Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 1(2)
Science and Research Campus
ISSN: 1735-2126

Investigation kinetic oxidation of PS by $K_2S_2O_8$ and $AgNO_3$ catalyst

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ABSTRACT

In this research oxidation kinetic panceuo.s (P.S) by $S_2O_8^{-2}$ at the presence of $AgNO_3$ as catalyst was studied.The method was spectrophotometer following absorption spectrum (P.S) in wave length of 518 nm. After improving the condition such as PH, P.S concentration, $K_2S_2O_8$ concentration, ionic strength, temperature, rate constant, activation energy, constant frequency, order reaction and thermo dynamical values as $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ for catalyst and non catalyst were determined.The results show that oxidation rate P.S by means of $S_2O_8^{-2}$ would be increased by the addition of $AgNO_3$ and silver ion would function as a positive catalyst in this reaction.

INTRODUCTION

The subject of chemical kinetics is concerned with the quantitative study of the rates of chemical reactions and of the factors upon which they depend. The first kinetic measurements, however, may be said to have been those of Wilhelmy, who in 1850 measured the rate of inversion of sucrose important result at which he arrived was that the rate of reaction at any instant was proportional to the concentration of sucrose remaining at that time[1-3].

A similar conclusion was reached in 1862 by Berthelot and St .Gilles [4]; their investigation concerned mainly the equilibrium between ethanol, acetic acid, ethyl acetate, and water, but they obtained some data on the rate of combination of the acid and alchol and concluded that the rate in this case was proportional to the product of the two concentrations. In the years 1865 to 1867 Harcourt and Esson [5] published the results of their investigations on the reaction between potassium permanganate and oxalic acid

The subject of chemical kinetics covers a very wide range. It includes empirical studies of the effects of concentration, temperature, and hydrostatic pressure on reactions of various type; such studies may be of practical value in connection with technical processes [6-7]. In the differential method, which was suggested by Vant Hoff [8], one deals with the actual rates of reactions as determined by measuring the slopes of concentration – time curves. The rate of a reaction may be related to the concentration of a reactant by the equation $\upsilon=kc^n$. Taking either Common or natural Logarithms, $\log \upsilon = \log k + n \log c$. If, therefore, the velocity is measured at various values of the reactant concentration, a double – logarithmic plot of the velocity against the concentration may give a straight line. If so, the slope is the order of the reaction with respect to the substance whose concentration is being varied, and the intercept on the $\log \upsilon$ axis is equal to $\log k$. By the early part of the last century there had been discover a number of reactions whose rates were influenced by the presence of a substance that remained unchanged at the end of the process .These reactions include the conversion of starch into sugars, the rate of which was influenced acids; the decomposition of alchols and of hydrogen peroxide, influenced by metallic surfaces; and the formation of ammonia in the presence of spongy platinum. Such reactions were classified by Berzelius [9] in 1836 under the collective title of catalyzed processes and were regarded by him as taking place under the influence of a catalytic force [10 – 15]. This research studies rate dependency with factors such as concentration, temperature, catalyst, ionic strength and PH effect and tries to single out the role of each on the above mentioned factors in the rate of reaction .Different methods are used in kinetic studies and also to determine thermodynamic constant which their selection are based on the type of the reaction, such as spectroscopy, NMR, IR, Raman and electrochemical.

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EXPERIMENTAL METHOD

1. Procedure:

In this research sample and blank solutions were used to study kinetic quantities. Different volumes of $K_2S_2O_8$ and Ag NO_3 were added to 10 ml flask by means of numbered pipets 0.5 to 5 ml

The volume of the solution was diluted 7 to 8 ml by means of pure water, than 1 ml of P.S was added to the flask. The timer started working as the last drop of P.S fell down; the volume was 10 ml through the use of pure water.

We stirred it. Some of the resulted liquid was put in to spectrophotometer cell and the absorption change was recorded in 518nm wave length in a time interval between 30 to 300 seconds after the starting point of the reaction. To prepare the blank solution the same method and materials were used by Ag NO_3 was not added to the solution. All the needed containers and solution were bathed for half and hour with the same temperature to achieve temperature equilibrium.

2. The study of parameters and improvement of the conditions.

The parameters used to improve the conditions of the above mentioned reaction are the followings; PH effect, P.S concentration, $K_2S_2O_8$ concentration, ionic power and temperature

A single agent method was used to study the above mentioned parameters, all the other parameters were constant and the only parameter which was to be improved was changed. To improve concentration parameters, different volumes of the intended material were added to the solution and to keep the volume constant (10ml) the amount of pure water was changed

3. Absorption spectrum P.S solution:

P.S solution in wave length 518nm had the highest absorption (λ_{max}=518nm).The reaction of P.S solution with $K_2S_2O_8$ solution is noticeable; there for the absorption changes are low, but the absorption rate severaly decreases whenever Ag^+ is added and the rate of reaction is increased.

4-The effect of PH:

The PH effect on the absorption changes of sample and blank solutions were studied using buffers made from PH=2 to PH=7

For the production of sample solution , 0.5 ml of the intended buffer solution and 5 ml of $K_2S_2O_8$ 0.04 molar and 1 ml of $AgNo_3$ 100ppm were add to a 10 ml flask , then the solution was diluted to the 8 ml volume by means of pure water after that 1 ml of P.S 2.62×10^{-4} molar ,was added exactly at the time when the last drop of P.S fell down , chronometer was switched on the volume of flask was increased to 10 ml by means of pure water , the solution was stirred ,some of it was transfered to cell and the sample solution absorption changes in the time interval between 30 to 300 seconds were read. The blank solution which locked silver nitrate was produced in the same way and its absorption changes were measured

The PH changes have no important effect on absorption changes in the above mentioned reaction .So the reaction was done with of buffer later on. It is necessary to mention that PH more than 7 was not studied because of silver hydroxide deposit

5- The effect of concentration P.S

For the production of sample solution 5 ml of $K_2S_2O_8$ 0.04 molar and 1 ml of Ag NO_3 500 ppm were added to a 10 ml flask and the solution was diluted to 7 ml volume the different volume of P.S were added to the solution

The result of this study shows that an increase in the concentration of P.S from 1.3×10^{-6} to 1.3×10^{-5} molar results in the increase in the sample solution absorption changes and the absorption changes go Ir respective of P.S concentration later on. In the blank solution approximate absorption changes were seen by means of the increase of concentration. The concentration of 3.9×10^{-5} was selected to continue the study

6 -The ionic strength effect:

NaCl (3 molar) was used to study ionic strength in the improved condition of solutions concentration and also $AgNO_3$ 500 ppm. To prepare sample solution 4.5 ml of $K_2S_2O_8$ 0.04 molar and 1 ml of $AgNO_3$ 500 ppm and different volumes of sodium nitrate 3 molar were added to a 10 ml flask. The results shows that an increase in the amount of ionic strength decrease in the sample solutions absorption change and the blank solutions absorption changes are independent from ionic strength

7 - Improved conditions and suggested methods:

The mentioned studies showed that the most appropriate condition for the reaction of oxidation of P.S by $K_2S_2O_8$ at the presence of $AgNO_3$ catalyst in $K_2S_2O_8$, 0.18 mol and P.S 3.9×10^{-5} and the time of reaction is 300 seconds at the temperature of 40^0C, the selected wave length for the absorption rate of the solution was 518nm

8 – Determining the order reaction.

To determine the order of reaction to the other types, the concentration of all the other types remain constant except the concentration of the intended type, so we have (X+Y+Z+… $\rightarrow$ …) for the reaction:

$Rate = K[X]^m[Y]^n[Z]^p\ldots\ldots$

If we take Ln from the two sides of the equation:

$Ln\ R = Ln\ k + m\ Ln[X] + n\ Ln[Y] + p\ Ln\ [Z] + \ldots$

If for example we want to determine the order of compound X, the other part of the equation is a constant quantity and as the rate of reaction is based on absorption changes, we have

$Ln\ \Delta A = m\ Ln\ x + \text{const}$

Therefore the slope of the curve $Ln\Delta A$ based on $Ln\ [x]$ is equal to the order of the reaction

9 – Determining the order of reaction P.S

9-1: In non catalyst reaction calculate the order of reaction P.S we have:

$$P.S+S_2O_8^{2-} \xrightarrow{K} prod.$$
$$R=K\,[P.S]^{m}\,[S_2O_8^{2-}]^{n}$$
$$Ln\,R= Ln\,K+ m\,Ln\,[P.S] + n\,Ln\,[S_2O_8^{2-}]$$
$$Ln\,A= m\,Ln\,[P.S] +const$$

9-2: In catalyst reaction

The results of the experiment are presented in table1 and figure1 . In catalyst environment the order of P.S was determined as following

$$P.S+S_2O_8^{-2} +Ag^{+} \xrightarrow{k} prod.$$
$$R = k\,[P.S]^{m'}\,[S_2O_8]^{n'}\,[Ag^{+}]^{p'}$$
$$Ln\,R= Ln\,K+ m'\,Ln\,[P.S] +n'\,Ln\,[S_2O_8^{2-}] +p'Ln\,[Ag^{+}]$$
$$Ln\,\Delta A= m'\,Ln\,[P.S] +const$$

Considering the figure m'= 0.97 was achieved.

Table 1. Determination of order reaction P.S by catalyst and non catalyst solutions

[P.S]	Ln[P.S]	ΔA(blank)	LnΔA(blank)	ΔA(sample)	LnΔA(sample)
5.91×10^{-5}	-9.73	0.049	-3.01	1.15	0.139
4.93×10^{-5}	-9.91	0.045	-3.1	0.79	-0.23
3.94×10^{-5}	-10.14	0.032	-3.44	0.72	-0.328
2.95×10^{-5}	-10.43	0.021	-3.85	0.56	-0.579
1.97×10^{-5}	-10.83	0.018	-3.97	0.35	-1.049
0.98×10^{-5}	-11.3	0.009	-4.71	0.19	-1.66

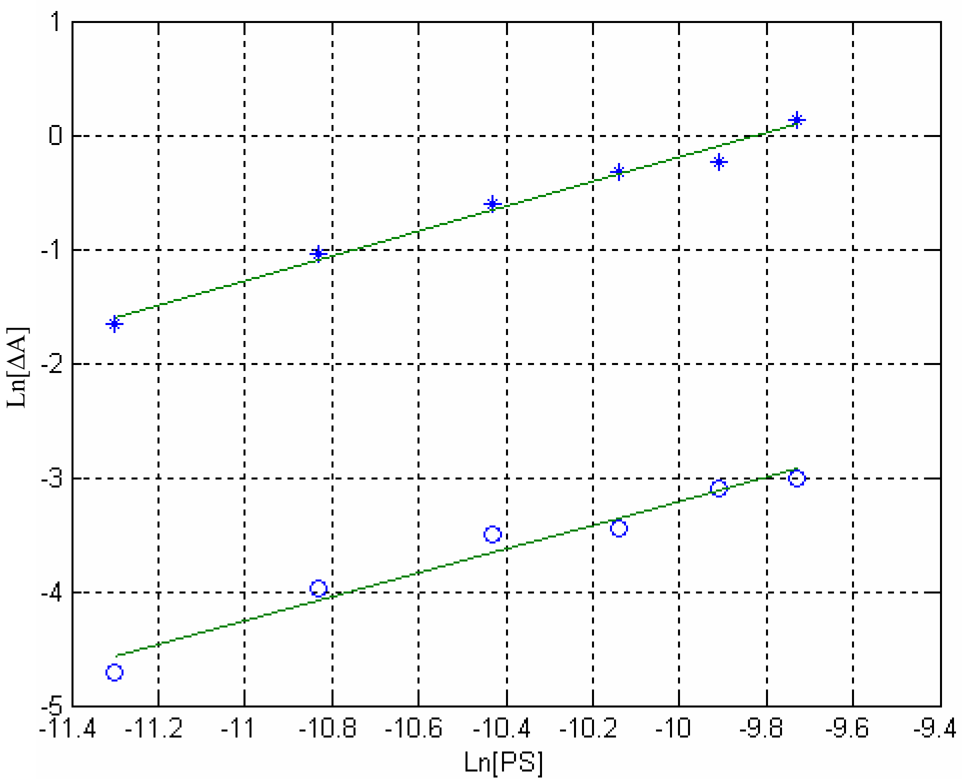

Fig. 1. ln ΔA versus ln[PS]
: catalyst reaction
: Non catalyst reaction
Condition : $[k_2S_2O_8]$=0.018 ,T=40 Ċ

RESULTS AND DISCUSSION

In the first experimental part , the good was achieving improved conditions and concentrations including; The PH effect, $S_2O_8^{2-}$ concentrations in order to increase the precission, so in determination of improved concentrations, all the other types concentrations remained constant and just the intended type concentration was changed therefore a proper concentration for each type was achieved

In determination of reactions proper temperature, a temperature which had the maximum absorption changes of catalyst and non catalysts solution was selected. As it could be understood that the absorption changes of catalyst and non catalyst solution increases with the increase in the amount of temperature.In non catalyst solution, the absorption change is very minute to the 40 ^{0}C (the rate is slow) so a temperature lower than40 ^{0}C is not a proper temperature for non catalyst reaction. As temperature increased above 40 ^{0}C the necessary energy for the reaction was provided and the rate of the reaction increased .In catalyst solution too the temperature increase to 40 ^{0}C resulted in the increase in the absorption change (rate increase) and remained constant later on. On the other hand it can be said that in catalyst solution two factors influence the rate of the reaction ,the first is catalyst and the other is temperature increase, these two factors cause the catalyst reaction to have a remarkable improvement in the first , two or three minutes. By studying the effect of ionic strength on the process of the reaction we found out that the non catalyst solutions absorption change is very small with the increase of non catalyst system includes. A natural compound (P.S) and $S_2O_8^{2-}$ according to equation $\text{Log } K = \text{Log } K_0 + 1.018\ Z_A Z_B \sqrt{\mu}$. when ever one of factors is uncharged for example (P.S) $Z_A Z_B = 0$ and the rate reaction changes is very low with the increase of ionic strength. In the second experimental section the kinetic quantities such as the rate of reaction for all the species, rate of reaction constant, activation energy, Arinus constant, $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ were calculated and the results are presented in table 2

CONCLUSIONS

In catalyst solution we can conclude that in the rate determination state Ag^+ and $S_2O_8^{2-}$ interfere and two particles with opposite charges have key role in improvement of the reaction in such a condition the rate reaction decrease with increase of ionic strength, because these reaction as they would have lower electric charges.

Table2. Kinetic quantities catalyst and non catalyst reaction

Subject	Non catalyst reaction	Catalyst reaction
$n_{p.s}$	0.94	0.97
n_{k2s2o8}	1.12	0.76
$n_{Ag\,No3}$	—	0.8
n_{total}	2.06	2.53
$E_a^{\#}$	64.72kj.mol^{-1}	23.94kj.mol^{-1}
K	1.31×10^{-3} mol$^{-1.06}$L$^{1.06}$S^{-1}	1242 mol$^{-1.53}$L$^{1.53}$S^{-1}
$\Delta S^{\#}$	-0.1kj.mol^{-1}	-0.11kj.mol^{-1}
$\Delta H^{\#}$	62..11kj.mol^{-1}	21.32kj.mol^{-1}
$\Delta G^{\#}$	93.41kj.mol^{-1}	55.76kjmol^{-1}
A	4.2×10^{7} mol$^{-1.06}$L$^{1.06}$S^{-1}	1.4×10^{7} mol$^{-1.53}$L$^{1.53}$S^{-1}

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