

# Oxidation of Glycine by Ce(IV) in Nitric Acid

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## ABSTRACT

The kinetics of oxidation of glycine by Ce(IV) in nitric acid media has been carried out to explore the active kinetic species in the oxidation of glycine. A decrease in rate with increase in [Ce(IV)] is observed, such behaviour is analysed and presented on the basis of dimerisation of Ce(IV). The reaction has been studied at constant pH using acetic acid and sodium acetate buffer. The effect of varying concentration [Oxidant] and [Substrate] keeping [acetic acid] and [sodium acetate] constant. The presence of free radical in the reaction has been identified mechanism consistent with the observation is proposed and an appropriate rate law is derived.

**Keywords:** Kinetics, Glycine, Oxidation, Ce(IV)-dimer, Nitric acid.

## I. INTRODUCTION

The biological importance of amino acids proved from its metabolic role which includes the biosynthesis of poly peptides, proteins and synthesis of nucleotides [1]. The oxidation of glycine is important and received much attention due to its use in the inhibitory neurotransmitter in the central nervous system especially in the brain stem, spinal cord and retina. When glycine receptors activate, chloride enters the neuron via ionotropic receptors causing an inhibitory postsynaptic potential [2,3]. Glycine is a building block of various chemical compounds. Cell function involving the formation of DNA and RNA is glycine dependent due to its role in purine biosynthesis and improves the sleep [4]. The study of its behaviour towards oxidation can give a new area to understand the mechanism of protein and amino acid modification.

Many reports are available on kinetics of oxidation of glycine by many oxidants namely N-bromoanisamide [5], tributylammonium chlorochromate [3], tripropylammonium fluorochromate [6], iron(III)-1,10-phenanthroline complex [7], chloramine-T [8], vanadium(V) [9], manganese(III) [10], n-

bromosuccinimide [11], cerium(IV) [12], pyridinium dichromate [13] and pyridinium bromochromate [14,15].

Cerium(IV) is known oxidant in acid medium having reduction potential of the couple cerium(IV)/cerium(V) 1.70 volt. The formation of cerium(IV) complex in the form of active species in different acids were proposed.

The aim of present work is to propose the most probable cerium (IV) species reactive in the oxidation of glycine in nitric acid. The study has attracted the attention due to the specific zwitterionic nature.

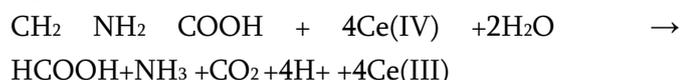
## II. METHODS AND MATERIAL

G.R. MERCK grade Glycine was used as received. The freshly prepared solution of glycine by dissolving a weight quantity of the sample in a known volume of distilled water and kept in a dark coloured glass container to avoid any photochemical reaction. The solutions were freshly prepared and standardised against standard solution. The solution of cerium (IV) ammonium nitrate LOBA (GR) was also freshly prepared and standardised against a standard solution

of ammonium ferrous sulphate Sarabhai (GR).The nitric acid BDH,AnalaR solution was standardised against a standard alkali.The nitro ferroin (G.F.Smith) solution was used with suitable dilution.

**A. Stoichiometry**

The stoichiometry in the oxidation of glycine was determine under the experimental condition to those similar condition of the kinetic study [Glycine] > 10[CeIV)].A number of reaction mixtures containing a known excess of cerium (IV) over glycine was kept at room temperture in nitric acid. The amount of Ce(IV) left revealed that 1:4 stoichiometry between glycine and cerium (IV) exists acoording to following equation.



**B. Test for Free Radical:**

The reaction mixture was degassed with nitrogen before the reaction was initiated. The addition of acrylonitrile in the partially oxidised mixture results the formation of viscous / curdy type precipitate.The observation indicated the presence of free radical in the reaction mixture.

**C. Evaluation of Rate Constant :**

Since the substrate concentration was always in excess,pseudo-first-order rate constant  $k_{\text{obs}}$  with respect to to cerium (IV) was evaluated using first order rate expression.In particular run the values was found to have a decreasing tendency in the starting of the reaction,thus it was not possible to obtain the constant value of rate constant at the initial stage.

Hence  $(-\frac{dc}{dt})$  value was calculated from the plots between remaining ceric ammonium nitrate and time.

The value of  $k_{\text{obs}}$  was calculated by deviding

$(-\frac{dc}{dt})$  value of concentration of cerium (IV) at which  $(-\frac{dc}{dt})$  was obtained.

**III. RESULTS AND DISCUSSIONS**

We have initiated the oxidation of glycine without any catalyst in nitric acid. Unfortunately the reaction between glycine and cerium(IV) in nitric acid was too slow to measure at acid concentration 0.50 mol dm<sup>-3</sup>. The aim of our study to investigate the dependence of reaction rate on initial cerium (IV) concentration at same nitric acid concentration as we have used in the oxidation of acetone[15].

The cerium (IV) has a tendency to coordinate with the ligands through N-atom and carboxalate group.The possibility of glycine to found the complex with cerium(IV) is greater than the oxidation of glycine by cerium(IV) in nitric acid.

Due to these reasons we have obtained the kinetic condition by using buffer solution of constant pH nearly equal to the isoelectric point of glycine(pH=5.89).The results obtained are given below.

**A. Dependence of Rate on Initial Cerium (IV) Concentration:**

The effect of cerium (IV) concentration  $k_{\text{obs}}$  was investigated at constant concentration of hydrogen ion and alcohol and ionic strength at constant pH.The effect of varying initial cerium(IV) was investigated over a range 0.0014-0.0056 mol dm<sup>-3</sup>.The plot between  $k_{\text{obs}}$  and [cerium(IV)]<sup>-1</sup> was found to be linear which passed through origin. The result obtained are given in table 1 and the plot between  $k_{\text{obs}}$  and [cerium(IV)]<sup>-1</sup> is represented in Figure 1.

**Table 1.** Dependence of  $k_{\text{obs}}$  on Initial Cerium (IV) Concentration at 298K ( $\mu=0.90$  mol dm<sup>-3</sup>)

[H<sup>+</sup>] = 0.575 mol dm<sup>-3</sup> [NO<sub>3</sub><sup>-</sup>] = 0.575 mol dm<sup>-3</sup>

10 <sup>3</sup> [Ce(IV)] mol dm <sup>-3</sup>	Glycine 10 <sup>4</sup> $k_{\text{obs}}$ (s <sup>-1</sup> )
1.4	2.23
2.1	1.48
2.8	1.08

4.2	0.74
5.6	0.57

[Glycine] = 0.40 mol dm<sup>-3</sup> [Acetic acid] = 0.10 mol dm<sup>-3</sup>  
 [Sodium acetate] = 0.19 mol dm<sup>-3</sup>

$$k_{\text{obs}} \text{ v/s } [\text{Ce(IV)}]^{-1}$$

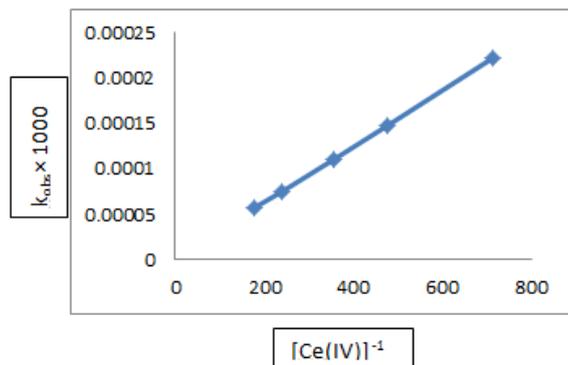


Figure1

### B. Dependence of Rate on Initial Glycine Concentration:

The effect of varying initial glycine was investigated over a range 0.4-1.6 mol dm<sup>-3</sup>. The results obtained followed the first order with respect to (glycine). A plot between  $k_{\text{obs}}$  and [Glycine] was linear which passed through the origin. The data obtained are given in Table 2 and the representative plot is given in Figure.2

**Table 2.** Dependence of  $k_{\text{obs}}$  on Initial Glycine Concentration at 298 K, ( $\mu=0.90$  mol dm<sup>-3</sup>)

[H<sup>+</sup>] = 0.575 mol dm<sup>-3</sup> [NO<sub>3</sub><sup>-</sup>] = 0.575 mol dm<sup>-3</sup>  
 $10^3 [\text{Ce(IV)}] = 1.40$  mol dm<sup>-3</sup> [Acetic acid] = 0.10 mol dm<sup>-3</sup>  
 [Sodium acetate] = 0.19 mol dm<sup>-3</sup>

[Glycine] mol dm <sup>-3</sup>	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
0.4	0.20
0.6	0.30
0.8	0.40
1.2	0.57
1.6	0.80

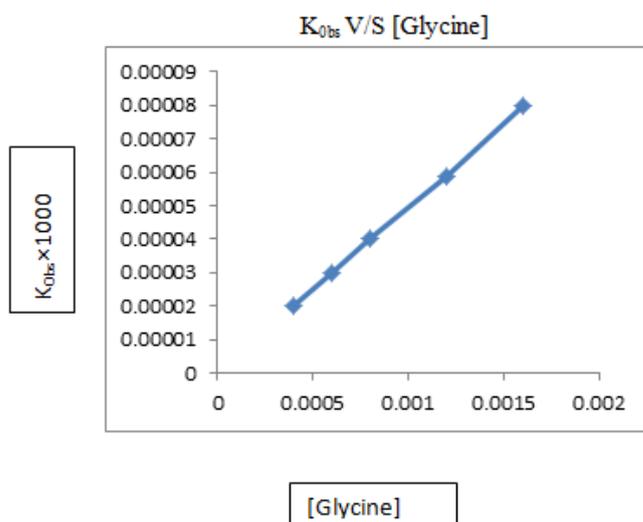


Figure 2

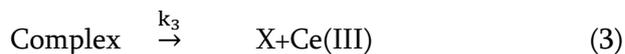
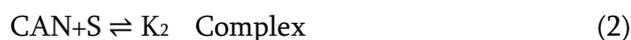
### C. Mechanism

Many reports are available [5-15] in the literature on the kinetics of oxidation of amino acids by a variety of metal and non-metal oxidants. Generally the oxidation of amino acids involves the cleavage of a C-H bond as well as of N-H bond in the rate determining step. In acidic medium amino acids exist in its protonated form which is resistant to the attack of an oxidant. In our study it is not possible that the protonated form or a mixture of protonated, zwitterionic and neutral form.

At constant pH in nitric acid medium it is reasonable to assume that the cerium may form the complex with amino acid or undergo dimerisation as in the case of acetone[15]. Hence we suggest the following mechanism for the oxidation of glycine.



(CAN)



$$-\frac{d[\text{Ce(IV)}]}{dt} = k_3 K_2 [\text{CAN}] [\text{S}] \quad (5)$$

Now it is assumed as a major approximation that the ceric ammonium nitrate depending upon the acid [16]. may form complex or remains in dimeric form with cerium (IV). The concentration of cerium (IV) is

negligible in comparison to the contraction of CAN,Ce(IV)-dimer and Ce(IV)-amino acid complex. The rate of disappearance of cerium(IV) may be given by equation (5)

or

$$k_{obs} = \frac{k_3 K_2 [S]}{k_3 K_2 [S] + K_1 [Ce(IV)]} \quad (6)$$

The equation (6) can be rearranged in the form of equation (7)

$$k_{obs} = \frac{1}{1 + \frac{K_1 [Ce(IV)]}{k_3 K_2 [S]}} \quad (7)$$

Now under our experimental conditions the ratio of [Ce(IV)] and [Substrate] is nearly 10<sup>-2</sup>. Hence the equation (7) can be approximated to equation (8) without any serious error.

$$k_{obs} = \frac{k_3 K_2 [S]}{K_1 [Ce(IV)]} \quad (8)$$

The equation (8) is the rate law in agreement with our results, the plot between 1/[Ce(IV)] vs k<sub>obs</sub> is a straight line having intercept value zero. Similarly the plot between [Glycine] k<sub>obs</sub> is linear in nature.

At constant cerium(IV) concentration the rate law can be written as

$$k_{obs} = A \cdot [Glycine] \quad (9)$$

where  $A = \frac{k_3 K_2 [S]}{K_1 [Ce(IV)]}$  is the slope value for the plot [Glycine] vs k<sub>obs</sub>. Secondly the slope value A' for the plot [Ce(IV)]<sup>-1</sup> vs k<sub>obs</sub>.

$$A' = \frac{k_3 K_2 [S]}{K_1}$$

It is interpreted as an indication for the correctness of the proposed mechanism that the slope values obtained for both curves should follow the relation.

$$\frac{k_3 K_2}{K_1} = \frac{A'}{[S]} = A \cdot [Ce(IV)] = X \quad (10)$$

The values of X calculated from the curves are compared for both the reactants and substrates. It is to be noted that there is a satisfactory agreement between two values. The values are given below.

**Table 3**

Curve	Slope	[S] or [Ox]	'X' value
[Ce(IV)] <sup>-1</sup> vs k <sub>obs</sub>	0.003×10 <sup>-4</sup>	0.40	7.5×10 <sup>-7</sup>
[s] vs k <sub>obs</sub>	5.00×10 <sup>-4</sup>	0.0014	7.0×10 <sup>-7</sup>

Finally it should be pointed out that without considering the formation of dimeric cerium(IV) it is difficult to explain the differing dependence of the rate on the initial cerium(IV) in the oxidation of glycine in the present study and also in the case of catalysed oxidations.

#### IV. CONCLUSION

The reaction between cerium (IV) and glycine in nitric acid medium at 298<sup>o</sup> K has specific nature due to decrease in the rate of reaction with increasing initial concentration of cerium(IV). The cerium (IV)-dimer in nitric acid as a reactive specie in the oxidation of glycine has been observed with the justification of experimental results.

#### V. ACKNOWLEDGEMENT

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#### VI. REFERENCES

- [1]. Barret G C. Amino acids, peptides and proteins. Royal society of Chem. UK. 1998, 29.
- [2]. Lynch JW. Molecular structure and function of glycine receptor chloride channel. Physiological reviews. 2004, vol. 84 (4).
- [3]. Prabhakar K.; Hussain S. Kinetics of oxidation and mechanism of glycine by tributylammonium chlorochromate in acid medium. Int. J. Phar. Phceu. Rea. 2017, vol. 10(3), 224-234.
- [4]. Yamadera W.; Inagawa.; Chiba S.; Bannai M.; Takahashi M.; Nakayama K. Glycine ingestion improves subjective sleep quality in human volunteers, correlating with polysomnographic

- changes. Sleep and Biological Rhythms. 2007, vol.5,(2),126-131.
- [5]. Malviya LN.;Siriah VK.;Badole MK. Kinetics and mechanism of oxidation of glycine by N-bromoanisamide. Int.J. Inn.Sci.Engg.Tech.2015, vol .2,(12),565-570.
- [6]. Kempe Gowda BK.;Prashanth PA. Kinetics of oxidation of  $\alpha$ -amino acids by Tripropylammonium florochromate (TriPAFC) in acid medium. Int.J.Chem.Tech.Rea.2011, vol.3,(4),190 6-913.
- [7]. Partha Sarathi TVN.;kumar AK.;Kishore KK.;Vani P. Kinetics and mechanism of oxidation of glycine by iron(III)-1,10 phenanthroline complex in perchloric acid medium. J.Chem.Sci. 2005, vol.117,(4),329-332.
- [8]. Grover N.;kambo N.;Upadhyay SK. Kinetics and mechanism of palladium(II) catalysed oxidation of some  $\alpha$ -amino acids by chloramine-T in perchloric acid. Indian.J.Chem. 2002, vol.41A,2482-2488.
- [9]. Joshi SK.;Kandpal ND. Kinetics of Ruthenium (III) catalysed oxidation of amino acids by vanadium(v) in aqueous perchloric acid. Phy.Chem A.Indian.J. 2006, vol.1 (4),106-111.
- [10]. Singh R.;Tamta DK.;Joshi SK.;Chandra N.;Kandpal ND. Oxidation of amino acids by manganese (III) in aqueous sulphuric acid. J.Chem.Pharm.Res. 2011, vol.3,(1),529-535.
- [11]. Singh AK.;Singh RK.;Srivastava J.;Rahmani S.;Yadav S. Kinetic and mechanistic studies of oxidation of glycine and valine by N-bromosuccinimide using chloro complex of Rh(III) in its nano-concentration range as homogeneous catalyst. Indian.J.Chem.2012, vol.51A,681-689.
- [12]. Sumathi T.;Shanmugasundram P.;Chandramohan G.;Deepa D.;Renganathan R. A kinetic and mechanistic study on the silver(I)-catalysed oxidation of L-Glycine by cerium (IV) in sulphuric acid medium. Int.J.Chem.Sci.Tech. 2012, vol.2,(3),44-51.
- [13]. Rathor S.;Dhangarh BK. Kinetics and mechanism of oxidative transformation of some amino acid by pyridinium dichromate in DMF-Water medium. Int.J.Sci.Res. 2015, vol.6. (2),352-354.
- [14]. Hasin BL.;Nalwaya.;Jain A. Kinetics of oxidation of glycine by pyridinium brochromate in acetic acid medium. J.Ind.Chem.Soc.2002, vol.79,(7),587-589.
- [15]. Chandra B.;Pandey K.; Kandpal ND. Kinetics and mechanism of cerium (IV) Oxidation of acetone in nitric acid. J.Chem& Chemi.Sci.2018, vol.8,(1),48-54.
- [16]. Tamta DK.;Chandra B.;Joshi SK.;Kandpal ND. Oxidation of sugars by Ce (IV) in aqueous sulphuric acid: kinetic and viscometric approach. Int.J.Res.App.Natu. &So. Sci.2017, vol.5, (8),51-58.