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Kinetics and Mechanism of Oxidation of 2-(2-Methoxyethoxy)ethanol and 2-(2-Ethoxyethoxy)ethanol by Ditelluratoargentate(III) in Alkaline Medium

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Oxidation of 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol by ditelluratoargentate(III) in alkaline liquids has been studied spectrophotometrically in the temperature range of 293.2 - 313.2 K. The first-order rates with respect to reductant and Ag(III) were all found. 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 $H_4TeO_6^{2-}$. There was a positive salt effect and no free radicals were detected. In view of this, the $Ag(H_3TeO_6)(H_2O)_2$ is assumed to be the active species. A plausible mechanism is proposed and the rate equations derived from the mechanism can explain all the experimental observations activation parameters and the rate constant of the rate-determining step were calculated.

Keywords: Ditelluratoargentate(III), 2-(2-Methoxyethoxy)ethanol, 2-(2-Ethoxyethoxy)ethanol, Redox reaction, Kinetics mechanism.

INTRODUCTION

Recently, studies on the transition metals in a higher oxidation state have been one of the most active area and more and more researchers have devoted themselves to the study of the higher oxidation state of transition metal ions. Metal chelates, such as ditelluratocuprate(III)[1,2], diperiodatocuprate(III)[3,4], diperiodatoargentate(III)[5,6], ditelluratoargentate(III)[7], diperiodatonickelat (IV)[8] are good oxidants in a medium with an appropriate pH. The research is focus on the kinetics of oxidation of small molecules by ditelluratoargentate(III), such as alcohols, aldehydes[9], carboxylic acid (salt)[10] amine[11], phosphate[12] and trinitride[13]. Diperiodatoargentate(III) also has a strong coagulation and flocculation, which can effectively remove the excess algae in the water and degradation of liver toxins in the water, moreover it has no residue toxicity and such outstanding advantages as without causing secondary pollution of drinking water. The researches are still not enough in this area and the reaction dynamics about supernormal oxidation state of transition metals deserves further investigation. In the present paper, the mechanism of oxidation of 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol by ditelluratoargentate (III) is reported.

Both 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol are colourless liquids and high boiling-point solvents which means they have a wide application, such as non-polluting cleaning agents, extraction agents, diluent, medicine, additives and solvent, *etc*.

EXPERIMENTAL

All chemicals used were of A.R. grade and double distilled water was used throughout the work. Solutions of ditelluratoargentate(III) and reductants were always freshly prepared before use. The stock solution of ditelluratoargentate (III) was prepared and standardized by the method given by Gupta *et al.*[14]. The concentration of ditelluratoargentate (III) was derived from its absorption at $\lambda = 351$ nm. KNO_3 and KOH were used to maintain ionic strength and alkalinity of the reaction, respectively.

The measurements of the kinetic were performed on a UV-visible spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell-holder kept at a constant temperature (± 0.1 ºC) by circulating water from a thermostat (DC-2010, Baoding, China).

Kinetics measurements: All kinetic measurements were carried out under pseudo-first-order conditions. Solution (2 mL) containing required concentration of Ag(III), OH^-, $H_4TeO_6^{2-}$ and ionic strength and reductant solution (2 mL) of requisite concentration were mixed at the desired temperature. The complete fading of ditelluratoargentate (III) color (reddish brown) marked the completion of the reaction. The product of oxidation was identified as ketone by its characteristic spot test[15].

RESULTS AND DISCUSSION

Under the conditions of $[reductant]_0 >> [DTA]_0$, the plots of $\ln(A_t\text{-}A_\infty)$ *vs.* time were straight lines, indicating the reaction was first order with respect to [ditelluratoargentate(III)], where A_t and A_∞ were 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 (r = 0.999). Deviations in duplicate determinations were generally less than ± 3 %.

Rate dependence on the [reductant]: At constant [ditelluratoargentate(III)], [OH^-], [$H_4TeO_6^{2-}$], ionic strength μ and temperature, k_{obs} values increased with the increase in concentration of reductants and the plot of k_{obs} *vs.* concentration of reductants was a straight line passing through the origin ($r \geq 0.998$), indicating that it was the first order with respect to [reductant] (Figs. 1 and 2).

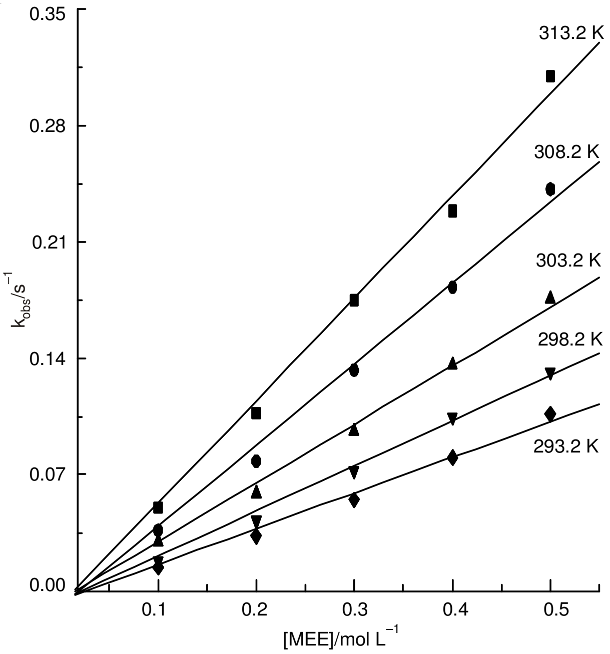

Fig. 1. Plots of k_{obs} *vs.* [2-(2-methoxyethoxy)-ethanol] at different temperatures [ditelluratoargentate(III)] = 6.27×10^{-4} mol L^{-1}, [$H_4TeO_6^{2-}$] = 1.00×10^{-3} mol L^{-1}, [OH^-] = 1.00×10^{-2} mol L^{-1}, μ = 4.30×10^{-2} mol L^{-1}

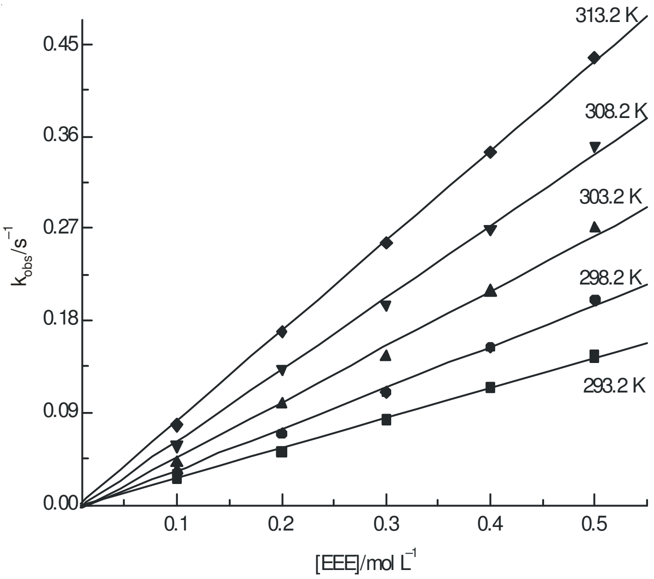

Fig. 2 Plots of k_{obs} *vs.* [2-(2-ethoxyethoxy)-ethanol] at different temperatures [ditelluratoargentate(III)] = 6.27×10^{-4} mol L^{-1}, [$H_4TeO_6^{2-}$] = 1.00×10^{-3} mol L^{-1}, [OH^-] = 1.00×10^{-2} mol L^{-1}, μ = 4.30×10^{-2} mol L^{-1}

Rate dependence on [$H_4TeO_6^{2-}$]: Under the condition of $[\text{reductant}]_0 >> [\text{ditelluratoargentate (III)}]_0$, at constant [reductant], [OH^-], ionic strength and temperature, k_{obs} values decreased with the increase in concentration of $H_4TeO_6^{2-}$ and the order with respect to [$H_4TeO_6^{2-}$] was found to be fractional (in the temperature range of 293.2-313.2 K), which revealed that [$H_4TeO_6^{2-}$] was produced in equilibrium before the rate-determining step. The plots of $1/k_{obs}$ *vs.* [$H_4TeO_6^{2-}$] at different temperatures were all straight lines without passing through the origin (Figs. 3 and 4).

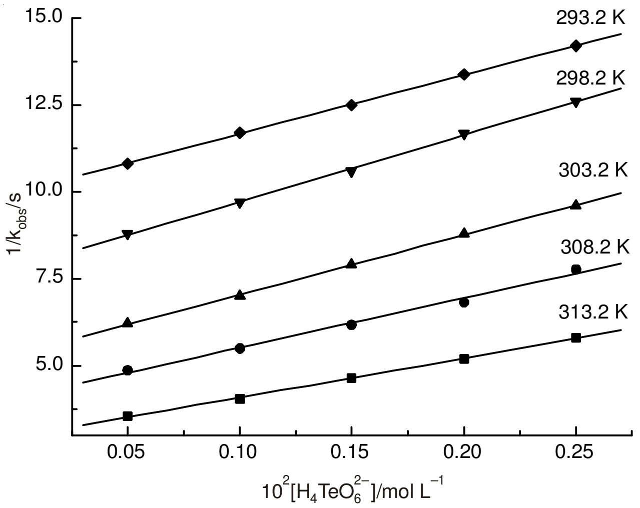

Fig. 3. Plot of $1/k_{obs}$ *vs.* $10^2[H_4TeO_6^{2-}]$ at different temperatures [ditelluratoargentate(III)] = 6.27×10^{-4} mol L^{-1}, [2-(2-methoxyethoxy)ethanol] = 3.00×10^{-1} mol L^{-1}, [OH^-] = 1.00×10^{-2} mol L^{-1}, μ = 4.30×10^{-2} mol L^{-1} (r = 0.998)

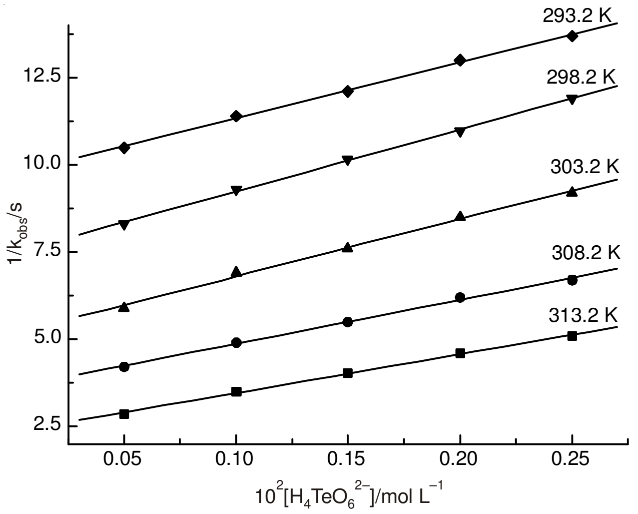

Fig. 4. Plots of $1/k_{obs}$ *vs.* $10^2[H_4TeO_6^{2-}]$ at different temperatures [ditelluratoargentate(III)] = 6.27×10^{-4} mol L^{-1}, [EEE] = 3.00×10^{-1} mol L^{-1}, [OH^-] = 1.00×10^{-2} mol L^{-1}, μ = 4.30×10^{-2} mol L^{-1} (r = 0.998)

Rate dependence on the [OH^-]: At fixed concentrations of ditelluratoargentate (III), $H_4TeO_6^{2-}$, reductant, ionic strength μ and temperature (298.2 K), the value of k_{obs} increased with increasing concentration of OH^-. The order with respect to [OH^-] was fractional and the plots of $1/k_{obs}$ *vs.* $1/[OH^-]$ was linear (Fig. 5).

Rate dependence on the ionic strength (μ): The effect of ionic strength on the reaction was studied in the range of 1.50×10^{-2} to 7.50×10^{-2} mol L^{-1} at constant [ditelluratoargentate

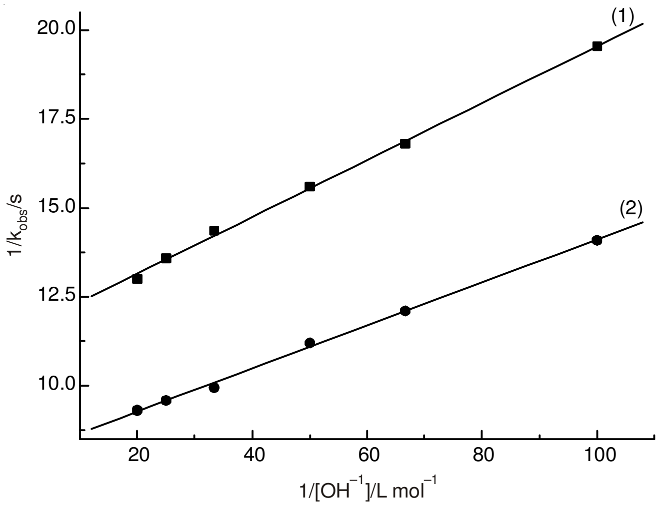

Fig. 5. Plots of $1/k_{obs}$ *vs.* $1/[OH^-]$ at 298.2 K [ditelluratoargentate (III)] = 6.27×10^{-4} mol L^{-1}, $[H_4TeO_6^{2-}] = 1.00 \times 10^{-3}$ mol L^{-1}, μ = 4.30×10^{-2} mol L^{-1}. (1) [MEE] = 3.00×10^{-1} mol L^{-1}, (r = 0.999) (2) [EEE] = 3.00×10^{-1} mol L^{-1}, (r = 0.999)

(III)], [reductant], $[OH^-]$, $[H_4TeO_6^{2-}]$ and temperature. The experimental results indicated that the rate constant k_{obs} increased with increased in ionic strength μ (Table-1), which showed that there was positive salt effect that consistent with the common regulation of the kinetics[16].

TABLE-1
INFLUENCE OF VARIATION IONIC STRENGTH μ

10^2 μ/mol L^{-1}		1.50	3.00	4.50	6.00	7.50
$10^2 k_{obs}$/s^{-1}	2-(2-methoxyethoxy)-ethanol	7.53	8.5	9.53	10.5	11.4
	2-(2-ethoxyethoxy)-ethanol	8.14	10.10	11.88	13.43	15.34

[reductant] (MEE and EEE) = 3.00×10^{-1}mol L^{-1}, [DTA] = 6.27×10^{-4} mol L^{-1}, $[OH^-] = 1.00 \times 10^{-2}$ mol L^{-1}, $[H_4TeO_6^{2-}] = 1.00 \times 10^{-3}$ mol L^{-1}

Reaction mechanism: In an alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier[17] ($pK_w = 14$).

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

$$H_4TeO_6^{2-} + OH^- \rightleftharpoons H_3TeO_6^{3-} + H_2O \qquad \lg \beta 2 = -1.00 \quad (2)$$

The distribution of all species of telluride in aqueous alkaline solution is calculated from (1) and (2). In the alkaline medium, $[OH^-] = 0.01$ mol L^{-1}, the equations give: $[H_4TeO_6^{2-}]$: $[H_5TeO_6^-]$: $[H_3TeO_6^{3-}]$ = 1000:89:1, in the concentration range of OH^- used in this work, the $H_5TeO_6^-$ and $H_3TeO_6^{3-}$ species can be neglected and the main species of telluride is $H_4TeO_6^{2}$. According to the literature[18] the main species of ditelluratoargentate (III) is $[Ag(H_4TeO_6)_2]^-$ over the experimental concentration range of $[OH^-]$.

According to the above experimental facts, the following reaction mechanism is proposed.

$$[Ag(H_4TeO_6)_2]^- + OH^- + H_2O \overset{K_1}{\rightleftharpoons} \left[Ag(H_3TeO_6)(H_2O_2)\right] + H_4TeO_6^{2-} \qquad (1)$$

$$[Ag(H_3TeO_6)(H_2O)_2] + \text{reductant} \xrightarrow[\text{slow}]{k} [Ag(I) + H_4TeO_6^{2-} + 2H_2O + C_6H_{10}O] \qquad (2)$$

Reactions (1) is dissociation and coordination equilibrium, the reaction rates of which is generally fast, reaction (2) is an electron-transfer reaction, the reaction rates of which are generally slow. Hence, eqn. (2) as a rate control step had been proposed here. $[Ag\ (III)]_t$ stands for all forms of Ag (III) complex which exists in the equilibrium and R′ stands for the reductant.

$$-d[Ag(III)]_t / dt = k[Ag(H_3TeO_6)][\text{reductant}] \qquad (3)$$

$$-d\left[Ag\ (III)\right]_t / dt = \frac{kK_1[R'][OH^-]}{K_1[OH^-] + [H_4TeO_6^{2-}]} \qquad (4)$$

$$[Ag\ (III)]_t = k_{obs}[Ag\ (III)]_t$$

The expression of k_{obs} is obtained by (4):

$$k_{obs} = \frac{kK_1[R'][OH^-]}{K_1[OH^-] + [H_4TeO_6^{2-}]} \qquad (5)$$

Re-arranging eqn. 5 leads to eqn. 6:

$$\frac{1}{k_{obs}} = \frac{1}{k[R']} + \frac{[H_4TeO_6^{2-}]}{kK_1[R']}\frac{1}{[OH^-]} \qquad (6)$$

Eqns. 4-6 suggest that the order in [reductant] and [Ag(III)] are found to be one each and in OH^- and $H_4TeO_6^{2-}$ be fractional and inverse fractional respectively, which conform to the observations. All above indicated that the mechanism we have proposed is more plausible. Eqn. (6) indicates that the plots of $1/k_{obs}$ *vs.* $1/[OH^-]$ and $1/k_{obs}$ *vs.* $[H_4TeO_6^{2-}]$ are straight lines and activation energy and the thermodynamic parameters are evaluated by the method given earlier[19] (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
10^2 k/mol^{-1} L s^{-1}	MEE	33.37	42.72	62.66	81.30	112.84
	EEE	34.22	44.66	64.60	92.34	143.06
Thermodynamic activation parameters	MEE	Ea/(kJ mol^{-1}) = 46.99, ΔH$^{\neq}$/(kJ mol^{-1}) = 44.51, ΔS$^{\neq}$/(J K^{-1} mol^{-1}) = -102.35, T = 298.2 K				
	EEE	Ea/(kJ mol^{-1}) = 51.82, ΔH$^{\neq}$/(kJ mol^{-1}) = 49.34, ΔS$^{\neq}$/(J K^{-1} mol^{-1}) = -85.81, T = 298.2 K				

Plot of ln k *vs.* T^{-1} have following intercept (a) slope (b) and relative coefficient (r): MEE: a = 18.15, b = -5652.29, r = 0.998; EEE: a = 20.14, b = -6233.15, r = 0.998

Conclusion

Base on the former discussion and results, we can know that the rate constants k of the rate-determining step and the activation parameters for 2-(2-methoxyethoxy)-ethanol and 2-(2-ethoxyethoxy)-ethanol are contiguous. Both of 2-(2-methoxyethoxy)-ethanol and 2-(2-ethoxyethoxy)-ethanol form the same intermediate compounds with ditelluratoargentate (III) and the rate of 2-(2-ethoxyethoxy)-ethanol is a little quicker than that of 2-(2-methoxyethoxy)-ethanol. The reason is that the electron-donating ability of 2-(2-ethoxyethoxy)-ethanol is larger than that of 2-(2-methoxyethoxy)-ethanol. The transition complex formation between 2-(2-ethoxyethoxy)-ethanol and ditelluratoargentate (III) is more stable than that of 2-(2-methoxyethoxy)-ethanol[20].

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