Oxidation of 2-(2-Methoxyethoxy)ethanol and 2-(2-Ethoxyethoxy)ethanol by Diperiodatocuprate(III) in Alkaline Medium-A Kinetic and Mechanistic Study

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The kinetics of oxidation of 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol by diperiodatocuprate(III) (DPC) in alkaline liquids had been investigated spectrophotometrically in the temperature range of 20 ℃ to 40 ℃. It was found that the reaction was pseudo-first order in [DPC] and $1 < n_{ap} < 2$ in the concentration of reductants. The pseudo-first order rate constant k_{obs} decreased rapidly with an increase in [OH$^-$] to a certain value, then increasing with the continuous increase in [OH$^-$]. In addition, the k_{obs} decreased with an increase in [IO$_4^-$]. There was no salt effect. The rate of 2-(2-ethoxyethoxy)ethanol was higher than 2-(2-methoxyethoxy)ethanol in stronger alkaline medium. A plausible mechanism 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 298.2 K along with rate constants of the rate-determining step were calculated.

Key Words: Kinetics, Oxidation, Diperiodatocuprate(III), 2-(2-Methoxyethoxy)ethanol, 2-(2-Ethoxyethoxy)ethanol.

INTRODUCTION

In recent years, studies on the transition metals in a higher oxidation state have been the most active area. Transition metals generally can be stabilized by chelation with polydentate ligands, such as ditelluratocuprate(III)[1,2], diperiodato-cuprate(III)[3,4], diperiodatoargentate(III)[5,6], ditelluratoargentate(III)[7], diperio-datonickelate(IV)[8] are good oxidants in a medium with an appropriate pH. As a kind of oxidation reagents, Cu(III) complex has been used widely in many biological systems involving electron-transfer processes[9] and organic mixture qualitative analysis[10]. Because Cu(III) is in the highest oxidation state and the reaction is complicated in the kind of reaction system, it is of significance to have a further study on this kind of reaction system. In the present paper, the mechanism of oxidation of 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)-ethanol by diperiodatocuprate(III) is reported.

Both 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyeth-oxy)ethanol (EEE) are colourless liquids and high boiling-point solvents so that they have a wide application. Such as printing, dyeing, resin, cellulose and coatings, *etc*. In addition, 2-(2-methoxyethoxy)ethanol can be used for the extracting agent for hydrocarbon and chemical reagent in chemical analysis.

EXPERIMENTAL

All the reagents used were A.R. Grade and double-distilled water was used throughout the work. Diperiodato-

cuprate(III) (DPC) was prepared and standardized by the method reported by Jaiswal[11]. The purity of the complex was checked by comparing UV-visible spectrum with literature data, which showed a characteristic absorption peak at 415 nm. KNO$_3$ and KOH were used to maintain ionic strength and alkaliniy of the reaction, respectively. Moreover, solutions of DPC and reductants were always freshly prepared before use.

Kinetics measurements and apparatus: The kinetics were followed under pseudo-first order conditions, solution (2 mL) containing required concentration of DPC, OH$^-$, IO$_4^-$ and ionic strength and reductant solution (2 mL) of requisite concentration were mixed at the desired temperature. The progress of the reaction was followed by measuring the decrease in absorbance of DPC at 415 nm. The kinetic measurements were performed on a UV-visible spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell holder kept at constant temperature (± 0.1 ℃) by circulating water from a thermostat (DC-2010, Baoding Xinhua Inc., China). It was verified that there was negligible interference from other reagents at this wavelength.

RESULTS AND DISCUSSION

Product analysis: Under the kinetic conditions the product of oxidation was identified as aldehyde by its characteristic spot test[12].

Evaluation of pseudo-first order rate constants: Under the conditions of [reductant]$_0$ ([MEE]$_0$ and [EEE]$_0$) >>

$[Cu(III)]_0$, the plots of $\ln(A_t-A_\infty)$ *versus* time were straight lines($r \geq 0.999$) (Fig. 1), indicating the order in DPC to be unity. The pseudo-first-order rate constants k_{obs} were evaluated by using the equation $\ln(At-A_\infty) = -k_{obst} + b(constant)$. The k_{obs} values were the average value of at least three independent experiments and reproducibility was within ± 5 %.
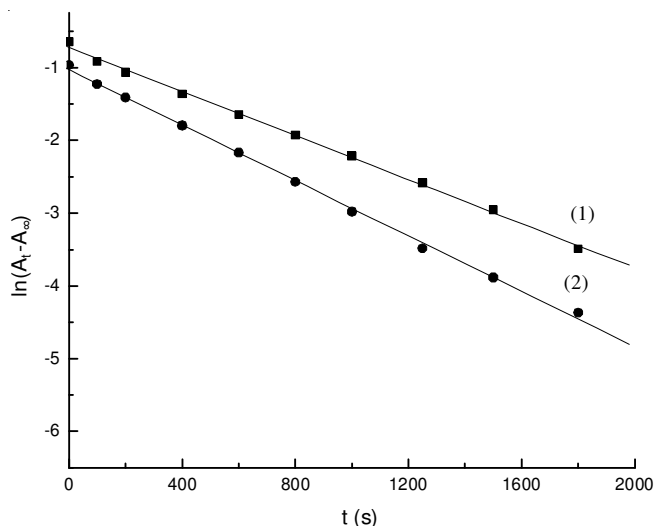

Fig. 1. Plot of $\ln (A_t-A_\infty)$ *vs* t at T = 298.2 K; [DPC] = 6.99×10^{-5} mol L^{-1}, $[IO_4^-]$ = 1.00×10^{-3} mol L^{-1}, $[OH^-]$ = 1.00×10^{-2} mol L^{-1}, μ = 3.11×10^{-2} mol L^{-1}, [reductant] = 4.00×10^{-2} mol L^{-1} (1) [MEE]: k_{obs}= 1.512×10^{-3}s^{-1} (2) [EEE]: k_{obs} = 1.904×10^{-3}s^{-1}

Rate dependence on the [reductant]: The [reductant] was varied in the range of 0.25 mol L^{-1} to 0.60 mol L^{-1} at different temperature keeping all other [reactants] constant. The order nap of [reductant] was found to be $1 < n_{ap} < 2$ form the slopes of $\ln k_{obs}$ *versus* ln[reductant] plots. Besides, the k_{obs} value increased with the increasing [reductant]. The plots of [reductant]/k_{obs} *versus* 1/[reductant] were straight lines (r = 0.998) (Figs. 2 and 3).

Rate dependence on the [OH$^-$]: The effect of [OH$^-$] on the reaction had been studied in the range of 5.00×10^{-3} mol L^{-1}

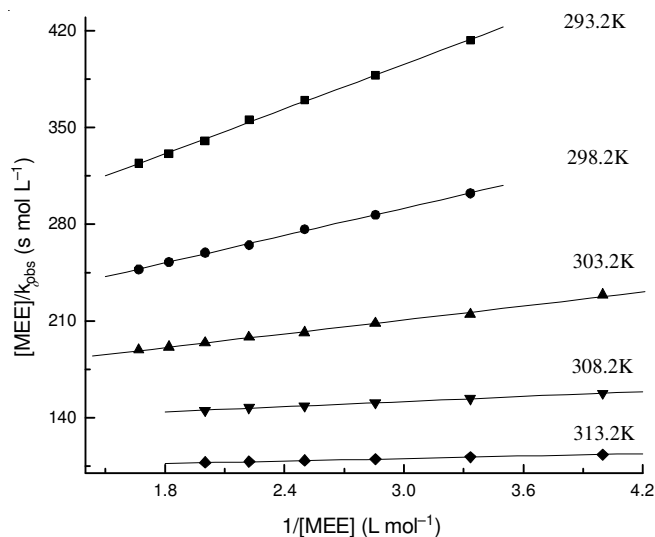Fig. 2. Plots of [MEE]/k_{obs}^{-1} *vs*. [MEE]$^{-1}$ (r = 0.998)· [DPC] = 6.99×10^{-5} mol L^{-1}, $[IO_4^-]$ = 1.00×10^{-3} mol L^{-1}, $[OH^-]$ = 1.00×10^{-2} mol L^{-1}, μ = 3.11×10^{-2} mol L^{-1}
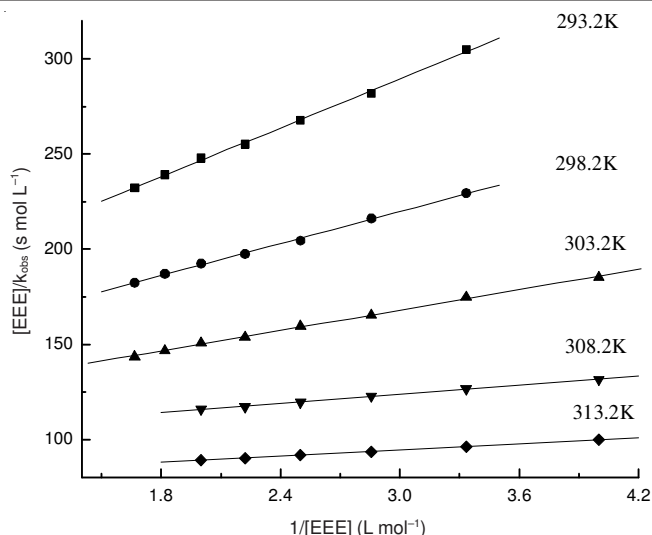
Fig. 3. Plots of [EEE]/k_{obs}^{-1} *vs*. [EEE]$^{-1}$ (r = 0.998); [DPC] = 6.99×10^{-5} mol L^{-1}, $[IO_4^-]$ = 1×10^{-3} mol L^{-1}, $[OH^-]$ = 1.00×10^{-2} mol L^{-1}, μ = 3.11×10^{-2} mol L^{-1}

to 25.00×10^{-3} mol L^{-1} at constant [DPC], [reductant], $[IO_4^-]$, μ and temperature. It was found that k_{obs} decreased rapidly with the increaseing [OH$^-$] to a certain value, then increasing with the continuous increase in [OH$^-$]. The plot of k_{obs} *vs*. [OH$^-$] was curved line (Fig. 4). The concentration of OH$^-$ was about 7.50×10^{-3} mol L^{-1} for MEE at the turning point in which the rate was the slowest, but [OH$^-$] was about 2.50×10^{-3} mol L^{-1} with respect to EEE at the turning that the rate was the slowest.
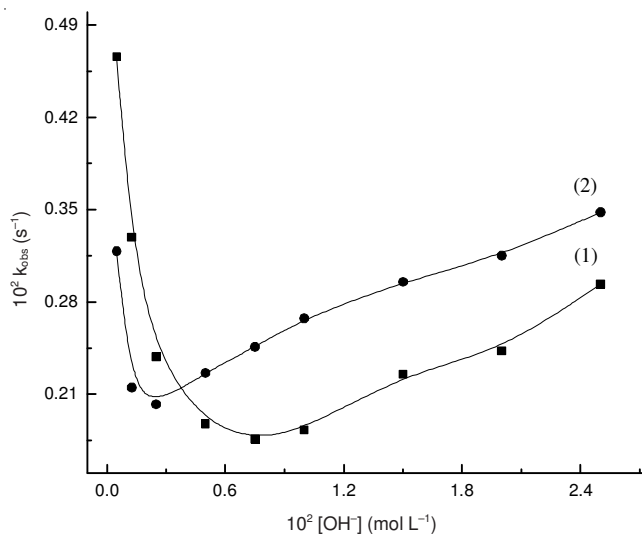

Fig. 4. Plots of 10^2k_{obs} *vs*. 10^2[OH$^-$] at 303.2 K; [DPC] = 6.99×10^{-5} mol L^{-1}, $[IO_4^-]$ = 1.00×10^{-3} mol L^{-1}, μ = 3.11×10^{-2} mol L^{-1}, [reductant] = 4.00×10^{-1} mol L^{-1}, (1) [MEE] (2)[EEE]

Rate dependence on the [IO$_4^-$]: The [IO$_4^-$] was varied from 1.00×10^{-3} mol L^{-1} to 3×10^{-3} mol L^{-1} range at constant [DPC], [reductant], [OH$^-$], μ and temperature. The k_{obs} values increased with the decreasing concentration of IO$_4^-$. The order with respect to IO$_4^-$ was found to be a negative fraction, which reveals that IO$_4^-$ was produced in equilibrium before the rate controlling step. A plot of k_{obs}^{-1} *versus* [IO$_4^-$] was straight line with a positive intercept (Fig. 5).
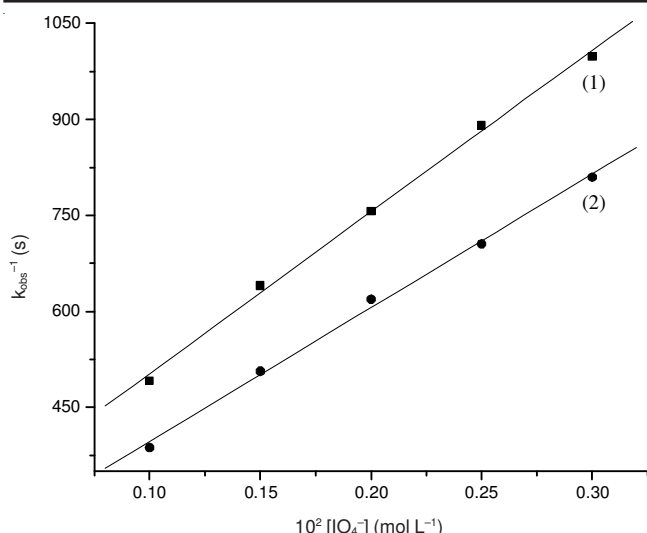
Fig. 5.   Plots of k_{obs}^{-1} *vs.* $10^2[IO_4^-]$ at 303.2 K, (r = 0.998); [DPC] = 6.99 × 10^{-5} mol L^{-1}, $[OH^-]$ = 1.00 × 10^{-2} mol L^{-1}, μ = 3.11 × 10^{-2} mol L^{-1}, [reductant] = 4.00 × 10^{-1} mol L^{-1} (1)[MEE] (2)[EEE]
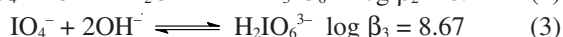
Rate dependence on ionic strength (μ): The effect of ionic strength on the reaction was studied in the range of 1.50 × 10^{-2} mol L^{-1} to 7.50 × 10^{-2} mol L^{-1} at constant [DPC], [reductant], $[OH^-]$, $[IO_4^-]$ and temperature. The experimental results indicated that the rate constant k_{obs} changed slightly with increased in ionic strength (μ) (Table-1), which showed that there was no salt effect.

TABLE-1
INFLUENCE OF VARIATION IONIC STRENGTH (μ) AT 303.2 K

10^2 μ/mol L^{-1}		1.50	3.00	4.50	6.00	7.50
$10^3 k_{obs}/s^{-1}$	MEE	19.78	20.56	21.41.	21.72	22.07
	EEE	24.75	24.90	25.35	26.03	26.42
[reductant] ([MEE] and [EEE]) = 4.00 × 10^{-1} mol L^{-1}, [DPC] = 6.99 × 10^{-5} mol L^{-1}, $[OH^-]$ = 1.00 × 10^{-2} mol L^{-1}, $[IO_4^-]$ = 1.00 × 10^{-3} mol L^{-1}						

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 DPC. And blank experiments in reaction system gave no polymeric suspensions.

Reaction mechanism: In aqueous periodate solution, equilibria (1)-(3) were detected and the corresponding equilibrium constants at 273.2 K were determined by Aveston[13].

$$2IO_4^- + 2OH^- \rightleftharpoons H_2I_2O_{10}^{4-} \quad \log \beta_1 = 15.05 \quad (1)$$

$$IO_4^- + OH^- + H_2O \rightleftharpoons H_3IO_6^{3-} \quad \log \beta_2 = 6.21 \quad (2)$$

$$IO_4^- + 2OH^- \rightleftharpoons H_2IO_6^{3-} \quad \log \beta_3 = 8.67 \quad (3)$$

The distribution of all species of periodate in aqueous alkaline solution can be calculated from equilibriums (1)-(3). In the concentration of OH^- range used in this work the dimer and IO_4^- species of periodate can be neglected. The equations (4)-(5) can be obtained from (2) and (3) as below:

$$[H_2IO_6^{3-}] = \frac{\beta_3[OH^-]^2}{1 + \beta_2[OH^-] + \beta_3[OH^-]^2}[IO_4^-]_{ex} = f([OH^-])[IO_4^-]_{ex} \quad (4)$$
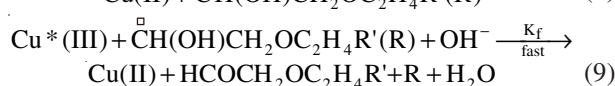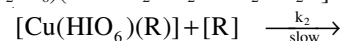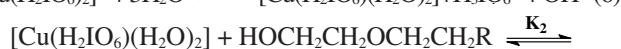
$$[H_3IO_6^{2-}] = \frac{\beta_2[OH^-]}{1 + \beta_2[OH^-] + \beta_3[OH^-]^2}[IO_4^-]_{ex} = \phi([OH^-])[IO_4^-]_{ex} \quad (5)$$

here $[IO_4^-]_{ex}$ representsed the concentration of original overall periodate and equals approximately to the sum of $[H_2IO_6^{3-}]$ and $[H_3IO_6^{2-}]$.

In weaker alkaline medium such as $[OH^-]$ = 5.00 × 10^{-3} mol L^{-1}, $[H_2IO_6^{3-}]$: $[H_3IO_6^{2-}]$=1.44:1.00, so the main species of periodate were $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$, consistent with the result calculated from Crouthamel's data by Murthy[14]. In stronger alkaline medium such as $[OH^-]$ = 5.00 × 10^{-2} mol L^{-1}, $[H_2IO_6^{3-}]$: $[H_3IO_6^{2-}]$ = 14.40 : 1.00, so the main species of periodate was $H_2IO_6^{3-}$.

According to the above discussion, the two plausible mechanisms of oxidation were proposed as follows: (R respectively standed for MEE and EEE; R' respectively standed for OCH_3 and OCH_2CH_3).

Mechanism I ----In weaker alkaline medium:

$$[Cu(H_2IO_6)_2]^{3-} + 3H_2O \xrightleftharpoons{K_1} [Cu(H_2IO_6)(H_2O)_2] + H_3IO_6^{2-} + OH^- \quad (6)$$

$$[Cu(H_2IO_6)(H_2O)_2] + HOCH_2CH_2OCH_2CH_2R \xrightleftharpoons{K_2}$$
$$[Cu(H_2IO_6)(HOCH_2CH_2OCH_2CH_2R)] + 2H_2O \quad (7)$$

$$[Cu(HIO_6)(R)] + [R] \xrightarrow[slow]{k_2}$$
$$Cu(II) + \overset{\circ}{C}H(OH)CH_2OC_2H_4R'(R) \quad (8)$$

$$Cu*(III) + \overset{\circ}{C}H(OH)CH_2OC_2H_4R'(R) + OH^- \xrightarrow[fast]{K_f}$$
$$Cu(II) + HCOCH_2OC_2H_4R' + R + H_2O \quad (9)$$

The Cu*(III) stand for any kind of which Cu^{3+} existed in equilibrium. The total concentration of Cu(III) can be written as:(subscripts T and e stand for total concentration and at equilibrium respectively).

$$Cu*(III) = [Cu(H_2IO_6)(H_2O)_2]_e + [Cu(H_2IO_6)_2]^{3-}_e + [Cu(H_2IO_6)(R)]_e$$

Since reaction (8) was the rate-determining step, the rate of disappear of $[Cu(III)]_T$ was represented as:

$$-\frac{d[Cu(III)]_T}{dt} = \frac{2k_1K_1K_2[R]^2}{K_1 + [H_3IO_6^{2-}][OH^-] + K_1K_2[R]}[Cu(III)]_T$$
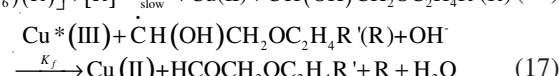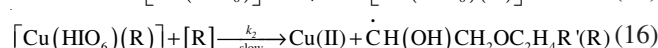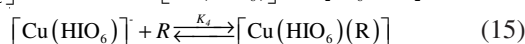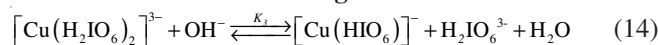$$(10)$$

$$= k_{obs}[Cu(III)]_T$$

$$k_{obs} = \frac{2k_1K_1K_2[R]^2}{K_1 + [H_3IO_6^{2-}][OH^-] + K_1K_2[R]} \quad (11)$$

Re-arranging eqn. (11) leaded to eqns. (12) and (13)

$$\frac{[R]}{k_{obs}} = \frac{1}{2k_1} + \frac{K_1 + [H_3IO_6^{2-}][OH^-]}{2k_1K_1K_2} \times \frac{1}{[R]} \quad (12)$$

$$\frac{1}{k_{obs}} = \frac{K_1K_2[R] + K_1}{2k_1K_1K_2[R]^2} + \frac{[OH^-]}{2k_1K_1K_2[R]^2} \times [H_3IO_6^{2-}] \quad (13)$$

Mechanism II---In stronger alkaline medium:

$$[Cu(H_2IO_6)_2]^{3-} + OH^- \xrightleftharpoons{K_3} [Cu(HIO_6)]^- + H_2IO_6^{3-} + H_2O \quad (14)$$

$$[Cu(HIO_6)]^- + R \xrightleftharpoons{K_4} [Cu(HIO_6)(R)] \quad (15)$$

$$[Cu(HIO_6)(R)] + [R] \xrightarrow[slow]{k_2} Cu(II) + \overset{\cdot}{C}H(OH)CH_2OC_2H_4R'(R) \quad (16)$$

$$Cu*(III) + \overset{\cdot}{C}H(OH)CH_2OC_2H_4R'(R) + OH^-$$
$$\xrightarrow[fast]{K_f} Cu(II) + HCOCH_2OC_2H_4R' + R + H_2O \quad (17)$$

where Cu*(III) stand for any kind of form which Cu(III) existed in equilibrium. The total concentration of Cu(III) can be written as:(subscripts T and e stand for total concentration and at equilibrium respectively).

$$Cu^*(III) = \left[Cu(HIO_6)\right]_e^- + \left[Cu(H_2IO_6)_2\right]_e^{3-} + \left[Cu(HIO_6)(R)\right]_e$$
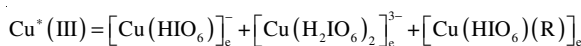
Reaction (17) was the rate-determining step. Similarly, the rate of the reaction can be derived as:

$$-\frac{d[Cu(III)]_T}{dt} = \frac{2k_2K_3K_4[OH^-][R]^2}{K_3[OH^-] + [H_2IO_6^{3-}] + K_3K_4[OH^-][R]}[Cu(III)]_T \tag{18}$$

$$= k_{obs}[Cu(III)]_T$$

$$k_{obs} = \frac{2k_2K_3K_4[OH^-][R]^2}{K_3[OH^-] + [H_2IO_6^{3-}] + K_3K_4[OH^-][R]} \tag{19}$$

Re-arranging equation (19) leaded to equations (20) and (21).

$$\frac{[R]}{k_{obs}} = \frac{1}{2k_2} + \frac{K_3[OH^-] + [H_2IO_6^{3-}]}{2k_2K_3K_4[OH^-]} \times \frac{1}{[R]} \tag{20}$$

$$\frac{1}{k_{obs}} = \frac{K_3K_4[R] + K_3}{2k_2K_3K_4[R]^2} + \frac{[H_2IO_6^{3-}]}{2k_2K_3K_4[OH^-][R]^2} \tag{21}$$

Equations (1)-(5) and our calculated results were given, which can explain why k_{obs} decreased rapidly with increase in [OH⁻] up to a certain value. After the point, it increased gradually with the continuous increasing in [OH⁻].

Equations (10) and (18) suggested that the order with respect to Cu(III) was unity. Eqns. (11) and (19) showed that the order in [reductant] was found to be $1 < n_{ap} < 2$. The rate constants of the rate-determining step at different temperature were determined by the intercept of the plots of [reductant]/k_{obs} *vs.* 1/[reductant] which were straight lines. Eqns. (13) and (21) showed that the plots of $1/k_{obs}$ *versus* [IO₄⁻] should also be linear. The rate equations derived from the two simultaneous mechanisms were consistent with our experimental results. Hence activation energy and the thermodynamic parameters were evaluated at 298.2 K by the method given earlier[15] (Table-2).

TABLE-2
RATE CONSTANTS (*k*) AND ACTIVATION PARAMETERS
OF THE RATE-DETERMINING STEP

T (K)		293.2	298.2	303.2	308.2	313.2
10^3 k/ s⁻¹	MEE	2.14	2.59	3.11	3.75	4.91
	EEE	3.11	3.68	4.37	5.00	6.37
Thermodynamic activation parameters	MEE	E_a/(kJ mol⁻¹) = 30.99, $\Delta H^{\neq}$/(kJ mol⁻¹)= 28.55, $\Delta S^{\neq}$/(J K⁻¹ mol⁻¹) = -198.86				
	EEE	E_a/(kJ mol⁻¹)= 26.59, $\Delta H^{\neq}$/(kJ mol⁻¹)= 24.15, $\Delta S^{\neq}$/(J K⁻¹ mol⁻¹) = -210.71				

The plot of ln k *vs* 1/T have following intercept (a) slope (b) and relative coefficient (r); MEE: a = 6.54, b = -3727.05, r = -0.995 ; EEE: a = 5.12, b = -3197.63, r = -0.995.

Conclusion

Through the comparative study of oxidation of 2-(2-methoxy ethoxy)ethanol (MEE) and 2-(2-ethoxyethoxy)-ethanol (EEE) by diperiodatocuprate(III), it is found that both the MEE and EEE formed the same intermediate compounds with Cu(III). In addition, the values of the activation parameters with respect to MEE is larger than that of EEE, which indicated the reactivity of EEE is higher than MEE. The reason is that the electron-donating ability of EEE is larger than that of MEE. Moreover, The transition complex formation between EEE and DTA is more stable than that of MEE. The above conclusions are consistent with experimental results.

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