

## RESEARCH ARTICLE

# Kinetics Study of the Reaction between Serine and N-Bromosuccinimide in the Presence of Palladium (Pd<sup>2+</sup>)

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## ABSTRACT

The oxidation of serine using N-bromosuccinimide (NBS) has been studied at fix pH value. The reaction presents a first-order reaction with respect to both substrate and oxidant. It is noted that the rate of reaction increases with increasing the palladium ion concentration. The addition of the reaction product (succinimide) affects the oxidation reaction rate. The protonated Br<sup>+</sup> or NBrS and NBrS are used to be the reactive species of the N-bromosuccinimide. Furthermore, intermediate compounds are noticed through the reaction. Finally, a mechanism for the oxidation reaction is suggested in this work.

**Keywords:** Kinetics, Oxidation process, Amino acid, N-bromosuccinimide.

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**Conflict of interest:** None

## INTRODUCTION

N-bromosuccinimide (NBS) is considered as one of the oxidants that are used widely in oxidizing organic compounds.<sup>1</sup> It has been used for the study of kinetics and mechanism of oxidation of esters<sup>2</sup>, alcohols, and ketones in acidic media.<sup>2</sup> N-chloro, N-Bromo, and N-iodo compounds also reacted with compounds of double bonds to add halide or will be as granary noun of halide in aqueous solution. This group of compounds such as N-chlorosuccinimide, Bromamine-T, N-chloronicotinamide, Chloramine-T, N-bromophtalimide.<sup>3</sup> Sometimes it behaves like a base, nucleophile, hypohalite species, etc.<sup>4</sup>

The transition metals (Pt group) are very interested in chemist.<sup>5,6</sup> The oxidation state of Pd is 0 and +2.<sup>7,8</sup> Palladium(II) chloride (PdCl<sub>2</sub>) has been used successively as a catalyst.<sup>9,10</sup>

The research suggests a reaction mechanism according to the steps involved in the reaction between NBS and Serine, then determines the reactions rate law, and determines the effects of catalyst on the reaction.

## EXPERIMENTAL

The procedure of the experimental work was accomplished as follows: suitable amounts of the prepared solution were put in separate vessels of glass and maintained for 15 minutes (at least) in a bath of thermo-stated water at 35°C. A known amount of every single reactant was added and mixed together in a specific vessel of glass. Then, a requisite amount of water (double distilled) was added to the mixture. Next, the produced reaction mixture was placed in the bath of thermos-stated

water kept at 35°C constant temperature in uncertainties of ± 5%. The reaction was launched by adding a requisite quantity of oxidation solution, which was placed individually in the same bath of water. It is worthy to note that the kinetic measurements (all of them) were accomplished under first-order conditions within a concentration of serine in excess over NBrS at a constant ionic strength. The constants of the first-order rate (k<sub>obs</sub>) were calculated from the slope of the log absorbance-time plots. The solution of the NBrS was noticed to be thermally stable in the visible region. The different mixtures of the reaction with the different concentration sets of the reactants were kept at 35°C for 24 hours, where the NBrS was in excess over serine at constant catalyst concentration, acidity, and constant ionic strength. After reaction completion, the remaining NBrS was estimated for the different sets of the experiment. The results of this work showed that one serine mole consumes two NBrS moles. The oxidation products were recognized as carbon dioxide, 2-hydroxyethanal, ammonia, and Br. The mixture of reaction was handled with acidified 2 and 4-dinitrophenyl hydrazine solution, which was used for hydrazine yielding.

Serine solution and sulphuric acid were prepared in doubly distilled water, while PdCl<sub>2</sub> was prepared in HCl (0.20 mol dm<sup>-3</sup>) 2, 4-Dinitrophenylhydrazine was used for the test of aldehyde.

## RESULT AND DISCUSSION

The reaction was carried out without Pd catalyst, and the rate of the reaction was calculated, and it was slow compared

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with the rate of reaction when Pd catalyst had been used. (Figure 1)

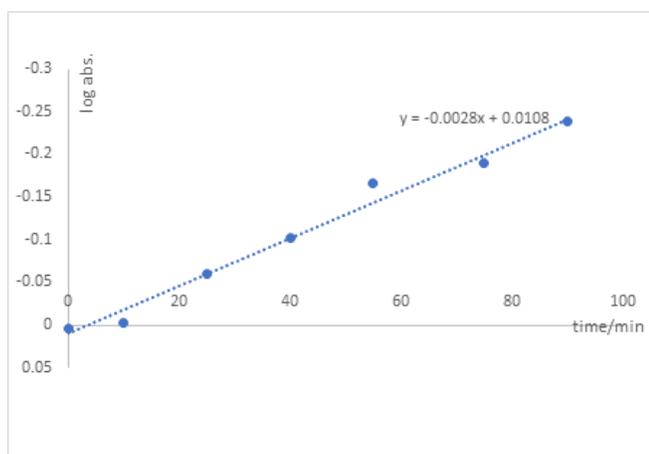
The influence of NBrS was studied in this work. The NBS concentration was ranged from  $5.0 \times 10^{-3}$  to  $5.0 \times 10^{-4}$  M with using  $5 \times 10^{-2}$  M of [serine],  $[H^+] = 1.0$  M,  $I = 1.0$  M at 35°C. The first-order rate constant ( $k_{obs}$ ) is independent of the initial concentration of NBrS as shown in Table 1.

In order to study, the effect of serine concentrations on rates of reaction, serine was changed from 0.03 to 0.09 M using  $[NBrS] = 5.0 \times 10^{-3}$  M,  $[H^+] = 1.0$  M,  $I = 1.5$  M and  $[Pd(II)] =$

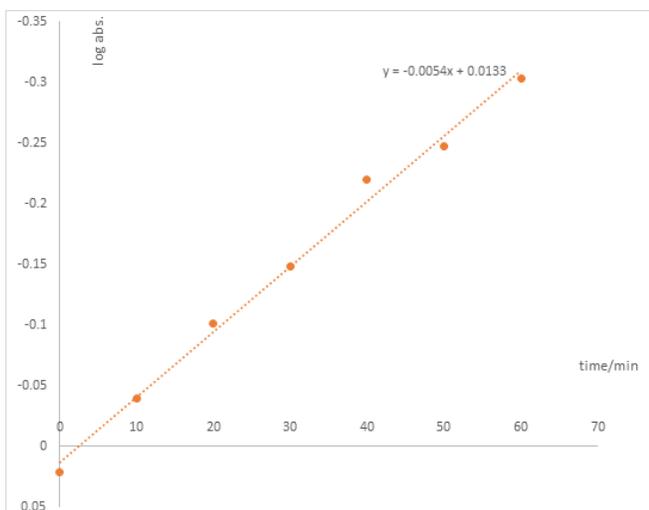
$5 \times 10^{-5}$  M. The constant ( $k_{obs}$ ) has increased with increasing the serine concentration as listed in Table 2 and Figures 2-5.

The serine order of reaction is fractional, which was obtained from performing the linear regression to the  $\log k_{obs} - \log [\text{serine}]$  data. The influence of adding Pd (II) concentration to the reaction mixture had been also investigated, and an increase in the rate was noticed up to  $5 \times 10^{-5}$  (Table 3).

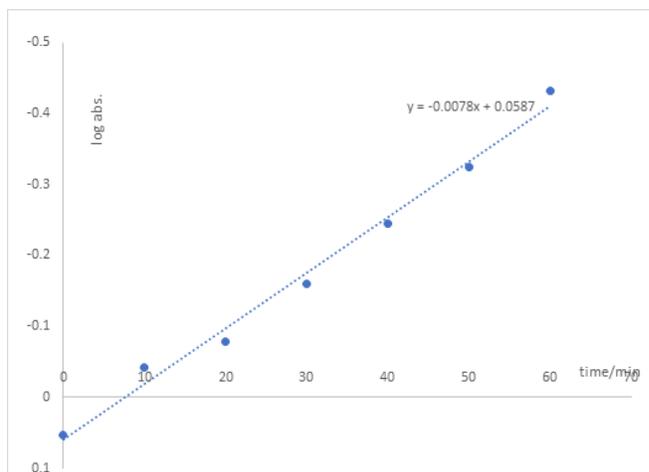
The ionic strength influence was investigated using a constant concentration of NBrS, [serine], [Pd (II)], and temperature. The ionic strength (i) ranged from 1.2 to 2.0 M, using NaClO<sub>4</sub> to fix the ionic strength. A slight increase in the



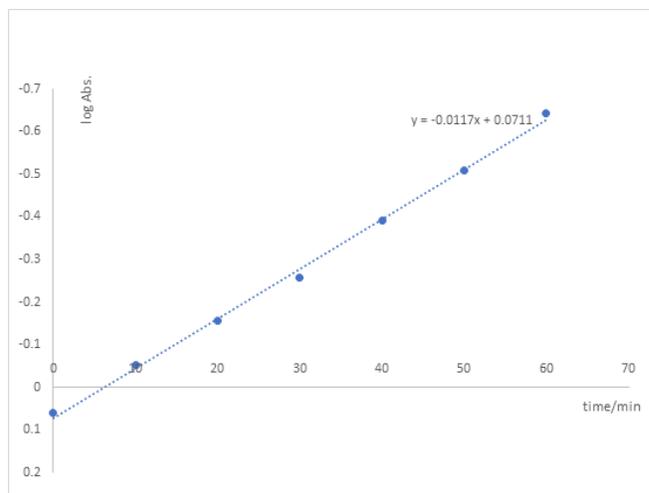
**Figure 1:** Shows the first order relation for the reaction between serine and NBrS at 35°C, in the absence of pd, {Ser.}=0.05M,  $[NBrS] = 3 \times 10^{-3}$  M



**Figure 2:** Shows the first order relation for the reaction between serine and NBrS at 35°C,  $[pd] = 5 \times 10^{-5}$  M, {Ser.}=0.03M,  $[NBrS] = 3 \times 10^{-3}$  M



**Figure 3:** Shows the first order relation for the reaction between serine and NBrS at 35°C,  $[pd] = 5 \times 10^{-5}$  M, {Ser.}=0.05M,  $[NBrS] = 3 \times 10^{-3}$  M



**Figure 4:** Shows the first order relation for the reaction between serine and NBrS at 35°C,  $[pd] = 5 \times 10^{-5}$  M, {Ser.}=0.07M,  $[NBrS] = 3 \times 10^{-3}$  M

**Table 1:** The effect of using different concentrations of NBrS on the rate of reaction at [serine] =  $5 \times 10^{-2}$  M,  $[Pd(II)] = 5 \times 10^{-5}$  M and  $[H^+] = 1.0$  M and constant temperature of 35°C.

$10^3 [NBrS]$	0.5	1.0	5.0
$10^3 k/min$	6.85	8.11	7.80

**Table 2:** Shows the results of using different concentrations of serine on the reaction rate at constant concentrations of  $NBrS = 5 \times 10^{-3}$  M,  $Pd(II) = 5 \times 10^{-5}$  M, and  $H^+ = 1.0$  M and a constant temperature of 35°C.

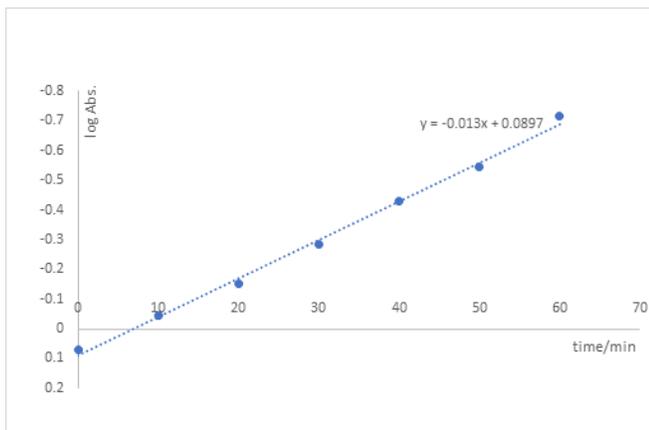
$10^2 [Serine]/M$	3.0	5.0	7.0	9.0
$10^3 k/min$	5.4	7.80	11.7	13

**Table 3:** Gives the data of using different Pd II concentrations on the reaction rate at constant concentrations of NBrS=5x10<sup>-3</sup> M, serine=5x10<sup>-2</sup> M and H<sup>+</sup> = 1.0 M, and constant temperature of 35°C.

10 <sup>5</sup> [Pd II]/M	1.0	3.0	5.0
10 <sup>3</sup> k /min	1.8	2.05	2.28

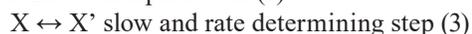
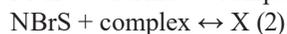
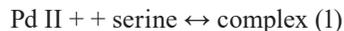
**Table 4:** The effect of using different concentrations of HSO<sup>4-</sup> on the rate of reaction at constant concentrations of NBrS=5x10<sup>-3</sup> M, Pd II =5x10<sup>-5</sup> M, and serine = 5x10<sup>-2</sup> M and constant temperature of 35°C.

[HSO <sub>4</sub> <sup>-</sup> ]/ M	0.2	0.6	0.8	1.0
(k)/min <sup>-1</sup>	0.013	0.0085	0.00805	0.0078

**Figure 5:** Shows the first order relation for the reaction between serine and NBrS at 35°C, [pd]=5x10<sup>-5</sup> M, {Ser.}=0.09M, [NBrS]=3x10<sup>-3</sup> M

reaction rate was obtained when increasing the ionic strength. The effect of adding the catalyst in the thermostated water bath at 35°C for 24 hours in the existence of exceeded serine over NBrS and fixed ionic strength and acidity was investigated under kinetic conditions.

Adding 2,4-dinitrophenylhydrazine into the reaction mixture had produced a hydrazone precipitation derivative of an aldehyde with a brown color; serine is protonated in an acidic medium, owing to the presence of H<sup>+</sup> is in the pre-equilibrium step of the reaction. To explain the first-order dependence on NBrS, it is assumed that NBrS oxidize the complex is a slow step to producing Pd(II) substrate complex, which decomposes fastly to the catalyst, CO<sub>2</sub>, ammonia, and aldehyde (Offner and Skoog, 1996). The suggested mechanism and the derived rate law was suggested.



The conversion of intermediate (X) to a N-Bromo derivative of the substrate (X') is derived as:

$$R = [\text{NBrS}][\text{Serine}]/[\text{HSO}_4^-]$$

#### Effect of [HSO<sub>4</sub><sup>-</sup>]

Using different [HSO<sub>4</sub><sup>-</sup>] = 0.2 - 1.0 M at [NBrS] = 5.0x10<sup>-3</sup> M, [serine] = 5.0x10<sup>-2</sup> M, [Pd(II)] = 5.0x10<sup>-5</sup> M and ionic strength of 1.50 M at 35°C. Plot of 1/k<sub>obs</sub> against [HSO<sub>4</sub><sup>-</sup>] give straight line, Results are given in Table 4.

#### Effect of Added Products

The product Succinimide was added to the reaction in ranged from 1.0 x 10<sup>-4</sup> to 5.0 x 10<sup>-3</sup> M at fixed [NBrS]= 5.0 x 10<sup>-3</sup> M,

[Ser] = 5.0 x 10<sup>-2</sup> M, [H<sup>+</sup>] = 1.0 M and I = 1.50 M at 35°C. The effect on the rate of reaction was negligible.

## CONCLUSION

The extent of the great importance and the distinctive role of kinetic chemistry in general and of amino acids and (Serine) in particular has been mentioned in our research, especially the medicinal and pharmaceutical importance where kinetic chemistry plays an important role in stability and incompatibility.

pH can be controlled by using N-Bromo-succinimide (NBS) as the granary noun of positive halide.

Kinetics is a rate process. It has many applications, including stability, incompatibility, dissolution, absorption, distribution, elimination processes, drug action, and other acts.

The oxidation of serine has received much attention because of strengthening the immune system by providing antibodies and synthesizing fatty acid sheath around nerve fibers.

In our experiment, the reaction was carried out without a Pd catalyst, and the rate of the reaction was calculated, and it was slow compared with the rate of reaction when Pd catalyst was used.

The first-order rate constant (k<sub>obs</sub>) has increased with increasing the serine concentration

(at constant concentrations of NBrS=3x10<sup>-3</sup> M, Pd II=5x10<sup>-5</sup> M, and H<sup>+</sup> = 1.0 M and a constant temperature of 35°C).

It is independent of the initial concentration of NBrS (at constant concentrations of serine=5x10<sup>-2</sup> M, Pd II =5x10<sup>-5</sup> M and H<sup>+</sup> = 1.0 M and constant temperature of 35°C).

The reaction rate is inversely proportional to the HSO<sub>4</sub><sup>-</sup> ion concentration.

## REFERENCES

- Salman NY, Mahdi SA, Al-Niami KH. Kinetic and mechanistic study of glycine oxidation by N-bromosuccinimide using MN2+ as catalyst., *Biochem. Cell. Arch.* 2020;20, Supplement 2.
- Katre YR, Singh AK, Patil S, Joshi GK. Kinetic studies on the mechanism of oxidation of DL-serine by chloramine-T in micellar system. *Oxidation Communications.* 2006 Jan 1;29(1):129.
- Narender M, Reddy MS, Rao KR. A mild and efficient oxidative deprotection of THP ethers with NBS in the presence of β-cyclodextrin in water. *Synthesis.* 2004 Aug;2004(11):1741-1743.
- Thiagarajan V, Venkatasubramaniam N. Kinetics of bromination of anisole by N-bromosuccinimide (NBS), *Indian J. Chem.* 1970;8:809.
- Carbtree RH. *The Organometallic Chemistry of Transitions Metals*, 4th ed., John Wiley and Sons, New Jersey, 1. 2005.

6. Hartley FR. Chemistry of the Platinum Group Metals; Recent Developments, Elsevier, Amsterdam, New York, 11, 1991.
7. Canty A. Handbook of Organopalladium Chemistry of Organic Synthesis, E. I. Negishi, Eds., John Wiley & Sons, New York, 2002. 189.
8. Mureinik R.J and Pross E., Coord J,(1978). Chem., 8, 127.
9. Srivastava S. and Singh P. (2008). Bull. Catal. Soc. Ind., 7, 12.
10. Srivatava S. and Singh P., Oxid J. ,(2008). Commun. Book-4, 31, 853.
11. M. S. Sherrill C. B. King and SpoonerR.C, (1943).Test of aldehyde, J. Am. Chem. Soc. 65, 170.