

碱性介质中二(高碘酸根)合铜(Ⅲ)酸根氧化乙二醇独丁醚
的反应动力学及机理

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在 25℃ ~ 40℃ 区间用分光光度法在碱性介质中研究了二(高碘酸根)合铜(Ⅲ)酸根配离子(DPC)氧化乙二醇独丁醚(EGB)的反应动力学。结果表明: 反应对 DPC 为一级, 对 EGB 是 $1 < n_{ap} < 2$ (n_{ap} 代表表观反应级数); 在保持准一级条件 ($[EGB]_0 \gg [Cu(III)]_0$) 下, 表观速率常数, k_{obs} , 在弱碱性介质中, 随 $[OH^-]$ 增大而减小, 在较强碱性介质中随 $[OH^-]$ 增大而增大, 随着 $[IO_4^-]$ 增加而减小; 无盐效应。提出了含有自由基过程的反应机理, 由假设的两种同时进行的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(高碘酸根)合铜(Ⅲ)酸根 乙二醇独丁醚 氧化还原反应 动力学及机理
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Kinetics and Mechanism of Oxidation of Ethylene Glycol Monobutyl
Ether by Diperiodatocuprate (Ⅲ) in Alkaline Medium

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Copper (Ⅲ) has received extensive attention recently because of its apparent involvement in various biological processes. Amounts of work have been reported. But 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. Investigation on them will certainly provide us with more dynamical parameters, and will provide theoretical foundation for the reaction route design of the organic synthesis and quantitative analysis of analytical chemistry.

The kinetics of oxidation of ethylene glycol monobutyl ether (EGB) by diperiodatocuprate (Ⅲ) complex (DPC) was studied spectrophotometrically between 25℃ and 40℃ in alkaline medium. All kinetic measurements were carried out under pseudo-first order conditions. The reaction process was monitored automatically by recording the varying curve of absorbance (A) of reaction solution with time (t) at 415nm with a spectrometer.

The reaction rate showed first order dependence in DPC and $1 < n_{ap} < 2$ in EGB. It was found that under the conditions of the pseudo-first order ($[EGB]_0 \gg [Cu(III)]_0$), the rate constant, k_{obs} , changed differently under different $[OH^-]$. At low $[OH^-]$, k_{obs} decreased with increase in $[OH^-]$, but when $[OH^-]$ increased to enough extent, k_{obs} increased with increase in $[OH^-]$, and then it decreased with increase in $[IO_4^-]$. There is no effect of addition of salt like KNO_3 . Free radicals were observed in the process of reaction. A plausible mechanism involving free radical was proposed. The rate equations derived from two simultaneous mechanisms can explain all experimental observations. The activation parameters along with the rate constants of the rate-determining step were calculated.

Keywords: diperiodatocuprate (Ⅲ) ethylene glycol monobutyl ether redox reaction
kinetics and mechanism

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0 Introduction

Transition metals in a higher oxidation state generally can be stabilized by chelation with suitable polydentate ligands. Metal chelates such as diperiodatocuprate (III)^[1], ditelluratocuprate (III)^[2], diperiodatonickelate (IV)^[3] are good oxidants in a medium with an appropriate pH value. DPC has been used in the estimation of sugars and organic acids^[4]. The use of DPC as oxidizing agents in the investigation of some organic compounds such as diethanolamine^[5] etc have been reported. However, there is no report on the kinetics of oxidation reaction of EGB by DPC. We have therefore studied the oxidation of EGB by DPC in alkaline medium in order to get an insight into the mechanism of oxidation of the substrates.

1 Material and Methods

All reagents used were of A. R. grade. All solution was prepared with twice distilled water. Solution of DPC and EGB were always freshly prepared before use. The stock solution of DPC in a strong alkaline medium was prepared by the method given by Jaiswal^[4]. Its electronic spectrum was found to be consistent with that reported by Jaiswal. The concentration of DPC obtained by its absorption at $\lambda = 415$. 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 UV-8500 spectrophotometer (Shanghai) fitted with a 501 thermostat ($\pm 0.1^\circ\text{C}$, Shanghai). Details of the determinations are described elsewhere^[6]. The product of oxidation was identified as the corresponding aldehyde by spot test^[7].

2 Results and Discussion

2.1 Evaluation of Pseudo-First-Order Rate Constants

Under the conditions $[\text{EGB}]_0 \gg [\text{Cu(III)}]_0$, the plots of $\ln(A_t - A_\infty)$ versus time t were linear ($r \geq 0.9998$) indicating that the reaction is first order with respect to Cu(III) , where A_t and A_∞ were the absorbance at time t and at infinite time, respectively. The pseu-

do-first order rate constants, k_{obs} , were evaluated by the method of least squares. We used generally 8 ~ 10 A_t values within three times half life period to calculate k_{obs} , k_{obs} values were at least averaged values of three independent experiments and reproducibility is within $\pm 5\%$.

2.2 Effect of Varying [EGB]

At constant $[\text{Cu(III)}]$, $[\text{OH}^-]$, $[\text{IO}_4^-]$, and ionic strength μ and temperature, k_{obs} values increase with the increase in $[\text{EGB}]$ and the order with respect to EGB was found to be $1 < n_{\text{ap}} < 2$. The plot of $[\text{EGB}]/k_{\text{obs}}$ versus $1/[\text{EGB}]$ was linear ($r \geq 0.996$) (Fig. 1).

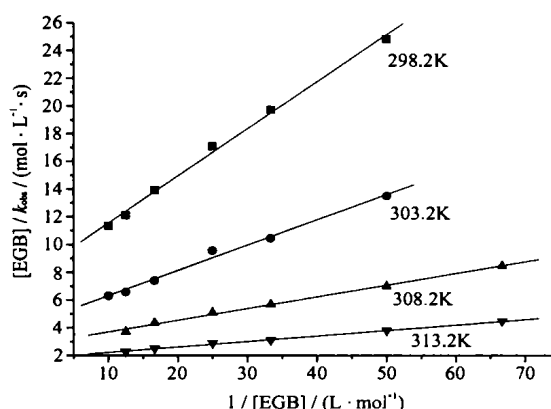


Fig. 1 Plots of $[\text{EGB}]/k_{\text{obs}}$ vs $1/[\text{EGB}]$ at different temperatures

$$[\text{Cu(III)}] = 8.953 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1},$$

$$[\text{IO}_4^-] = 1.606 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1},$$

$$[\text{OH}^-] = 1.025 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1},$$

$$\mu = 1.186 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

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

At constant $[\text{Cu(III)}]$, $[\text{EGB}]$, $[\text{IO}_4^-]$, ionic strength μ and temperature, k_{obs} values decreased rapidly with increase in $[\text{OH}^-]$, and then increased with increase in $[\text{OH}^-]$. The concentration of OH^- was about $0.020 \text{ mol} \cdot \text{L}^{-1}$ at the turning point in which the rate was the slowest (Fig. 2).

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

At fixed $[\text{Cu(III)}]$, $[\text{OH}^-]$, $[\text{EGB}]$, ionic strength μ and temperature, k_{obs} values decreased with the increase in $[\text{IO}_4^-]$, and the order with respect to IO_4^- was found to be negative fractional order. The plot of $1/k_{\text{obs}}$ versus $[\text{IO}_4^-]$ was linear ($r = 0.997$) (Fig. 3).

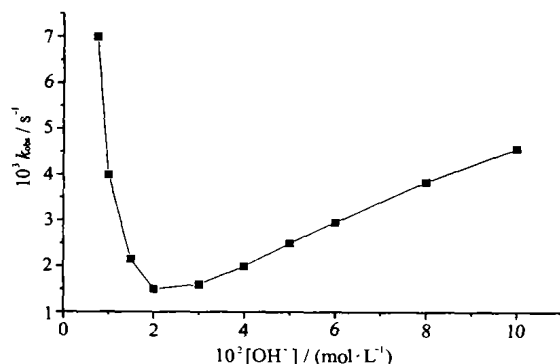


Fig. 2 Plot of k_{obs} vs $[\text{OH}^-]$ at $T = 303.2\text{K}$
 $[\text{Cu(III)}] = 8.953 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$,
 $[\text{IO}_4^-] = 1.606 \times 10^{-3} \text{mol} \cdot \text{L}^{-1}$,
 $[\text{EGB}] = 0.040 \text{mol} \cdot \text{L}^{-1}$,
 $\mu = 0.102 \text{mol} \cdot \text{L}^{-1}$

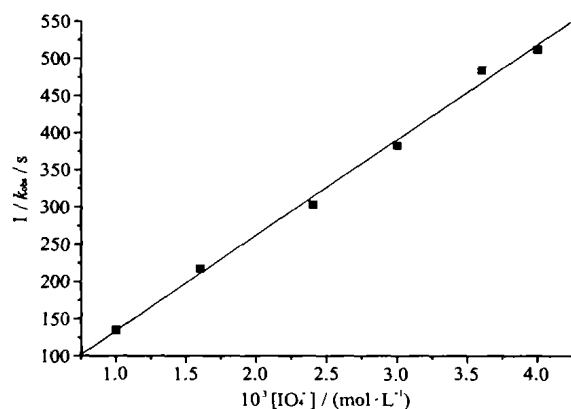


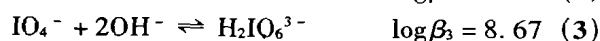
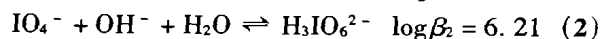
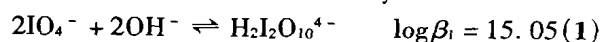
Fig. 3 Plot of $1/k_{\text{obs}}$ vs $[\text{IO}_4^-]$ at $T = 303.2\text{K}$
 $[\text{Cu(III)}] = 7.958 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$,
 $[\text{EGB}] = 0.050 \text{mol} \cdot \text{L}^{-1}$,
 $[\text{OH}^-] = 0.010 \text{mol} \cdot \text{L}^{-1}$,
 $\mu = 1.400 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$

2.5 Effect of Varying Ionic Strength μ

Table 1 reveals that ionic strength μ has negligible effect on the rate.

Acrylamide was added under the protection of nitrogen 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 aqueous periodate solution equilibria (1) ~ (3) were detected and the corresponding equilibrium constants at 273.2K were determined by Aveston^[8].



The distribution of all species of periodate in aqueous alkaline solution can be calculated from equilibria (1) ~ (3). In the $[\text{OH}^-]$ range used in this work the dimer and IO_4^- species of periodate can be neglected. Neglecting the concentration of ligand dissociated from Cu(III) and the species of periodate other than $\text{H}_2\text{IO}_6^{3-}$ and $\text{H}_3\text{IO}_6^{2-}$, Eqs. (4) and (5) can be obtained from (2) and (3):

$$\begin{aligned} [\text{H}_2\text{IO}_6^{3-}] &= \frac{\beta_3 [\text{OH}^-]^2}{1 + \beta_2 [\text{OH}^-] + \beta_3 [\text{OH}^-]^2} [\text{IO}_4^-] \\ &= f([\text{OH}^-]) [\text{IO}_4^-]_{\text{ex}} \end{aligned} \quad (4)$$

$$\begin{aligned} [\text{H}_3\text{IO}_6^{2-}] &= \frac{\beta_2 [\text{OH}^-]}{1 + \beta_2 [\text{OH}^-] + \beta_3 [\text{OH}^-]^2} [\text{IO}_4^-]_{\text{ex}} \\ &= \phi([\text{OH}^-]) [\text{IO}_4^-]_{\text{ex}} \end{aligned} \quad (5)$$

Here $[\text{IO}_4^-]_{\text{ex}}$ represents the original overall entering periodate and equals approximately to the sum of $[\text{H}_2\text{IO}_6^{3-}]$ and $[\text{H}_3\text{IO}_6^{2-}]$.

In weaker alkaline medium such as $[\text{OH}^-] = 5.00 \times 10^{-3} \sim 1.00 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{IO}_6^{3-}] : [\text{H}_3\text{IO}_6^{2-}] = (1.44 \sim 2.89) : 1.00$, so the main species of periodate are $\text{H}_2\text{IO}_6^{3-}$ and $\text{H}_3\text{IO}_6^{2-}$, consistent with the result calculated from Crouthamel's data^[9] by Murthy. In stronger alkaline medium such as $[\text{OH}^-] = 5.00 \times 10^{-2} \sim 0.10 \text{mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{IO}_6^{3-}] : [\text{H}_3\text{IO}_6^{2-}] = (14.4 \sim 28.9) : 1.00$, so the main species of periodate is $\text{H}_2\text{IO}_6^{3-}$.

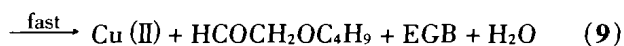
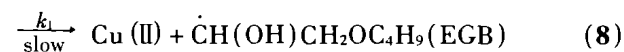
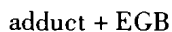
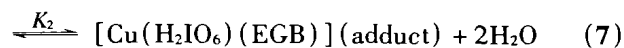
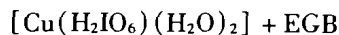
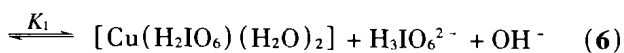
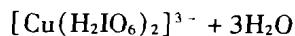
Based on the above discussion and the previous work^[1,10,11], two simultaneous reaction mechanism were proposed:

Mechanism I — In weaker alkaline medium:

Table 1 Rate Dependence on Ionic Strength at $T = 303.2\text{K}$

$10^2 \mu / (\text{mol} \cdot \text{L}^{-1})$	1.186	2.372	3.558	4.744	5.930
$10^3 k_{\text{obs}} / \text{s}^{-1}$	4.182	3.986	4.063	4.281	4.116

$[\text{Cu(III)}] = 8.953 \times 10^{-5} \text{mol} \cdot \text{L}^{-1}$, $[\text{IO}_4^-] = 1.606 \times 10^{-3} \text{mol} \cdot \text{L}^{-1}$,
 $[\text{EGB}] = 0.040 \text{mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = 1.025 \times 10^{-2} \text{mol} \cdot \text{L}^{-1}$



Where $\text{Cu}^*(\text{III})$ stand for any kind of form which Cu(III) existed in equilibrium. Subscripts T and e stand for total concentration and at equilibrium respectively. $[\text{Cu}(\text{III})]_{\text{T}} = [\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2]_{\text{e}} + [\text{Cu}(\text{H}_2\text{IO}_6)_2]_{\text{e}}^{3-} + [\text{adduct}]_{\text{e}}$. Reaction (8) was the rate-determining step.

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

$$\begin{aligned} -\frac{d[\text{Cu}(\text{III})]_{\text{T}}}{dt} &= \frac{2k_1K_1K_2[\text{EGB}]^2}{K_1 + [\text{H}_3\text{IO}_6^{2-}][\text{OH}^-] + K_1K_2[\text{EGB}]} [\text{Cu}(\text{III})]_{\text{T}} \\ &= k_{\text{obs}}[\text{Cu}(\text{III})]_{\text{T}} \end{aligned} \quad (10)$$

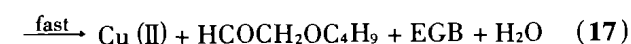
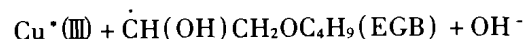
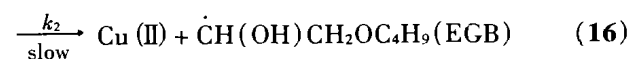
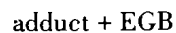
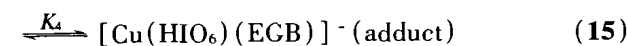
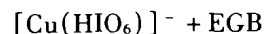
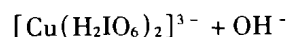
$$k_{\text{obs}} = \frac{2k_1K_1K_2[\text{EGB}]^2}{K_1 + [\text{H}_3\text{IO}_6^{2-}][\text{OH}^-] + K_1K_2[\text{EGB}]} \quad (11)$$

Rearranging Eq. (11) leads to Eqs. (12) and (13):

$$\frac{[\text{EGB}]}{k_{\text{obs}}} = \frac{1}{2k_1} + \frac{K_1 + [\text{H}_3\text{IO}_6^{2-}][\text{OH}^-]}{2k_1K_1K_2} \frac{1}{[\text{EGB}]} \quad (12)$$

$$\begin{aligned} \frac{1}{k_{\text{obs}}} &= \frac{K_1K_2[\text{EGB}] + K_1}{2k_1K_1K_2[\text{EGB}]^2} \\ &\quad + \frac{[\text{OH}^-]}{2k_1K_1K_2[\text{EGB}]^2} [\text{H}_3\text{IO}_6^{2-}] \end{aligned} \quad (13)$$

Mechanism II — In stronger alkaline medium:



Where $\text{Cu}^*(\text{III})$ stand for any kind of form which

Cu(III) existed in equilibrium. So we obtained the following equation: $[\text{Cu}(\text{III})]_{\text{T}} = [\text{Cu}(\text{HIO}_6)]_{\text{e}}^- + [\text{Cu}(\text{H}_2\text{IO}_6)_2]_{\text{e}}^{3-} + [\text{adduct}]_{\text{e}}$. Reaction (16) was the rate-determining step. Similarly, the rate of the reaction can be derived as:

$$\begin{aligned} -\frac{d[\text{Cu}(\text{III})]_{\text{T}}}{dt} &= \frac{2k_2K_3K_4[\text{OH}^-][\text{EGB}]^2}{K_3[\text{OH}^-] + [\text{H}_2\text{IO}_6^{3-}] + K_3K_4[\text{EGB}][\text{OH}^-]} [\text{Cu}(\text{III})]_{\text{T}} \\ &= k_{\text{obs}}[\text{Cu}(\text{III})]_{\text{T}} \end{aligned} \quad (18)$$

$$k_{\text{obs}} = \frac{2k_2K_3K_4[\text{OH}^-][\text{EGB}]^2}{K_3[\text{OH}^-] + [\text{H}_2\text{IO}_6^{3-}] + K_3K_4[\text{EGB}][\text{OH}^-]} \quad (19)$$

Rearranging Eq. (19) leads to Eqs. (20) and (21):

$$\frac{[\text{EGB}]}{k_{\text{obs}}} = \frac{1}{2k_2} + \frac{K_3[\text{OH}^-] + [\text{H}_2\text{IO}_6^{3-}]}{2k_2K_3K_4[\text{OH}^-]} \frac{1}{[\text{EGB}]} \quad (20)$$

$$\frac{1}{k_{\text{obs}}} = \frac{K_3 + K_3K_4[\text{EGB}]}{2k_2K_3K_4[\text{EGB}]^2} + \frac{[\text{H}_2\text{IO}_6^{3-}]}{2k_2K_3K_4[\text{OH}^-][\text{EGB}]^2} \quad (21)$$

Based on equations (1) ~ (5) and our calculated results, the influence of the change in $[\text{OH}^-]$ is discussed as follows. In weaker alkaline medium, the advantageous active substrate is $[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2]$. As $[\text{OH}^-]$ increase in the system, the reaction (6) is inhibited, k_{obs} decreases rapidly. When $[\text{OH}^-]$ continues to increase, $[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2]$ decreases and $[\text{Cu}(\text{HIO}_6)]^-$ increases gradually. When $[\text{OH}^-]$ increases to a certain extent, the decrease in rate caused by the decrease in $[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2]$ equals to the increase in rate caused by the increase in $[\text{Cu}(\text{HIO}_6)]^-$. So the turning point ($0.02\text{mol} \cdot \text{L}^{-1}$) in which the rate is the slowest appears. After the point, the main active substrate is $[\text{Cu}(\text{HIO}_6)]^-$ and it increases with the continuous increase in $[\text{OH}^-]$. So k_{obs} increases gradually.

Eqs. (11) and (19) show that the order in EGB was found to be $1 < n_{\text{ep}} < 2$. Eqs. (12) and (20) suggest that the plots of $[\text{EGB}]/k_{\text{obs}}$ versus $1/[\text{EGB}]$ should be linear. From their intercepts the rate-determining step constants (k) at different temperatures were evaluated. Eqs. (13) and (21) show that the plots of $1/k_{\text{obs}}$ versus $[\text{IO}_4^-]$ should also be linear. The rate equations derived from the two simultaneous mechanisms are consistent with our experimental results. The activation parameters data of EGB obtained

Table 2 Rate Constants (k) of the Rate-Determining Step and Activation Parameters

T/K	298.2	303.2	308.2	313.2	activation parameters (298.2K)
$10^2 k / (\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1})$	6.148	11.12	17.50	27.41	$E_a = 77.08 \pm 3.12 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta H^\ddagger = 74.60 \pm 3.12 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta S^\ddagger = -17.69 \pm 0.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

The slope, intercept and the correlation coefficient of the plot $\ln k$ vs $1/T$ are -9271.12 , 28.33 , 0.998 , respectively.

by the method given earlier^[12] are listed in Table 2.

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