

Kinetics and Mechanism of Oxidation of 1,3–Butylene Glycol by Dihydroxyditelluratoargentate(III) in Alkaline Medium

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The kinetics of oxidation of 1,3-butylene glycol (β – BG) by dihydroxyditelluratoargentate(III) were studied spectrophotometrically between 298.2 and 313.2 K in alkaline medium. The reaction rate showed pseudo-first order dependence in oxidant and fractional order in β -BG. The pseudo-first order rate constant k_{obs} increased with an increase in the concentration of OH^- and a decrease in the concentration of TeO_4^{2-} . There was a negative salt effect and no free radicals were detected. Thus, the dihydroxy-monotelluratoargentate(III) species is assumed to be the active species. The activation parameters along with the rate constants of the rate-determining step were calculated.

Key Words: Dihydroxyditelluratoargentate(III), 1,3–Butylene glycol, Redox reaction, Kinetics and mechanism.

Introduction

The study of the highest oxidation state of transition metals has intrigued many researchers recently. Transition metals in a higher oxidation state generally can be stabilized by chelation with suitable polydentate ligands. Metal chelates such as diperiodatoargentate(III)¹, ditellurargentate(III)², ditelluratocuprate(III)³ and diperiodat-onickelate(IV)⁴ are good oxidants in a medium with an appropriate pH value. 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 performed³, but no further information on the kinetics is available. In this paper, the mechanism of oxidation of β – BG by dihydroxyditelluratoargentate(III) is reported.

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Chemicals and apparatus

All reagents used were of A.R. grade. All solutions were prepared with twice distilled water. Solutions of dihydroxyditelluroargentate(III) and $\beta - BG$ were always freshly prepared before use. The stock solution of dihydroxyditelluroargentate(III) in a strong alkaline medium was prepared and standardized by the method reported earlier⁷. The concentration of dihydroxyditelluroargentate(III) was derived by its absorption at $\lambda = 351$ nm. The ionic strength was maintained by adding KNO_3 solution and the pH value was regulated with KOH solution.

All kinetics measurements were carried out under pseudo-first order conditions. A solution (2 mL) containing concentrations of $[Ag(III)]$, $[OH^-]$ and $[TeO_4^{2-}]$ with ionic strength μ and a reductant solution (2 mL) of an appropriate concentration were transferred separately to the upper and lower branch tubes of a type 2-cell reactor. After thermal equilibration at the desired temperature in a thermobath (made in Shanghai), the 2 solutions were mixed well and immediately transferred to a 1 cm rectangular cell quartz in a constant temperature cell-holder (± 0.1 °C). The reaction process was monitored automatically by recording the disappearance of Ag(III) with time (t) at 351 nm with a UV-8500 spectrophotometer (made in Shanghai). All other species did not absorb significantly at this wavelength.

After completion of the reaction, the oxidation product was identified⁸ as an aldehyde alcohol, precipitated as 2,4-dinitrophenylhydrazone derivative. By gravimetric analysis, it was found that 1 mol of reductant consumed 1 mol of Ag(III).

Results and Discussion

Evaluation of pseudo-first-order rate constants

Under the conditions of $[Reductant]_{0i} \ll [Ag(III)]_0$. The plots of $\ln(A_t - A_{\infty})$ versus time are 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 least-squares method ($re \geq 0.999$). To calculate k_{obs} generally 8-10 A_t values within 3 times the half-life were used. k_{obs} values were at least averaged values of three independent experiments and reproducibility was within $\pm 5\%$.

Rate dependence on $[\beta - BG]$

At fixed $[Ag(III)]$, $[OH^-]$, $[TeO_4^{2-}]$, ionic strength μ and temperature, k_{obs} values increased with the increase in $[\beta - BG]$ and the order in $[\beta - BG]$ was found to be fractional (Table 1). The plots of $1/k_{obs}$ vs. $1/[\beta - BG]$ are straight lines with a positive intercept ($re \geq 0.999$) (Figure).

Table 1. $10^3 k_{obs} / s^{-1}$ varying with different $[\beta - BG]$ at different temperatures $[Ag(III)] = 4.658 \times 10^{-4}$ mol/L; $[TeO_4^{2-}] = 0.001$ mol/L; $[OH^-] = 0.02$ mol/L; $\mu = 0.04$ mol/L.

C(mol/L)	0.1	0.125	0.16	0.25	0.5	b	r
T(K)							
298.2	3.053	3.731	4.726	6.466	11.44	0.811	0.999
303.2	4.968	5.94	7.269	10.35	17.32	0.777	0.999
308.2	7.552	8.913	10.6	15.16	25.48	0.759	0.999
313.2	11.71	13.97	16.89	22.38	34.69	0.668	0.999

b and r respectively stand for the slope and the relative coefficient of the plot of $\ln k_{obs}$ vs. $\ln C$

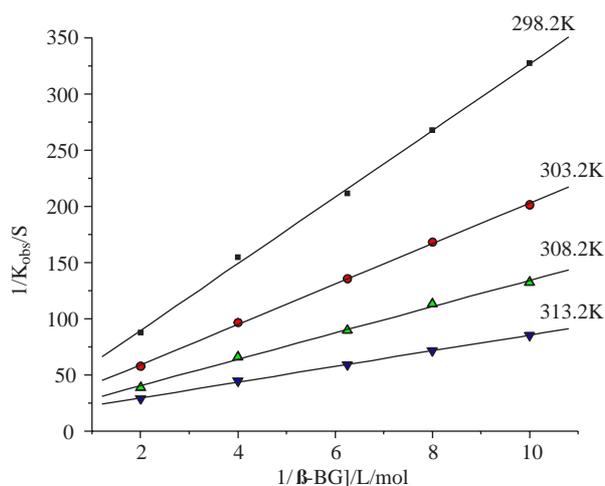


Figure. The plots of $1/k_{obs}$ vs. $1/[\beta - BG]$ at different temperatures $[Ag(III)]=4.658 \times 10^{-4}$ mol/L; $[TeO_4^{2-}] = 0.001$ mol/L; $[OH^-]=0.02$ mol/L; $\mu=0.04$ mol/L.

Rate dependence on $[TeO_4^{2-}]$

At fixed $[Ag(III)]$, $[OH^-]$, $[\beta - BG]$, ionic strength μ and temperature, k_{obs} decreased with the increase in $[H_4TeO_6^{2-}]$. The plots of $1/k_{obs}$ vs. $[H_4TeO_6^{2-}]$ are straight lines with a positive intercept ($r \geq 0.999$) (Table 2).

Table 2. $10^2 k_{obs} / s^{-1}$ varying with different $[TeO_4^{2-}]$ at 303.2 K $[Ag(III)]=4.658 \times 10^{-4}$ mol/L; $[\beta - BG]=0.4$ mol/L; $[OH^-]=0.02$ mol/L; $\mu=3.35 \times 10^{-2} \times 10^{-4}$ mol/L.

$10^3 [TeO_4^{2-}] / mol/L$	0.9	1.5	2.5	3.5	4.5	b	r
$10^2 k_{obs} / s^{-1}$	1.613	1.368	1.089	0.902	0.785	0.45	0.994

b and r respectively stand for the slope and the relative coefficient of the plot of $\ln k_{obs}$ vs. $\ln C$

Rate dependence on $[OH^-]$ and ionic strength μ

At fixed $[Ag(III)]$, $[H_4TeO_6^{2-}]$, $[\beta - BG]$, ionic strength μ and temperature. k_{obs} increased with the increase in $[OH^-]$. The plots of $1/k_{obs}$ vs. $1/[OH^-]$ are lines ($r \geq 0.999$) (Table 3). The rate decreased feebly with the addition of KNO_3 solution (Table 4), which indicates a negative salt effect consistent with the common regulation of the kinetics⁹.

Table 3. $10^2 k_{obs} / s^{-1}$ varying with different $[OH^-]$ at 303.2 K $[Ag(III)]=4.658 \times 10^{-4}$ mol/L; $[\beta - BG]=0.4$ mol/L; $[TeO_4^{2-}]=0.001$ mol/L; $\mu=5.30 \times 10^{-2} \times 10^{-4}$ mol/L.

$10^2 [OH^-] / mol/L$	1.0	1.25	1.67	2.5	5.0	b	r
$10^2 k_{obs} / s^{-1}$	1.136	1.206	1.293	1.390	1.482	0.2	0.996

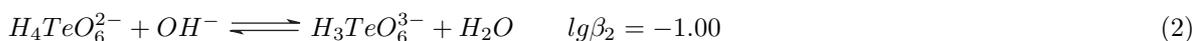
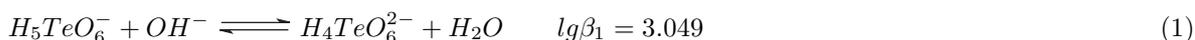
b and r respectively stand for the slope and the relative coefficient of the plot of $\ln k_{obs}$ vs. $\ln C$

Table 4. $10^2 k_{obs} / s^{-1}$ varying with different μ at 303.2 K [Ag(III)]= 4.658×10^{-4} mol/L; $[TeO_4^{2-}] = 0.001$ mol/L; $[OH^-] = 0.02$ mol/L; $[\beta - BG] = 0.4$ mol/L.

$10 \mu / \text{mol/L}$	0.3	0.6	0.9	1.2	1.5
$10^2 k_{obs} / s^{-1}$	1.753	1.504	1.361	1.274	1.197

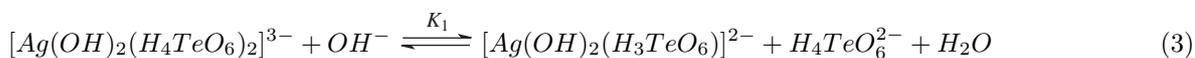
Free radical detection and the mechanism

In the alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier¹⁰ (here $pK_w = 14$)



The distribution of all species of tellurate in aqueous alkaline solution can be calculated from equilibria (1)-(2). In alkaline medium such as $[OH^-] = 0.1-0.01$ mol·L⁻¹, $[H_4TeO_6^{2-}]:[H_5TeO_6^-]:[H_3TeO_6^{3-}]L \cong 1000-100:89.3-0.893:1$, and so in the concentration of OH^- range used in this work, $H_5TeO_6^-$ and $H_3TeO_6^{3-}$ can be neglected, and the main tellurate species is $[H_4TeO_6^{2-}]$. According to a previous report¹¹ the main species was $[Ag(OH)_2(H_4TeO_6)_2]^{3-}$ over the experimental range of $[OH^-]$.

The addition of acrylonitrile or acrylamide to the reaction mixture under nitrogen atmosphere neither changed the rate nor initiated any polymerization, showing no free radicals in the reaction. In our study, we also think there was a similar type of 1-step 2-electron transfer mechanism. According to the above experimental facts, we present the mechanism of the reaction below:



Reactions (3) and (4) belong to dissociation and coordination equilibrium, whose reaction rates are generally faster. Reaction (5) belongs to a electron-transfer reaction, whose reaction rate is generally slower, and so reaction (5) is the rate-determining step.

$$-d[Ag(III)]_t/dt = k[adduct]^{2-}$$

where $[Ag(III)]_t$ stands for any kind of form of Ag(III) complexes that existed in equilibrium.

$$\begin{aligned} -d[Ag(III)]_t/dt &= \frac{kK_1K_2[OH^-][CH_3CH_2OHCH_2CH_2OH]}{[H_4TeO_6^{2-}] + K_1[OH^-] + K_1K_2[OH^-][CH_3CH_2OHCH_2CH_2OH]} [Ag(III)]_t \\ &= k_{obs}[Ag(III)]_t \end{aligned} \quad (7)$$

$$k_{obs} = \frac{kK_1K_2[OH^-][CH_3CH_2OHCH_2CH_2OH]}{[H_4TeO_6^{2-}] + K_1[OH^-] + K_1K_2[OH^-][CH_3CH_2OHCH_2CH_2OH]} \quad (8)$$

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{K_1[OH] + [H_4TeO_6^{2-}]}{kK_1K_2[OH]} \frac{1}{[CH_3CH_2OHCH_2CH_2OH]} \quad (9)$$

$$\frac{1}{k_{obs}} = \frac{K_1 + K_1K_2[CH_3CH_2OHCH_2CH_2OH]}{kK_1K_2[CH_3CH_2OHCH_2CH_2OH]} + \frac{[H_4TeO_6^{2-}]}{kK_1K_2[CH_3CH_2OHCH_2CH_2OH][OH^-]} \quad (10)$$

From equation (9), the plots of $1/k_{obs}$ vs. $1/[\beta - BG]$ are straight lines and the rate constants of the rate-determining step at different temperatures were obtained from the intercept of the straight line. Equation (10) suggests that the plot of $1/k_{obs}$ vs. $[H_4TeO_6^{2-}]$ is a straight line. Activation energy and the thermodynamic parameters were evaluated by the method given earlier¹² (Table 5).

Table 5. Rate constants (k) and activation parameters of the rate-determining step.

Constants	T/K				Activation parameters (298.2 K)		
	298.2	303.2	308.2	313.2	E_a (KJ/mol)	$\Delta H^\#$ (KJ/mol)	$\Delta S^\#$ (J/mol)
$10^2 k/s^{-1}$							
argentate (III)	3.286	4.280	5.447	6.417	35.12±0.534	32.64±0.534	-163.7±0.686
cuprate(III)	0.904	1.566	2.182	3.345	66.45±4.2	63.97±4.2	-69.24±5.1

The plot of $\ln k$ vs. $1/T$ have the following intercept (a) slope (b) and relative coefficient (r) argentate (III): a=10.766 b=-4223.939.

Based on the above discussion and comparing to our previous work⁸ and the reactions mechanism of the argentate(III) and cuprate(III), we know that rate constants (k) of the rate-determining step of argentate(III) are bigger than those of cuprate(III). We think that the oxidations of the reductant by dihydroxyditelluroargentate(III) take place by an inner-sphere mechanism, unlike dihydroxyditellurocuprate(III), which reacts by an outer-sphere mechanism. In the alkaline solutions dihydroxyditelluroargentate(III) reacts faster than the corresponding reactions with dihydroxyditellurocuprate(III), so the reactions by an inner-sphere mechanism path react faster than the reactions by an outer-sphere mechanism path in this medium, which is in keeping with the previous viewpoint¹³. Our work can also prove it.

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