SciencePG
Science Publishing Group

Kinetic and Thermodynamic Studies of the Oxidation of Xylose in the Presence and Absence of Catalysts by Peroxdisuphate

Mawia Hassan Elsaim[1, 2, *], Jubrallah Elhaj[3], Ibrahim Mukhta[4]

[1]Department of Chemistry, Faculty of Science and Technology, Merowe University of Technology, Merowe, Sudan

[2]Department of Chemistry, College of Science, Beijing University of Chemical Technology, Beijing, China

[3]Department of Chemistry, Faculty of Education, Dalanj University, Dalanj, Sudan

[4]Department of Chemistry, Faculty of Education, University of Khartoum, Khartoum, Sudan

Email address:
Maelsaimhu7@gmail.com (M. H. Elsaim), maelsaimhu@yahoo.com (M. H. Elsaim)
[*]Corresponding author

Abstract: Sugars containing either aldehyde (aldose), ketone (ketose) or hemiacetal groups can be oxidized and are classified as reducing sugars. As oxidation of carbohydrates is widely studied under the field of organic chemistry, the present work deals with the study of the redox reactions between peroxodisulphate and xylose underuncatalyzed and catalyzed conditions. The kinetic study of the above reactions showed that these reactions followed first order with respect to peroxodisulphate and the silver nitrate ion catalyst and a fractional order of (0.2) with respect to xylose. Ag catalyst was used to increase the rate of reaction in case of xylose where reactions proceed very slowly with respect to time as compared to other sugars used. The oxidation showed that configuration of sugars has some bearing on rate of oxidation. At lower concentration of oxidants, the linear dependence of reaction rate tends towards new order at their higher concentration. The rate of reaction was affected at elevated temperature where thermodynamic activation parameters like activation energy (Ea), enthalpy change of activation ($\Delta H\#$), free energy change of activation ($\Delta G\#$) and entropy change of activation ($\Delta S\#$) were determined by Arrhenius and Erying equations. The analysis of the reaction products using IR revealed the presence of formaldehyde and formic acid. A mechanism of the reactions was proposed to explain the experimentally observed rate law and the products.

Keywords: Oxidation, Kinetic, Xylose, Peroxodisulphate

1. Introduction

Chemical kinetics is a branch of chemistry, which studies the rate of reaction whereby various chemical reactions take place in different conditions. Kinetics takes into consideration the time required for transformation of reactants from one state to another. Some reactions take place rapidly within fraction of seconds while some are extremely slow like rusting of iron. Reactions, which take reasonable time for completion, can be studied conveniently by suitable methods. Kinetics is concerned with series of all physical and chemical processes, which comes during the course of chemical reactions [1-3]. Several researchers had made

pioneering work in chemical kinetics. Kinetic study covers the effect of concentration, temperature and pressure on different types of reactions. Based on the type of reaction wide.

Variety of experimental techniques had been used to investigate. Kinetics is useful in study of gas, liquid and solid phase reactions. Especially liquid phase reactions are studied the most due to higher interest of organic and inorganic chemists particularly engineers from industries [4-5]. Various factors such as concentration, catalyst, dielectric constant, salt, ionic strength, temperature and free radicals [6] were accounted by different researchers. Potassium hexacyanoferrate (III) was used for reading palimpsests and old manuscripts in nineteenth century. The compound has

widespread use in blueprint drawing and in photography (Cyanotype process). Iron and copper toning involve the use of potassium ferricyanide. Potassium ferricyanide is used as an oxidizing agent to remove silver from negatives and positives, a process called dot etching. In color photography, potassium ferricyanide is used to reduce the size of color dots without reducing their number, as a kind of manual color correction. The compound is also used to harden iron and steel, in electroplating, dyeing wool, as a laboratory reagent and as a mild oxidizing agent in organic chemistry. It is used in black and white photography with sodium thiosulfate (hypo) to reduce the density of a negative or gelatin silver print where the mixture is known as farmer's reducer; this can help offset problems from over exposure of the negative or brighten the highlights in the print. Potassium ferricyanide is also one of two compounds present in ferroxyl indicator solution (along with phenolphthalein) which turns blue (Prussian blue) in the presence of Fe^{2+} ions and which can therefore be used to detect metal oxidation that will lead to rust. It is possible to calculate the number of moles of Fe^{2+} ions by using a colorimeter because of the very intense prussian blue color of $Fe^4[Fe(CN)_6]^3$. Potassium ferricyanide is often used in physiology experiments as a means of increasing a solution's redox potential (E°'~ 436 mV at pH7). As such it can oxidize reduced cytochrome C (E° ~ 247 mV at pH 7) in intact isolated mitochondria. Sodium dithionite is usually used as a reducing chemical in such experiments (E°' ~ −420 mV at pH 7). Potassium ferricyanide is used in many amperometric biosensors as an electron transfer agent replacing an enzyme's natural electron transfer agent such as oxygen with the enzyme glucose oxidase. It is used as ingredient in many commercially available blood glucose meters for diabetics use. Potassium ferricyanide is combined with potassium hydroxide (or sodium hydroxide as a substitute) and water to formulate [7]. Therefore, we have chosen to study the oxidation of xylose in presence of light. The present work deals the redox reaction of peroxodisulphate with xylose was studied from the following viewpoints:- To establish the rate laws for the reaction between $[S_2O_8^{-2}]$ and xylose, to study the effect of temperature and to evaluate the thermodynamic Parameters, to investigate the effect of catalyst and surface and analyze the reaction products.

2. Martial and Methods

2.1. Kinetic Measurements

Was found that the reactions between $[S_2O_8^{-2}]$ and xylose at ordinary temperature were slow unless a catalyst was present [11]. The suitable measurable rate of the redox reaction was carried out at 70°C, Thus for a reason the temperature range of (60-80°C) was chosen. The aim of carrying-out the kinetic measurements was to establish an appropriate rate law for the reactions investigated. This required a set of runs to be carried out in which the concentration of one of the two reactants was changed while keeping the concentration of the other constant.

2.2. Preparation of Solutions

The redox reactions of peroxodisulphate with organic compounds required the use of double distilled water, because it is highly susceptible to impurities in solution and often leads to erratic values. Double distilled water was obtained by redistilling water over alkaline potassium permanganate in Pyrex glass. Solutions used in the work were prepared in the following manner: Potassium peroxodisulphate 6.76 gms of $K_2S_2O_8$ was dissolved in 250 cm^3 of double distilled water to get 0.10 mol dm^{-3} solution. The solutions were always freshly prepared fresh and never used after more than 48hours from the time of preparation. These solutions were, kept at room temperature (30-40°C) in the dark. 3.83 gms required weight of xylose was dissolved in 250 cm^3 of distilled water to give a molar solution. A 0.01 molar of sodium thiosulphate solution was prepared by dissolving 2.84g of $Na_2S_2O_3.5H_2O$ (B. D. H) in 1000 of distilled water, it was then standardized against standard solution of $K_2S_2O_8$ and kept for 4-5 days as stock solution. 20 gms of Potassium iodide was dissolved in 100 cm^3 of distilled water to get 20% freshly prepared solution. A 0.10 M of sodium bicarbonate solution was prepared by dissolving 4.20 gms of $NaHCO_3$ (BDH) in 500 cm^3 of distilled water. A 0.50 molar of sulphuric acid solution was prepared by dissolving 1 cm^3 of H_2SO_4 (BDH) in 35 cm^3 of distilled water. 0.17 gms of $AgNO_3$ (BDH) was dissolved in 100 cm^3 of double distilled water to get 0.01 M of silver nitrate solution. 1 gms of soluble starch was dissolved in 30 cm^3 distilled water and heated. This is used as an indicator. BDH Laboratory reagent 10gms of 2,4-dinitrophenylhydrazine were dissolved in 30 cm^3 of double distilled water. 5 cm^3 methanol and 10 cm^3 of concentrated sulphuric acid were, added to obtain a complete solution.

2.3. Estimation of Peroxodisulphate

A 50 cm^3 of the substrate and 50 cm^3 of the peroxodisulphate solutions were placed in the thermostat for about 20 minutes. These solutions were transferred to the 250 cm^3 round bottom flask. The residual peroxodisulphate was estimated by an iodometric method which was modified [8, 9]. A 5 cm^3 of the reaction mixture containing the residual peroxodisulphate was added to 250 cm^3 conical flask containing a solution mixture of: 5 cm^3 of sodium bicarbonate solution. 1 cm^3 of sulphuric acid solution and 5 cm^3 of 20% potassium iodide solution. Then it was placed in the dark for 20 minutes until all iodine was liberated. After that, drops of starch were added and the liberated iodine was titrated against standard thiosulphate solution [12].

2.4. Investigation of the Reaction Products

Known weights of potassium peroxodisulphate were, allowed to react with equal weights of the substrates at 70°C. The reaction mixture was left under reflux conditions for five days. The reaction mixture was then taken and subjected to

fractional separation of the products. A volatile fraction collected by distillation over the temperature range 97-105°C. This fraction was collected in a tube closed with rubber and placed in an ice bath. Due to volatility of the product. The analysis by IR confirmed formaldehyde and Formic acid. The presence of formaldehyde and formic acid was further confirmed as follow: Formaldehyde, its 2, 4-dinitrophenylhydrazone derivative was prepared by adding 2,4-dinitrophenylhydrazine to the fraction of distillate which was recrystallized from ethanol to give a m. p. 166-167°C.

3. Results and Discussion

3.1. Kinetic Order with Respect to Peroxodisulphate

Table 1 show the data of the experiments in which the concentration of peroxodisulphate was varied from 15×10^{-3} to 40×10^{-3} M and the concentration of xylose $HO-CH_2-(CH-OH)_3-CH-OH$ is kept constant at 20×10^{-3} M at 70°C. These experiments were carried out in duplicates. In each experiment, the observed rate law (R) was calculated in the manner outlined from titer value. While, the integrated rate law and means calculated the observed rate constant (k_0) value are obtained. figure 1 represents the plot of the rate average against peroxodisulphate concentration. It is observed that R varies linearly with the $[S_2O_8^{2-}]$. From the plot of figure 1 equation 1 is obtained: $R=k_0[S_2O_8^{2-}]$ value of $k_0=1.10 \times 10-4$ s^{-1} was obtained from the slope of figure 1. In which k_0 was independent of $[S_2O_8^{2-}]$.

Table 1. *Variation of R vs $[S_2O_8^{2-}]$.*

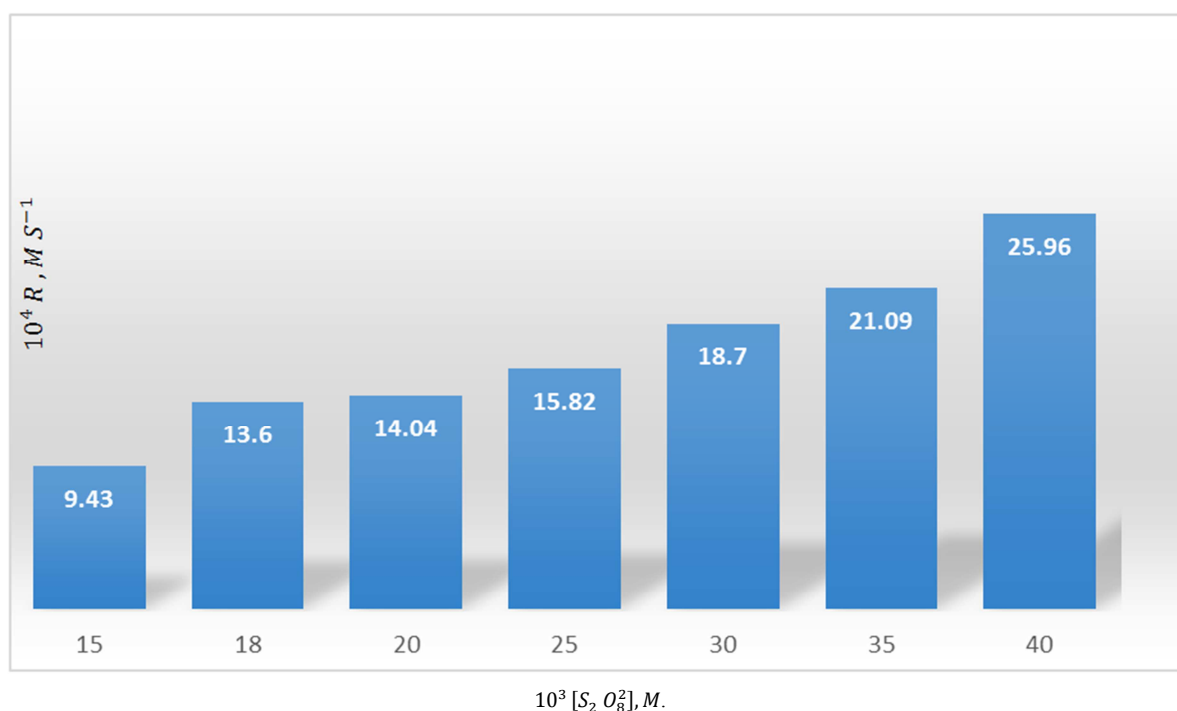| $[S_2O_8]^{2-}$M$\times 10^{-3}$	15.0	18.0	20.0	25.0	30.0	35.0	40.0
R$\times 10^4$ MS^{-1}	09.43	13.60	14.04	15.82	18.70	21.09	25.96
$K_0 \times 10^4$S^{-1}	1.33	1.20	1.10	1.02	1.00	1.04	1.00

Xylose=20×10^3M Temp=70°C.

Figure 1. *Plot of R VS $[S_2O_8]^2$.*

3.2. Kinetic Order with Respect to Xylose

In a second set of kinetic runs, xylose–peroxodisulphate reaction was studied at a constant concentration of peroxodisulphate=20×10^{-3}M, and varying the concentration of xylose -$C_5H_{10}O_5$- from 2.5×10^{-3} to 25×10^{-3} M at 70°C. The

rates and the rate constant were calculated in the manner out lined table 2 and figure 2 shows the plot of the mean rates against the concentration of xylose and indicates that the order with respect to xylose was 0.2.

Table 2. *Variation of R vs xylose.*

$[S_2O_8]^{2-}$M$\times 10^{-3}$	2.5	5.0	8.0	10.0	15.0	20.0	25.0
R$\times 10^4$ MS^{-1}	14.11	14.13	14.07	14.01	14.09	14.04	14.07
$K_0 \times 10^4$S^{-1}	1.14	1.13	1.06	1.04	1.28	1.06	1.11

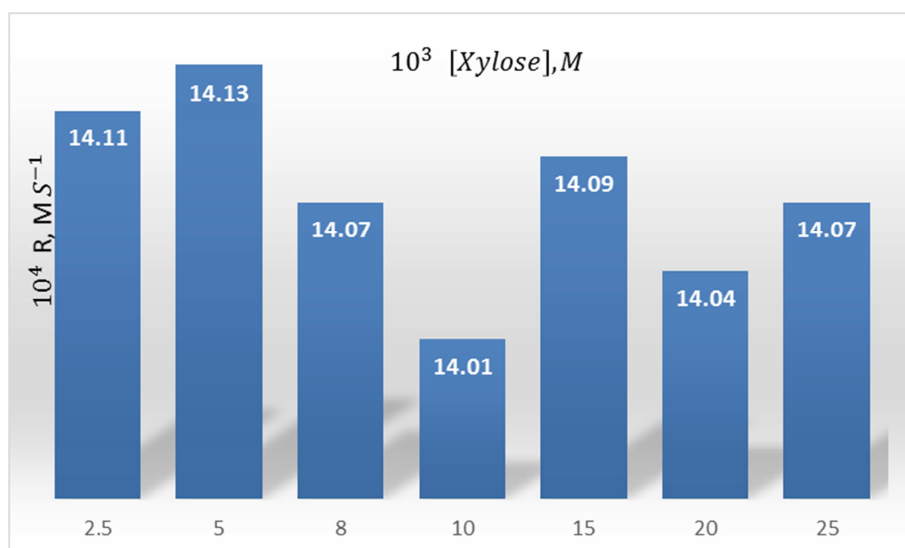$[S_2O_8^{2-}]$=20×10^3M Temp=70°C.

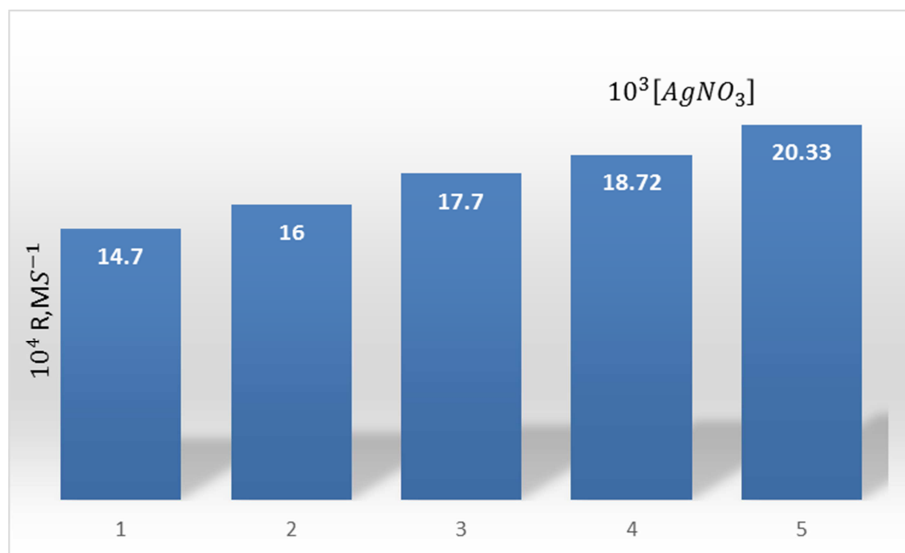***Figure 2.*** *Plot of R VS Xylose.*

3.3. Kinetic Order with Respect to Silver Nitrate

Table 3 and figure 3 show order dependence of the average rate on Ag(I) concentration when it is varied between 10×10^{-3} to 50×10^{-3} M at 70°C, while keeping peroxodisulphate and xylose concentration constant at 20×10^{-3} M. The average rate

observed first order rate constant can be expressed as: $R = k_0[Ag^+]$. This indicates that the reaction follows first order in Ag^+, and the k_0 values increase linearly with increasing of the silver concentrations figure 3.

Table 3. *Variation of R vs [AgNO₃].*

$[S_2O_8]^{2-}M \times 10^{-3}$	1	2	3	4	5
$R \times 10^4$ MS^{-1}	14.70	16.00	17.70	18.72	20.33
$K_0 \times 10^4 S^{-1}$	1.02	1.11	1.52	1.80	1.81

$[S_2O_8^{2-}] = 20 \times 10^3$ M xylose 20×10^3 M Temp=70°C.

Figure 3. *Plot of R Vs [AgNO₃].*

3.4. Effect of Temperature

The reaction was studied over temperature range 60–80°C at concentration of $[S_2O_8^{2-}] = 20 \times 10^{-3}$ M and xylose concentration=20×10^{-3} M. The value of R and k_0 at these temperatures were obtained. Their value together with the

mean ones are given in tables 4. By using Arrhenius equation and from the slope and intercept of the line with y-axis in figure 4 the energy change of activation $\Delta Ea^{\#}$ and frequency factor A were calculated. These values were further used to calculate the entropy change of activation $\Delta S^{\#}$ and free energy of activation $\Delta G^{\#}$ for the reaction by using the

equation. The results are summarized in table 4. $k = A\ e^{-\Delta E/RT}$

$\Delta G^{\#} = \Delta E^{\#} - T\Delta S^{\#}$

$-\Delta E^{\#} = 2.303 \times slope \times 8.3\ Joule$

Table 4. Summary of Effect of Temperature.

T °C	t ^{0}K	1\T 10^3 K	$K_0 \times 10^4$	Logk_0	5+logk_0	T °C
60	333	3.00	0.85	-4.07	0.93	
65	338	2.96	0.92	-4.04	0.96	
70	343	2.92	1.06	-3.97	0.03	
75	348	2.87	1.35	-3.87	1.13	
80	353	2.83	1.76	-3.75	1.25	

Table 5. Thermodynamic parameters of activation of k_0 path.

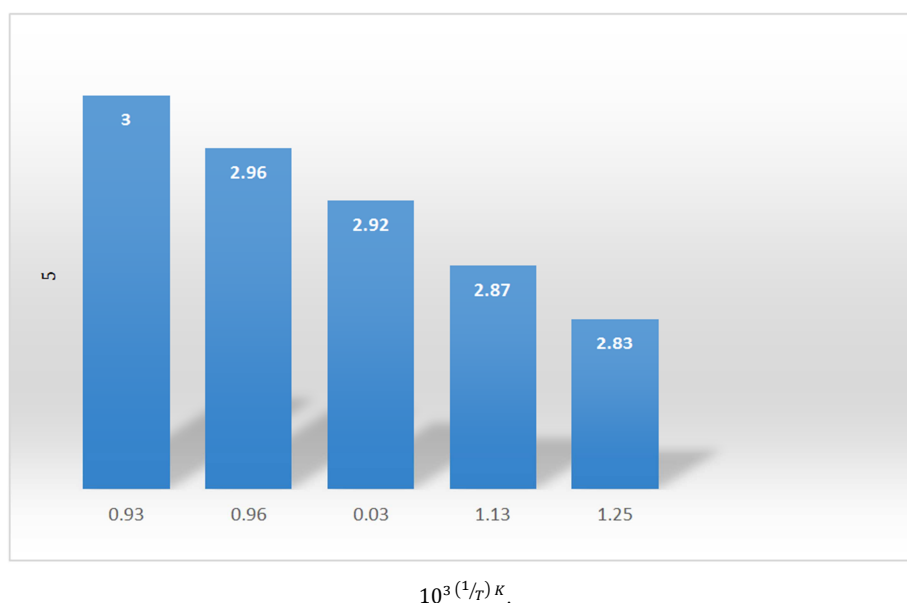| $\Delta Ea^{\#}$, kJ mol-1	A, M s^{-1}	$\Delta S^{\#}$, J/K	$G^{\#}$, kJ mol^{-1}
40.29	1.49×10^{-2}	282.52	56.61

Figure 4. Plot of log K VS 1\T.

3.5. Effect of Surface

To the reaction mixture containing peroxodisulphate concentration=xylose concentration=20×10^{-3}M at 70°C different surfaces (glass rods and cotton wool) were added and their effect on the reaction was studied. The results are shown in table 6. The surface effect shows that there is small effect on the reaction rates.

Table 6. Effect of Surface.

Surface added	Weight (g)	$R \times 10^4$, M s^{-1}	$k_0 \times 10^4$, s^{-1}
No surface	--------	14.04	1.06
Glass rod	6.0	15.98	1.18
Cotton wool	1.0	16.32	1.43

4. Conclusion

The present study deals with a systematic study of the redox reaction of peroxodisulphate with xylose under uncatalyzed condition over temperature range 60-80°C and in the presence of Ag(I) as a catalyst at 70°C. It is well known that peroxodisulphate decomposes thermally in the absence of reducing substance, therefor there are two main paths for the reaction:- Path(1): represents the thermal decomposition of peroxodisulphate. Path(II) represents the bimolecular reaction of peroxodisulphate with reducing substrate. In the present work, no attempt was made to estimate the extent of path (I) and path (II). Two main aspects of the study were involved. (a) A kinetic study (b) An investigation of the product of the reaction. They were all found to have fractional (0.2) order in substrate and first order with respect to peroxodisulphate concentration. The kinetic study of oxidation of xylose by peroxodisulphate showed that these reactions followed 0.2 order in xylose and first order in peroxodisulphate and the catalyst Ag(I).

The variation of the observed first order rate constant with temperature was studied over the range 60-80°C, from the value of K_0 at different temperatures, the energy of activation $Ea^{\#}$, the frequency factor A, the entropy of activation $\Delta S^{\#}$ and free energy of activation $\Delta G^{\#}$ were evaluated for all the reactions under study. The reactions were studied in the presence of surface (cotton wool and glass rods) and found to be sensitive to these surfaces which indicates its radical

character.

References

[1]   Finar L. L., Organic Chemistry Vol. 1: The Fundamental Principles, Sixth Edition (1973).

[2]   Brand Hans, Brand Elzbieta, Goliath Buissness Knowledge on Demand (2002).

[3]   Singh M. P., Singh H. S., Tiwari S. C., Gupta K. C., Singh A. K., Singh V. P. and Singh R. K., (1975). Oxidation of D-glucose, D-xylose, D-fructose, L-arabinose and L- sorbose by ammoniacal silver nitrate, *Ind. J. of Chem.* 13, 819-22.

[4]   Prashanth P. A., Mantelingu K., Anandamurthy A. S., Anitha N., Rangaswamy and Rangappa K. S., (2001). Kinetics and mechanism of oxidation of hexoses by bromamine-T in alkaline medium, *J. Ind. Chem. Soc.*, 78.

[5]   Chandrashekar, Venkatesha B. M. and Ananda S., (2012). Kinetics of Oxidation of Vitamin-B_3 (Niacin) by Sodium N-bromo benzenesulphonamide (Bromamine-B) in HCl Medium and Catalysis by Rum (III) ion, *Res. J. chem. sci.,* 2 (8), 26-30.

[6]   Sarasan Geetha and Pathak Namrata, (2014). Effect of Acetic Acid on Chlorination of some Phenols by Chloramine-T: A Kinetic Approach, *Res. J. chem. sci.,* 4 (3), 86-89.

[7]   Johnson, R. L., Tratnyek, P. G. and Johnson, R. O. (2008). Persulfate persistence under thermal activation conditions", Environ. Sci. Technol., 42 (24), 9350-9356.

[8]   Huie, R. E. and Neta, P. (1984). Chemical behavior of SO_3- and SO_5- radicals in aqueous solutions", *J. Phys. Chem.*, 88 (23), 5665-5669.

[9]   Deepa D. and Chandramohan G., (2012). Kinetic and Mechanistic Study on the Oxidation of Indole-3-Propionic Acid in Acetic Acid Medium *Res. J. Chem. Sci.,* 2 (10), 70-74.

[10] Ghosh Manoj Kumar and Rajput Surendra K., (2012) Unanalyzed Oxidation of Dextrose by Cerium (IV) in Aqueous Acidic Medium-A Kinetic and Mechanistic Study, *Res. J. Chem. Sci.,* 2 (11), 55-60.

[11] Junlian Qiao, Liying Feng, Hongyu Dong, Zhiwei Zhao, Xiaohong Guan. Overlooked Role of Sulfur-Centered Radicals During Bromate Reduction by Sulfite. Environmental Science & Technology 2019, 53 (17), 10320-10328. DOI: 10.1021/acs.est.9b01783.

[12] Rama Rao. K, Rambabu. R, Raghu Babu. K. International Journal of Innovative Research in Science Engineering and Technology Vol 2, Issue 11, 2013. Titrimetric estimation of ascorbic acid, hydrazine, sodium sulphite, thiosulphate and vanadium (II) with chloramine-Tas an acidimetric reagent in EDTA medium.