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Thermodynamic and Kinetic Study of Glycine Oxidation in Aqueous Acetic Acid Medium

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ABSTRACT

In the current study, the kinetics and the mechanism of oxidation of glycine by N-bromoanisamide in an acidic medium is studied. The reaction was conducted in pseudo first-order conditions in the presence of excess glycine and the reaction progress was monitored iodometrically. The findings demonstrate that the reaction is of first-order kinetics with respect to the oxidant and that it is influenced by glycine concentration. The rise in the concentration of hydrogen ions will cause the reaction rate to decrease indicating that there is protonation equilibria of glycine. Ionic strength was also seen to have little impact, but the dielectric constant of the medium had a strong impact on the rate of reaction. When anisamide is added, it retards the reaction, which is an indication that there is a pre-equilibrium step that involves the product. The stoichiometric analysis proves the 1:1 ratio of mole between glycine and the oxidant.

Keywords: *Glycine, Oxidation, Reaction Rate, Temperature, Acetic Acid.*

I. Introduction

In living organisms, α-amino acid oxidation is a crucial metabolic process. This encompasses a wide range of critical events, including the Krebs Cycle, oxidative deamination, oxidative catabolism, and oxidative metabolism. Additionally, the medical and biotechnological communities are especially interested in the uncatalyzed oxidation reactions of α-amino acids involving a variety of oxidants. The oxidation of microcystins and other very hazardous amino acid derivatives generated by certain freshwater cyanobacteria is especially crucial since these compounds are present in wastewater. Dissolved amino acids in wastewater must be removed or oxidatively degraded in order for the wastewater to be treated.

Nevertheless, several reaction systems employ distinct mechanisms. Because various oxidants produce different byproducts, studying the oxidation of amino acids is intriguing in and of itself. Many researchers have used oxidants in higher oxidation states of non-metals like iodine, bromine, chlorine, and transition metals like chromium, manganese, osmium, and ruthenium to study the kinetics of oxidation of various amino acids, including alanine, arginine, leucine, isoleucine, proline, valine, glycine, and many more.

Amino acids are building blocks of proteins; the smallest of them is glycine. The fact that it is achiral makes it distinct from all other proteinogenic amino acids. Its short side chain of only one hydrogen atom allows it to fit into both hydrophilic and hydrophobic environments. Glycine is an amphoteric molecule in water; its proton potential is around 2.4 at low pH and 9.6 at high pH (exact pKa values are temperature and ionic strength dependent). Since it is biosynthesised in the body from serine, an amino acid produced from 3-phosphoglycerate, lycine is not a dietary need for humans. One of glycine's primary roles is as a protein precursor; for example, it and hydroxyproline are required to build the collagen helix at regular intervals. In addition to its role as an inhibitory neurotransmitter in the central nervous system, glycine is also a metabolic intermediate.

II. Review of Literature

N, Afsar & Manivannan, S. (2020) An investigation was conducted on the rate of trichloroisocyanuric acid's (TCICA) oxidation of leucine, an alpha-amino acid, in a solvent medium consisting of 50% acetic acid and 50% water (v/v), with chloride ions present. The oxidation occurred in first order in all three cases (LEU, TCICA, and fractional order), and it sloped downwards with regard to [H+]. 2-Methyl butanal is the primary byproduct of oxidation. The reaction is of the dipole-dipole type when the rate of the reaction rises as the water content of the solvent medium increases. The reactive oxidising species has been hypothesised to be HOCl. An appropriate method has been suggested.

Vivekanandan, K & Nagarajan, Aathi. (2016) At 303 K, researchers examined the rate of glycine, alanine, and valine oxidation using N-iodosuccinimide in an acetic acid-water medium with hydrochloric acid. With regard to the oxidant and [H+], the reaction exhibits inverse first order. There is a little positive correlation between the rate and the [amino acid] concentration, suggesting a first-order dependency. While adding salts to the reaction media (e.g., potassium chloride, sodium chloride, or KCl) does not affect the rate, raising the temperature does. Oxidation of the amino acids produced ammonia, carbon dioxide, and aldehydes in that order. We isolated and identified the goods that we received. We have calculated the activation parameters. The kinetic observations are supported by a proposed mechanism.

Vivekanandan, K. & Narayanan, R. (2014) A study was conducted to examine the kinetics of glycine oxidation by nicotinium dichromate in an aqueous media containing perchloric acid. When tested with different concentrations of oxidant, substrate, and perchloric acid, the reaction was determined to be first order, fractional order, and second order, respectively. The carbonyl compound was formed by converting amino acid. There was a completely insignificant change in the rate as the ionic strength increased. Acryliconitrile did not show signs of polymerisation. An obvious catalytic effect on the pace of the reaction was produced by the addition of Mn2+ ions. At four distinct temperatures, we measured the reaction rates and assessed the thermodynamic characteristics.

Vaijayanthi, S. & Mathiyalagan, N. (2013) Researchers have studied the rate of oxidation of alanine, glycine, leucine, phenyl alanine, and valine in an aqueous acetic acid medium with hydrochloric acid using N-chloropyrazinamide (NCPZA). The observed rate of oxidation is first order in [NCPZA], [H+] and [Cl^-]. There is no order in relation to [amino acid]. As the acetic acid percentage rises, the oxidation rate also rises. As the ionic strength increases, the reaction rate goes up a notch, but as pyrazinamide is added, it slows down. Analysing the reaction at various temperatures allowed us to assess the Arrhenius and thermodynamic activation parameters from the Arrhenius plot. The observed kinetic data have been accounted for by deducing an appropriate rate law and proposing a reaction mechanism that is very likely to occur.

Hiran, B.L. et al., (2012) At 40°C, the kinetics of glycine oxidation by pyridinium chlorochromate in a DMF-water combination with perchloric acid have been investigated. It was discovered that the reaction rate was first-order dependent on [PCC], [glycine], and [H+]. A protonated chromium(VI) species is likely involved in the rate-determining phase, since the oxidation rate increases with increasing acidity. Formaldehyde has been recognised as the end result of oxidation. As the solvent's polarity (the dielectric constant of the medium) increased, the reaction rate dropped, suggesting that an ion-dipole type of interaction was involved in the step that determined the rate. We have tested the activation settings. We have suggested a viable mechanism based on the experimental results.

III. Materials and Method

The acetic acid solution of N-bromoanisamide was iodometrically standardised after its preparation. All of the chemicals utilised were of AR grade, and they included Glycine (E. Merck), NaClOR4R, perchloric acid, and others. We used double distilled water to make all of the solutions. The study was conducted using glacial acetic acid and de-ionized water as solvents. kept track of by iodometrically measuring the amount of unconsumed oxidant using starch as the indication.

The temperature was kept at the desired level using a thermostated water bath. The reaction was observed at a constant temperature of 308K. In each kinetic run, an excess of glycine over oxdant was maintained to preserve pseudo first order conditions. Unconsumed oxidant was measured iodometrically with starch as the indication to track the reaction's progress.

IV. Results and Discussion

An appropriate aldehyde was produced by oxidising glycine. Based on product analysis and stoichiometric calculations, the following reaction may be expressed as followed.

$$CH_2(NH_2)COOH + CH_3OC_6H_4CONHBr + H_2O \longrightarrow HCHO + CH_3OC_6H_4CONH_2 + CO_2 + NH_3 + HBr$$

Effect of Oxidant Variation

Several studies have examined the oxidation kinetics of glycine at different starting oxidant concentrations and constant concentrations of other reactants. (Table 1) The straight line that results from plotting log (a-x) with time suggests that the rate is dependent on the oxidant at a first-order rate.

Table 1: Effect of Oxidant on The Reaction Rate

Glycine = 2.0 x10^{-2} M; HClO4 = 0.01 M; Temp.= 308 K0

[Hg(AcO)R2R] = 0.002M; Solvent; water-acetic acid (v/v) 30 %

Oxidant × 10^{-3} M	**k × 10^{-3} min^{-1}**
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

As the concentration of glycine increases, the rate of reaction also increases linearly (as shown in table 2) A straight line passing through the origin was obtained when plotting 1/kRobsR vs 1/[Substrate], suggesting a first-order dependency on substrate.

Effect of [H +] Variation

At constant concentrations of oxidant, substrate, and other reagents, we varied the starting concentration of HClOR4 to study the influence of the reaction rate on the concentration of H+.As the concentration of HClOR4 R increases, the kRobs Rvalues drop somewhat. (Table 2)

Effect of Acetic Acid Variation

The influence of the reaction medium's dielectric constant was investigated by incorporating acetic acid into the mixture while maintaining a constant concentration of the other reactants. Increasing the concentration of acetic acid in the solvent slows down the reaction rate. (Table 2)

Table 2: Effect of Substrate on The Reaction Rate

$[Hg(AcO)_2]$ = 0.002M; Oxidant = 1.0 x10-3 M

Temp.= 308 K^0; Solvent; water-acetic acid (v/v) 30 %

Substrate×10^{-2} M	HClO ×10^{-2} M	CHR3RCOOH %	k×10^{-3} min^{-1}
0.5	1.0	30	1.285
1.0	1.0	30	1.392
1.5	1.0	30	1.558
2.0	1.0	30	1.737
2.5	1.0	30	1.994
3.0	1.0	30	2.332
2.0	0.25	30	2.166
2.0	0.50	30	2.047
2.0	0.75	30	1.889
2.0	1.0	30	1.733
2.0	1.25	30	1.511
2.0	1.50	30	1.345
2.0	1.0	30	1.735
2.0	1.0	40	2.646
2.0	1.0	50	3.547
2.0	1.0	60	5.421

Effect of Temperature Variation: -

The reaction has been investigated at temperatures ranging from 308 to 323 K, with the findings documented in table 3. Table 4 displays the results of calculating the substrate's activation energy using the Arrhenius equation, which was then used to compute a number of additional thermodynamic parameters.

Table-3: Effect of Temperature on The Reaction Rate

Oxidant = 1.0 x10^{-3} M; Glycine = 2.0 x10^{-2} M; HClO4 = 1.0 x10^{-2} M

[Hg(AcO)R2R] = 0.002M; Solvent; water-acetic acid (v/v) 30 %

Temperature K	k × 10^{-3} min^{-1}
308	1.735
313	2.645
318	3.547
323	5.419

Table 4: Activation Parameters for The Oxidation of Glycine

Substrate	ERa (k.Jmol^{-1})	ΔH* (k.Jmol^{-1})	ΔS* (JK-1mol^{-1})	ΔG* (kJ.mol^{-1})
Glycine	58.22	55.71	108.95	89.29

V. Conclusion

The mechanistic and thermodynamic information about glycine oxidation by N-bromoanisamide in acidic medium is investigated kinetically. The reaction is first-order kinetic with respect to the oxidant and is concentration-dependent with respect to substrate concentration, which confirms the occurrence of an intermediate complex in the rate-limiting reaction. The concentration of the hydrogen ions on the inhibition effect shows the presence of protonated species that controls the rate of the reaction. Ionic strength does not have much influence on the reaction, but dielectric constant of the media has a significant effect, which shows the significance of solvent effects. The retardation that is observed in the presence of anisamide indicates that there is a reversible pre-equilibrium between reaction products. The reviewed activation parameters justify the practicability of the suggested mechanism.

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