Kinetics and mechanism of oxidation of diethylene glycol by dihydroxyditellutoargentate (III) in alkaline medium

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The kinetics of oxidation of diethylene glycol (DG) by dihydroxyditelluratoargentate(III) (DDA) is studied spectrophotometrically between 298.2K and 313.2K in alkaline medium. A mechanism involving a one–step two–electron transfer has been proposed The activation parameters and the rate constants of the rate-determining step are calculated.

Recently, study of chemistry of the highest oxidation state of transition metals has intrigued many researchers. Transition metals in a higher oxidation state generally can be stabilised by chelation with suitable polydentate ligands. Metal chelates such as ditelluratoargentate(III)[1] and ditelluratocuprate(III)[2] are good oxidants in a medium with an appropriate pH value. The use of complexes as an oxidant in analytical chemistry has been reported,[3,4] but no further information on the kinetics is available. In this paper, the mechanism of oxidation of DG by DDA is reported.

Chemicals and apparatus

All reagents were of A.R. grade. All solutions were prepared with twice-distilled water. Solutions of DDA and DG were prepared freshly. The stock solution of DDA in a strong alkaline medium was prepared and standardised by the method reported earlier.[5] The concentration of DDA was derived by its absorption at λ=351nm. The ionic strength was maintained by adding KNO_3 solution and the pH value was regulated with KOH solution.

Measurements of the kinetics were performed using a UV-8500 spectrophotometer (Shanghai) fitted with a 501 thermostat ($\pm$0.1K,Shanghai). Details of the determinations were described elsewhere.[6]

Product analysis and stoichiometry

The oxidation product as the corresponding aldehyde was identified by a spot test.[7] Solutions having known concentrations of Ag(III) were mixed with an excess of DG. The completion of the reaction was marked by the complete disappearance of the Ag(III) colour. After completion of the reaction, the product was transformed into a precipitated 2,4-dinitro-phenyl hydrazine derivative. It was found that one mole of DG consumed one mole of Ag(III) by weight.

Results and discussion

Evaluation of pseudo-first order rate constants:
Under the conditions of $[Reductant]_0 >> [Ag(III)]_0$, the plots of $\ln(A_t-A_\infty)$ versus time are linear, indicating that 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 ($r\geq0.999$). To calculate k_{obs} generally 8–10 A_t values within three times of the half-life were used. k_{obs} values of three independent experiments were averaged at least and reproducibility is within $\pm5\%$.

Rate dependence on [DG]: At fixed $[Ag(III)]$, $[OH^-]$, $[H_4TeO_6^{2-}]$, ionic strength μ and temperature, k_{obs} values increased with the increase of [DG]. The plots of k_{obs} versus [DG]

are straight lines which pass though the grid origin, so indicating that the reaction is first order in DG (Table1).

Rate dependence on $[TeO_4^{2-}]$: At fixed $[Ag(III)]$, $[OH^-]$, $[DG]$, ionic strength μ and temperature, k_{obs} values decreased with increase of $[H_4TeO_6^{2-}]$.The plots of $1/k_{obs}$ versus $[H_4TeO_6^{2-}]$ are straight lines with a positive intercept (Table 2).

Rate dependence on $[OH^-]$ and ionic strength μ: At fixed $[Ag(III)]$, $[H_4TeO_6^{2-}]$, $[DG]$, ionic strength μ and temperature, k_{obs} values increased with increase of $[OH^-]$.The plot of $1/k_{obs}$ versus $1/[OH^-]$ is linear (Table 3). The rate does not change by the addition of KNO_3 solution (Table 4), which indicate there is no salt effect, which is consistent with the common regulation of the kinetics.[8]

Table 1 $10^3 k_{obs}/s^{-1}$ varying with different [DG] at different temperatures

$[Ag(III)]=1.511\times10^{-3}mol/l; [TeO_4^{2-}]=9\times10^{-4}mol/l; [OH^-]=1.5\times10^{-2}$ mol/l;μ=0.018mol/l

C(mol/l)	0.02	0.04	0.06	0.08	0.1
T(K)					
298.2	3.321	7.257	11.21	15.46	18.73
303.2	5.681	10.97	17.52	22.96	28.88
308.2	7.488	16.22	23.58	31.19	39.83
313.2	7.497	18.18	26.94	34.43	43.23

Table 2 $10^3 k_{obs}/s^{-1}$ varying with different $[TeO_4^{2-}]$ at different temperatures

$[Ag(III)]=1.511\times10^{-3}mol/l;$ $[DG]=0.04mol/l;[OH^-]=0.04mol/l;$ μ=0.06mol/l

C(mol/l)	0.001	0.002	0.003	0.004	0.005
T (K)					
298.2	14.46	11.45	8.881	7.764	6.257
303.2	21.31	15.81	12.52	10.24	8.296
308.2	28.98	22.03	16.99	13.94	11.71
313.2	45.88	32.24	22.38	18.98	15.29

Table 3 $10^2 k_{obs}/s^{-1}$ varying with different $[OH^-]$ at 303.2K
$[Ag(III)]=1.511\times10^{-3}mol/l;[DG]=0.05mol/l;[TeO_4^{2-}]=9\times10^{-4}mol/l;$ μ=0.053mol/l

$10^2[OH^-]/mol/l$	1.0	2.0	3.0	4.0	5.0
$10^2 k_{obs}/s^-$	1.105	1.632	1.919	2.081	2.357

Table 4 $10^2 k_{obs}/s^{-1}$ varying with different μ at 303.2K
$[Ag(III)]=1.511\times10^{-3}mol/l;[TeO_4^{2-}]=9\times10^{-4}mol/l;[OH^-]=0.02mol/l;$ $[DG]=0.03mol/l$

$10 \mu/mol/l$	0.023	0.04	0.06	0.08	0.1
$10^2 k_{obs}/s^-$	1.672	1.688	1.684	1.688	1.685

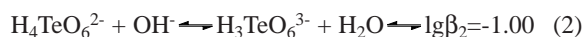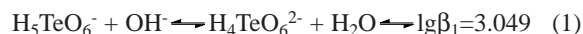* Correspondence. E-mail: shanjinhuaner@yahoo.com

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

Constants	T/K				Activation parameters (298.2K)		
	298.2	303.2	308.2	313.2	E_a(KJ/mol)	$\Delta H^{\#}$ (KJ/mol)	$\Delta S^{\#}$(J/(mol K))
k/(mol^{-1}/l/s^{-1})	0.559	0.921	1.286	2.414	73.23±0.73	48.44±0.73	−12.62±0.73

The plot of ln$k$ vs $1/T$ has following intercept (a) slope (b).
argentate (III):a=28.94 b=−8808.
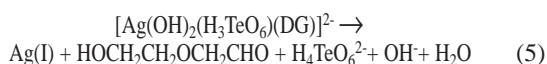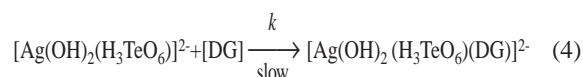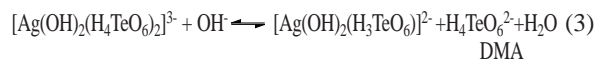
Free radical detection and the mechanism

In the alkaline medium (where pK_w=14), the dissociation equilibrium of telluric acid was given earlier [9] as:

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

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

The distribution of all species of tellurate in aqueous alkaline solution can be calculated from equilibria(1) and (2). In alkaline medium such as [OH$^-$]=0.1–0.01mol l^{-1}, [H$_4$TeO$_6^{2-}$]:[H$_5$TeO$_6^-$]:[H$_3$TeO$_6^{3-}$]≅1000-100:89.3–0.893:1, so in the OH$^-$ concentration range used in this work, H$_5$TeO$_6^-$ and H$_3$TeO$_6^{3-}$ can be neglected, the main tellurate species is [H$_4$TeO$_6^{2-}$]. According to a report[10] the main tellurium species is [Ag(OH)$_2$(H$_4$TeO$_6$)$_2^{3-}$] over the experimental range of [OH$^-$].

The fractional and inverse fractional order dependence of k_{obs} on [OH$^-$] and [TeO$_4^{2-}$] respectively indicate that OH$^-$ ions would be present in a preequilibrium with DDA, and then [Ag(OH)$_2$(H$_4$TeO$_6$)$_2^{3-}$](DDA) loses a H$_4$TeO$_6^{2-}$ ligand from its coordination sphere forming a transition complex [Ag(OH)$_2$(H$_3$TeO$_6$)]$^{2-}$ (DMA), which is the active species of the Ag complex.

The addition of acrylonitrile or acrylamide to the reaction mixture under N$_2$ neither changed the rate nor initiated any polymerisation, showing no free radical in the reaction. In our study, we also believe a similar type of a one-step two-electron transfer mechanism[11] operates. According to the above experimental facts, we suggest that the mechanism of the reaction is as below:

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

$$[Ag(OH)_2(H_3TeO_6)]^{2-} + [DG] \xrightarrow[\text{slow}]{k} [Ag(OH)_2(H_3TeO_6)(DG)]^{2-} \quad (4)$$

$$[Ag(OH)_2(H_3TeO_6)(DG)]^{2-} \rightarrow$$
$$Ag(I) + HOCH_2CH_2OCH_2CHO + H_4TeO_6^{2-} + OH^- + H_2O \quad (5)$$

Reaction (3) involving dissociation and deprotonation, whose reaction rates are generally fast.[8] Reaction (4) is an electron-transfer reaction, whose reaction rate is generally slow, so reaction (4) is the rate-determining step. Thus we have for the kinetic equations:

$$-d[Ag(III)]_t/dt=k[DMA]_e[DG] \quad (6)$$

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

$$-d[Ag(III)]_t/dt = \frac{kK[OH^-][DG]}{[H_4TeO_6^{2-}]+K_1[OH^-]} [Ag(III)]_t=k_{obs}[Ag(III)]_t \quad (7)$$

$$\frac{1}{k_{obs}} = \frac{1}{k[DG]} + \frac{1}{kK[DG]} \frac{[H_4TeO_6^{2-}]}{[OH^-]} \quad (8)$$

From equation (8), the plots of $1/k_{obs}$ vs. [H$_4$TeO$_6^{2-}$] are straight lines and the rate constants of the rate-determining step at different temperature are obtained from the intercept of the straight line. Activation energy and the thermodynamic parameters are calculated by the method given earlier[12] (Table 5).

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