

碱性介质中二(碲酸根)合铜(Ⅲ)酸根氧化乙二醇一乙醚的反应动力学及机理

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在碱性介质中用分光光度法研究了二过碲酸合铜(Ⅲ)配离子(DTC)氧化乙二醇一乙醚(EGE)的反应动力学及机理, 反应速率表明: 反应对 DTC 为准一级, 对 EGE 为分数级; 在保持准一级条件 ($[EGE] \gg [DTC]$) 下, 表观速率常数随着 OH^- 浓度的增加而增大, 随着 TeO_4^{2-} 浓度的增加而减小; 有负的盐效应。据此提出了包括配离子和 EGE 形成络合物的前期平衡的反应机理, 由假设反应机理推出的速率方程能很好的解释全部实验现象, 进一步求得速控步的速率常数和活化参数。

关键词: 二碲酸合铜(Ⅲ)离子 乙二醇一乙醚 氧化还原反应 动力学及机理
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Kinetics and Mechanism of Oxidation Ethylene Glycol Monoethylether by Ditelluratocuprate (Ⅲ) in Alkaline Medium

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The kinetics of the oxidation of ethylene glycol monoethyl ether (EGE) by ditelluratocuprate (Ⅲ) complex (DTC) was studied in alkaline medium with spectrophotometry. The reaction rate showed pseudo-first order dependence in oxidation and fractional order in EGE. It was found that the pseudo-first order (under the condition: $[EGE] \gg [DTC]$) rate constants k_{obs} increased with the increase in $[OH^-]$ and decrease in $[TeO_4^{2-}]$. There is a negative salt effect. A mechanism involving a preequilibrium of a adduct formation between the complex and EGE was proposed. The rate equation derived from the mechanism can explain all the experimental results. The activation parameters along with the rate constants of the rate-determining step were calculated.

Keywords: ditelluratocuprate (Ⅲ) ethylene glycol monoethylether redox reaction
kinetics and mechanism

0 Introduction

Recently, studies on the transition metals in a higher oxidation state have been the most active area.

Investigations on them such as Cu (Ⅲ)^[1], Ag (Ⅲ)^[2], Ni (Ⅳ)^[3] etc will certainly provide us with more valuable information.

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Transition metals in a higher oxidation state generally can be stabilized by chelation with suitable polydentate ligands. Metal chelation such as diperiodatocuprate (III), diperiodatoargenate (III) and dihydroxydiperiodatonickelate (IV) complexes are stable and strong oxidants in a medium with an appropriate pH value. The use of Cu (III) as an oxidizing agent is well known in analytical chemistry in the estimation of sugars, glycerols, amino acids, proteins, carboxylic acids, carbonyl compounds and alcohols^[4,5]. Cu (III) is also shown to be an intermediate in the Cu (II) -catalyzed oxidation of amino acids by peroxodisulphate^[6]. Because Cu (III) is in the highest oxidation state and the reaction is complicated in this system, it is of significance to have a further study on this kind of reaction system. In the present paper, the mechanism of oxidation of Ethylene glycol monoethyl ether (EGE) by ditelluratocuprate (III) (DTC) is reported.

1 Material and Methods

All the chemicals used were A. R. grade. All solutions were prepared with twice-distilled water. The stock solution of DTC was prepared by the method given by Jaiswal and Yadava^[4]. Its electronic spectrum was found to be consistent with that reported by Jaiswal and Yadava. The concentration of DTC was obtained by its absorption at $\lambda = 405\text{nm}$. The ionic strength was maintained by adding KNO_3 solution and the pH value was regulated with KOH solution.

Measurements of the kinetics were performed using a Shimadzu UV-265 spectrophotometer (Japan) fitted with a Shimadzu TB-85 thermostat ($\pm 0.1^\circ\text{C}$). Details of the determinations are described elsewhere^[7]. The oxidation product was identified as the corresponding aldehyde by spot test^[8].

2 Results and Discussions

2.1 Evaluation of Pseudo-First-Order Rate Constants

Constants

Under the condition of $[\text{EGE}]_0 \gg [\text{DTC}]_0$, the plots of $\ln(A_\infty - A_t)$ vs. time t for more than three half lives of the reaction were good straight lines ($r \geq$

0.9999), indicating the order in DTC to be unity. The pseudo-first-order rate constants k_{obs} were calculated by using the least-squares method. The rate constants reported here are average of three independent runs. Deviations in duplicate determinations are generally less than $\pm 5\%$.

2.2 Effect of Varying [EGE]

Under the condition of $[\text{EGE}] \gg [\text{DTC}]$, at constant $[\text{DTC}]$, $[\text{TeO}_4^{2-}]$, $[\text{OH}^-]$, ionic strength I and temperature, k_{obs} values increased with the increase in concentration of EGE and the order with respect to EGE was found to be fractional (in the temperature range of $20 \sim 40^\circ\text{C}$, $n_{\text{app}} = 0.79 \sim 0.9$). The plots of $1/k_{\text{obs}}$ vs. $1/[\text{EGE}]$ were straight lines with a positive intercept ($r > 0.994$) (Fig. 1).

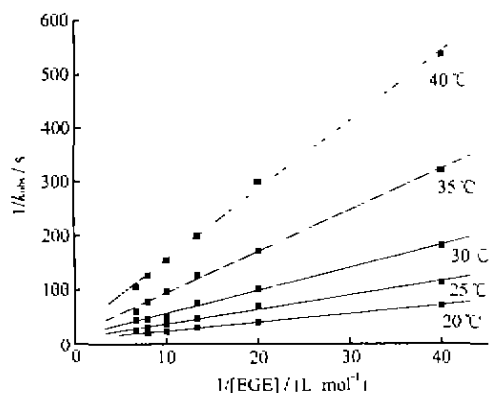


Fig. 1 Plots of $1/k_{\text{obs}}$ vs. $1/[\text{EGE}]$ at different temperatures
 $[\text{Cu (III)}] = 1.822 \times 10^{-4} \text{mol} \cdot \text{L}^{-1}$;
 $[\text{TeO}_4^{2-}] = 1.905 \times 10^{-3} \text{mol} \cdot \text{L}^{-1}$;
 $[\text{OH}^-] = 1.68 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$;
 $I = 0.02785 \text{mol} \cdot \text{L}^{-1}$

2.3 Effect of Varying $[\text{OH}^-]$

At constant $[\text{DTC}]$, $[\text{TeO}_4^{2-}]$, $[\text{EGE}]$, ionic strength I and temperature, k_{obs} increased with the increase in $[\text{OH}^-]$ and the order with respect to OH^- was found to be fractional order ($n_{\text{app}} = 0.53$). The plot of $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ was a straight line ($r = 0.991$) (Fig. 2).

2.4 Effect of Varying $[\text{TeO}_4^{2-}]$

The experimental results indicate k_{obs} decreased with the increase in $[\text{TeO}_4^{2-}]$, and the order with respect to TeO_4^{2-} was found to be fractional order, $n_{\text{app}} = -0.89$. The plot of $1/k_{\text{obs}}$ vs. $[\text{TeO}_4^{2-}]$

Table 1 Influence of Variation of I

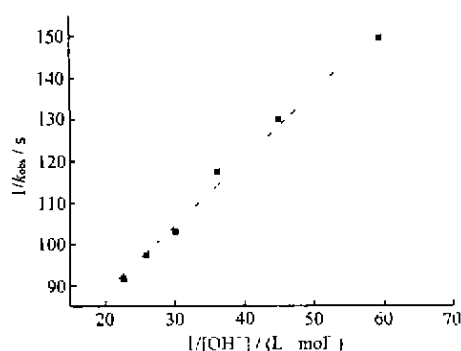
$10^3 I$	2.785	3.783	4.783	5.783	6.783	7.783
$10^3 k_{obs}$	9.736	8.9303	8.1165	7.5354	6.8726	6.4343

$[Cu(III)] = 1.822 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $[EGF] = 0.05 \text{ mol} \cdot \text{L}^{-1}$, $[TeO_4^{2-}] = 1.905 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$,
 $[OH^-] = 1.68 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$; $t = 30^\circ\text{C}$.

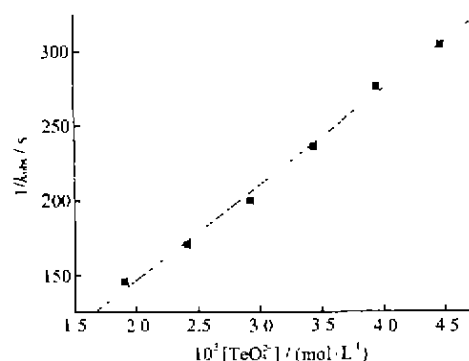
Table 2 Rate Constants of Rate-Determining Step and Activation Parameters

T/K	293.2	298.2	303.2	308.2	313.2	activation parameters (25°C)
$k/(\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1})$	0.01817	0.02684	0.03437	0.04749	0.06182	$E_a = 45.77 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta H = 43.29 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta S = -130.19 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Linear regression of $\ln k$ vs. $1/T$ gives slope, $a = -5503.87$, intercept, $b = 14.7979$; $r = 0.9986$

Fig. 2 Plot of $1/k_{obs}$ vs. $1/[OH^-]$

$[Cu(III)] = 1.822 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$
 $[EGE] = 0.05 \text{ mol} \cdot \text{L}^{-1}$, $I = 0.03055 \text{ mol} \cdot \text{L}^{-1}$
 $[TeO_4^{2-}] = 1.905 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $t = 30^\circ\text{C}$

Fig. 3 Plot of $1/k_{obs}$ vs. $[TeO_4^{2-}]$

$[Cu(III)] = 1.822 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$
 $[EGE] = 0.05 \text{ mol} \cdot \text{L}^{-1}$
 $I = 0.03277 \text{ mol} \cdot \text{L}^{-1}$
 $[OH^-] = 1.68 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$; $t = 30^\circ\text{C}$

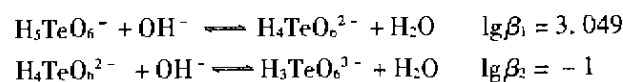
was a straight line ($r = 0.996$) (Fig. 3).

2.5 Effect of Varying I

The rate was decreased by added KNO_3 solution (Table 1), which indicate there was a negative salt effect which consistent with the common regulation of the kinetics^[9].

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

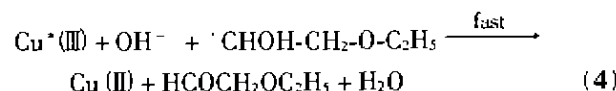
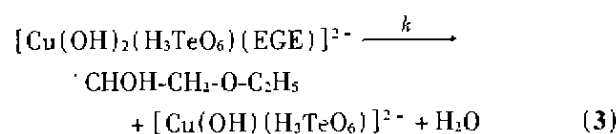
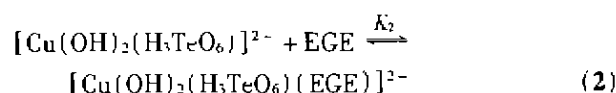
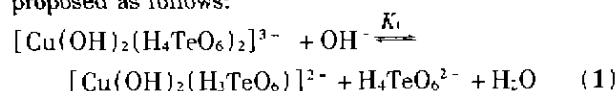
In the alkaline medium, the dissociative equilibrium of the $[TeO_4^{2-}]$ was given earlier^[10], (here $pK_a = 14$)



Hence the main tellurate species was $H_4TeO_6^{2-}$.

In view of the experiments, the mechanism was

proposed as follows:



Where $Cu^*(III)$ stand for any kind of form which Cu^{3+} existed in equilibrium.

$$-d[Cu(III)]_T/dt = 2k[Cu(OH)_2(H_3TeO_6)(EGE)]^{2-} \quad (I)$$

$$[Cu(III)]_T = [Cu(OH)_2(H_4TeO_6)_2]^{3-} + [Cu(OH)_2(H_3TeO_6)]^{2-} + [Cu(OH)_2(H_3TeO_6)(EGE)]^{2-} = [DTC]_0$$

Where T and e stand for total concentration and equilibrium concentration respectively.

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

where

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

Re-arranging equation (III) leads to equation (IV) ~ (V)

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

$$\frac{1}{k_{\text{obs}}} = \frac{1}{2k} + \left(\frac{1}{2kK_2} + \frac{[\text{H}_4\text{TeO}_6^{2-}]}{2kK_1K_2[\text{OH}^-]} \right) \cdot \frac{1}{[\text{EGE}]} \quad (\text{V})$$

From the equation (IV), the plots of $1/k_{\text{obs}}$ vs. $1/[\text{EGE}]$ is straight line ($r > 0.99$), and the rate constants of rate-determining at different temperatures were obtained from the intercepts of the straight lines. Equation (V) suggests that the plot 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, which conform to the observation. Activation energy and the thermodynamic parameters ($t = 25^\circ\text{C}$) were evaluated by the method given earlier^[11].

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