Kinetics of oxidation of 1,4-butylene glycol by dihydroxydiperiodatoargentate(III) in alkaline medium

Jin-Huan Shan*, Sheng-Min Li, Shu-Ying Huo, Wen-Jie Zhao, Shi-Gang Shen and Han-Wen Sun

Key Laboratory of Analytical Science and Technology of Hebei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P R China

Kinetics of oxidation of 1,4-butylene glycol by dihydroxydiperiodatoargentate(III) in alkaline liquid has been investigated by spectrophotometry in the 298.2–318.2K range. The order in oxidant was pseudo first order and the order with respect to 1,4-butylene glycol was $1<n_{ap}<2$. The associated rate law was: $-d[Ag(III)]_t/dt = \{kK_1K_2[OH^-][HOCH_2CH_2CH_2CH_2OH]^2[Ag(III)]_t\}/\{[H_2IO_4^{3-}] + K_1[OH^-] + K_1K_2[OH^-][HOCH_2CH_2CH_2CH_2OH]\} = k_{obs}[Ag(III)]_t$. A plausible mechanism involving a pre-equilibrium of adduct formation between the complex and reductant was proposed. The activation parameters along with rate constants of the rate-determining step were calculated.

Keywords: 1,4-butylene glycol(BDO), dihydroxydiperiodatoargentate(III)(DPA), kinetics, reaction mechanisms, redox reactions

Transition metals in a higher oxidation state can generally be stabilised by chelation with suitable polydentate ligands. Metal chelates in the highest oxidation state such as dihydroxyditellutoargentate(III),[1] diperiodatonickelate(IV)[2] are good oxidants in a medium with an appropriate pH value. In addition, 1,4-butylene glycol is a basic material in chemical industry, which can be used to produce tetrahydrofuran, polybutylene terephthalate, butyrolactone and polyurethane. Understanding of the mechanisms of oxidation of 1,4-butylene glycol by some transition metals in a higher oxidation state will provide a theoretical foundation for the design of reaction routes in organic synthesis and provide us with more dynamical parameters. In this paper, the kinetics and a plausible mechanism of oxidation of 1,4-butylene glycol by DPA are reported.

Experimental

All reagents used were of A.R. grade and were prepared using doubly distilled water. The solution of DPA was prepared and standardised by the method reported earlier.[3] The concentration of DPA was derived from its absorption at $\lambda = 362$nm. The solution of DPA was always freshly prepared. The ionic strength μ was maintained by adding aqueous KNO_3 and the pH value was regulated with KOH solution. The apparatus and kinetics measurements were described previously.[4]

Results

Under the conditions of $[Reductant]_0 >> [Ag(III)]_0$, the plots of $\ln(A_t - A_\infty)$ versus time were linear, indicating that the reaction was pseudo-first-order with respect to [Ag(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 ($r \geq 0.999$). Generally 8–10 A_t values within three times the half-life were used to calculate k_{obs}. k_{obs} values of at least three independent experiments were averaged and reproducibility is within ±5 %.

k_{obs} values increased with an increase in [reductant] at constant [Ag(III)], $[OH^-]$, $[IO_4^-]$, ionic strength and temperature. (Table 1). The plots of $[BDO]/k_{obs}$ versus 1/[BDO] were straight linear with a positive intercept, so indicating that the reaction order was $1< n_{ap} <2$.

At constant [Ag(III)], [reductant], $[IO_4^-]$, ionic strength and temperature, k_{obs} values increased with an increase in $[OH^-]$ (Table 2), the plots of $1/k_{obs}$ versus $f([OH^-])/[OH^-]$ were linear ($r = 0.998$) and the order with respect to $[OH^-]$ was found to be fractional ($n_{ap} = 0.71$, $r = 0.995$). At constant [Ag(III)], [reductant], $[OH^-]$, ionic strength and temperature, k_{obs} values decreased with an increase in $[IO_4^-]$ (Table 2), the plot of $1/k_{obs}$ versus $[IO_4^-]_{ex}$ were linear and the order with respect to $[IO_4^-]_{ex}$ was found to be fractional order ($n_{ap} = -0.50$, $r = -0.993$). The rate decreased upon the addition of aqueous KNO_3 (Table 2), and the plot of $\log k_{obs}$ versus $I^{1/2}$ was linear with negative slope ($r = 0.999$), which is consistent with the negative salt effect.[5]

The addition of acrylonitrile to the reaction mixture under a N_2 atmosphere neither changed the rate nor initiated any polymerisation, which showed that there was no free radical in the reaction. The products were the corresponding aldehyde alcohols determined by their characteristic spot test,[6] and they were quantified by gravimetric analysis, in which they were transformed into 2,4-dinitrophenyldrazone derivatives. The molar ratio of reductant and Ag(III) was 1: 1.

Discussion

In aqueous periodate solution equilibria (1)–(3) were detected and the corresponding equilibrium constants at 273.2K were determined by Aveston.[7]

Table 1 10^4 $k_{obs}(s^{-1})$varying with different [BDO] at different temperatures; $[Ag(III)] = 7.158 \times 10^{-5}$mol/l; $[IO_4^-] = 2.000 \times 10^{-3}$mol/l; $[OH^-] = 0.100$ mol/l; $\mu = 0.102$ mol/l

	C(mol/l)								
T/K	0.100	0.125	0.160	0.250	0.500	n_{ap}	*r*	*a*	r_1
298.2	2.207	3.174	5.079	10.42	31.96	1.66	0.999	85.79	0.998
303.2	3.330	4.696	7.238	15.50	42.06	1.59	0.999	71.94	0.997
308.2	5.095	7.406	11.40	22.23	58.05	1.51	0.998	57.25	0.999
313.2	7.146	10.43	15.19	28.82	78.13	1.47	0.999	47.20	0.998
318.2	17.54	23.59	32.09	56.34	122.6	1.21	0.999	36.56	0.998

n_{ap} and *r* are for the slope and relative coefficient, respectively, of the plot of $\ln k_{obs}$ versus $\ln C$, *a* and r_1 are the intercept and relative coefficient, respectively, of the plot of $[BDO]/k_{obs}$ versus 1/[BDO].

---

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

Table 2 k_{obs} (s^{-1}) varying with the different $[IO_4^-]$,$[OH^-]$, μ at 313.2K,[Ag(III)] = 7.158 × 10^{-5}mol/l

C_{BDO} (mol/l)	$10^{-3}[IO_4^-]$ mol/l	$[OH^-]$ mol/l	μ mol/l	10^3k_{obs}/s
0.500	1.000	0.100	0.105	9.743
0.500	2.000	0.100	0.105	7.521
0.500	3.000	0.100	0.105	5.772
0.500	4.000	0.100	0.105	4.969
0.500	4.500	0.100	0.105	4.659
0.500	0.002	0.020	0.202	2.230
0.500	2.000	0.040	0.202	3.883
0.500	2.000	0.060	0.202	5.257
0.500	2.000	0.080	0.202	6.717
0.500	2.000	0.100	0.202	7.146
0.500	2.000	0.120	0.202	7.854
0.500	2.000	0.140	0.202	9.121
0.500	2.000	0.160	0.202	10.29
0.500	2.000	0.080	0.082	7.517
0.500	2.000	0.080	0.182	7.006
0.500	2.000	0.080	0.282	6.590
0.500	2.000	0.080	0.382	6.282
0.500	2.000	0.080	0.482	5.995

$$2IO_4^- + 2\,OH^- \rightleftharpoons H_2I_2O_{10}^{4-} \quad \log\beta_1 = 15.05 \quad (1)$$

$$IO_4^- + OH^- + H_2O \rightleftharpoons H_3IO_6^{2-} \quad \log\beta_2 = 6.21 \quad (2)$$

$$IO_4^- + 2\,OH^- \rightleftharpoons H_2IO_6^{3-} \quad \log\beta_3 = 8.67 \quad (3)$$

The distribution of all species of periodate in aqueous alkaline solution can be calculated from equilibria (1)–(3). In the $[OH^-]$ range used in this work the dimer and IO_4^- species of periodate can be neglected ($H_2IO_6^{3-}$:$H_3IO_6^{2-}$:$H_2I_2O_{10}^{4-}$:$[IO_4^-]$≅ 2.89–28.84:1.00:0.11–1.40 × 10^{-2}:6.2 × 10^{-5}~6 × 10^{-4}), the main species of periodate are $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$. Equations (4) and (5) can be obtained from Eqns (2) and (3):

$$[H_2IO_6^{\ 3-}] = \frac{\beta_3[OH^-]^2}{1+\beta_2[OH^-]+\beta_3[OH^-]^2}[IO_4^{\ -}]_{ex} = f([OH^-])[IO_4^{\ -}]_{ex} \quad (4)$$

$$[H_3IO_6^{\ 2-}] = \frac{\beta_2[OH^-]}{1+\beta_2[OH^-]+\beta_3[OH^-]^2}[IO_4^{\ -}]_{ex} = \phi([OH^-])[IO_4^{\ -}]_{ex} \quad (5)$$

Here $[IO_4^-]_{ex}$ represents the concentration of original overall periodate ion and equals approximately to the sum of [$H_2IO_6^{3-}$] and $[H_3IO_6^{2-}]$. Based on our previous work,[4] the formula of the Ag(III) periodate complex may be represented by the less protonated $[Ag(OH)_2(H_2IO_6)_2]^{5-}$. So we propose the reaction mechanism of the reaction as shown below:

$$\underset{\text{A}}{\begin{matrix}[Ag(OH^-)_2(H_2IO_6)_2]^{5-}\\ +\ OH^-\end{matrix}} \xrightleftharpoons{K_1} \underset{\text{B}}{\begin{matrix}[Ag(OH^-)_2(HIO_6)]^{3-}\\ +\ OH^- + H_2IO_6^{3-} + H_2O\end{matrix}} \quad (6)$$

$$[Ag(OH^-)_2(HIO_6)]^{3-} + BDO \xrightleftharpoons{K_2} \underset{\text{adduct}}{[Ag(OH^-)_2(HIO_6)(BDO)]^{3-}} \quad (7)$$

$$\begin{matrix}[Ag(OH^-)_2(HIO_6)(BDO)]^{3-}\\ +\ BDO\end{matrix} \xrightarrow[\text{slow}]{k} \begin{matrix}[Ag(OH^-)_2(HIO_6)(BDO)]^{3-}\\ BDO\end{matrix} \quad (8)$$

$$[Ag(OH^-)_2(HIO_6)(BDO)]^{3-}BDO \xrightarrow{\text{fast}} \begin{matrix}Ag(I) + BDO +\\ HOCH_2CH_2CH_2CHO\end{matrix} \quad (9)$$

As the rate of the disappearance of $[Ag(III)]_t$ is monitored and $[Ag(III)]_t = [A]_e + [B]_e + [adduct]_e$, reaction (8) is the rate-determining step:

$$-d[Ag(III)]_t/dt = k\cdot[adduct]_e\cdot[BDO]$$

$$= \frac{kK_1K_2[OH^-][BDO]^2[Ag(III)]}{[H_2IO_6^{3-}]+K_1[OH^-]+K_1K_2[OH^-][BDO]} = k_{obs}\cdot[Ag(III)]_t \quad (10)$$

$$k_{obs} = \frac{kK_1K_2[OH][BDO]^2}{[H_2IO_6^{3-}]+K_1[OH^-]+K_1K_2[OH^-][BDO]} \quad (11)$$

Substituting eqn(4) into eqn (11), we can get the following:

$$\frac{[BDO]}{k_{obs}} = \frac{1}{k} + \frac{f([OH^-])[IO_4^-]_{ex} + K_1[OH^-]}{kK_1K_2[OH^-]}\cdot\frac{1}{[BDO]} \quad (12)$$

$$\frac{1}{k_{obs}} = \frac{1+K_2[BDO]}{kK_2[BDO]^2} + \frac{[IO_4^-]_{ex}}{kK_1K_2[BDO]^2}\cdot\frac{f([OH^-])}{[OH^-]} \quad (13)$$

$$\frac{1}{k_{obs}} = \frac{1+K_2[BDO]}{kK_2[BDO]^2} + \frac{f\ [OH^-]}{kK_1K_2[BDO]^2[OH^-]}[IO_4^-]_{ex} \quad (14)$$

Equation (12) shows that the order in [BDO] should be $1< n_{ap} <2$ and the plots of $[BDO]/k_{obs}$ versus [BDO] should be linear. Equation (13) suggests that the plot of $1/k_{obs}$ versus $f([OH^-])/[OH^-]$ should be linear and equation (14) shows that the plot of $1/k_{obs}$ versus$[IO_4^-]_{ex}$ should also be linear. From intercepts of Table 1 the rate-determining step constants (*k*) at different temperature were evaluated. The activation parameters (298.2K) data of 1,4-butylene glycol were evaluated by the method given earlier.[8] (Table 3).

Table 3 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	318.2	*E*a (kJ/ mol^{-1})	Δ*H*# (kJ/ mol^{-1})	Δ*S*# (J mol^{-1} K^{-1})
10^3k (mol^{-1}/l/s^{-1})	11.66	13.90	17.47	21.19	27.35	33.34	30.86	178.78

The plot of ln*k* *vs*1/T has the following regression equation: ln*k* = 8.96–4010.24 (1/*T*) (*r* = 0.997).

Received 16 August 2005; accepted 28 November 2005
Paper 05/3443

References

1 J.H. Shan, S.Y. Huo, F. Wang *et al.*, *J. Chem. Res. (S),*2004,**10,**674.
2 S. Chandra and K.L. Yadava, *Talanta.*, 1986,**15**,349.
3 A. Balikungeri, M. Pelletier and D. Monnier, *Inorg. Chim. Acta.*, 1977, **22,**7.
4 J.H. Shan, J. Qian, T.Y. Zhai *et al.,Chinese. J. Inorg. Chem.,* 2003, **19,** 843.
5 J.J. Jin, *Kinetic Principles of Chemical Reaction in Liquid Phase*, Shanghai: Science Technique Press, 1984, p.186.
6 F. Feigl, *Spot Tests in Organic Analysis*, Elsevier Publishing Co, New York, 1956, p.208.
7 J. Aveston, *J. Chem. Soc. (A)*, 1969, 273.
8 J.H. Shan and T.Y. Liu, *Acta Chim. Sin.*. 1994, **52,** 1140.