Kinetics and Mechanism of Oxidation of Sarcosine by Diperiodatocuprate(III) Complex in Alkaline Medium

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The kinetics of oxidation of sarcosine by diperiodatocuprate(III) (DPC) was studied with spectrophotometry in a temperature range of 292.2—304.2 K. The reaction between diperiodatocuprate(III) and sarcosine in alkaline medium exhibits 1∶1 stoichiometry (DPC∶sarcosine). The reaction was found to be first order with respect to both DPC and sarcosine. The observed rate constant (k_{obs}) decreased with the increase of the [IO$_4^-$], decreased with the increase of the [OH$^-$], and then increased with the increase of the [OH$^-$] after a turning point. There was no salt effect, and free radicals were detected. Based on the experimental results, a mechanism involving the diperiodatocuprate(III) (DPC) as the reactive species of the oxidant has been proposed. The activation parameters, as well as the rate constants of the rate-determining step, have been calculated.

Keywords diperiodatocuprate(III), sarcosine, kinetics and mechanism, redox reaction

Introduction

In recent years, the study of the highest oxidation state of transition metals has intrigued many researchers. This can provide new and valuable information in some fields. Transition metals in a higher oxidation state can generally be stabilized by chelation with suitable polydentate ligands, while metal chelates, such as diperiodatocuprate(III),[1] ditelluratocuprate(III),[2] diperiodatonickelate(IV),[3] are good oxidants in a medium with an appropriate pH value. These complexes, such as Ag(III), Cu(III) and Ni(IV) complexes, can be used as an oxidation reagent in organic chemistry and analytical chemistry.[4,5] As a kind of oxidation reagents, those complexes have been used widely in kinetic study.[6]

Sarcosine is an important and interesting compound, which finds a number of applications in the syntheses of biochemical reagent, daily chemical, amino acid surfactant, health caring medicine, *etc*. The study of sarcosine becomes important because of its biological significance. In this paper, the kinetics and mechanism of oxidation of sarcosine by diperiodatocuprate(III) is presented.

Experimental

Reagents and apparatus

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Solution of $[\mathrm{Cu(H_2IO_6)_2}]^{3-}$ (DPC) and reductant were always freshly prepared before use. The stock solution of DPC in a strong alkaline medium was prepared by the method given by Jaiswal.[7] The concentration of DPC was derived from its absorption at $\lambda=415$ nm. The ionic strength μ was maintained by adding $\mathrm{KNO_3}$ solution and the pH value of the reaction mixture was regulated with KOH solution. The study was performed with a TU-1900 UV-Vis spectrophotometer fitted with a DC-2010 thermostat (± 0.1 K, China)

Kinetics measurements and product analysis

All kinetics measurements were carried out as previously.[6] The way for product analysis was similar to previous study.[8] After completion of the reaction, the main reaction products were identified as aldehyde[9] by a spot test, amino acid[10] by ninhydrin reagent and Cu(II) by its spot test.[11] When added Nessler's reagent into the solution of the product, however, there was not any phenomenon.

Results and discussion

Evaluation of pseudo-first order rate constants

Under the conditions of [sarcosine]$_0$>>[Cu(III)]$_0$, the plots of $\ln(A_t-A_\infty)$ versus time were straight lines, and details of the evaluation are described in our previous work.[12]

Rate dependence on [sarcosine]

At constant temperature, k_{obs} values increase by increasing the concentration of sarcosine while keeping the concentration of [Cu(III)], [OH$^-$], [IO$_4^-$], and μ constant. The order with respect to [sarcosine] was unity;

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the plots of k_{obs} versus [sarcosine] are straight lines which pass the grid origin at different temperatures (Figure 1).

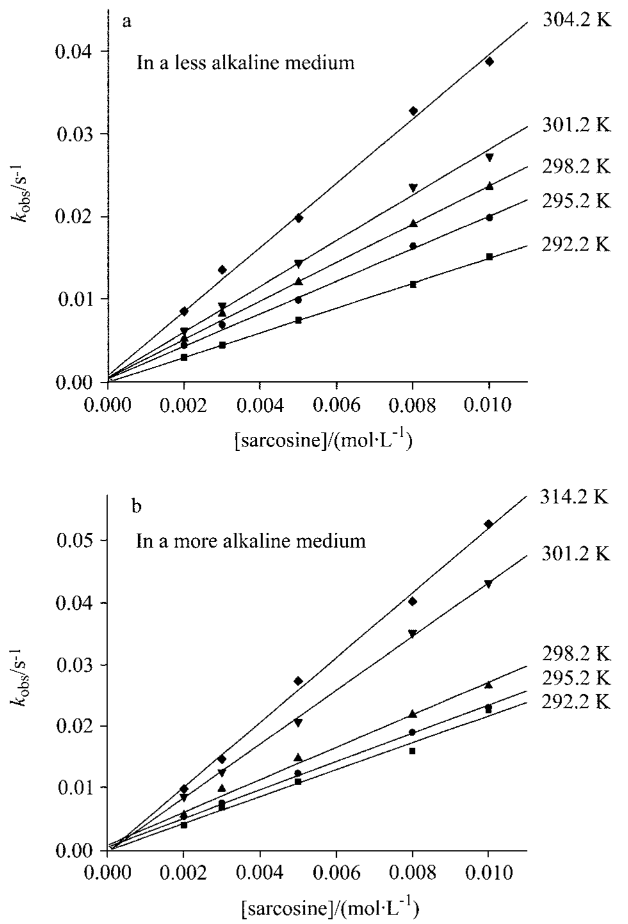

Figure 1 Plots of k_{obs} vs. [sarcosine] at different temperatures. (a) [Cu(III)]$=6.5\times10^{-5}$ mol•L^{-1}, [OH$^-$]$=1.0\times10^{-2}$ mol/L, [IO$_4^-$]$=1.0\times10^{-3}$ mol•L^{-1}, $\mu=0.08$ mol•L^{-1}; (b) [Cu(III)]$=6.5\times10^{-5}$ mol•L^{-1}, [OH$^-$]$=5.0\times10^{-2}$ mol•L^{-1}, [IO$_4^-$]$=1.0\times10^{-3}$ mol•L^{-1}, $\mu=0.08$ mol•L^{-1}

Rate dependence on [OH$^-$]

At constant [Cu(III)], [sarcosine], [IO$_4^-$], μ and temperature, k_{obs} values decreased rapidly with the increase in [OH$^-$], and then increased slowly with the increase in [OH$^-$]. The concentration of OH$^-$ was about 0.05 mol•L^{-1} at the turning point at which the rate was the slowest (Table 1).

Table 1 Rate dependence on [OH$^-$] at $T=298.2$ K^a

10[OH$^-$]/(mol•L^{-1})	0.050	0.080	0.10	0.15	0.20	0.50	1.0	1.5	2.0	2.5
$10^2k_{obs}/s^{-1}$	2.47	1.72	1.60	1.51	1.42	1.30	1.51	1.70	1.95	2.27

^{a} [Cu(III)]$=6.5\times10^{-5}$ mol•L^{-1}, [sarcosine]$=5.0\times10^{-3}$ mol•L^{-1}, [IO$_4^-$]$=1.0\times10^{-3}$ mol•L^{-1}, $\mu=0.30$ mol•L^{-1}.

Rate dependence on [IO$_4^-$] and ionic strength (μ)

At constant concentration of [Cu(III)], [sarcosine], [OH$^-$], μ and temperature, the experimental results indicate that k_{obs} decreases while increasing the concentration of [IO$_4^-$]. The order with respect to [IO$_4^-$] was negative fractional and the plot of $1/k_{obs}$ versus [IO$_4^-$] was linear (Figure 2). The addition of KNO$_3$ solution, to adjust the ionic strength of the reaction at constant [DPC], [sarcosine], [IO$_4^-$], [OH$^-$] and temperature, had no effect on the rate (Table 2). It showed that there was no salt effect, which was consistent with the common regulation of the kinetics [13].

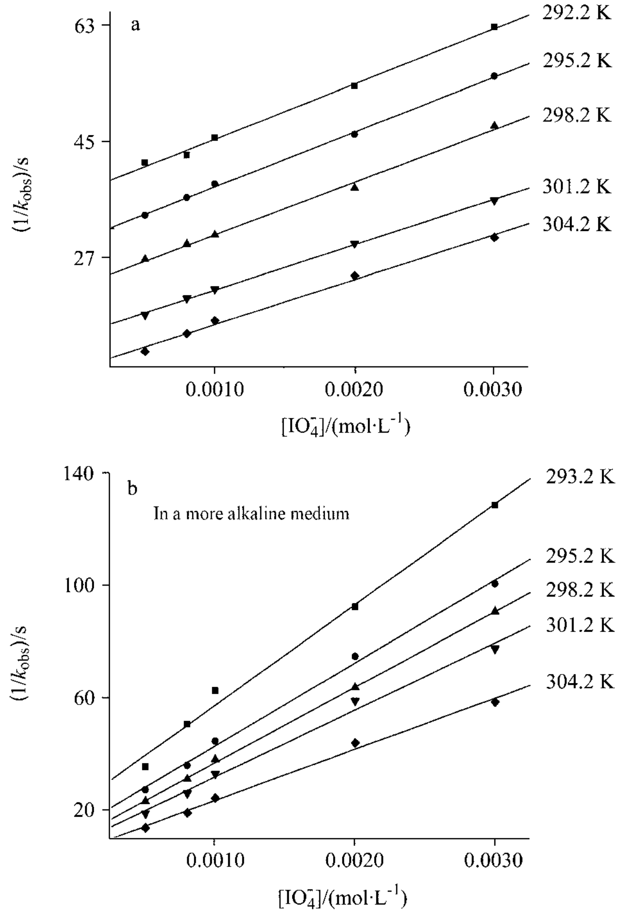

Figure 2 Plots of $1/k_{obs}$ vs. [IO$_4^-$] at 298.2 K. (a) In a less alkaline medium: [Cu(III)]$=6.5\times10^{-5}$ mol•L^{-1}, [sarcosine]$=1.0\times10^{-2}$ mol•L^{-1}, [OH$^-$]$=0.01$ mol•L^{-1}, $\mu=0.07$ mol•L^{-1}; (b) In a more alkaline medium: [Cu(III)]$=6.5\times10^{-5}$ mol/L, [sarcosine]$=1.0\times10^{-2}$ mol•L^{-1}, [OH$^-$]$=0.05$ mol•L^{-1}, $\mu=0.07$ mol•L^{-1}.

Table 2 The dependence of rate on μ at 298.2 K^a

μ/(mol•L^{-1})	0.07	0.1	0.2	0.3	0.4	0.5	0.6
$10^2k_{obs}/s^{-1}$	2.30	2.15	2.13	2.38	2.72	2.47	2.58

^{a} [Cu(III)]$=6.5\times10^{-5}$ mol•L^{-1}, [sarcosine]$=1.0\times10^{-2}$ mol•L^{-1}, [OH$^-$]$=0.05$ mol•L^{-1}, [IO$_4^-$]$=1.0\times10^{-3}$ mol•L^{-1}.

Reaction mechanism

In aqueous periodate solution, Eqs. (1)—(3) were detected and the corresponding equilibrium constants at 298.2 K were determined by Aveston.[14]

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

$$IO_4^- + OH^- + H_2 \rightleftharpoons H_3IO_6^{2-} \qquad \lg\beta_2 = 6.21 \qquad (2)$$

$$IO_4^- + 2OH^- + H_2 \rightleftharpoons H_2IO_6^{3-} \qquad \lg\beta_3 = 8.67 \qquad (3)$$

The distribution of all species of periodate in alkaline solution can be calculated from Eqs. (1)—(3). In the $[OH^-]$ range used in this work, the dimer and $[IO_4^-]$ species of periodate can be neglected. The main species of periodate are $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$. Eqs. (4) and (5) can be obtained from Eqs. (1—3)

$$[H_2IO_6^{3-}] = \frac{\beta_3[OH^-]}{1+\beta_2+\beta_3[OH^-]}[IO_4^-]_{ex} = f([OH^-])[IO_4^-]_{ex} \qquad (4)$$

$$[H_3IO_6^{2-}] = \frac{\beta_2}{\beta_2+\beta_3[OH^-]}[IO_4^-]_{ex} = j([OH^-])[IO_4^-]_{ex} \qquad (5)$$

where $[IO_4^-]_{ex}$ represents the concentration of original overall periodate ion.

Based on the above discussion, two simultaneous reaction mechanisms were proposed.

Mechanism I (In a less alkaline medium):

$$\begin{aligned}&[Cu(H_2IO_6)_2]^{3-} + 3H_2O \overset{K_1}{\rightleftharpoons} \\ &[Cu(H_2IO_6)(H_2O)_2] + H_3IO_6^{2-} + OH^-\end{aligned} \qquad (6)$$

MPC

$$\begin{aligned}&[Cu(H_2IO_6)(H_2O)_2] + CH_3NHCH_2COO^- \xrightarrow[\text{slow}]{k_1} \\ &Cu(II) + complex\end{aligned} \qquad (7)$$

$$\begin{aligned}&Cu^*(III) + complex \xrightarrow[\text{fast}]{} \\ &Cu(II) + HCOH + NH_2CH_2COO^-\end{aligned} \qquad (8)$$

The total concentration of Cu(III) is

$$[Cu(III)]_t = [Cu(H_2IO_6)_2^{3-}]_e + [Cu(H_2IO_6)(H_2O)_2]_e$$

here "e" and "t" mean the equilibrium concentration of the all kinds of Cu(III) complexes and the total concentration of Cu(III) complexes, respectively. Eq. (7) is the rate-determining step, and the rate equation can be expressed as below:

$$\frac{-d[Cu(III)]_t}{dt} = \frac{2k_1K_1[R^-]}{[H_3IO_6^{2-}][OH^-]+K_1} \times [Cu(III)]_t = k_{obs}[Cu(III)]_t \qquad (9)$$

$$k_{obs} = \frac{2k_1K_1[R^-]}{[H_3IO_2^{2-}][OH^-]+K_1} \qquad (10)$$

Then substitute Eq. (5) for $[H_3IO_6^{2-}]$ in Eq. (10):

$$k_{obs} = \frac{2k_1K_1[R^-]}{j([OH^-])[OH^-][IO_4^-]_{ex}+K_1} \qquad (11)$$

$$\frac{1}{k_{obs}} = \frac{1}{2k_1[R^-]} + \frac{j([OH^-])[OH^-]}{2k_1K_1[R^-]}[IO_4^-]_{ex} \qquad (12)$$

Mechanism II (in a more alkaline medium):

$$\begin{aligned}&[Cu(H_2IO_6)_2]^{3-} + OH^- \overset{K_2}{\rightleftharpoons} \\ &[Cu(HIO_6)]^- + H_2IO_6^{3-} + H_2O\end{aligned} \qquad (13)$$

MPA

$$\begin{aligned}&[Cu(HIO_6)]^- + CH_3NHCH_2COO^- \xrightarrow[\text{slow}]{k_2} \\ &Cu(II) + complex\end{aligned} \qquad (14)$$

$$\begin{aligned}&Cu^*(III) + complex \xrightarrow[\text{fast}]{} \\ &Cu(II) + HCOH + NH_2CH_2COO^-\end{aligned} \qquad (15)$$

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

$$[Cu(III)]_t = [DPC]_e + [MPC]_e$$

Subscripts t and e stand for total concentration and concentration at equilibrium, respectively.

As the rate of the disappearance of $[Cu(III)]_t$ was monitored, the rate of the reaction can be derived as:

$$\frac{-d[Cu(III)]}{dt} = \frac{2k_1K_1[OH^-][R^-]}{[H_3IO_6^{2-}][OH^-]+K_1} \times [Cu(III)]_t = k_{obs}[Cu(III)]_t \qquad (16)$$

$$k_{obs} = \frac{2k_2K_2[R^-][OH^-]}{K_2[OH^-]+[H_2IO_6^{3-}]} \qquad (17)$$

Then substitute Eq. (4) for $[H_2IO_6^{3-}]$ in Eq. (17):

$$\frac{1}{k_{obs}} = \frac{1}{2k_2[R^-]} + \frac{f([OH^-])}{2k_2K_2[R^-][OH^-]}[IO_4^-]_{ex} \qquad (18)$$

In this report, Eqs. (10) and (17) can explain why k_{obs} values decreased rapidly with the increase in $[OH^-]$

up to 0.05 mol•L^{-1}. After that point, it increased gradually with the continuous increase in [OH$^-$]. Eqs. (12) and (18) show that the plots of $1/k_{\text{obs}}$ versus $[\text{IO}_4^-]_{\text{ex}}$ should also be linear. Eqs. (10) and (17) show that the order in sarcosine should be first order and the k_{obs} versus [sarcosine] should be linear. The rate equations derived from the reaction mechanisms are consistent with our experimental results. The activation energy and the thermodynamic parameters (298.2 K) were evaluated by the previously published method[15] (Table 3).

Conclusion

Among various species of Cu(III) in alkaline liquids, monoperiodatocuprate is considered as the active species for the title reaction. The rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to the slow step of the reaction were computed. The positive value of $\Delta^{\neq}S$ suggests that the reactant is more order than the intermediate complex.

Table 3 Rate constants (k) and the activation parameters for the rate-determining step at T=298.2 K^a

Temperature/K	k_1/(mol^{-1}•L•s^{-1})	Thermodynamic activation parameters (298.2 K)				
		E_a/(kJ•mol^{-1})	$\Delta^{\neq}H$/(kJ•mol^{-1})	$\Delta^{\neq}S$/(J•K^{-1}•mol^{-1})	K_1/(mol^2•L^{-2})	K_2
In the less alkaline medium						
292.2	1.358	82.81	80.33	31.96	7.0×10^{-5}	
295.2	1.699					
298.2	2.242					
301.2	3.362					
304.2	5.198					
In the more alkaline medium						
292.2	2.317	82.44	79.96	61.22		1.731×10^{-5}
295.2	3.733					
298.2	5.021					
301.2	6.282					
304.2	9.511					

^{a} In the less alkaline medium, the plot of ln k vs. $1/T$ has the following intercept (a), slope (b), and relative coefficient (r): $r=-0.99$, $a=34.31$, $b=-9959.78$. In the more alkaline medium, the plot of ln k vs. $1/T$ has the following intercept (a), slope (b), and relative coefficient (r): $r=-0.99$, $a=37.83$, $b=-9915.70$.

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