Oxidation of Neopentyl Glycol by Diperiodatocuprate(III) in Alkaline Medium-A Kinetic and Mechanistic Study

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The kinetics of oxidation of neopentyl glycol by diperiodatocuprate(III) in alkaline medium had been studied spectrophtometrically in the different of temperatures range of 25-45 °C. The reaction of neopentyl glycol is the first order in each [diperiodatocuprate(III)] by experiment determination. The rate constant k_{obs} increased with increase in [OH$^-$] and [neopentyl glycol]. However, with the increase of the temperature, the k_{obs} decreased with increase in [IO$_4^-$]. 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 298.2 K were calculated.

Keywords: Kinetics, Diperiodatocuprate(III), Oxidation, Neopentyl glycol.

INTRODUCTION

Diperiodatocuprate(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. 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 and it was well recognized as an analytical reagent[3]. Diperiodatocuprate(III) is a square-planar d^8 complex, so Cu(III) is a high oxidation state that its significance to have a further study. Alcohols had been oxidized by diperiodatocuprate(III)[4], We report here the kinetics of the oxidation of neopentyl glycol by diperiodatocuprate(III).

Neopentyl glycol becomes important because of many applications in industrial production. Such as neopentyl glycol can be used for production of plasticizers, resins, high lubricant additive and as well as in organic synthesis. In addition, neopentyl glycol is a better solvent, it can be used to select the separation of aromatic and naphthenic hydrocarbons. Due to no hydrogen atom at the β position on neopentyl glycol, it has high chemical stability and thermal stability. It can also be used as analgesic ibuprofen synthesis in the pharmaceutical industry.

EXPERIMENTAL

All chemicals used were of reagent A.R. grade. Double distilled water was prepared and used throughout the work.

The diperiodatocuprate(III) crystals is prepared[5,6] by oxidizing Cu(II) in the alkaline medium and standardized by the method of Jaiswal and Yadava[7]. 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, diperiodatocuprate(III) and reducing agent need to extemporaneous so that to maintain always freshly daily. KOH and KNO$_3$ were employed to maintain the required alkalinity and ionic strength in reaction solutions, respectively.

Kinetics measurements: All kinetics measurements were performed under pseudo-first order conditions. The reaction containing required quantities of concentration of diperiodatocuprate(III) (2 mL), OH$^-$, IO$_4^-$ and ionic strength and reductant solution (2 mL) 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 Jensovsky[8]. The first peak is observed at 415 nm and the second at 265 nm for the diperiodatocuprate(III), respectively. The concentration of the diperiodatocuprate(III) has an absorption peak at 415 nm, as a function of time. The ionic strength was controlled by KNO$_3$ 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.

When the complete disappearance of the colour 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 $[reductant]_0 >> 20[Cu(III)]_0$, the plots of $\ln(A_t-A_\infty)$ *versus* time were straight lines, indicating that the reaction is the first order in diperiodatocuprate(III), which using the equation $\ln (A_t-A_\infty) = -k_{obs} t + b$ (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 [reductant]: At fixed [DPC], [OH⁻], [IO₄⁻] and μ, the [neopentyl glycol] was varied in the range of 6×10^{-2} to 3×10^{-1} mol L⁻¹ at different temperatures. The plots of $\ln k_{obs}$ *versus* ln c (reductant) were linear (r ≥ 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 ≥ 0.998) (Fig. 1).
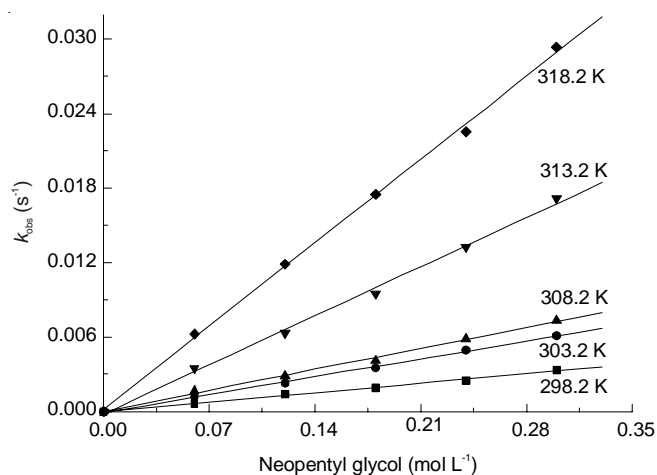

Fig. 1. Plots of k_{obs} *vs.* [neopentyl glycol] (r ≥ 0.998); [DPC] = 4.52×10^{-5} mol L⁻¹, [IO₄⁻] = 1×10^{-3} mol L⁻¹, [OH⁻] = 1×10^{-2} mol L⁻¹, $\mu = 2.10 \times 10^{-2}$ mol L⁻¹

Rate dependence on [OH⁻]: The [OH⁻] was varied in the range of 5×10^{-3} to 25×10^{-3} mol L⁻¹, the k_{obs} increased with increasing [OH⁻] at constant diperiodatocuprate(III), [reductant], [IO₄⁻], μ and temperature. The plots of $1/k_{obs}$ *versus* $1/[OH⁻]$ proved to be straight lines (Fig. 2).

Rate dependence on [IO₄⁻]: At fixed diperiodatocuprate(III), [OH⁻], [reductant] and μ, the [IO₄⁻] was varied in the range of 0.50×10^{-3} to 2.50×10^{-3} mol L⁻¹ at different temperatures that found to be the plots of $1/k_{obs}$ *versus* [IO₄⁻] were linear (Fig. 3). The experimental results showing that the k_{obs} decreased with increase in [IO₄⁻].

Rate dependence on 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 (Table-1).

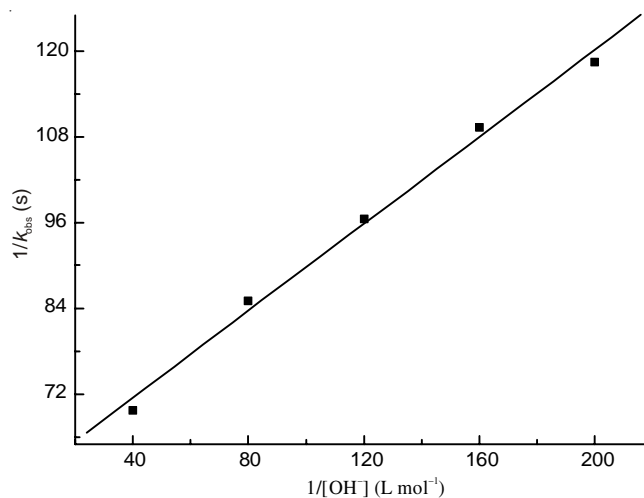Fig. 2. Plots of $1/k_{obs}$ *vs.* $1/[OH⁻]$ at 303.2 K; [DPC] = 4.52×10^{-5} mol L⁻¹, [IO₄⁻] = 1×10^{-3} mol L⁻¹, $\mu = 2.10 \times 10^{-2}$ mol L⁻¹, [neopentyl glycol] = 1.80×10^{-1} mol L⁻¹, (r ≥ 0.997)
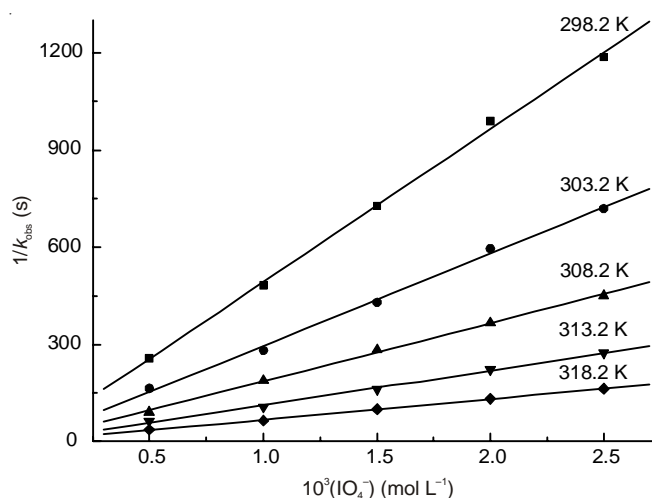
Fig. 3. Plots of $1/k_{obs}$ *vs.* [IO₄⁻] at different temperatures, [DPC] = 4.52×10^{-5} mol L⁻¹, [neopentyl glycol] = 1.80×10^{-1} mol L⁻¹, [OH⁻] = 1×10^{-2} mol L⁻¹, $\mu = 2.10 \times 10^{-2}$ mol L⁻¹, (r ≥ 0.999)

TABLE-1
RATE DEPENDENCE ON THE IONIC STRENGTH (μ) AT 313.2 K

$10^2 \mu$(mol L⁻¹)	1.50	3.00	4.50	6.00	7.50
$10^3 k_{obs}$ (s⁻¹)	13.96	7.54	5.97	4.95	4.28

[DPC] = 4.52×10^{-5} mol L⁻¹, [IO₄⁻] = 1×10^{-3} mol L⁻¹, [OH⁻] = 1×10^{-2} mol L⁻¹ [neopentyl glycol] = 1.80×10^{-1} mol L⁻¹

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

$$2IO_4^- + 2OH^- \rightleftharpoons H_2I_2O_{10}^{4-} \qquad \log \beta_1 = 15.05 \qquad (1)$$
$$IO_4^- + OH^- + H_2O \rightleftharpoons H_3IO_6^{2-} \qquad \log \beta_2 = 6.21 \qquad (2)$$
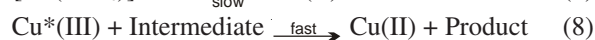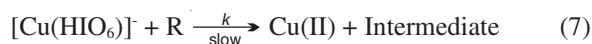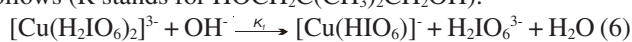$$IO_4^- + 2OH^- \rightleftharpoons H_2IO_6^{3-} \qquad \log \beta_3 = 8.67 \qquad (3)$$
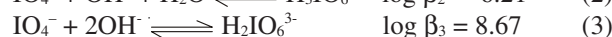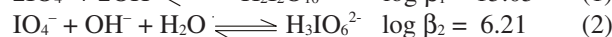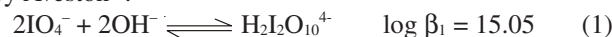
The distribution of all the species of periodate in aqueous alkaline solution can be calculated from eqn. 1-3. In an alkaline medium such as [OH⁻] = 1×10^{-2} mol L⁻¹, $[H_2IO_6^{3-}]:[H_3IO_6^{2-}]:[H_2I_2O_{10}^{4-}]:[IO_4^-] = 2.9:1.0:0.02:6 \times 10^{-5}$ and at the OH⁻ employed in this study, $H_2I_2O_{10}^{4-}$ and IO_4^- can be neglected, so the main periodate species exists as $[H_2IO_6^{3-}]$ and $[H_3IO_6^{2-}]$, we chose the former and this conclusion has supported by literature[11].

According to eqn. 1-3 can be obtained to eqn. 4-5:

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

$$= f([OH^-])[IO_4{}^-]_{ex} \quad (4)$$

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

$$= \phi([OH^-])[IO_4{}^-]_{ex} \quad (5)$$

It is known that $[H_2IO_6{}^{3-}]$ was protonated and coordinated with central ion to form $[Cu(H_2IO_6)_2]^{3-}$. Based on the experimental results and discussion, the mechanism was poposed as follows (R stands for $HOCH_2C(CH_3)_2CH_2OH$).

$$[Cu(H_2IO_6)_2]^{3-} + OH^- \xrightarrow{K_1} [Cu(HIO_6)]^- + H_2IO_6{}^{3-} + H_2O \quad (6)$$

$$[Cu(HIO_6)]^- + R \xrightarrow[slow]{k} Cu(II) + Intermediate \quad (7)$$

$$Cu^*(III) + Intermediate \xrightarrow{fast} Cu(II) + Product \quad (8)$$

The Cu*(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:

$$[Cu(III)]_T = [Cu(H_2IO_6)_2]^{3-}_e + [Cu(HIO_6)]^-_e$$

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

$$-\frac{d[Cu(III)]_T}{dt} = \frac{2kK_1[R][OH^-]}{K_1[OH^-]+[H_2IO_6{}^{3-}]}$$

$$[Cu(III)]_T = k_{obs}[Cu(III)]_T \quad (9)$$

$$k_{obs} = \frac{2kK_1[R][OH^-]}{K_1[OH^-]+[H_2IO_6{}^{3-}]} \quad (10)$$

The eqn. 4 substituted into eqn. 10 can be obtained to the following equation:

$$\frac{1}{k_{obs}} = \frac{1}{2k[R^-]} + \frac{f([OH^-])}{2kK_1[R][OH^-]}[IO_4{}^-]_{ex} \quad (11)$$

$$\frac{1}{k_{obs}} = \frac{1}{2k[R^-]} + \frac{[IO_4{}^-]_{ex}}{2kK_1[R]}\frac{f([OH^-])}{[OH^-]} \quad (12)$$

From the eqn. 10 can be knows the plots k_{obs} vs. [reductants] was straight lines passing through the origin at different temperature. The eqn. 11 and 12 suggest that the plots

of $1/k_{obs}$ vs. $f([OH^-])/[OH^-]$ and $1/k_{obs}$ vs. $[IO_4{}^-]$ were also straight lines, in addition, the k_{obs} decreased with increase in $[IO_4{}^-]$ and k_{obs} increased with increase in $[OH^-]$. Activation energy and the thermodynamic parameters were evaluated at 298.2 K by the method given earlier[12] (Table-2).

TABLE-2
RATE CONSTANTS (k) AND ACTIVATION
PARAMETERS OF THE RATE-DETERMINING STEP

T(K)	$10^2 k$ (mol^{-1} L s^{-1})	Thermodynamic activation parameters
298.2	5.10	
303.2	8.80	E_a = 70.28 kJ mol^{-1}
308.2	13.20	$\Delta H^{\neq}$ = 67.80 kJ mol^{-1}
313.2	21.80	$\Delta S^{\neq}$ = -38.24 J K^{-1} mol^{-1}
318.2	33.40	

The plot of ln k vs 1/T have following intercept (a) slope (b) and relative coefficient (r), a = 25.85, b = -8453.26, r = 0.998

Conclusion

Through the previous studies, we found that many different types of reductants have been oxidized by diperiodatocuprate(III). 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 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 that 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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