

Research Article

The Oxidation of 2-(2-Methoxyethoxy)ethanol and 2-(2-Ethoxyethoxy)ethanol by Ditelluratocuprate(III): A Kinetic and Mechanistic Study

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The oxidation of 2-(2-methoxyethoxy)ethanol (MEE) and 2-(2-ethoxyethoxy)ethanol (EEE) by ditelluratocuprate(III) (DTC) had been studied spectrophotometrically in alkaline medium. The reaction between 20°C and 40°C showed first-order dependence in DTC and fractional order in MEE and EEE. The rate constant k_{obs} of the pseudo-first-order reaction decreased with an increase of $[\text{TeO}_4^{2-}]$, whereas adding $[\text{OH}^-]$ enhanced the constant. In addition, the reaction had a negative salt effect. The rate of EEE was higher than that of MEE. A suitable assumption involving preequilibria before the rate-controlling step and a free radical mechanism was proposed, based on the kinetic data. Activation parameters and the rate constant of the rate-determining step were calculated.

1. Introduction

Recently, more and more researchers have devoted themselves to the study of the higher oxidation state of transition metal. Cu(III), Ag(III), and Ni(IV) can be stabilized by chelation with polydentate ligands, such as ditelluratocuprate(III) [1, 2], diperiodatocuprate(III) [3, 4], diperiodatoargentate(III) [5, 6], ditelluratoargentate(III) [7], diperiodatonickelate(IV) [8] which are good oxidants in a medium with an appropriate pH. As early as 1844, the researchers have begun to study Cu(III) complex. Now, the use of Cu(III) not only plays a prominent role in many biological systems involving electron-transfer processes, but also makes contribution as an oxidation agent in organic mixture qualitative analysis [9]. Hence, the further research of Cu(III) is significant. In the present paper, the mechanism of oxidation of 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol by ditelluratocuprate(III) is reported.

Both 2-(2-methoxyethoxy)-ethanol and 2-(2-ethoxyethoxy)-ethanol are colorless liquids and high boiling point solvents so that they have a wide application such as printing, dyeing, resin, cellulose, and coatings. In addition, 2-(2-methoxyethoxy)-ethanol can be used for the extracting

agent for hydrocarbon and chemical reagent in chemical analysis.

2. Experimental Section

2.1. Materials. All chemicals used were of AR grade, and double distilled water was used throughout the work. Ditelluratocuprate(III) (DTC) was prepared and standardized by the method reported by Chandra and Yadava [10, 11]. The purity of the complex was checked by comparing UV-Vis spectrum with the 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.

2.1.1. Kinetics Measurements and Apparatus. The kinetics were followed under pseudo-first-order conditions. Solution (2 mL) containing required concentration of DTC, OH^- , and TeO_4^{2-} and ionic strength and reductant solution (2 mL) of requisite concentration were transferred separately to the upper and lower branch tubes of a λ type two-cell reactor.

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

T/K	[MEE]/mol·L ⁻¹					n_{ap}	r_1	r_2
	0.01	0.02	0.03	0.04	0.05			
293.2	2.25	3.89	5.84	6.86	8.28	0.18	0.998	0.998
298.2	3.98	6.90	9.39	10.94	13.60	0.25	0.998	0.999
303.2	8.21	12.85	17.32	19.47	21.21	0.40	0.995	0.998
308.2	13.75	21.12	24.72	27.87	29.71	0.52	0.991	0.999
313.2	22.77	31.63	37.77	40.32	43.59	0.60	0.994	0.999

r_1 and r_2 , respectively stand for the relative coefficient of the plots of $\ln k_{\text{obs}}$ versus $\ln [\text{MEE}]$ and the plots of k_{obs}^{-1} versus $[\text{MEE}]^{-1}$; n_{ap} stand for the order in MEE.

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

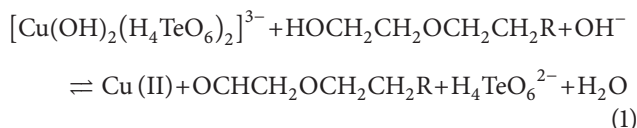
T/K	[EEE]/mol·L ⁻¹					n_{ap}	r_1	r_2
	0.01	0.02	0.03	0.04	0.05			
293.2	2.22	4.12	6.30	7.24	9.12	0.13	0.997	0.999
298.2	3.95	6.54	9.70	11.61	13.95	0.15	0.999	0.999
303.2	5.06	9.80	13.39	15.91	18.61	0.19	0.996	0.999
308.2	8.04	14.94	20.39	22.60	29.42	0.22	0.994	0.998
313.2	11.64	21.07	29.65	31.76	39.31	0.25	0.992	0.998

r_1 and r_2 , respectively stand for the relative coefficient of the plots of $\ln k_{\text{obs}}$ versus $\ln [\text{EEE}]$ and the plots of k_{obs}^{-1} versus $[\text{EEE}]^{-1}$; n_{ap} stand for the order in EEE.

After thermostating the solutions at the desired temperature, the two solutions rapidly mixed and put into the galss absorption cell. The progress of the reaction was followed by measuring the decrease in absorbance of DTC at 405 nm. The kinetic measurements were performed on a UV-vis spectrophotometer, which had a cell holder kept at constant temperature ($\pm 0.1^\circ\text{C}$) by circulating water from a thermostat. It was verified that the effect of other reagents at 405 nm was negligible.

3. Results and Discussion

3.1. Stoichiometric and Product Analysis. Stoichiometric studies revealed that 1 mol of DTC consumed 1 mol of reductants by adding dropwise DTC of known concentrations to $0.1 \text{ mol}\cdot\text{L}^{-1}$ reductants until no further decolorization was observed [12]



Under the kinetic conditions, the product of oxidation was identified as an aldehyde by its characteristic spot test [13].

3.2. Evaluation of Pseudo-First-Order Rate Constants. Under the conditions of $[\text{reductant}]_0$ ($[\text{MEE}]_0$ and $[\text{EEE}]_0$) \gg $[\text{Cu}(\text{III})]_0$, the plots of $\ln(A_t - A_\infty)$ versus time were straight lines ($r \geq 0.9993$), indicating the order in DTC to be unity. The pseudo-first-order rate constants k_{obs} were evaluated by using the equation $\ln(A_t - A_\infty) = -k_{\text{obs}}t + b$ (constant).

The k_{obs} values were the average value of at least three independent experiments, and reproducibility was within $\pm 5\%$.

3.3. Rate Dependence on the [Reductant]. The [reductant] was varied in the range of 1.00×10^{-2} to $5.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ at different temperature keeping all other [reactants] constant. The order n_{ap} in reductant were calculated as fractional order from the slopes of the plots of $\ln k_{\text{obs}}$ versus $\ln[\text{reductant}]$ (Tables 1 and 2). Besides, the k_{obs} value increased with the increasing [reductant]. The plots of k_{obs}^{-1} versus $[\text{reductant}]^{-1}$ were straight lines ($r \geq 0.998$).

3.4. Rate Dependence on the $[\text{OH}]^-$. The effect of $[\text{OH}]^-$ on the reaction had been studied in the range of $5.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ to $25.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ at constant [DTC], [reductant], $[\text{TeO}_4^{2-}]$, μ , and temperature (Table 3). It was found that k_{obs} values increased with the increasing $[\text{OH}]^-$ and the order with respect to $[\text{OH}]^-$ was fractional. The plot of k_{obs}^{-1} versus $[\text{OH}]^{-1}$ was linear with a positive intercept ($r \geq 0.999$).

3.5. Rate Dependence on the $[\text{TeO}_4^{2-}]$. The $[\text{TeO}_4^{2-}]$ was varied from $0.50 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ to $2.50 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ range at constant [DTC], [reductant], $[\text{OH}]^-$, μ , and temperature (Table 3). The k_{obs} increased with the decreasing concentration of TeO_4^{2-} . The order with respect to TeO_4^{2-} was found to be a negative fraction, which revealed that TeO_4^{2-} was produced in equilibrium before the rate-controlling step. In addition, the plot of k_{obs}^{-1} versus $[\text{TeO}_4^{2-}]$ was also straight line with a positive intercept ($r \geq 0.998$).

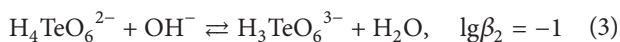
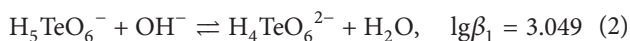
TABLE 3: Effect of $[\text{OH}^-]$, $[\text{TeO}_4^{2-}]$, and μ on the reaction at 298.2 K.

$10^5 [\text{DTC}]$ (mol·L ⁻¹)	[Reductant] (mol·L ⁻¹)	$\mu \times 10^2$ (mol·L ⁻¹)	$10^3 [\text{TeO}_4^{2-}]$ (mol·L ⁻¹)	$10^3 [\text{OH}^-]$ (mol·L ⁻¹)	MEE $10^3 k_{\text{obs}}/\text{s}^{-1}$	EEE $10^3 k_{\text{obs}}/\text{s}^{-1}$
7.16	0.03	3.80	1.00	5.00	7.17	8.20
7.16	0.03	3.80	1.00	10.00	7.94	9.69
7.16	0.03	3.80	1.00	15.00	8.27	10.18
7.16	0.03	3.80	1.00	20.00	8.45	10.68
7.16	0.03	3.80	1.00	25.00	8.53	10.86
7.16	0.03	3.80	0.50	2.50	9.49	13.24
7.16	0.03	3.80	1.00	2.50	7.13	10.14
7.16	0.03	3.80	1.50	2.50	5.84	7.54
7.16	0.03	3.80	2.00	2.50	4.90	6.73
7.16	0.03	3.80	2.50	2.50	4.27	5.86
7.16	0.03	1.50	1.00	2.50	8.89	12.34
7.16	0.03	3.00	1.00	2.50	7.56	9.61
7.16	0.03	4.50	1.00	2.50	7.03	9.17
7.16	0.03	6.00	1.00	2.50	6.45	8.68
7.16	0.03	7.50	1.00	2.50	5.19	7.66

3.6. Rate Dependence on the Ionic Strength μ . The effect of ionic strength on the reaction was studied from $1.50 \times 10^{-2} \text{ mol·L}^{-1}$ to $7.50 \times 10^{-2} \text{ mol·L}^{-1}$ at constant [DTC], [reductant], $[\text{OH}^-]$, $[\text{TeO}_4^{2-}]$, and temperature (Table 3). The experimental results indicated that the rate constant decreased with the increasing μ which showed that there was negative salt which was consistent with the common regulation of the kinetics [14].

3.7. 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 might be produced in the oxidation by DTC. And blank experiments in reaction system gave no polymeric suspensions.

3.8. Reaction Mechanism. In the alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier (here $\text{pK}_w = 14$)

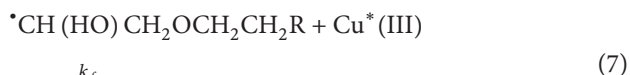
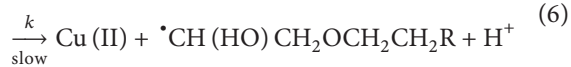
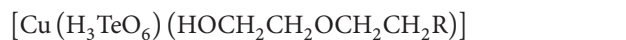
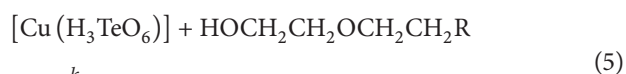
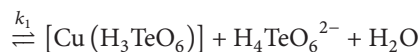


Hence, the main tellurate species was $\text{H}_4\text{TeO}_6^{2-}$ in the concentration of OH^- range used in this work.

The fractional order in OH^- determined that OH^- took part in a preequilibrium with Cu(III) before the rate-determining step. The plot of k_{obs}^{-1} versus $[\text{TeO}_4^{2-}]$ was straight line with a positive intercept indicating a dissociation equilibrium in which the Cu(III) lost a tellurate ligand $\text{H}_4\text{TeO}_6^{2-}$ from its coordination sphere forming an active species monotelluratocuprate(III) complex (MTC). The order with respect to reductant was fractional, which

indicated complex formation between reductant and MTC. In addition, the plot of k_{obs}^{-1} versus $[\text{reductant}]^{-1}$ was straight line with a positive intercept proving the kinetic evidence for the formation of 2:1 complex.

In alkaline solution studied, $(\text{H}_2\text{TeO}_6)_4^-$ protonated easily and coordinated with central ion formed $[\text{Cu}(\text{H}_4\text{TeO}_6)_2]^-$. The plausible mechanism of oxidation was proposed as follows (R, resp. stand for OCH_3 and OCH_2CH_3):



The $\text{Cu}^*(\text{III})$ stands for any kind of which Cu^{3+} existed in equilibrium. The total concentration of Cu(III) at time t can be written as

$$[\text{Cu(III)}]_t = [\text{Cu}(\text{H}_4\text{TeO}_6)_2]_e^- + [\text{Cu}(\text{H}_3\text{TeO}_6)]_e + [\text{Cu}(\text{H}_3\text{TeO}_6)(\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{R})]_e \quad (8)$$

TABLE 4: Rate constants (k) and activation parameters of the rate-determining step.

T (K)		293.3	298.2	303.2	308.2	313.2
$10^2 k/s^{-1}$	MEE	1.16	1.48	1.78	2.11	2.77
	EEE	1.92	2.49	3.12	3.79	4.27
Thermodynamic activation parameters	MEE	$E_a/(kJ \cdot mol^{-1}) = 32.11$, $\Delta H^\ddagger/(kJ \cdot mol^{-1}) = 29.63$, and $\Delta S^\ddagger/(J \cdot K^{-1} \cdot mol^{-1}) = -142.52$				
	EEE	$E_a/(kJ \cdot mol^{-1}) = 31.01$, $\Delta H^\ddagger/(kJ \cdot mol^{-1}) = 28.53$, and $\Delta S^\ddagger/(J \cdot K^{-1} \cdot mol^{-1}) = -141.86$				

The plots of $\ln k$ versus $1/T$ has the following: intercept (a), slope (b), and relative coefficient (r).

MEE: $a = 13.32$, $b = -3863.18$, and $r = -0.996$; EEE: $a = 13.41$, $b = -3730.92$, and $r = -0.993$.

Since reaction (6) was the rate-determining step, the rate of disappearance of $[Cu(III)]_t$ was represented as

$$-\frac{d[Cu(III)]_t}{dt} = \frac{2kK_1K_2 [OH^-] [RCH_2CH_2OCH_2CH_2OH]}{[H_4TeO_6^{2-}] + K_1 [OH^-] + K_1K_2 [OH^-] [RCH_2CH_2OCH_2CH_2OH]} \times [Cu(III)] = k_{obs} [Cu(III)] \quad (9)$$

Rearranging (9) leads to

$$\begin{aligned} \frac{1}{k_{obs}} &= \frac{1}{2k} + \frac{[H_4TeO_6^{2-}] + K_1 [OH^-]}{2kK_1K_2 [OH^-]} \\ &\times \frac{1}{[RCH_2CH_2OCH_2CH_2OH]}, \\ \frac{1}{k_{obs}} &= \frac{1}{2k} + \frac{1}{2kK_2 [RCH_2CH_2OCH_2CH_2OH]} \\ &+ \frac{[H_4TeO_6^{2-}]}{2kK_1K_2 [RCH_2CH_2OCH_2CH_2OH]} \times \frac{1}{[OH^-]}. \end{aligned} \quad (10)$$

Equation (9) suggested that the order with respect to $Cu(III)$ was unity. From (10), the rate constants of the rate-determining step at different temperature were determined by the intercept of the plots of k_{obs}^{-1} versus $[reductant]^{-1}$ which were straight lines. Hence, the activation energy and the thermodynamic parameters were evaluated by the method given earlier at 298.2 K (Table 4). In addition, (11) indicated that the plots of k_{obs}^{-1} versus $[OH^-]^{-1}$ and k_{obs}^{-1} versus $[H_4TeO_6^{2-}]$ were also straight lines. All of the previous conclusions were consistent with experimental results.

4. Conclusion

Through the comparative study of oxidation of 2-(2-methoxy ethoxy)-ethanol (MEE) and 2-(2-ethoxyethoxy)-ethanol (EEE) by ditelluratocuprate(III), we found that both the MEE and the EEE formed the same intermediate compounds with $Cu(III)$. In addition, the values of the activation parameters with respect to MEE were larger than those of EEE, which indicated that the reactivity of EEE was higher than that of MEE. The reason was that the electron-donating

ability of EEE was larger than that of MEE, which indicated that the former was more stable than the latter. The previous conclusions were consistent with experimental results.

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