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Kinetics and Mechanism of Oxidation of 1,2-Butanediol by Argentate(III) Complex in Alkaline Medium

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The kinetics of oxidation of 1,2-butanediol by dihydroxyditellutoargentate(III) (DDA) is studied spectrophotometrically. The reaction rate shows first order dependence in DDA and $1 < n_{ap} < 2$ order in 1,2-butanediol. It is found that the pseudo-first order rate constant k_{obs} increases with the increase in concentration of OH^- and decreases with the increase in concentration of TeO_4^{2-}. There is a negative salt effect; no free radical is detected. In view of this, the dihydroxymonotelluratoargentate(III) species is assumed to be the active species. A plausible mechanism involving a two-electron transfer is proposed and the rate equations derived from mechanism explains all experimental results. The activation parameters along with the rate constants of the rate-determining step are calculated.

Keywords: Dihydroxyditellutoargentate(III), 1,2-Butanediol, Redox reaction, Kinetics and mechanism

INTRODUCTION

Transition metals in a higher oxidation state can generally be stabilized by chelation with suitable polydentate ligands in a medium at an appropriate pH. In a strong base medium, the kinetics and mechanism of oxidation of iodide [1], arsenite [2], thiosulfate [3], 4-t-butylphenolate anion [4] by $Ag(OH)_4^-$, have been studied. However, the resultant compounds were metastable and decomposed at room temperature ($[OH^-] = 1.2$ M with a half-life of approximately 1.5 h) [5].

Tetraglycine [6] and *vic*-dioximethe [7] complexes of Ag(III) have been prepared from $Ag(OH)_4^-$. Another Ag(III) complex species, [ethylenebis(biguanide)silver(III)], is stable in aqueous solution over a wide pH range [8], and Ag(III) complexes were stabilized in alkaline medium by periodate or tellurate ions [9]. These type of complexes have been reported as good oxidizing agents for analytical chemistry, such as in the determination of some sugars, carboxylic acid and inorganic ions [10]. The oxidation of a number of organic compounds and lower oxidation state metals by ditelluratoargentate(III) complexes has also been performed [11]. In these reaction systems, the reductants are monohydroxy compounds, and the reductant order is unity. However, in our study reaction system [12], 1,2-butanediols are polyhydroxy compounds, and we found the reaction order to be one to two. So the kinetics system is not perfect and no further information on the kinetics is available. In this paper, the kinetics and mechanism of oxidation of 1,2-butanediol (Butdiol) by dihydroxyditellutoargentate(III) is reported.

EXPERIMENTAL

Materials

All reagents used were of analytical reagent grade. All solutions were prepared with doubly distilled water. A solution of $[Ag(OH)_2(H_4TeO_6)_2]^{3-}$ (DDA), (9.315×10^{-2} M), was

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*Corresponding author. E-mail: huoshuyinger@yahoo.com.cn prepared and standardized by a previously reported method [9], and the UV spectrum was found to be consistent with the report. The concentration of DDA was calculated from its absorption at $\lambda = 351$ nm ($\varepsilon = 1.58 \times 10^3$ l mol^{-1} cm^{-1}). The solution of DDA was freshly prepared before use with doubly-distilled water. The ionic strength (μ) was maintained by adding KNO_3 (1.0 M), and the pH of the reaction mixture was regulated with KOH (1.112×10^{-1}). Measurements of the kinetics were performed using a UV-8500 spectrophotometer (Shanghai) fitted with a 501 thermostat (±0.1 °C, Shanghai).

Kinetics Measurements and Product Analysis

All kinetics measurements were carried out under pseudo-first order conditions, $[\text{1,2-butanediol}]_0 \geqslant [\text{Ag(III)}]_0$. A solution (2 ml) containing a known concentration of Ag(III), OH^-, TeO_4^{2-}, of known ionic strength, and a 1,2-butanediol solution (2 ml) were transferred separately to the upper and lower branch tubes of a two-cell reactor. After thermal equilibration at the desired temperature (±0.1 °C) in a thermobath (Shanghai), the two solutions were mixed well and immediately transferred to a 1 cm rectangular quartz cell in a temperature-regulated cell-holder. The reaction process was monitored automatically by recording the disappearance of the Ag(III) complex over time (*t*) at 351 nm with a UV-8500 spectrophotometer (made in Shanghai). No other species absorbed significantly at this wavelength.

After completion of the reaction, the oxidation product was identified [13] as an hydroxyl aldehyde, which was precipitated as a 2,4-dinitrophenyldrazone derivative and Ag(I), the product of Ag(III) [14].

RESULTS AND DISCUSSION

By gravimetric analysis, we found that one mole of 1,2-butanediol consumed one mole Ag(III). The addition of acrylonitrile or acrylamide to the reaction mixture under a nitrogen atmosphere neither changed the rate nor initiated any polymerization, showing the lack of free radicals in the reaction [15]. Under the employed conditions, a one-step/two-election transfer mechanism is in operation.

Under the conditions of $[\text{1,2-butanediol}]_0 >> [\text{Ag(III)}]_0$, the plots of $\ln(A_t\text{-}A_\infty)$ *vs.* time were straight lines, indicating the reaction is first order with respect to the Ag(III) complex, 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 ($r \geqslant 0.999$). Generally, 8-10 A_t values within three times the half-lives were used to calculate k_{obs} values. The k_{obs} values were the average values of at least three independent experiments. The reproducibility is within ±5%.

At a fixed concentration of $[\text{Ag(III)}] = 9.315 \times 10^{-4}$ M, $[TeO_4^{2-}] = 1.0 \times 10^{-3}$ M, $[OH^-] = 2.0 \times 10^{-2}$ M, $\mu = 2.3 \times 10^{-2}$ M, the values of k_{obs} were determined at different temperatures along with different concentrations of 1,2-butanediol. The k_{obs} values increased with an increase in concentration of 1,2-butanediol at all temperatures. The reaction order in 1,2-butanediol was found to be $1 < n_{ap} < 2$ (Table 1). The plots of $[\text{1,2-butanediol}]/k_{obs}$ *vs.* $1/[\text{1,2-butanediol}]$ were straight lines with a positive intercept.

At fixed concentrations of $[\text{Ag(III)}] = 9.315 \times 10^{-4}$ M, $[OH^-] = 2.0 \times 10^{-2}$ M, $[\text{1,2-butanediol}] = 8.0 \times 10^{-2}$ M, and $\mu = 3.5 \times$

Table 1. $10^3\,k_{obs}$ (s^{-1}) at Different 1,2-Butanediol Concentrations and Different Temperatures

[Butdiol] (M)	2.0×10^{-2}	2.5×10^{-2}	3.3×10^{-2}	5.0×10^{-2}	1.0×10^{-1}	a[a]	R[a]
T (K)							
298.2	3.161	4.294	6.266	10.66	24.27	1.26	0.999
303.2	4.565	5.970	8.766	14.46	3.235	1.22	0.999
308.2	6.273	8.540	12.25	20.33	44.29	1.21	0.999
313.2	9.300	12.38	17.38	28.42	62.24	1.18	0.999

[a] a and R stand for the slope and relative coefficient, respectively, of the plot of $\ln k_{obs}$ *vs.* $\ln[\text{1,2-butanediol}]$.

10^{-2} M and T = 303.2 K, the values of k_{obs} were determined. The value of k_{obs} decreased with the increase in concentration of $H_4TeO_6^{2-}$. The plots of $1/k_{obs}$ *vs*. $H_4TeO_6^{2-}$ were straight lines with positive intercepts (Table 2).

At fixed concentrations of [Ag(III)] = 9.315×10^{-4} M, $[H_4TeO_6^{2-}] = 1.0 \times 10^{-3}$ M, [1,2-butanediol] = 8.0×10^{-2} M, and $\mu = 5.3 \times 10^{-2}$ M and T = 303.2 K, the value of k_{obs} increased with the increase in concentration of OH^-. The orders with respect to OH^- were found to be fractional .The plots of $1/k_{obs}$ *vs*. $1/[OH^-]$ were staight lines ($r \geq 0.99$) (Table 3).

At fixed concentrations of [Ag(III)] = 9.315×10^{-4} M $[H_4TeO_6^{2-}] = 1.0 \times 10^{-3}$ M, $[OH^-] = 2.0 \times 10^{-2}$ M, [1,2-butanediol] = 8.0×10^{-2} M, and T = 303.2 K, the value of k_{obs} decreased with an increase in $[KNO_3]$ (Table 4), which indicates that there was a negative salt effect.

REACTION MECHANISM

In an alkaline medium, the electric dissociation equilibrium of telluric acid is $pK_w = 14$ [16].

$$H_5TeO_6^- + OH^- \rightleftharpoons H_4TeO_6^{2-} + H_2O \quad \log\beta_1 = 3.05 \quad (1)$$

$$H_4TeO_6^{2-} + OH^- \rightleftharpoons H_3TeO_6^{3-} + H_2O \quad \log\beta_2 = -1.00 \quad (2)$$

The distribution of all species of tellurate in aqueous alkaline solution can be calculated from the equilibriums (1) and (2). In an alkaline medium, $[OH^-] = 0.01$ M, the equation can be calculated: $([H_4TeO_6^{2-}]:[H_5TeO_6^-]:[H_3TeO_6^{3-}] = 1000:89:1)$. Hence, 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 [12], the main DDA species was $[Ag(OH)_2(H_4TeO_6)_2]^{3-}$ over the experimental concentration range of $[OH^-]$.

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

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

$$[Ag(OH)_2(H_3TeO_6)]^{2-} + Butdiol \xrightleftharpoons{K_2} [Ag(OH)_2(H_3TeO_6)]^{2-}\cdot[Butdiol] \quad (4)$$

$$[Ag(OH)_2(H_3TeO_6)]^{2-}\cdot[Butdiol] + Butdiol \xrightarrow[slow]{k} [Ag(OH)_2(H_3TeO_6)(Butdiol)]^{2-}[Butdiol] \quad (5)$$

$$[Ag(OH)_2(H_3TeO_6)(Butdiol)]^{2-}[Butdiol] \xrightarrow{fast} Ag(I) + RCHO + Butdiol + H_4TeO_6^{2-} + OH^- + H_2O \quad (6)$$

Table 2. Rate Dependence on $[H_4TeO_6^{2-}]$

$10^3\,[H_4TeO_6^{2-}]$ (M)	1.0	2.0	3.0	4.0	5.0	C[a]	r[a]
$10^2\,k_{obs}\,(s^{-1})$	2.58	1.83	1.55	1.34	1.21	-0.47	0.999

[a]c and r stand for the slope and relative coefficient, respectively, of the plot of $\ln k_{obs}$ *vs*. $\ln[H_4TeO_6^{2-}]$.

Table 3. Rate Dependence on $[OH^-]$

$10^2\,[OH^-]$ (M)	1.00	1.25	1.67	2.50	5.00	[a]d	[a]r
$10^2\,k_{obs}\,(s^{-1})$	1.48	1.73	2.07	2.56	3.22	0.48	0.999

[a]d and r stand for the slope and relative coefficient, respectively, of the plot of $\ln k_{obs}$ *vs*. $\ln[OH^-]$.

Table 4. Rate Dependence on Ionic Strength

$10^2\,[\mu]$ (M)	2.3	4.6	6.9	9.2	11.5
$10^2 k_{obs}\,(s^{-1})$	2.45	2.04	1.88	1.86	1.75

Reaction (3) and (4) are dissociation and coordination equilibria, the reaction rates of which are generally fast; reaction (5) is one of the electron-transfer reactions, which generally have slow reaction rates, so reaction (5) is the rate-determining step.

$$-d[\mathrm{Ag(III)}]_t/dt = k[\mathrm{Adduct}]\,[\mathrm{Butdiol}]$$

where $[\mathrm{Ag(III)}]_t$ stands for any form of Ag(III) complex which exists in the equilibrium.

$$-d[\mathrm{Ag(III)}]_t/dt = \frac{kK_1K_2[\mathrm{OH^-}][\mathrm{Butdiol}]^2}{[\mathrm{H_4TeO_6}^{2-}] + K_1[\mathrm{OH^-}] + K_1K_2[\mathrm{OH^-}][\mathrm{Butdiol}]}[\mathrm{Ag(III)}]_t$$

$$= k_{\mathrm{obs}}[\mathrm{Ag(III)}]_t \tag{7}$$

$$\frac{1}{k_{\mathrm{obs}}} = \frac{K_1 + K_1K_2[\mathrm{Butdiol}]}{kK_1K_2[\mathrm{Butdiol}]^2} + \frac{[\mathrm{H_4TeO_6}^{2-}]}{kK_1K_2[\mathrm{Butdiol}]^2[\mathrm{OH^-}]} \tag{8}$$

$$\frac{[\mathrm{Butdiol}]}{k_{\mathrm{obs}}} = \frac{1}{k} + \frac{K_1[OH] + [H_4TeO_6^{2}\ ]}{kK_1K_2[OH]}\frac{1}{[\mathrm{Butdiol}]} \tag{9}$$

$$\frac{1}{k_{\mathrm{obs}}} = \frac{K_1 + K_1K_2[\mathrm{Butdiol}]}{kK_1K_2[\mathrm{Butdiol}]^2} + \frac{[\mathrm{H_4TeO_6}^{2-}]}{kK_1K_2[\mathrm{Butdiol}]^2[\mathrm{OH^-}]} \tag{10}$$

From equation (9), plots of [1,2-butanediol]/k_{obs} *vs.* 1/[1,2-butanediol] should be straight lines, which is consistent with the experimental phenomena. The rate constants of the rate-determining step, 0.28, 0.359, 0.49, and 0.675, were obtained from the intercept of the straight lines at 298.2, 303.2, 308.2, and 313.2 K. Equation (10) suggests that a plot of 1/k_{obs} *vs.* $[\mathrm{H_4TeO_6}^{2-}]$ is a straight line, which is also consistent with the experimental phenomena. The activation energy and the thermodynamic parameters, $E\mathrm{a}$ = 46.28 kJ mol^{-1}, $\triangle H^{\ddagger}$ = 43.8 kJ mol^{-1}, $\triangle S^{\ddagger}$ = -110.5 J mol^{-1} K^{-1}, were evaluated by a previously published method [17]. In the reaction, the Ag(III) complex and OH$^-$ combine to form the DMA complex in Eq. 3. DMA and 1,2-butanediol then form the adduct complex in Eq. 4, which means the entropy is reduced, so $\triangle S^{\ddagger}$ has a negative value. $\triangle H^{\ddagger}$ has a positive value, so the rate of this reaction increases with the increase in temperature, which is consistent with the experimental phenomena (Table 1).

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