

KINETICS AND MECHANISM OF OXIDATION OF PENTAERYTHRITOL BY DITELLURATOARGENTATE(III) IN ALKALINE MEDIUM

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ABSTRACT

The kinetics of oxidation of pentaerythritol by ditelluratoargentate (III) (DTA) in alkaline liquids has been studied spectrophotometrically in the temperature range of 293.2 K-313.2 K. The reaction rate showed first-order dependence in DTA and fractional order with respect to pentaerythritol. It was found that the pseudo-first-order rate constant k_{obs} increased with an increase in concentration of OH^- and a decrease in concentration of $\text{H}_4\text{TeO}_6^{2-}$. There was a negative salt effect and no free radicals were detected. A plausible mechanism involving a two-electron transfer is proposed and the rate equations derived from the mechanism can explain all the experimental results. The rate equations derived from mechanism can explain all experimental observations. The activation parameters along with the rate constants of the rate-determining step were calculated.

Keywords: Ditelluratoargentate(III)(DTA), pentaerythritol, redox reaction, reaction kinetics, mechanism, fractional order, k_{obs} , OH^- , $\text{H}_4\text{TeO}_6^{2-}$, rate equations.

INTRODUCTION

Many researchers from many countries are interested in the study of the highest oxidation state of transition metals, which in a higher oxidation state generally can be stabilized by chelation with suitable polydentate ligands. These studies can provide new and valuable information in some fields. Metal chelates, such as diperiodatoargentate (III)¹, ditelluratoargentate (III)², and ditelluratocuprate (III)³, are good oxidants in a medium with an appropriate pH. The oxidation of a number of organic compounds and metals in lower oxidation state by Ag (III) has also been performed¹. The use of Ag (III) as an oxidation agent is well known in analytical chemistry in the estimation of glucose, sugars and organic acids. The research is focus on the kinetics of oxidation of small molecules by DTA, such as alcohols, aldehydes⁴, carboxylic acid (salt)⁵ amine⁶, phosphate⁷ and trinitride⁸. In this paper, the mechanism of the oxidation of pentaerythritol by DTA is reported.

EXPERIMENTAL

Materials

All the reagents used were A.R. grade. All solutions were prepared with doubly distilled water. Solution of DTA was prepared and standardized by the method reported earlier⁹. Its UV spectrum was found to be consistent with that reported. The concentration of DTA was derived from its absorption at $\lambda = 351$ nm. The solution of DTA was prepared with double-distilled water. The ionic strength μ was maintained by adding the solution of KNO_3 and the pH of the reaction mixture was regulated with the solution of KOH . The kinetic measurements were performed on a UV-vis spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell-holder kept at a constant temperature ($\pm 0.1^\circ\text{C}$) by circulating water from a thermostat (DC-2010, Baoding, China). None of the other species absorbed significantly at this wavelength.

Kinetics measurements

All kinetic measurements were carried out under pseudo-first-order conditions. A solution of Ag (III), OH^- and $\text{H}_4\text{TeO}_6^{2-}$ with known concentrations was mixed with an excess of reductant. The complete fading of DTA color (reddish brown) marked the completion of the reaction. The product of oxidation was identified as ketone by its characteristic spot test¹⁰.

RESULTS AND DISCUSSION

Evaluation of Pseudo-First Order Rate Constants

Under the conditions of $[\text{reductant}]_0 \gg [\text{Ag(III)}]_0$, the plots of $\ln(A_t - A_\infty)$ vs time were straight lines, indicating the reaction was first order with respect to $[\text{Ag(III)}]$, where A_t and A_∞ were 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 ($r \geq 0.999$). The reproducibility was within $\pm 3\%$.

Rate dependence on [reductant]

At fixed concentration of Ag (III), OH^- , $\text{H}_4\text{TeO}_6^{2-}$ and ionic strength μ , the values of k_{obs} were determined at different temperatures. The plot of $\ln k_{\text{obs}}$ vs $\ln[\text{reductant}]$ was a straight line ($r \geq 0.998$), and from the slope of such plots,

the order with respect to reductant was found to be fractional. The plots of $[\text{pentaerythritol}]/k_{\text{obs}}$ vs $[\text{pentaerythritol}]$ at different temperatures were straight lines (Figure 1).

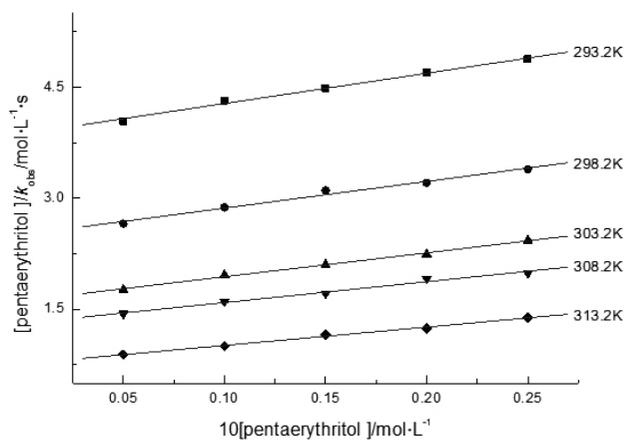


Figure 1: Plots of $[\text{pentaerythritol}]/k_{\text{obs}}$ vs. $10[\text{pentaerythritol}]$ ($r \geq 0.995$) $[\text{Ag(III)}] = 4.11 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[\text{H}_4\text{TeO}_6^{2-}] = 1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, ionic strength (μ) = $3.80 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$

Rate dependence on $[\text{H}_4\text{TeO}_6^{2-}]$

At constant $[\text{Ag(III)}]$, $[\text{reductant}]$, $[\text{OH}^-]$, ionic strength μ and temperature (298.2 K), the experimental results indicated that k_{obs} decreased while the $[\text{H}_4\text{TeO}_6^{2-}]$ increased. The order with respect to $\text{H}_4\text{TeO}_6^{2-}$ was derived to be an inverse fraction, which revealed that $\text{H}_4\text{TeO}_6^{2-}$ was produced in equilibrium before the rate-determining step. The plot of $1/k_{\text{obs}}$ vs $[\text{H}_4\text{TeO}_6^{2-}]$ was a straight line (Figure 2).

Rate dependence on $[\text{OH}^-]$

At fixed concentrations of Ag (III), $\text{H}_4\text{TeO}_6^{2-}$, reductant, ionic strength μ and temperature (298.2 K), the value of k_{obs} increased with increasing concentration of OH^- . The order with respect to $[\text{OH}^-]$ was fractional and the plot of $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ was linear (Figure 3).

Rate dependence on the ionic strength μ

With other conditions fixed, the reaction rate decreased with the addition of KNO_3 solution (Table 1), which indicated that there was negative salt effect which was consistent with the common regulation of the kinetics¹¹.

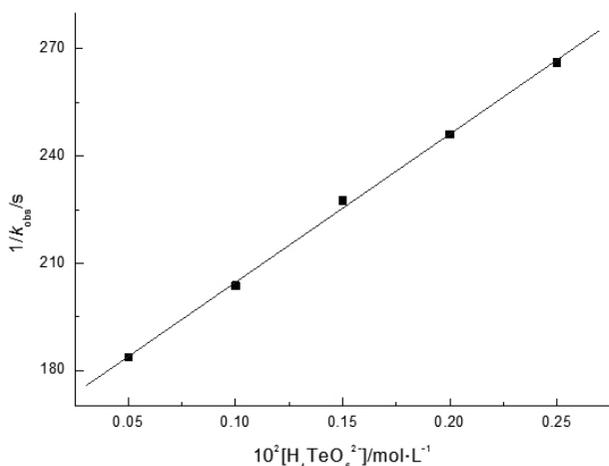


Figure 2: Plot of $1/k_{obs}$ vs $10^2[H_4TeO_6^{2-}]$ at 298.2 K. $[Ag(III)] = 4.11 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, [pentaerythritol] = $1.50 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[OH^-] = 1.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, ionic strength (μ) = $3.80 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, temperature (K) = 298.2 K. ($r=0.999$).

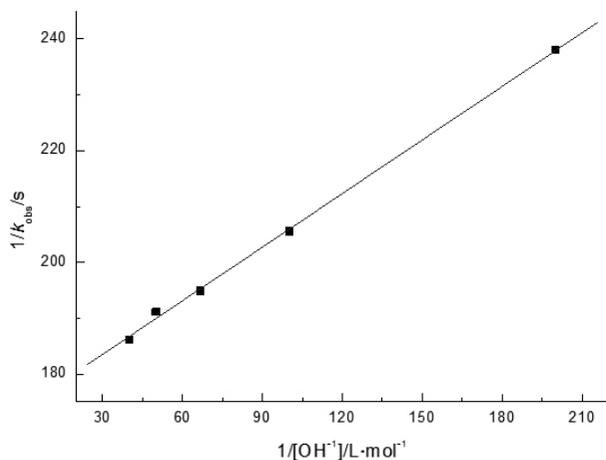


Figure 3: Plot of $1/k_{obs}$ vs $1/[OH^-]$ at 298.2 K. $[Ag(III)] = 4.11 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, [pentaerythritol] = $1.50 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[H_4TeO_6^{2-}] = 1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, ionic strength (μ) = $3.80 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, temperature (K) = 298.2 K. ($r=0.999$).

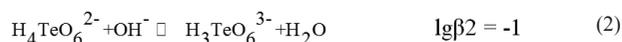
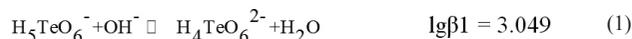
Table 1: Rate dependence on ionic strength (μ).

$10^2\mu / \text{mol}\cdot\text{L}^{-1}$	1.50	3.00	4.50	6.00	7.50
$10^3k_{obs} / \text{s}^{-1}$	5.31	5.09	4.75	4.50	4.20

$[Ag(III)] = 4.11 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, [reductant] = $1.50 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[OH^-] = 1.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[H_4TeO_6^{2-}] = 1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, temperature (K) = 298.2 K.

Reaction mechanism

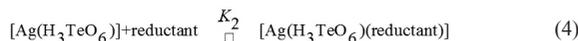
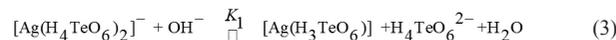
In alkaline medium, the electric dissociation equilibrium of telluric acid is given earlier ¹²($pK_w = 14$).



The distribution of all species of telluride in aqueous alkaline solution is calculated from (1) and (2). In the alkaline medium, $[OH^-] = 0.01 \text{ mol}\cdot\text{L}^{-1}$, the equations give: $[H_4TeO_6^{2-}] : [H_3TeO_6^{3-}] : [H_2TeO_6^{4-}] = 1000:89:1$, in the concentration range of OH^- used in this work, the $H_3TeO_6^{3-}$ and $H_2TeO_6^{4-}$ species

can be neglected, and the main species of telluride is $H_4TeO_6^{2-}$. According to the literature¹³, the main species of DTA is $[Ag(H_4TeO_6)_2]^-$ over the experimental concentration range of $[OH^-]$.

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



The reductant reacted with $[Ag(H_3TeO_6)]$ firstly, the pre-equilibrium was established, and then the intermediate, $[Ag(H_3TeO_6)(\text{reductant})]$, was generated. The reaction order with respect to reductant was fractional, which was known from the rate law, so equation (5) as a rate control step had been proposed here.

$$-d[Ag(III)]_t / dt = k[Ag(H_3TeO_6)(\text{reductant})] \quad (6)$$

$[Ag(III)]_t$ stands for all forms of Ag (III) complex which exists in the equilibrium and R' stands for the reductant.

$$-d[Ag(III)]_t / dt = \frac{kK_1K_2 [R'] [OH^-]}{K_1K_2 [R'] [OH^-] + K_1 [OH^-] + [H_4TeO_6^{2-}]} [Ag(III)]_t = k_{obs} [Ag(III)]_t \quad (7)$$

$$k_{obs} = \frac{kK_1K_2 [R'] [OH^-]}{K_1K_2 [R'] [OH^-] + K_1 [OH^-] + [H_4TeO_6^{2-}]} \quad (8)$$

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

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{[H_4TeO_6^{2-}] + K_1 [OH^-]}{kK_1K_2 [OH^-]} \frac{1}{[R']} \quad (9)$$

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

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

From (10), the plots $[R']/k_{obs}$ vs $[R']$ are straight lines and the rate constants of the rate-determining step at different temperature are obtained from the slope of the straight line. Equation (11) indicates that the plots of $1/k_{obs}$ vs $1/[OH^-]$ and $1/k_{obs}$ vs $[H_4TeO_6^{2-}]$ are straight lines. Activation energy and the thermodynamic parameters are evaluated by the method given earlier¹⁴ (Table 2).

Table 2: Rate constants (k) and activation parameters of the rate-determining step.

T/K	293.2	298.2	303.2	308.2	313.2
$10^2k / \text{s}^{-1}$	2.44	2.77	3.09	3.55	4.03
Thermodynamic activation parameters(298.2K)	$E_a / (\text{kJ}\cdot\text{mol}^{-1}) = 18.67$, $\Delta H^\ddagger / (\text{kJ}\cdot\text{mol}^{-1}) = 16.19$, $\Delta S^\ddagger / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = -219.14$				

The plot of $\ln k$ vs $1/T$ has the following intercept (a) slope (b) and correlation coefficient (r): a = 4.11, b = -2294.11, r = 0.999.

From the thermodynamic parameters of table 2, a low value of E_a could indicate a large rate of the reaction. However, because of the lower value of the entropy the rate of reaction is not so large. This conclusion is supported by equation (12).

$$k = \frac{k_B T}{h} e^n (c^\ominus)^{1-n} \exp\left[\frac{\Delta_r^\ddagger S_m(c^\ominus)}{R}\right] \exp\left(-\frac{E_a}{RT}\right) \quad (12)$$

CONCLUSION

All the experimental results indicate that higher temperature and pH, lower $H_4TeO_6^{2-}$, and higher concentrations of the reductant, speed the reaction significantly. Our discussion and studies provide theoretical basis and valuable information of applications of pentaerythritol.

REFERENCES

1. A. Kumar, Vaishali, P. Ramamurthy, *Ion. Int. J. Chem. Kinet.* **32**, 286-293, (2000)
2. T. R. Prasad, B. Sethuram, T. N. Rao, *J. Ind. Chem.* **21A**, 169-170, (1982)
3. J. J. Wu, L. Y. Huang, Y. X. Lin, *Journal of Huaqiao University (Natural Science Edition)*. **21 (1)**, 34-39, (2000)
4. T. Raviprasad, B. Sethuram, R. Navaneeth, *J. Ind. Chem. Sect A.* **18A (1)**, 40-42, (1979)
5. K. K. Sen Gupta, B. K. Nandy, S. Sen Gupta, *J. Ind. Chem. Sect A*, **36A (3)**, 190-196, (1997)
6. J. H. Shan, L. Wang, S. G. Shen, B. S. Liu, H. W. Sun, *Journal of Hebei University*. **21 (1)**, 53-56, (2001)
7. J. H. Shan, L. Wang, S. G. Shen, H. W. Sun, A. Z. Wang, *Chem. Res. Chin. Univ.* **16 (3)**, 218-222, (2000)
8. K. K. Sen Gupta, B. Ghosh, *J. Chem. Res. Synop.* **6**, 178-179, (1992)
9. K. K. Sen Gupta, B. K. Nandy, S. Sen Gupta, *J. Chem. Soc. Dalton Trans.* **7**, 1227-1232, (1995)
10. F. Feigl, *Spot Tests in Organic Analysis*. Elsevier Publishing Co., New York, 1956, pp. 208.
11. J. J. Jin, "Kinetics principle of chemical reaction in liquid phase," Shanghai: Science Technique Press, 1966; pp. 186. (in Chinese).
12. J. Aveston, *J. Chem. Soc. A.* 273, (1969).
13. H. G. Mukherjee, B. Mandal, S. De, *J. Ind. Chem.* **23(A)**, 481, (1984).
14. J. J. H. Shan, T. Y. Liu, *Acta Chim. Sinica.* **52**, 1140, (1994).