CATALYTIC ACTIVITY OF 4-HYDROXY-2,2,6,6-TETRAMETHYL-PIPERIDIN-1-OXYL IN HOMOGENEOUS ELECTROOXIDATION OF HYDROXYLAMINE

He XIA and Hulin LI[1,*]

Department of Chemistry, Lanzhou University, Lanzhou 730000, People Republic of China; e-mail: [1] e-mail: lihl@lzu.edu.cn

Received January 22, 1998
Accepted June 11, 1998

4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (**1**) shows catalytic electroactivity in homogeneous oxidation of hydroxylamine on a glassy carbon electrode. Kinetic parameters of the electrode reaction were measured and an catalytic reaction mechanism for the electrooxidation was proposed. Possible application of electrocatalytic activity of **1** in determination hydroxylamine was also discussed.
Key words: Catalytic electrooxidation; Hydroxylamine; 4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl; Electrochemistry; Cyclic voltammetry.

Recently we have reported the first employment of organic mediator 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (**1**, TEMPOL) in the electrocatalytic oxidation of hydrazine[1]. From a mechanistic viewpoint, it would be valuable to investigate the effect of **1** on electrochemical behaviour of other relevant compounds containing nitrogen donor such as hydroxylamine. NH_2OH is an important compound in chemical industry[2]. Its anodic oxidation is of great interest for electrochemists and has been investigated under various conditions[3–6]. However, few organic mediators have been investigated as catalysts in its electrooxidation. Herein, we report electrochemical oxidation of NH_2OH in the presence of **1**.

EXPERIMENTAL

4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl radical (ACROS, U.S.A.) was used as received. Hydroxylamine hydrochloride, analytical grade (Beijing Chemical Reagent Company, China) was used without further purification.

All electrochemical experiments were carried out using electrochemical analyzer (BAS100B, U.S.A.). A glassy carbon electrode with an area of 0.10 cm^2 was used as working electrode. A Pt

* The author to whom correspondence should be addressed.

wire was employed as the counter electrode. An Ag|AgCl|saturated KCl electrode served as the reference electrode and all potentials in the text refer to it.

Glassy carbon electrode was polished with 0.1 μm alumina, rinsed with distilled water and sonicated in water for 3–5 min, dried thoroughly before every use. Supporting electrolyte solution was 0.1 M KCl and phosphate buffer solution. All solution were thoroughly flushed with high purity nitrogen that had been passed through a 1 m column containing Mn(II) dispersed on vermiculite before every electrochemical experiment, and all experiments were carried out at room temperature.

RESULTS AND DISCUSSION

*Electrocatalytic Activities of **1** in the Oxidation of NH_2OH*

Figure 1 demonstrates the catalysis of **1** in the electrooxidation of NH_2OH. In our experiment, no well defined peak of NH_2OH electrooxidation appears in the potential range of 0.3–0.9 V in the absence of **1** as shown in Fig. 1, curve *2*. Howerver, an irreversible oxidation peak emerges at about +0.60 V in a $4 . 10^{-4}$ M solution of **1**, as shown in Fig. 1, curve *3*, which is very close to the anodic potential of the oxidation of **1** (Fig. 1, curve *1*). This indicates that **1** exhibits a catalytic activity in the electrooxidation of NH_2OH. It can be assumed that **1** is easily oxidized at the glassy carbon electrode (GCE) forming an oxoammonium cation which can subsequently react with NH_2OH.

The catalytic peak current (I_{pa}) increases with the increase in the concentration of the **1**. At a given level depending on the concentration of NH_2OH, I_{pa} varies little with the catalyst concentration. The peak potential shifs towards negative values with the increase in the catalyst concentration, which indicates the nature of an electrocatalytic mechanism.

The I_{pa} of NH_2OH oxidation increases linearly with the square root of the sweep rate below 500 mV s^{-1} (Fig. 2), as expected for a diffusion-controlled reaction. At a higher

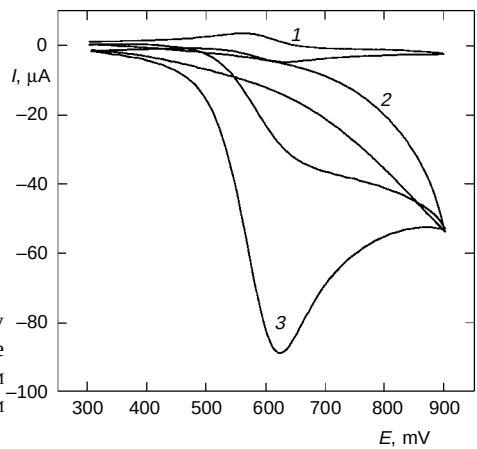


FIG. 1
Cyclic voltammogram of $4.0 . 10^{-4}$ M **1** at a glassy carbon electrode in the absence (*1*) and presence (*3*) of $4.0 . 10^{-3}$ M NH_2OH in 0.1 M KCl and 0.1 M phosphate buffer (pH 7.04). Curve *2*: $4.0 . 10^{-3}$ M NH_2OH without **1**. Sweep rate 20 mV s^{-1}

sweep rate (1 V s^{-1}), no peak current can be observed. Hence, the catalytic current is completely kinetically controlled at higher sweep rates. This is another characteristic of an electrocatalytic process. The peak potential E_{pa} is proportional to log ν as can be seen in Fig. 3; the slope of the plot is $\partial E_p/\partial(\log \nu) = 43.5$ mV. The Tafel slope b may be estimated from the equation for the totally irreversible diffusion-controlled process[7]:

$$E_p = (b \log \nu)/2 + \text{const.} \qquad (1)$$

Hence, $b = 2 \cdot 43.5 = 87$ mV. From the equation

$$b = 2.3RT/n\alpha F \qquad (2)$$

we can calculate $n\alpha = 0.60$. If $n = 1$, then $\alpha = 0.60$. The number of electrons involved in the catalytic electrooxidation of NH_2OH can be estimated using the following equation[8]:

$$I_p = (2.99 \cdot 10^5)\, n(\alpha n)^{1/2} A C_0 D_0^{1/2} \nu^{1/2} . \qquad (3)$$

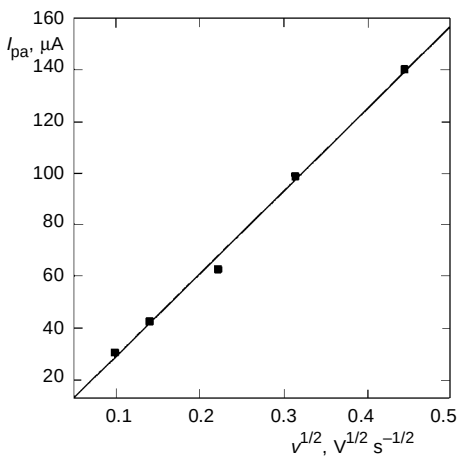


FIG. 2
Plot of peak current *vs* square root of sweep rate. $c_{NH_2OH} = 2 \cdot 10^{-3}$ mol l^{-1}, $c_{TEMPOL} = 5 \cdot 10^{-4}$ mol l^{-1}, pH 7.04

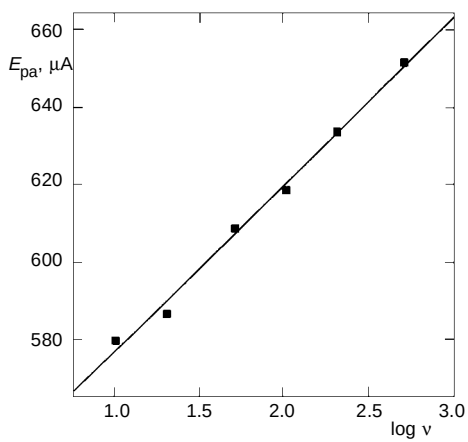


FIG. 3
Plot of E_{pa} (mV) *vs* log ν (ν in mV s^{-1}). $c_{NH_2OH} = 2 \cdot 10^{-3}$ mol l^{-1}, $c_{TEMPOL} = 5 \cdot 10^{-4}$ mol l^{-1}, pH 7.04

When A (the electrode area), C_0 (the concentration of substrate), and D_0 (the diffusion coefficient of NH_2OH, $D_{NH_2OH} = 1.4 \cdot 10^{-5}$ cm^2 s^{-1}) are known, the value of $n(\alpha n)^{1/2}$ (where n is the total number of electrons involved in the oxidation and αn is a parameter reflecting the irreversibility of the reaction) can be derived. Combining the two slopes in Figs 2 and 3 gives values of αn (0.60) and n (1.9) for NH_2OH oxidation.Thus, the well-known[3] two-electron oxidation of NH_2OH giving N_2O occurs as follows:

$$2\ NH_2OH + 4\ OH^- \rightarrow N_2O + 5\ H_2O + 4\ e^- \quad (A)$$

The plot of log I_{pa} *vs* log c_{NH_2OH} is a straight line with a slope close to unity (Fig. 4), indicating that the catalytic reaction obeys the first-order kinetics with respect to NH_2OH.

A series of voltammograms was recorded at various pH values. If pH < 3, the electrooxidation of NH_2OH catalyzed by **1** cannot occur and only a redox voltammogram of **1** can be obtained. If pH > 3, the peak current increases with the increase in pH. In the pH range 6.98–9.12, the peak current is almost constant with increasing pH. In addition, the **1** catalysis in alkaline media is affected in a complex way due to an irreversible electrooxidation of **1**.

The differential pulse voltammograms of **1** in the absence and presence of NH_2OH are shown in Fig. 5. The rate constant caculated from the plot[9] is $(3.86 \pm 0.2) \cdot 10^4$ dm^3 mol^{-1} s^{-1}.

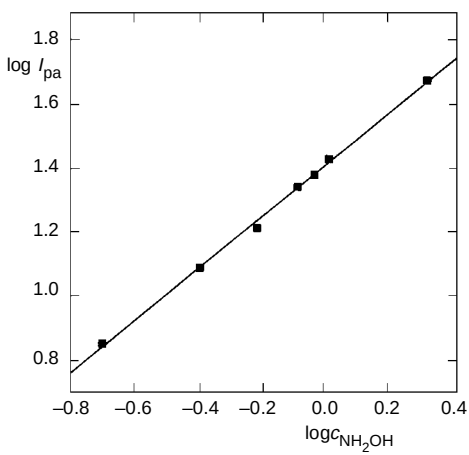


FIG. 4

Effect of NH_2OH concentration (mmol l^{-1}) on the peak current I_{pa} (μA) in 0.1 M KCl and 0.1 M phosphate buffer solution (pH 7.04) containing $5 \cdot 10^{-4}$ M **1**. Sweep rate 20 mV s^{-1}

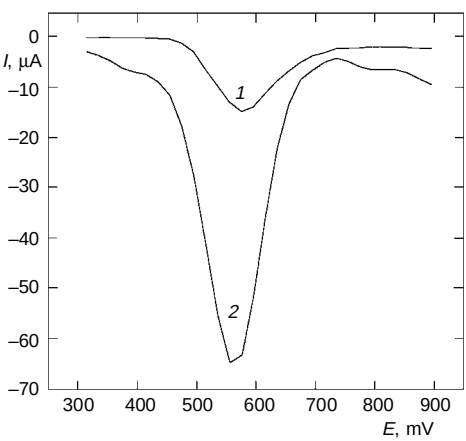
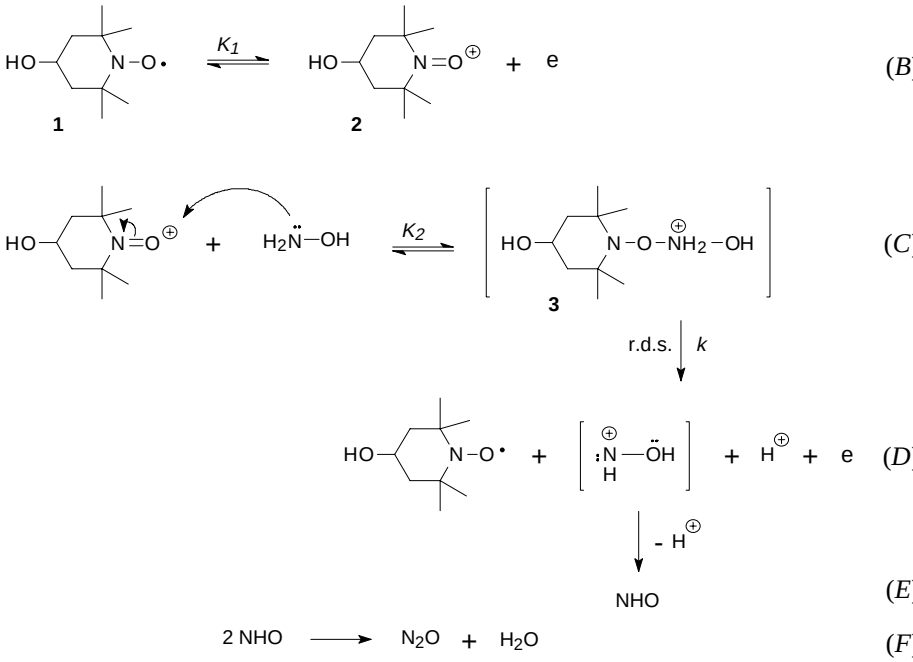


FIG. 5

Differential pulse voltammograms of $4.0 \cdot 10^{-4}$ M **1** in the absence (*1*) and presence (*2*) of $4 \cdot 10^{-3}$ M hydroxylamine in 0.1 M phosphate buffer (pH 7.04) and 0.1 M KCl solution

*Reaction Mechanism for **1**-Catalyzed Electrooxidation of Hydroxylamine*

Based on experimental results and discussion, the following mechanism is proposed:



Compound **1** is oxidized at the GCE to the oxoammonium salt which, in turn, oxidize NH_2OH. Reaction (*D*) is the rate-determining step (r.d.s.) in which one H^+, one NH_2OH and one electron are involved. The cation intermediate **3** formed in reaction (*C*) is further oxidized releasing **1** to keep the electrooxidation going.

In the rate-determining step, the catalytic NH_2OH oxidation current is given by Eq. (*4*):

$$I = k[\mathbf{3}]\, e^{[\alpha F(E - E\mathrm{eq})/RT]} \,. \qquad (4)$$

After introducting the equilibrium equations

$$[\mathbf{3}] = K_2[NH_2OH][\mathbf{2}] \text{ and } [\mathbf{2}] = K_1[\mathbf{1}] \qquad (5)$$

into Eq. (*4*), the following equation is obtained:

$$I = kK_1K_2[NH_2OH][\mathbf{1}]\ e^{[\alpha F(E - E\mathrm{eq})/RT]}\ . \qquad (6)$$

It can be seen from Eq. (*6*) that the oxidation obeys the first-order kinetics with respect to NH_2OH. The reaction mechanism proposed is consistent with the experimental results obtained.

Cyclic Voltammetric Determination of NH_2OH by Catalytic Electrooxidation

Hydroxylamine is known to be a reducing agent routinely used in industrial and pharmaceutical processes. It has also been identified as an intermediate in many biological processes[10]. Determination of hydroxylamine is, therefore, very important both in biological studies and in industrial processes.

In the above experiments we have found that in the presence of **1** trace amounts of NH_2OH could be oxidized and the corresponding anodic current could be enhanced. This observation can be employed for developing a simple and rapid method for analysis of NH_2OH in aqueous solutions.

A calibration graph for the determination of NH_2OH was constructed under optimum conditions (Fig. 6). A good linearity was observed in the range of NH_2OH concentration $1 . 10^{-5}$–$2 . 10^{-3}$ mol l^{-1}. The regression equations for the line and the correlation coefficient obtained by the least-squares method are $I_{pa} = 4.758 + 22.43c$ and $r = 0.9985$ (c in $1 . 10^{-3}$ mol l^{-1}, I_{pa} in μA). Since the standard deviation for the background signal is $3 . 10^{-6}$ M NH_2OH ($n = 20$), the detection limit is $1 . 10^{-5}$ M NH_2OH.

In interference tests, common ions and compounds such as Na^+, K^+, Cl^-, PO_4^{3-}, Mg^{2+}, F^-, Br^-, Cl^-, CO_3^{2-}, SO_4^{2-}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, urea, oxalic acid,

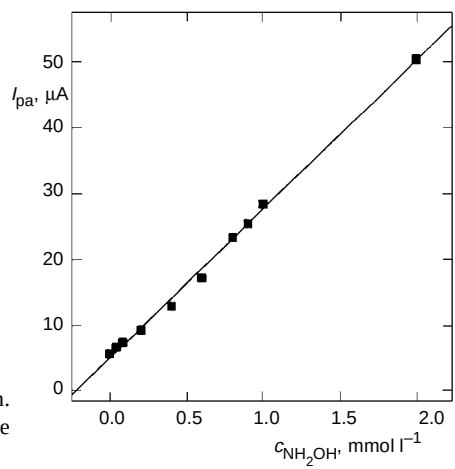


FIG. 6
Plot of peak current *vs* NH_2OH concentration. Concentration of **1** is $5 . 10^{-4}$ mol l^{-1}. Sweep rate 20 mV s^{-1}

glycine, nitrate, and ammonia (20-fold excess) show almost no effect on the catalytic currents of NH_2OH at pH 7.04.

Summarizing, we found that **1** shows an excellent catalytic activity in the homogeneous electrooxidation of NH_2OH. The reaction mechanism of this oxidation is similar to that of hydrazine[1]. The linear relationship between I_{pa} and the NH_2OH concentration over the range of $1 . 10^{-5}$–$2 . 10^{-3}$ mol l^{-1} can be used for determination of NH_2OH.

REFERENCES

1. Xia H., Li H. L.: *J. Electroanal. Chem.* **1997**, *430*, 183.
2. Cuisia D. G., Hwa C. M., Jacob J. T., Salutsky M. L.: U.S. 4 067 690; *Chem. Abstr.* **1978**, *88*, 141457.
3. Zhang J. J., Tse Y. H., Pietro W. J., Lever A. B. P.: *J. Electroanal. Chem.* **1996**, *406*, 203; and references therein.
4. Sultan S. M., Bishop E.: *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3661.
5. Kokkinidis G.: *J. Electroanal. Chem.* **1985**, *189*, 155.
6. Zagal J. H.: *Coord. Chem. Rev.* **1992**, *119*, 89.
7. Zhang J. J., Lever A. B. P., Pietro W. J.: *Inorg. Chem.* **1994**, *33*, 1392.
8. Bard A. J., Faulkner L. R.: *Electrochemical Methods, Fundamentals and Applications.* Wiley, New York 1980.
9. Kim M. H., Birke R. L.: *Anal. Chem.* **1983**, *55*, 522.
10. Kolasa T., Wardencki W.: *Talanta* **1974**, *21*, 845.