

# Kinetics and mechanism of oxidation of glycine by N-bromoanisamide

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## Abstract

Oxidation of glycine by N-bromoanisamide has been studied in acidic medium. The rate of the reaction is inhibited by an increase in the hydrogen ion concentration due to the protonation equilibria of the amino acids. Variation of ionic strength of the medium has no significance effect, whereas variation of dielectric constant of the medium has significant effect on the rate of reaction. The rate is retarded by addition of anisamide. The stoichiometric studies revealed 1:1 mole ratio. Thermodynamic parameters have been calculated and reported based on the temperature effect and a possible operative mechanism is proposed and the derived rate law was verified graphically.

Keywords: glycine; N-bromoanisamide; perchloric acid; mechanism;

## 1. Introduction:

N-halo compounds are very effective oxidants due to their specific oxidizing nature and ability to act as sources of halonium ions, hypohalite species and nitrogen anions, which act as both bases and nucleophiles. A lot of works have been reported on the oxidation of organic compounds by N-halo compounds<sup>1-4</sup>. Numerous reports are available on kinetics of oxidation of amino acids by variety of oxidants<sup>5-11</sup>.

As similar to other N-halo compounds, N-bromoanisamide also a potent oxidant and only few works have been done on N-bromoanisamide<sup>12-15</sup> as an oxidant. A literature search showed no reports on the mechanism of oxidation of amino acid by N-bromoanisamide. We now report the kinetics and mechanism of oxidation of glycine by N-bromoanisamide in acidic medium.

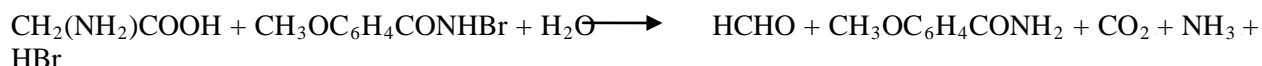
## 2. Materials and Method:

N-bromoanisamide was prepared and its acetic acid solution was standardised iodometrically. The reagents employed were Glycine (E. Merck), NaClO<sub>4</sub>, perchloric acid and all other reagents used were of AR grade. All solutions were prepared in doubly distilled water. Water (de-ionized) and glacial acetic acid were used as the solvent through the work.

A thermostated water bath was used to maintain the desired temperature. The reaction was studied at constant temperature 308K. Pseudo first order condition were maintained in each kinetic run by keeping an excess of the glycine over oxidant. The progress of the reaction was monitored by measuring unconsumed oxidant iodometrically using starch as the indicator.

### 3. Results and Discussion:

The oxidation of glycine resulted in the formation of corresponding aldehyde. Product analysis and stoichiometric determinations indicates that the following reaction may be written as.



#### Effect of oxidant variation:-

The kinetics of oxidation of glycine has been studied at various initial concentration of the oxidant and at fixed concentration of other reactants. (table-1).The plot of  $\log(a-x)$  versus time yields a straight line indicating a first order dependence of rate on oxidant

**Table-1:** Effect of oxidant on the reaction rate

Glycine =  $2.0 \times 10^{-2}$  M;  $\text{HClO}_4$  = 0.01 M; Temp.= 308 K<sup>0</sup>  
 $[\text{Hg}(\text{AcO})_2]$  = 0.002M; Solvent; water-acetic acid (v/v) 30 %

Oxidant $\times 10^{-3}$ M	k $\times 10^{-3}$ min <sup>-1</sup>
0.25	1.734
0.50	1.732
0.75	1.733
1.00	1.735
1.25	1.737
1.50	1.736

#### Effect of substrate variation:-

The rate of reaction increases linearly with an increase in the concentration of glycine. (table-2) The plot of  $1/k_{\text{obs}}$  versus  $1/[\text{Substrate}]$  gave linear line passing through origin indicating a first order dependence on substrate.

#### Effect of $[\text{H}^+]$ variation:-

The dependence of the reaction rate on the concentration of  $H^+$  was studied at constant concentration of oxidant, substrate and other reagents, and varying the initial concentration of  $HClO_4$ . The  $k_{obs}$  values decrease slightly with increase in the  $HClO_4$  concentration. (table-2).

**Effect of Acetic acid variation:-**

The effect of dielectric constant of reaction medium was studied by adding acetic acid in the reaction medium at constant concentration of other reactants. The rate of reaction decreases by increasing the portion of acetic acid in the solvent medium. (table-2)

**Table-2:** Effect of Substrate,  $HClO_4$   $CH_3COOH$  on the reaction rate

$$[Hg(AcO)_2] = 0.002M; \quad \text{Oxidant} = 1.0 \times 10^{-3} M$$

$$\text{Temp.} = 308 K^0; \text{Solvent; water-acetic acid (v/v) } 30 \%$$

Substrate $\times 10^{-2} M$	$HClO_4 \times 10^{-2} M$	$CH_3COOH \%$	$k \times 10^{-3} \text{ min}^{-1}$
0.5	1.0	30	1.286
1.0	1.0	30	1.396
1.5	1.0	30	1.562
2.0	1.0	30	1.735
2.5	1.0	30	1.990
3.0	1.0	30	2.328
2.0	0.25	30	2.164
2.0	0.50	30	2.051
2.0	0.75	30	1.888
2.0	1.0	30	1.735
2.0	1.25	30	1.509
2.0	1.50	30	1.341
2.0	1.0	30	1.735
2.0	1.0	40	2.645
2.0	1.0	50	3.547
2.0	1.0	60	5.419

**Effect of temperature variation:-**

The reaction has been studied in the temperature range 308-323 K and the results are recacorded in (table-3). Using Arrhenius equation the energy of activation for substrate has been calculated and this value subsequently utilized in computing various other thermodynamic parameters, all the results are presented in (table-4).

**Table-3:** Effect of Temperature on the reaction rate

Oxidant =  $1.0 \times 10^{-3}$  M; Glycine =  $2.0 \times 10^{-2}$  M;  $\text{HClO}_4$  =  $1.0 \times 10^{-2}$  M  
 $[\text{Hg}(\text{AcO})_2]$  = 0.002M; Solvent; water-acetic acid (v/v) 30 %

Temperature K	$k \times 10^{-3} \text{ min}^{-1}$
308	1.735
313	2.645
318	3.547
323	5.419

**Table-4:** Activation parameters for the oxidation of Glycine

Substrate	$E_a$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	$\Delta H^*$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	$-\Delta S^*$ ( $\text{JK}^{-1}\text{mol}^{-1}$ )	$\Delta G^*$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
Glycine	58.24	55.68	108.98	89.25

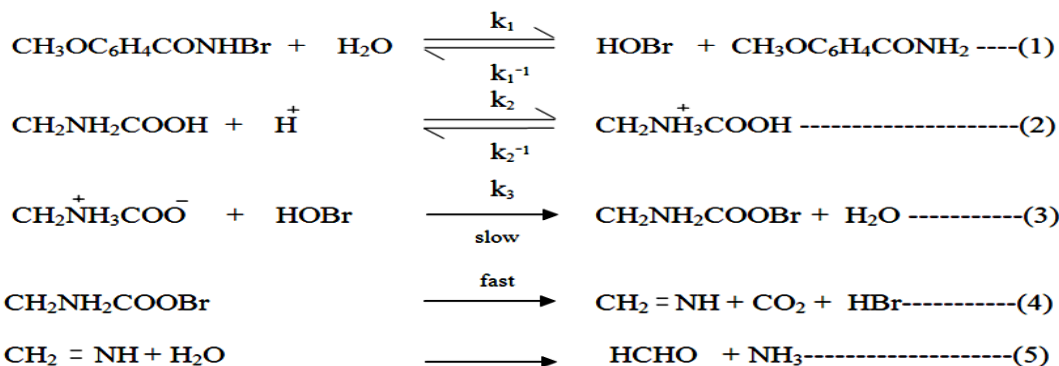
#### Effect of Variation of ionic strength, and anisamide

Variation of ionic strength has been studied by varying concentration of sodium perchlorate ( $\text{NaClO}_4$ ). It was found that there is no substantial change in the reaction rate on varying the ionic strength. Addition of anisamide (one of the reaction product) at constant concentration of oxidant, glycine and other reactants decreases the rate of reaction. The retardation of reaction rate on the adding of anisamide suggest a pre-equilibrium step that involves a process in which anisamide is one of the product.

#### 4. Reaction Mechanism:

Based on the above mentioned experimental observation, the following reaction mechanism is suggested in which the protonated hydroxy acid react with active form of the oxidant HOBr in the rate determining step.

The proposed mechanism for the title reaction is



From the above mechanism, the following rate law is derived.

$$\text{Rate} = K_1 k_3 [\text{NBA}] [\text{SH}^+] / K_2 [\text{Anisamide}]$$

### 5. Conclusion:

Kinetic studies demonstrate that the complex formed between substrate and oxidant in the slow rate determining step, decompose to give product. The experimental stoichiometry is in good agreement first order to oxidant and fractional order to substrate at higher concentration is supported by derived rate law.

### 6. References:

1. Thenraja, D., Subramaniam, P. and Srinivasan, C. 2002. *J. Chem. Soc. Perkin Trans 2*: 2125-2129.
2. Mukaiyama, T., Mastsuo, J. I., Lida, D. and Kitagawa, H. 2001. *Chem. Lett.* **8**: 846-847.
3. Nadh, R. V., Sundar, B. S. and Radhakrishnamurthi, P. S. 2001. *Russ. J. Phy. Chem.* **75**(2):174.
4. Nadh, R. V., Sundar, B. S. and Radhakrishnamurthi, P. S. 2000. *Oxid. Commun.* **23**(1):102.
5. Farook, N. A. M., Prabakaran, Rahini, S. Senthil, R. K. Rajamahendran, G. and Gopalakrishanan, B. 2004. *E-J Chem.* **1**(2):127-131
6. Farook, N. A. M., Seyed Dammen, G. A., Murugesan, A. and Kanagaraj, M. 2004. *E-J Chem.* **1**(2):132-136.
7. Katre, Y. R., Solanki, S. K., Patil, S. and Joshi, G. K. 2005. *Asian J. Chem.* **17**(1):423-428.
8. Joshi, G. K., Katre, Y. R. and Singh, A. K., Singh, A., 2006. *J. Surf. Deter.* **9**(3): 231-235.

9. Singh, A. K., Singh, R. K., Srivastava, J., Rahmani, S. and Yadav, S. 2012. *Ind. J. Chem.* **51A**:681-689.
10. Vaijyanthi, S. P. and Mathiyalagan.2013. *Int. Lett. Chem. Phy. Astro.***16**:1-8.
11. Nadh, R. V. and Sireesha, M. 2015. *Bulg. Chem. Comm.* **47**(1): 13-21.
12. Badole M. K., Malviya, L. N., and Siriah V. K. 2012. *Asian J. Chem.* **24**(12): 5939-5940.
13. Badole M. K., Malviya, L. N., and Siriah V. K. 2012 *Orient. J. Chem.* **28**(3): 1433-1436.
14. Malviya L. N., Siriah V. K. and Badole M. K. 2013 *J. App.Chem.* **2**(3): 636-639.
15. Malviya L. N., Siriah V. K. and Badole M. K. 2013. *Int. J. Sci. & Res. Pub.* **3**(9): 1-5.