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Kinetics And Mechanism Of Oxidation Of 1, 2-Butanediol By Diperiodatocuprate (III) In Alkaline Medium

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ABSTRACT

The kinetics of oxidation of 1,2-butanediol(α-BG) by diperiodatocuprate (III)(DPC) in aqueous alkaline medium have been studied by spectrophotometry in a temperature range of 298.2K-313.2K. The reaction was found to be pseudo-first order(k_{obs}) with respect to DPC and $1<n_{ap}<2$ to α-BG. It was found that under the condition of the pseudo-first order ($[\alpha\text{-BG}]_0 >> [DPC]_0$), the observed rate constant k_{obs} increased with an increase in concentration of$[OH^-]$ and a decrease in concentration of $[IO_4^-]$. There is a weak negative salt effect. Based on the experimental results, a probable reaction mechanism of oxidation is proposed. The rate equation derived from the mechanism can explain all the experimental phenomena. The activation parameters along with the rate constants of the rate-determining step were calculated.

KEYWORDS

Diperiodatocuprate(III);
1,2-Butanediol;
Redox reaction;
Kinetics and mechanism.

INTRODUCTION

Recently, the study of the highest oxidation state of transition metals intrigued many researchers, which can provide new and valuable information in some fields. Transition metals in a higher oxidation state generally can be stabilized by chelation with suitable polydentate ligands. Metal chelates such as ditelluratocuprate(III)[1] , diperiodatocuprate(III)[2,3,4], diperiodato argentate(III)[4], ditelluratoargentate (III)[5], diperiodatonickelate(IV)[6] and iron(VI)[7] usually exists as FeO_4^{2-},they are all good oxidants in a medium with an appropriate pH value. The use of Cu(III) as an oxidation agent is also known in some sugars and organic acid qualitative analysis[8]. We have therefore studied the oxidation of α-BG by DPC in alkaline medium in order to get an insight into the mechanism of oxidation of the substrates.

EXPERIMENTAL

Reagents and instrumentation

All reagents used such as $K_2S_2O_8$, $CuSO_4 \cdot 5H_2O$, KIO_4, KOH and α-BG were of A.R. grade. The stock solution of DPC in a strong alkaline medium was prepared by the method given by literature[4]. All solutions were prepared with twice distilled water. Solution of DPC and α-BG were always freshly prepared before use. 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-1900 spectrophotometer(Beijing) fitted with a 501 thermostat (±0.1^{0}C, Shanghai).

Kinetics measurements

All kinetics measurements were carried out under pseudo-first order conditions. Solution(2mL) containing definite concentration of Cu(III), OH^-, IO_4^- and ionic strength and solution(2mL) of α-BG appropriate concentration were transferred separately to the upper and lower branch tubes of a λ type two-cell reactor. After it was thermally equilibrated at desired temperature in a thermobath, the two solutions were mixed well and immediately transferred into a 1 cm thick rectangular cell quartz in a constant temperature cell-holder(±0.1^{0}C). The reaction process was monitored automatically by recording the disappearance of Cu(III) with time(t) at 415nm, and none of other reactants and products absorbed significantly at this wavelength. It is obtained about the dynamic information of the reaction system.

Product analysis and free radical detection

Under the conditions employed, the oxidation product was identified as the corresponding aldehyde alcohol by spot test[9].

Acrylamide was added under the protection of nitrogen atmosphere during the course of reaction. The appearance of white polyacrylamide was consistent with free radical intermediates in the oxidation by Cu(III) complexes. Blank experiments in reaction system gave no polymeric suspensions.

RESULTS AND DISCUSSION

Evaluation of pseudo-first-order rate constants

Under the condition of $[\alpha\text{-BG}]_0 >> [Cu(III)]_0$, the plots of $\ln(A_t - A\infty)$ versus time t were linear(r=0.999) indicating that the reaction is first order with respect to Cu(III), where A_t and $A\infty$ were the absorbance at time t and at infinite time respectively. The pseudo-first order rate constants, k_{obs}, were evaluated by the method of least squares. We used generally 15A_t values within three times half life period to calculate k_{obs}, k_{obs} values were at least averaged values of three independent experiments and reproducibility is within ±5%.

Rate dependence on [α-BG]

At constant [Cu(III)], [OH^-], [IO_4^-], and ionic strength μ and temperature, k_{obs} values increase with the increase in[α-BG] and the order with respect to α-BG was found to be $1<n_{ap}<2$ (TABLE 1). The plot of $[\alpha\text{-BG}]/k_{obs}$ versus $1/[\alpha\text{-BG}]$ was linear(r=0.999) (Figure 1).

TABLE 1: 10^2k_{obs} varying with different concentrations of α-BG at different temperatures

$10^2C/mol \cdot L^{-1}$ T/K	0.50	0.83	1.25	1.60	2.25	n_{ap}	r
298.2	0.235	0.571	1.061	1.600	2.647	1.617	0.999
303.2	0.430	0.977	1.850	2.635	4.300	1.541	0.999
308.2	0.626	1.452	2.634	3.876	6.288	1.528	0.999
313.2	0.952	2.128	3.841	5.425	8.674	1.498	0.999

$[Cu(III)]=1.49\times10^{-4} mol \cdot L^{-1}$, $[IO_4^-]=0.90\times10^{-3} mol \cdot L^{-1}$, $[OH^-]=0.05\ mol \cdot L^{-1}$, $\mu=0.10 mol \cdot L^{-1}$, n_{ap} and r stand for slope and relative coefficient, respectively, of the plot of $\ln k_{obs}$ vs ln[α-BG]

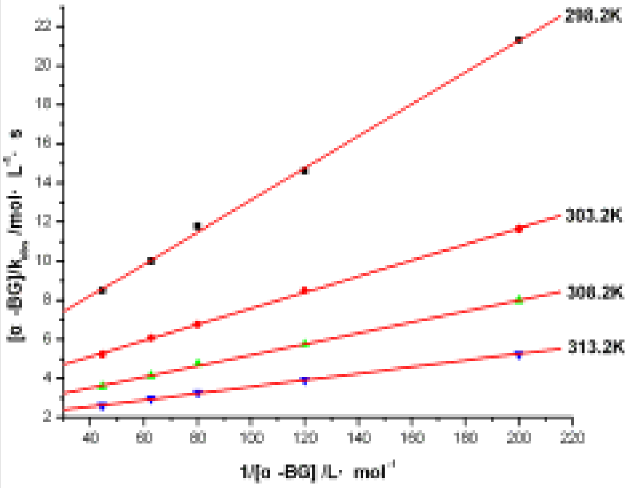

Figure 1: Plots of[α-BG]/k_{obs} vs.1/[α-BG] at different temperatures[Cu(III)]= 1.49×10^{-4}mol·L^{-1}, [IO_4^-]=0.90×10^{-3}mol·L^{-1},[OH^-]=0.05mol·L^{-1}, μ=0.10mol· L^{-1}

Rate dependence on [OH^-]

At constant[Cu(III)], [α-BG], [IO_4^-], ionic strength μ and temperature, k_{obs} values increase with the increasing concentration of [OH^-] and the order with respect to OH^- was found to be fractional order (TABLE 2).

TABLE 2: 10^3k_{obs} varying with different concentrations of 10^2[OH^-] at T=303.2K

10^2 [OH^-]/ mol·L^{-1}	2.50	5.00	6.25	7.50	10.00
10^3k_{obs}/ s^{-1}	0.720	1.317	1.601	1.939	2.699

[Cu(III)]=1.49×10^{-4}mol·L^{-1}, [α-BG]=1.25×10^{-2}mol·L^{-1}, [IO_4^-]=0.90×10^{-3}mol·L^{-1}, μ=0.10mol·L^{-1}

Rate dependence on [IO_4^-]

At fixed[Cu(III)], [OH^-], [α-BG], ionic strength μ and temperature, k_{obs} values decrease with the increasing concentration of [IO_4^-]. The plot of 1/k_{obs} versus[IO_4^-] was linear(r=0.999)(Figure 2).

Rate dependence on ionic Strength μ

At fixed[Cu(III)], [α-BG], [OH^-], [IO_4^-] and temperature, k_{obs} values decreased with the increase in ionic strength μ(TABLE 3)., There is a weak negative salt effect[10].

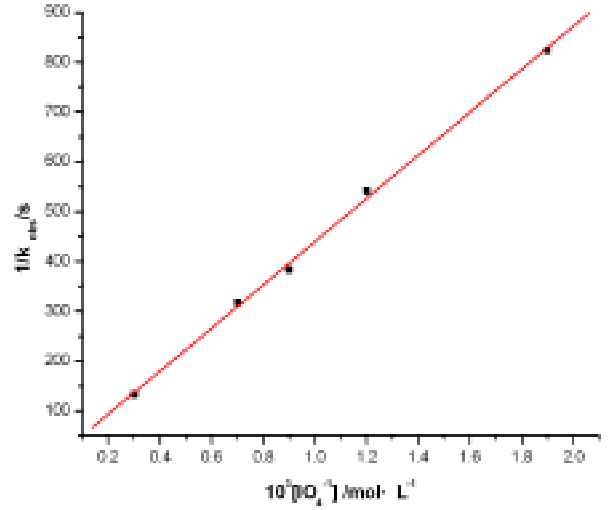

Figure 2: Plots of 1/k_{obs} vs. 1/[IO_4^-]] at T=303.2K [Cu(III)]=1.49×10^{-4}mol·L^{-1}, [α-BG]=1.25×10^{-2} mol·L^{-1}[OH]=0.05 mol·L^{-1}, μ=0.10mol·L^{-1}

TABLE 3: 10^3k_{obs} varying with different ionic strength at T=303.2K

μ/mol·L^{-1}	0.10	0.20	0.30	0.40	0.50
10^3k_{obs}/s^{-1}	3.377	2.406	2.249	2.154	2.102

[Cu(III)]=1.49x10-4mol·L^{-1}, [α-BG]=1.25x10-2mol·L^{-1}, [OH-]=0.05mol· L^{-1}, [IO4-]=0.90x10-3mol·L^{-1}

DISCUSSIONS

In aqueous periodate solution equilibria (1)-(3) were detected and the corresponding equilibrium constants at 273.2K were determined by Aveston[11].

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

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

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

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. Neglecting the concentration of ligand dissociated from Cu(III) and the species of periodate other than $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$, Eq. (4) and (5) can be obtained from(1), (2) and (3):

$$[H_2IO_6^{3-}]=[\beta_3\times[OH^-]/(\beta_2+\beta_3\times[OH^-])]\times[IO_4^-]_{ex} = f([OH^-])\times[IO_4^-]_{ex} \tag{4}$$

$$[H_3IO_6^{2-}]=[\beta_2/(\beta_2+\beta_3\times[OH^-])]\times[IO_4^-]_{ex} = F([OH^-])\times[IO_4^-]_{ex} \tag{5}$$

Here $[IO_4^-]_{ex}$ represents the original overall entering periodate and equals approximately to the sum of [$H_2IO_6^{3-}$] and [$H_3IO_6^{2-}$].

Calculated from(4) and (5), when [OH^-]=0.025 ~0.125mol·L^{-1} the relationship between [$H_2IO_6^{3-}$], [$H_3IO_6^{2-}$] and $[IO_4^-]_{ex}$ as follow (TABLE 4)

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TABLE 4: The existence of$[IO_4^-]_{ex}$ varying with different$[OH^-]$ at T=303.2K

$10[OH^-]/\ mol \cdot L^{-1}$	0.25	0.50	0.63	0.75	1.00	1.25
$[H_2IO_6^{3-}]/[IO_4^-]_{ex}$	0.878	0.935	0.948	0.956	0.966	0.973
$[H_3IO_6^{2-}]/[IO_4^-]_{ex}$	0.122	0.065	0.052	0.044	0.034	0.027

Shi[14] were all considered that the main species of periodate in the reaction is$[Cu(OH)_2(H_3IO_6)_2]^{3-}$. Based on the above discussion, we come to a conclusion that when the main species of periodate is $[Cu(OH)_2(H_2IO_6)_2]^{5-}$:

In view of the above discussion, a possible reaction mechanism was proposed:

$$[Cu(OH)_2(H_2IO_6)_2]^{5-} + OH^- \xleftrightarrow{K_1} [Cu(OH)_2(HIO_6)(H_2IO_6)]^{6-} + H_2O\ DPC \qquad (6)$$

$$[Cu(OH)_2(HIO_6)(H_2IO_6)]^{6-} \xleftrightarrow{K_2} [Cu(OH)_2(HIO_6)]^{3-} + H_2IO_6^{3-} \qquad (7)$$

$$[Cu(OH)_2(HIO_6)]^{3-} + CH_3CH_2CHOHCH_2OH \xleftrightarrow{K_3} [Cu(OH)_2(HIO_6)(\alpha\text{-}BG)]^{3-}\ \alpha-BG \qquad (8)$$

$$[Cu(OH)_2(HIO_6)(\alpha\text{-}BG)]^{3-} + \alpha-BG \xrightarrow[slow]{K} Cu(II) + (\alpha\text{-}BG)\ CH_3CH_2CH(OH)CH(OH)E \qquad (9)$$

$$Cu*(III) + OH^- \xrightarrow{fast} Cu(II) + \alpha\text{-}BG + CH_3CH_2CH(OH)CHO + H_2O \qquad (10)$$

Here $Cu^*(III)$ stand for any kind of form which Cu(III) existed in equilibrium. Subscripts T and e stand for total concentration and equilibrium concentration respectively. Reaction(9) was the rate determining step.

$$[Cu(III)]T = [Cu(OH)_2(H_2IO_6)_2]^{5-}e + [Cu(OH)_2(HIO_6)(H_2IO_6)]_2\text{-}e + [Cu(OH)_2(HIO_6)]^{3-}e + [Cu(OH)_2(HIO_6)(\alpha\text{-}BG)]^{3-}e$$

$$= \left(\frac{[H_2IO_6^{3-}]}{K_1K_2K_3[OH][\alpha-BG]} + \frac{[H_2IO_6^{3-}]}{K_2K_3[\alpha-BG]} + \frac{1}{K_3[\alpha-BG]} + 1\right)[Cu(OH)_2(HIO_6)(\alpha-BG)]^{3-}{}_e \qquad (11)$$

$$\therefore [Cu(OH)_2(HIO_6)(\alpha-BG)]^{3-}{}_e = \left(\frac{K_1K_2K_3[OH][\alpha-BG] \bullet [Cu(III)]_T}{[H_2IO_6^{3-}] + K_1[H_2IO_6^{3-}][OH^-] + K_1K_2K_3[\alpha-BG]}\right. \qquad (12)$$

$$-d[Cu(III)_T/dt = 2K[Cu(OH)_2(HIO_6)(\alpha-BG)]^{3-}[\alpha-BG$$

$$= \frac{2kK_1K_2K_3[OH^-][\alpha-BG]^2}{[H_2IO_6^{3-}] + K_1[OH^-][H_2IO_6^{3-}]K_1K_2[OH^-] + K_1K_2K_3[OH^-][\alpha-BG]} \bullet [Cu(III)]_T = K_{obs}[Cu(III)]_T \qquad (13)$$

$$\therefore K_{obs} = \frac{2kK_1K_2K_3[OH^-][\alpha-BG]^2}{[H_2IO_6^{3-}] + K_1[OH^-][H_2IO_6^{3-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][\alpha-BG]} \qquad (14)$$

$$\frac{[\alpha-BG]}{K_{obs}} = \frac{1}{2K} + \frac{[H_2IO_6^{3-}] + K_1[OH^-][H_2IO_6^{3-}] + K_1K_2[OH^-]}{2kK_1K_2K_3[OH^-][\alpha-BG]} \qquad (15)$$

$$\frac{1}{K_{obs}} = \frac{1 + K_3[\alpha-BG]}{2kK_3[\alpha-BG]^2} + \frac{1 + K_1[OH^-]}{2kK_1K_2K_3[OH^-][\alpha-BG]^2} \bullet [H_2IO_6^{3-}] \qquad (16)$$

$$\frac{1}{K_{obs}} = \frac{[H_2IO_6^{3-}]}{2kK_1K_2K_3[\alpha-BG]^2} \bullet \frac{1}{[OH^-]} + \frac{K_1[H_2IO_6^{3-}] + K_1K_2 + K_1K_2K_3[\alpha-BG]}{2kK_1K_2K_3[\alpha-BG]^2} \qquad (17)$$

Substituting for Eq.(4) into Eq.(16) and (17):

$$\frac{1}{K_{obs}} = \frac{1 + K_3[\alpha-BG]}{2kK_3[\alpha-BG]^2} + \frac{f([OH^-])(1 + K_1[OH^-])}{2kK_1K_2K_3[OH^-][\alpha-BG]^2} \bullet [IO_4^-]_{ex} \qquad (18)$$

$$\frac{1}{K_{obs}} = \frac{[IO_4^{3-}]_{ex}}{2kK_1K_2K_3[\alpha-BG]^2} \bullet \frac{f([OH^-])}{[OH]} + \frac{K_1[H_2IO_6^{3-}] + K_1K_2 + K_1K_2K_3[\alpha-BG]}{2kK_1K_2K_3[\alpha-BG]^2} \qquad (19)$$

$$\frac{1}{K_{obs}} = \frac{[IO_4^-]_{ex}}{2kK_1K_2K_3[\alpha-BG]^2} \bullet \frac{\phi([OH^-])}{[OH]} + \frac{K_1[H_2IO_6^{3-}] + K_1K_2 + K_1K_2K_3[\alpha-BG]}{2kK_1K_2K_3[\alpha-BG]^2} \qquad (20)$$

Eq. (13) and (14) show that first order dependence in DPC and $1<n_{ap}<2$ in α-BG. From the Eq. (15) we could see that the plots of $[\alpha\text{-BG}]/k_{obs}$ versus $1/[\alpha\text{-BG}]$ should be linear with positive intercept, from their intercepts the rate-determining step constants(k) was evaluated, then the activation energy and thermodynamic parameters(t=25°C) were evaluated by the previously published method [15] (TABLE 5). Eq. (18) suggests that the plots of $1/k_{obs}$ versus$[IO_4^-]_{ex}$ should be linear and eq.(19) suggests that the plots of $1/k_{obs}$ versus $f([OH^-])/[OH^-]$ should also be linear(Figure 3), it is in accord with the result of the experiment. If the main species of periodate is$[Cu(OH)_2(H_3IO_6)_2]^{3-}$, eq (20) suggests that the plot of $1/k_{obs}$ versus $\Phi([OH^-])/[OH^-]$ was a liner, it is different from the result of the experiment, so we trend

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

T/K	298.2	303.2	308.2	313.2	Activation parameters(298.2K)
					Ea=51.37kJ·mol^{-1}
10^2k/	10.07	14.36	20.91	26.66	ΔH≠48.89kJ·mol^{-1}
Mol^{-1}dm^{3}S^{-1}					ΔS≠-99.94J·k^{-1}mol^{-1}

r=0.997, A=18.437, B=-6178.81 for the line regression of ln*k* vs.1/T

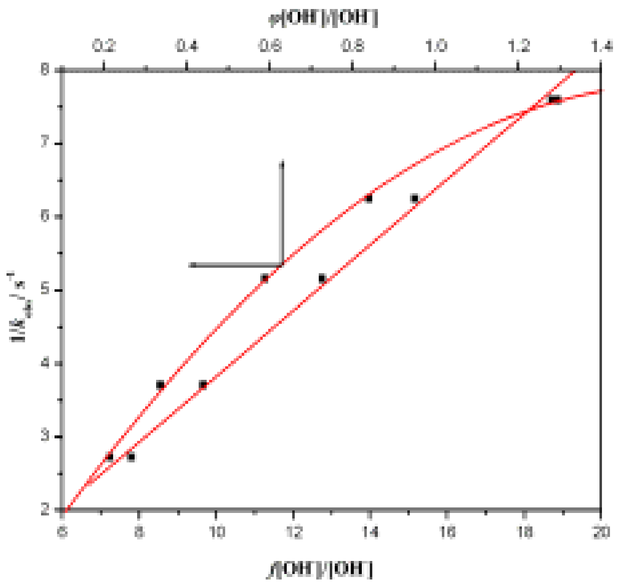

Figure 3: Plots of f([OH$^-$])/[OH$^-$] & Φ([OH$^-$])/[OH$^-$] vs. 1/k_{obs} at T=303.2K[Cu(III)]= 1.49×10^{-4}mol·L^{-1}, [α-BG]=1.25×10^{-2} mol·L^{-1}, [IO_4^-]=0.90×10^{-3}mol·L^{-1}, μ=0.10mol·L^{-1}

10^3k_{obs} varying with different concentrations of 10^3 [IO_4^-] at T=303.2K

10_3[IO4-] mol·L^{-1}	0.30	0.70	0.90	1.20	1.90
10^3k_{obs}/s^{-1}	7.565	3.145	2.606	1.849	1.213

[Cu(III)]=1.49×10^{-4}mol·L^{-1}, [α-BG]=1.25×10^{-2} mol·L-1, [OH$^-$]=0.05 mol· L^{-1}, μ=0.10mol·L^{-1}

towards $[Cu(OH)_2(H_2IO_6)_2]^{5-}$, it is consistent with our experimental results.

CONCLUSION

Under our experimental conditions, the reaction rate of oxidation of α-BG by DPC in alkaline medium is found to be first order to DPC and 1<n_{ap}<2 to α-BG. k_{obs} values decrease with the increasing concentration of [IO_4^-], increase with the increasing concentration of [OH$^-$] and decrease slightly with the increase of the ionic strength. The activation energy is 51.37 kJ·mol^{-1}. The result also validate that the chelate in low-protonize existent form should be more reasonable.

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