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SHORT COMMUNICATION

KINETICS AND MECHANISM OF OXIDATION OF 2-AMINO-1-BUTANOL BY DIPERIODATOARGENTATE(III) IN ALKALINE MEDIUM

Jin Huan Shan*, He Ye Wang, Chang Ying Song and Fang Wang

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

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ABSTRACT. The kinetics of oxidation of 2-amino-1-butanol (AB) by diperiodatoargentate(III) (DPA) has been studied spectrophotometrically in alkaline media in the temperature range 288.2-303.2 K. The reaction is first order with respect to [DPA] and fractional order with respect to [AB]. The observed rate constant (k_{obs}) decreased with increasing [IO_4^-] and increased with increasing [OH^-]. Increasing ionic strength of the media decreased the rate. The rate and equilibrium constants involved in the mechanism were calculated. There is good agreement between the observed and calculated rate constants under varying experimental conditions. The activation parameters for the slow step were computed and discussed. Thermodynamic quantities were also determined.

KEY WORDS: 2-Amino-1-butanol, Diperiodatoargentate(III), Kinetics, Reaction mechanism

INTRODUCTION

Aminoalcohols are an important and widely used class of organic compounds. They have been used as intermediate agents in the production of various other chemical compounds such as acidic gas absorbents, surfactants, pesticides and pharmaceuticals. 2-Amino-1-butanol (AB) is an important aminoalcohol. The kinetics and mechanisms of oxidation of 2-amino-1-butanol can provide some valuable information for chemical industry and organic synthesis.

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline media with a reduction potential of 1.74 V [1]. Some researchers have studied the kinetics of oxidation of some amino acids, reducing sugars and amines by DPA [2-7]. In this paper, the kinetics and mechanisms of oxidation of 2-amino-1-butanol by DPA are presented.

EXPERIMENTAL

Materials and reagents

All chemicals used were of A.R. grade and doubly distilled water was used throughout the work. The stock solution of 2-amino-1-butanol was prepared by dissolving an appropriate amount of sample in doubly distilled water. KNO_3 and KOH were used to maintain the ionic strength and alkalinity of the reaction, respectively. The stock standard solution of IO_4^- was prepared by dissolving KIO_4 in doubly distilled water and kept for 24 h to attain equilibrium.

Preparation of DPA

DPA was prepared by oxidizing Ag(I) in the presence of KIO_4 as described elsewhere [8]: the mixture of 8 g of KOH and 3.42 g of $NaIO_4$ in 100 mL of water along with 1.36 g $AgNO_3$ was heated just to boiling and 3 g of $K_2S_2O_8$ was added in several small amounts with stirring. The mixture was then allowed to cool. It was filtered through a medium porosity fritted glass filter. The complex was characterized from its UV spectrum, exhibiting two peaks at 253 and 362 nm. These spectral features were identical to those reported earlier for DPA [8].

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*Corresponding author. E-mail: shanjinhuaner@yahoo.com.cn; fax: 86-0312-5079525

Kinetic measurements

The kinetic measurements were performed on a UV-vis spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell holder to keep constant temperature (± 0.1°C) by circulating water from a thermostat (BG-chiller E_{10}, Beijing Biotech Inc., Beijing). The reactions were followed under pseudo-first-order conditions, using an excess of 2-amino-1-butanol over DPA at 288.2-303.2 K. The reaction was initiated by mixing DPA with the 2-amino-1-butanol solution which also contained KNO_3, KOH and KIO_4. The progress of the reaction was monitored spectrophotometrically at 362 nm, which is the maximum absorption wavelength of DPA. It was verified that there was almost no interference from other species in the reaction mixture at 362 nm.

Product analysis and free radical detection

The product was $CH_3CH_2COCH_2OH$, which was identified by its characteristic spot test [9]. It was quantified by gravimetric analysis by transformation into the 2,4-dinitrophenyldrazone derivative. The stoichiometry is [2-amino-1-butanol]/[DPA] = 1:1. Furthermore, the addition of acrylonitrile or acrylamide to the reaction mixture under nitrogen atmosphere neither changed the rate nor initiated any polymerization, showing that no free radicals are involved in the reaction. The reaction equation is

$$[Ag(OH)_2(H_2IO_6)_2]^{5-} + CH_3CH_2CHNH_2CH_2OH \longrightarrow Ag(I) + CH_3CH_2COCH_2OH + NH_3 + H_2O + 2H_2IO_6^{3-} \quad (1)$$

RESULTS AND DISCUSSION

Evaluation of pseudo-first order rate constants

Under the conditions of $[AB]_0 >> [Ag(III)]_0$, plots of $\ln(A_t\text{-}A_\infty)$ versus time were linear, indicating that the reaction is first order with respect to [Ag(III)]. Here, A_t and A_∞ are the absorbance at time t and infinite time, respectively. The plots were linear up to 85 % completion of reaction ($r \geq 0.999$). The values of k_{obs} were average values of at least three independent experiments and reproducibility of k_{obs} was ± 5%.

Effect of [AB]. The effect of [AB] on the reaction was studied at constant [DPA], $[OH^-]$, $[IO_4^-]$ and ionic strength (μ) in the range of 288.2-303.2 K. The [AB] varied from 0.010 to 0.050 mol L^{-1}. The values of k_{obs} increased with increasing [AB] (Table 1). The order with respect to 2-amino-1-butanol was found to be fractional and the plots of k_{obs} versus [AB] are consistent with non-linear equation (2) at different temperatures:

$$k_{obs} = \frac{a[AB]}{b[AB]+c} \quad (2)$$

Here a, b and c are constants under fixed experimental conditions.

Effect of $[IO_4^-]$. The effect of $[IO_4^-]$ on the reaction was studied at constant [DPA], $[OH^-]$, [AB] and ionic strength in the range of 288.2-303.2 K. The rate constants decreased with increasing $[IO_4^-]$ at different temperatures and the pseudo first-order rate constants are given in Table 2. The order with respect to $[IO_4^-]$ was found to be inverse fractional order, which reveals that IO_4^- is produced in equilibria before the rate determining step. Plots of k_{obs} versus $[IO_4^-]$ are consistent with non-linear equation (3) at different temperatures:

$$k_{obs} = \frac{e}{d + f[IO_4^-]} \tag{3}$$

Here e, d and f are constants under fixed experimental conditions.

Effect of [OH⁻]. The effect of [OH^-] on the reaction was studied at constant [DPA], [IO_4^-], [AB] and ionic strength at 298.2 K. The rate constants increased with increasing [OH^-] (Table 3).

Effect of ionic strength, μ. The effect of μ on the reaction was studied at constant [DPA], [IO_4^-], [OH^-] and [AB] at 298.2 K. The rate decreased with addition of KNO_3, which is consistent with a negative salt effect [10] (Table 4).

Table 1. k_{obs} varying with different [2-amino-1-butanol] at different temperatures.

T	288.2 K		293.2 K		298.2 K		303.2 K	
[AB] (mol L^{-1})	10^2k_{obs} (s^{-1})		10^2k_{obs} (s^{-1})		10^2k_{obs} (s^{-1})		10^2k_{obs} (s^{-1})	
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
0.010	1.01	0.92	1.34	1.31	1.71	1.69	2.33	2.19
0.020	1.78	1.77	2.49	2.50	3.25	3.19	4.07	4.12
0.030	2.58	2.55	3.60	3.57	4.53	4.55	5.87	5.83
0.040	3.14	3.27	4.54	4.56	5.65	5.77	7.34	7.37
0.050	3.99	3.93	5.49	5.46	6.95	6.88	8.72	8.75

[Ag(III)] = 5.19×10^{-5} mol L^{-1}; [IO_4^-] = 2.00×10^{-3} mol L^{-1}; [OH^-] = 0.030 mol L^{-1}; μ = 0.232 mol L^{-1}.

Table 2. k_{obs} varying with different 10^3 [IO_4^-] at different temperatures.

T	288.2 K		293.2 K		298.2 K		303.2 K	
10^3[IO_4^-]	10^2k_{obs} (s^{-1})		10^2k_{obs} (s^{-1})		10^2k_{obs} (s^{-1})		10^2k_{obs} (s^{-1})	
(mol L^{-1})	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
0.50	3.82	4.08	5.94	6.27	8.52	8.41	11.0	11.13
1.00	3.50	3.77	5.44	5.57	7.54	7.30	10.2	9.51
2.00	3.09	3.27	4.10	4.56	5.91	5.77	7.40	7.37
3.00	2.74	2.88	3.59	3.86	5.02	4.77	6.24	6.01
4.00	2.46	2.60	2.96	3.34	4.29	4.06	5.23	5.08
4.50	2.37	2.45	2.83	3.13	4.03	3.79	4.95	4.71

[Ag(III)] = 5.19×10^{-5} mol L^{-1}; [OH^-] = 0.030 mol L^{-1}; [AB] = 0.040 mol L^{-1}; μ = 0.232 mol L^{-1}.

Table 3. k_{obs} varying with [OH^-] at 298.2 K.

[OH^-] (mol·L^{-1})		0.030	0.060	0.080	0.100	0.130	0.160
10^2k_{obs} (s^{-1})	Found	6.20	7.22	7.54	8.17	8.97	9.31
	Calculated	5.77	7.19	7.70	8.05	8.41	8.65

[Ag(III)] = 5.19×10^{-5} mol L^{-1}; [IO_4^-] = 2.00×10^{-3} mol L^{-1}; [AB] = 0.040 mol L^{-1}; μ = 0.232 mol L^{-1}.

Table 4. k_{obs} varying with ionic strength at 298.2 K.

μ (mol L^{-1})	0.132	0.232	0.332	0.432	0.532
10^2k_{obs} (s^{-1})	7.72	6.11	5.47	4.70	4.33

[Ag(III)] = 5.19×10^{-5} mol L^{-1}; [IO_4^-] = 2.00×10^{-3} mol L^{-1}; [OH^-] = 0.030 mol L^{-1}; [AB] = 0.040 mol L^{-1}.

Reaction mechanism

In aqueous solution periodate equilibria (4)-(6) were observed and the corresponding equilibrium constants at 298.2 K were determined by Aveston [11]

$$2IO_4^- + 2\,OH^- \rightleftarrows H_2I_2O_{10}^{4-} \quad \log\beta_1 = 15.05 \tag{4}$$

$$IO_4^- + OH^- + H_2O \rightleftarrows H_3IO_6^{2-} \quad \log\beta_2 = 6.21 \tag{5}$$

$$IO_4^- + 2\,OH^- \rightleftarrows H_2IO_6^{3-} \quad \log\beta_3 = 8.67 \tag{6}$$

The distribution of all species of periodate in aqueous alkaline solution can be calculated from equilibria (4)-(6). In the $[OH^-]$ range used in this work, the amount of dimeric and IO_4^- species is negligible. The main species of periodate are $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$, consistent with the result calculated from Crouthamel's data [12] by Murthy [13]. Equations (7) and (8) can be obtained from (6) and (5):

$$[H_2IO_6^{3-}] = \frac{\beta_3[OH^-]}{\beta_2+\beta_3[OH^-]}[IO_4^-]_{ex} = f([OH^-])[IO_4^-]_{ex} \tag{7}$$

$$[H_3IO_6^{2-}] = \frac{\beta_2}{\beta_2+\beta_3[OH^-]}[IO_4^-]_{ex} = \phi([OH^-])[IO_4^-]_{ex} \tag{8}$$

Here, $[IO_4^-]_{ex}$ represents the stochiometric concentration of periodate ion and is approximately equal to the sum of $[H_2IO_6^{3-}]$ and $[H_3IO_6^{2-}]$. Based on this distribution, the formula of the Ag(III) periodate complex may be represented by either $[Ag(OH)_2(H_3IO_6)_2]^{3-}$ or the less protonated $[Ag(OH)_2(H_2IO_6)_2]^{5-}$. We prefer to represent DPA with the latter, which is closer to that suggested by Mukherjee [14].

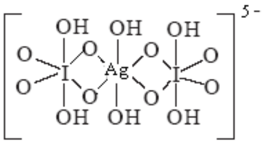
Based on the above discussion, the following reaction mechanism is proposed:

$$\underset{\text{DPA}}{[Ag(OH)_2(H_2IO_6)_2]^{5-}} + OH^- \overset{K_1}{\rightleftharpoons} \underset{\text{MPA}}{[Ag(OH)_2(HIO_6)]^{3-}} + H_2IO_6^{3-} + H_2O \tag{9}$$

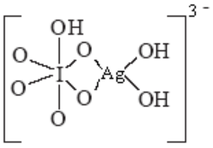
$$[Ag(OH)_2(HIO_6)]^{3-} + \underset{\text{AB}}{CH_3CH_2CHNH_2CH_2OH} \overset{K_2}{\rightleftharpoons} \underset{\text{Complex(C)}}{[Ag(OH)_2(CH_3CH_2CHNH_2CH_2OH)(HIO_6)]^{3-}} \tag{10}$$

$$\text{Complex(C)} \xrightarrow[\text{slow}]{k} Ag\,(I) + CH_3CH_2COCH_2OH \tag{11}$$

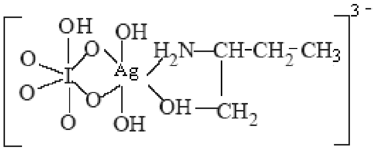
The structure of DPA, MPA and Complex(C) may be proposed as below:



DPA



MPA



Complex (C)

The rate of the disappearance of $[Ag(III)]_t$ is monitored and $[Ag(III)]_t = [DPA]_e + [MPA]_e + [C]_e$. Reactions (9) and (10) are pre-equilibria. Reaction (11) is an electron-transfer reaction, the rate of which is generally slower, so reaction (11) is the rate determining step:

$$-\mathrm{d}\,[\mathrm{Ag(III)}]_t/\mathrm{d}t = k\,[\mathrm{Complex}]$$

$$= \frac{kK_1K_2[\mathrm{OH}^-][\mathrm{AB}]}{K_1K_2[\mathrm{OH}^-][\mathrm{AB}] + K_1[\mathrm{OH}^-] + [\mathrm{H}_2\mathrm{IO}_6^{3-}]}\cdot[\mathrm{Ag(III)}]_t$$

$$= k_{\mathrm{obs}}\cdot[\mathrm{Ag(III)}]_t \qquad (12)$$

where

$$k_{\mathrm{obs}} = \frac{kK_1K_2[\mathrm{OH}^-][\mathrm{AB}]}{K_1K_2[\mathrm{OH}^-][\mathrm{AB}] + K_1[\mathrm{OH}^-] + [\mathrm{H}_2\mathrm{IO}_6^{3-}]} \qquad (13)$$

Eq (14) can be obtained from eqs (13) and (7)

$$k_{\mathrm{obs}} = \frac{kK_1K_2[\mathrm{AB}]}{K_1K_2[\mathrm{AB}] + K_1 + \dfrac{f(\mathrm{OH}^-)}{[\mathrm{OH}^-]}[\mathrm{IO}_4^-]_{\mathrm{ex}}} \qquad (14)$$

Equation (13) shows that the order in [AB] should be fractional, and Eq. (14) is identical to empirical Eq. (2) if a = kK_1K_2, b = K_1K_2, c = (K_1 + {f (OH^-)/[OH^-]}{[IO_4^-]$_{ex}$}). At the same time, Eq. (14) is equivalent to empirical Eq. (3), if d = kK_1K_2[AB], e = (K_1K_2[AB] + K_1), f = f(OH^-)/ [OH^-]. From the correlations above we can obtain (a/b) = k and (d/e) = (kK_2[AB])/(K_2[AB]+1), then combined with Eq. (14), the values of the rate constants (k) and the equilibrium constants (K_1, K_2) at different temperatures can be calculated (Table 5). The activation parameters at 298.2 K and the values of thermodynamic quantities were evaluated by the method given earlier [15, 16] (Table 5).

Table 5. Thermodynamic activation parameters for the oxidation of 2-amino-1-butanol by diperiodatoargentate(III) in alkaline medium.

(A) Effect of temperatures on rate constant		(B) Effect of temperatures on equilibrium constants		
T (K)	k (L mol^{-1} s^{-1})	T (K)	K_1 (L mol^{-1})	K_2 (mol L^{-1})
288.2	0.217	288.2	0.131	6.45
293.2	0.253	293.2	0.076	9.87
298.2	0.297	298.2	0.055	12.6
303.2	0.350	303.2	0.045	15.6
(C) Activation parameters (298.2 K)		(D) Thermodynamic quantities from K_1 and K_2		
Parameters	Values	Thermodynamic quantities	Values from K_1	Values from K_2
Ea	23.2 kJ mol^{-1}	ΔH (kJ mol^{-1})	-51.6	42.0
$\Delta^{\neq}S$	-185 J K^{-1} mol^{-1}	ΔS (J K^{-1} mol^{-1})	-197	162
$\Delta^{\neq}H$	20.7 kJ mol^{-1}	$\Delta G_{298.2}$ (kJ mol^{-1})	7.19	-6.27

In the pre-equilibrium reaction (9), DPA deprotonated by OH^- produces MPA and a free periodate species, which is evidenced by a decrease in rate with increasing [IO_4^-]. It may be expected that MPA will be more important in the reaction than DPA. Equilibrium constant K_2 is greater than K_1. The tendency towards formation of complex (C) is greater than for DPA deprotonation in alkaline media.

Based on the above discussion and comparing to our previous work [6], the rate constants and activation parameters of α-butylene glycol (α-BG, and the structure $CH_3CH_2CHOHCH_2OH$) is oxidized by DPA were obtained earlier: $k_{298.2\,K}$ = 0.0928 L mol^{-1} s^{-1}, $k_{303.2\,K}$ = 0.149 L mol^{-1} s^{-1}, E_a = 60.2 kJ mol^{-1}, $\Delta^{\neq}H$ = 57.7 kJ mol^{-1}, $\Delta^{\neq}S$ = -71.0 J K^{-1} mol^{-1} [6]. Compared with oxidation of α-BG by DPA, the rate constants of rate determining step are higher at the same temperature and the activation energy is lower. We conclude that the active group is –NH_2, and the reaction rate changes with the active group. The reason is that the formation of a pentacyclic intermediate complex by MPA and AB is easier than by DPA and α-BG. The former is more stable, which is consistent with the experimental results. This phenomenon is consistent with the hard-soft acid-base principle.

CONCLUSIONS

The active species of DPA is understood to be for the title reaction. The rate constants of the slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters were also computed. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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