

## Kinetics and Mechanism of Oxidation of 2-Aminoethanol and 3-Amino-1-propanol by Diperioatoargentate(III) in Alkaline Medium

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The kinetics of oxidation of 2-aminoethanol and 3-amino-1-propanol by diperioatoargentate(III) (DPA) were carried out spectrophotometrically in alkaline medium in the temperature range of 293.2-308.2 K. The reaction showed first order with respect to [DPA] and each reductant. The observed rate constant ( $k_{obs}$ ) decreased with the increase of  $[IO_4^-]$  and increased with the increase of  $[OH^-]$ . Increasing ionic strength of the medium decreased the rate. Investigations of the reaction at different temperatures allowed the determination of the activation parameters for the slow step of proposed mechanism. The proposed mechanism and the derived rate laws found consistent with the observed kinetics.

**Keywords:** Diperioatoargentate(III) (DPA), 2-Aminoethanol, 3-Amino-1-propanol, Kinetics and mechanism, Rate constants

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### INTRODUCTION

Alcohol amines 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 gases absorbents, surfactants, pesticides and pharmaceuticals. 2-Aminoethanol (2-AE) and 3-amino-1-propanol (3-AP) are important alcohol amines. The kinetics and mechanism of oxidation of 2-AE and 3-AP can provide some valuable information for chemical industry and organic synthesis.

Diperioatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential 1.74 V [1]. Some researchers have studied DPA as an oxidizing agent for the kinetics of oxidation of some organic substrates, such as amino acids, reducing sugars and amines [2-7]. In this paper, the kinetics and mechanism of oxidation of 2-aminoethanol and 3-amino-1-propanol by DPA(III) is 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 reductant was prepared by dissolving an appropriate amount of sample in doubly distilled water. The reductant was used from its stock solution.  $KNO_3$  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 the equilibrium.

#### Kinetic Measurements

The kinetic measurements were performed on a UV-Vis spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell holder kept at constant temperature ( $\pm 0.1$  °C) by circulating water from a thermostat (BG-chiller E<sub>10</sub>, Beijing Biotech Inc., Beijing). The reactions were followed under pseudo-first-order conditions, using an excess of the reductant

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over DPA in the temperature range of 293.2-308.2 K. The reaction was initiated by mixing DPA with the reductant solution which also contained  $\text{KNO}_3$ ,  $\text{KOH}$  and  $\text{KIO}_4$ . 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 the selected wavelength.

### Product Analysis

The products were the corresponding aldehyde alcohols, which were identified by their characteristic spot test [8]. They were quantified by gravimetric analysis, *via* their transformation into 2,4-dinitrophenyldrazone derivatives. The stoichiometry is the same in both cases, that is,  $[\text{reductant}]/[\text{DPA}] = 1:1$ .

## RESULTS AND DISCUSSION

### Evaluation of Pseudo-First Order Rate Constants

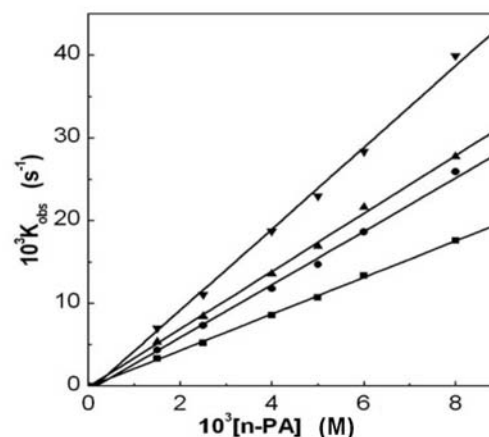
Under the conditions of  $[\text{Reductant}]_0 \gg [\text{Ag(III)}]_0$ , the plots of  $\ln(A_t - A_\infty)$  vs. time are linear, indicating the reaction is first order with respect to  $[\text{Ag(III)}]$ , where  $A_t$  and  $A_\infty$  are the absorbance at time  $t$  and at infinite time, respectively. The pseudo-first-order rate constants  $k_{\text{obs}}$  were calculated by the method of least squares ( $r \geq 0.999$ ,  $S < 0.01$ ,  $S$  is the standard deviation). To calculate  $k_{\text{obs}}$ , generally 8-10 values of  $A_t$  within three times the half-life were used. The values of  $k_{\text{obs}}$  were average values of at least three independent experiments and reproducibility of  $k_{\text{obs}}$  is within the experimental error  $\pm 5\%$ .

### Effect of Reductant Concentration

The effect of  $[\text{reductant}]$  on the reaction was studied at

constant  $[\text{DPA}]$ ,  $[\text{OH}^-]$  and  $[\text{IO}_4^-]$  and ionic strength ( $\mu$ ) in the range of 293.2-308.2 K. The substrates, 2-aminoethanol and 3-amino-1-propanol were varied in the range of 0.004-0.030 M and 0.0015-0.0080 M, respectively. The values of  $k_{\text{obs}}$  increased with increase in  $[\text{reductant}]$  and the plots of  $k_{\text{obs}}$  vs.  $[\text{reductant}]$  were straight lines which passed through the grid origin at different temperatures (Table 1 and Fig. 1), from which the corresponding equation can be gotten:

$$k_{\text{obs}} = m [\text{reductant}] \quad (1)$$



**Fig. 1.** Plots of  $k_{\text{obs}}$  vs.  $[\text{3-AP}]$ . 293.2 K (■), 298.2 K (●), 303.2 K (▲), 308.2 K (▼). Conditions:  $[\text{Ag(III)}] = 5.186 \times 10^{-5}$  M;  $[\text{OH}^-] = 0.030$  M;  $[\text{IO}_4^-] = 0.002$  M;  $\mu = 0.232$  M.

From the Eq. (1), we can obtain that the order was found to be unity with respect to  $[\text{reductant}]$ .

**Table 1.**  $10^2 k_{\text{obs}}$  Varying with Different  $[\text{2-AE}]$  at Different Temperatures

T (K)	$10^2 [\text{2-AE}]$ (M)						$n_{\text{ap}}$	$r$
	0.400	0.600	0.800	1.000	2.000	3.000		
293.2	0.498	0.752	0.973	1.220	2.377	4.079	1.03	0.999
298.2	0.662	1.091	1.349	1.662	3.481	5.241	1.00	0.999
303.2	0.914	1.318	1.741	2.272	4.419	6.824	1.01	0.999
308.2	1.264	1.852	2.538	3.088	6.442	9.987	1.02	0.999

$n_{\text{ap}}$  and  $r$  stand for the slope and correlation coefficient, respectively, of the plot of  $\ln k_{\text{obs}}$  vs.  $\ln[\text{2-AE}]$   $[\text{Ag(III)}] = 5.186 \times 10^{-5}$  M;  $[\text{OH}^-] = 0.030$  M;  $[\text{IO}_4^-] = 0.002$  M;  $\mu = 0.232$  M.

### Effect of $\text{IO}_4^-$ Concentration

The effect of  $[\text{IO}_4^-]$  on the reaction was studied at constant [DPA],  $[\text{OH}^-]$ , [reductant] and ionic strength in the temperature range of 293.2-308.2 K. The rate constants decreased with increase in  $[\text{IO}_4^-]$  and the plot of  $1/k_{\text{obs}}$  vs.  $[\text{IO}_4^-]$  exhibits linearity (Table 2 and Fig. 2.), which correspond to the equation:

$$1/k_{\text{obs}} = a + b [\text{IO}_4^-] \quad (2)$$

The order in  $[\text{IO}_4^-]$  was derived to be an inverse fraction which reveals that  $\text{IO}_4^-$  is produced in equilibria before the rate-determining step.

### Effect of $\text{OH}^-$ Concentration

The effect of  $[\text{OH}^-]$  on the reaction was studied at constant [DPA],  $[\text{IO}_4^-]$ , [reductant] and ionic strength at 303.2 K. The rate constants increased with the increase of  $[\text{OH}^-]$  and the plots of  $1/k_{\text{obs}}$  vs.  $f(\text{OH}^-)/[\text{OH}^-]$  were consistent with the corresponding linear equation: (Table 3 and Fig. 3).

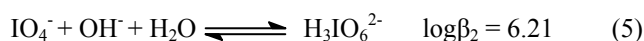
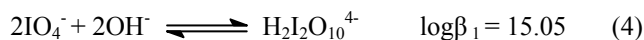
$$1/k_{\text{obs}} = a + c f(\text{OH}^-)/[\text{OH}^-] \quad (3)$$

### Effect of Ionic Strength

The effect of  $\mu$  on the reaction was studied at constant [DPA],  $[\text{IO}_4^-]$ ,  $[\text{OH}^-]$  and [reductant] at 303.2 K, the rate was decreased with the addition of aqueous  $\text{KNO}_3$ , which is consistent with the negative salt effect [9] (Table 4).

### Reaction Mechanism

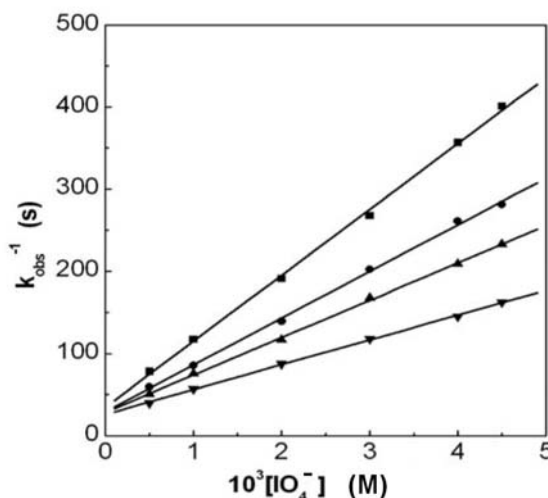
In periodate aqueous solution equilibria (4)-(6) were observed and the corresponding equilibrium constants at 298.2 K were determined by Aveston [10] as



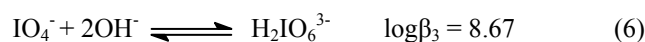
**Table 2.**  $10^2 k_{\text{obs}}$  Varying with Different  $[\text{IO}_4^-]$  at Different Temperatures<sup>a</sup>

T (K)	$10^3 [\text{IO}_4^-]$ (M)				
	0.500	1.000	2.000	3.000	4.000
293.2	1.151	1.096	0.989	0.929	0.864
298.2	1.571	1.484	1.326	1.219	1.146
303.2	2.279	2.077	1.801	1.595	1.528
308.2	3.021	2.822	2.510	2.216	2.056

<sup>a</sup> $[\text{Ag(III)}] = 5.186 \times 10^{-5} \text{ M}$ ;  $[\text{OH}^-] = 0.030 \text{ M}$ ;  $[\text{2-AE}] = 0.008 \text{ M}$ ;  $\mu = 0.232 \text{ M}$ .



**Fig. 2.** Plots of  $k_{\text{obs}}^{-1}$  vs.  $[\text{IO}_4^-]$ . 293.2 K (■), 298.2 K (●), 303.2 K (▲), 308.2 K (▼). Conditions:  $[\text{Ag(III)}] = 5.186 \times 10^{-5} \text{ M}$ ;  $[\text{OH}^-] = 0.030 \text{ M}$ ;  $[\text{3-AP}] = 0.0025 \text{ M}$ ;  $\mu = 0.232 \text{ M}$ .

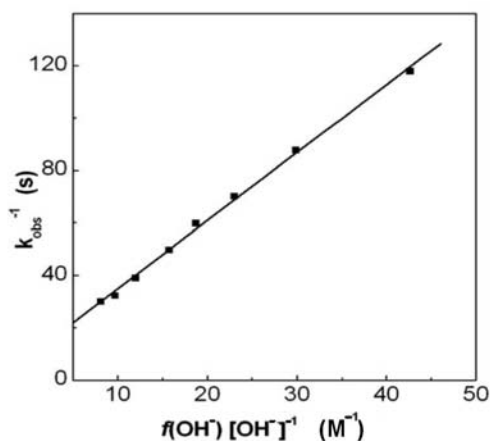


The distribution of all species of periodate in aqueous alkaline solution can be calculated from equilibria (4)-(6). In

**Table 3.**  $k_{\text{obs}}$  Varying with  $[\text{OH}^-]$  at 303.2 K<sup>a</sup>

$[\text{OH}^-]$ (M)	0.020	0.030	0.040	0.050	0.080	0.100	0.120
$10^2 k_{\text{obs}}$ ( $\text{s}^{-1}$ )	1.539	1.751	1.923	2.041	2.319	2.413	2.465

<sup>a</sup> $[\text{Ag(III)}] = 5.186 \times 10^{-5} \text{ M}$ ;  $[\text{IO}_4^-] = 0.002 \text{ M}$ ;  $[\text{2-AE}] = 0.008 \text{ M}$ ;  $\mu = 0.232 \text{ M}$ .



**Fig. 3.** Plots of  $k_{\text{obs}}^{-1}$  vs.  $f(\text{OH}^-)/[\text{OH}^-]$  at 303.2 K. Conditions:  $[\text{Ag(III)}] = 5.186 \times 10^{-5} \text{ M}$ ;  $[\text{IO}_4^-] = 0.002 \text{ M}$ ;  $[\text{3-AP}] = 0.0025 \text{ M}$ ;  $\mu = 0.232 \text{ M}$ .

the  $[\text{OH}^-]$  range used in this work the amount of dimer and  $\text{IO}_4^-$  species of periodate is neglected. The main species of periodate are  $\text{H}_2\text{IO}_6^{3-}$  and  $\text{H}_3\text{IO}_6^{2-}$ , consistent with the result calculated from Crouthamel's data [11] by Murthy. Eqs. (7) and (8) can be obtained from (6) and (5):

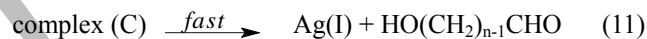
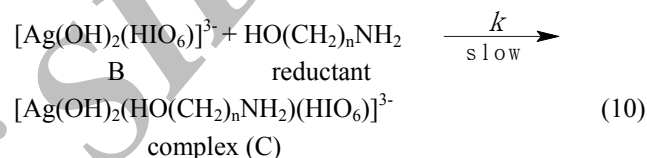
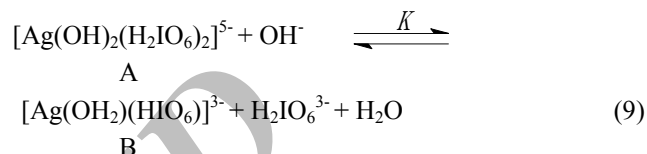
$$[\text{H}_2\text{IO}_6^{3-}] = \frac{\beta_3[\text{OH}^-]}{\beta_2 + \beta_3[\text{OH}^-]} [\text{IO}_4^-]_{\text{ex}} = f([\text{OH}^-]) [\text{IO}_4^-]_{\text{ex}} \quad (7)$$

$$[\text{H}_3\text{IO}_6^{2-}] = \frac{\beta_2}{\beta_2 + \beta_3[\text{OH}^-]} [\text{IO}_4^-]_{\text{ex}} = \varphi([\text{OH}^-]) [\text{IO}_4^-]_{\text{ex}} \quad (8)$$

Here  $[\text{IO}_4^-]_{\text{ex}}$  represents the concentration of original overall periodate ion and is approximately equal to the sum of  $[\text{H}_2\text{IO}_6^{3-}]$  and  $[\text{H}_3\text{IO}_6^{2-}]$ . Based on such distribution, the formula of Ag(III) periodate complex may be represented by either  $[\text{Ag}(\text{OH})_2(\text{H}_3\text{IO}_6)_2]^{3-}$  or the less protonated

$[\text{Ag}(\text{OH})_2(\text{H}_2\text{IO}_6)_2]^{5-}$ . We preferred to represent DPA with the latter, which is closer to that suggested by Mukherjee [12].

Based on the above discussion, a possible reaction mechanism was proposed as:



$n = 2$ , the reductant is 2-AE and  $n = 3$ , is 3-AP.

As the rate of the disappearance of  $[\text{Ag(III)}]_t$  is monitored and  $[\text{Ag(III)}]_t = [\text{A}]_e + [\text{B}]_e$ . The reaction (10) is the rate-determining step:

$$\begin{aligned} -d[\text{Ag(III)}]_t/dt &= k [\text{B}][\text{reductant}] \\ &= \frac{kK[\text{OH}^-][\text{reductant}]}{[\text{H}_2\text{IO}_6^{3-}] + K[\text{OH}^-]} \cdot [\text{Ag(III)}]_t = k_{\text{obs}} \cdot [\text{Ag(III)}]_t \end{aligned} \quad (12)$$

$$k_{\text{obs}} = \frac{kK[\text{OH}^-][\text{reductant}]}{[\text{H}_2\text{IO}_6^{3-}] + K[\text{OH}^-]} \quad (13)$$

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{IO}_4^-]_{\text{ex}} f(\text{OH}^-)}{kK[\text{reductant}][\text{OH}^-]} + \frac{1}{k[\text{reductant}]} \quad (14)$$

**Table 4.**  $k_{\text{obs}}$  Varying with Ionic Strength at 303.2 K<sup>a</sup>

$\mu$ (M)	0.132	0.232	0.332	0.432	0.532
(2-AE) $10^2 k_{\text{obs}}$ ( $\text{s}^{-1}$ )	2.080	1.762	1.646	1.497	1.397
(3-AP) $10^3 k_{\text{obs}}$ ( $\text{s}^{-1}$ )	8.970	8.516	8.336	8.235	8.014

<sup>a</sup> $[\text{Ag(III)}] = 5.186 \times 10^{-5} \text{ M}$ ;  $[\text{OH}^-] = 0.030 \text{ M}$ ;  $[\text{IO}_4^-] = 0.002 \text{ M}$ ;  $[\text{2-AE}] = 0.008 \text{ M}$ ,  $[\text{3-AP}] = 0.0025 \text{ M}$ .

**Table 5.** Rate Constants (*k*) and Activation Parameters of the Rate-Determining Step

T (K)	<i>k</i> (M <sup>-1</sup> s <sup>-1</sup> )		Activation parameters (298.2 K)	
	2-AE	3-AP	2-AE	3-AP
293.2	1.50 ± 0.01	10.16 ± 0.50	<i>E</i> <sub>a</sub> = 50.28 ± 1.36 kJ mol <sup>-1</sup>	<i>E</i> <sub>a</sub> = 23.95 ± 1.98 kJ mol <sup>-1</sup>
298.2	2.06 ± 0.03	12.63 ± 0.38	Δ <i>H</i> <sup>‡</sup> = 47.79 ± 1.36 kJ mol <sup>-1</sup>	Δ <i>H</i> <sup>‡</sup> = 21.45 ± 1.99 kJ mol <sup>-1</sup>
303.2	2.99 ± 0.10	14.48 ± 0.82	Δ <i>S</i> <sup>‡</sup> = -78.41 ± 4.52 J mol <sup>-1</sup> K <sup>-1</sup>	Δ <i>S</i> <sup>‡</sup> = -152.06 ± 6.63 J mol <sup>-1</sup> K <sup>-1</sup>
308.2	4.04 ± 0.05	16.50 ± 0.71		

The regression equations of [2-AE] and [3-AP] are shown:  $\ln k = 21.02 - 6047.38/T$  ( $r = 0.999$ ) and  $\ln k = 12.17 - 2880.64/T$  ( $r = 0.993$ ), respectively.

Equation (13) shows that the order in [reductant] should be first order, the plots of  $k_{\text{obs}}$  vs. [reductant] should be linear, passing through the grid origin. Equation (13) is equivalent to the empirical Eq. (1) if  $m = kK[\text{OH}^-]/([\text{H}_2\text{IO}_6^{3-}] + K[\text{OH}^-])$ . Equation (14) suggests that the plot of  $1/k_{\text{obs}}$  vs.  $[\text{IO}_4^-]_{\text{ex}}$  should be linear and shows that the plots of  $1/k_{\text{obs}}$  vs.  $f(\text{OH}^-)/[\text{OH}^-]$  should also be linear at different temperatures. In addition, the Eq. (14) is identical to empirical Eq. (2) and Eq. (3), if  $a = \frac{1}{k[\text{reductant}]}$ ,  $b = \frac{f(\text{OH}^-)}{kK[\text{reductant}][\text{OH}^-]}$ ,  $c = \frac{[\text{IO}_4^-]_{\text{ex}}}{kK[\text{reductant}]}$ .

From the intercepts of Eq. (14) at different temperatures, the rate-determining step constants (*k*) were evaluated. The activation parameter (at 298.2 K) of each reductant were evaluated by the method given earlier [13] (Table 5). In our experiments, we found that there were greater influence on the rate of 3-AP than that of 2-AE varying with  $[\text{IO}_4^-]$  and  $[\text{OH}^-]$ . So the rate constants (*k*) and activation parameters of the rate-determining step vary considerably.

The moderate values of Δ*H*<sup>‡</sup> and Δ*S*<sup>‡</sup> are both favorable for electron transfer processes. The negative value of Δ*S*<sup>‡</sup> indicates that the complex (C) is more ordered than the reactants [14] and supports the view that the rate-limiting step consists in the formation of an intermediate complex and does not involve the breaking of a bond.

## CONCLUSIONS

The active species of DPA is understood to be  $[\text{Ag}(\text{OH})_2(\text{HIO}_6)]^{3-}$  for the title reaction. Rate constant of the slow step involved in the mechanism was evaluated and activation parameters with respect to slow step of reaction were computed, respectively. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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