MECHANISTIC INVESTIGATION OF OXIDATION OF SOME AMINO ACIDS BY BIS(DIHYDROGEN TELLURATE)ARGENTATE(III) ION IN ALKALINE MEDIUM. A KINETIC STUDY

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(Received: February 24, 2009 - Accepted: July 1, 2009)

ABSTRACT

The oxidation of leucine, isoleucine and valine by bis(dihydrogen tellurate)argentate(III) ion was studied by stopped-flow technique. It was both first order with respect to Ag(III) complex and amino acids. A plausible mechanism was proposed from the kinetics study. And the rate equations derived from mechanism can explain all experimental phenomena. The activation parameters along with the second order rate constants were calculated.

Keywords: Bis(dihydrogen tellurate)argentate(III), amino acid, Kinetics and mechanism, Redox reactions

INTRODUCTION

Transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands, such as diperiodatargentate(III),^[1] [ethylenebis(biguan-ide) silver(III)].^[2] These complexes exist in a suitable aqueous solution. Ag(III) complexes were stabilized in alkaline medium by periodate or tellurate ions.^[3] These complexes, Ag(III), Cu(III), Ni(IV), can be used as an oxidation reagents in organic chemistry and analytical chemistry.^[4,5] As oxidation reagents, these complexes have been extensively studied.

Amino acid act not only as the building blocks in biological molecules,^[6] but they also play a significant role in metabolism, and play key roles in many neuro-chemical response mechanisms, such as memory, appetite control and pain transmission.^[7,8] Amino acids can undergo many types of reaction depending on whether a particular amino acid contains non-polar groups or polar substituents. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants, these oxidation reactions display diverse reaction mechanisms, oxidative deamination and decarboxylation decarboxylation.^[9-19] Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant.

EXPERIMENTAL SECTION

Reagents

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Amino acid was changed to Potassium salt by adding KOH solution, molar ratio of amino acid and KOH is 1:2. Solution of bis(dihydrogen tellurate)argentate(III) ion was standardized by the method reported earlier.^[3] Its UV spectrum has a characteristic absorption band at 350 nm, which was found to be consistent with the reported. The concentration of bis(dihydrogen tellurate)argentate(III) was derived by its absorption at $\lambda=350$ nm. Solution of bis(dihydrogen tellurate)argentate(III) was always freshly prepared before use with doubly-distilled water. The ionic strength I was maintained by adding KNO₃ solution and the pH value of the reaction mixture was regulated with KOH solution.

Synthesis of bis(dihydrogen tellurate)argentate(III)

AgNO₃ (2.72 g), H₆TeO₆ (7.34 g), K₂S₂O₈ (13 g) and KOH (18 g) were taken in a 500 ml round bottomed flask. 150 ml of demineralised water were added. The mixture was heated to boiling while stirring. After 10 minutes of boiling an orangish-yellow froth was obtained and the mixture was heated for another 10 minutes. The mixture was left to cool to room temperature and filtered through a Gooch crucible. The solution was cooled in an ice bath to eliminate as much of potassium sulphate as possible and the solution filtered again while cold. The resulting orangish-red clear filtrate was left to attain room temperature. In order to isolate the complex, 80 ml of NaNO₃ saturated solution were added to the solution and the mixture left to crystallise. Almost immediately crystals started appearing and crystallisation is complete when the supernatant liquid is colourless. The crystals were filtered and washed several times with demineralised water until the complex itself starts dissolving, which is indicated by the orange-red drops being formed under the crucible. In this way one can be sure of eliminating sodium and potassium hydroxide since this complex is insoluble in concentrated hydroxide solution and the Ag(III) complex, Na₅[Ag(H₂TO₆)₂], was obtained.

Apparatus and Kinetics Measurements

Since the reaction rate was too fast to be monitored by the usual methods, kinetic measurements were performed on a rapid kinetic technique (stopped-flow SX20, Applied Photophysics Limited, United Kingdom), attached with a circulating water from a thermostat (BG-chiller E10, Baijing Biotech Inc., Beijing).

All reactions were monitored under pseudo-first order conditions, with at least a ten-fold excess of amino acids. The reactions were started by the mixing of equal volumes (128 μ l) of a solution of the Ag(III) complex with a solution of the amino acid directly in the stopped-flow instrument. The reaction of the amino acid with the Ag(III) complex was monitored as a decrease of absorbance at the maximum absorbance at 350 nm. Observed rate constants were calculated by a fit of a single exponential function to the kinetic traces. Reported pseudo-first-order rate constants, k_{obs} , are mean values of at least five independent kinetic runs, using a standard least-squares minimizing routine.

Product Analysis

Solution having known concentrations of [Ag(III)], [OH⁻] and [H₄TeO₆²⁻] were mixed with an excess of amino acid. The completion of the reaction was marked by the complete disappearance of the Ag(III) color.^[20] After completion of the reaction, the main reaction products were identified as aldehydes by a spot test,^[21] and ammonia by Nessler's reagent.

Free radical trapping experiment

Under the reaction conditions used for kinetic measurements, a 50 mL solution of amino acid containing 10% acrylonitrile was mixed with a 25 mL Ag(III) solution in a 3-neck flask; both solutions were bubbled for 30 min with nitrogen gas before mixing. By stirring the reaction mixture for 4 h under the protection of nitrogen gas, no precipitates of polyacrylonitrile could be noticed. This observation implies that involvement of free radicals in the reaction course is improbable.

RESULTS AND DISCUSSION

Protolytic equilibria

Under the reaction conditions used in the present work, i.e., 0.02 mol/L < [OH⁻] < 0.1 mol/L, we ensure that [OH⁻] remains constant during the reaction course. Protolysis constants of amino acids have been reported to be: pKa (α -COOH) = 2.33, and pKa ($-\text{NH}_3^+$) = 9.74 for leucine, pKa (α -COOH) = 2.32, and pKa ($-\text{NH}_3^+$) = 9.76 for isoleucine, pKa (α -COOH) = 2.29, and pKa ($-\text{NH}_3^+$) = 9.72 for valine.^[22] It can be calculated on the basis of the equilibrium constants that the amino acids are in the anionic form RCH₂(H₂N)COO⁻ in the alkaline medium we used. Several protolytic equilibria of the tellurate in aqueous media have been described in the literature.^[23] The following two equilibria, together with equilibrium constants, were reported for potassium tellurate dissolved in aqueous alkaline medium.

Based on the K_{a2} equilibrium constants, if [OH⁻] = 0.01 mol·L⁻¹, [H₄TeO₆²⁻]:[H₃TeO₆³⁻]:[H₅TeO₆⁻] = 1000:89:1. Hence in the concentration range of OH⁻ used in this work, the H₅TeO₆⁻ and H₃TeO₆³⁻ can be neglected. The

calculations reveal that under our experimental conditions $\text{H}_4\text{TeO}_6^{2-}$ is the predominant species whereas the $\text{H}_3\text{TeO}_6^{3-}$ and H_5TeO_6^- make a very minor contribution to the total tellurate speciation.

Influence of $[\text{OH}^-]$ and $[\text{H}_4\text{TeO}_6^{2-}]$ on the reaction rates

At fixed concentration of $[\text{Ag(III)}]$ $[\text{OH}^-]$ [amino acid] ionic strength I and temperature, the value of k_{obs} decreased with the increase concentration of $\text{H}_4\text{TeO}_6^{2-}$. The plot of $1/k_{\text{obs}}$ versus $[\text{H}_4\text{TeO}_6^{2-}]$ was straight line with a positive intercept (Table 1). shows that tellurate is the product of the pre-equilibrium. The equation (3) can be expressed as:

The second order rate constant, k' , was calculated, and $1/k'$ versus $[\text{H}_4\text{TeO}_6^{2-}]$ was also a straight line (Figure 1, Figure 2 and Figure 3).

At fixed concentration of $[\text{Ag(III)}]$ $[\text{H}_4\text{TeO}_6^{2-}]$ [amino acid] ionic strength I and temperature, the value of k_{obs} decreased with the increase of the $[\text{OH}^-]$. The plot of $1/k_{\text{obs}}$ versus $[\text{OH}^-]$ was a straight line (Table 2), and the influence of $[\text{OH}^-]$ on the reaction rates comes from the form of tellurate species in the aqueous alkaline medium. The second order rate constants were calculated and $1/k'$ versus $[\text{OH}^-]$ was also a straight line (Figure 4, Figure 5 and Figure 6). The value of k_{obs} increased on addition of KNO_3 solution (Table 3)

Table 1. $k_{\text{obs}}/\text{s}^{-1}$ varying with different $[\text{H}_4\text{TeO}_6^{2-}]$ at 298.2 K.

C/(mol/L)		0.001	0.002	0.003	0.004	0.005	0.006
leucine	$10^2 k_{\text{obs}}$	8.762	8.348	8.037	7.778	7.460	7.247
	k'	2.503	2.385	2.296	2.222	2.131	2.071
isoleucine	$10^2 k_{\text{obs}}$	9.891	9.345	8.971	8.495	8.135	7.785
	k'	2.826	2.670	2.563	2.427	2.324	2.224
valine	$10^2 k_{\text{obs}}$	9.292	8.921	8.596	8.235	7.945	7.711
	k'	2.655	2.549	2.456	2.353	2.27	2.203

$[\text{Ag(III)}]=1.651 \times 10^{-4} \text{ mol/L}$, $[\text{OH}^-]=2.00 \times 10^{-2} \text{ mol/L}$, [amino acid] $=3.50 \times 10^{-2} \text{ mol/L}$, $I=0.20 \text{ mol/L}$, $T=298.2 \text{ K}$

Table 2. $k_{\text{obs}}/\text{s}^{-1}$ varying with different $[\text{OH}^-]$ at 298.2 K.

C/(mol/L)		0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11
leucine	$10^2 k_{\text{obs}}$	8.102	5.997	5.185	4.290	3.731	3.493	3.119	2.877	2.682	2.451
	$10k'$	23.15	17.13	14.81	12.26	10.66	9.980	8.911	8.220	7.663	7.003
isoleucine	$10^2 k_{\text{obs}}$	9.441	7.577	6.415	5.436	4.744	4.081	3.645	3.412	3.086	2.750
	$10k'$	26.97	21.65	18.33	15.53	13.55	11.66	10.41	9.749	8.817	7.857
valine	$10^2 k_{\text{obs}}$	8.225	6.548	5.557	4.737	4.209	3.826	3.520	3.217	3.030	2.812
	$10k'$	23.50	18.71	15.91	13.53	12.03	10.93	10.06	9.191	8.657	8.034

$[\text{Ag(III)}]=1.651 \times 10^{-4} \text{ mol/L}$, $[\text{H}_4\text{TeO}_6^{2-}]=3.00 \times 10^{-3} \text{ mol/L}$, [amino acid] $=3.50 \times 10^{-2} \text{ mol/L}$, $I=0.23 \text{ mol/L}$, $T=298.2 \text{ K}$.

Table 3. $k_{\text{obs}}/\text{s}^{-1}$ varying with different ion strength at 298.2 K.

I/(mol/L)		0.08	0.18	0.28	0.38	0.48
$10^2 k_{\text{obs}}$	leucine	7.312	8.185	8.087	8.113	7.973
	isoleucine	8.732	10.07	10.15	9.506	9.617
	valine	7.977	8.965	9.075	8.827	8.798

$[\text{Ag(III)}]=1.651 \times 10^{-4} \text{ mol/L}$, $[\text{OH}^-]=2.00 \times 10^{-2} \text{ mol/L}$, $[\text{H}_4\text{TeO}_6^{2-}]=3.00 \times 10^{-3} \text{ mol/L}$, [amino acid] $=3.50 \times 10^{-2} \text{ mol/L}$, $T=298.2 \text{ K}$

Figure 1: a plot of $1/k'$ versus $[H_4TeO_6^{2-}]$ for the oxidation of leucine by Ag(III) complex at 298.2 K.

Figure 3: a plot of $1/k'$ versus $[H_4TeO_6^{2-}]$ for the oxidation of valine by Ag(III) complex at 298.2 K.

Figure 2: a plot of $1/k'$ versus $[H_4TeO_6^{2-}]$ for the oxidation of isoleucine by Ag(III) complex at 298.2 K.

Figure 4: a plot of $1/k'$ versus $[OH^-]$ for the oxidation of leucine by Ag(III) complex at 298.2 K.

Figure 5: a plot of $1/k'$ versus $[OH^-]$ for the oxidation of isoleucine by $Ag(III)$ complex at 298.2 K.

Figure 6: a plot of $1/k'$ versus $[OH^-]$ for the oxidation of valine by $Ag(III)$ complex at 298.2 K.

Table 4. k_{obs}/s^{-1} varying with different [amino acid] at different temperatures

C/(mol/L)		0.02	0.04	0.06	0.08	0.10	n_{ap}	R
Amino acid	T/(K)	$10^2 k_{obs}$						
leucine	293.2	3.094	6.278	9.095	12.17	15.87	1.00	0.999
	298.2	4.566	9.001	13.64	18.07	22.66	1.00	0.999
	303.2	7.019	14.23	21.34	28.03	35.51	1.00	0.999
	308.2	10.21	20.55	30.77	40.80	51.32	1.00	0.999
	313.2	15.85	31.76	47.95	63.97	79.90	1.00	0.999
isoleucine	293.2	3.224	6.471	9.792	13.19	16.26	1.00	0.999
	298.2	5.245	10.48	15.66	21.01	26.06	1.00	0.999
	303.2	8.191	16.34	24.41	32.60	40.82	1.00	0.999
	308.2	11.53	23.03	34.56	46.21	57.72	1.00	0.999
	313.2	18.26	36.56	54.61	73.05	91.32	1.00	0.999
valine	293.2	3.116	6.356	9.542	12.61	15.99	1.01	0.999
	298.2	5.026	10.25	15.28	20.44	25.25	1.00	0.999
	303.2	7.881	15.71	23.61	31.33	39.13	1.00	0.999
	308.2	11.05	22.21	33.23	44.46	55.25	1.00	0.999
	313.2	19.18	38.35	57.11	76.53	95.65	0.97	0.998

$[Ag(III)] = 1.651 \times 10^{-4}$ mol/L, $[OH^-] = 2.00 \times 10^{-2}$ mol/L, $[H_4TeO_6^{2-}] = 3.00 \times 10^{-3}$ mol/L, [amino acid] = 3.50×10^{-2} mol/L, $I = 0.33$ mol/L, n_{ap} is the apparent reaction order, which are the slopes of the plot of $\ln k_{obs}$ versus $\ln [\text{amino acid}]$ at different temperature, and R is the relative coefficient

Influence of [amino acid] on the reaction rates

At fixed concentration of $[Ag(III)]$ $[OH^-]$ $[H_4TeO_6^{2-}]$ ionic strength I. The values of k_{obs} were determined at different temperature and amino acid concentrations. The k_{obs} values were found to increase with increase concentration of amino acid at all temperatures, the order with respect to amino acid is unity, which were the slopes of the plots of $\ln k_{obs}$ versus $\ln[\text{amino acid}]$, and plots of k_{obs} versus $[\text{amino acid}]$ were straight lines through the origin at different temperature (Table 4), from which it can be known that a molecular of amino acid participated in the rate controlled step, Equation (4) can be obtained as below:

Reaction Mechanism

According to the kinetics, the reaction mechanism can be expressed as below:

So the equation can be obtained:

$$[Ag(III)]_{Tot} = [A]_e + [B]_e \quad (9)$$

where "e" means equilibrium concentration of the kinds of Ag(III) species.

$$r = -d[Ag(III)]_{Tot}/dt = k_{obs}[Ag(III)]_{Tot}$$

$$= k \cdot [B]_e \cdot [\text{amino acid}] = k' [Ag(III)]_{Tot} \cdot [\text{amino acid}] \quad (10)$$

Where k' is the second order rate constant.

Then k_{obs} can be expressed as:

$$k_{obs} = \frac{kK_1K_{a2}[\text{amino acid}]}{[H_4TeO_6^{2-}][OH^-] + K_1K_{a2}} = k' [\text{amino acid}] \quad (11)$$

Where,

$$k' = \frac{kK_1K_{a2}}{[H_4TeO_6^{2-}][OH^-] + K_1K_{a2}} \quad (12)$$

Equation (13),(14) can also be obtained:

$$\frac{1}{k_{obs}} = \frac{1}{k'[\text{amino acid}]} + \frac{[H_4TeO_6^{2-}][OH^-]}{k'K_1K_{a2}} \quad (13)$$

$$\frac{1}{k'} = \frac{1}{k} + \frac{[H_4TeO_6^{2-}][OH^-]}{K_1K_{a2}} \quad (14)$$

From the equation presented above, it is demonstrated that a plot of k_{obs} versus $[\text{amino acid}]$ is a straight line, which through the origin. The plots of $1/k_{obs}$ versus $[OH^-]$ and $[H_4TeO_6^{2-}]$ are all straight line. The plots of $1/k'$ versus $[OH^-]$ and $[H_4TeO_6^{2-}]$ are all straight line too. So the rate law obtained from reaction mechanism can explain all these experimental phenomena. The activation parameters were obtained by a fit of the natural logarithm of

rate constant of the rate determining step, $\ln(k')$ versus $1/T$ to the Arrhenius equation (Table 5).

CONCLUSION

In this study, the oxidation of leucine, isoleucine and valine by bis(dihydrogen tellurate)argentate(III) was investigated using the stopped-flow technique. The rate law for the proposed reaction mechanism explains all the experimental observations. The reactions products in basic medium are aldehydes. The results support the notion that the Ag(III) complex can be used as a reagent for a transformation of peptides and proteins in alkaline medium. Studies are in progress toward this direction. And the reaction is similar to the metabolizability of the amino acid in the human body. So we can learn more about the reaction of amino acid in the body.

Table 5: the second order rate constants at different temperature and activation parameters of these reactions at 298 K.

amino acid	T/K	$k'/(mol^{-1} \cdot L \cdot s^{-1})$	activation parameters
Leucine	293.2	1.548	$E_a = 62.47 \pm 1.43$ KJ/mol
	298.2	2.266	$H^\ddagger = 59.99 \pm 1.43$ KJ/mol
	303.2	3.536	$S^\ddagger = -36.82 \pm 4.74$ J/(mol·K)
	308.2	5.121	$k = 3.268 \pm 0.663$ L/(mol·s)
	313.2	7.969	$K_1 = (1.988 \pm 1.696) \times 10^{-5}$ mol/L
isoleucine	293.2	1.627	$E_a = 64.74 \pm 1.59$ KJ/mol
	298.2	2.617	$H^\ddagger = 62.26 \pm 1.59$ KJ/mol
	303.2	4.081	$S^\ddagger = -28.25 \pm 5.24$ J/(mol·K)
	308.2	5.766	$k = 4.634 \pm 1.648$ L/(mol·s)
	313.2	9.126	$K_1 = (1.536 \pm 0.881) \times 10^{-5}$ mol/L
valine	293.2	1.583	$E_a = 66.82 \pm 2.66$ KJ/mol
	298.2	2.540	$H^\ddagger = 64.34 \pm 2.66$ KJ/mol
	303.2	3.926	$S^\ddagger = -21.52 \pm 8.81$ J/(mol·K)
	308.2	5.540	$k = 3.234 \pm 0.464$ L/(mol·s)
	313.2	9.565	$K_1 = (2.458 \pm 1.458) \times 10^{-5}$ mol/L

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