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Kinetics and mechanism of oxidation of methyl α -D-mannopyranoside and methyl α -D-glucopyranoside by ditelluratoargentate(III) in alkaline medium

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Abstract : Oxidation of Methyl α -D-mannopyranoside and Methyl α -D-glucopyranoside by ditelluratoargentate (III) (DTA) in alkaline liquids has been studied spectrophotometrically in the temperature range of 293.2 K-313.2 K. It is first-order rate with respect to DTA, while fractional order in reductant. The rate constant k_{obs} of pseudo-first order reaction decreased with the increase of $[\text{TeO}_4^{2-}]$, whereas adding

$[\text{OH}^-]$ enhanced the constant. In view of this, a mechanism based on the experimental result is proposed, and the constants involved in the mechanism were evaluated. © Global Scientific Inc.

Keywords : Ditelluratoargentate(III)(DTA); Methyl α -D-mannopyranoside; Methyl α -D-glucopyranoside; Kinetics; Mechanism.

INTRODUCTION

Both Methyl α -D-mannopyranoside and Methyl α -D-glucopyranoside are white powder and soluble in water, and they have applied in many aspects.

Methyl α -D-mannopyranoside is a kind of important raw material of vitamin B₆ and diuretic medicine. It can also improve the nutritional value of food, such as bread, ice cakes, dairy products, carbonated drinks, ice cream and other food. Methyl α -D-glucopyranoside has excellent chemical properties, widely used in adhesives, cosmetics, paint, surfactant and other industries.

Recently, using a transition metal in its unusual oxidation state as an oxidizing agent which can be stabi-

lized by co-ordination of it with a suitable anion such as periodate or tellurate^[1-8] has been well-known in chemistry in the estimation of sugar, amino acid and protein, etc. For instance, the kinetics of oxidation of small molecules by DTA, such as amine^[9], alcohols, trinitride^[10], phosphate^[11], carboxylic acid (salt)^[12] and aldehydes^[13].

Ditelluratoargentate (III) also integrates the properties, such as adsorption, deodorization, flocculation, and oxidizing sterilization. As the understanding of Ag(III) is further developed, the further research of its application value has significance.

In the present paper, the mechanism of oxidation of Methyl α -D-mannopyranoside and Methyl α -D-

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glucopyranoside by ditelluratoargentate (III) were studied in detail.

EXPERIMENTAL

Material and methods

All the chemicals used were of reagent grade and doubly distilled water was used throughout the study. The solutions of DTA and reductants were always freshly prepared before use with stock solution. The stock solution of DTA was prepared and standardized by the method given by Gupta et al.^[14]. Its UV-Visible spectrum was found to be consistent with that reported. The

concentration of DTA was obtained by its absorption at $\lambda = 351$ nm. The PH value was regulated with KOH solution and the ionic strength was maintained by adding KNO_3 solution.

The kinetics were followed under pseudo-first order conditions by keeping a large excess of [reductant] with respect to [DTA]. Kinetic measurements were performed on a TU 1901 spectrophotometer (Beijing Puxi Inc., China) fitted with a DC 2010 thermostat (± 0.1 K, Baoding, China) which had a cell-holder kept at a constant temperature ($\pm 0.1^\circ\text{C}$) by circulating water from it (Baoding, China). The product of oxidation was identified as ketone by its characteristic spot test^[15].

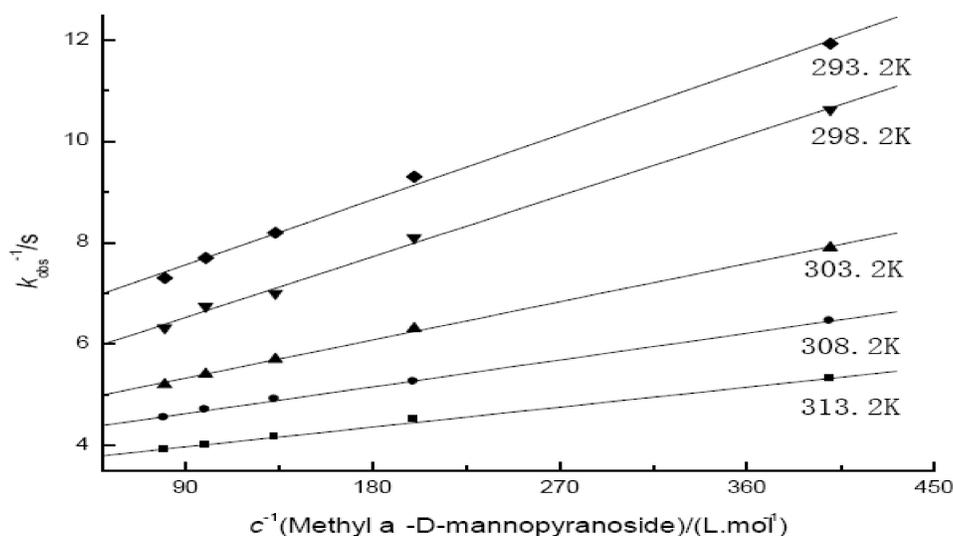


Figure 1 : Plots of $1/k_{\text{obs}}$ versus $1/[\text{Methyl } \alpha\text{-D-mannopyranoside}]$ at different temperatures, $[\text{DTA}] = 2.27 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{H}_4\text{TeO}_6^{2-}] = 1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$

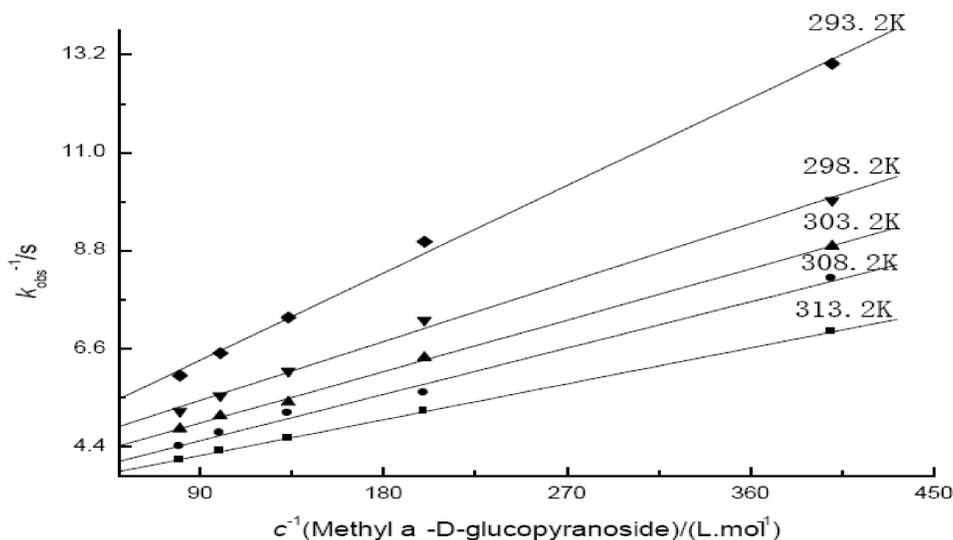


Figure 2 : Plots of $1/k_{\text{obs}}$ versus $1/[\text{Methyl } \alpha\text{-D-glucopyranoside}]$ at different temperatures, $[\text{DTA}] = 2.27 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{H}_4\text{TeO}_6^{2-}] = 1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$

RESULTS AND DISCUSSION

Evaluation of pseudo-first order rate constant

Under the conditions of $[\text{reductant}]_0$ ([Methyl α -D-mannopyranoside] $_0$ and [Methyl α -D-glucopyranoside] $_0$) \gg $[\text{DTA}]_0$, and the plots of $\ln(A_t - A_\infty)$ vs time t for more than three half lices of the reaction were straight lines ($r \geq 0.999$), indicating the order in DTA to be unity. The pseudo-first-order rate constants k_{obs} were evaluated by using the least-squares method. Deviations in duplicate determinations were generally less than $\pm 3\%$.

Effect of varying of the [reductant]

At constant $[\text{DTA}]$, $[\text{H}_4\text{TeO}_6^{2-}]$, $[\text{OH}^-]$ and ionic strength μ , at different temperature (293.2K-313.2K) and different [reductant] ([Methyl α -D-mannopyranoside] and [Methyl α -D-glucopyranoside]) (0.0025-0.0125 mol/L), the plot of $1/k_{obs}$ versus $1/[\text{reductant}]$ were straight lines ($r \geq 0.997$), indicating that it was fractional order with respect to [reductant] (Figure 1 and Figure 2).

Effect of varying of the $[\text{H}_4\text{TeO}_6^{2-}]$

The $[\text{TeO}_4^{2-}]$ was varied from 0.5×10^{-3} to 2.5×10^{-3} mol·L $^{-1}$ range at constant $[\text{DTA}]$, [reductant] ([Methyl α -D-mannopyranoside] and [Methyl α -D-glucopyranoside]), $[\text{OH}^-]$, ionic strength of 3.80×10^{-2} mol·L $^{-1}$ and the temperature of 298.2 ± 0.1 K fixed.

The k_{obs} values decreased with the increase in concentration of TeO_4^{2-} and the order with respect to $[\text{TeO}_4^{2-}]$ was found to be fractional, which reveals that TeO_4^{2-} is produced in equilibrium before the rate controlling step. A plot of $1/k_{obs}$ versus $[\text{TeO}_4^{2-}]$ was a straight line without passing through the origin (Figure 3 and Figure 4).

Effect of varying of the $[\text{OH}^-]$

Under the concentrations of DTA, $\text{H}_4\text{TeO}_6^{2-}$, reductant ([Methyl α -D-mannopyranoside] and [Methyl α -D-glucopyranoside]), ionic strength of 3.80×10^{-2} mol·L $^{-1}$ and the temperature of 298.2 ± 0.1 K fixed. It was found that k_{obs} values increased with the increasing $[\text{OH}^-]$. The order with respect to $[\text{OH}^-]$ was fractional. The plots of $1/k_{obs}$ vs. $1/[\text{OH}^-]$ was a straight line without passing through the origin (Figure 5 and Figure 6).

Effect of varying of ionic strength

The influence of variation ionic strength on the reaction was studied in the rang of 1.50×10^{-2} mol·L $^{-1}$ to 7.50×10^{-2} mol·L $^{-1}$ at constant $[\text{DTA}]$, [reductant] ([Methyl α -D-mannopyranoside] and [Methyl α -D-glucopyranoside]), $[\text{H}_4\text{TeO}_6^{2-}]$, $[\text{OH}^-]$ and temperature ($T=298.2\text{K}$). The experimental results indicated that the rate constant k_{obs} increased with the increasing $[\text{KNO}_3]$ (TABLE 1), which determined to have positive salt effect that consistent with the common regulation of the kinetics^[16].

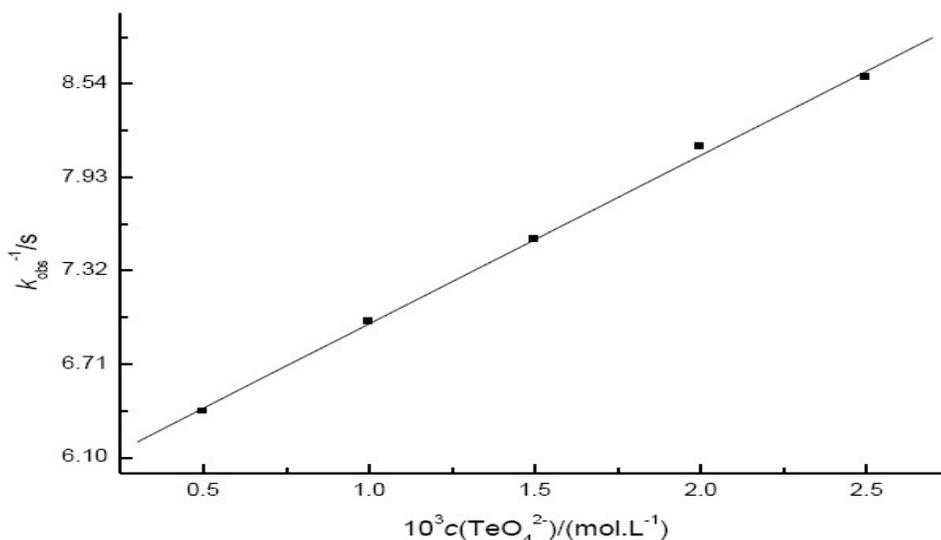


Figure 3 : Plot of $1/k_{obs}$ vs $10^3[\text{H}_4\text{TeO}_6^{2-}]$ at the temperature of 298.2 ± 0.1 K, $[\text{DTA}] = 2.27 \times 10^{-4}$ mol·L $^{-1}$, [Methyl α -D-mannopyranoside] = 7.50×10^{-3} mol·L $^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-2}$ mol·L $^{-1}$, $\mu = 3.80 \times 10^{-2}$ mol·L $^{-1}$ ($r = 0.999$)

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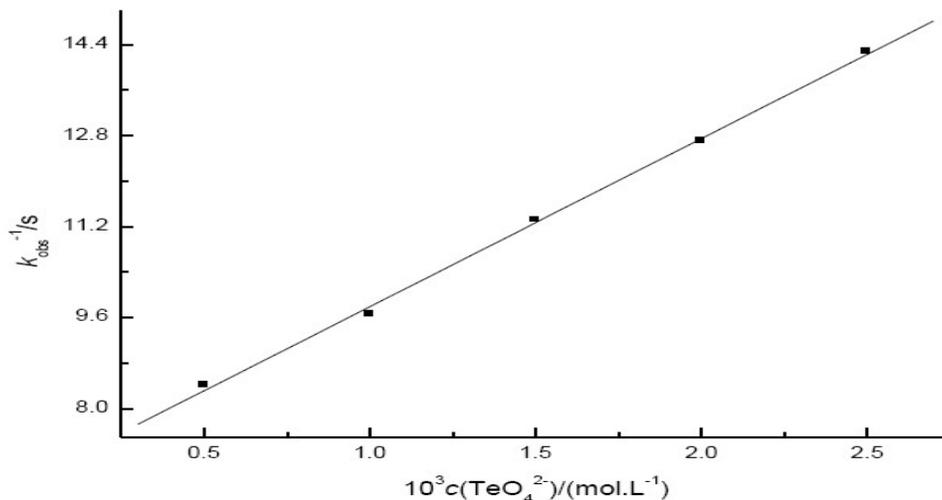


Figure 4 : Plots of $1/k_{\text{obs}}$ vs $10^2[\text{H}_4\text{TeO}_6^{2-}]$ at the temperature of 298.2 ± 0.1 K, $[\text{DTA}] = 2.27 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{Methyl } \alpha\text{-D-glucopyranoside}] = 7.50 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ($r = 0.999$)

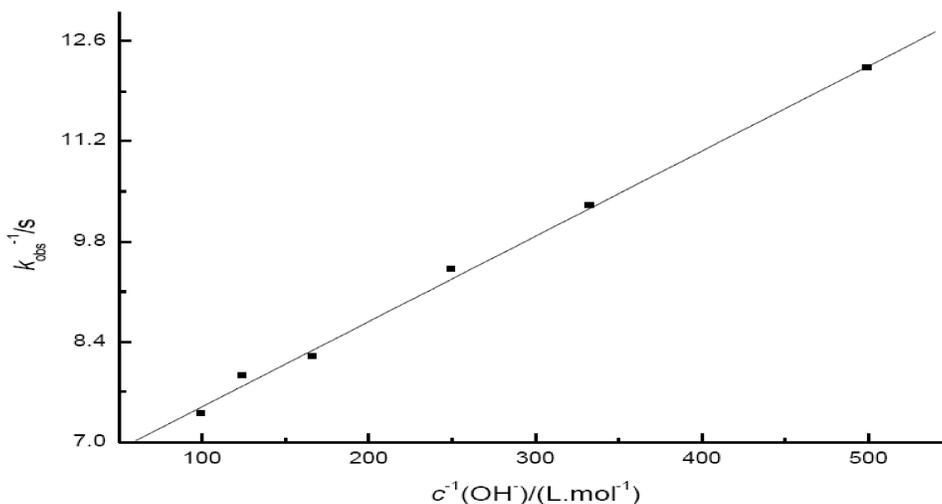


Figure 5 : Plots of $1/k_{\text{obs}}$ vs $1/[\text{OH}^-]$ at the temperature of 298.2 ± 0.1 K, $[\text{DTA}] = 2.27 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_4\text{TeO}_6^{2-}] = 1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[\text{Methyl } \alpha\text{-D-mannopyranoside}] = 7.50 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, ($r = 0.998$)

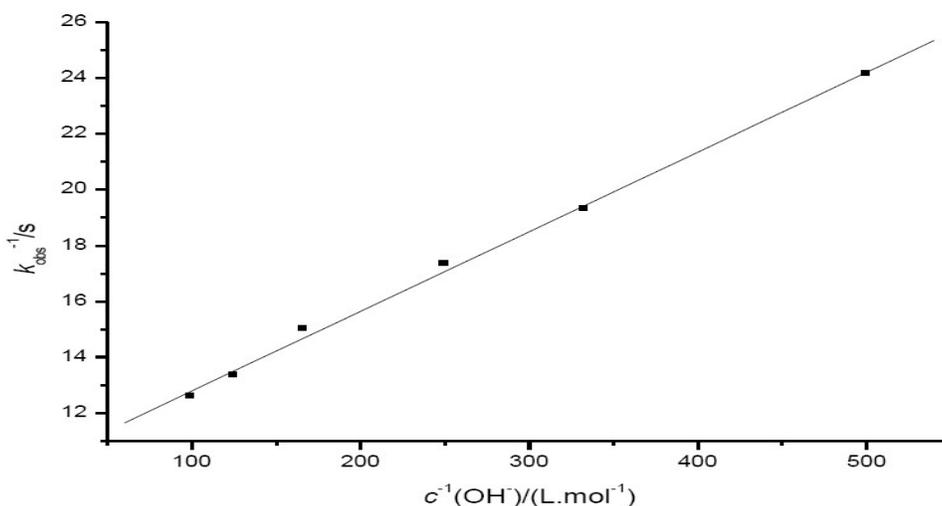


Figure 6 : Plots of $1/k_{\text{obs}}$ vs $1/[\text{OH}^-]$ at the temperature of 298.2 ± 0.1 K, $[\text{DTA}] = 2.27 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_4\text{TeO}_6^{2-}] = 1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[\text{Methyl } \alpha\text{-D-glucopyranoside}] = 2.50 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, ($r = 0.999$)

TABLE 1 : Effect of varying of ionic strength μ (T=298.2K)

$10^2 \mu / \text{mol} \cdot \text{L}^{-1}$		1.50	3.00	4.50	6.00	7.50
$10^2 k_{\text{obs}} / \text{s}^{-1}$	Methyl α -D-mannopyranoside	12.27	13.33	14.71	16.13	17.31
	Methyl α -D-glucopyranoside	9.06	9.51	9.90	10.42	10.89

[reductant] ([Methyl α -D-mannopyranoside] and [Methyl α -D-glucopyranoside]) = $2.50 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, [DTA] = $2.27 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, [OH⁻] = $1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, [H₄TeO₆²⁻] = $1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$

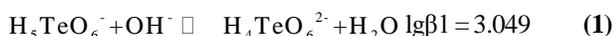
TABLE 2 : The rate-determining step's rate constants (k) and activation parameters

$T(\text{K})$		293.2	298.2	303.2	308.2	313.2
$10^2 K / \text{s}^{-1}$	Methyl α -D-mannopyranoside	16.30	18.98	22.12	24.51	28.25
	Methyl α -D-glucopyranoside	24.75	25.11	26.46	28.36	29.53
Thermodynamic activation parameters	Methyl α -D-mannopyranoside	Ea/(kJ·mol ⁻¹)= 20.71, ΔH^\ddagger /(kJ·mol ⁻¹)= 18.23, ΔS^\ddagger /(J·K ⁻¹ ·mol ⁻¹)= -237.47, T = 298.2 K				
	Methyl α -D-glucopyranoside	Ea/(kJ·mol ⁻¹)= 8.51, ΔH^\ddagger /(kJ·mol ⁻¹)= 6.03, ΔS^\ddagger /(J·K ⁻¹ ·mol ⁻¹)= -247.29, T = 298.2 K				

The intercept (a), slope (b) and relative coefficient (r) of the plot $\ln k$ vs T^{-1} are : Methyl α -D-mannopyranoside: a=6.69, b= -2491.24, r= 0.998; Methyl α -D-glucopyranoside: a=2.05, b= -1023.83, r= 0.998

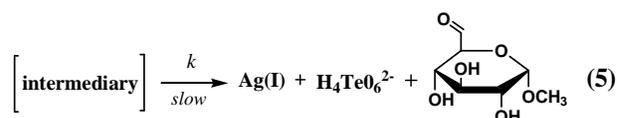
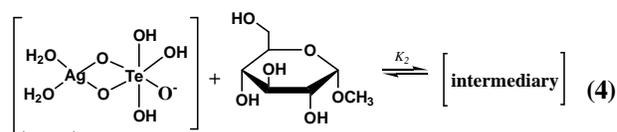
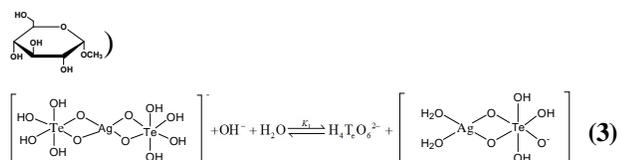
MECHANISM

In the alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier^[17] (here pKw = 14).



From equilibria (1)-(2), the distribution of all species of tellurate can be calculated in aqueous alkaline solution. In an alkaline medium, such as [OH⁻] = 0.01 mol·L⁻¹, the equations give: [H₄TeO₆²⁻]: [H₅TeO₆⁻]: [H₃TeO₆³⁻] = 1000:89:1. Hence, in the concentration of OH⁻ range used in this work, the H₅TeO₆⁻ and H₃TeO₆³⁻ species can be neglected, and the main species of telluride is H₄TeO₆²⁻. In the reaction system, [H₄TeO₆²⁻]_{ex} >> [Ag(III)], and the dissociation of H₄TeO₆²⁻ from DTA was very little, so in this solution, [H₄TeO₆²⁻]_{ex} · H⁺ / [H₄TeO₆²⁻] [H₄TeO₆²⁻]_{ex} stands for the extra H₄TeO₆²⁻. According to the report^[18] the main species of DTA is [Ag(H₄TeO₆)₂]⁻ over the experimental concentration range of [OH⁻].

According to the above experimental facts, the following reaction mechanism is proposed. (such as



Reactions (3) and (4) are dissociation and coordination equilibrium, the reaction rates of which are generally fast, reaction (5) is an electron-transfer reaction, the reaction rates of which are generally slow. Hence, reaction (5) is the rate-determining step.

$$-d[\text{Ag(III)}]_t / dt = k[\text{intermediary}] \quad (6)$$

[Ag(III)]_t stands for any form of Ag(III) complex which exists in the equilibrium and R' stands for both of the reductants.

$$-d[\text{Ag(III)}]_t / dt = \frac{kK_1K_2 [\text{R}'] [\text{OH}^-]}{K_1K_2 [\text{R}'] [\text{OH}^-] + K_1 [\text{OH}^-] + [\text{H}_4\text{TeO}_6^{2-}]}$$

$$[\text{Ag(III)}]_t = k_{\text{obs}} [\text{Ag(III)}]_i \quad (7)$$

$$k_{\text{obs}} = \frac{kK_1K_2 [\text{R}'] [\text{OH}^-]}{K_1K_2 [\text{R}'] [\text{OH}^-] + K_1 [\text{OH}^-] + [\text{H}_4\text{TeO}_6^{2-}]} \quad (8)$$

Re-arranging equation (8) leads to equation (9-11):

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k} + \frac{[\text{H}_4\text{TeO}_6^{2-}] + K_1 [\text{OH}^-]}{kK_1K_2 [\text{OH}^-]} \frac{1}{[\text{R}']} \quad (9)$$

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$$\frac{[R']}{k_{\text{obs}}} = \frac{[R']}{k} + \frac{[H_4TeO_6^{2-}] + K_1[OH^-]}{kK_1K_2[OH^-]} \quad (10)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1 + K_2[R']}{kK_2[R']} + \frac{[H_4TeO_6^{2-}]}{kK_1K_2[R'] [OH^-]} \quad (11)$$

From the equation (11), the plots $[R']/k_{\text{obs}}$ vs $[R']$ are straight lines and the rate constants of the rate-determining step at different temperature were obtained from the slope of the straight line. Equation (11) indicated that the plots of k_{obs}^{-1} vs. $[OH^-]^{-1}$ and k_{obs}^{-1} vs. $[H_4TeO_6^{2-}]$ were straight lines. Activation energy and the thermodynamic parameters were evaluated by the method given earlier (TABLE 2).

CONCLUSION

Through the previous studies, we found that DTA can oxidize different types of reductions. Based on the experimental results, we found that both the Methyl α -D-mannopyranoside and Methyl α -D-glucopyranoside formed the analogical intermediate compounds with Ag(III). When the reductants' active groups are on the different positions, the rate of the reaction is different. The value of the activation parameters with respect to Methyl α -D-mannopyranoside was larger than that of Methyl α -D-glucopyranoside, which indicated that the reactivity of Methyl α -D-glucopyranoside is higher than Methyl α -D-mannopyranoside^[19]. The reason was that the steric stability of Methyl α -D-mannopyranoside was larger than that of Methyl α -D-glucopyranoside, which indicated the latter was easier to react with Ag(III) than the former. This phenomenon is consistent with experimental results.

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