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Oxidation of triethylene glycol and tetraethylene glycol by ditelluratocuprate(III) in alkaline medium - A kinetic and mechanistic study

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ARTICLE INFORMATION

ABSTRACT

The kinetics of oxidation of triethylene glycol (TEG) and tetraethylene glycol (TTEG) by ditelluratocuprate(III) (DTC) in alkaline liquids were investigated spectrophotometrically in the temperature range of 20°C to 40°C. It was found that the reaction followed pseudo-first order in DTC and less than unit order in reductants. The rate constant k_{obs} of pseudo-first order reaction decreased with an increase of $[TeO_4^{2-}]$, whereas adding $[OH^-]$ enhanced the constant. In addition, there was a negative salt effect. A suitable assumption involving pre-equilibriums before the rate controlling step and a free radical mechanism was proposed from the kinetics study. The rate equations derived from mechanism can explain all experimental phenomena. Moreover, the activation parameters at 298.2K and rate constants of the rate-determining step were evaluated.

1. Introduction

Triethylene glycol (TEG) is a colorless liquid with sweetish smell. It is mainly used as textile auxiliaries, plasticizing agent, diesel fuel additives, rocket fuel and so on. In addition, it has a wide range of applications in many fields, such as medicine, coating, textile, printing, dyeing, papermaking, cosmetics, metal processing, *etc*. But TEG is toxic, some researches demonstrated that the acute lethal toxicity of TEG had bad effect on skin and eye [1,2]. Tetraethylene glycol (TTEG) is a colorless viscous liquid. It can mixed dissolve with water, ethanol, hydrocarbon and oils. TTEG's production and used as a solvent, plasticizer, lubricant, softening agent for paper tissue, a ceramic paste [3] printing ink binder and a liquid desiccant for natural gas. Moreover, tetraethylene glycol to the eye and the upper respiratory tract has slightly stimulation [4].

Since Vrtis [5] successfully prepared and isolated Cu(III) complex, more and more researchers have been interested in the study of the higher oxidation state of transition metal which can be stabilized by chelation with polydentate ligands, such as ditelluratocuprate(III) [6,7], diperiodatocuprate(III) [8,9], diperiodatoargentate(III) [10,11], ditelluratoargentate(III) [12], diperiodatonickelate(IV) [13] are good oxidants in a medium with an appropriate pH. Now, Cu(III) complex is regarded as very effective and interesting oxidising agent. In addition, the use of Cu(III) not only plays an prominent role in many biological systems [14,15], but also makes contribution as an oxidation agent in organic mixture qualitative analysis [16]. Hence, the further research of Cu(III) has significance.

In this paper, the kinetics and mechanism of oxidation of triethylene glycol and tetraethylene glycol by ditellurato cuprate(III) (DTC) were studied in detail.

2. Experimental

2.1. Materials

All chemicals used were of A.R. grade and double distilled water was used throughout the work. Ditelluratocuprate(III) (DTC) was prepared and standardized by the method reported [17,18]. The purity of the complex was checked by comparing UV-Vis spectrum with literature data, which showed a characteristic absorption peak at 405 nm. KNO_3 and KOH were used to maintain ionic strength and alkalinity of the reaction, respectively. Besides, solutions of DTC and reductants were always freshly prepared before using.

2.2. Kinetics measurements and apparatus

The kinetics was followed under pseudo-first order conditions by keeping a large excess of [reductant] with respect to [DTC]. Solution (2 mL) containing required concentration of DTC, OH^-, TeO_4^{2-} was mixed with solution (2 mL) requisite concentration of reductant and ionic strength at the desired temperature. With the complete fading of DTC color (yellowness) marked the completion of the reaction. 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 (±0.1 °C) by circulating water from a thermostat (DC-2010, Baoding Xinhua Inc., China). It was verified that there was negligible interference from other reagents at 405nm. The product of oxidation was identified as aldehyde by its characteristic spot test [19].

3. Results and discussion

3.1. Evaluation of pseudo-first order rate constants

Under the conditions of [reductant]$_0$ ([TEG]$_0$ and [TTEG]$_0$) >> [Cu(III)]$_0$, the plots of ln(A$_t$-A$_\infty$) versus time were straight lines(r ≥ 0.998), indicating the reaction was first order in DTC. The pseudo-first-order rate constants k_{obs} were evaluated by using the equation ln(A$_t$-A$_\infty$)= -k_{obs}t + b (constant). The k_{obs} values were the average value of at least three independent experiments, and reproducibility was within ±5%.

3.2. 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 order n$_{ap}$ of [reductant] ([TEG] and [TTEG]) was calculated as fractional order form the slopes of ln k_{obs} versus ln [reductant] plots. Besides, the k_{obs} value increased with the increasing [reductant]. The plots of k_{obs}^{-1} versus [reductant]$^{-1}$ were straight lines (r ≥ 0.998) (Figure 1 and Figure 2).
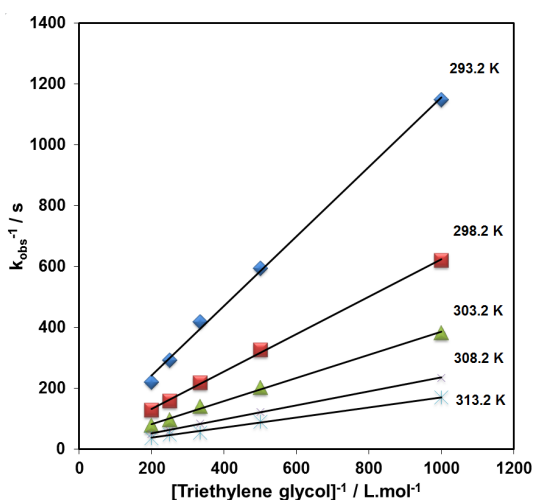

Figure 1. Plots of k_{obs}^{-1} *vs.* [Triethylene glycol]$^{-1}$; [DTC] = 7.16×10^{-5} mol/L, [TeO$_4^{2-}$] = 1.00×10^{-2} mol/L, [OH$^-$] = 1.00×10^{-2} mol/L (r ≥ 0.998).
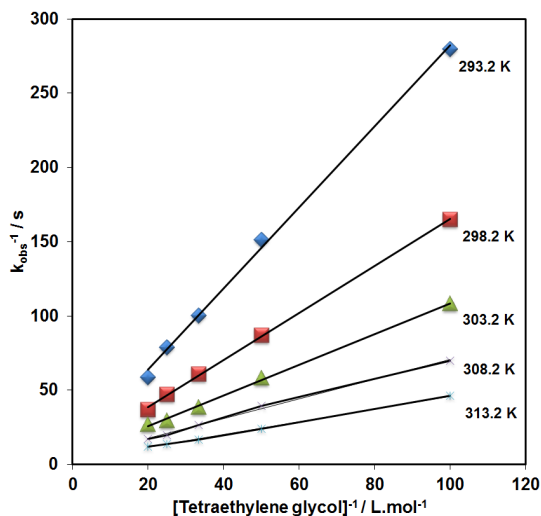
Figure 2. Plots of k_{obs}^{-1} *vs.* [Tetraethylene glycol]$^{-1}$; [DTC] = 7.16×10^{-5} mol/L, [TeO$_4^{2-}$] = 1.00×10^{-2} mol/L, [OH$^-$] = 1.00×10^{-2} mol/L (r ≥ 0.998).

3.3. Rate dependence on the [OH$^-$]

The effect of [OH$^-$] on the reaction has been studied in the range of 0.50×10^{-2} to 2.50×10^{-2} mol/L at constant [DTC], [reductant], [TeO$_4^{2-}$], μ and temperature. It was found that k_{obs} values increased with the increaseing [OH$^-$] (Table 1) and the order with respect to [OH$^-$] was fractional. The plot of k_{obs}^{-1} *vs.* [OH$^-$]$^{-1}$ was linear with a positive intercept (r ≥ 0.998).

3.4. Rate dependence on the [TeO$_4^{2-}$]

The [TeO$_4^{2-}$] was varied from 0.50×10^{-3} to 2.50×10^{-3} mol/L range at constant [DTC], [reductant], [OH$^-$], μ and temperature. The k_{obs} values increased with the decreasing concentration of TeO$_4^{2-}$ (Table 1). The order with respect to TeO$_4^{2-}$ was found to be a negative fraction, which reveals that TeO$_4^{2-}$ is produced in equilibrium before the rate controlling step. A plot of k_{obs}^{-1} versus 10^2 [TeO$_4^{2-}$] was straight line with a positive intercept (r ≥ 0.997).
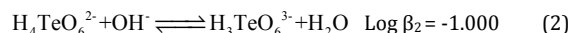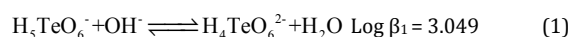
3.5. Rate dependence on ionic strength μ

The effect of ionic strength on the reaction was studied in the range of 1.50×10^{-2} mol/L to 7.50×10^{-2} mol/L at constant [DTC], [reductant], [OH$^-$], [TeO$_4^{2-}$] and temperature. The experimental results indicated that the rate constant decreased with the increasing of ionic strength (Table 1), which showed that there was negative salt that consistent with the common regulation of the kinetics [20].

3.6. Free radical detection

To study the possible presence of a free radical during the reaction, a known amount of acrylamide was added under the protection of nitrogen atmosphere. The polymerization clearly appeared which indicated that free radical intermediates may be produced in the oxidation by DTC. And blank experiments in reaction system gave no polymeric suspensions.

3.7. Reaction mechanism

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

$$H_5TeO_6^- + OH^- \rightleftharpoons H_4TeO_6^{2-} + H_2O \quad Log\ \beta_1 = 3.049 \qquad (1)$$

$$H_4TeO_6^{2-} + OH^- \rightleftharpoons H_3TeO_6^{3-} + H_2O \quad Log\ \beta_2 = -1.000 \qquad (2)$$

From equilibriums (1)-(2), The distribution of all species of tellurate can be calculated in aqueous alkaline solution. In alkaline medium such as [OH$^-$] = 0.01 mol/L, [H$_4$TeO$_6^{2-}$]:[H$_5$TeO$_6^-$]:[H$_3$TeO$_6^{3-}$]=1000:89:1. Hence, in the concentration of OH$^-$ range used in this work, the H$_5$TeO$_6^-$ and H$_3$TeO$_6^{3-}$ species can be neglected, and the main tellurate species was H$_4$TeO$_6^{2-}$.

The fractional order in OH$^-$ determined that OH$^-$ took part in a pre-equilibrium with Cu(III) before the rate-determing step. The plot of k_{obs}^{-1} versus [TeO$_4^{2-}$] was line with a positive intercept indicating a dissociation equilibrium in which the Cu(III) lost a tellurate ligand H$_4$TeO$_6^{2-}$ from its coordination sphere forming a active specie monotelluratocuprate(III) complex (MTC). The order with respect to reductant was fractional, which indicated complex formation between reductant and MTC. In alkaline solution, (H$_2$TeO$_6$)$_4^-$ protonated easily and formed [Cu(H$_4$TeO$_6$)$_2$]$^-$ by coordinating with central ion.

The plausible mechanism of oxidation was proposed as follows (Equation 3-6) (R, respectively stand for CH$_2$O(CH$_2$)$_2$OCH$_2$ and CH$_2$O(CH$_2$)$_2$O(CH$_2$)$_2$OCH$_2$).

Table 1. Effect of [OH⁻], [TeO₄²⁻] and μ on the reaction at 293.2K.

10^5[DTC], (mol/L)	[Reductant], (mol/L)	$\mu \times 10^2$, (mol/L)	10^3[TeO₄²⁻], (mol/L)	10^3[OH⁻], (mol/L)	TEG, $10^3 k_{obs}$/s⁻¹	TTEG, $10^3 k_{obs}$/s⁻¹
7.16	0.01	3.80	1.00	5.00	8.15	2.95
7.16	0.01	3.80	1.00	10.00	9.33	3.70
7.16	0.01	3.80	1.00	15.00	9.63	4.12
7.16	0.01	3.80	1.00	20.00	9.84	4.38
7.16	0.01	3.80	1.00	25.00	10.03	4.52
7.16	0.01	3.80	0.50	10.00	15.79	4.68
7.16	0.01	3.80	1.00	10.00	12.06	3.75
7.16	0.01	3.80	1.50	10.00	9.33	3.10
7.16	0.01	3.80	2.00	10.00	8.32	2.74
7.16	0.01	3.80	2.50	10.00	7.18	2.46
7.16	0.01	1.50	1.00	10.00	12.16	4.37
7.16	0.01	3.00	1.00	10.00	11.14	3.82
7.16	0.01	4.50	1.00	10.00	10.96	3.63
7.16	0.01	6.00	1.00	10.00	9.56	3.20
7.16	0.01	7.50	1.00	10.00	8.22	2.93

Table 2. Rate constants (k) and the activation parameters for the rate-determining step *.

T (K)		293.2	298.2	303.2	308.2	313.2
$10^2 k$/s⁻¹	TEG	3.89	5.23	7.21	9.45	11.83
	TTEG	5.48	7.13	9.73	11.61	16.62
Thermodynamic	TEG	E_a (kJ/mol)= 43.05, ΔH‡ (kJ/mol)= 40.61, ΔS‡(J/K·mol) = -133.37				
activation parameters	TTEG	E_a (kJ/mol)= 41.29, ΔH‡ (kJ/mol)= 38.85, ΔS‡(J/K·mol) = -136.67				

* The plot of ln *k vs* T^{-1} have following intercept (a) slope (b) and relative coefficient (r): triethylene glycol: a = 14.42, b = -5177.58, *r* = -0.998; tetraethylene glycol: a = 14.02, b = -4966.19, *r* = -0.995.

$$\left[Cu\left(H_4TeO_6\right)_2\right]^- + OH^- \underset{}{\overset{K_I}{\rightleftharpoons}} \left[Cu\left(H_3TeO_6\right)\right] + H_4TeO_6{}^{2-} + H_2O \tag{3}$$

$$\left[Cu(H_3TeO_6)\right] + HOCH_2RCH_2OH \overset{K_2}{\rightleftharpoons} \left[Cu\left(H_3TeO_6\right)\left(HOCH_2RCH_2OH\right)\right] \tag{4}$$

$$\left[Cu\left(H_3TeO_6\right)\left(HOCH_2RCH_2OH\right)\right] \xrightarrow[\text{slow}]{k} Cu\left(II\right) + \bullet CH\left(HO\right)RCH_2OH \tag{5}$$

$$Cu^*\left(III\right) + OH^- + \bullet CH\left(HO\right)RCH_2OH \xrightarrow[\text{fast}]{k_f} OCHRCH_2OH + Cu\left(II\right) + H_2O \tag{6}$$
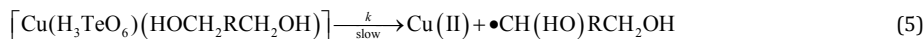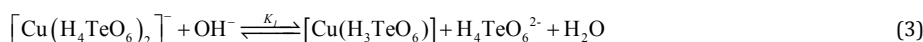
The Cu*(III) standed for any kind of which Cu³⁺ existed in equilibrium. The total concentration of Cu(III) can be written as: (subscripts T and e stand for total concentration and equilibrium concentration respectively).

$$\left[Cu\left(III\right)\right]_t = \left[Cu\left(H_4TeO_6\right)_2\right]_e^- + \left[Cu\left(H_3TeO_6\right)\right]_e$$
$$+ \left[Cu\left(H_3TeO_6\right)\left(HOCH_2RCH_2OH\right)\right]_e \tag{7}$$

Since reaction (5) was the rate-determining step, the rate of disappear of [Cu(III)]ₜ was represented as:

$$-\frac{d\left[Cu(III)\right]_t}{dt} = 2k\left[Cu\left(H_3TeO_6\right)\left(HOCH_2RCH_2OH\right)\right] \tag{8}$$

$$-\frac{d\left[Cu(III)\right]_t}{dt} =$$
$$= \frac{2kK_IK_2\left[OH^-\right]\left[HOCH_2RCH_2OH\right]\left[Cu(III)\right]}{\left[H_4TeO_6{}^{2-}\right] + K_I\left[OH^-\right] + K_IK_2\left[OH^-\right]\left[HOCH_2RCH_2OH\right]} =$$
$$= k_{obs}\left[Cu(III)\right] \tag{9}$$

$$k_{obs} = \frac{2kK_IK_2\left[OH^-\right]\left[HOCH_2RCH_2OH\right]}{\left[H_4TeO_6{}^{2-}\right] + K_I\left[OH^-\right] + K_IK_2\left[OH^-\right]\left[HOCH_2RCH_2OH\right]} \tag{10}$$

Re-arranging equation (10) led to equation (11, 12).

$$\frac{1}{k_{obs}} = \frac{1}{2k} + \frac{\left[H_4TeO_6{}^{2-}\right] + K_I\left[OH^-\right]}{2kK_IK_2\left[OH^-\right]} \times \frac{1}{\left[HOCH_2RCH_2OH\right]} \tag{11}$$

$$\frac{1}{k_{obs}} = \frac{1 + K_2\left[HOCH_2RCH_2OH\right]}{2kK_2\left[HOCH_2RCH_2OH\right]}$$
$$+ \frac{\left[H_4TeO_6{}^{2-}\right]}{2kK_IK_2\left[HOCH_2RCH_2OH\right]} \times \frac{1}{\left[OH^-\right]} \tag{12}$$

From the equation (9), the order with respect to Cu(III) was unity. The equation (11) suggested that the rate constants of the rate-determining step at different temperature were determined by the intercept of the plots k_{obs}^{-1} vs [reductant]⁻¹ which were straight lines. Equation (12) indicated that the plots of k_{obs}^{-1} *vs* [OH⁻]⁻¹ and k_{obs}^{-1} *vs* [H₄TeO₆²⁻] were straight lines. In addition, activation energy and the thermodynamic parameters were evaluated at 298.2K by the method given earlier (Table 2).

4. Conclusion

In this study, we found that both the triethylene glycol (TEG) and tetraethylene glycol (TTEG) formed the same intermediate compounds with Cu(III) in the reaction system, which could be due to their similar structure. In addition, the values of the activation parameters with respect to TEG was

larger than that of TTEG, which indicated the reactivity of TTEG was higher than TEG. The reason was that the electron-donating ability of TTEG was larger than that of TEG, which indicated the former was more stable than the latter. The above conclusions were consistent with experimental results.

Acknowledgement

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