



Oxidation Of 1,2-Butanediol By Cu(III) Complex In Alkaline Medium: A Kinetics And Mechanism Study

C.Y.Song*, J.H.Shan, S.G.Shen

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, (CHINA)

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ABSTRACT

The kinetics of oxidation of 1,2-butylene glycol by dihydroxyditellurocuperate(III) is studied spectrophotometrically between 298.2 and 313.2K in alkaline medium. A mechanism involving a two-step one-electron transfer process has been proposed, and the rate equation can be expressed as: $k_{obs} = 2kK_1[OH^-][CH_3CH_2CHOHCH_2OH]/(K_1[OH^-] + [H_4TeO_6^{2-}])$. The activation parameters and the rate constants of the rate-determining step are calculated. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Dihydroxyditellurocuperate(III);
1,2-Butanediol;
Kinetics;
Mechanism;
Redox.

INTRODUCTION

Transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands, such as diperiodatargentate(III)^[1] ditelluratocuprate(III)^[2], which can be used as oxidants in the organic synthesis chemistry and titrimetric analysis. For example, Cu(III) is shown to be an intermediate in the Cu(II)-catalysed oxidation of amino acids by peroxydisulphate^[3], also can be used for the titrimetric determination of some reducing sugars, organic acids^[4]. Moreover, the kinetics and mechanism study of this system can make the theories of coordination chemistry perfectly^[5]. In the kinetic study, Cu(III) complexes used as an oxidant has been reported^[6], but the reaction system is simple, and telluric acid has two equilibrium in the alkaline medium, we want to know the complexes' form of Cu(III) and telluric acid through the study. For these purpose, the kinetics and mechanism of oxidation of 1,2-butanediol by Cu(III) complexes has been studied in this paper.

EXPERIMENTAL

Chemical reagents and apparatus

All reagents are of A.R. grade. All solutions are prepared with twice distilled water. Solutions of Cu(III) complex and 1,2-butanediol are prepared freshly before use. The stock solution of Cu(III) complex in a strong alkaline medium is prepared and standardized by the method reported earlier^[7,8]. The concentration of Cu(III) is derived by its absorption at $\lambda=405\text{nm}$ ($\epsilon=1 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). The ionic strength is maintained by adding KNO_3 solution and the pH value is regulated with KOH solution.

TU-1900 spectrophotometer (Beijing); Refrigerated circulator baths(Beijing)

Kinetics method

All kinetics measurements were carried out under pseudo-first order conditions. Solution (2 mL) containing concentrations of $[\text{Cu(III)}]$, $[\text{OH}^-]$, $[\text{H}_4\text{TeO}_6^{2-}]$ with

ionic strength μ and a reductant solution (2 mL) of appropriate concentration were transferred separately to the upper and lower branch tubes of a type two-cell reactor. After it was thermally equilibrated at desired temperature in thermobath, the 2 solutions were mixed well and transferred into a 1 cm thick glass cell immediately with a constant temperature cell-holder. The reaction process was monitored automatically by recording the disappearance of Cu(III) complexes with time (t) at 405 nm with a TU-1900 spectrophotometer. All other species did not absorb significantly at this wavelength.

Product analysis and stoichiometry

The oxidation product as the corresponding aldehyde was identified by spot test^[9]. Solutions having known concentrations of Cu(III) was mixed with an excess of 1,2-butanediol. The completion of the reaction was marked by the completion disappearance of Cu(III) color. After completion of the reaction, the product was transformed into a precipitate 2,4-dinitro-phenyl drazine derivative. It was found that one mole of reductant consumed two moles of Cu(III) by weighing.

RESULTS AND DISCUSSIONS

Evaluation of pseudo-first order rate constants

Under the conditions of $[\text{Reductant}]_0 \gg [\text{Cu(III)}]_0$. The plots of $\ln(A_t - A_\infty)$ versus time are lines, indicating the reaction is first order with respect to $[\text{Cu(III)}]$, where A_t and A_∞ are the absorbance at time t and at infinite time respectively. The pseudo-first-order rate constants k_{obs} are calculated by the method of least squares ($r \geq 0.999$). To calculate k_{obs} generally 8-10 A_t values within three times the half-life are used. k_{obs} values of the three independent experiments are averaged at least and reproducibility is within $\pm 5\%$.

Rate dependence on [1,2-butanediol]

At fixed $[\text{Cu(III)}]$, $[\text{OH}^-]$, $[\text{H}_4\text{TeO}_6^{2-}]$, ionic strength μ and temperature, k_{obs} values increased with the increase in [1,2-butanediol]. The plots of k_{obs} versus [1,2-butanediol] are straight lines which though the grid origin, which indicates that the reaction is first order with respect to 1,2-butanediol. (TABLE 1)

TABLE 5: Rate constants (k) and activation parameters of the rate-determining tep (T=298.2K)

T (K)/(mol ⁻¹ ·L·s ⁻¹)	298.2	303.2	308.2	313.2	Ea(KJ·mol ⁻¹)	ΔH^\ddagger (KJ·mol ⁻¹)	ΔS^\ddagger (J·mol ⁻¹ ·K ⁻¹)
1,2-butanediol	1.09	1.66	2.25	3.44	60.81	58.33	-48.87

The plots of $\ln k$ vs $1/T$ have following intercept(a) slope(b) and relative coefficient(r); a=24.58, b=-7314.3, r=0.991

TABLE 1 : $10^3 k_{\text{obs}}/s^{-1}$ varying with different [1,2-butanediol] at different temperatures

C/(mol/L)	0.005	0.01	0.015	0.02	0.025
T					
298.2K	4.06	8.16	13.2	18.6	21.4
303.2K	5.13	13.4	20.3	28.8	35.2
308.2K	8.84	18.9	29.1	41.7	50.0
313.2K	12.6	29.1	43.3	61.2	70.9

$[\text{Cu(III)}]=8.818 \times 10^{-5} \text{ mol/L}$, $[\text{OH}^-]=3.00 \times 10^{-3} \text{ mol/L}$, $[\text{H}_4\text{TeO}_6^{2-}]=2.064 \times 10^{-3} \text{ mol/L}$, $\mu=0.109 \text{ mol/L}$

TABLE 2 : k_{obs}/s^{-1} varying with the different $[\text{H}_4\text{TeO}_6^{2-}]$

$10^3 C/(\text{mol/L})$	0.564	1.164	1.764	2.364	2.964
$10^3 k_{\text{obs}}$	19.7	10.9	8.14	5.03	4.18

$[\text{Cu(III)}]=8.818 \times 10^{-5} \text{ mol/L}$, $[\text{OH}^-]=3.00 \times 10^{-3} \text{ mol/L}$, [1,2-butanediol]=0.005 mol/L, T=303.2K, $\mu=0.0619 \text{ mol/L}$

TABLE 3 : $10^3 k_{\text{obs}}/s^{-1}$ varying with the different $[\text{OH}^-]$

$10^3 C/(\text{mol/L})$	3.00	3.78	5.11	7.86	17.0
T					
298.2K	4.09	4.66	5.39	6.98	9.79
303.2K	6.03	6.85	8.18	10.2	15.2
308.2K	9.89	10.8	12.6	15.6	21.7
313.2K	15.1	16.7	19.5	24.2	34.9

$[\text{Cu(III)}]=8.818 \times 10^{-5} \text{ mol/L}$, $[\text{H}_4\text{TeO}_6^{2-}]=2.064 \times 10^{-3} \text{ mol/L}$, $\mu=0.409 \text{ mol/L}$, [1,2-butanediol]=0.006 mol/L, T=303.2K

TABLE 4 : k_{obs}/s^{-1} varying with the different μ

$10^2 C/(\text{mol/L})$	5.92	10.9	20.9	30.9	40.9
$10^3 k_{\text{obs}}$	9.41	6.28	5.24	4.51	4.14

$[\text{Cu(III)}]=8.818 \times 10^{-5} \text{ mol/L}$, $[\text{OH}^-]=3.00 \times 10^{-3} \text{ mol/L}$, [1,2-butanediol]=0.005 mol/L, $[\text{H}_4\text{TeO}_6^{2-}]=2.264 \times 10^{-3} \text{ mol/L}$, T=303.2K

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

At fixed $[\text{Cu(III)}]$, $[\text{OH}^-]$, [1,2-butanediol], ionic strength μ and temperature, k_{obs} values decreased with the increase in $[\text{H}_4\text{TeO}_6^{2-}]$. The plots of $1/k_{\text{obs}}$ versus $[\text{H}_4\text{TeO}_6^{2-}]$ are straight lines with a positive intercept indicating the order with respect to $\text{H}_4\text{TeO}_6^{2-}$ were found to be fractional order. (TABLE 2)

Rate dependence on $[\text{OH}^-]$ and ionic strength μ

At fixed $[\text{Cu(III)}]$, $[\text{H}_4\text{TeO}_6^{2-}]$, [1,2-butanediol], ionic strength μ and temperature, k_{obs} values increased with the increase in $[\text{OH}^-]$. The plot of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ is a line (TABLE 3). The rate decreased by the addition of KNO_3 solution (TABLE 4), which indicates that there was a negative salt effect.

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Free radical detection and the mechanism

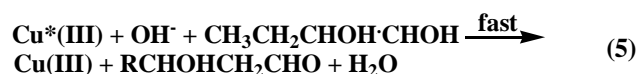
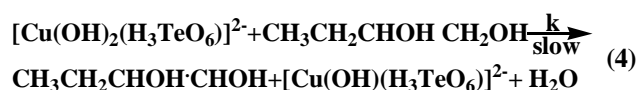
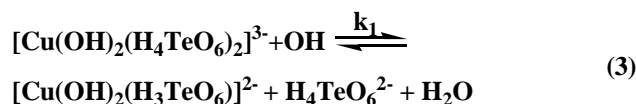
In the alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier (here $pK_w = 14$)^[10].



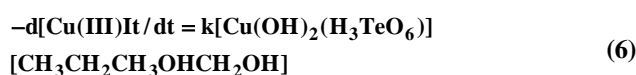
The distribution of all species of tellurate in aqueous alkaline solution can be calculated from equilibriums (1), (2). In alkaline medium such as $[\text{OH}^-] = 0.1 - 0.01 \text{ mol} \cdot \text{L}^{-1}$, $[\text{H}_4\text{TeO}_6^{2-}] : [\text{H}_5\text{TeO}_6^-] : [\text{H}_3\text{TeO}_6^{3-}] \cong 1000 - 100 : 89.3 - 0.893 : 1$, so in the concentration of OH^- range used in this work, H_5TeO_6^- and $\text{H}_3\text{TeO}_6^{3-}$ can be neglected, the main tellurate species is $[\text{H}_4\text{TeO}_6^{2-}]$. So we think the main species is $[\text{Cu}(\text{OH})_2(\text{H}_4\text{TeO}_6)_2]^{3-}$ over the experimental range of $[\text{OH}^-]$.

The fractional and inverse fractional order dependence of k_{obs} on $[\text{OH}^-]$ and $[\text{TeO}_4^{2-}]$ respectively indicate that OH^- ions would be present in a pre-equilibrium and then $[\text{Cu}(\text{OH})_2(\text{H}_4\text{TeO}_6)_2]^{3-}$ loses a $\text{H}_4\text{TeO}_6^{2-}$ ligand from its coordination sphere forming a transition complex $[\text{Cu}(\text{OH})_2(\text{H}_3\text{TeO}_6)]^{2-}$, which is the activity species of the Cu complex.

The addition of acrylonitrile or acrylamide to the reaction mixture under nitrogen atmosphere the polymerization happened in the reaction, showing free radical produced in the reaction. In our study, we also believe a similar type of a two-step one-electron transfer mechanism. According to the above experimental facts, we bring forward the mechanism of the reaction below:



Reaction (3) is a pre-equilibrium. Reaction (4) belongs to electron-transfer reaction, whose reaction rate is generally slower, so reaction (4) is the rate-determining step.



Where $[\text{Cu}(\text{III})]_t$ stands for any kind of form of Cu(III) complexes which existed in equilibrium.

Then we get:

$$k_{\text{obs}} = \frac{2kK_1[\text{OH}^-][\text{CH}_3\text{CH}_2\text{CHOHCH}_2\text{CH}_2\text{OH}]}{K_1[\text{OH}^-] + [\text{H}_4\text{TeO}_6^{2-}]} \quad (7)$$

From equation (7), the plots of $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ are straight lines and the rate constants of rate-determining step at different temperature are obtained from the intercept of the straight line. Activation energy and the thermodynamic parameters are calculated. (TABLE 5).

CONCLUSIONS

In our previous work, we study the kinetics and mechanism of oxidation of 1,2-ethanediol by ditellurate(III) in alkaline medium, we know that the rate constants of rate-determining step are 10.24, 13.10, 17.51, 21.50, 25.13, 32.34 $\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ at 293.2, 295.2, 297.2, 299.2, 301.2, 303.2K respectively. So the rate constants of rate-determining step of 1,2-ethanediol are larger than those of 1,2-butanediol. The reason for this is the steric effect of 1,2-butanediol is larger than that of 1,2-ethanediol's, then the formation of a hexa-cyclic intermediate adduct compound by 1,2-ethanediol is more stable than that of 1,2-butanediol, so the rate of 1,2-ethanediol is larger than the rate of 1,2-butanediol which is consist with the phenomena of the experiment.

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