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Kinetics and Mechanism of Oxidation of 1-Methoxy-2-propanol and 1-Ethoxy-2-propanol by Ditelluratoargentate(III) in Alkaline Medium

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The kinetics of oxidation of 1-methoxy-2-propanol and 1-ethoxy-2-propanol by ditelluratoargentate(III) in alkaline liquids has been studied spectrophotometrically in the temperature range of 293.2 K-313.2 K. The reaction rate showed first order dependence in ditelluratoargentate(III) and fractional order with respect to 1-methoxy-2-propanol or 1-ethoxy-2-propanol. 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 negative salt effect and no free radicals were detected. A plausible mechanism involving a two-electron transfer is proposed and the rate equations derived from the mechanism can explain all the experimental results. The rate equations derived from mechanism can explain all experimental observations. The activation parameters along with the rate constants of the rate-determining step were calculated.

Key Words: Ditelluratoargentate(III), 1-Methoxy-2-propanol, 1-Ethoxy-2-propanol, Redox reaction, Kinetics mechanism.

INTRODUCTION

Recently, many researchers are interested in the study of the highest oxidation state of transition metals which in a higher oxidation state generally can be stabilized by chelation with suitable polydentate ligands. Metal chelates, such as diperiodato-argentate(III)[1], ditelluratoargentate (III)[2], ditelluratocuprate(III)[3] and diperiodatonickelate(IV)[4], are good oxidants in a medium with an appropriate pH. The use of complexes as good oxidizing agents in analytical chemistry has been reported[5,6]. The oxidation of a number of organic compounds and metals in lower oxidation state by Ag(III) has also been performed[3]. However, the reaction system is relatively complex because of Ag(III) in the highest valence state, no further information on the kinetics is available, it is necessary to study this reaction system in the future. In this paper, the mechanism of the oxidation of 1-methoxy-2-propanol and 1-ethoxy-2-propanol by ditelluratoargentate(III) (DTA) is reported. Both of 1-methoxy-2-propanol and 1-ethoxy-2-propanol which serve as thinners, solvent and dispersant are used in coatings, inks, printing, dyeing, pesticide, cellulose and acrylic acid industry, *etc*. In addition, they can also be used as fuel antifreeze, cleaning agents, the extractant, non-ferrous metal dressing agent and organic synthetic materials *etc*.

EXPERIMENTAL

All the reagents used were A.R. grade. All solutions were prepared with doubly distilled water. Solution of ditellurato-

argentate(III) was prepared and standardized by the method reported earlier[7]. Its UV spectrum was found to be consistent with that reported. The concentration of ditelluratoargentate(III) was derived from its absorption at $\lambda = 351$ nm. The solution of ditelluratoargentate(III) was prepared with double-distilled water before using. The ionic strength μ was maintained by adding the solution of KNO_3 and the pH of the reaction mixture was regulated with the solution of KOH. The kinetic measurements were performed on a UV-VIS 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). None of the other species absorbed significantly at this wavelength.

Kinetics measurements and product analysis: All kinetics measurements were carried out under pseudo-first order conditions. A solution of Ag(III), OH⁻ and $H_4TeO_6^{2-}$ with known concentrations was mixed with an excess of reductants. With the complete fading of ditelluratoargentate(III) colour (reddish brown) marked the completion of the reaction. The product of oxidation was identified as ketone by its charac-teristic spot test[8].

RESULTS AND DISCUSSION

Evaluation of pseudo-first order rate constants: Under the conditions of [reductant]₀ >> [Ag(III)]₀, the plots of ln(A_t-A_∞) *versus* time were straight lines, indicating the reaction is first order with respect to [Ag(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} were calculated by the method of least squares ($r \geq 0.999$). The k_{obs} values were the average values of at least three independent experiments. The reproducibility was within ± 5 %.

Rate dependence on the [reductant]: At fixed concentration of Ag(III), OH⁻, $H_4TeO_6^{2-}$ and ionic strength μ, the values of k_{obs} were determined at different temperatures. The plots of $\ln k_{obs}$ *versus* ln[reductant] were linear ($r \geq 0.997$) and from the slope of such plots, the order with respect to reductant was found to be fractional. The plots of [reductant]/k_{obs} *vs.* [reductant] at different temperatures were straight lines (Figs. 1 and 2).
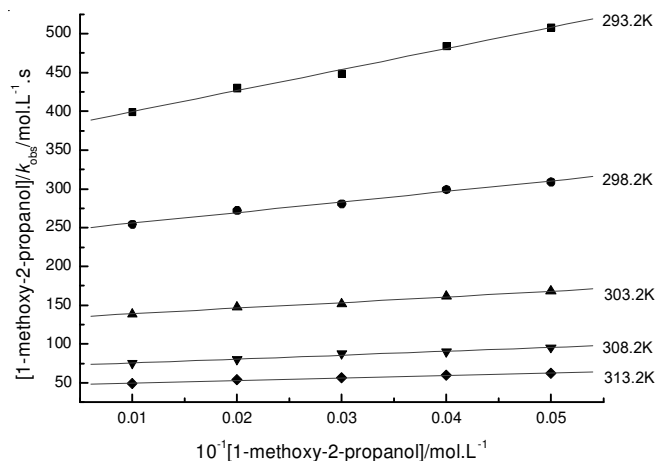

Fig. 1. Plots of [1-methoxy-2-propanol]/k_{obs} *vs.* 10^{-1}[1-methoxy-2-propanol] ($r \geq 0.995$); [Ag(III)] = 4.75×10^{-4} mol L⁻¹, [OH⁻] = 1.00×10^{-2} mol L⁻¹, [$H_4TeO_6^{2-}$] = 1.00×10^{-3} mol L⁻¹, μ = 3.80×10^{-2} mol L⁻¹
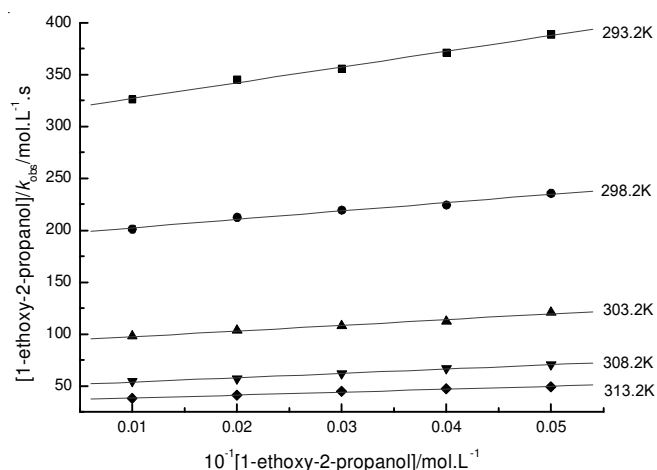
Fig. 2. Plots of [1-ethoxy-2-propanol]/k_{obs} *vs.* 10^{-1}[1-ethoxy-2-propanol] ($r \geq 0.996$); [Ag(III)] = 4.75×10^{-4} mol L⁻¹, [OH⁻] = 1.00×10^{-2} mol L⁻¹, [$H_4TeO_6^{2-}$] = 1.00×10^{-3} mol L⁻¹, μ = 3.80×10^{-2} mol L⁻¹

Rate dependence on the [OH⁻]: At fixed concentrations of Ag(III), $H_4TeO_6^{2-}$, reductant, ionic strength μ and temperature, the value of k_{obs} increased with increasing concentration of OH⁻. The order with respect to [OH⁻] was fractional and the plot of 1/k_{obs} *vs.* 1/[OH⁻] was linear (Fig. 3).

Rate dependence on the [$H_4TeO_6^{2-}$]: At constant [Ag(III)], [reductant], [OH⁻], μ and temperature, the experimental results indicate that k_{obs} decreases while increasing the [$H_4TeO_6^{2-}$]. The order with respect to $H_4TeO_6^{2-}$ was derived to

be an inverse fraction, which reveals that $H_4TeO_6^{2-}$ is produced in equilibrium before the rate-determining step. A plot of 1/k_{obs} *versus* [$H_4TeO_6^{2-}$] was a straight line (Fig. 4).
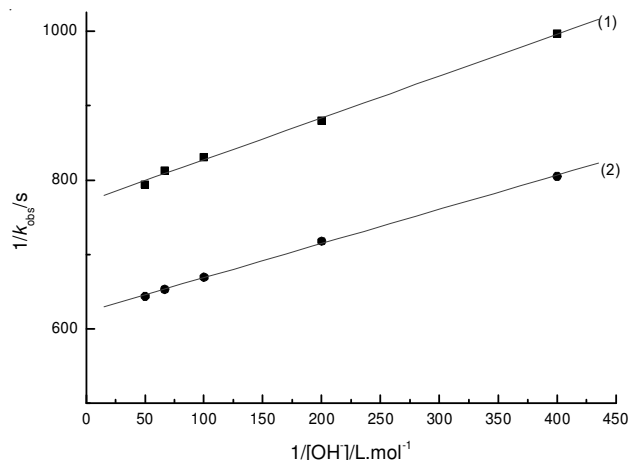

Fig. 3. Plots of 1/k_{obs} *vs.* 1/[OH⁻] at 298.2 K; [Ag(III)] = 4.75×10^{-4} mol L⁻¹, [$H_4TeO_6^{2-}$] = 1.00×10^{-3} mol L⁻¹, μ = 3.80×10^{-2} mol L⁻¹; (1) [1-methoxy-2-propanol] = 3.00×10^{-2} mol L⁻¹ ($r = 0.999$). (2) [1-ethoxy-2-propanol] = 3.00×10^{-2} mol L⁻¹ ($r = 0.999$)
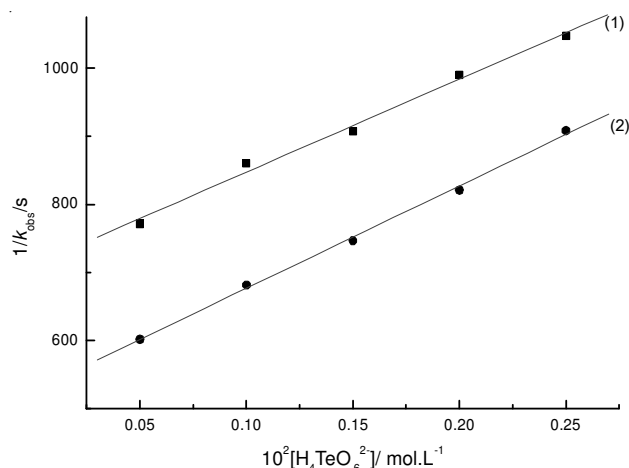
Fig. 4. Plots of 1/k_{obs} *vs.* 10^2[$H_4TeO_6^{2-}$] at 298.2 K; [Ag(III)] = 4.75×10^{-4} mol L⁻¹, [OH⁻] = 1.00×10^{-2} mol L⁻¹, μ = 3.80×10^{-2} mol L⁻¹; (1) [1-methoxy-2-propanol] = 3.00×10^{-2} mol L⁻¹ ($r = 0.998$); (2) [1-ethoxy-2-propanol] = 3.00×10^{-2} mol L⁻¹ ($r = 0.999$).

Rate dependence on the ionic strength: With other conditions fixed, the reaction rate was decreased by the addition of KNO₃ solution (Table-1), which indicate there is negative salt effect, which consistent with the common regulation of the kinetics[9].
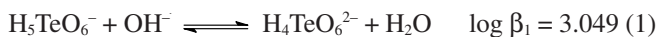
<table>
<tr><td colspan="6" align="center">TABLE-1
RATE DEPENDENCE ON IONIC STRENGTH (μ)</td></tr>
<tr><td colspan="2">10^2μ/ mol L⁻¹</td><td>1.50</td><td>3.00</td><td>4.50</td><td>6.00</td><td>7.50</td></tr>
<tr><td rowspan="2">$10^3 k_{obs}$
/s⁻¹</td><td>1-methoxy-2-propanol</td><td>1.23</td><td>1.20</td><td>1.15</td><td>1.07</td><td>0.91</td></tr>
<tr><td>1-ethoxy-2-propanol</td><td>1.65</td><td>1.56</td><td>1.46</td><td>1.43</td><td>1.37</td></tr>
<tr><td colspan="7">[Ag(III)] = 4.75×10^{-4} mol L⁻¹, [reductant] = 3.00×10^{-2} mol L⁻¹, [OH⁻] = 1.00×10^{-2} mol·L⁻¹, [$H_4TeO_6^{2-}$] = 1.00×10^{-3} mol·L⁻¹</td></tr>
</table>

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

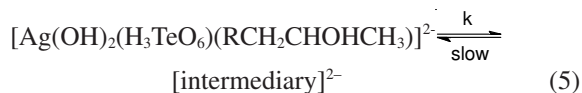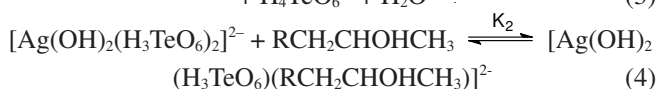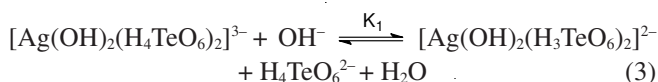$$H_5TeO_6^- + OH^- \rightleftharpoons H_4TeO_6^{2-} + H_2O \quad \log \beta_1 = 3.049 \quad (1)$$
$$H_4TeO_6^{2-} + OH^- \rightleftharpoons H_3TeO_6^{3-} + H_2O \quad \log \beta_2 = -1 \quad (2)$$

The distribution of all species of tellurate in aqueous alkaline solution can be calculated from the equilibriums (1) and (2). In the alkaline medium, [OH$^-$] = 0.01 mol L^{-1}, the equation can be calculated: [$H_4TeO_6^{2-}$]:[$H_5TeO_6^-$]:[$H_3TeO_6^{3-}$] = 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 tellurate species was $H_4TeO_6^{2-}$. According to the literature[11], the main ditelluratoargentate(III) species was [Ag(OH)$_2$(H$_4$TeO$_6$)$_2$]$^{3-}$over the experimental concentration range of [OH$^-$].

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

$$[Ag(OH)_2(H_4TeO_6)_2]^{3-} + OH^- \xrightarrow{K_1} [Ag(OH)_2(H_3TeO_6)_2]^{2-}$$
$$+ H_4TeO_6^{2-} + H_2O \quad (3)$$

$$[Ag(OH)_2(H_3TeO_6)_2]^{2-} + RCH_2CHOHCH_3 \xrightarrow{K_2} [Ag(OH)_2$$
$$(H_3TeO_6)(RCH_2CHOHCH_3)]^{2-} \quad (4)$$

$$[Ag(OH)_2(H_3TeO_6)(RCH_2CHOHCH_3)]^{2-} \xrightarrow[\text{slow}]{k}$$
$$[\text{intermediary}]^{2-} \quad (5)$$

$$[\text{intermediary}]^{2-} \xrightarrow[\text{fast}]{k_f} Ag(I) + RCH_2COCH_3 \quad (6)$$

Reactions (3) and (4) are dissociation and coordination equilibrium, the reaction rates of which are generally fast, reaction (5) is an electron-transfer reaction, the reaction rates of which are generally slow. Hence, reaction (5) is the rate-determining step.

$$-d[Ag(III)]_t/dt = k[\text{intermediary}] \quad (7)$$

[Ag(III)]$_t$ stands for any form of Ag(III) complex, which exists in the equilibrium and stands for both of the reductants.

$$-d[Ag(III)]_t = \frac{kK_1K_2[R'][OH^-]}{K_1K_2[R'][OH^-]+K_1[OH^-]+[H_4TeO_6^{2-}]}$$
$$[Ag(III)]_t = k_{obs}[Ag(III)]_t \quad (8)$$

$$k_{obs} = \frac{kK_1K_2[R'][OH^-]}{K_1K_2[R'][OH^-]+K_1[OH^-]+[H_4TeO_6^{2-}]} \quad (9)$$

Re-arranging equation (9) leads to equation (10-12):

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{[H_4TeO_6^{2-}]+K_1[OH^-]}{kK_1K_2[OH^-]}\frac{1}{[R']} \quad (10)$$

$$\frac{[R']}{k_{obs}} = \frac{[R']}{k} + \frac{[H_4TeO_6^{2-}]+K_1[OH^-]}{kK_1K_2[OH^-]} \quad (11)$$

$$\frac{1}{k_{obs}} = \frac{1+K_2[R']}{kK_2[R']} + \frac{[H_4TeO_6^{2-}]}{kK_1K_2[R'][OH^-]} \quad (12)$$

From the equation (11), the plots [R']/k$_{obs}$ $vs.$ [R'] are straight lines and the rate constants of the rate-determining step at different temperature were obtained from the slope of the straight line. Equation (12) indicates that the plots of 1/k$_{obs}$ $vs.$ 1/[OH$^-$] and 1/k$_{obs}$ $vs.$ [H$_4$TeO$_6^{2-}$] are straight lines. Activation energy and the thermodynamic parameters were evaluated by the method given earlier (Table-2).

Conclusion

Base on the former discussion and results, we can know that the rate constants of the rate-determining step and the activation parameters for 1-methoxy-2-propanol and 1-ethoxy-2-propanol are contiguous. Both of 1-methoxy-2-propanol and 1-ethoxy-2-propanol form the same intermediate compounds with Ag(III) and the rate of 1-ethoxy-2-propanol is a little quicker than that of 1-methoxy-2-propanol. The reason is that electronic ability of ethoxy radical is more than that of methoxy radical and 1-ethoxy-2-propanol and ditelluratoargentate(III) are more likely to form complex.

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