Kinetics and Mechanism of the Oxidation of β-Alanine by Dihydroxydiperiodatoargentate(III) in an Alkaline Medium

J.H. Shan*, S.M. Li, S.Y. Huo, S.G. Shen and H.W. Sun

Key Laboratory of Analytical Science and Technology of Hebei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

The kinetics of the oxidation of β**-**alanine by dihydroxydiperiodatoargentate(III) (DPA) in an alkaline medium was studied by spectrophotometry in a temperature range of 298.2 K-318.2 K. The reaction rate showed pseudo-first order dependence in the oxidant and $1 < n_{ap} < 2$ in the reductant. A plausible mechanism involving a pre-equilibrium of adduct formation between the complex and reductant is proposed. The rate equations derived from the mechanism explain all experimental observations. The activation parameters along with the rate constants of the rate-determining step were calculated.

INTRODUCTION

Transition metals in higher oxidation states generally can be stabilized by chelation with suitable polydentate ligands. Metal chelates such as diperiodatoargentate(III) [1], ditellurato-argentate(III) [2], diperiodatonickelate(IV) [3] are good oxidants in a medium with an appropriate pH. The usefulness of complexes as oxidizing agents in the field of analytical chemistry has been reported [4]. The oxidation of a number of organic compounds and metals in lower oxidation states by Ag(III) has also been performed [1], but no further information on the kinetics is available. Because of the high oxidation state of Ag(III) and the complexity of the reaction in this kind of reaction system, further study of this type of reaction system would be significant. Such an investigation would provide us with more dynamic parameters, as well as a theoretical foundation for the design of a reaction route in organic syntheses and quantitative analyses in analytical chemistry.

In this paper, the mechanism of oxidation of β-alanine by dihydroxydiperiodatoargentate(III) is reported.

EXPERIMENTAL

Materials

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. The solution of $[Ag(OH)_2(H_2IO_6)_2]^{5-}$ (DPA) was prepared and standardized as previously reported [5]. Its UV spectrum was found to be consistent with that reported. The concentration of DPA was derived by its absorption at $\lambda = 362$ nm. The DPA solution was always freshly prepared before use. The ionic strength (μ) was maintained by adding KNO_3 solution and the pH value of the reaction mixture was regulated with KOH solution.

Apparatus and Kinetics Measurements

All kinetics measurements were carried out under pseudo-first order conditions. Two ml of the DPA solution containing a known concentration of Ag(III), OH⁻, and IO_4^-,

---

* Corresponding author. E-mail:shanjinhuaner@yahoo.com.cn

with a known μ was transferred to the upper branch tube of a type two-cell reactor and 2 ml of reductant solution with an appropriate concentration was transferred to the lower branch tube of the reactor. After thermal equilibration in a thermobath (Techcomp Scientific Instrument Co., Ltd., Shanghai), the two solutions were mixed well and immediately transferred to a 1-cm thick rectangular cell quartz in a cell-holder kept at a constant temperature (±0.1 °C). The reaction process was monitored automatically by recording the disappearance of Ag(III) with time (*t*) at 362 nm with a UV-8500 spectrophotometer (Techcomp Scientific Instrument Co., Ltd., Shanghai) (Fig. 1). None of the other species absorbed significantly at this wavelength.

Product Analysis

A solution with a known concentration of Ag(III) and OH^- was mixed with an excess of β-alanine, The completion of the reaction was marked by the complete discharge of the Ag(III) color. After completion of the reaction, the products of the oxidation were identified as ammonia and the corresponding aldehyde acid by their characteristic spot test [6].

RESULTS AND DISCUSSION

Evaluation of Pseudo-First Order Rate Constants

Under the conditions of $[Reductant]_0 \gg [Ag(III)]_0$, the plots of $\ln(A_t-A_\infty)$ versus time are linear, indicating the reaction is first order with respect to [Ag(III)], where A_t and A_∞ are the absorbance at time *t* and at infinite time, respectively. The pseudo-first-order rate constants, k_{obs}, were calculated by the method of least squares (r ≥ 0.999). To calculate k_{obs} generally 8-10 A_t values within three times the half-life were used. k_{obs} values were at least averaged values of three independent experiments and reproducibility is within ±5%.

Rate Dependence on β-Alanine

At fixed [Ag(III)], [OH⁻], [IO₄⁻], μ, and temperature, k_{obs} values increased with an increase in [Ala] and the order in the concentration of [Ala] was found to be $1 < n_{ap} < 2$ (Fig. 2). The plots of $[Ala]^2/k_{obs}$ versus [Ala] are straight linear with a positive intercept (Table 1) .
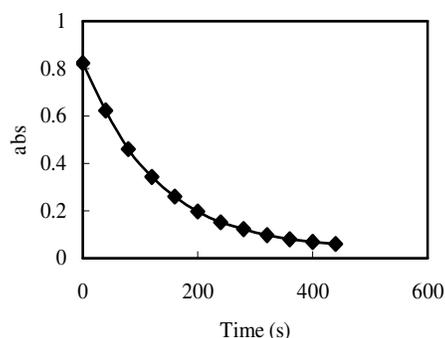
Fig. 1. The absorbance of Ag(III) over time: Ag(III), 7.16×10^{-5} M; IO_4^-, 2.00×10^{-3} M; OH^-, 0.06 M; Ala, 6.00×10^{-2} M; μ, 0.162 M; T, 303.2 K.
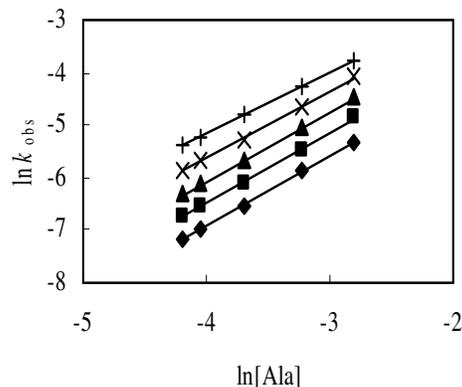
Fig. 2. $\ln k_{obs}$ versus ln[Ala]: Ag(III), 7.16×10^{-5} M; IO_4^-, 2.00×10^{-3} M; OH^-, 0.06 M; μ, 0.142 M; T = (◆) 298.2, (■) 303.2, (▲) 308.2, (✕) 313.2, (+) 318.2 K.

Rate Dependence on [OH⁻]

At constant [Ag(III)], [Ala], [IO₄⁻], μ and temperature, k_{obs} values decreased with an increase in [OH⁻], and then increased with the increase in [OH⁻], The concentration of OH⁻ was approximately 0.045 M at the turning point, at which the rate was the slowest (Fig. 3).

Rate Dependence on [IO₄⁻] and Ionic Strength

At constant [Ag(III)], [Ala], [OH⁻], μ and temperature, k_{obs}

Table 1. Variation in $10^3 \, k_{obs}$ (s^{-1}) at Different Concentrations of Ala and Different Temperatures

10^2 [Ala] (M) T (K)	1.50	1.75	2.50	4.00	6.00	8.00	n_{ap}	r	b	r_1
298.2	0.7535	0.9410	1.438	2.778	4.920	7.014	1.34	0.999	9.291	0.997
303.2	1.213	1.464	2.219	4.258	7.819	10.61	1.32	0.999	6.153	0.994
308.2	1.808	2.229	3.420	6.455	11.51	16.63	1.33	0.999	3.969	0.995
313.2	2.857	3.494	5.035	9.713	16.70	23.46	1.27	0.999	2.930	0.997
318.2	4.594	5.337	8.175	14.26	23.17	32.63	1.18	0.999	2.252	0.999

Ag(III), 7.16×10^{-5} M; IO_4^-, 2.00×10^{-3} M; OH^-, 0.06 M; μ, 0.142 M; n_{ap} and r stand for the slope and relative coefficient, respectively, of the plot of $\ln k_{obs}$ *vs*. $\ln C$, b and r_1 stand for the slope and relative coefficient, respectively, of the plot of $[Ala]^2/k_{obs}$ versus [Ala].
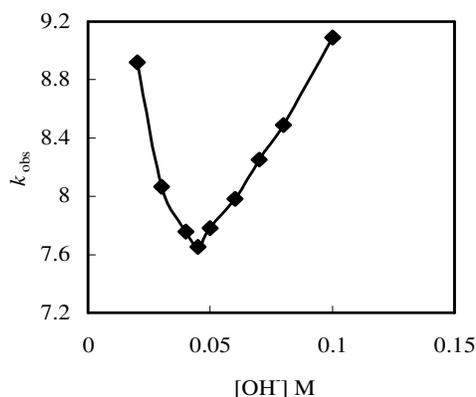
Fig. 3. k_{obs} versus [OH^-], Ag(III), 7.16×10^{-5} M; IO_4^-, 2.00×10^{-3} M; Ala, 0.06 M; μ, 0.162 M; T, 303.2 K.

values decreased with an increase in [IO_4^-] and the plots of $1/k_{obs}$ versus [IO_4^-] were linear (r = 0.9997). The order with respect to [IO_4^-] was found to be fractional ($n_{ap \, (IO4-)}$ = -0.886, r = 0.9994). The rate did not change upon the addition of the KNO_3 solution, which indicates there was no salt effect, consistent with the common regulation of the kinetics [7] (Table 2).

Discussion of the Reaction Mechanism

In aqueous periodate solutions, equilibria (1-3) were observed and the corresponding equilibrium constants at 273.2 K were determined by Aveston [8].

Table 2. Variation of k_{obs} (s^{-1}) with Varying [IO_4^-] and μ at 30 °C; Ag(III), 7.16×10^{-5} M

[Ala] (M)	10^3[IO_4^-] (M)	[OH^-] (M)	μ (M)	$10^3 \, k_{obs}$ (s^{-1})
0.060	1.00	0.06	0.124	14.18
0.060	2.00	0.06	0.124	8.011
0.060	3.00	0.06	0.124	5.425
0.060	4.00	0.06	0.124	4.239
0.060	4.50	0.06	0.124	3.728
0.050	2.00	0.06	0.112	6.192
0.050	2.00	0.06	0.212	6.002
0.050	2.00	0.06	0.312	6.054
0.050	2.00	0.06	0.412	5.934
0.050	2.00	0.06	0.512	6.066

$$2IO_4^- + 2OH^- \rightleftharpoons H_2I_2O_{10}^{4-} \quad \log \beta_1 = 15.05 \quad (1)$$

$$IO_4^- + OH^- + H_2O \rightleftharpoons H_3IO_6^{2-} \quad \log \beta_2 = 6.21 \quad (2)$$

$$IO_4^- + 2OH^- \rightleftharpoons H_2IO_6^{3-} \quad \log \beta_3 = 8.67 \quad (3)$$
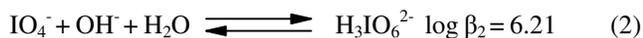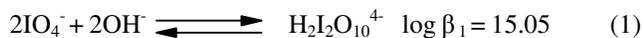
The distribution of all species of periodate in aqueous alkaline solution can be calculated from equilibria (1-3). In the $[OH^-]$ range used in this work, the amount of dimer and IO_4^- species of periodate is negligible ($[H_2IO_6^{3-}]$:$[H_3IO_6^{2-}]$:$[H_2I_2O_{10}^{4-}]$:$[IO_4^-] \cong 2.9\text{-}29{:}1.0{:}0.02\text{-}0.2{:}6 \times 10^{-5}\text{-}6 \times 10^{-4}$). The main species of periodate are $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$, consistent with the result calculated from Crouthamel's data [9] by Murthy. Eqs. (4) and (5) can be obtained from (2) and (3):

$$[H_2IO_6^{3-}] = \frac{\beta_3[OH^-]^2}{1 + \beta_2[OH^-] + \beta_3[OH^-]^2}[IO_4^-]_{ex} = f([OH^-])[IO_4^-]_{ex} \quad (4)$$

$$[H_3IO_6^{2-}] = \frac{\beta_2[OH^-]}{1 + \beta_2[OH^-] + \beta_3[OH^-]^2}[IO_4^-]_{ex} = \phi([OH^-])[IO_4^-]_{ex} \quad (5)$$

Here $[IO_4^-]_{ex}$ represents the concentration of the original overall periodate ion and is approximately equal to the sum of $[H_2IO_6^{3-}]$ and $[H_3IO_6^{2-}]$. In the $[OH^-]$ range used in this work, $[H_2IO_6^{3-}]$:$[H_3IO_6^{2-}] = 5.8\text{-}28.4{:}1.00$, so the main species of periodate is $H_2IO_6^{3-}$. Based on such distribution, the formula of the Ag(III) periodate complex may be represented by either $[Ag(OH)_2(H_3IO_6)_2]^{3-}$ or the less protonated ionic species $[Ag(OH)_2(H_2IO_6)_2]^{5-}$. We preferred to use the latter to represent DPA because it is closer to that suggested by Mukherjee [10].

Based on the above discussion, two simultaneous reaction mechanisms were proposed:

Mechanism I. In a less alkaline medium:
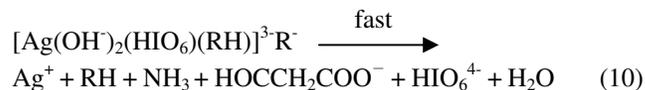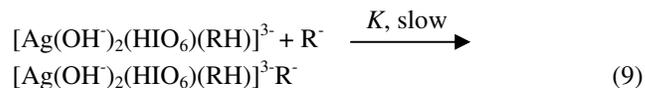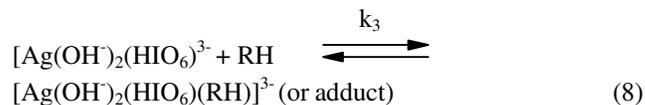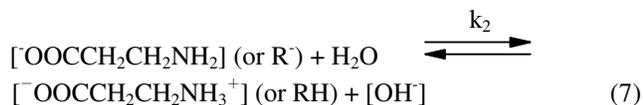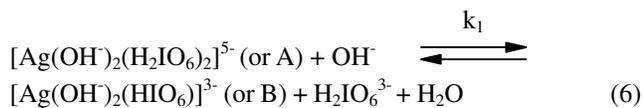
$$[Ag(OH^-)_2(H_2IO_6)_2]^{5-} \text{ (or A)} + OH^- \overset{k_1}{\rightleftharpoons}$$
$$[Ag(OH^-)_2(HIO_6)]^{3-} \text{ (or B)} + H_2IO_6^{3-} + H_2O \quad (6)$$

$$[^-OOCCH_2CH_2NH_2] \text{ (or R}^-\text{)} + H_2O \overset{k_2}{\rightleftharpoons}$$
$$[^-OOCCH_2CH_2NH_3^+] \text{ (or RH)} + [OH^-] \quad (7)$$

$$[Ag(OH^-)_2(HIO_6)]^{3-} + RH \overset{k_3}{\rightleftharpoons}$$
$$[Ag(OH^-)_2(HIO_6)(RH)]^{3-} \text{ (or adduct)} \quad (8)$$

$$[Ag(OH^-)_2(HIO_6)(RH)]^{3-} + R^- \overset{K, \text{ slow}}{\longrightarrow}$$
$$[Ag(OH^-)_2(HIO_6)(RH)]^{3-}R^- \quad (9)$$

$$[Ag(OH^-)_2(HIO_6)(RH)]^{3-}R^- \overset{fast}{\longrightarrow}$$
$$Ag^+ + RH + NH_3 + HOCCH_2COO^- + HIO_6^{4-} + H_2O \quad (10)$$

The total concentration of Ag(III) at time t can be written as $[Ag(III)]_t = [A]_e + [B]_e + [\text{adduct}]_e$. Since reaction (9) is the rate-determining step, the rate of disappearance of $[Ag(III)]_t$ is monitored as:

$$-d[Ag(III)]_t/dt = k[\text{adduct}]_e[R^-] =$$

$$= \frac{kK_1K_2K_3[R^-]^2[Ag(III)]_t}{[H_2IO_6^{3-}] + K_1[OH^-] + K_1K_2K_3[R^-]} = k_{obs}[Ag(III)]_t \quad (11)$$

$$k_{obs} = \frac{kK_1K_2K_3[R^-]^2}{[H_2IO_6^{3-}] + K_1[OH^-] + K_1K_2K_3[R^-]} \quad (12)$$

$$\frac{[R^-]^2}{k_{obs}} = \frac{[R^-]}{k} + \frac{[H_2IO_6^{3-}] + K_1[OH^-]}{kK_1K_2K_3[OH^-]} \quad (13)$$

Mechanism II. In a more alkaline medium:
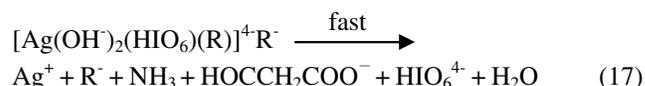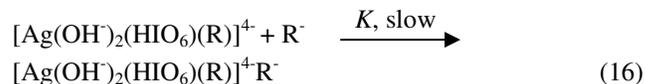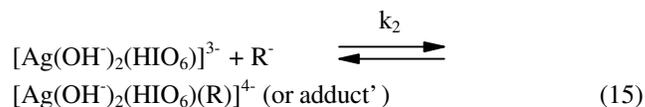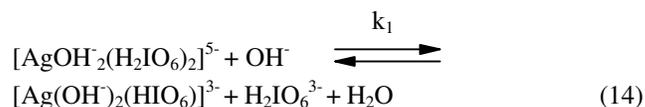
$$[AgOH^-_2(H_2IO_6)_2]^{5-} + OH^- \overset{k_1}{\rightleftharpoons}$$
$$[Ag(OH^-)_2(HIO_6)]^{3-} + H_2IO_6^{3-} + H_2O \quad (14)$$

$$[Ag(OH^-)_2(HIO_6)]^{3-} + R^- \overset{k_2}{\rightleftharpoons}$$
$$[Ag(OH^-)_2(HIO_6)(R)]^{4-} \text{ (or adduct')} \quad (15)$$

$$[Ag(OH^-)_2(HIO_6)(R)]^{4-} + R^- \overset{K, \text{ slow}}{\longrightarrow}$$
$$[Ag(OH^-)_2(HIO_6)(R)]^{4-}R^- \quad (16)$$

$$[Ag(OH^-)_2(HIO_6)(R)]^{4-}R^- \overset{fast}{\longrightarrow}$$
$$Ag^+ + R^- + NH_3 + HOCCH_2COO^- + HIO_6^{4-} + H_2O \quad (17)$$

The total concentration of Ag(III) at time t can be written as

$[Ag(III)]_t = [A]_e + [B]_e + [adduct']_e$. Since reaction (9) is the rate-determining step, the rate of disappearance of $[Ag(III)]_t$ is monitored as:

$$-d[Ag(III)]_t/dt = k\,[adduct']_e \cdot [R^-]$$

$$= \frac{kK_1K_2[OH^-][R^-]^2[Ag(III)]_t}{[H_2IO_6^{3-}] + K_1[OH^-] + K_1K_2[OH^-][R^-]} = k_{obs}[Ag(III)]_t$$

(18)

$$k_{obs} = \frac{kK_1K_2[OH^-][R^-]^2}{[H_2IO_6^{3-}] + K_1[OH^-] + K_1K_2[OH^-][R^-]}$$

(19)

$$\frac{1}{k_{obs}} = \frac{f(OH^-)[IO_4^-]}{kK_1K_2[OH^-][R^-]^2} + \frac{K_2[R^-]+1}{kK_2[R^-]^2}$$

(20)

$$\frac{[R^-]^2}{k_{obs}} = \frac{[R^-]}{k} + \frac{[H_2IO_6^{--}] + K_1[OH^-]}{kK_1K_2[OH^-]}$$

(21)

In this report, Eqs. (12) and (19) can explain k_{obs} values decreased rapidly with the increase in $[OH^-]$ up to 0.045 M. After that point, it increased gradually with the continuous increase in $[OH^-]$. Equation (20) shows that the plots of $1/k_{obs}$ versus $[IO_4^-]$ should also be linear. Equation (21) shows that the order in Ala should be $1 < n_{sp} < 2$ and $[Ala]^2/k_{obs}$ versus $[Ala]$ should be linear. The rate equations derived from the reaction mechanisms are consistent with our experimental results. Based on the slope in Fig. 4, the rate-determining step constants (k) at different temperatures were evaluated, then activation energy and the thermodynamic parameters (298.2 K) were evaluated
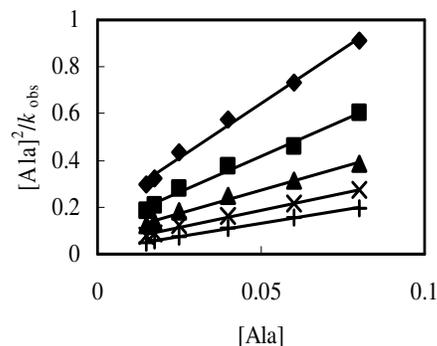
Fig. 4. The plots of $[Ala]^2/k_{obs}$ versus $[Ala]$: Ag(III), 7.16×10^{-5} M; IO_4^-, 2.00×10^{-3} M; OH^-, 0.06 M; μ, 0.142 M; T = (◆) 298.2, (■) 303.2, (▲) 308.2, (✕) 313.2, (✚) 318.2 K.

by the previously published method [11] (Table 3).

REFERENCES

[1]   A. Kumar, V.P. Ramamurthy, Int. J. Chem. Kin. 32 (2000) 286.

[2]   T. Raviprasad, B. Sethuram, T.N. Rao, Indian J. Chem. A 18 (1979) 40.

[3]   S. Chandra, K.L. Yadava, Talanta 15 (1986) 349.

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

[5]   A. Balikungeri, M. Pelletier, D. Monnier, Inorg. Chem. Acta 22 (1977) 7.

[6]   F. Feigl, Spot Tests in Organic Analysis, Elsevier Publishing Co., New York, 1956, p. 208.

[7]   J.J. Jin, Kinetics Principle of Chemical Reaction in

Table 3. Rate Constants (k) and Activation Parameters of the Rate-determining Step

Constants	T (K)					Activation parameters (298.2 K)		
	298.2	303.2	308.2	313.2	318.2	Ea (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
$10^2 k$ (M^{-1}s^{-1})	0.108	0.163	0.252	0.341	0.444	56.15	53.67	-83.25

The plot of ln$k$ vs.1/T has the following regression equation: ln$k$ = 20.45-6753.20 (1/T) (r = 0.996).

Liquid Phase, Shanghai: Science Technique Press, 1984, p. 186.

[8] J. Aveston, J. Chem. Soc. A (1969) 273.

[9] C.E. Crouthamel, H.V. Meek, D.S. Martin *et al*. J. Am. Chem. Soc. 71 (1949) 3031; 73 (1951) 82.

[10] H.G. Mukherjee, B. Mandal, De S. Indian J. Chem. 23A (1984) 426.

[11] J.H. Shan, T.Y. Liu, Acta Chim. Sinica 52 (1994) 1140.