therefore, it is, concluded that the order of reaction is one with respect to oxidant in each substrates.

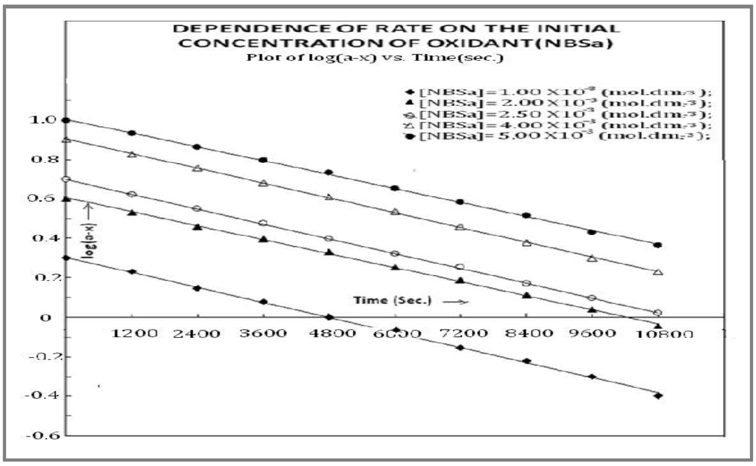


Figure 1. Dependence of rate on the initial concentration of oxidant (NBSa)

Dependence of rate on the concentration of substrate: The effect of the concentration of substrates on the reaction rate was investigated by varying their concentration, while the concentration of other reactants was kept constant on their respective temperature. The results are recorded in the figure 2.

Perusal of above tables those pseudo first-order rate constant increases with increase in the concentration of substrate. The plot of k1 versus [substrate] are obtained linear passing through origin at low concentration but at higher concentrations it tend zero order (Figure 2). The double reciprocal plot between 1/k1 and 1/[substrate] is obtained linear with intercept on y-axis (Figure 3).

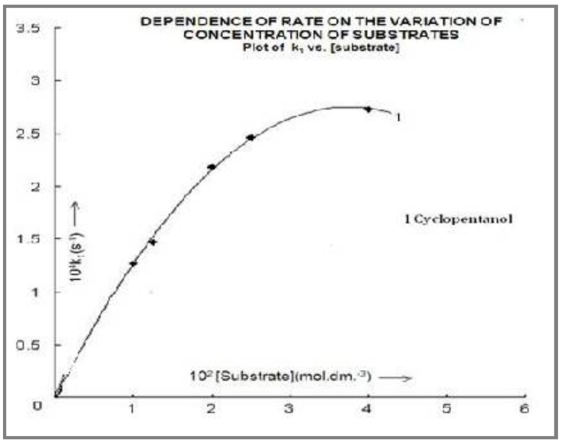


Figure 2. Dependence of rate on the variation of concentration of substrates.

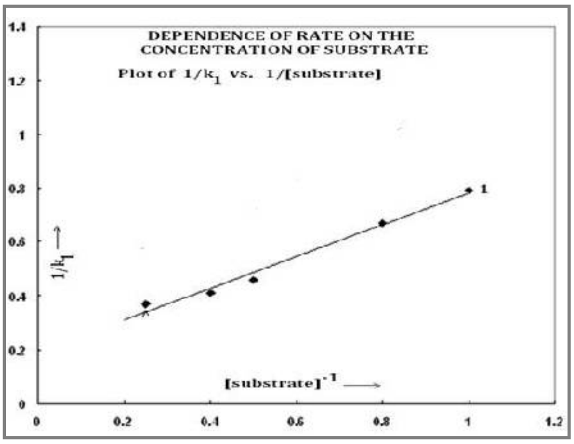


Figure 3. Dependence of rate on the concentration of substrates.

Dependence of rate on the variation of the concentration of sulphuric acid: The effect of the concentration of Sulphuric acid on the reaction rate was investigated by varying their concentration, while the concentration of other reactants was kept constant on their respective temperature. The results are shown in figure 4 and 5.

It is evident that the first-order rate constant slightly increases with increase concentration of sulphuric acid i.e. reactions are not fully acid catalyzed. The plot of k_1 vs. $[H^+]$ is obtained linear with the positive unit slope and intercepting on y-axis, confirming that the effect of Sulphuric acid is negligible (Figure 5).

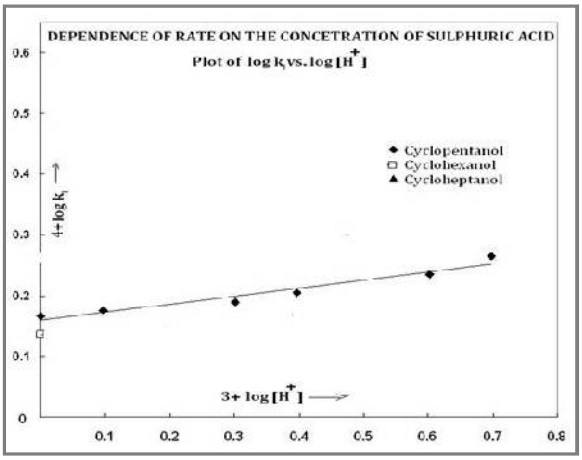


Figure 4. Dependence of rate on the variation of concentration of sulphuric acid.

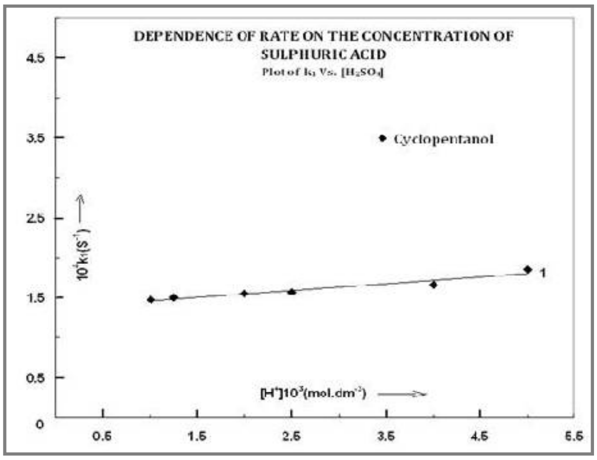


Figure 5. Dependence of rate on the concentration of sulphuric acid.

It is evident that the first-order rate constant slightly increases with increase concentration of sulphuric acid i.e. reactions are not fully acid catalyzed. The plot of k_1 vs. $[H^+]$ is obtained linear with the positive unit slope and intercepting on y-axis, confirming that the effect of Sulphuric acid is negligible (Figure 5).

Dependence of rate on the dielectric constant of the medium In order to study the effect of solvent polarity, on the rate of reaction between cyclic alcohols and NBSa, experiments were carried out by taking four and five fold composition of binary mixture of acetic acid water; maintaining the concentration of other reactants constant. Perusal of figure 6 shows that the first-order rate constant increases with increase % of composition of acetic acid i.e. rate increases with increase in dielectric constant of the medium. The plot of log k1 versus 10^3/D was obtained linear with positive slope in each substrate (Figure 6).

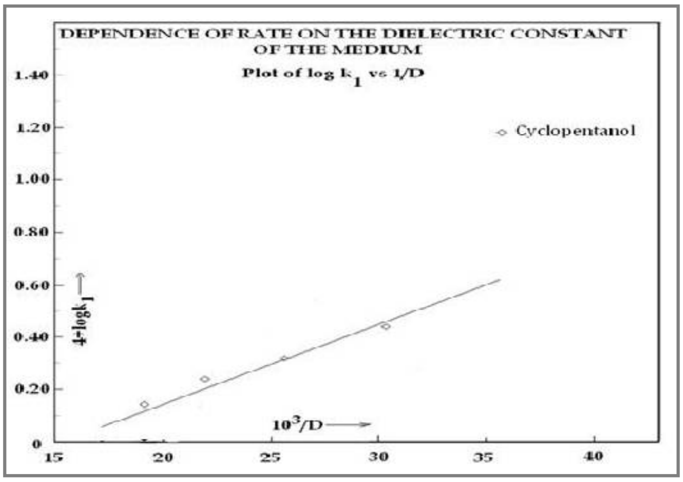


Figure 6. Dependence of rate on the dielectric constant of the medium.

Dependence of rate on the concentration of reductant product saccharin the effect of the added concentration of reductant product saccharin on the reaction rate was investigated by varying their concentration, while the concentration of other reactants was kept constant on their respective temperature. Perusal of figure shows that the first-order rate constant decreases with increase added concentration of saccharin i.e. rate decreases with increase in concentration of saccharin. The plot of log k_1 versus 1/[saccharin] was obtained linear in each substrate (Figure 7).

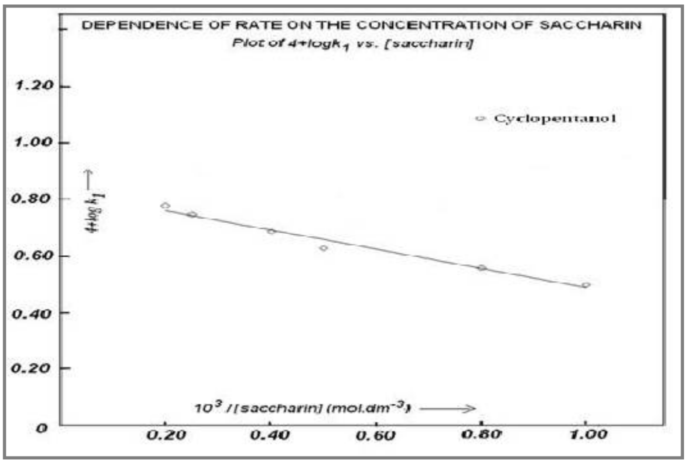


Figure 7. Dependence of rate on the concentration of saccharin.

Dependence of rate on the concentration of phosphotungustic acid (PTA) Perusal of table 6 shows that the first-order rate constant increases with increase concentration of i.e. rate increases with increase in concentration of phosphotungustic acid (PTA). The plot of k1 versus [PTA] was obtained linear with positive slope in each substrate (Figure 8).

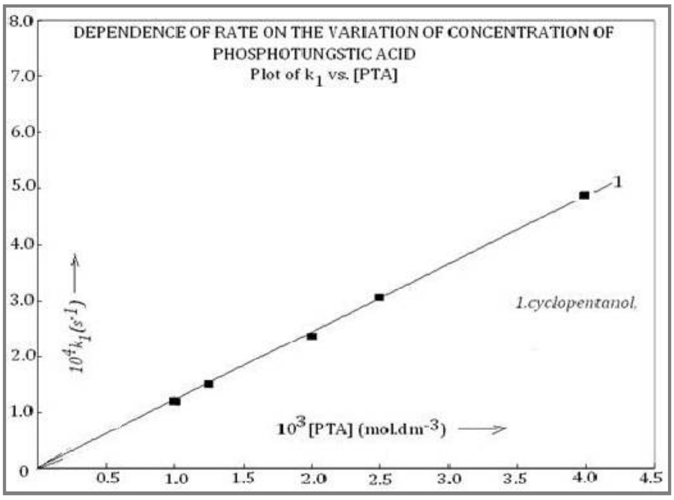


Figure 8. Dependence of rate on the variation of concentration of phosphotungustic acid.

Dependence of rate on the concentration of mercuric acetate the effect of the added concentration of mercuric acetate on the reaction rate was investigated by varying their concentration, while the concentration of other reactants was kept constant on their respective temperature. The results are recorded in the figure 9. Perusal of figure 9, the rate constant k_1, slightly increases with increase in the concentration of Hg $(OAc)_2$. Therefore, it is concluded that Hg $(OAc)_2$ negligible effect shows on the rate of reaction.

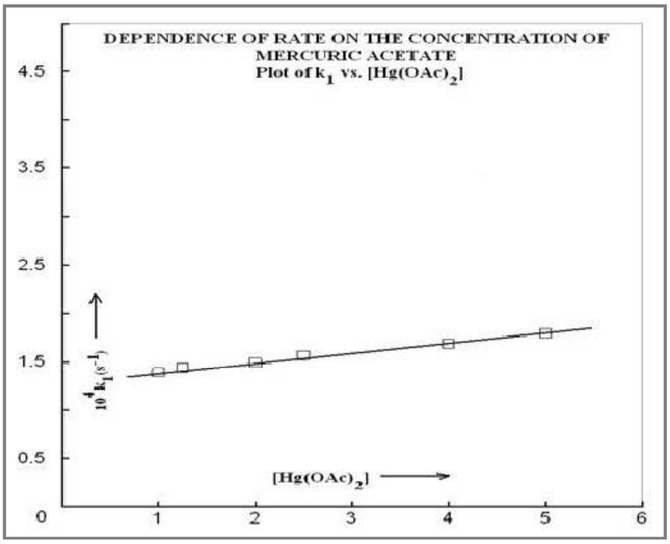


Figure 10. Dependence of rate on the concentration of mercuric acetate.

Dependence of rate on variation of temperature the dependence of rate on temperature was studied at four different temperatures for cyclic alcohols with NBSa while keeping the concentration of other reactants constant. It is clear from figure that the rate of reaction increases with increase in temperature (Figure 10-15).

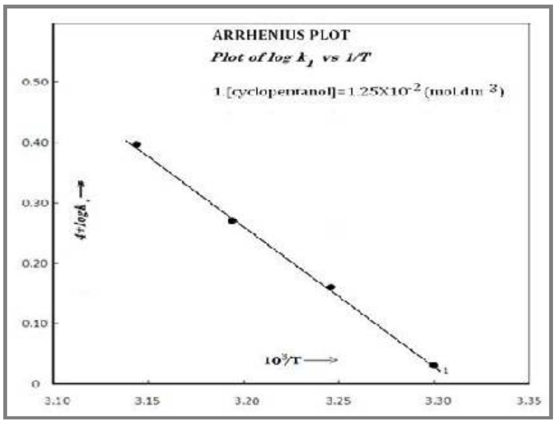


Figure 10. Arrhenius plot.

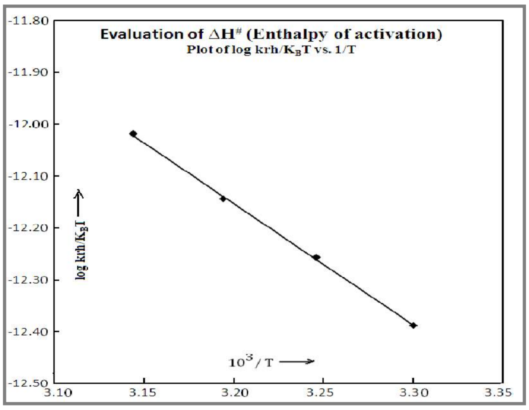


Figure 11. Evaluation of ΔH.

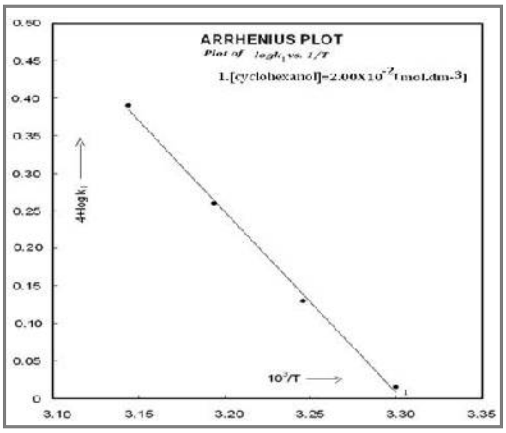


Figure 12. Arrhenius plot.

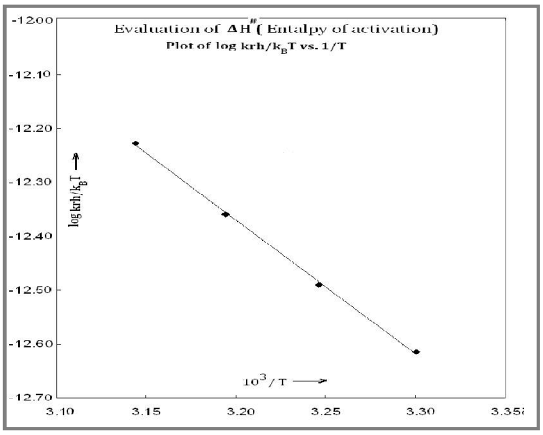


Figure 13. Evaluation of ΔH

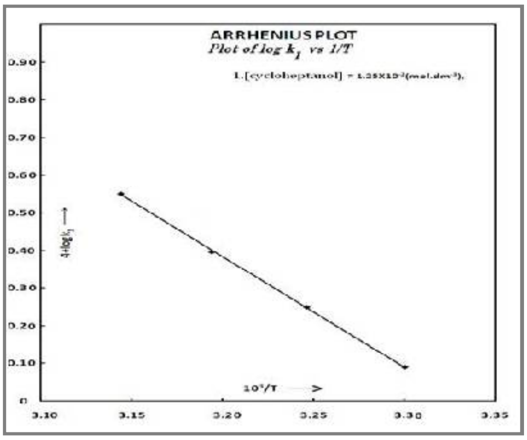


Figure 14. Arrhenius plot.

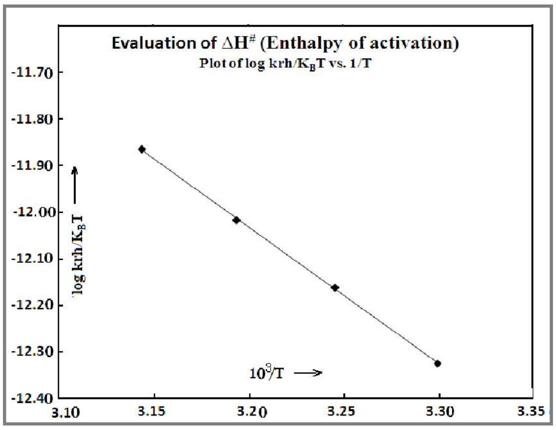
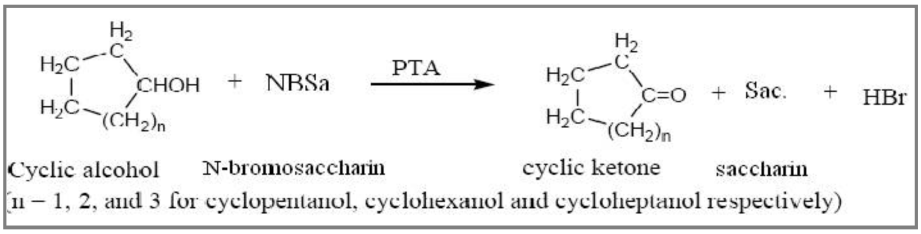


Figure 15. Evaluation of ΔH

Thermodynamic Parameters Various activation parameters namely temperature coefficient, energy of activation, frequency factor, free energy, enthalpy of activation and entropy of activation for each reaction are calculated. The Arrhenius plot had drawn between log k1 vs. the reciprocal of absolute temperature. The value of energy of activation (Ea) is calculated from the slope of Arrhenius plot. The frequency factor (A) is calculated using graphical value of Ea. The enthalpy of activation (ΔH#) is evaluated from the slope of the plot between the krh / kBT and 1/T. Where, kr is specific rate constant. The value of free energy of activation (ΔG#) and entropy of activation (ΔS#) is calculated by using Erying equation. These parameters are summarized in the (figure 10-15). Stoichiometry and Product Analysis The stoichiometry of the reaction of oxidation of cyclic alcohols (viz. cyclopentanol, cyclohexanol and cycloheptanol) by NBSa in presence of phosphotungstic acid, in aqueous-acetic acid medium was determined in duplicate at their experimental temperature by following procedure. In stoichiometric determination, the experiments were planned and designed in which the oxidant concentration was in excess (Δ10 times) over the concentration of substrate. The binary composition of H_2O and CH_3COOH were taken similar to their respective runs. The calculation volume of the reactants were mixed and maintained in a thermostat at the experimental condition of temperature, for sufficient time that is until there is no change in NBSa concentration. The NBSa un-reacted in each reaction mixture is, then estimated separately, periodically by titrating a definite volume of the reaction mixture iodometrically. Thus, the quantity of NBSa used up to oxidize a definite quantity of each cyclic alcohol completely is calculated. From these stoichiometric data, it is found that for complete oxidation of one mole of each cyclic alcohol, one mole of NBSa is required. The stoichiometric equations empirically can therefore, be represented as:



(n = 1, 2, and 3 for cyclopentanol, cyclohexanol and cycloheptanol respectively)

Product Analysis the final oxidation products of the reactions, under investigation were qualitatively identified by existing conventional methods. Test of free radicals the reactions of cyclic alcohol with NBSa showed an induction period. 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. Identification of oxidation main end-products A 0.25 M solution of 2, 4-dinitrophenylhydrazine, may be used for the preparation of derivatives of keto compounds. Dissolve 25 g of 2, 4-dintrophenylhydrazine in 300 mL of 85 % perchloric acid in a 600 mL beaker on a stream bath , dilute the solution with 200ml 95% ethanol , allow to stand and filter through a sintered glass funnel . it must be emphasized that this reagent is not suitable for the routine detection of carbonyl compounds since it also gives a precipitate in cold with certain amine, esters, and other compounds; if, however, a dilute solution of the ketonic compound in ethyl alcohol is treated with a few drops of the reagent and mixture diluted with water and heated, the precipitate produced with ketonic compounds generally not dissolves. Collect the crystals of 2, 4-dinitrophenylhydrazone of cyclic ketones and re-crystallized again wash, dried it, and then determine the melting points. Test for saccharin, reduction product of NBSa the 50 mL of reaction mixture (Test solution) was treated with few drops of concentrated H_2SO_4 followed by addition of 0.30 g. of resorcinol. On warming, the colors of the solution turn dark green which disappeared on subsequently cooling. The green fluorescence re-appeared on making alkaline of NaOH solution which confirms the presence of saccharin.

CONCLUSION

The present proposed study envisaged with the kinetics of reactions involving the redox system. NBSA is an effective and economically cheap oxidant to syntheses easily in laboratory and also available in market. The N-Bromosaccharin can be successfully exploited as an input technology. The psycho-economic activity of this oxidant is limited and scanty need to be explored widely. The >N-Br bond undergoes heterolytic fission in polar medium producing brominium (Br^+) ion , a mild oxidant than chloronium ion (Cl^+) ion , observed that NBSA could be successfully used as both an oxidizing agent as well as bromination for allylic and benzylic substances. In presence of mineral acids like perchloric and sulphuric acids the HOBr, protonated NBSA (NBSA H+) & H_20+Br may exist as oxidant species, one cannot ignore the existence of acetate complexes in acetic acid medium as CH_3COOBr and $CH_3CO.O$+HBr.While cyclic alcohols are actually saturated cyclic hydroxy alcohols in which hydroxy group is attached through carbon atom of different size of ring, exhibit a variety of chemical reactions. The study of such reactions is of great significance and the interest because of its vast implication in understanding the nature of chemical processes involve. Although the kinetics and mechanism of oxidation of cyclic alcohols with NBSA has been received much attention and attracted to chemists in several laboratories. The current survey of literature reveals that similar studies on the mechanism of phosphotungustic acid catalyzed oxidation of cyclic alcohols with NBSA is lacking till date; this inspired me to probe into this task of investigation of oxidation reaction mechanism in acetic acid –water medium.

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