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Oxidation of pentaerythritol by diperodatocuprate(III) in alkaline medium-a kinetic and mechanistic study

Jinhuan Shan*, Qianqian Wang

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, (P.R.CHINA)

E-mail: hbushanjh@163.com

Abstract : The kinetic of oxidation of Pentaerythritol by Diperodatocuprate(III)(DPC) in alkaline medium had been studied spectrophotometrically in the different of temperatures range of 20°C-40°C. The reaction of Pentaerythritol is the first order in each [DPC] by experiment determination. The rate constant k_{obs} increased with increase in [OH⁻] and [pentaerythritol] with increasing of the temperature. However, the k_{obs} decreased with increase in [IO₄⁻]. In addition, there was a nega-

tive salt effect. The reaction constants which involved in the different steps of the mechanisms are calculated. Activation parameters which controlled by slow step of the mechanism are discussed and thermodynamic quantities are determined. Therefore, the activation parameters at 298.2K were calculated.
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Keywords : Kinetics and mechanistic; Diperodatocuprate(III); Oxidation; Pentaerythritol.

INTRODUCTION

Diperodatocuprate(III)(DPC)^[1,2] had been reported by many researches. It is one-electron oxidants in the study of kinetics and mechanism of various compounds in alkaline medium. In recent years, the periodate complexes of copper in its trivalent state has been widely used in the analysis of several organic compounds. As the kinetics of self-decomposition, these complexes were studied in some details and it was well recognized^[3] as an analytical reagent. Diperodatocuprate(III) is square-planar d⁸ complex, so Cu(III) is a high oxidation state that its significance to have a further study. Alcohols had been oxidized by

diperodatocuprate(III)(DPC)^[4], We report here the kinetics of the oxidation of Pentaerythritol by diperodatocuprate(III)(DPC).

Pentaerythritol becomes important because of the widely of applications. It is mainly used in the coatings industry and alkyd resin coatings which enabling make the hardness, gloss and durability of the paint film can be improved. It also can be used as manufacture of plastic stabilizers and plasticizers. Because of pentaerythritol having a high degree of symmetry, it is often used as a polyfunctional compound is prepared to take the raw material. In addition, it can be used for pharmaceuticals, pesticides and other production.

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EXPERIMENTAL

All chemicals used were of reagent A.R. grade. Double distilled water was prepared and used throughout the work. The diperiodatocuprate (III)(DPC) crystals is prepared^[5,6] by oxidizing Cu(II) in the alkaline medium and standardized reported by the method^[7] of Jaiswal and Yadava. The crystals dissolving into a solution, then the purity of the complex was characterized by its UV/Visible spectrum, which showed a broad absorption peak at 415 nm. However, DPC and reducing agent need to be extemporaneous so that to maintain always freshly daily. KOH and KNO₃ were employed to maintain the required alkalinity and ionic strength in reaction solutions, respectively.

Kinetics measurements and apparatus

All kinetics measurements were performed under pseudo-first order conditions. The reaction containing required quantities of concentration of DPC (2mL), OH⁻, IO₄⁻ and ionic strength and reductant solution (2mL) of maintain the required concentration were transferred separately to the upper and lower branch tubes of a λ type two-cell reactor. The results obtained the absorption spectra of the diperiodatocuprate(III) well agree with those observed by L. Jensovsky^[8]. The first peak is observed at 415nm and the second at 265nm for the diperiodatocuprate(III) respectively. The concentra-

tion of the diperiodatocuprate(III) has an absorption peak at 415nm, as a function of time. The ionic strength was controlled by KNO₃ solution and the PH was maintained by adding KOH solution. The kinetic measurements were performed on a UV-visible spectrophotometer (TU-1901, Beijing Puxi Inc., China), which had a cell holder kept at constant temperature (±0.1°C) by circulating water from a thermostat (DC-2006, Baoding, China). Other agents did not affect at the wavelength.

Product analysis

When the complete disappearance of the color that marked the reaction was terminated. The main product of oxidation was identified as corresponding aldol by its spot test^[9].

RESULTS AND DISCUSSION

Under the conditions of $[\text{reductant}]_0 \gg 20[\text{Cu(III)}]_0$, the plots of $\ln(A_t - A_\infty)$ versus time were straight lines, indicating that the reaction is the first order in DPC, which using the equation $\ln(A_t - A_\infty) = -k_{\text{obs}}t + b(\text{constant})$. The pseudo-first-order rate constants k_{obs} were calculated by the method of least-squares. The k_{obs} values were the average value of at least three independent experiments, and reproducibility is within ±5%.

Rate dependence on the [reductant]

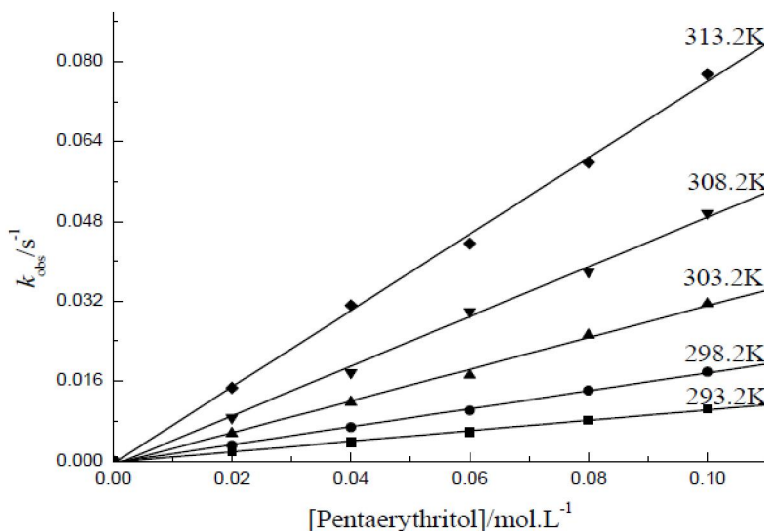


Figure 1 : Plots of k_{obs} vs. [pentaerythritol] ($r = 0.998$); $[\text{DPC}] = 4.52 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $[\text{IO}_4^-] = 1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\mu = 3.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$

At fixed [DPC], [OH⁻], [IO₄⁻] and μ , the [pentaerythritol] was varied in the range of 2.00×10^{-2} to 1.00×10^{-1} mol·L⁻¹ at different temperatures. The plots of $\ln k_{\text{obs}}$ versus $\ln c(\text{reductant})$ were linear ($r \geq 0.998$), according to the slopes of five plots showing that the reductant was found to be first order. Moreover, the k_{obs} increase with the increase of reactant concentration. The plots of k_{obs} versus [reductant] were straight lines passing through the origin ($r \geq 0.998$) (Figure 1).

Rate dependence on the [OH⁻]

The [OH⁻] was varied in the range of 5.00×10^{-3} to 25.00×10^{-3} mol·L⁻¹ at different temperatures, the k_{obs} increased with increasing [OH⁻] at constant [DPC], [reductant], [IO₄⁻] and μ . The plots of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ proved to be straight lines with a positive intercept (Figure 2).

Rate dependence on the [IO₄⁻]

At fixed [DPC], [OH⁻], [reductant] and μ , the [IO₄⁻] was varied in the range of 0.50×10^{-3} to 2.50×10^{-3} mol·L⁻¹, it was found to be the plots of $1/k_{\text{obs}}$ versus [IO₄⁻] were linear (Figure 3). The experimental results showing that the k_{obs} decreased with increase in [IO₄⁻].

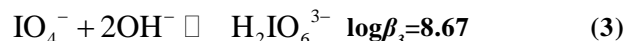
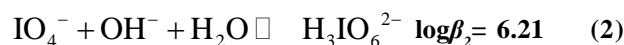
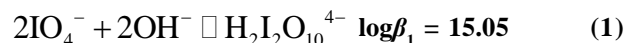
Rate dependence on the μ

Under other conditions fixed, the ionic strength

of the concentration was varied from 1.50×10^{-2} to 7.50×10^{-2} mol·L⁻¹, It was found that there was a negative salt effect, thus indicate that the k_{obs} was decreased with the ionic strength (TABLE1).

Reaction mechanism

In the alkaline medium, periodate acid radical of equilibrium constants was given earlier at 298.2K by Aveston^[10].



The distribution of all the species of periodate in aqueous alkaline solution can be calculated from Equation (1)-(3). In an alkaline medium such as [OH⁻] = 1.00×10^{-2} mol·L⁻¹, [H₂IO₆³⁻]:[H₃IO₆²⁻]:[H₂I₂O₁₀⁴⁻]:[IO₄⁻] = 2.9:1.0:0.02:6 × 10⁻⁵, and at the OH⁻ employed in this study, H₂I₂O₁₀⁴⁻ and IO₄⁻ can be neglected, so the main periodate species exists as [H₂IO₆³⁻] and [H₃IO₆²⁻], we chose the former and this conclusion has supported by literature^[11].

According to equation (1)-(3) can be obtained to equation (4)-(5):

$$[\text{H}_2\text{IO}_6^{3-}] = \frac{\beta_3 [\text{OH}^-]^2}{1 + \beta_2 [\text{OH}^-] + \beta_3 [\text{OH}^-]^2} [\text{IO}_4^-]_{\text{ex}} = f([\text{OH}^-]) [\text{IO}_4^-]_{\text{ex}} \quad (4)$$

$$[\text{H}_3\text{IO}_6^{2-}] = \frac{\beta_2 [\text{OH}^-]}{1 + \beta_2 [\text{OH}^-] + \beta_3 [\text{OH}^-]^2} [\text{IO}_4^-]_{\text{ex}} = \phi([\text{OH}^-]) [\text{IO}_4^-]_{\text{ex}} \quad (5)$$

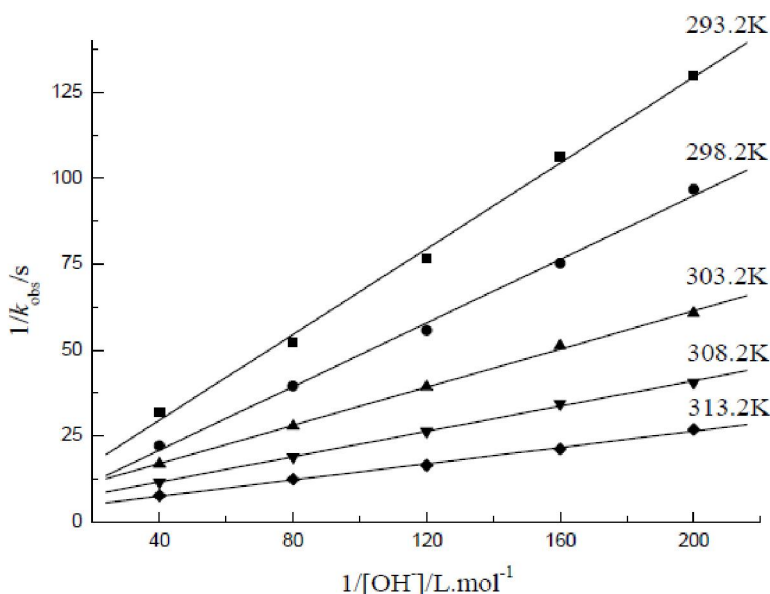


Figure 2 : Plots of $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ at different temperatures ($r \geq 0.998$), [DPC] = 4.52×10^{-5} mol·L⁻¹, [pentaerythritol] = 6.00×10^{-2} mol·L⁻¹, [IO₄⁻] = 1.00×10^{-3} mol·L⁻¹, $\mu = 3.00 \times 10^{-2}$ mol·L⁻¹

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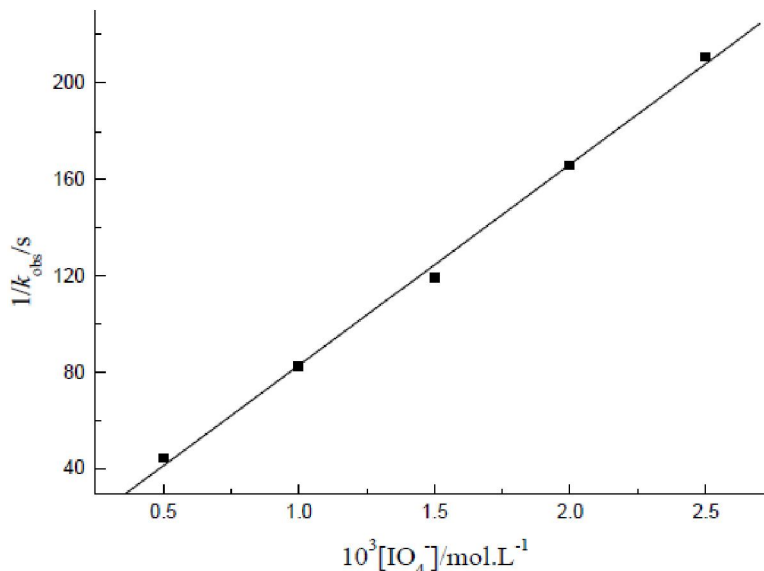


Figure 3 : Plots of $1/k_{\text{obs}}$ vs. $[\text{IO}_4^-]$ at 303.2K, $[\text{DPC}]=4.52 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $[\text{pentaerythritol}]=6.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[\text{OH}^-]=1.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $\mu=3.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, ($r \geq 0.998$)

TABLE 1 : Rate dependence on the ionic strength (μ) at 313.2K

$10^3 \mu / \text{mol}\cdot\text{L}^{-1}$	1.50	3.00	4.50	6.00	7.50
$10^3 k_{\text{obs}} / \text{s}^{-1}$	21.52	12.83	11.62	10.09	8.61

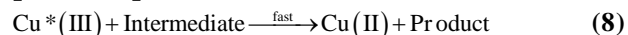
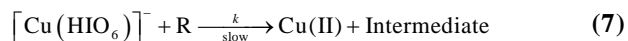
$[\text{DPC}]=4.52 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $[\text{IO}_4^-]=1.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{OH}^-]=1.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $[\text{pentaerythritol}]=6.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$

TABLE 2 : Rate constants (k) and Activation parameters of the rate-determining step

T(K)	$10^2 k (\text{mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1})$	Thermodynamic activation parameters
293.2	17.16	$E_a = 34.13 \text{ kJ}\cdot\text{mol}^{-1}$ $\Delta H^\ddagger = 31.65 \text{ kJ}\cdot\text{mol}^{-1}$ $\Delta S^\ddagger = -151.59 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
298.2	21.74	
303.2	28.14	
308.2	33.63	
313.2	42.68	

The plot of $\ln k$ vs $1/T$ have following intercept (a) slope (b) and relative coefficient (r), $a=12.23$, $b= -4104.70$, $r= 0.998$.

It is known that $[\text{H}_2\text{IO}_6^{3-}]$ was protonated and coordinated with central ion to form $[\text{Cu}(\text{H}_2\text{IO}_6)_2]^{3-}$. Based on the experimental results and discussion, the mechanism was proposed as follows (R stands for $\text{C}(\text{CH}_2\text{OH})_4$).



The $\text{Cu}^*(\text{III})$ stand for any kind of which Cu^{3+} existed in equilibrium, (6)-(8), subscripts T and e represents the total concentration and at equilibrium concentration respectively, The total concentration of Cu (III) can be written as:

$$[\text{Cu}(\text{III})]_{\text{T}} = [\text{Cu}(\text{H}_2\text{IO}_6)_2]_{\text{e}}^{3-} + [\text{Cu}(\text{HIO}_6)]_{\text{e}}^-$$

Due to (8) was the rate-determining step, the rate law of the reaction was derived as follows:

$$-\frac{d[\text{Cu}(\text{III})]_{\text{T}}}{dt} = \frac{2kK_1[\text{R}][\text{OH}^-]}{K_1[\text{OH}^-] + [\text{H}_2\text{IO}_6^{3-}]} [\text{Cu}(\text{III})]_{\text{T}} = k_{\text{obs}} [\text{Cu}(\text{III})]_{\text{T}} \quad (9)$$

$$k_{\text{obs}} = \frac{2kK_1[\text{R}][\text{OH}^-]}{K_1[\text{OH}^-] + [\text{H}_2\text{IO}_6^{3-}]} \quad (10)$$

The equation (4) substituted into equation (10) can be obtained to the following equation:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{2k[\text{R}]} + \frac{f([\text{OH}^-])}{2kK_1[\text{R}][\text{OH}^-]} [\text{IO}_4^-]_{\text{ex}} \quad (11)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{2k[\text{R}]} + \frac{[\text{IO}_4^-]_{\text{ex}} f([\text{OH}^-])}{2kK_1[\text{R}][\text{OH}^-]} \quad (12)$$

From the equation (10) can be known the plots k_{obs} vs [reductants] was straight lines passing through

the origin at different temperature, the equation (11) and (12) suggest that the plots of $1/k_{\text{obs}}$ vs $f([\text{OH}^-])$ and $1/k_{\text{obs}}$ vs $[\text{IO}_4^-]$ were also straight lines, in addition, the k_{obs} decreased with increase in $[\text{IO}_4^-]$ and k_{obs} increased with increase in $[\text{OH}^-]$. Activation energy and the thermodynamic parameters were evaluated at 298.2K by the method given earlier^[12] (TABLE 2).

CONCLUSION

Through the previous studies, we found that many different types of reductants have been oxidized by DPC(III). On the bases of above discussion and results, we can know that the rate constant of the rate-determining step and activation parameters with respect to the rate-determining step of the reaction were computed. Through the deep study of the reaction system, it can be good to verify the extraordinary of the transition metal complexes present with low protonated form. According to the experimental determination, we can be found there is a obvious negative salt effect, which is because of the "ion atmosphere" can be contain the effects between ions of the reaction, it makes activated complex more unstable. All the mechanism described is consistent with mechanistic and kinetic studies.

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