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KINETICS AND MECHANISM OF RUTHENIUM(III)-CATALYZED OXIDATION OF GLYCINE BY CERIUM(IV) IONS IN ACIDIC MEDIUM

SAMSON O. OWALUDE^{1*}, EZEKIEL O. ODEBUNMI¹, ADEDIBU C. TELLA¹, CHRISTIANA A. BAMIGBOYE², AYINDE². ADEBAYO² AND ADENIYI S. OGUNLAJA³

^aDepartmentof Chemistry, University of Ilorin, P. M. B. 1515, Ilorin, Nigeria ^bDepartmentof Industrial Chemistry, University of Ilorin, P. M. B. 1515, Ilorin, Nigeria ^cDepartment of Chemistry, Nelson Mandela Metropolitan University, PO Box 77000, Port Elizabeth 6031, South Africa

Abstract

Kinetics of oxidation of glycine in acidic solution of cerium(IV) ions in presence of ruthenium(III) ions were studied. The reactions were found to be first-order with respect to [glycine], [Ru(III)] and [Ce(IV)]. The rate is proportional to $[H^+]$ while the rates was decreased with increasing [Ce(IV)], [HSO4⁻] and ionic strength of the medium. The observed kinetic data and the spectroscopic evidence lead to the conclusion that HCHO, (NH_3^+) ,-COOH, $[RuCl_2(H_2O)_4]^+$ and $Ce(SO_4)_2$ were the reactive species of glycine, Ru(III) chloride and cerium(IV) ions, respectively. Based on the kinetic data, the mechanism of the reaction for the catalytic path was proposed. It was found that Ru(III) chloride forms an intermediate complex, which subsequently reacts with the active form of Ce(IV) to yield the product with regeneration of Ru(III). Activation parameters were evaluated and provided further support to the proposed mechanism.

Keywords: Kinetics, cerium(IV), glycine, ruthenium(III) chloride, activation parameters, catalysis

Introduction

L-Glycine is a neurotransmitter inhibitor in the central nervous systemmost especially in the spinal cord and retina.¹ The study of the kinetics and mechanism of oxidation of *L*-glycine is therefore of immense importance. Kinetic studies on the oxidation of glycine by one-electron, two-electron and a series of multi-electron oxidants have been reported.^{2,6}

The mechanism of action of these catalysts have been proposed in some cases based on the formation of intermediate complexes⁷, while in others the results were analyzed on the basis of formation of free radicals.⁸ Oxidation reactions using Ru(III) as catalyst involves several active species of ruthenium depending on the reaction media and oxidation states of ruthenium.⁹⁻¹⁰ Therefore we investigated the kinetics and mechanism of Ru(III) catalyzed oxidation of glycine by cerium(IV) in aqueous sulphuric acid medium in order to clarify the mechanism by identifying the active forms of Ru(III), cerium(IV) and glycine.

Experimental

All chemicals were procured from BDH or Sigma Aldrich. Ce(IV) solution was prepared by dissolving cerium(IV) ammonium sulphate in 0.1 mol dm⁻³ sulphuric acid and was standardized with iron(II) ammonium sulphate solution.¹⁴ 0.1 mol dm⁻³ glycine stock solution was prepared freshly before use by dissolving 0.7506 g in 100 mL of double distilled water. Stock solution of Ru (III) (0.01 mol dm⁻³) was prepared by dissolving 0.2074 g RuCl₃ in 100 mL of 0.20 mol dm⁻³ HCl and the concentration was always checked using EDTA titration.¹¹

Cyclic Voltammetry Studies

The electrochemical oxidation analysis was done using an *Epsilon* Version 1.30.64 system. Three electrode systems were employed: a platinum wire (3 M KCl in water) was used as the reference

^{*} Email: sowalude@gmail.com

electrode, a platinum electrode served as the working electrode, and the counter electrode. The instrumental parameters for CV sweeps were as follows: potential range from 0 to+1 V; modulation time: 0.05 s; interval time: 2 s; scan rate: 50 mV/s, and pulse amplitude: 100 mV.

Spectral measurement

UV-Vis absorption spectrum of 0.01 mol dm⁻³ solution of Ce(IV) was measured from 300 to 800 nm region. The wavelength corresponding to maximum absorbance (λ_{max}) was found to be 395 nm.

Kinetic measurements

Kinetic experiments were performed at 35 ± 0.5 °C and I=0.20 mol dm⁻³ by following a reported procedure.⁹ The reaction was carried out under pseudo-first order conditions, with glycine in excess of the oxidant and the progress of the reaction was monitored by estimating the decrease in the absorbance of Ce(IV) ion at time intervals at a wavelength of 395 nm using a Beckman Coulter DU 730 UV–Vis spectrophotometer. The reaction was deemed to be completed when Ce(IV)-glycine solution turned from yellow to colorless. Kinetic runs were followed for more than 80% completion of the reaction and the observed first-order rate constants, log [Cerium(IV)] *vs* time. The calculated rate constants were averages of at least three measurements and were reproducible to within $\pm 5\%$.

Product analyses

The reaction mixture was kept under the reaction condition for 24 hr a few drops of freshly prepared Tollen's reagent was added, and deposition of silver as a thin film silver generated from HCHO on the inner surface of the beaker was observed. CO₂ and NH₃ liberated during the reaction were identified using standard procedures.¹²

Evidence for the formation of Ce(III) product

Cyclic voltammetry (CV) studies were carried out, CV studies showed reversible redox peak Ce(III)/Ce(IV) for both systems. The cerium complex before use exhibited a pair of well-defined reversible redox peaks at ~630 mV and ~151 mV, which are attributed to the oxidation and reduction processes. The Ce complex after use in the presence of glycine also exhibited a similar well-defined reversible redox peaks at ~620 mV and ~150 mV.

Stoichiometry

The reaction mixture containing the excess of Ce(IV) concentration over glycine with both solutions prepared in 0.10 mol dm⁻³ H₂SO₄ at a constant ionic strength of 0.20 mol dm⁻³, maintained by NaSO₄, was kept at 25 ± 2 °C for 48 hr. The unreacted Ce(IV) was then analyzed spectrophotometrically.

Polymerization study

Formation of free radicals in the reaction was investigated by the addition of a known quantity of aqueous 20% acrylamide into the reaction mixture at the initial stage and the mixture was kept in an inert atmosphere for 24 hr. Control experiments did not show gel formation of gel. On further dilution the reaction mixture with methanol, no precipitate was formed thus confirming the absence of free radicals in the reaction.

Results and Discussion

Variation of Kobs with reactant concentration

The reactions were studied at different initial Ce(IV) concentrations with all other parameters kept constant. The observed rate constants (k_{obs}) were then obtained from the slope of log[Ce(IV)] vs time plots. The values of k_{obs} show (Table 1) that the observed rate constants were almost constant with increasing initial concentrations of Ce(IV) which is an indication that the order with respect to Ce(IV) was unity.¹³ In another set of experiments, the observed rate constants (k_{obs}) were evaluated at different initial concentrations of the glycine keeping all other parameters constant.

[H ⁺]	[Glycine] [RuCl ₃] \times 10 ⁷ μ		[Ce(IV)] x 10 ³		$k_{ m obs} imes 10^4$
(mol dm ⁻³)	(mol dm ⁻³)	(mol dm ⁻³)	(mol dm ⁻³)	(mol dm ⁻³)	(S ⁻¹)
0.05	0.015	5.0	0.20	1.0	5.62
0.10	0.015	5.0	0.20	1.0	5.05
0.15	0.015	5.0	0.20	1.0	4.60
0.20	0.015	5.0	0.20	1.0	4.31
0.25	0.015	5.0	0.20	1.0	4.06
0.30	0.015	5.0	0.20	1.0	3.77
0.35	0.015	5.0	0.20	1.0	2.47
0.10	0.035	5.0	0.20	1.0	3.40
0.10	0.050	5.0	0.20	1.0	4.96
0.10	0.065	5.0	0.20	1.0	6.43
0.10	0.095	5.0	0.20	1.0	9.00
0.10	0.150	5.0	0.20	1.0	13.92
0.10	0.015	1.0	0.20	1.0	1.39
0.10	0.015	3.0	0.20	1.0	1.76
0.10	0.015	7.0	0.20	1.0	2.16
0.10	0.015	9.0	0.20	1.0	2.40
0.10	0.015	11.0	0.20	1.0	2.93
0.10	0.015	13.0	0.20	1.0	3.06
0.10	0.015	5.0	0.20	2.0	5.83
0.10	0.015	5.0	0.20	3.0	5.81
0.10	0.015	5.0	0.20	4.0	4.98
0.10	0.015	5.0	0.20	6.0	5.88
0.10	0.015	5.0	0.20	7.0	5.76
0.10	0.015	5.0	0.05	1.0	5.62
0.10	0.015	5.0	0.10	1.0	5.05
0.10	0.015	5.0	0.15	1.0	4.60
0.10	0.015	5.0	0.25	1.0	4.06
0.10	0.015	5.0	0.30	1.0	3.77
0.10	0.015	5.0	0.35	1.0	2.47

Table 1: Effect of various parameters on the observed first-order rate constants k_{obs} forRu(III) catalyzed oxidation of glycine by Ce(IV) at 35 °C.

Variation of *K*_{obs} with [H⁺]

The effects of variation of acidity on the rate of the reaction were investigated at different initial concentration of perchloric acid at fixed ionic strength of 0.1 mol dm⁻³ with other parameters maintained constant. The rate constants decreased with increasing acid concentration which is attributed to the protonation of Ru(III) in the acidic medium.¹⁴

Variation of *k*_{obs} with ionic strength

The effect of ionic strength was studied by varying the Na_2SO_4 concentration in the reaction medium from 0.05 to 0.35 mol dm⁻³ while maintaining constant the other parameters. The results revealed a slight decrease in rate constant with increase in Na_2SO_4 concentration. This may be attributed to the removal of active species of Ce(IV) as concentration of SO_4^{2-} increases in agreement with literature reports.¹⁵

 $Ce(SO_4)_2 + SO_4^{2-} \underbrace{\longrightarrow} Ce(SO_4)_3^{2-} (1)$

Variation of *k*_{obs} with [HSO₄⁻]

The effect of $[HSO_4^-]$ on the rate was investigated at different initial concentration of NaHSO₄ between 0.1-2.3 mol dm⁻³ while maintaining constant the other parameters. The rate constants decreased with increase in the concentration of HSO_4^- . This is consistent with the effect of increase in the concentration of SO_4^{2-} as represented by equation (1).

Variation of kobs with Ru(III) ion concentration

The oxidation reaction was carried out in the presence of different initial concentrations of ruthenium trichloride. The concentration of Ru(III) ion was varied from 1.0×10^{-7} mol dm⁻³ to 13.0×10^{-7} mol dm⁻³ at the pH of 1.0 while maintaining constant the other parameters. The rate constant increased with increase in the concentration of the Ru(III) ion. The reaction rate was found to be proportional to [Ru(III)].¹⁶

Variation of *K*_{obs} with temperature

The oxidation reactions in the presence of Ru(III) chloride and without Ru(III) were carried out at different temperatures between 15-75°C while maintaining constant the other parameters. The observed first-order rate constants both cases increased with increase in temperature. The rate constants, k_2 and k_5 , corresponding to the slow steps of the mechanism were obtained from the relation $k = k_{obs}/[glycine]$ at different temperatures and were used to calculate the activation parameters. The entropy of activation in each case was found to be negative, suggesting the compactness of the transition state as compared to the ground state.

Table 2: Effect of temperature on the observed first-order rate constants for the Ru(III)-catalyzed and uncatalyzed oxidation of glycine by Ce(IV) ions in acidic medium. [Glycine] = $0.015 \text{ mol dm}^{-3}$, [Na₂SO₄] = 0.20 mol dm^{-3} , [Ce (IV)] = $0.001 \text{ mol dm}^{-3}$, [H⁺] = 0.1 mol dm^{-3} , [RuCl₃] = $5 \times 10^{-7} \text{ mol dm}^{-3}$

Temp. (K)	$k_{\rm obs} \times 10^4 { m s}^{-1}$ (uncatalyzed path)	$k_2 \times 10^2$ mol dm ⁻³ s ⁻¹	$k_{obs} \times 10^4 s^{-1}$ (catalyzed path)	k2×10 ² mol dm ⁻³ s ⁻¹
288	0.15	0.10	0.71	0.47
298	0.23	0.16	1.63	1.09
308	0.45	0.31	2.69	1.79
318	0.70	0.47	3.99	2.66
328	1.00	0.67	5.70	3.80
338	1.62	1.08	8.55	5.70
348	2.62	1.75	14.00	9.33

Reactive species of the glycine

The amino acid glycine in acidic medium can be protonated at both the amino group and the carboxylic group.⁶ The pK value for the amino group on glycine has been reported as greater than 9.1 and that for the carboxylic group as 2.35.⁶ The pH of the medium of the reaction was maintained below 2.0 throughout the studies; in that condition the NH₂ group of glycine will be protonated as -NH₃⁺ according to the following equilibrium:

 $NH_2CH_2COOH + H^+$ $NH_3^+CH_2COOH (2)$

The reactive species of glycine in Ru(III)-catalyzed oxidation of glycine by Ce(IV) ion in acidic medium was NH₃+CH₂COOH.

Reactive species of Ce(IV) ion

In sulphuric acid media Ce(IV) was reported to exist in different Ce(IV)-sulphate forms such as $Ce(OH)^{3+}$, $Ce(SO_4)_{4^{2+}}$, $Ce(SO_4)_{2}$, $Ce(SO_4)_{2}(HSO_4)$ and $H_3Ce(SO_4)_{4}$.^{7-10,23-25} Among these different Ce(IV)-sulphato species, the kinetically active one has been reported as Ce(SO_4)_2. On the basis of the observed kinetic data of the active species of Ce(IV) was considered as Ce(SO_4)_2.

Reactive species of Ru(III) chloride

Ru(III) chloride in aqueous solution exists in the form of a number of chloro complexes and the species that have been characterized in solution are $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{.2+26}$ The species $[RuCl_4(H_2O)_2]^-$ was reported as the most stable in highly acidic medium

below the pH of 0.4 and at higher pH between 0.4-2.0, $[RuCl_2(H_2O)_4]^+$ become the most stable.²⁷ The stability of all the ruthenium species decreases with increasing pH and all the other unstable species were converted to $[RuCl_2(H_2O)_4]^+$ within this pH range (0.4-2.0).²⁷ This stable species was always in equilibrium with its hydrolyzed form $[RuCl_3(H_2O)_3OH]$ as represented by equation 5 below:

 $[RuCl_2(H_2O)_4]^+ + H_2O \quad \fbox{RuCl_2(H_2O)_3OH]} + H_3O^+ (3)$

In strong acidic medium the following equilibrium reaction has been reported

 $[RuCl_2(H_2O)_3OH] + H^+$ [RuCl_2(H_2O)_4]⁺ (4)

Throughout the reaction, the $[H^+]$ was maintained at 0.1 mol dm⁻³, therefore the species $[RuCl_2(H_2O)_4]^+$ is considered as the active species of Ru(III) chloride in these reactions. The negative effect of $[H^+]$ observed in this experiment can therefore be explained in terms of formation of $[RuCl_2(H_2O)_4]^+$ according to the equilibrium expressed in equation 4.

Evidence for the formation of complexes in the reactions under investigation

Formation of a complex between the amino acid and RuCl₃ proposed in step 4 (4) of the mechanism was further investigated using spectrophotometric technique. The UV-visspectrumrecorded for the solution of Ce(IV) and RuCl₃ in acidic medium RuCl₃ and glycine was reported. It was found that there was an increase in absorbance from 0.38 to 0.82 with a shift in λ_{max} towards longer wavelength from 313 to 329 nm, an indication of a complex formation between Ru(III) and glycine.^{28,29} This provides extra evidence for the formation of complex species [Ru(III)-Glycine] between the Ru(III) catalyst and glycine.³⁰ Similar experiment performed in the absence of RuCl₃ did not show any significant increase in absorbance and λ_{max} , an indication that no complex formation between Ce(IV) and glycine in agreement with the proposed mechanism. The platinum group metals have been reported as active promoters of the N–H bond activation³¹ and the proposed complex formation between Ru(III) and glycine in this study is therefore plausible. The observed increase in the rate with increase in Ru(III) concentration also supports the formation of an intermediate complex between Ru(III) and glycine.²⁰

Reaction mechanism

Based on the kinetic data that revealed a first-order dependence in Ce(IV), glycine and Ru(III) chloride, an inverse dependence on H^+ ion concentration the following mechanism is proposed for the Ru(III)-catalyzed oxidation of glycine:

$$NH_{2}CH_{2}COOH + H^{+} \stackrel{K_{1}}{\leftrightarrow} NH_{3} CH_{2}COOH (5)$$

$$NH_{2}CH_{2}COOH + 2Ce(SO_{4})_{2} \stackrel{k_{2}}{\underset{slow}{\longrightarrow}} HCHO + NH_{3} + CO_{2} + 2Ce(III) (6)$$

$$[RuCl_{2}(H_{2}O)_{2}OH] + H^{+} \stackrel{k_{3}}{\underset{\approx}{\longrightarrow}} RuCl_{2} [RuCl_{2}H_{2}O)_{4}]^{+} (7)$$

$$NH_{3}^{+}CH_{2}COOH + [RuCl_{2}(H_{2}O)_{4}^{+} \stackrel{k_{4}}{\underset{\approx}{\longrightarrow}} Complex (C) (8)$$

$$Complex (C) + 2Ce(SO_{4})_{2} \stackrel{k_{5}}{\underset{slow}{\longrightarrow}} HCHO + NH_{3} + CO_{2} + 2Ce(III) (9)$$

According to the mechanism, the reactive species of *L*-glycine formed an intermediate complex with the reactive species of the catalyst which then reacts in a slow step with one mole of the active form of Ce(SO₄)₂ to give the products Ce(III), HCHO, CO₂ and NH₃ in a slow step. Spectrophotometric evidence lend further support to the formation of an intermediate complex between Ru(III) and *L*-glycine. The kinetic results obtained in the present study is consistent with the 1-electron reduction of Ce(IV) as established by the cyclic voltammetry results and by other several authors.^{3,7-12} The dependence of the reaction rate on the ionic strength of the medium showed a marginal decrease as μ increases from 0.05 to 0.35 mol dm.⁻³ Such negligible effect of ionic strength on the reaction rate is consistent with reactions between reactants bearing opposite sign in which one is a neutral molecule.⁴ In this case as expressed in equation 10 of the mechanism, the rate determining step involved a cationic

40

intermediate complex C and neutral Ce(SO₄)₂ molecule in agreement with the kinetic data. Ru(III) catalyst has been reported to be very ineffective in sulphuric acid because of the absence of the known active form of Ru(III), [Ru(H₂O)₆]³⁺, in many reactions conducted in media other than acidic.³² The small difference obtained between the activation energy values for the uncatalyzed path and the catalyzed path in this study is also consistent with this assertion. Equation (6) is in agreement with the kinetic results on the variation of *kobs* with Ru(III) chloride. The negative entropy of activation, Δ S, obtained in this study suggests the compactness of the transition state compared to the ground state.²²

The kinetics of reaction are described in rate law given below:

The rate of disappearance of Ce(IV) according to the above mechanism may be derived as follows:

Rate = $2k_2 [GLY^+][Ce(IV)] + 2k_5[C][Ce(IV)]$ (10)

For the uncatalyzed path, the rate is given by:

Rate₁ = $2k_2 [GLY^+][Ce(IV)]$ (11)

The total glycine concentration $([GLY]_T)$ will be the addition of the protonated glycine $([GLY^+])$ and the free glycine ([GLY]), therefore,

 $[GLY]_{T} = [GLY^{+}] + [GLY] \quad (12)$

And from equation 5

 $[GLY^+] = K_1[GLY][H^+]$ (13)

Substitute for [GLY]^T in equation 12

 $[GLY]_T = K_1[GLY][H +] + [GLY] (14)$

Hence,

 $[GLY] = \frac{[GLY]_T}{1 + k_1[H^+]} (15)$

The rate of reaction for this path is therefore,

 $Rate_{1} = \frac{2k_{2}[GLY]_{T}[Ce(IV)]}{1 + k_{1}[H^{+}][GLY]_{T}} (16)$

For the catalyzed path, the rate of the reaction is given by:

Rate $2 = 2k_5[C][Ce(IV)]$ (17)

and application of steady state approximation to [C] yields

$$[C] = \frac{k_4 [GLY^+] [Ru(III)^+]}{k_{-4} + 2k_5 [Ce(IV)]^2} (18)$$

Where $[Ru(III)^+]$ is the protonated Ru(III) molecule according to equation (7) in the mechanism. The total glycine concentration in this path is:

 $[GLY]_T = [GLY^+] + [C], [GLY^+] = [GLY]_T - [C]$ (20)

Putting this value of [GLY⁺] in equation 20 and solving for [C] yields:

$$[C] = \frac{k_4 [CLY]_T [Ru(III)^+]}{k_{-4} + 2k_5 [Ce(IV)]^2 + k_4 [Ru(III)^+]} (21)$$

Step 4 of the mechanism is very fast compared to the rate determining step 5, therefore the inequality $k_{4} > 2k_5 [Ce(IV)]^2$ may be taken as valid and under very low Ru(III) concentration as in the present study the term k4 [Ru(III)] is negligible. Under this condition, equation (20) reduces to:

 $[C] = K4 [GLY]_T [Ru (III)^+]$ (21)

Where $K_4 = \frac{k_4}{k_4}$

From equation (7),

 $[Ru (III)^+] = K_3 [Ru (III)] [H^+] (22)$

Therefore,

 $[C] = K_3K_4 [GLY]_T [Ru(III)] [H^+]$ (23)

And the rate of the catalyzed path will be given by

Rate₂ = $2k_5K_3K_4$ [GLY]_T [Ru(III)] [H⁺] [Ce(IV)] (24)

The overall rate of the reaction is therefore,

$$Rate = \left\{ \frac{2k_2[GLY]_T[Ce(IV)]}{1 + k_1[H^+]} + 2k_5k_3k_4[GLY]_T[Ru(III)][H^+[Ce(IV)] \right\} (25)$$

The rate law is therefore reduced to:

 $Rate = 2[GLY]_{T}[Ce(IV)] x \left\{ \frac{k_{2}}{1+k_{1}[H^{+}]} + k_{5}k_{3}k_{4}[Ru(III)][H^{+}] \right\} (26)$

The rate law in equation 26 agrees with the kinetic results *i.e.* the first-order rate dependence on Ce(IV) and glycine concentrations. The proportionality of the rate on $(k+k_x [Ru(III)])$ as obtained in Fig. 4 where $k = k_2/(1+K_1[H^+])$ and $k_x = k_5K_3K_4[H^+]$. The decrease in rate observed with respect to increase in [H⁺] also conforms to equation 26.

Conclusions

The following conclusions were drawn from the observed kinetic data and spectra information collected for the Ru(III)-catalyzed oxidation of glycine by Ce(IV) ions in acidic medium:

- i. The reactive species of Ce(IV), Ru(III) chloride and glycine under the present reaction condition are Ce(SO₄)₂, [RuCl₂(H₂O)₄]⁺ and NH₃⁺CH₂COOH, respectively.
- ii. The existence of the complex specie between $[RuCl_2(H_2O)_4]^+$ and $NH_3^+CH_2COOH$ is supported by the spectral information collected.
- iii. The observed negative entropy of activation for the oxidation of glycine supports the formation of rigid activated complex as proposed in step 10 of the reaction mechanism.
- iv. A rate law consistent with the mechanism was derived.

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42

SAMSON O. OWALUDE, EZEKIEL O. ODEBUNMI, ADEDIBU C. TELLA et al

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