

## Research Letter

# Kinetics and Mechanism of Oxidation of Leucine and Alanine by Ag(III) Complex in Alkaline Medium

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Kinetics and mechanism of oxidation of leucine and alanine by Ag(III) complex were studied spectrophotometrically in alkaline medium at constant ion strength. The reaction was in first order with respect to Ag(III) complex and amino acids (leucine, alanine). The second-order rate constant,  $k$ , decreased with the increasing in  $[\text{OH}^-]$  and  $[\text{IO}_4^-]$ . A plausible mechanism was proposed from the kinetics study, and the rate equations derived from mechanism can explain all experimental phenomena. The activation parameters were calculated at 298.2 K.

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## 1. Introduction

Transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands, such as diperiodatargentate(III) [1–4], [ethylenebis(biguanide)silver(III)] [5, 6]. These complexes were stable in a suitable aqueous solution. Ag(III) complexes were stabilized in alkaline medium by periodate or tellurate ions [7, 8]. These complexes such as Ag(III), Cu(III), and Ni(IV) complex can be used as an oxidation reagents in organic chemistry and analytical chemistry [9–11]. As a kind of oxidation reagents, those complexes have been used widely in kinetic study [12].

The kinetics and mechanism of oxidation of some amino acids have been studied by some researchers. However, the mechanism is different in the different reaction systems [13–23]. In order to perfect the mechanism of oxidation of amino acids, the kinetics and mechanism of oxidation of alanine and leucine by  $[\text{Ag}(\text{HIO}_6)_2]^{5-}$  have been studied in this paper.

## 2. Experimental

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Solution of

$[\text{Ag}(\text{HIO}_6)_2]^{5-}$  (DPA) was prepared and standardized by the method reported earlier [7, 8]. Solution of DPA was always freshly prepared before used.

**2.1. Apparatus and Kinetics Measurements and Product Analysis.** All kinetics measurements were carried out as previously [12]. The way for product analysis was similar to previous study [24]. After completion of the reaction, the products of oxidation were identified as ammonia and the corresponding ketone by their characteristic spot test [25].

## 3. Result and Discussion

**3.1. Kinetics.** The pseudo-first-order rate constants  $k_{\text{obs}}$  were calculated by the method as previously [12].

$k_{\text{obs}}$  values increased with the increase in [AA], the plots of  $k_{\text{obs}}$  versus [AA] are straight line which pass the grid origin at different temperatures (Table 1), the order with respect to [AA] was unity. Thus, an overall second-order rate law described by (1) is established here, where  $k'$  represents observed second-order rate constant:

$$r = k_{\text{obs}}[\text{Ag(III)}] = k'[\text{Ag(III)}][\text{AA}]. \quad (1)$$

TABLE 1:  $k_{\text{obs}}$  varied with different [AA] at different temperatures.

[AA]/(mol/L)	0.01	0.02	0.03	0.04	0.05
T/(K)	$10^3 k_{\text{obs}}/(\text{s}^{-1})$ for oxidation of leucine				
298.2	2.740	5.360	7.789	10.17	13.69
303.2	4.066	7.973	11.29	15.92	19.64
308.2	6.775	12.04	18.18	24.62	31.11
313.2	8.258	15.25	22.50	32.40	38.30
T/(K)	$10^3 k_{\text{obs}}/(\text{s}^{-1})$ for oxidation of alanine				
298.2	5.872	10.37	15.87	22.14	29.05
303.2	8.671	14.38	23.24	31.97	40.89
308.2	12.47	22.52	33.46	44.47	59.78
313.2	17.71	32.76	47.18	65.98	93.53

[Ag(III)] =  $2.965 \times 10^{-5}$  mol/L,  $[\text{OH}^-]$  = 0.06 mol/L,  $[\text{IO}_4^-]$  =  $5.00 \times 10^{-4}$  mol/L,  $\mu$  = 0.15 mol/L.

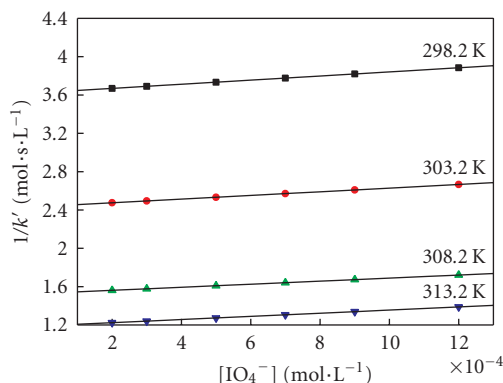


FIGURE 1: The second-order rate constant,  $k'$ , as a function of the concentration of  $\text{IO}_4^-$  at different temperatures for oxidation of leucine.

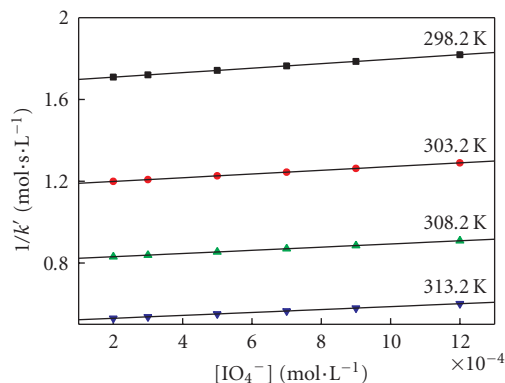
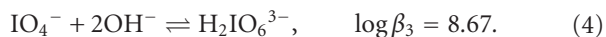
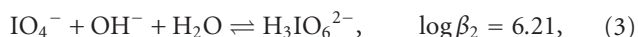
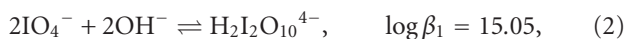


FIGURE 2: The second-order rate constant,  $k'$ , as a function of the concentration of  $\text{IO}_4^-$  at different temperatures for oxidation of alanine.

$k'$  values decreased with the increase in  $[\text{IO}_4^-]$ . The plot of  $1/k'$  versus  $[\text{IO}_4^-]$  was a straight line (Figures 1 and 2). The values of  $k'$  decreased with the increase in  $[\text{OH}^-]$  and the plots of  $1/k'$  versus  $f(\text{OH})[\text{OH}^-]$  were line (Figures 3 and 4).

**3.2. Reaction Mechanism.** In aqueous periodate solution, (2)–(4) were detected and the corresponding equilibrium constants at 273.2 K were determined by Aveston [26] as follows:



The distribution of all species of periodate in alkaline solution can be calculated from (2)–(4). In the  $[\text{OH}^-]$  range used in this work, the dimer and  $\text{IO}_4^-$  species of periodate can be neglected. The main species of periodate are  $\text{H}_2\text{IO}_6^{3-}$

and  $\text{H}_3\text{IO}_6^{2-}$ . Equation (5) can be obtained from (2), (3), (4) as follows:

$$[\text{H}_2\text{IO}_6^{3-}] = \frac{\beta_3[\text{OH}^-]^2}{1 + \beta_2[\text{OH}^-] + \beta_3[\text{OH}^-]^2} \quad (5)$$

$$[\text{IO}_4^-]_{\text{ex}} = f([\text{OH}^-])[\text{IO}_4^-]_{\text{ex}},$$

where  $[\text{IO}_4^-]_{\text{ex}}$  represents the concentration of original overall periodate ion.

From the discussion above, the reaction mechanism was proposed as below:

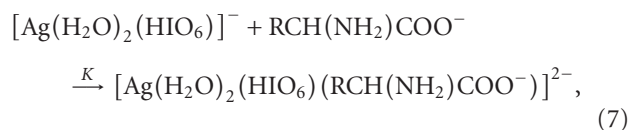
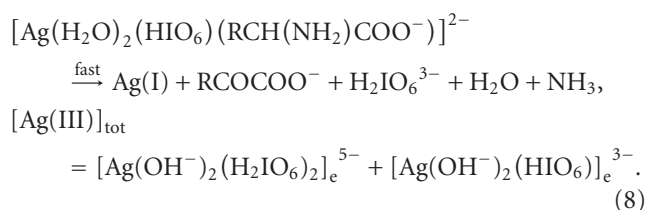


TABLE 2: Thermodynamic activation parameters for the oxidation of leucine and alanine by Ag(III) complex in alkaline medium.

Thermodynamic activation parameters			
Reaction for oxidation of leucine			
Temperature (K)	$10k/(\text{M}^{-1} \cdot \text{s}^{-1})$		
298.2	2.75	$E_a/(\text{KJ} \cdot \text{mol}^{-1})$	$59.34 \pm 4.37$
303.2	4.10	$\Delta H^\ddagger/(\text{KJ} \cdot \text{mol}^{-1})$	$56.86 \pm 4.37$
308.2	6.54	$\Delta S^\ddagger/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$-64.83 \pm 14.3$
313.2	8.40	$10^3 K_1/(\text{mol} \cdot \text{L}^{-1})^2$	$7.09 \pm 0.42$
Reaction for oxidation of alanine			
Temperature (K)	$10k/(\text{M}^{-1} \cdot \text{s}^{-1})$		
298.2	5.93	$E_a/(\text{KJ} \cdot \text{mol}^{-1})$	$60.95 \pm 3.15$
303.2	8.47	$\Delta H^\ddagger/(\text{KJ} \cdot \text{mol}^{-1})$	$58.47 \pm 3.15$
308.2	12.3	$\Delta S^\ddagger/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$53.40 \pm 10.31$
313.2	19.4	$10^3 K_1/(\text{mol} \cdot \text{L}^{-1})^2$	$6.44 \pm 0.49$

R means  $(\text{CH}_3)_2\text{CHCH}_2$ —for leucine and H—for alanine



Here “e” and “tot” mean the equilibrium concentration of the all kinds of Ag(III) complexes and the total concentration of all kinds of Ag(III) complexes, respectively. The reaction (7) is the rate-determining step,  $k$  means the rate-determining step constant, the rate equation can be expressed as below:

$$\begin{aligned}
 & \frac{-d[\text{Ag(III)}]_T}{dt} \\
 & = k_{\text{obs}} \cdot [\text{Ag(III)}]_{\text{tot}} \\
 & = k' [\text{Ag}(\text{H}_2\text{O})_2(\text{HIO}_6)^-] \cdot [\text{RCH}(\text{NH}_2)\text{COO}^-] \\
 & = \frac{kK_1[\text{R}][\text{Ag(III)}]_{\text{tot}}}{K_1 + [\text{H}_2\text{IO}_6^{3-}][\text{OH}^-]}, \quad (9)
 \end{aligned}$$

$$k_{\text{obs}} = \frac{kK_1[\text{R}]}{K_1 + [\text{H}_2\text{IO}_6^{3-}][\text{OH}^-]}. \quad (10)$$

Then substitute (5) for  $[\text{H}_2\text{IO}_6^{3-}]$  in (10) is as follows:

$$k_{\text{obs}} = \frac{kK_1[\text{R}]}{K_1 + f([\text{OH}^-])[\text{IO}_4^-]_{\text{ex}}[\text{OH}^-]}, \quad (11)$$

$$k' = \frac{kK_1}{K_1 + f([\text{OH}^-])[\text{IO}_4^-]_{\text{ex}}[\text{OH}^-]}. \quad (12)$$

From (12), the plot of  $1/k'$  versus  $f(\text{OH}) \cdot [\text{OH}^-]$  is a straight line, and  $1/k'$  versus  $[\text{IO}_4^-]_{\text{ex}}$  is straight line too, which can explain all the experimental phenomena, and the activation parameters according to  $k$  are calculated [27] (see Table 2).

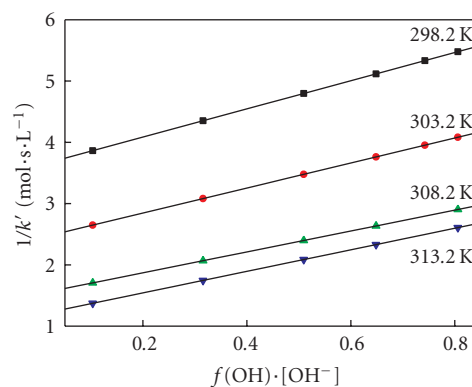


FIGURE 3: The second-order rate constant,  $k'$ , as a function of the concentration of  $\text{OH}^-$  at different temperatures for oxidation of leucine.

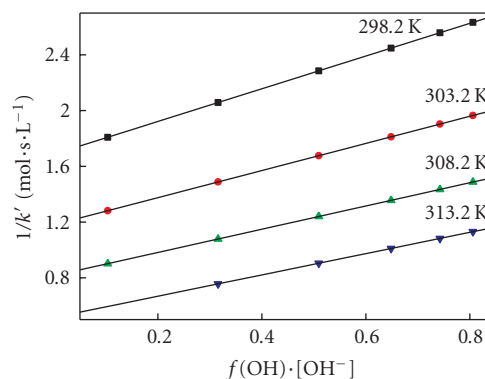


FIGURE 4: The second-order rate constant,  $k'$ , as a function of the concentration of  $\text{OH}^-$  at different temperatures for oxidation of alanine.

## 4. Conclusion

Through the kinetics study, we supposed a simple reaction mechanism, which can explain the reaction very well. Activation parameters and rate determining step constant were calculated from the rate law derived from the proposed

reaction mechanism. The negative value of  $\Delta S^\ddagger$  suggested that intermediate complex is more in order than the reactants. The higher rate constant for the rate determining step indicates that the oxidation presumably occurs via innersphere mechanism. The pre-equilibrium constants,  $K_1$ , are calculated at 298.2 K, which are smaller values. This also shows that rate law from equilibrium hypothesis is suitable for the reaction mechanism.

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