

Electrochemical Reduction Characteristics of α -Nitronaphthalene in Sulfuric Acid Solution

Chun An MA, Wen Kui ZHANG*, Yong Ping GAN, Hui HUANG,
Mei Chao LI, Shao Ping TONG

Department of Applied Chemistry, Zhejiang University of Technology, Hangzhou 310014

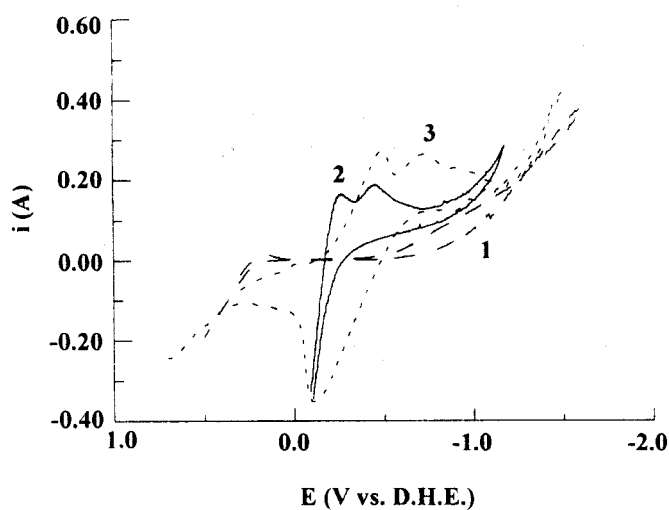
Abstract: The electrochemical reduction characteristics of α -nitronaphthalene in sulfuric acid solution were first reported in this paper. The results showed that the 1-amino-5-naphthol can be prepared by electrodeduction from α -nitronaphthalene and reduction peak corresponding to the reaction of α -nitronaphthalene to 1-amino-5-naphthol was in the range of -0.40~-0.60V(vs. D.H.E) on the amalgamated copper cathode in the presence of SnCl_2 additives. The mechanism of α -nitronaphthalene electroreduction to 1-amino-5-naphthol was also investigated, the overall electroreduction reaction was composed of two intermediate steps and two intermediate products existed in solution. The electrochemical reduction mechanism was similar to that of nitrobenzene to *para*-aminophenol.

Keywords: Electrochemical reduction, α -nitronaphthalene, 1-amino-5-naphthol.

1-Amino-5-naphthol is an important intermediate product for organic synthesis¹. It was traditionally synthesized from α -nitronaphthalene by chemical method. However, the chemical method needs two steps and produces a large quantity of wastewater, indicating the higher energy consumption and pollution. In this paper, the electrochemical reduction of α -nitronaphthalene to 1-amino-5-naphthol was first put forward, the electrochemical reduction characteristics of α -nitronaphthalene to 1-amino-5-naphthol were studied and the reaction mechanism was proposed as well.

The experiments were performed on an EG&G Model 273A electrochemical system. A dynamic hydrogen electrode (DHE) was used as a reference electrode; an amalgamated copper electrode (1.35 cm^2) was used as working electrode and platinum plate as counter electrode. In the course of the experiment, the solution was agitated by bubbling of pure nitrogen. All chemicals used were of chemical reagents grade.

Figure 1 shows the cyclic voltammograms of α -nitronaphthalene in 7.9 M sulfuric acid solution at 110 °C. As shown in **Figure 1**, two adjacent reduction peaks appeared in the range of -0.30 ~ -0.50V (vs. DHE) without additives and -0.40 ~ -0.60V (vs. DHE) in the presence of SnCl_2 additives. It indicates that α -nitronaphthalene can be reduced electrochemically on amalgamated copper electrode. With the addition of SnCl_2 , the reduction current increased and the peak position shifted to negative direction, indicating that SnCl_2 gives a catalytic effect on the reduction reaction.

Figure 1 Cyclic voltammogram of α -nitronaphthalene in acid solution

Scan rate: 100mV/s; Temperature: 110°C

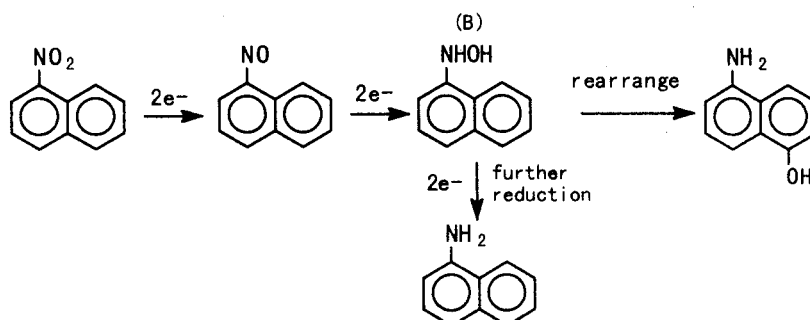
Catholyte:

Curve 1 - 7.9M H₂SO₄

Curve 2 - 7.9M H₂SO₄+0.03 M α -nitronaphthalene

Curve 3 - 7.9M H₂SO₄+0.03M α -nitronaphthalene +1.5%SnCl₂

The electrolysis experiment was carried out in 7.9 M sulfuric acid solution under the voltage range of -0.40 ~ -0.60 V (vs. DHE) in the presence of SnCl₂ additives. The experimental results show that the electrolytic products of α -nitronaphthalene were mainly consisted of 1-amino-5-naphthol under the above electrolytic conditions and the yield reached to 65% at 65°C. This means that the reduction peak appeared in cyclic voltammogram corresponds to the conversion of α -nitronaphthalene to 1-amino-5-naphthol. Further investigation disclosed the mechanism of α -nitronaphthalene electroreduction to 1-amino-5-naphthol as follows:

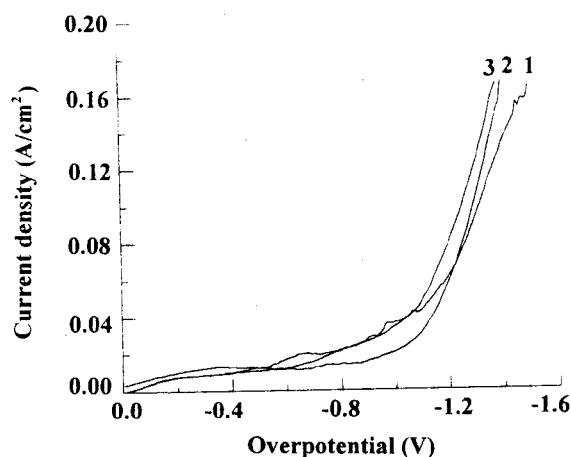


The electroreduction of α -nitronaphthalene to 1-amino-5-naphthol was 4e reaction, there existed two intermediate steps and two intermediate products in sequence. The

direct reduction product of α -nitronaphthalene was designated as B, after rearrangement in sulfuric acid solution under high temperature, B transformed into 1-amino-5-naphthol. If intermediate product B was further reduced electrochemically, it would transform into naphthylamine. If 1-amino-5-naphthol product is preferred, the synthesis conditions must be controlled. The above reaction mechanism was similar to that of nitrobenzene to *para*-aminophenol, also involving two intermediate steps and two intermediate products²⁻⁴.

Figure 2 depicts the polarization curves of α -nitronaphthalene on amalgamated copper electrode at different temperatures. Depending on the polarization curves at different temperatures, the exchange current density of the reduction reaction of α -nitronaphthalene to 1-amino-5-naphthol can be calculated according to the Tafel equation⁵. The value in exchange current density was calculated to about 1.1 mA/cm².

Figure 2 Polarization curves of α -nitronaphthalene on amalgamated copper electrode at different temperatures



Catholyte: 7.9M H₂SO₄+0.03 M α -nitronaphthalene
Curve 1 — 90°C; Curve 2 — 100°C; Curve 3 — 110°C

Further investigations show that the control step for the reduction of α -nitronaphthalene to 1-amino-5-naphthol was the electrons transfer instead of diffusion of α -nitronaphthalene or its intermediate products out of the electrodes.

The conclusions were arrived at as follows:

- (1) α -nitronaphthalene can be reduced electrochemically to 1-amino-5-naphthol on amalgamated copper electrode.
- (2) The electroreduction of α -nitronaphthalene to 1-amino-5-naphthol was 4e reaction, there existed two intermediate steps and two intermediate products in sequence. The electroreduction mechanism was similar to that of nitrobenzene to *para*-aminophenol.

Acknowledgment

This work is supported by The Natural Science Foundation of Zhejiang province and this is gratefully acknowledged.

References

1. Merck Index (2nd edition), 10457; 11465.
2. J. Schulze *et al.* *Z. Chem.*, **1980**, 20 (12) 436.
3. H.C. Rance, J. M. Coulson, *Electrochimica Acta*, **1969**, (14) 283.
4. J. Marquez, D. Pletcher, *J. Applied Electrochemistry*, **1980**, (10) 567
5. H.Q. Wu, Y.F. Li, *Electrochemical Kinetics*, High Education Press and Springer Press, **1998**, P41.

Received 10 January 1999

Revised 9 October 1999