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Research Article

INVESTIGATION OF KINETIC OXIDATION OF PANCEAU S (PS) BY $K_2S_2O_8$ AND $Pb(NO_3)_2$ AS CATALYST

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ABSTRACT

In this research oxidation kinetic of Panceuo S (p.s) by $K_2S_2O_8$ in the presence of $Pb(NO_3)_2$ as catalyst was studied. The method was spectrophotometry following absorption spectrum (P.S) in wave length of 520nm. 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 thermodynamically 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 $K_2S_2O_8$ would be increased by the addition $Pb(NO_3)_2$would function as a positive catalyst in this reaction.

Keywords: *Kinetic; Oxidation; Panceuo S; Catalyst*

INTRODUCTION

Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. Peter and Cato (1864) pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances (Chang, 2005).

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero-order reactions (for which reaction rates are independent of concentration), first-order reactions, and second-order reactions, and can be derived for others.

In consecutive reactions, the rate-determining step often determines the kinetics. In consecutive first-order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation.

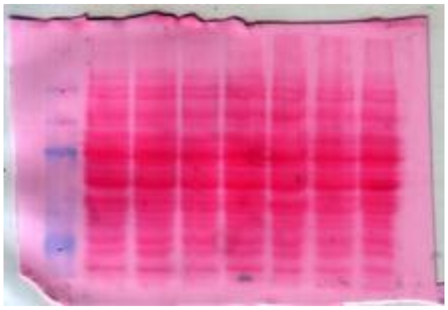
The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction (Ames, 2010; Laidler, 1984; Logan, 1982; Chang, 2005).

Properties of Ponceau S

Ponceau S, Acid Red 112, or C.I. 27195 is a sodium salt of a diazo dye of a light red color, that may be used to prepare a stain for rapid reversible detection of protein bands on nitrocellulose or polyvinylidene fluoride (PVDF) membranes (Western blotting), as well as on cellulose acetate membranes.

A Ponceau S stain is useful because it does not appear to have a deleterious effect on the sequencing of blotted polypeptides and is therefore one method of choice for locating polypeptides on Western blots for blot-sequencing. http://en.wikipedia.org/wiki/Ponceau_S - cite_note-Al-1 It is also easily reversed with water washes, facilitating subsequent immunological detection.

The stain can be completely removed from the protein bands by continued washing.[1] Common stain formulations include 0.1% (w/v) Ponceau S in 5% acetic acid or 2% (w/v) Ponceau S in 30% tri –chloro acetic acid and 30% sulfosalicylic acid.



A nitrocellulose membrane stained with Ponceau S dye for protein detection during western blotting. The blue bands on the left are protein markers for various molecular weights (Figure 1).

Application

Ponceau S stain comes ready-to-use and is designed for rapid (5 min) staining of protein bands on nitrocellulose or PVDF membranes (Western blots) and also for staining protein on cellulose acetate membranes. Ponceau S staining on nitrocellulose and PVDF is reversible by washing the stained membrane with 0.1 M NaOH for 1 min. The stained and destained membrane can then be immunologically detected (Western blotting). A product information sheet is supplied which includes the staining procedure for cellulose acetate, nitrocellulose, and PVDF (Al-Amoudi *et al.,* 2013).

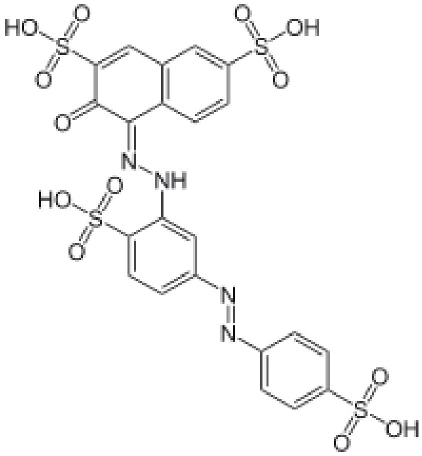


Figure 1: Structure of P.S

Experimental

1. Procedure

In this research sample and blank solutions were used to study kinetic quantities. Different volumes of $K_2S_2O_8$ and $Pb(No_3)_2$ 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 520nm 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 $Pb(N0_3)_2$ was not added to the solution. All the needed containers and solution were bathed for half an 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 520nm had the highest absorption .The reaction of P.S solution with $K_2S_2O_8$ solution is noticeab1e; there for the absorption changes are low. but the absorption rate severely decreases whenever Pb^{2+} 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 frompH=2 to pH=7.

For the production of sample solution, 0.5 ml of the intended buffer solution and 5 ml of
$K_2S_20_8$ 0.04 molar and I ml of $Pb(N0_3)_2$ 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 transferred 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 Pb^{2+} hydroxide deposit.

5- The Effect of Concentration P.S

For the production of sample solution 5 ml of $K_2S_20_8$ 0.04 molar and 1 ml of Pb $(N0_3)_2$ 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 Irrespective 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 Pb $(N0_3)_2$ 500 ppm. To prepare sample solution 4.5 ml of $K_2S_20_8$ 0.04 molar and 1 mil of Pb $(N0_3)_2$ 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 $K_2S_20_8$ at the presence of Pb $(N0_3)_2$ catalyst in $K_2S_20_8$ 0.18 mol and P.S 3.9 *10^{-5} and the time of reaction is 300 seconds at the temperature of 40°C, the selected wave length for the absorption rate of the solution was 520nm.

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+… …) for the reaction:

$\text{Rate} = K[X]^m[y]^n\,[Z]^P \ldots.$

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

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

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

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

Therefore the slope of the curve Ln ΔA 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:

$P.S + S_2O_8^{-2K}$ prod. $\longrightarrow$

$R=K\,[P.s]^{m}\,[S_2O_8^{2-}]\,n$

$\text{Ln } R = \text{Ln } K + m \text{ Ln } [P.S] + n \text{ Ln } [S_2O_8^{2-}]$

$\text{Ln } A = m \text{ Ln } [P.S] + \text{const}$

9-2: In catalyst reaction

The results of the experiment are presented in table-1, 2 and figure 2. In catalyst environment the order of P.S was determined as following

$P.S + S_2O_8^{-2} + Ag^{+K}$ prod. $\longrightarrow$

$R = k\,[P.S]^{m'}\,[S_2O_8]^{n'}\,[Pb^{2+}]^{p'}$

$\text{Ln } R = \text{Ln } K + m' \text{ Ln } [P.S] + n' \text{ Ln } [S_2O_8^{2-}] + p' \text{Ln } [Pb^{2}+]$

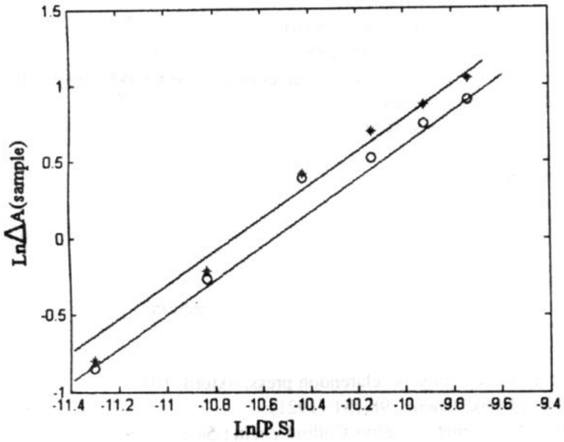
$\text{Ln } \Delta A = m' \text{ Ln } [P.S] + \text{const}$

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

[P. S]	**Ln[P.S]**	**ΔA(sample)**	**LnΔA(sample)**
$5.91\text{x}10^{-5}$	-9.736	2.467	0.903
$4.93\text{x}10^{-5}$	-9.918	2.124	0.753
$3.94\text{x}10^{-5}$	-10.14	1.741	0.524
$2.95\text{x}10^{-5}$	-10.43	1.357	0.395
$1.97\text{x}10^{-5}$	-10.83	0.766	-266
$0.98\text{x}10^{-5}$	-11.3	0.427	-0.850

Table 2: Determination of order reaction P.S by non catalyst solutions

[P. S]	**Ln[P.S]**	**ΔA(sample)**	**LnΔA(sample)**
$5.91\text{x}10^{-5}$	-9.736	2.834	1.041
$4.93\text{x}10^{-5}$	-9.918	2.406	0.877
$3.94\text{x}10^{-5}$	-10.14	2.015	0.700
$2.95\text{x}10^{-5}$	-10.43	1.531	0.425
$1.97\text{x}10^{-5}$	-10.83	0.806	-0.215
$0.98\text{x}10^{-5}$	-11.3	0.449	-0.800



***catalyst reaction Condition: [$K_2S_2O_8$] = 0.018, T=40 ^{O}C**
Figure 2: O Non catalyst reaction

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 precession, 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.

Table 3: Kinetic quantities catalyst and non catalyst reaction

Subject	**Non catalyst reaction**	**Catalyst reaction**
n $_{P.S}$	1.15	1.35
n $_{K2S2O8}$	1.3	1.6
n $_{Pb(no3)2}$	–	0.4
n $_{total}$	2.45	2.95
$E_a^{\#}$	46.28kj .mol^{-1}	23.26kj.mol^{-1}
K	8.66x10^{-2} Mol$^{.1.45}$L$^{1.45}$S^{-1}	23150.70 Mol$^{-2.35}$L$^{2.35}$S^{-1}
$\Delta S^{\#}$	-0. 154kj.mol^{-1}	-0.11989kj.mol^{-1}
$\Delta H^{\#}$	43.51 kj.mol^{-1}	20.497kj. mol^{-1}
$\Delta G^{\#}$	94.78kj. mol^{-1}	6.422kj mol^{-1}
A	15.7 mol^{-1}L$^{1.45}$S^{-1}	10336 mol^{-1}L$^{2.35}$S^{-1}

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°C (the rate is slow) so a temperature lower than 40 °C is not a proper temperature for non catalyst reaction. As temperature increased above 40°C the necessary energy for the reaction was provided and the rate of the reaction increased. In catalyst solution to the temperature increase to 40 °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 $\text{Log } K = \text{Log } K_o + 1.018\, Z_A Z_B \sqrt{\mu}$. whenever 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 catalyst solution we can conclude that in the rate determination state $pb^{2+}$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.

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 3.

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