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Mechanistic Investigation of Oxidation of Glycine and Alanine by Bis(dihydrogen-tellurto)argentite(III) Ion in Alkaline Medium. A Kinetic Study

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The oxidation of glycine and alanine by bis(dihydrogen-tellurto)argentite(III) ion was studied by stopped-flow spectrophotometery. The reaction is of first order in Ag(III) complex and has less than unit order in glycine and alanine. A plausible mechanism was proposed form the kinetic studies. The rate equations derived from mechanism found to explain all experimental phenomena. The activation parameters with respect to the rate determining step of the mechanism were calculated.

Keywords: Bis(dihydrogen-tellurto)argentite(III), Glycine, Alanine, Kinetics and mechanism, Redox reactions

INTRODUCTION

Amino acids can undergo many types of reactions 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 [1-13]. Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant.

Ag(III) complexes is stable in alkaline medium, which can be used as an oxidation reagent in analytical chemistry [14]. These complexes have been used widely in kinetic studies and the kinetics and mechanism of oxidation of some chemical reagents by Ag(III) complexes had been studied [15-19]. However, oxidation of glycine and alanine by bis(dihydrogen-tellurto)argentite(III) has not been reported. In this paper, the oxidation of glycine and alanine by bis(dihydrogen-tellurto)argentite(III) in alkaline medium has been studied.

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EXPERIMENTAL

Reagents

All the reagents used were of A.R. Grade and all solutions were prepared with doubly distilled water. Glycine and alanine were changed to their potassium salts by adding KOH solution at an amino acid to KOH molar ratio of 1:2. Solutions of bis(dihydrogen-tellurto)argentite(III) ion were standardized by the method reported earlier [20]. The UV spectrum of the complex has a characteristic absorption band at 350 nm, which was found to be consistent with that reported. The concentration of bis(dihydrogen-tellurto)argentite(III) was derived by its absorption at 350 nm. Solutions of bis(dihydrogen-tellurto)argentite(III) were always freshly prepared before use with doubly-distilled water. The ionic strength was maintained by adding KNO_3 solution and the pH of reaction mixtures was maintained with KOH solution.

Synthesis of Bis(dihydrogen-tellurto)argentite(III)

$AgNO_3$ (2.72 g), H_6TeO_6 (7.34 g), $K_2S_2O_8$ (13 g) and KOH (18 g) were taken in a 100 ml round bottomed flask and 50 ml of demineralized water was added. The mixture was heated to boiling while stirring. After 10 min of boiling, an orangish-yellow froth was obtained and the mixture was heated for another 10 min. The mixture was left to cool to room temperature and filtered through a Gooch crucible. The solution was then cooled in an ice bath to eliminate as much of potassium sulfate 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, 40 ml of $NaNO_3$ saturated solution were added to the solution and the mixture left to crystallize. Almost immediately, crystals started appearing and crystallization is completed when the supernatant liquid is colorless. The crystals were filtered and washed several times with demineralized 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 make sure about elimination of sodium and potassium hydroxides since this complex is insoluble.

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 reaction was started by mixing of equal volumes (128 µl) of a solution of the Ag(III) complex with a solution of amino acid directly in the stopped-flow instrument. The reaction of the amino acid with the Ag(III) complex was monitored as a decrease in absorbance at the complex maximum absorbance at 350 nm. The observed rate constants were calculated by fit of a single exponential function to the kinetic traces. The reported pseudo-first-order rate constants, k_{obs}, are mean values of at least five independent kinetic runs, using a standard least-squares minimizing subroutine.

Product Analysis

A solution having known concentrations of [Ag(III)], [OH^-] and [$H_4TeO_6^{2-}$] was mixed with an excess of amino acid, and the completion of the reaction was marked by the complete discharge of Ag(III) color [21]. After completion of the reaction, the main reaction products were identified as $RCOCOO^-$ (R = H for glycine, $-CH_3$ for alanine) by a spot test [22], and ammonia was identified 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 flushed 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 unlikely.

RESULTS AND DISCUSSION

Protolytic Equilibria

Under the reaction conditions used in the present work, *i.e.*, 0.02 M < [OH^-] < 0.11 M, we ensure that [OH^-] remains constant during the reaction course. Protolysis constants of glycine and alanine have been reported to be: pK_a (α-COOH) = 2.34, and pK_a ($-NH_3^+$) = 9.6 for glycine, pK_a (α-COOH) = 2.35, and pK_a ($-NH_3^+$) = 9.69 for alanine [23]. From these equilibrium constants, it can be calculated that the amino acid is existing in the form of RCH_2COO^- (R = H for glycine, $-CH_3$ for alanie) in the alkaline medium used. Several protolytic equilibriums have been described for aqueous tellurate chemistry [24]. Following are reported two equilibriums together with the corresponding equilibrium constants, were potassium tellurate was dissolved in aqueous alkaline medium, at $pK_w = 14$.

$$H_5TeO_6^- + OH^- \underset{}{\overset{K_{a1}}{\rightleftharpoons}} H_4TeO_6^{2-} + H_2O \qquad \log Ka_1 = 3.049 \quad (1)$$

$$H_3TeO_6^{3-} + H_2O \underset{}{\overset{K_{a2}}{\rightleftharpoons}} H_4TeO_6^{2-} + OH^- \qquad \log Ka_2 = 1.00 \quad (2)$$

Based on the above equilibrium constants, if [OH^-] = 0.01 M,

$[H_4TeO_6^{2-}]$:$[H_5TeO_6^{-}]$:$[H_3TeO_6^{3-}]$ = 1000:89:1; hence, at the concentration range of OH^- used in this work, the amount of $H_5TeO_6^-$ and $H_3TeO_6^{3-}$ spices are negligible and the main tellurate specie is $[H_4TeO_6^{2-}]$.

Influence of $[OH^-]$ and $[H_4TeO_6^{2-}]$ on the Reaction Rates

At fixed concentrations of Ag(III), OH^- and amino acid and fixed ionic strength and temperature, the value of k_{obs} decreased with the increasing $[H_4TeO_6^{2-}]$. The plot of $1/k_{obs}$ *vs*. $[H_4TeO_6^{2-}]$ was found to be a straight line with a positive intercepts (Figs. 1 and 2). It illustrated that tellurate is the product of the pre-equilibrium. Thus, Eq. (3) can be expressed as:

$$[Ag(H_2TeO_6)_2]^{5-} + 2H_2O \overset{K_1}{\rightleftharpoons} [Ag(OH)(H_2O)(H_2TeO_6)]^{2-} + H_3TeO_6^{3-} \quad (3)$$

Meanwhile, at fixed concentrations of Ag(III), $H_4TeO_6^{2-}$ and amino acid and fixed ionic strength and temperature, the value of k_{obs} decreased with an increase in $[OH^-]$. The plot of $1/k_{obs}$ *vs*. $[OH^-]$ was also a straight line (Figs. 3 and 4). The k_{obs} values increased upon addition of KNO_3 solution, as shown in Table 1.

Influence of [Amino Acid] on the Reaction Rates

At fixed concentrations of Ag(III), OH^- and $H_4TeO_6^{2-}$ and fixed ionic strength, the values of k_{obs} were determined at different temperatures and amino acid concentrations. The k_{obs} values were found to increase with increasing concentration of amino acid at all temperatures. The order, slope for the plot of ln k_{obs} *vs*. ln [amino acid], is less than unity. The plots of $1/k_{obs}$ *vs*. 1/[amino acid] were straight lines at different temperatures (Table 2), which it can be known that a molecule of amino acid participated in another pre-equilibrium step, Eq. (4) can be obtained as:

$$[Ag(OH)(H_2O)(H_2TeO_6)]^{2-} + RCH_2(NH_2)COO^- \overset{K_2}{\rightleftharpoons} \text{adduct} + H_2O \quad (4)$$

Reaction Mechanism

According to the kinetic results obtained, following

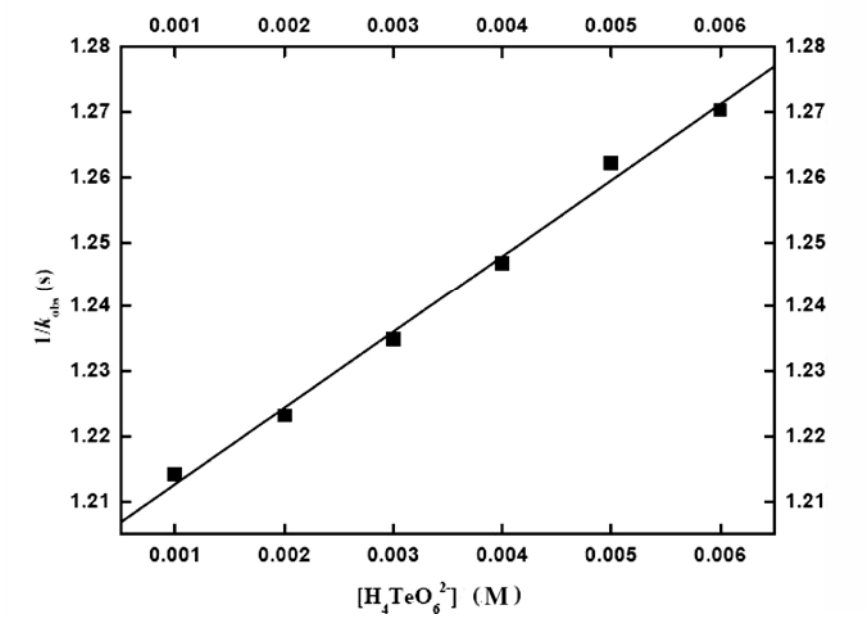


Fig. 1. Plot of $1/k_{obs}$ *vs*. $[H_4TeO_6^{2-}]$ for the oxidation of glycine by Ag(III) complex at 298.2 K. Reaction conditions: [Ag(III)] = 1.651×10^{-4} M, $[OH^-] = 2.00 \times 10^{-2}$ M, [glycine] = 5.00×10^{-2} M, I = 0.09 M, T = 298.2 K.

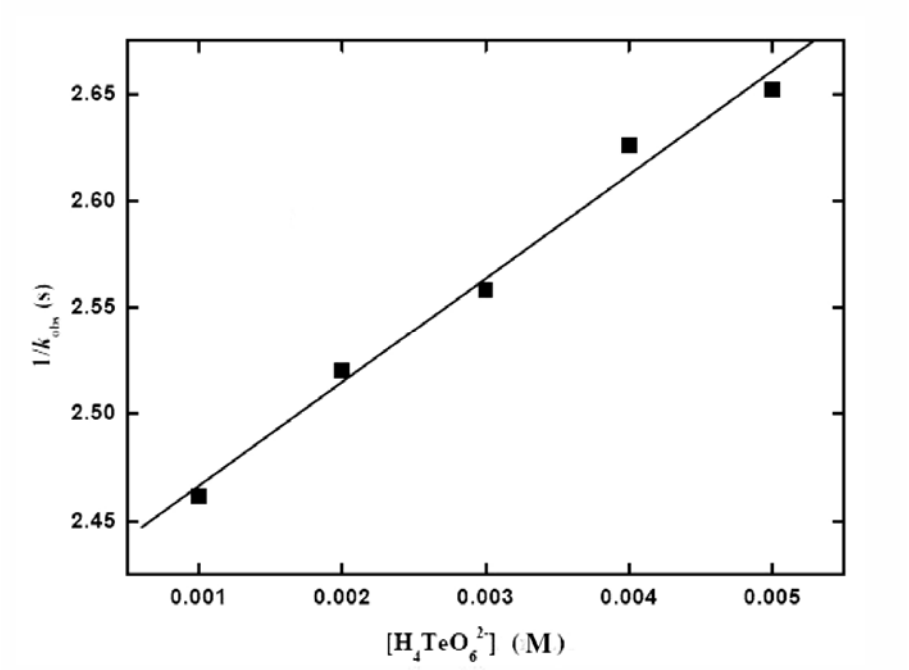


Fig. 2. Plot of $1/k_{obs}$ *vs*. $[H_4TeO_6^{2-}]$ for the oxidation of alanine by Ag(III) complex at 298.2 K. Reaction conditions: [Ag(III)] = 1.651×10^{-4} M, $[OH^-] = 2.00 \times 10^{-2}$ M, [glycine] = 5.00×10^{-2} M, I = 0.09M, T = 298.2 K.

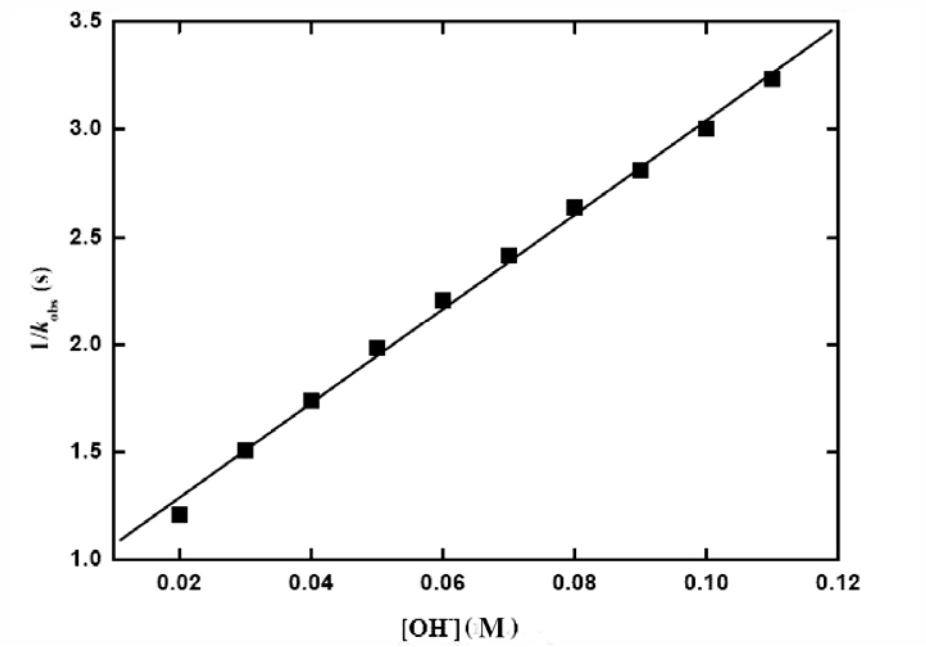


Fig. 3. Plot of $1/k_{obs}$ *vs*. $[OH^-]$ for the oxidation of glycine by Ag(III) complex at 298.2 K, Reaction conditions: [Ag(III)] = 1.651×10^{-4} M, $[H_4TeO_6^{2-}] = 3.00 \times 10^{-3}$ M, [glycine] = 5.00×10^{-2} M, I = 0.17 M, T = 298.2 K.

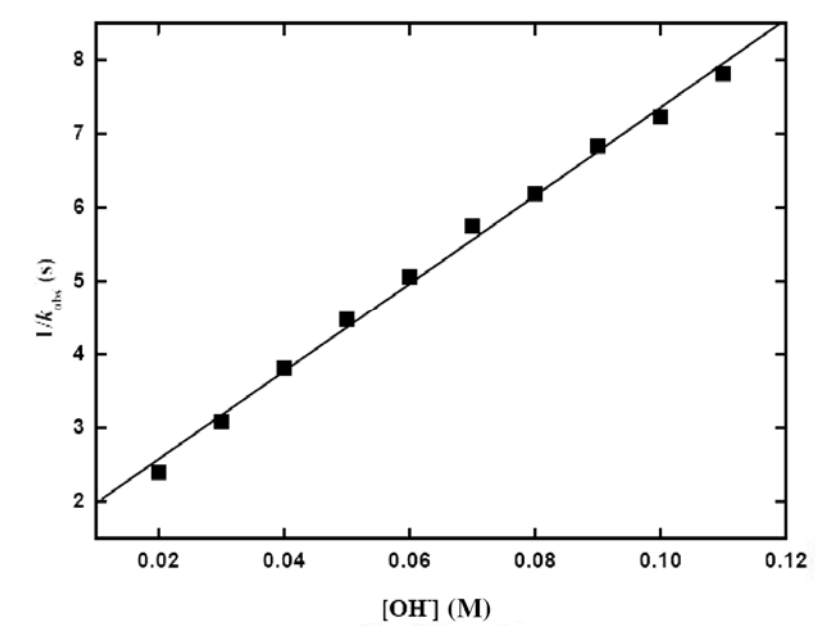


Fig. 4. Plot of $1/k_{obs}$ *vs.* $[OH^-]$ for the oxidation of alanine by Ag(III) complex at 298.2 K. Reaction conditions: [Ag(III)] = 1.651×10^{-4} M, $[H_4TeO_6^{2-}] = 3.00 \times 10^{-3}$ M, [alanine] = 5.00×10^{-2} M, I = 0.17 M, T = 298.2 K.

Table 1. Values of k_{obs} at Various Ion Strengths[a]

C (M)		0.08	0.18	0.28	0.38	0.48
$10k_{obs}$ (s^{-1})	Glycine	7.142	7.985	8.005	8.112	8.152
	Alanine	3.481	3.661	3.719	3.940	4.243

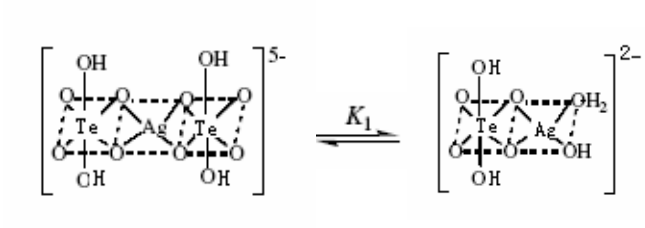
[a]Reaction conditions: [Ag(III)] = 1.651×10^{-4} M, $[OH^-] = 2.00 \times 10^{-2}$ M, $[H_4TeO_6^{2-}] = 3.00 \times 10^{-3}$ M, [amino acid] = 5.00×10^{-2} M T = 298.2 K.

Table 2. Values of k_{obs} at Various Amino Acid Concentrations and Different Temperatures[a]

C (M)	0.02	0.04	0.06	0.08	0.10
T (K)			$10k_{obs}$ (s^{-1}) for Glycine		
293.2	2.668	4.689	6.223	8.287	9.847
298.2	3.859	6.854	8.909	11.53	13.69
303.2	5.547	9.461	12.63	16.83	20.34
308.2	8.109	13.73	18.59	24.01	29.33
313.2	11.17	19.26	26.38	33.79	41.87
T (K)			$10k_{obs}$ (s^{-1}) for Alanine		
293.2	1.328	2.387	3.207	4.088	4.842
298.2	1.818	3.144	4.669	5.765	6.858
303.2	2.585	4.583	6.348	9.047	10.02
308.2	4.162	7.221	10.36	13.17	16.45
313.2	6.253	11.08	14.91	19.55	23.92

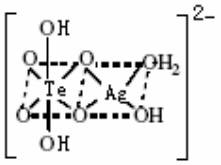
[a]Reaction conditions: [Ag(III)] = 1.651×10^{-4} M, $[OH^-] = 2.00 \times 10^{-2}$ M, $[H_4TeO_6^{2-}] = 3.00 \times 10^{-3}$ M, I = 0.33 M.

reaction mechanism can be suggested:



+ $H_3TeO_6^{3-}$ (5)

$$H_3TeO_6^{3-} + H_2O \underset{}{\overset{K_{a2}}{\rightleftharpoons}} H_4TeO_6^{2-} + OH^- \quad (6)$$



+ $RCH_2(NH_2)COO^-$ $\overset{K_2}{\rightleftharpoons}$

adduct + H_2O (7)

adduct $\xrightarrow{k}$ intermediate (8)

intermediate $\xrightarrow{fast}$ Ag(I) + $RCHOCOO^-$ + NH_3 + $H_4TeO_6^{2-}$ + OH^- (9)

Thus, based on the above equations, one may have:

$$[Ag(III)]_{Tot} = [H_3TeO_6^{3-}]_e + [H_4TeO_6^{2-}]_e + [adduct]_e \quad (10)$$

where "e" means equilibrium concentration of the species indicated.

The rate of reaction can be written as:

$$r = -d[Ag(III)]_{Tot}/dt = k_{obs}[Ag(III)]_{Tot} = k\,[adduct]_e \quad (11)$$

where k_{obs} and k are the observed rate constant and rate determining step rate constant, respectively. Then k_{obs} can be expressed as:

$$k_{obs} = \frac{kK_1K_2K_{a2}[\text{amino acid}]}{[H_4TeO_6^{2-}][OH^-] + K_1K_{a2} + K_1K_2K_{a2}[\text{amino acid}]} \quad (12)$$

Rearrangement of Eq. (13) gives:

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{[H_4TeO_6^{2-}][OH^-] + K_1K_{a2}}{kK_1K_2K_{a2}} \frac{1}{[\text{amino acid}]} \quad (13)$$

According to Eq. (13), the plots of $1/k_{obs}$ *vs*. $[OH^-]$ at fixed $[H_4TeO_6^{2-}]$ and $1/k_{obs}$ *vs*. $[H_4TeO_6^{2-}]$ at fixed $[OH^-]$ should give straight lines. It is also clear that a plot of $1/k_{obs}$ *vs*. 1/[amino acid] at fixed $[H_4TeO_6^{2-}]$ and $[OH^-]$ is also a straight line with a positive intercept, from which the rate determining step rate constants can be calculated. The activation parameters with respect to rate determining step were obtained by a fit of the natural logarithm of rate constant of the rate determining step, ln(*k*) *vs*. 1/T to the Arrhenius equation (Table 3 and Fig. 5).

Table 3. The Values of *k* at Different Temperatures and Corresponding Activation Parameters at 298.2 K

Amino acid	T (K)	k (s^{-1})	Activation parameters
Glycine	293.2	2.494 ± 0.069	Ea = 53.60 ± 2.66 kJ mol^{-1}
	298.2	3.268 ± 0.037	$\Delta H^{\ddagger}$ = 51.12 ± 2.66 kJ mol^{-1}
	303.2	4.739 ± 0.045	$\Delta S^{\ddagger}$ = -63.362 ± 8.73 J mol^{-1} K^{-1}
	308.2	6.667 ± 0.029	
	313.2	10.31 ± 0.018	
Alanine	293.2	1.291 ± 0.066	Ea = 61.27 ± 3.28 kJ mol^{-1}
	298.2	2.028 ± 0.103	$\Delta H^{\ddagger}$ = 58.79 ± 3.28 kJ mol^{-1}
	303.2	3.344 ± 0.087	$\Delta S^{\ddagger}$ = -41.80 ± 10.81 J mol^{-1} K^{-1}
	308.2	4.739 ± 0.049	
	313.2	6.411 ± 0.028	

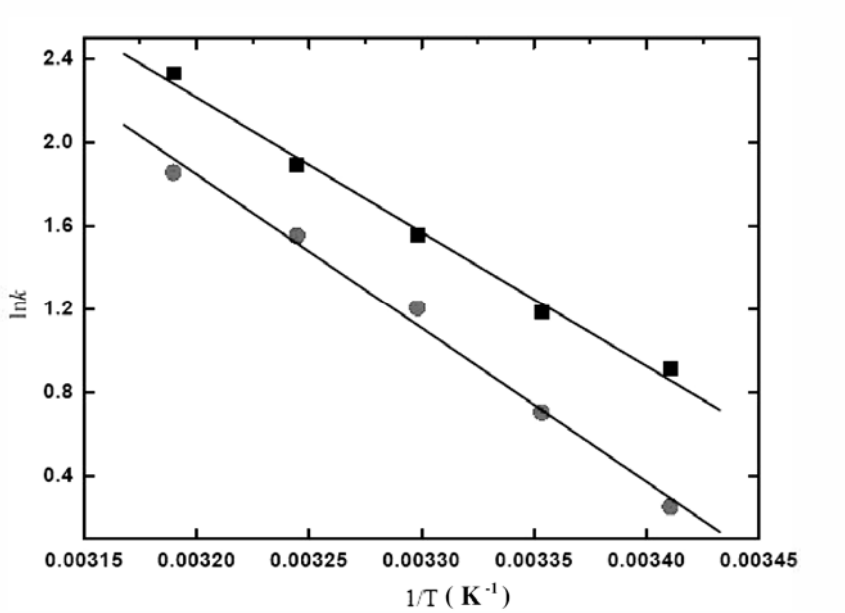


Fig. 5. Arrhenius' plots for oxidation of glycine and alanine with bis(dihydrogen-tellurto)argentite(III) complex: (■) glycine, (●) alanine.

CONCLUSIONS

In this paper, the oxidation of glycine and alaine by bis(dihydrogen-tellurto)argentite(III) was investigated by stopped-flow spectrophotometery. From the results of kinetic studies, a possible reaction mechanism was proposed. According to the rate law derived from the proposed mechanism can explain all the experimental phenomena, which suggest that the mechanism is suitable for this reaction. The reactions take place in alkaline medium and the product is $RCOCOO^-$ (R = H for glycine, $-CH_3$ for alanine). These features implicate that the Ag(III) complex might be used as a reagent for modifications of peptides and proteins in alkaline medium. In fact, the reaction is similar to the metabolizability of the amino acids in the human body. Studies are in progress toward this direction, so that we may learn more about the reaction of amino acid in human body.

REFERENCES

[1] H. Shi, S. Shen, H. Sun, J. Inorg. Biochem. 101 (2007) 165.

[2] S. Huo, C. Song, J. Shan, J. Chil. Chem. Soc. 52 (2007) 1102.

[3] D. Bilehal, R. Kulkarni, S. Nandibewoor. J. Mol. Catal. A 232 (2005) 21.

[4] B.T. Gowda, P. Jagan, M. Rao, Bull. Chem. Soc. Jpn. 62 (1989) 3303.

[5] Y.R. Katre, A.K. Singh, S. Patil, G.K. Joshi, Oxidation Commun. 29 (2006) 129.

[6] Y.R. Katre, A.K. Singh, G.K. Joshi, S. Patil, Oxidation Commun. 29 (2006) 137.

[7] A. Kumar, P. Kumar, P. Ramamurthy, Polyhedron 18 (1999) 773.

[8] N. Nalwaya, A. Jain, B.L. Hiran, Kin. Catal. 45 (2004) 345.

[9] R.M. Rodriguez, J.D Andres, E.B. Brillas, J.A. Garrido, J.P. Benito, New J. Chem. 12 (1988) 143.

[10] R.T. Mahesh, M.B. Bellakki, S.T. Nandibewoor, J. Chem. Res. 1 (2005) 13.

[11] S.A. Chimatadar, A.K. Kini, S.T. Nandibewoor, Oxidation Commun. 29 (2006) 147.

[12] R.M. Mulla, H.M. Gurubasavaraj, S.T. Nandibewoor, Polish J. Chem. 77 (2003) 1833.

[13] S.-Y. Huo, C.-Y. Song, Y.-J. Zhen, Trans. Metal Chem. 32 (2007) 936.

[14] P.K. Jaiswal, K.L. Yadava, Talanta 17 (1970) 236.

[15] S. Jin-Huan, H. Shu-Ying, S. Shi-Gang, S. Han-Wen,

W. An-Zhou, Chem. J. Chin. Univ. 26 (2005) 706.
[16] J.H. Shan, S.Y. Huo, S.G. Shen, H.W. Sun, J. Serb. Chem. Soc. 70 (2005) 585.
[17] V. Seregar, T.M. Veeresh Sharanappa, T. Nandibewoor, Polyhedron. 26 (2007) 1731.
[18] C.V. Hiremath, T.S. Kiran, T. Nandibewoor, J. Mol. Catal. A 248 (2006) 163.
[19] A. Das, S. Mukhopadhyay, Polyhedron. 23 (2004) 895.
[20] A. Balikungeri, M. Pelletier, D. Minnier, Inorg. Chim. Acta 22 (1977) 7.
[21] T.S. Shi, J.T. He, T.H. Ding, J. Chem. Kin. 23 (1991) 815.
[22] F. Feigl, Spot Tests in Organic Analysis, Elsevier Publishing Co., New York, P208, 1956.
[23] Q.Y. Xing, F.F. Pei, R.Q. Xu, J. Pei, Basic Organic Chemistry, 3th ed., Higher Education Press, Beijing, 2005, p. 980
[24] The Teaching and Research Section of Analytical Chemistry in Zhongnan Mining Institute, Handbook of Analytical Chemistry, Beijing: Science publishing Co., 1984, p. 567.