Kinetics and Mechanism of Oxidation of N,N-Dimethylethanolamine by Diperiodatocuprate(III) Complex in Alkaline Medium

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The kinetics and mechanisms of the oxidation of N,N-dimethylethanolamine (DMEA) by diperiodatocuprate(III) (DPC) in aqueous alkaline medium was studied with spectrophotometry in a temperature range of 293.2-313.2 K. The reaction shows first order dependence on [DPC] and fractional order with respect to [N,N-dimethylethanolamine]. The observed rate constant (k_{obs}) decreased with increasing [IO_4^-] and increased with increasing [OH^-]. Increasing ionic strength of the medium decreased the rate. Free radicals were observed in the process of reaction. A mechanism involving the diperiodatocuprate(III)) as the reactive species of the oxidant has been proposed. The rate constants of the rate-determining step and the activation parameters were calculated.

Key Words: Diperiodatocuprate(III), N,N-Dimethylethanolamin, Kinetics and Mechanism, Redox reaction.

INTRODUCTION

Amino alcohols are important and widely used class of organic compounds. They have been used as intermediate agents in the production of various other chemical compounds such as coatings, surfactants, pesticides and pharmaceuticals. N,N-dimethylethanolamine (DMEA) is an important amino alcohol.

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(I), Cu(III) and Ni(IV) complex 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]. The kinetics and mechanism of oxidation of some hydroxy acids have been studied by some researchers. However, the mechanism is different in the different reaction systems[7,8]. The kinetics and mechanisms of oxidation of DMEA can provide some valuable information for chemical industry and organic synthesis.

EXPERIMENTAL

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Solution of [$Cu(H_2IO_6)_2$]$^{3-}$ (DPC) and reductant were always freshly pre-

pared before use. The stock solution of diperiodatocuprate(III) in a strong alkaline medium was prepared by the method given by Jaiswal[9]. The study was performed with a 4802 UV-Vis spectrophotometer fitted with a DC-2010 thermostat (± 0.1 K, China).

Kinetics measurements: All kinetics measurements were carried out as reported[6]. The product analysis was done similar to previous study[10]. The oxidation product was identified as the corresponding aldehyde and Cu(II) by spot test[11].

RESULTS AND DISCUSSION

Evaluation of pseudo-first order rate constants: Under the conditions of [DMEA]$_0$ >> [Cu(III)]$_0$, the plots of ln (A$_t$-A$_\infty$) *versus* time were straight lines. The details of the evaluation are described in our previous work[12].

Rate dependence on [DMEA]: At constant temperature, k_{obs} values increase by increasing the concentration of DMEA while keeping the [Cu(III)], [OH$^-$], [IO$_4^-$] and μ constant. The order with respect to DMEA was fractional. The plots of $1/k_{obs}$ *vs.* 1/ [DMEA] were straight lines with a positive intercept (Fig. 1).

Rate dependence on [OH$^-$]: At constant [Cu(III)], [DMEA], [IO$_4^-$], μ and temperature, k_{obs} values increased with the increase of [OH$^-$]. The order with respect to [OH$^-$] was fractional and the plot of $1/k_{obs}$ *vs.* f([OH$^-$])/[OH$^-$] was linear (Fig. 2).

Rate dependence on [IO$_4^-$]: At constant concentration of [Cu(III)], [DMEA], [OH$^-$], μ and temperature, the experimental

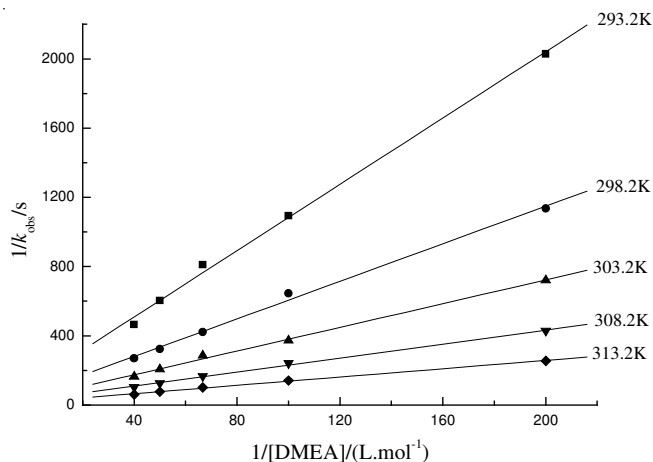Fig. 1. Plots of $1/k_{obs}$ vs. $1/$[DMEA]; [Cu(III)] = 7.5×10^{-5} mol/L; [OH⁻] = 2.5×10^{-2} mol/L; [IO$_4^-$] = 1.0×10^{-3} mol/L; $\mu = 3.6 \times 10^{-2}$ mol/L
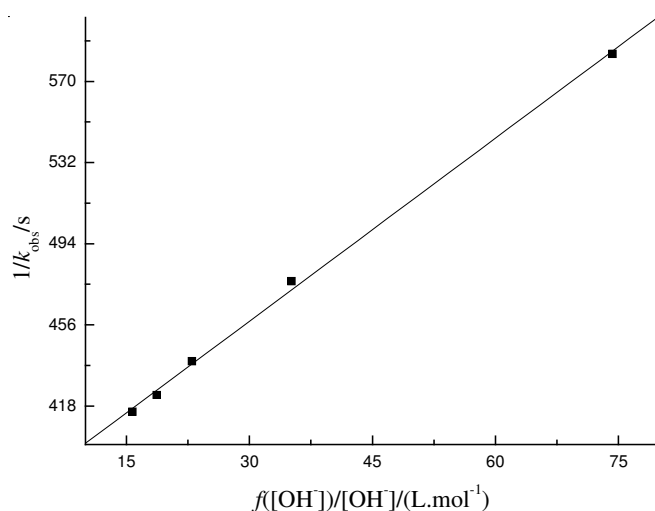

Fig. 2. Plot of $1/k_{obs}$ vs. f([OH⁻])/[OH⁻]; [Cu(III)] = 7.5×10^{-5} mol/L; [DMEA] = 2.0×10^{-2} mol/L; [IO$_4^-$] = 1.0×10^{-3} mol/L; $\mu = 6.1 \times 10^{-2}$ mol/L

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 (Fig. 3).
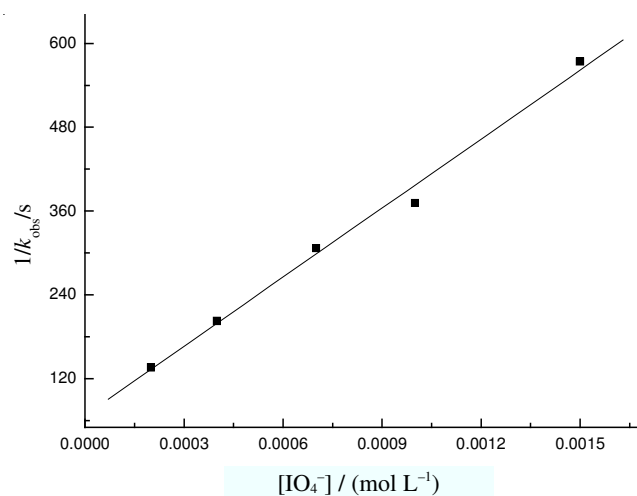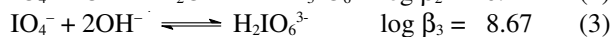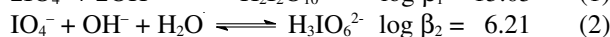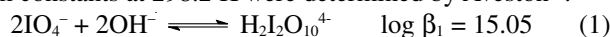

Fig. 3. Plot of $1/k_{obs}$ vs. [IO$_4^-$]; [Cu(III)] = 7.5×10^{-5} mol/L; [DMEA] = 2.0×10^{-2} mol/L; [OH⁻] = 2.5×10^{-2} mol/L; $\mu = 3.7 \times 10^{-2}$ mol/L

Rate dependence on the ionic strength and free radical detection: With other conditions fixed, the reaction rate dose not change by the addition of KNO$_3$ solution (Table-1), which indicate there is a negative salt effect. Acrylamide was added during the course of reaction, the appearance of white poly-acrylamide is consistent with free radical intermediates in the oxidation by Cu(III) complexes. Blank experiments in it was excluded gave no polymeric suspensions.

TABLE-1 RATE DEPENDENCE ON IONIC STRENGTH μ AT T=298.2 K					
μ (mol L^{-1})	0.036	0.076	0.125	0.175	0.225
$10^3 k_{obs}$ (s^{-1})	2.61	1.56	1.19	1.02	0.881
[Cu(III)]=7.5×10^{-5} mol/L; [DMEA]=2.0×10^{-2} mol/L; [OH⁻]=2.5×10^{-2} mol/L; [IO$_4^-$]=1.0×10^{-3} mol/L					

Reaction mechanism: In aqueous periodate solution, equilibria (1-3) were detected and the corresponding equilibrium constants at 298.2 K were determined by Aveston[13].

$$2IO_4^- + 2OH^- \rightleftharpoons H_2I_2O_{10}^{4-} \qquad \log \beta_1 = 15.05 \qquad (1)$$
$$IO_4^- + OH^- + H_2O \rightleftharpoons H_3IO_6^{2-} \qquad \log \beta_2 = 6.21 \qquad (2)$$
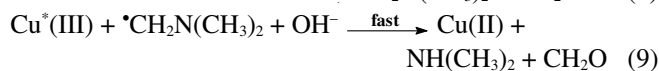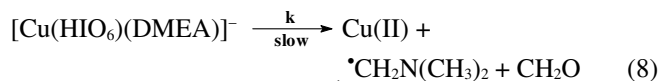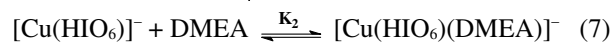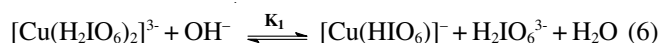$$IO_4^- + 2OH^- \rightleftharpoons H_2IO_6^{3-} \qquad \log \beta_3 = 8.67 \qquad (3)$$

The distribution of all species of periodate in 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. The main species of periodate are $H_2IO_6^{3-}$ and $H_3IO_6^{2-}$. Eqns. 4 and 5 can be obtained from eqns. 1-3:

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

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

(where [IO$_4^-$]$_{ex}$ represents the concentration of original overall periodate ion).

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

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

$$[Cu(HIO_6)]^- + DMEA \underset{K_2}{\rightleftharpoons} [Cu(HIO_6)(DMEA)]^- \quad (7)$$

$$[Cu(HIO_6)(DMEA)]^- \xrightarrow[slow]{k} Cu(II) + $$
$$^\bullet CH_2N(CH_3)_2 + CH_2O \quad (8)$$
$$Cu^*(III) + {}^\bullet CH_2N(CH_3)_2 + OH^- \xrightarrow{fast} Cu(II) + $$
$$NH(CH_3)_2 + CH_2O \quad (9)$$

The total concentration of Cu(III) is

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

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. The reaction (8) is the rate-determining step and the rate equation can be expressed as below:

$$-\frac{d[Cu(III)]_T}{dt} = \frac{2kK_1K_2[OH^-][DMEA]}{K_1[OH^-] + [H_2IO_6^{3-}] + K_1K_2[DMEA][OH^-]}[Cu(III)]_T$$
$$= k_{obs}[Cu(III)]_T \qquad (10)$$

$$\therefore k_{obs} = \frac{2kK_1K_2[OH^-][DMEA]}{K_1[OH^-]+[H_2IO_6^{3-}]+K_1K_2[DMEA][OH^-]} \quad (11)$$

$$\frac{1}{k_{obs}} = \frac{1}{2k} + \frac{K_1[OH^-]+[H_2IO_6^{3-}]}{2kK_1K_2[OH^-]} \frac{1}{[DMEA]} \quad (12)$$

$$\frac{1}{k_{obs}} = \frac{K_1+K_1K_2[DMEA]}{2kK_1K_2[DMEA]} + \frac{[H_2IO_6^{3-}]}{2kK_1K_2[DMEA]} \frac{1}{[OH^-]} \quad (13)$$

$$\frac{1}{k_{obs}} = \frac{K_1+K_1K_2[DMEA]}{2kK_1K_2[DMEA]} + \frac{[H_2IO_6^{3-}]}{2kK_1K_2[DMEA][OH^-]} \quad (14)$$

Then substitute eqn. 4 for $[H_3IO_6^{2-}]$ in the eqns. 12-14:

$$\frac{1}{k_{obs}} = \frac{1}{2k} + \frac{K_1[OH^-]+f([OH^-])[IO_4^-]_{ex}}{2kK_1K_2[OH^-]} \cdot \frac{1}{[DMEA]} \quad (15)$$

$$\frac{1}{k_{obs}} + \frac{K_1+K_1K_2[DMEA]}{2kK_1K_2[DMEA]} + \frac{[IO_4^-]_{ex}}{2kK_1K_2[DMEA]} \frac{f([OH^-])}{[OH^-]} \quad (16)$$

$$\frac{1}{k_{obs}} + \frac{K_1+K_1K_2[DMEA]}{2kK_1K_2[DMEA]} + \frac{1}{2kK_1K_2[DMEA]} \frac{f([OH^-])}{[OH^-]}[IO_4^-]_{ex} \quad (17)$$

In this report, eqn. 15 shows that the order in DMEA should be fractional order and $1/k_{obs}$ *vs.* $1/[DMEA]$ should be liner. From eqn. 16 shows that the plot of $1/k_{obs}$ *vs.* $f([OH^-])/[OH^-]$ should also be linear and eqn. 17 shows that the plot of $1/k_{obs}$ *versus* $[IO_4^-]_{ex}$ should be straight line too. 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[14] (Table-2).

TABLE-2
RATE CONSTANTS (k) AND ACTIVATION PARAMETERS OF THE RATE-DETERMINING STEP AT T = 298.2 K

Temp. (K)	k/(10^{-2} s^{-1})		Activation parameters (298.2 K)	
	DMEA	TEA	DMEA	TEA
293.2	0.3966	2.237	Ea=71.71 kJ mol^{-1}	Ea=42.63 kJ mol^{-1}
298.2	0.7846	3.049		
303.2	1.3220	4.102	$\Delta H^{\neq}$=69.23 kJ mol^{-1}	$\Delta H^{\neq}$=40.15 kJ mol^{-1}
308.2	1.7320	5.506	$\Delta S^{\neq}$=-53.78 J K^{-1} mol^{-1}	$\Delta S^{\neq}$=-139.33 J K^{-1} mol^{-1}
313.2	2.7870			

N,N-Dimethylethanolamine (DMEA), Triethanolamine* (TEA)
*Based on our previous work [Ref. 15].

The plot of ln k *vs.* 1/T has the following intercept (a), slope (b) and relative coefficient (r): r = -0.991, a = 23.99, b = -8625.22.

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 moderate values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are both favourable for electron transfer progress. The negative value of $\Delta S^{\neq}$ suggests that the intermediate complex is more order than the reactant.

Comparison N,N-dimethylethanolamin (DMEA) with triethanolamine (TEA) (Table-3), we found that the rate-determining step constants of triethanolamine (TEA) are larger than those for N,N-dimethylethanolamin (DMEA). Because the N,N-dimethylethanolamin (DMEA) embody two structures of methyl, which has the special steric hindrance.

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