Kinetics and Mechanism of Oxidation of 1-Methoxy-2-propanol and 1-Ethoxy-2-propanol by Ditelluratocuprate(III) in Alkaline Medium

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The kinetics of oxidation of 1-methoxy-2-propanol and 1-ethoxy-2-propanol by ditelluratocuprate(III) (DTC) in alkaline liquids has been studied spectrophotometrically in the temperature range of 293.2—313.2 K. The reaction rate showed first order dependence in DTC and fractional order with respect to 1-methoxy-2-propanol or 1-ethoxy-2-propanol. 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-} . There is a negative salt effect. A plausible mechanism involving a pre-equilibrium of a adduct formation between the complex and 1-methoxy-2-propanol or 1-ethoxy-2-propanol 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), 1-methoxy-2-propanol, 1-ethoxy-2-propanol, kinetics, mechanism, oxidation

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 can generally be stabilised by chelation with suitable polydentate ligands. Metal chelates such as ditelluratocuprate(III),^{1,2} diperiodatocuprate(III),³ diperiodatoar-gentate(III)⁴ and diperiodatonickelate(IV)⁵ 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.⁶ Many biological systems involve electrontransfer processes wherein Cu(III) plays an important role.⁷ 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 $[Cu(H_4TeO_6)_2]^{-1}$ and the mechanism involving a pre-equilibrium of an adduct formation between the complex and reductant was also proposed.⁸ 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.

Both of the reductants which serve as solvent, dis-

persant or thinners are used in coatings, inks, printing and dyeing, pesticide, cellulose and acrylic acid industry *etc.* In addition, they also can be used as fuel antifreeze, cleaning agents, the extractant, non-ferrous metal dressing agent and organic synthetic materials *etc.*

Experimental

Materials

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Solutions of $[Cu(H_4TeO_6)_2]^-$ (DTC) and reductants were always freshly prepared before using. The stock solution of DTC was prepared and standardized by the method given by Jaiswal and Yadava.^{9,10} Its electronic spectrum was found to be consistent with that reported by Jaiswal and Yadava.

Kinetics measurements and apparatus

All kinetics measurements were carried out under pseudo-first order conditions. Solution (2 mL) containing definite concentration of Cu(III), OH⁻, TeO₄²⁻ and ionic strength and reductant solution (2 mL) 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 KNO₃ solution and the pH of the reaction mixture was adjusted with a KOH solution. The kinetic measurements were performed on a UV-vis

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spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell holder kept at constant temperature $(\pm 0.1 \ ^{\circ}C)$ by circulating water from a thermostat (DC-2010, Baoding, China). All other species did not absorb significantly at this wavelength.

Product analysis

A solution with known concentrations of Cu(III), OH^- , TeO_4^{2-} was mixed with an excess of reductants. The complete fading of DTC color (reddish brown) marked the completion of the reaction. The product of oxidation was identified as ketone by its characteristic spot test.¹¹

Results and discussion

Evaluation of pseudo-first order rate constants

Under the conditions of $[reductant]_0 \gg [Cu(III)]_0$, the plots of $\ln(A_t - A_{\infty})$ versus time were straight lines, indicating the reaction is first order with respect to Cu(III), where A_t and A_{∞} are 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. Generally, more than $8A_t$ values within three times the half-lives were used to calculate k_{obs} . The k_{obs} values were the average value of at least three independent experiments, and reproducibility is within $\pm 5\%$.

Rate dependence on the [reductant]

At fixed concentration of Cu(III), OH^- , TeO_4^{2-} and ionic strength μ , the values of k_{obs} were determined at different temperatures. The plots of ln k_{obs} versus ln[reductant] were linear ($r \ge 0.996$), and from the slope of such plots, the order with respect to reductant was found to be fractional. In addition, the k_{obs} was found to be increased with the increase of reactant concentration. The plots of $1/k_{obs}$ vs. 1/[reductant] at different temperatures were straight lines (Figure 1 and Figure 2), the rate constants (k) of the rate-determining step were calculated from intercepts.

Rate dependence on the [OH⁻]

At constant [Cu(III)], [reductant], $[\text{TeO}_4^{2^-}]$, μ and temperature, k_{obs} values increased with the increase in [OH⁻]. The order with respect to [OH⁻] was fractional and the plot of $1/k_{obs}$ vs. $1/[\text{OH}^-]$ was linear with a positive intercept (Figure 3).

Rate dependence on the ionic strength

With other conditions fixed, the reaction rate was decreased by the addition of KNO₃ solution (Table 1), indicating there is negative salt effect which is consistent with the common regulation of the kinetics.¹²

Rate dependence on the $[TeO_4^{2-}]$

At constant [Cu(III)], [reductant], $[OH^-]$, μ and temperature, the experimental results indicate that k_{obs}



Figure 1 Plots of $1/k_{obs}$ vs. 1/[1-methoxy-2-propanol] ($r \ge 0.997$). [Cu(III)] = 3.93×10^{-5} mol·L⁻¹, [OH⁻] = 1.00×10^{-2} mol·L⁻¹, [TeO₄²⁻] = 1.00×10^{-3} mol·L⁻¹, $\mu = 1.90 \times 10^{-2}$ mol·L⁻¹.



Figure 2 Plots of $1/k_{obs}$ vs. 1/[1-ethoxy-2-propanol] ($r \ge 0.996$). [Cu(III)] = $3.93 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, [OH⁻] = $1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, [TeO₄²⁻] = $1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 1.90 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$.



Figure 3 Plots of $1/k_{obs}$ vs. $1/[OH^{-}]$ at 298.2 K. (1) $[Cu(III)] = 3.93 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-methoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[\text{TeO}_{4}^{2^{-}}] = 1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ (r = 0.998); (2) $[Cu(III)] = 3.93 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[\text{TeO}_{4}^{2^{-}}] = 1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $[\text{TeO}_{4}^{2^{-}}] = 1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-go}_{4}^{-1}] = 1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$,

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Table 1Rate dependence on ionic strength μ

		$10^2 \mu / (\text{mol} \cdot \text{L}^{-1})$					
		1.50	3.00	4.50 6.00	7.50		
$10^3 k_{\rm obs}/{\rm s}^{-1}$	(1) 1-methoxy-2-propanol	3.00	2.42	2.32 2.27	1.91		
	(2) 1-ethoxy-2-propanol	4.16	2.90	2.61 2.34	2.24		
(1) $[Cu(III)] = 3.93 \times 10^{-5} \text{ mol} \cdot L^{-1}$, [1-methoxy-2-propanol] =							
$3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[OH^{-}] = 1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[TeO_{4}^{2-}] =$							
$1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. (2) [Cu(III)] = $3.93 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$,							
[1-ethoxy-	2 -propanol] = 3.00×10^{-2}	mol•L	⁻¹ , [$OH^{-}] = 1.$	$\times 00$		

 $10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[\text{TeO}_4^{--}] = 1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

decreases while increasing the $[\text{TeO}_4^{2^-}]$. The order with respect to $\text{TeO}_4^{2^-}$ was derived to be an inverse fraction, which reveals that $\text{TeO}_4^{2^-}$ is produced in equilibrium before the rate-determining step. A plot of $1/k_{obs}$ versus $[\text{TeO}_4^{2^-}]$ was straight line with a positive intercept (Figure 4).



Figure 4 Plots of $1/k_{obs}$ vs. $[\text{TeO}_4^{2-}]$ at 298.2 K. (1) $[\text{Cu(III)}] = 3.93 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ (r = 0.998); (2) $[\text{Cu(III)}] = 3.93 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $[1\text{-ethoxy-2-propanol}] = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.80 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ (r = 0.999).

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 $pK_w = 14$).

$$H_{4}TeO_{6}^{2-}+OH^{-} \rightleftharpoons H_{4}TeO_{6}^{2-}+H_{2}O$$

$$\lg \beta_{1}=3.049$$
(1)

$$H_{4} TeO_{6}^{2-} + OH^{-} \rightleftharpoons H_{3} TeO_{6}^{3-} + H_{2}O$$

$$\lg \beta_{2} = -1$$
(2)

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, $[H_4TeO_6^{2^-}]$: $[H_5TeO_6^{2^-}]$: $[H_3TeO_6^{3^-}] = 1000$: 89 : 1, so in the concentration of OH⁻ range used in this work, $H_5TeO_6^{-}$ and $H_3TeO_6^{3^-}$ can be neglected, the main tellurate species was $H_4TeO_6^{2^-}$.

The fractional order in OH^- indicated that OH^- takes part in a pre-equilibrium with Cu(III) before the rate-determing 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 $H_4 TeO_6^{2-}$ from its coordination sphere and forms a reactive monotelluratocuprate(III) complex (MTC). The fractional order in reductant indicated complex formation between reductant and MTC, and the plot of $1/k_{obs}$ versus 1/[reductant] 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 reductant is proposed for the reaction.

In alkaline solution studied, $(H_2 \text{TeO}_6)_4^-$ was protonated easily and it coordinated with central ion forming $[\text{Cu}(H_4 \text{TeO}_6)_2]^-$. In view of the experiments, the mechanism was poposed as follows (R respectively stands for methoxy, ethoxy):

$$[\operatorname{Cu}(\operatorname{H}_{4}\operatorname{TeO}_{6})_{2}]^{-} + \operatorname{OH}^{-} \underbrace{K_{1}}_{[\operatorname{Cu}(\operatorname{H}_{3}\operatorname{TeO}_{6})]} + \operatorname{H}_{4}\operatorname{TeO}_{6}^{2-} + \operatorname{H}_{2}\operatorname{O}}$$
(3)

$$[Cu(H_{3}TeO_{6})] + RCH_{2}CHOHCH_{3} \xleftarrow{K_{2}}$$

$$[(Cu(H_{3}TeO_{6})(RCH_{2}CHOHCH_{3})]$$
(4)

$$[(Cu(H_{3}TeO_{6})(RCH_{2}CHOHCH_{3})] \xrightarrow{k} slow \rightarrow (5)$$

RCH₂•COHCH₃+[Cu(H₄TeO₆)]⁺

$$Cu^{*}(III)+OH^{-}+RCH_{2} \cdot COHCH_{3} \xrightarrow{K_{f}} Cu(II)+RCH_{2}COCH_{2}+H_{2}O$$
(6)

where $Cu^*(III)$ stands for any kind of form of Cu^{3+} complexes which existed in equilibrium and R' stands for reductant. Subscripts T and e stand for total and equilibrium concentration respectively.

$$[Cu(III)]_{T} = [Cu(H_{3}TeO_{6})]_{e} + [Cu(H_{3}TeO_{6})(RCH_{2}CHOHCH_{3})] + [Cu(H_{4}TeO_{6})_{2}]_{e}^{-}$$

Reaction (5) was the rate-determining step.

$$[Cu(H_{3}TeO_{6})(R')] = \frac{K_{1}K_{2}[Cu(III)]_{T}[OH^{-}][R']}{[H_{4}TeO_{6}^{2^{-}}] + K_{1}[OH^{-}] + K_{1}K_{2}[OH^{-}][R']}$$
(7)

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

$$-\frac{d[Cu(III)]_{T}}{dt} = 2k[Cu(H_{3}TeO_{6})(R')]$$
(8)

$$-\frac{d[\operatorname{Cu(III)}]_{\mathrm{T}}}{dt} = \frac{2kK_{1}K_{2}[\operatorname{Cu(III)}]_{\mathrm{T}}[\operatorname{OH}^{-}][\mathrm{R}^{\prime}]}{[\mathrm{H}_{4}\operatorname{TeO}_{6}^{2-}] + K_{1}[\operatorname{OH}^{-}] + K_{1}K_{2}[\operatorname{OH}^{-}][\mathrm{R}^{\prime}]}$$
$$= k_{\mathrm{obs}}[\operatorname{Cu(III)}]_{\mathrm{T}}$$

$$k_{obs} = \frac{2kK_1K_2[OH^-][R']}{[H_4TeO_6^{2-}] + K_1[OH^-] + K_1K_2[OH^-][R']}$$
(10)

Rearranging equation (10) leads to equations (11)—(13):

$$\frac{1}{k_{\rm obs}} = \frac{1}{2k} + \frac{[{\rm H}_{4}{\rm TeO}_{6}^{2^{-}}] + K_{1}[{\rm OH}^{-}]}{2kK_{1}K_{2}[{\rm OH}^{-}]} \frac{1}{[{\rm R}']}$$
(11)

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

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

From the equation (11), the plots $1/k_{obs}$ vs. 1/[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. Equations (12) and (13) suggest 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 were evaluated by the method given earlier (Table 2).

Conclusion

Base on the above discussion and results, we can know that the rate constants of the rate-determining step and the activation parameters for 1-methoxy-2-propanol and 1-ethoxy-2-propanol are very contiguous. In the reaction system, both the 1-methoxy-2-propanol and 1-ethoxy-2-propanol formed the same intermediate compounds with Cu(III). At the same time we also observed the rate of 1-methoxy-2-propanol is a little quicker than that of 1-ethoxy-2-propanol. In the reaction system, Compared with CH₃O—, CH₃CH₂O— has an excess CH₂ and steric effect is more larger. There is negative salt effect which is consistent with the common regulation of the kinetics.

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

				T/K				
		293.3	298.2	303.2	308.2	313.2		
$10^2 k/s^{-1}$	1-methoxy-2-propanol	0.6678	0.8802	1.1378	1.4005	1.7745		
	1-ethoxy-2-propanol	0.8231	1.0060	1.3257	1.8394	2.2699		
Thermodynamic	1-methoxy-2-propanol	$E_{\rm a} = 36.96 \text{ kJ} \cdot \text{mol}^{-1}, \Delta H^{\neq} = 34.48 \text{ kJ} \cdot \text{mol}^{-1}, \Delta S^{\neq} = -168.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$						
activation parameters	1-ethoxy-2-propanol	$E_{\rm a}$ =40.17 kJ•mol ⁻¹ , ΔH^{\neq} =37.69 kJ•mol ⁻¹ , ΔS^{\neq} =-156.48 J•K ⁻¹ •mol ⁻¹						

The plots of ln k vs. 1/T have following intercept (a), slope (b) and relative coefficient (r): 1-methoxy-2-propanol: a=10.17, b=-4445.78, r=0.999; 1-ethoxy-2-propanol: a=11.64, b=-4831.30, r=0.996.

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