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Oxidation of butylamine and isobutylamine by diperodatocuprate(III) in alkaline medium - A kinetic and mechanistic study

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ABSTRACT

The kinetics of oxidation of butylamine and isobutylamine by diperodatocuprate(III) (DPC) in alkaline medium has been studied spectrophotometrically in the temperatures range of 20-40 °C. All data follow pseudo-first order reaction in [DPC] under experimental conditions. It was found that the reaction showed pseudo-first order with respect to DPC and $1 < n_{ap} < 2$ to reductant. The rate constant k_{obs} increased with increase in [reductant], however, the k_{obs} decreased with increase in $[IO_4^-]$ and $[OH^-]$. In addition, there was a negative salt effect. Through the determined experimentally found that the rate of isobutylamine was higher than butylamine. The reaction constants involved in the different steps of the mechanisms are calculated. Activation parameters, which were controlled by slow step of the mechanism are discussed and thermodynamic quantities are determined. Therefore, the activation parameters at 298.2 K were calculated.

1. Introduction

It is well known that the studies of the supernormal oxidation states of transition metals were initially done in United States and India. Diperodatocuprate(III) had been reported by many researches [1-3]. 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 as an analytical reagent [4]. Diperiodatocuprate(III) is square-planar d^8 complex, so Cu(III) is a high oxidation state that its significance to have a further study. Amine had been oxidized by diperiodatocuprate(III) [5,6], we report here the kinetics of the oxidation of butylamine and isobutylamine by diperiodatocuprate(III).

Butylamine becomes important because of the widely of applications in production, such as butylamine applied in pharmaceutical intermediates which can be used for production of anti-diabetic drug and applied in pesticide intermediates which can be used for production of herbicide and insecticide. It is also applied in intermediates of rubber accelerator. In addition, butylamine is the developer of color photograph. Isobutylamine applied in synthetic intermediate of insecticide, corrosion inhibitor and rubber processing chemicals, it is also used as neutralizing agent and stabilizer which applied for mineral flotation agent, gasoline antiknock agent, polymerization catalyst and sulfobenzoic acid alkyl ester thirteen.

2. Experimental

2.1. Materials

All chemicals used were of reagent analytical reagent grade. Double distilled water was prepared and used throughout the work. The diperiodatocuprate(III) crystals is prepared [7,8] by oxidizing Cu(II) in the alkaline medium and standardized reported by the method of Chandra and Yadava [9]. 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 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.

2.2. Instrumentations

The kinetic measurements were performed on a UV-visible spectrophotometer (TU-1950, Beijing Puxi Inc., China), which had a cell holder kept at constant temperature (±0.1 °C) by circulating water from a thermostat (RA8, Germany). Other agents did not affect at the wavelength.

2.3. Kinetics measurements

All kinetics measurements were performed under pseudo-first order conditions. The reaction containing required quantities of concentration of DPC (2 mL), OH^-, IO_4^-, 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 diperiodato cuprate(III) well agree with those observed by L. Jensovsky [10]. 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.

3. Results and discussion

3.1. Evaluation of pseudo-first order rate constants

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 DPC, which using the equation $\ln(A_t-A_\infty) = -k_{obs} \times t + b$ (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%.

3.2. Rate dependence on the [reductant]

At fixed [DPC], $[OH^-]$, $[IO_4^-]$ and μ, the [butylamine] was varied in the range of 5.00×10^{-2} to 25.00×10^{-2} mol/L and the [isobutylamine] was varied in the range of 1.00×10^{-2} to 5.00×10^{-2} mol/L at different temperatures. The plots of ln k_{obs} versus ln c (reductant) were linear ($r \geq 0.999$), according to the slopes of five plots showing that the reaction order $1 < n_{ap} < 2$ dependence in reductant. Moreover, the k_{obs} increase with the increase of reactant concentration. The plots of $[reductant]/k_{obs}$ vs $1/[reductant]$ were straight line with a positive intercept (Figure 1 and 2).
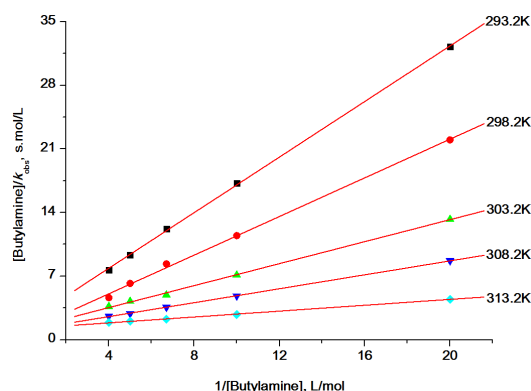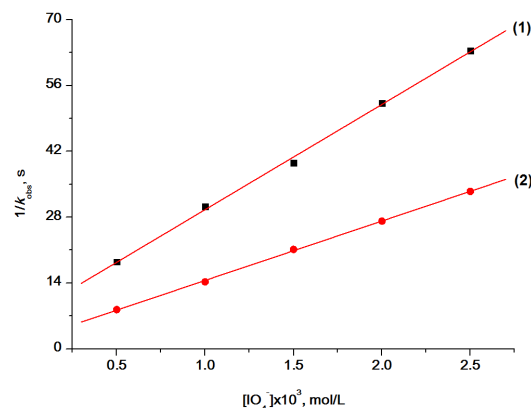

Figure 1. Plots of [butylamine]/k_{obs} vs. 1/[butylamine] ($r \geq 0.999$). [DPC] = 8.61×10^{-5} mol/L, $[IO_4^-]$ = 1.00×10^{-3} mol/L, $[OH^-]$ = 1.00×10^{-2} mol/L, μ = 3.00×10^{-2} mol/L.
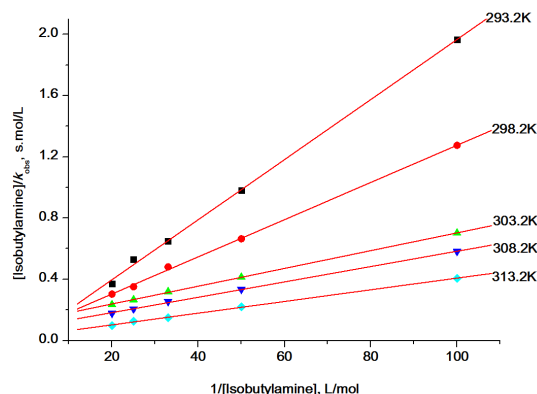
Figure 2. Plots of [isobutylamine]/k_{obs} vs. 1/[isobutylamine] ($r \geq 0.999$). [DPC] = 8.61×10^{-5} mol/L, $[IO_4^-]$ = 1.00×10^{-3} mol/L, $[OH^-]$ = 1.00×10^{-2} mol/L, μ = 3.00×10^{-2} mol/L.

3.3. Rate dependence on the $[IO_4^-]$

At fixed [DPC], $[OH^-]$, [reductant], μ and temperature, the $[IO_4^-]$ was varied in the range of 0.50×10^{-3} to 2.50×10^{-3} mol/L. It is found to be the plots of $1/k_{obs}$ versus $[IO_4^-]$ were straight line with a positive intercept (Figure 3). The experimental results showing that the k_{obs} decreased with increase in $[IO_4^-]$.

Figure 3. Plots of $1/k_{obs}$ vs. $[IO_4^-]$ at 303.2 K. [DPC] = 8.61×10^{-5} mol/L, $[OH^-]$ = 1.00×10^{-2} mol/L, μ = 3.00×10^{-2} mol/L. (1) [Butylamine] = 15.00×10^{-2} mol/L, ($r \geq 0.999$) (2) [Isobutylamine] = 3.00×10^{-2} mol/L, ($r \geq 0.999$)

3.4. Rate dependence on the $[OH^-]$

The $[OH^-]$ was varied in the range of 5.00×10^{-3} to 25.00×10^{-3} mol/L, the k_{obs} decreased with increasing $[OH^-]$ at constant [DPC], [reductant], $[IO_4^-]$, μ and temperature. The plots of $1/k_{obs}$ versus $[OH^-]$ proved to be straight line with a positive intercept (Figure 4).

3.5. Rate dependence on ionic strength μ

The ionic strength of the concentration was varied from 1.50×10^{-2} to 7.50×10^{-2} mol/L at constant [DPC], [reductant], $[OH^-]$, $[IO_4^-]$ and temperature, It was found that the reaction of [reductant] was a negative salt effect, thus indicate that the k_{obs} was decreased with the ionic strength [11] (Table 1).

4. Reaction mechanism

In the alkaline medium, periodate acid radical of equilibrium constants was given earlier at 298.2 K by Aveston [11].

Table 1. Influence of variation ionic strength μ at 303.2 K.

$\mu \times 10^2$, mol/L		1.50	3.00	4.50	6.00	7.50
$k_{obs} \times 10^2$, s^{-1}	Butylamine	4.67	3.41	2.72	2.46	2.28
	Isobutylamine	10.33	6.60	4.97	3.92	3.64

[DPC] = 8.61×10^{-5} mol/L, [OH$^-$] = 1.00×10^{-2} mol/L, [IO$_4^-$] = 1.00×10^{-3} mol/L. (1) [Butylamine] = 15.00×10^{-2} mol/L (2) [Isobutylamine] = 3.00×10^{-2} mol/L.

Table 2. Rate constants (k) and the activation parameters for the rate-determining step at 298.2 K.
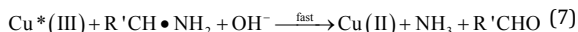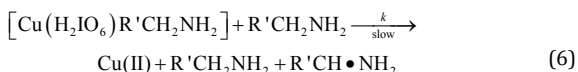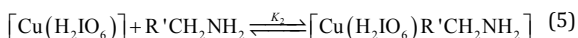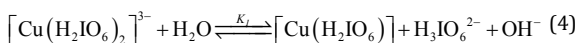
T, K		293.2	298.2	303.2	308.2	313.2
$k \times 10$, mol^{-1}.L.s^{-1}	Butylamine	5.59	7.03	8.88	10.27	12.47
K, mol^{-1}.L.s^{-1}	Isobutylamine	8.57	14.92	24.53	40.19	76.17
Thermodynamic activation parameters	Butylamine	Ea (kJ·mol^{-1}) = 30.05, $\Delta H^{\neq}$ (kJ·mol^{-1}) = 27.57, $\Delta S^{\neq}$ (J·K^{-1}·mol^{-1}) = -155.55				
	Isobutylamine	Ea (kJ·mol^{-1}) = 80.98, $\Delta H^{\neq}$ (kJ·mol^{-1}) = 78.51, $\Delta S^{\neq}$ (J·K^{-1}·mol^{-1}) = 40.38				

The plot of ln k *vs* 1/T have following intercept (a) slope (b) and relative coefficient (*r*). Butylamine: a = 11.75, b = -3614.89, *r* = -0.999; Isobutylamine: a = 35.32, b = -9740.79, *r* = -0.998.

$$2IO_4^- + 2OH^- \rightleftharpoons H_2I_2O_{10}^{4-} \qquad \log \beta_1 = 15.05 \qquad (1)$$

$$IO_4^- + OH^- + H_2O \rightleftharpoons H_3IO_6^{2-} \qquad \log \beta_2 = 6.21 \qquad (2)$$

$$IO_4^- + 2OH^- \rightleftharpoons H_2IO_6^{3-} \qquad \log \beta_3 = 8.67 \qquad (3)$$

The distribution of all the species of periodate in aqueous alkaline solution can be calculated from Equation (1-3). In an alkaline medium such as [OH$^-$] = 1.00×10^{-2} mol/L, [H$_2$IO$_6^{3-}$]:[H$_3$IO$_6^{2-}$]:[H$_2$I$_2$O$_{10}^{4-}$]:[IO$_4^-$] = 2.9:1.0:0.02:6×10^{-5}, and at the OH$^-$ employed in this study, H$_2$I$_2$O$_{10}^{4-}$ and IO$_4^-$ can be neglected, so the main periodate species exists as [H$_2$IO$_6^{3-}$] and [H$_3$IO$_6^{2-}$], we chose the former and this conclusion has supported by literature [12].

It is known that [H$_2$IO$_6^{3-}$] was protonated and coordinated with central ion to form [Cu(H$_2$IO$_6$)$_2$]$^{3-}$. Based on the experimental results and discussion, the mechanism was proposed as follows (R stands for butylamine and isobutylamine, R′ stands for CH$_3$(CH$_2$)$_2$ and (CH$_3$)$_2$CH, respectively).

$$\left[Cu\left(H_2IO_6\right)_2\right]^{3-} + H_2O \xrightleftharpoons{K_1} \left[Cu\left(H_2IO_6\right)\right] + H_3IO_6^{2-} + OH^- \quad (4)$$

$$\left[Cu\left(H_2IO_6\right)\right] + R'CH_2NH_2 \xrightleftharpoons{K_2} \left[Cu\left(H_2IO_6\right)R'CH_2NH_2\right] \quad (5)$$

$$\left[Cu\left(H_2IO_6\right)R'CH_2NH_2\right] + R'CH_2NH_2 \xrightarrow[slow]{k}$$
$$Cu(II) + R'CH_2NH_2 + R'CH \bullet NH_2 \quad (6)$$

$$Cu^*(III) + R'CH \bullet NH_2 + OH^- \xrightarrow{fast} Cu(II) + NH_3 + R'CHO \quad (7)$$

The Cu*(III) stand for any kind of which Cu^{3+} existed in Equilibrium (4-7), subscripts T and e represents the total concentration and at equilibrium concentration respectively.

The total concentration of Cu(III) can be written as:

$$\left[Cu(III)\right]_T = \left[Cu\left(H_2IO_6\right)_2\right]_e^{3-} + \left[Cu\left(H_2IO_6\right)\right]_e + \left[Cu\left(H_2IO_6\right)R'CH_2NH_2\right]_e \quad (8)$$

Due to Equation (6) was the rate-determining step, the rate law of the reaction was derived as follows:

$$-\frac{d\left[Cu(III)\right]_T}{dt} = \frac{2kK_1K_2[R]^2}{K_1 + \left[OH^-\right]\left[H_3IO_6^{2-}\right] + K_1K_2[R]}\left[Cu(III)\right]_T = k_{obs}\left[Cu(III)\right]_T \quad (9)$$

$$k_{obs} = \frac{2kK_1K_2[R]^2}{K_1 + \left[OH^-\right]\left[H_3IO_6^{2-}\right] + K_1K_2[R]} \quad (10)$$

The Equation (10) deformation can be obtained to Equation (11) and (12):

$$\frac{[R]}{k_{obs}} = \frac{1}{2k} + \frac{K_1 + \left[OH^-\right]\left[H_3IO_6^{2-}\right]}{2kK_1K_2} \times \frac{1}{[R]} \quad (11)$$

$$\frac{1}{k_{obs}} = \frac{K_1K_2[R] + K_1}{2kK_1K_2[R]^2} + \frac{\left[OH^-\right]}{2kK_1K_2[R]^2} \times \left[H_3IO_6^{2-}\right] \quad (12)$$

From the Equation (9) can be knows the reaction showed the first order dependence in DPC and the Equation (11) showed $1 < n_{ap} < 2$ dependence in reductant, which the plots [reductant]/k$_{obs}$ *vs* 1/[reductant] was straight lines with a positive intercept. The Equation (12) suggest that the plots of 1/k$_{obs}$ *vs* [OH$^-$] and 1/k$_{obs}$ *vs* [IO$_4^-$] were also straight lines, in addition, the k$_{obs}$ decreased with increase in [OH$^-$] and [IO$_4^-$]. Activation energy and the thermodynamic parameters were evaluated at 298.2 K by the method given earlier [13] (Table 2).
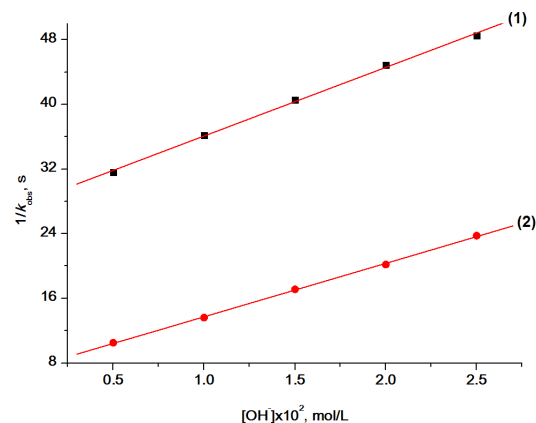
Figure 4. Plots of 1/k$_{obs}$ *vs.* [OH$^-$] at 303.2 K. [DPC] = 8.61×10^{-5} mol/L, [IO$_4^-$] = 1.00×10^{-3} mol/L, μ = 3.00×10^{-2} mol/L, (1) [Butylamine] = 15.00×10^{-2} mol/L, (*r* ≥ 0.999) (2) [Isobutylamine] = 3.00×10^{-2} mol/L, (*r* ≥ 0.999).

5. Conclusion

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 that the rate constants and the rate-determining step constants of isobutylamine are larger than butylamine, this is because of the complex formed with isobutylamine of the space steric hindrance is smaller than with butylamine so that increasing the reaction rate. In addition, there is an obvious negative salt effect in reductant, which is because of the "ion

atmosphere" can be contain the effects between ions of the reaction, it makes activated complex more unstable. For isobutylamine experimental values for $\Delta S^{\neq} > 0$, it may be related to the structure of the transition state is relatively loose. All the mechanism described is consistent with mechanistic and kinetic studies.

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