

Research Article

Kinetics and Mechanism of Silver(I)-Catalyzed Oxidations of α -Aminobutyric Acid by Platinum(IV) in Perchloric and Sulfuric Acid Solutions

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Abstract

The kinetics of oxidations of α -aminobutyric acid (ABA) by platinum(IV) has been investigated spectrophotometrically in perchloric and sulfuric acids solutions in the presence of silver(I) catalyst at a constant ionic strength of 1.0 mol dm⁻³ and at 25°C. The reactions were very slow to be measured in the absence of the catalyst. The reactions in both acids showed a first order dependence on [Pt^{IV}] and less than unit order dependences with respect to [ABA], [H⁺] and [Ag^I]. Increasing ionic strength and dielectric constant was found to decrease the oxidation rates. Under comparable experimental conditions, the oxidation rate of α -aminobutyric acid in perchloric acid solutions was approximately found to be twice that recorded in sulfuric acid solutions. A plausible oxidations mechanism has been proposed and the rate law expression has been derived. Both spectral and kinetic evidences revealed formation of 1:1 intermediate complexes between ABA and Ag^I in both acids before the rate-controlling step. Then the formed complexes react with the oxidant (Pt^{IV}) by an inner-sphere mechanism to give rise to the oxidation products of ABA which were identified as the corresponding aldehyde (propionaldehyde), ammonium ion and carbon dioxide. The activation parameters of the second order rate constants were evaluated and discussed.

Keywords: α -Aminobutyric acid; Oxidation; Silver(I) catalyst; Platinum(IV); Kinetics; Mechanism

Introduction

Amino acids play a significant role in the metabolism and the specific metabolic role of them includes the biosynthesis of polypeptides and proteins, as well as the synthesis of nucleotides. Oxidation of amino acids is a significant field of organic chemistry because of its bearing on the mechanism of amino acid metabolism. Kinetics of oxidation of amino acids by various oxidants in different media has been studied earlier [1-18], and they often undergo oxidative decarboxylation and deamination. α -Aminobutyric acid (ABA), is a non-proteinogenic alpha amino acid which is biosynthesised by transaminating oxobutyrate, a metabolite in isoleucine biosynthesis.

The chemistry of biologically active platinum(IV) complexes has increased interest in the last decades due to their remarkable anticancer properties [19-22]. Kinetic studies on the oxidation of inorganic and organic substrates using one of the platinum(IV) complexes such as hexachloroplatinate(IV) complex, [PtCl₆]²⁻, are scarce and limited to a few cases [10-16,23-26], in which [PtCl₆]²⁻ may behave as one or two electron oxidant, depending upon the substrate and experimental conditions. The knowledge of the reactivity of platinum(IV) compounds towards their reduction by potential bioreductant such as α -aminobutyric acid may be important for understanding the mechanism of where antitumor activity as well as for designing new compounds with the least side effect.

Transition metal ions have been widely employed as homogenous catalysts for oxidation of organic and inorganic substrates [7-17] by

different reaction pathways such as formation of complexes with the reactants, oxidation of a substrate, or the formation of free radicals [27]. Kinetic investigations on the oxidation of amino acids catalyzed by different metal ions are an important field of chemistry due to the role played by metals in biological systems.

Literature survey reveals that there are no reports about the kinetics of oxidation of α -aminobutyric acid by any oxidant. In view of the above mentioned arguments, we have carried out a detailed study on the kinetics and mechanism of oxidation of this important amino acid by biologically active platinum(IV) in different acid media, namely perchloric and sulfuric acids solutions in the presence of silver(I) catalyst. This work aims to study the selectivity of the studied amino acid towards platinum(IV) in acid media, to check the catalytic efficiency of Ag^I catalyst, and to elucidate a plausible reaction mechanism.

Experimental

Materials

Reagent grade chemicals and doubly distilled water were used throughout the work. A stock solution of α -aminobutyric acid was prepared afresh by dissolving the amino acid sample (E. Merck) in bidistilled water. Chloroplatinic acid solution (Johnson Matthey) was used without further purification. Required solution of the oxidant was freshly prepared before each experiment by proper dilution of its original solution which is standardized spectrophotometrically [28]. The solution was stored in a bottle away from light and re-

standardized periodically. Sodium perchlorate and sodium sulfate were used to vary the ionic strength in both perchloric and sulfuric acids solutions, respectively, and acetic acid to vary the dielectric constant of the reactions media.

Kinetic measurements

All kinetic investigations were conducted under pseudo-first-order conditions where α -aminobutyric acid was present in a large excess over that of platinum(IV). The ionic strength, I , of the reactions mixtures was adjusted to 1.0 mol dm^{-3} . The reactions temperature (25°C) was controlled within $\pm 0.1^\circ\text{C}$ unless stated otherwise. The reactions were initiated by rapid addition of known amounts of the pre-equilibrated Pt^{IV} to the reactions mixtures containing the required amounts of the investigated amino acid, perchloric or sulfuric acid, silver(I) nitrate, sodium perchlorate or sodium sulfate and water, thermostated at the same temperature. The solutions were then mixed and transferred to a cell with a path length of 1 cm . The courses of the reactions were followed spectrophotometrically by monitoring the decrease in the absorbance of Pt^{IV} at $\lambda = 261 \text{ nm}$, its absorption maximum, as a function of time using Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer with a cell compartment kept at constant temperature. The applicability of Beer's law was verified at 261 nm under the reaction conditions. The molar extinction coefficient, ϵ , was determined, $\epsilon = (1.32 \pm 0.04) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, and was found to be in a good agreement with that reported previously [28]. In addition, there is no interference from other reagents at this wavelength. It was observed that the oxidation reactions were very slow to be measured in the absence of silver(I) catalyst. The pseudo-first order rate constant values of the catalyzed reactions (k_c) were obtained from the linear portion of $\ln(\text{absorbance})$ versus time plots, which were the average of at least two independent kinetics runs and were reproducible to within $\pm 2-3\%$. Double logarithmic plots were used to determine the order with respect to each reactant. The concentration of the particular species being examined was varied while the concentrations of the other species were held fixed.

Results

Time-resolved spectra

Time-resolved spectra during the silver(I) catalyzed-oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions are shown in Figure 1 (a) and (b), respectively. The scanned spectra indicate gradual disappearance of the Pt^{IV} absorption band with time as a result of its reduction. A hypsochromic shift in the Pt^{IV} band of about 6 nm from 261 to 255 nm as well as two isosbestic points located at 245 and 280 nm are apparent in the spectra.

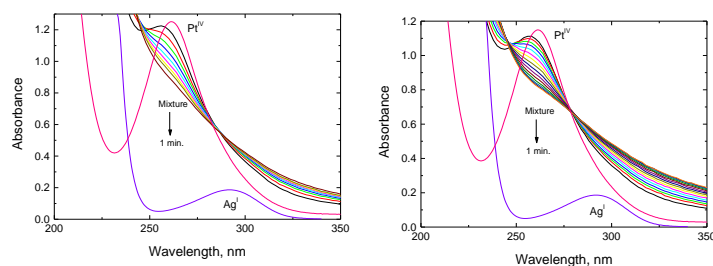


Figure 1: Time-resolved spectra during silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum (IV) in perchloric and sulfuric acids solutions. $[\text{ABA}] = 6.0 \times 10^{-3}$, $[\text{Pt}^{\text{IV}}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 0.5$, $[\text{Ag}^+] = 1.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

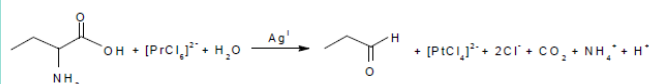
Stoichiometry and product identification

Different reactions mixtures with different sets of reactants containing various amounts of Pt^{IV} and α -aminobutyric acid in both acids solutions at fixed acidity, ionic strength, and temperature were allowed to react for about 24 h . After completion of the reactions, the unreacted $[\text{Pt}^{\text{IV}}]$ was assayed spectrophotometrically. Results indicated that one mole of the amino acid consumed one mole of Pt^{IV} in the predominant reactions, as represented in the following stoichiometric equation 1:

The product propionaldehyde was identified by spectral and chemical methods as reported earlier [29,30]. The byproducts are identified as ammonia by Nessler's reagent and carbon dioxide by lime water. On the other hand, the formation of $[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}$ was confirmed [10-16,26] by the observed black precipitate of platinum(II) hydroxide on addition of alkali to the reactions mixtures, according to the reaction, $[\text{PtCl}_4]^{2-} + 2\text{OH}^- = \text{Pt}(\text{OH})_2 + 4\text{Cl}^-$

Effect of $[\text{Pt}^{\text{IV}}]$

The concentration of the oxidant, platinum(IV), was varied in both acids in the range of 2.0×10^{-5} to $12.0 \times 10^{-5} \text{ mol dm}^{-3}$ at constant



Equation 1: Stoichiometric equation.

$[\text{ABA}]$, $[\text{Ag}^+]$, $[\text{H}^+]$, ionic strength and temperature. The non-variation in the observed first order rate constants at various concentrations of Pt^{IV} (Table 1) indicates that the order with respect to the oxidant is confirmed to be one.

Effect of $[\text{ABA}]$

The observed first order rate constant (k_c) was determined at different initial concentrations of the reductant α -aminobutyric acid keeping all other reactants concentration constant. The results showed that the rate constants in both acids increased with increasing the α -aminobutyric acid concentration as listed in Table 1. The plots of k_c versus $[\text{ABA}]$ in both acids were found to be linear with positive intercepts confirming less than unit order dependences with respect to the amino acid (Figure 2).

Effect of $[\text{H}^+]$

The rates of the reactions in both acids were measured at constant concentrations of ABA , Pt^{IV} , Ag^+ , ionic strength and temperature but with various $[\text{H}^+]$ ($0.1 - 1.0 \text{ mol dm}^{-3}$). The rates were found to increase as $[\text{H}^+]$ increased with less than unit order as found from the

Table 1: Effect of variation of $[Pt^{IV}]$, $[ABA]$, $[H^+]$, $[Ag^I]$ and ionic strength, I , on the observed first order rate constant (k_c) in the silver (I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions at 25°C.

$10^5 [HCP]$ (mol dm ⁻³)	$10^3 [ABA]$ (mol dm ⁻³)	$[H^+]$ (mol dm ⁻³)	$10^5 [Ag^I]$ (mol dm ⁻³)	I (mol dm ⁻³)	$10^5 k_c$ (s ⁻¹)	
					Perchloric	Sulfuric
2	6	0.5	1	1	27.2	15.2
4	6	0.5	1	1	29.1	14.7
6	6	0.5	1	1	28.4	13.9
8	6	0.5	1	1	27.4	14.1
10	6	0.5	1	1	26.9	13.7
12	6	0.5	1	1	28	14
8	2	0.5	1	1	11.2	6.1
8	4	0.5	1	1	18	9.3
8	6	0.5	1	1	27.4	14.1
8	8	0.5	1	1	37.1	18.2
8	10	0.5	1	1	43.3	23
8	12	0.5	1	1	50.7	26.3
8	6	0.1	1	1	10.4	6.3
8	6	0.3	1	1	20.4	10.9
8	6	0.5	1	1	27.4	14.1
8	6	0.7	1	1	36.2	17
8	6	0.9	1	1	42.5	21.4
8	6	1	1	1	49.7	24.2
8	6	0.5	0.4	1	12.1	7.2
8	6	0.5	0.7	1	18.6	10.3
8	6	0.5	1	1	27.4	14.1
8	6	0.5	1.5	1	33.7	19
8	6	0.5	2	1	41	23.9
8	6	0.5	2.5	1	51.2	28.4
8	6	0.5	1	1	27.4	14.1
8	6	0.5	1	1.2	24.3	12.2
8	6	0.5	1	1.4	22	9.8
8	6	0.5	1	1.6	18.9	7.1
8	6	0.5	1	1.8	16.2	5.3
8	6	0.5	1	2	14	4

Experimental Error \pm 3%

plots of $\log k_c$ versus $\log [H^+]$ (Figure 3).

Effect of $[Ag^I]$

The oxidation rates in both acids were measured with various concentrations of silver(I) catalyst ranging between 0.2×10^{-5} and 1.4×10^{-5} mol dm⁻³ at constant other variables. The oxidation rates were found to increase with increasing $[Ag^I]$ as listed in Table 1. The order with respect to $[Ag^I]$ was less than unity in both acids as found from the plots of $\log k_c$ versus $\log [Ag^I]$ as illustrated in Figure 4.

Effect of ionic strength and dielectric constant

The effect of ionic strength on the oxidation rates was investigated by the addition of sodium perchlorate in case of perchloric acid and sodium sulfate in case of sulfuric acid to the reactions media at constant concentrations of ABA, Pt^{IV} and Ag^I, and at constant

pH and temperature. The results showed that the rate constants decreased with increasing the ionic strength of the media, and the Debye–Hückel plots were found to be linear with negative slopes as shown in Figure 5.

Also, the effect of the dielectric constant (D) of the reactions media on the oxidation rates was examined by measuring the oxidation rates at different solvent compositions (v/v) of acetic acid and water. The rate constants were found to increase with the decrease in dielectric constant of the solvent mixture, i.e., increase in acetic acid content. The plots of $\log k_c$ versus $1/D$ was found to be linear with positive slopes as shown in Figure 6.

Effect of temperature

The oxidation rates were performed at four different temperatures in the range of 288 - 318 K, at constant concentrations of the reactants

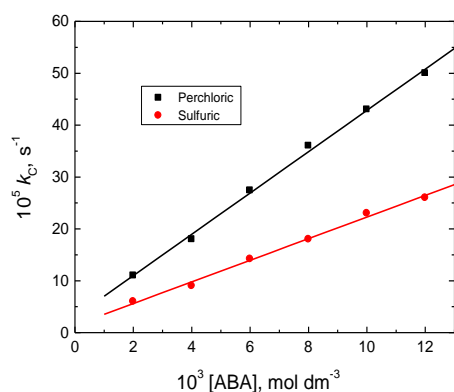


Figure 2: Plots of the observed first order rate constant (k_c) versus [ABA] in the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum (IV) in perchloric and sulfuric acids solutions. $[Pt^{IV}] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$, $[Ag^+] = 1.0 \times 10^{-5}$ and $I = 1.0$ mol dm^{-3} at 25°C.

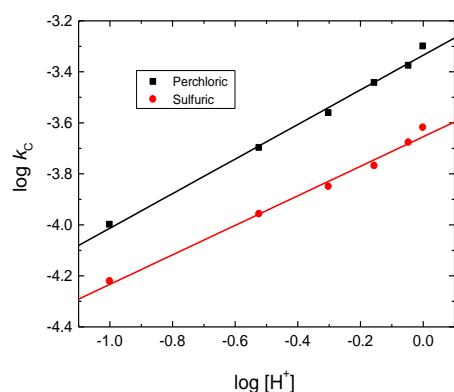


Figure 3: Plots of $\log k_c$ versus $\log [H^+]$ in the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions. $[ABA] = 6.0 \times 10^{-3}$, $[Pt^{IV}] = 8.0 \times 10^{-5}$, $[Ag^+] = 1.0 \times 10^{-5}$ and $I = 1.0$ mol dm^{-3} at 25°C.

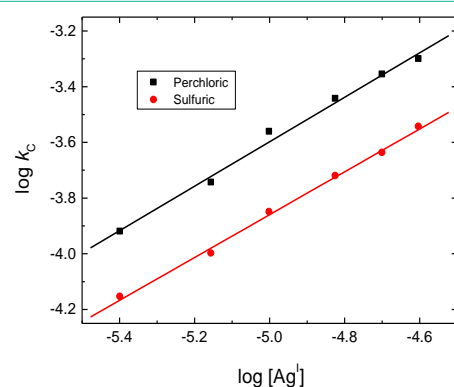


Figure 4: Plots of $\log k_c$ versus $\log [Ag^+]$ in the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions. $[ABA] = 6.0 \times 10^{-3}$, $[Pt^{IV}] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$ and $I = 1.0$ mol dm^{-3} at 25°C.

and other conditions being constant. The activation parameters of the second order rate constants (k_2) are calculated using Arrhenius and Eyring plots and are listed in Table 2.

Test for free radical intermediates

The involvement of free radicals in the oxidation reactions in

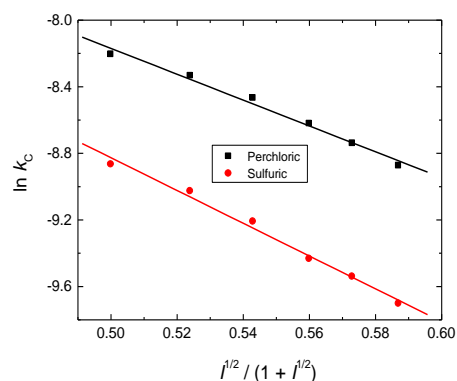


Figure 5: Debye-Hückel plots in the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions. $[ABA] = 6.0 \times 10^{-3}$, $[Pt^{IV}] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$, $[Ag^+] = 1.0 \times 10^{-5}$ and $I = 1.0$ mol dm^{-3} at 25°C.

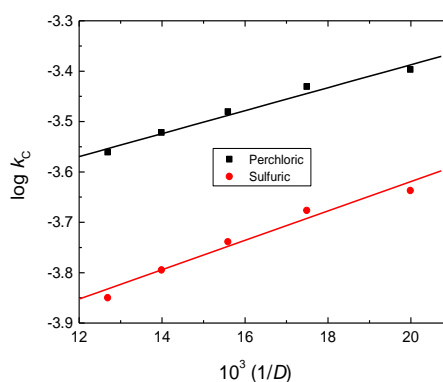


Figure 6: Plots of $\log k_c$ versus $1/D$ for the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions. $[ABA] = 6.0 \times 10^{-3}$, $[Pt^{IV}] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$, $[Ag^+] = 1.0 \times 10^{-5}$ and $I = 1.0$ mol dm^{-3} at 25°C.

Table 2: Activation parameters of the second order rate constants k_2 in the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions. $[ABA] = 6.0 \times 10^{-3}$, $[Pt^{IV}] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$, $[Ag^+] = 1.0 \times 10^{-5}$ and $I = 1.0$ mol dm^{-3} .

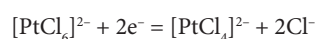
Acid	DS^\ddagger , $J \text{ mol}^{-1} K^{-1}$	H^\ddagger , $kJ \text{ mol}^{-1}$	ΔG_{298}^\ddagger , $kJ \text{ mol}^{-1}$	E_a^\ddagger , $kJ \text{ mol}^{-1}$
Perchloric	-76.03	49.21	71.87	50.47
Sulfuric	-89.17	48.97	75.54	48.12

Experimental error $\pm 2\%$

both acids was examined by the polymerization test. The reactions mixtures to which a known quantity of acrylonitrile scavenger has been added initially and was kept in inert atmosphere for 4 h. Upon diluting the reactions mixtures with methanol, there were no white precipitates formed, suggesting absence of free radicals intervention during the oxidation reactions. This indicates that the reactions were not routed through free radical path.

Discussion

It is also reported [31] that the platinum(IV) species in acid medium is present as $[PtCl_6]^{2-}$, which is assumed to be the principal reactive oxidant. The reduction of $[PtCl_6]^{2-}$ generally proceed as follows:



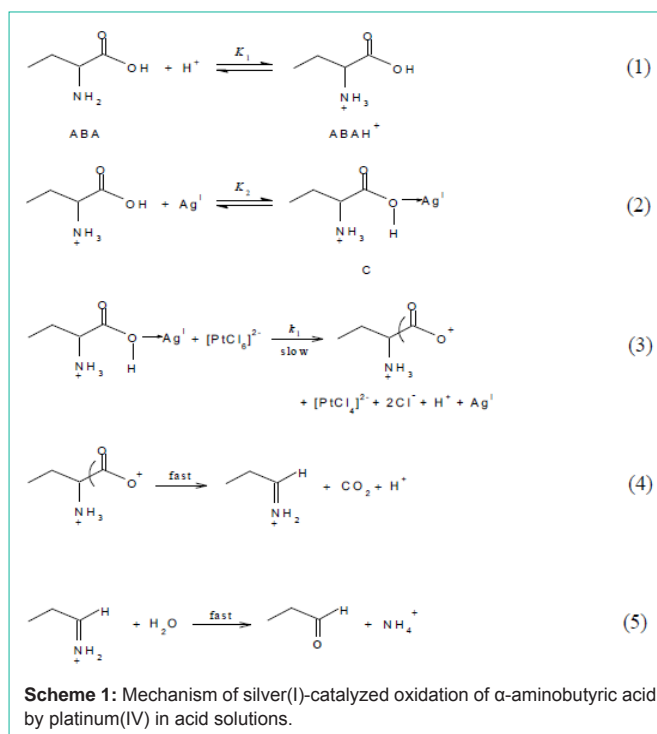
In this reduction process, octahedral Pt^{IV} is reduced to square planar Pt^{II} with release of two Cl⁻ ions. Therefore, this reaction is better classified as a reductive-elimination reaction [32,33]. Because platinum(IV) complexes are generally substitution-inert [34], initial complex formation between platinum(IV) and reductant prior to electron transfer can be excluded in reductive-elimination reactions.

Two alternative reaction mechanisms for the oxidation of amino acids by platinum(IV) may be considered. The first mechanism involves a simultaneous two-electron transfer in a single step. The second mechanism involves two successive one-electron transfer steps. If the transition states of the reductant and/or oxidant are unstable, a simultaneous two-electron transfer mechanism may be suggested, such as that in the oxidation of uranium(IV) by [PtCl₆]²⁻ [35]. In the present study, addition of acrylonitrile monomer to the reaction mixture failed to give polymerized products. It may be that a free radical such as the Pt^{III} species is too short-lived to interact with acrylonitrile to give the polymerized product under our experimental conditions. Consequently, the two-electron transfer mechanism seems plausible.

The investigated reactions between α-aminobutyric acid and platinum(IV) in both perchloric and sulfuric acids solutions have a 1:1 stoichiometry. The reactions exhibited a first order dependence with respect to [Pt^{IV}], less than unit order dependences with respect to [ABA], [H⁺] and [Ag^I]. The observed enhancement of the oxidation rates upon increasing acids concentration with the less than unit order dependences suggests that the protonated form of the amino acid may be considered as the kinetically reactive species in the rate-determining step, which plays the main role in the reactions kinetics. The less than unit order dependences with respect to both [ABA] and [Ag^I] suggests formation of an intermediate complex between ABA and Ag^I catalyst as reported earlier [12,13,16] owing to the availability of the electron pairs on both oxygen atom of the carboxylate group and nitrogen atom of the amine group in the amino acid. Within the protolytic amino acid system, the carboxylate and amine groups may act as nucleophiles, depending on pH of the medium. The protolytic group with the highest basicity interacts with the silver(I) catalyst. Thus, at low pH where the amine group is protonated, the carboxylate group should be able to attack Ag^I. Complexes formation was proved kinetically by the positive intercepts of the linear plots of [Ag^I] / kC versus 1 / [ABA] (Figure 7). Spectroscopic evidence to support complexes formation was obtained from the UV-Vis spectra where hypochromic shifts in the wavelength with the appearance of two isosbestic points as shown in Figure 1.

Based on the experimental results and the above-mentioned arguments, the oxidation mechanism illustrated in Scheme 1 suggests that the protonated amino acid combines with Ag^I to form an intermediate complex (C) which then reacts in a slow step with one mole of platinum(IV) to give rise to the products with regeneration of the catalyst Ag^I. The decrease in the oxidation rates upon increasing both ionic strength and dielectric constant of the reactions media suggests that the reactions in the rate-determining step occur between two oppositely charged ions [37-39], i.e. between the positively charged complex and [PtCl₆]²⁻.

According to the suggested mechanistic Scheme 1,



$$\text{Rate} = \frac{-d[\text{Pt}^{\text{IV}}]}{dt} = k_1[\text{C}][\text{Pt}^{\text{IV}}] \quad (6)$$

$$K_1 = \frac{[\text{ABAH}^+]}{[\text{ABA}][\text{H}^+]} \quad (7)$$

$$[\text{ABAH}^+] = K_1[\text{ABA}][\text{H}^+] \quad (8)$$

$$K_2 = \frac{[\text{C}]}{[\text{ABAH}^+][\text{Ag}^{\text{I}}]} = \frac{[\text{C}]}{K_1[\text{ABA}][\text{H}^+][\text{Ag}^{\text{I}}]} \quad (9)$$

$$[\text{C}] = K_1K_2[\text{ABA}][\text{H}^+][\text{Ag}^{\text{I}}] \quad (10)$$

Substituting Eq. (10) into Eq. (6) yields,

$$\text{Rate} = K_1K_1K_2[\text{ABA}][\text{H}^+][\text{Ag}^{\text{I}}][\text{Pt}^{\text{IV}}] \quad (11)$$

The total concentration of α-aminobutyric acid is given by,

$$[\text{ABA}]_{\text{T}} = [\text{ABA}]_{\text{F}} + [\text{ABAH}^+] + [\text{C}] \quad (12)$$

where [ABA]_T and [ABA]_F stand for total and free concentrations of the amino acid, respectively.

Substituting Eqs. (8) and (10) into Eq. (12) gives,

$$[\text{ABA}]_{\text{T}} = [\text{ABA}]_{\text{F}} + K_1[\text{ABA}]_{\text{F}}[\text{H}^+] + K_1K_2[\text{ABA}]_{\text{F}}[\text{H}^+][\text{Ag}^{\text{I}}] \quad (13)$$

$$[\text{ABA}]_{\text{T}} = [\text{ABA}]_{\text{F}}(1 + K_1[\text{H}^+] + K_1K_2[\text{H}^+][\text{Ag}^{\text{I}}]) \quad (14)$$

$$[\text{ABA}]_{\text{F}} = \frac{[\text{ABA}]_{\text{T}}}{1 + K_1[\text{H}^+] + K_1K_2[\text{H}^+][\text{Ag}^{\text{I}}]} \quad (15)$$

$$[\text{Ag}^{\text{I}}]_{\text{T}} = [\text{Ag}^{\text{I}}]_{\text{F}} + [\text{C}] \quad (16)$$

Substituting Eq. (8) into Eq. (10) and rearranging gives,

$$[\text{Ag}^{\text{I}}]_{\text{F}} = \frac{[\text{Ag}^{\text{I}}]_{\text{T}}}{1 + K_1K_2[\text{ABA}][\text{H}^+]} \quad (17)$$

In view of high [H⁺],

$$[H^+]_T = [H^+]_F \quad (18)$$

In addition,

$$[Pt^{IV}]_T = [Pt^{IV}]_F \quad (19)$$

Substituting Eqs. (15), (17)–(19) into Eq. (11) (and omitting ‘T’ and ‘F’ subscripts) gives,

$$\text{Rate} = \frac{k_1 K_1 K_2 [ABA][H^+][Ag^+][Pt^{IV}]}{(1 + K_1[H^+] + K_1 K_2 [H^+][Ag^+])(1 + K_1 K_2 [ABA][H^+])} \quad (20)$$

In view of low $[Ag^+]$ used, the term $K_1 K_2 [H^+][Ag^+]$ in the denominator of Eq. (20) can be neglected. Therefore, Eq. (20) becomes,

$$\text{Rate} = \frac{k_1 K_1 K_2 [ABA][H^+][Ag^+][Pt^{IV}]}{(1 + K_1[H^+])(1 + K_1 K_2 [ABA][H^+])} \quad (21)$$

Under pseudo-first-order conditions, the rate law can be expressed as,

$$\text{Rate} = \frac{-d[Pt^{IV}]}{dt} = k_c [Pt^{IV}] \quad (22)$$

Comparing Eqs. (21) and (22), the following relationship is obtained,

$$k_c = \frac{k_1 K_1 K_2 [ABA][H^+][Ag^+]}{(1 + K_1[H^+])(1 + K_1 K_2 [ABA][H^+])} \quad (23)$$

and with rearrangement it becomes,

$$\frac{[Ag^+]}{k_c} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2 [H^+]} \right) \frac{1}{[ABA]} + K' \quad (24)$$

$$\frac{[Ag^+]}{k_c} = \left(\frac{1}{k_1 K_1 K_2 [ABA]} \right) \frac{1}{[H^+]} + \frac{1}{k_1 K_2 [ABA]} + K' \quad (25)$$

where $K' = (1 + K_1[H^+]) / k_1$.

According to equations (24) and (25), the plots of $[Ag^+] / kC$ against $1/[ABA]$, at constant $[H^+]$, and $[Ag^+] / kC$ against $1/[H^+]$, at constant $[ABA]$, should be linear with positive intercepts on $[Ag^+] / kC$ axes. The experimental results satisfied this requirement as shown in Figures 7 and 8, respectively.

The activation parameters listed in Table 2 may be interpreted as follows. The obtained negative values of $DS \neq$ suggest that the reactions point towards the inner-sphere pathway [40]. The positive values of both $DH \neq$ and $DG \neq$ confirm endothermic formation of the intermediate complexes and their non-spontaneities, respectively.

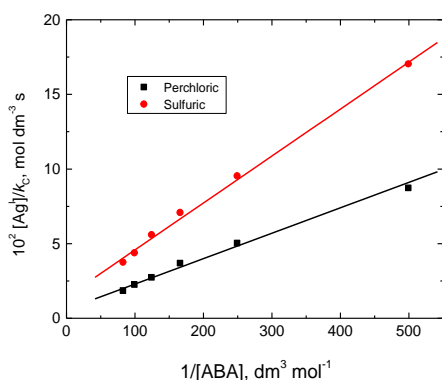


Figure 7: Verification of equation (24) in the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions. $[Pt^{IV}] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

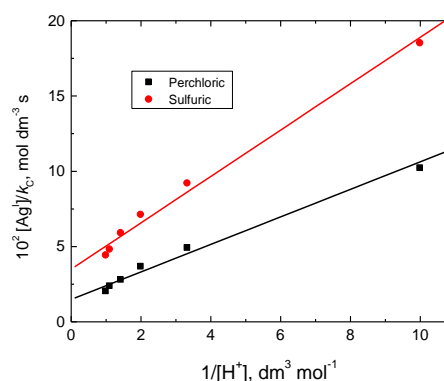


Figure 8: Verification of equation (25) in the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) in perchloric and sulfuric acids solutions. $[ABA] = 6.0 \times 10^{-3}$, $[Pt^{IV}] = 8.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

Conclusion

The kinetics of the silver(I)-catalyzed oxidations of α -aminobutyric acid by platinum(IV) has been investigated in perchloric and sulfuric acids solutions. The reactions were very slow to be measured in the absence of the catalyst. Under comparable experimental conditions, the oxidation rate of α -aminobutyric acid in perchloric acid solutions was approximately found to be twice that recorded in sulfuric acid solutions. The oxidation products of α -aminobutyric acid were identified as propionaldehyde, ammonium ion and carbon dioxide.

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