

Kinetics and Mechanism of Oxidation of 3-phenoxy-1,2-propanediol by Ditelluratocuprate(III) in Alkaline Medium

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Abstract

The kinetics of oxidation of 3-phenoxy-1,2-propanediol by ditelluratocuprate(III) (DTC) 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 DTC and fractional order with respect to 3-phenoxy-1,2-propanediol. 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 TeO_4^{2-} . The reaction rate changed with the position of hydroxyl group. There is a negative salt effect. A plausible mechanism involving a pre-equilibrium of an adduct formation between the complex and 3-phenoxy-1,2-propanediol was proposed. 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: Ditelluratocuprate(III) (DTC), Kinetics, Mechanism, 3-phenoxy-1,2-propanediol

1. Introduction

In recent years, the study of the higher oxidation state of transition metals has intrigued many researchers. This can provide new and valuable information in some fields. Transition metals in a higher oxidation state generally can be stabilized by chelation with suitable polydentate ligands. Metal chelates such as ditelluratocuprate(III) (Shan, J. H., Wei, H. Y., Wang, L., Liu, B. S., Shen, S. G., & Sun, H. W. 2001, Shan, J. H., Wang, L., Wei, H. Y., Shen, S. G., & Sun, H. W. 2002, Shan, J. H., Wang, L. P., & Sun, H. W. 2003), diperiodatocuprate(III) (Shan, J. H., Shen, S. G., & Ma, Z. G. 1998), diperiodatoargentate(III) (Shan, J. H., Wang, L., & Shen, S.G. 2001),

ditelluratoargentate(III) (Gupta, K. K. S., Nandy, B. K., & Bera, A. K. 1997), diperiodatonickelate(IV) (Shan, J. H., Wei, H. Y. & Wang, L. 2001) are good oxidants in a medium with an appropriate pH value. The use of Cu(III) as an oxidation agent is well known in analytical chemistry in the estimation of glucose, sugars and organic acids. The use of Cu(III) as an oxidation agent is also known in organic mixture qualitative analysis (Reddy, K. B., Sethuram, B., & Rao, T. N. 1981). Cu(III) is also shown to be an intermediate in the Cu(II)-catalyzed oxidation of amino acids by peroxodisulphate. Many biological systems involve electron-transfer processes wherein Cu(III) plays an important role (Feigl, F. 1956). Based on the studies of oxidation of some organic compounds by Cu(III) complex, Indian researchers proposed that in the alkaline medium the formula of DTC may be represented by $[\text{Cu}(\text{H}_4\text{TeO}_6)_2]^-$ and the mechanism involving a pre-equilibrium of an adduct formation between the complex and reductant was also proposed (Zhao, X. Z., Luo, Y. R. 1993). Because Cu(III) is in the higher oxidation state and the reaction is complicated in this kind of reaction system, it is of significance to have a further study on this kind of reaction system. Investigation on them will certainly provide us with more dynamical parameters, and will provide theoretical foundation for the design of reaction route in the organic synthesis and quantitative analysis in analytical chemistry.

2. Experimental

2.1 Materials and apparatus

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Solutions of $[\text{Cu}(\text{H}_4\text{TeO}_6)_2]^-$ (DTC) and 3-phenoxy-1,2-propanediol were always freshly prepared before using. The stock solution of DTC was prepared and standardized by the method given by Jaiswal and Yadava (Chandra, S., Yadava, K. L. 1968, Jaiswal, P. K., Yadava, K. L. 1973). Its electronic spectrum was found to be consistent with that reported by Jaiswal and Yadava.

2.2 Kinetics measurements

All kinetics measurements were carried out under pseudo-first order conditions. Solution (2mL) containing definite concentration of Cu(III), OH^- , TeO_4^{2-} and ionic strength and 3-phenoxy-1,2-propanediol solution (2mL) of appropriate concentration were transferred separately to the upper and lower branch tubes of a λ type two-cell reactor. The concentration of DTC was derived from its absorption at 405 nm. The ionic strength μ was maintained by adding KNO_3 solution and the pH of the reaction mixture was adjusted with a KOH solution. The kinetic measurements were performed on a UV-vis spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell holder kept at constant temperature ($\pm 0.1^\circ\text{C}$) by circulating water from a thermostat (DC-2010, Baoding, China).

2.3 Product analysis

A solution with known concentrations of Cu(III), OH^- , TeO_4^{2-} was mixed with an excess of 3-phenoxy-1,2-propanediol. With the complete fading of DTC color (reddish brown) marked the completion of the reaction. The product of oxidation was identified as aldehyde by its characteristic spot test (Feigl, F. 1966). It was found that one mole of 3-phenoxy-1,2-propanediol consumed two moles Cu(III) by weighting.

3. Results and discussion

3.1 Evaluation of Pseudo-First Order Rate Constants

Under the conditions of $[\text{3-phenoxy-1,2-propanediol}]_0 \gg [\text{DTC}]_0$, the plots of $\ln(A_t - A_\infty)$ versus time were straight lines, details of the evaluation are described in our previous work.

3.2 Rate Dependence on the [3-phenoxy-1,2-propanediol]

At constant temperature, k_{obs} values increase by increasing the concentration of 3-phenoxy-1,2-propanediol while keeping the $[\text{DTC}]$, $[\text{OH}^-]$, $[\text{TeO}_4^{2-}]$, and μ constant. The order with respect to 3-phenoxy-1,2-propanediol was fractional. The plots of $1/k_{\text{obs}}$ vs. $1/[\text{3-phenoxy-1,2-propanediol}]$ were straight lines with a positive intercept (**Figure 1**).

3.3 Rate Dependence on the $[\text{TeO}_4^{2-}]$ and $[\text{OH}^-]$

At constant $[\text{Cu(III)}]$, $[\text{3-phenoxy-1,2-propanediol}]$, $[\text{OH}^-]$, μ and temperature, the experimental results indicate that k_{obs} decreases while increasing the $[\text{TeO}_4^{2-}]$. The order with respect to $[\text{TeO}_4^{2-}]$ was negative fractional and the plot of $1/k_{\text{obs}}$ vs. $[\text{TeO}_4^{2-}]$ was linear (**Figure 2**).

At constant $[\text{Cu(III)}]$, $[\text{3-phenoxy-1,2-propanediol}]$, $[\text{TeO}_4^{2-}]$, μ and temperature, k_{obs} values increased with the increase in $[\text{OH}^-]$. 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**).

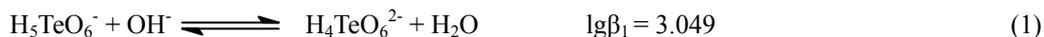
3.4 Rate Dependence on the Ionic Strength

With other conditions fixed, the reaction rate does not change by the addition of KNO₃ solution (**Table 1**), which indicate there is negative salt effect (Jin, J. J. 1984).

4. Reaction Mechanism

Acrylamide was added under the protection of nitrogen atmosphere during the course of reaction. The appearance of white polyacrylamide was consistent with free radical intermediates in the oxidation by Cu(III) complexes. Blank experiments in reaction system gave no polymeric suspensions.

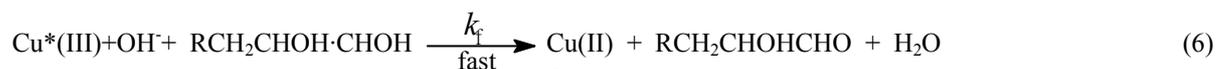
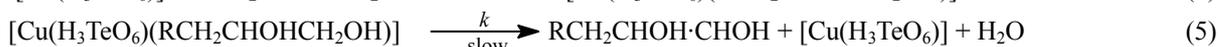
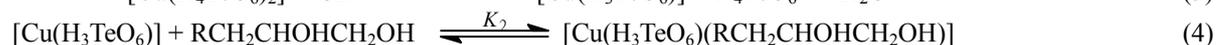
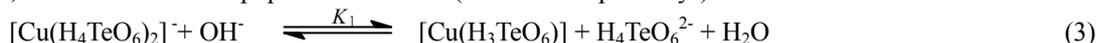
In the alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier. (here pK_w=14)



The distribution of all species of tellurate in aqueous alkaline solution can be calculated from equilibriums (1)-(2). In alkaline medium such as [OH⁻]=0.01 mol·L⁻¹, [H₄TeO₆²⁻]:[H₅TeO₆⁻]:[H₃TeO₆³⁻]=1000:89:1, so in the concentration of OH⁻ range used in this work, H₅TeO₆⁻ and H₃TeO₆³⁻ can be neglected, the main tellurate species was H₄TeO₆²⁻.

The fractional order in OH⁻ indicated that OH⁻ takes part in a pre-equilibrium with Cu(III) before the rate-determining step. The plot of 1/k_{obs} versus [TeO₄²⁻] is line with a positive intercept which indicates a dissociation equilibrium in which the Cu(III) loses a tellurate ligand H₄TeO₆²⁻ from its coordination sphere and forms a reactive monotelluratocuprate(III) complex (MTC). The fractional order in 3-phenoxy-1,2-propanediol indicated complex formation between 3-phenoxy-1,2-propanediol and MTC, and the plots of 1/k_{obs} versus 1/[3-phenoxy-1,2-propanediol] was straight line with a positive intercept providing kinetic evidence for the formation of 2:1 complex. Hence the following inner-sphere electron transfer mechanism involving a pre-equilibrium of an adduct formation between the complex and 3-phenoxy-1,2-propanediol is proposed for the reaction.

In alkaline solution, [Cu(H₂TeO₆)₂]⁵⁻ protonated easily and it coordinate with central ion. In view of the experiments, the mechanism was proposed as follows: (R stands for phenoxy-)



Where Cu*(III) stands for any kind of which Cu³⁺ existed in equilibrium and where R' stands for reductant. Subscripts T and e stand for total and equilibrium concentration respectively. [Cu(III)]_T=[Cu(H₃TeO₆)]_e+ [Cu(H₃TeO₆)(RCH₂CHOHCH₂OH)] + [Cu(H₄TeO₆)₂]_e. Reaction (5) was the rate-determining step.

$$[\text{Cu}(\text{H}_3\text{TeO}_6)(\text{R}')] = \frac{K_1 K_2 [\text{Cu}(\text{III})]_T [\text{OH}^-] [\text{R}']}{[\text{H}_4\text{TeO}_6^{2-}] + K_1 [\text{OH}^-] + K_1 K_2 [\text{OH}^-] [\text{R}']} \quad (7)$$

As the rate of the disappearance of Cu (III) was monitored, the rate law of the reaction can be derived as:

$$-\frac{d[\text{Cu}(\text{III})]_T}{dt} = 2k[\text{Cu}(\text{H}_3\text{TeO}_6)(\text{R}')] \quad (8)$$

$$\begin{aligned} -\frac{d[\text{Cu}(\text{III})]_T}{dt} &= \frac{2kK_1K_2[\text{Cu}(\text{III})]_T[\text{OH}^-][\text{R}']}{[\text{H}_4\text{TeO}_6^{2-}] + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][\text{R}']} \\ &= k_{\text{obs}}[\text{Cu}(\text{III})]_T \end{aligned} \quad (9)$$

$$k_{\text{obs}} = \frac{2kK_1K_2[\text{OH}^-][\text{R}']}{[\text{H}_4\text{TeO}_6^{2-}] + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][\text{R}']} \quad (10)$$

Re-arranging equation (10) leads to equation (11-13):

$$\frac{1}{k_{\text{obs}}} = \frac{1}{2k} + \frac{[\text{H}_4\text{TeO}_6^{2-}] + K_1[\text{OH}^-]}{2kK_1K_2[\text{OH}^-]} \frac{1}{[\text{R}']} \quad (11)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1 + K_2[\text{R}']}{2kK_2[\text{R}']} + \frac{[\text{H}_4\text{TeO}_6^{2-}]}{2kK_1K_2[\text{R}'][\text{OH}^-]} \frac{1}{[\text{R}']} \quad (12)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1 + K_2[\text{R}']}{2kK_2[\text{R}']} + \frac{[\text{H}_4\text{TeO}_6^{2-}]}{2kK_1K_2[\text{OH}^-][\text{R}']} \quad (13)$$

From the equation (11), the plots $1/k_{\text{obs}}$ vs $1/[\text{R}']$ are straight lines and the rate constants of the rate-determining step at different temperature were obtained from the intercept of the straight line. Equation (12) and (13) suggest that the plots of $1/k_{\text{obs}}$ vs $1/[\text{OH}^-]$ and $1/k_{\text{obs}}$ vs $[\text{H}_4\text{TeO}_6^{2-}]$ are straight lines. Activation energy and the thermodynamic parameters were evaluated by the method given earlier (**Table 2**).

5. Conclusion

Among various species of $\text{Cu}^*(\text{III})$ in alkaline liquids, monotelluratocuprate is considered as the active species for the title reaction. The rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to the slow step of the reaction were computed. The overall mechanistic sequence described here is consistent with product studies, mechanistic studies and kinetic studies.

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Table 1. Rate Dependence on ionic Strength at 298.2K

$10^2 \mu/M$	1	2	3	4	5
k_{obs}/s^{-1}	0.0321	0.0312	0.0275	0.0244	0.0235

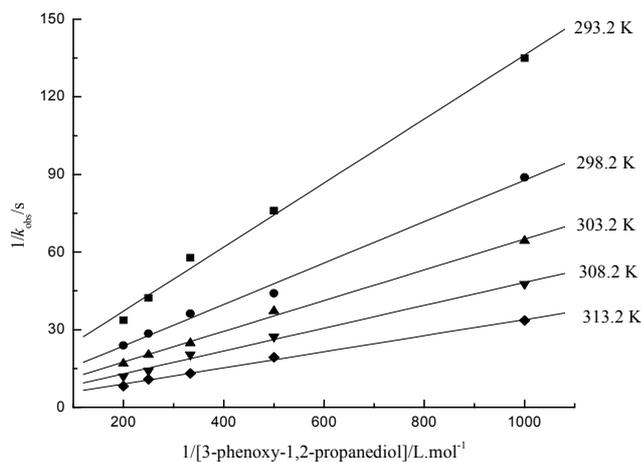
$[Cu(III)] = 4.04 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $[OH^-] = 5.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[TeO_4^{2-}] = 1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$,
 $[3\text{-phenoxy-1,2-propanediol}] = 3.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$

Table 2. Rate constants (k) and activation parameters of the rate-determining step at 298.2K

T/K	k/s^{-1}	Thermodynamic activation parameters (298.2 K)
293.2	0.0403	$E_a = 55.36 \text{ kJ}\cdot\text{mol}^{-1}$ $\Delta H^\ddagger = 52.88 \text{ kJ}\cdot\text{mol}^{-1}$ $\Delta S^\ddagger = -85.11 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
298.2	0.0648	
303.2	0.0872	
308.2	0.1216	
313.2	0.1803	

The plot of $\ln k$ vs $1/T$ have following intercept (a) slope (b) and relative coefficient (r)

$$a = 20.23 \quad b = -6658.86 \quad r = 0.998$$

Figure 1. Plots of $1/k_{\text{obs}}$ vs. $1/[3\text{-phenoxy-1,2-propanediol}]$ ($r \geq 0.996$)

$[Cu(III)] = 4.04 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $[OH^-] = 5.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[TeO_4^{2-}] = 1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $\mu = 1.20 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$

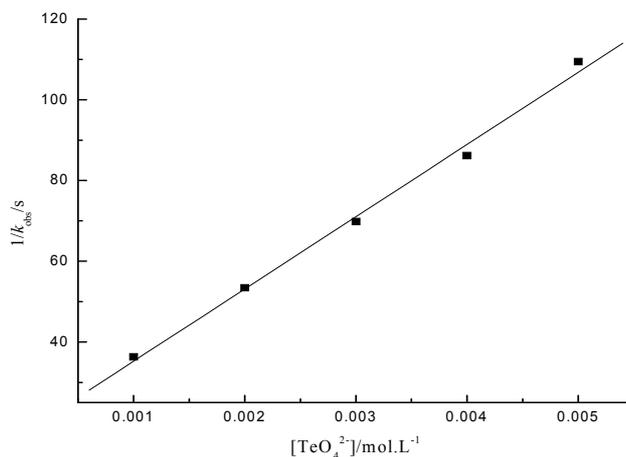


Figure 2. Plot of $1/k_{\text{obs}}$ versus $[\text{TeO}_4^{2-}]$ at 298.2 K ($r = 0.997$)

$[\text{Cu(III)}] = 4.04 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $[\text{OH}^-] = 5.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{3-phenoxy-1,2-propanediol}] = 3.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $\mu = 3.55 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$

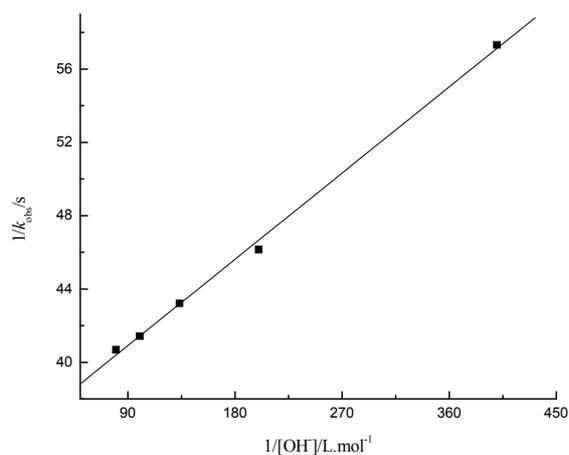


Figure 3. Plot of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ at 298.2 K ($r = 0.999$)

$[\text{Cu(III)}] = 4.04 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $[\text{TeO}_4^{2-}] = 1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{3-phenoxy-1,2-propanediol}] = 3.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $\mu = 3.55 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$