Anodic Oxidation of Aniline in Aqueous Alkaline Solution

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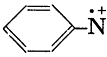
The anodic oxidation of aniline in an aqueous alkaline solution was studied. The anode materials were Ni, C, Pt, and Pb. An organic deposit (film) was formed on the anodes. The reaction mechanism was estimated through electrochemical measurements, chemical analysis, thin-layer chromatography, and UV, NMR, and IR spectrometries. The de-electronation of lone-pair electrons of the N atom in an aniline molecule caused the radical cation to be produced, , and this process was the rate-determining step. Some of the radical cations were found to couple together to produce azo-benzene *via* hydrazobenzene. The other radical cations led to *p*-amino diphenylamine by head-to-tail coupling; this product was de-electronated again to give the polymer with a quinoid structure.

Since Letheby[1] obtained aniline black through the anodic oxidation of aniline, many works have been presented on the anodic oxidation of aromatic compounds. Yasui[2] reported that aniline black was obtained from *p*-amino-diphenylamine and emeraldine in aqueous hydrochloric acid. Recently, discussion[3,4] was focussed on the reaction mechanism of the anodic oxidation of aniline derivatives in aqueous acidic solutions and also in nonaqueous solvents. Adams and his co-workers[5] observed the amino radical in the process of the anodic oxidation of aromatic amines. However, in an aqueous alkaline solution, the anodic oxidation of aniline has not been investigated. The present authors found film formation on the anode in an aqueous alkaline solution containing aromatic amines in their study of the electrochemical behavior of aniline derivatives.[6] In the present work, the anodic oxidation of aniline in an aqueous alkaline solution was carried out in order to elucidate the mechanism of this process by the analysis of the product and by electrochemical measurements.

Experimental

Test Electrode. The test electrodes were platinum, nickel, lead, and carbon. The metal electrodes were plates, 1 cm × 1 cm, equipped with a wire and sealed in glass tube. The carbon electrode was a carbon rod for spectroscopic analysis whose available area was made 1 cm^2 by blinding with Daifloil. The test electrodes were polished with emery paper, rinsed with a 1 N aqueous solution of potassium hydroxide and a 1 N aqueous solution of hydrochloric acid, and then immersed in a 10% aqueous solution of hydrazine. However, in the case of the lead electrode, the treatments with alkaline and acid were omitted.

Electrolytic Cell. The electrolytic cell was a H cell (100 m*l*) with a sintered glass disk diaphragm and a Luggine capillary connected to a reference electrode (Hg/HgO/1 N KOH). The counter electrode was a platinum plate (2 cm × 2.5 cm). Triangular potential waves were generated by using a potentiostat HP-E and a frequency function generator NS$_2$ (by Nichia Keiki Co., Ltd.). The temperature was 30°C.

Materials. An alkaline solution was prepared with a commercial, analytical-grade reagent and deionized water. The aniline was commercial and at an analytical grade, too.

Results and Discussion

Current-potential Curves of Aniline by Cyclic Voltammetry. A typical current-potential curve of aniline in 1 N potassium hydroxide, determined by cyclic voltammetry with a platinum electrode, is shown in Fig. 1.

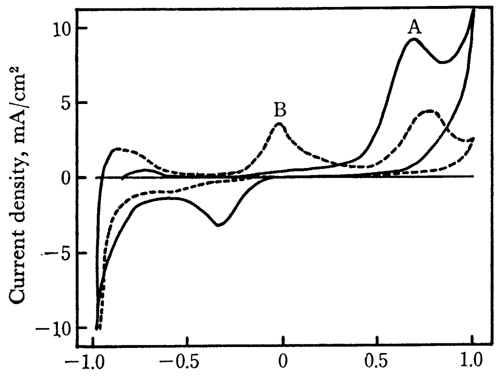


Fig. 1. Voltamgram of aniline in aqueous KOH solution. Potential sweep rate: 0.2 V/sec, 30°C, Electrode: Platinum plate, Electrolyte solution: 1 N KOH + 10^{-2} M aniline.

The potential sweep range was −1.0—+1.0 V (*vs.* Hg/HgO electrode); the potentials for the reactions of hydrogen and oxygen evolutions were outside this potential sweep range. The potential was anodically swept first from −1.0 V (*vs.* Hg/HgO electrode); then the direction of the current was reversed at +1.0 V, and the same procedures were repeated.

When aniline was absent in the solution, the current peaks, A and B in Fig. 1, were not observed. At the first anodic sweep with the existence of aniline, only the current peak A was ovserved; after the second sweep, both current peaks, A and B, were obtained.

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[1] H. Letheby, *J. Chem. Soc.*, **15**, 161 (1862).

[2] T. Yasui, This Bulletin, **10**, 305 (1935).

[3] S. Wawzonek, T. W. McIntyre, *J. Electrochem. Soc.*, **114**, 1025 (1967).

[4] T. Mizoguchi and R. N. Adams, *J. Amer. Chem. Soc.*, **84**, 2058 (1962).

[5] E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *ibid.*, **88**, 3498 (1966).

[6] H. Tamura, Y. Matsuda, and M. Iijima, *Kogyo Kagaku Zasshi*, **72**, 1077 (1969).

When the cyclic voltammetry was applied, the current peaks corresponding to A and B became lower and reddish-brown film was precipitated on the electrode as time passed. When the potential sweep range was only between −1.0 and +0.4 V, the B peak was not observed on the current-potential curve. From the results mentioned above, the two current peaks, A and B, might be assumed to be caused by the anodic reaction of aniline or the intermediate products. The anodic oxidation of aniline, therefore, might be initiated with the electrochemical reaction corresponding to the current peak A. Moreover, it can be assumed that the decrease of the current with cyclic sweeps might be caused by the increase in the resistance on the electrode resulting from the film formation. Therefore, as will be discussed later, this initial reaction is shown by Eq. (1):

$$C_6H_5\ddot{N}H_2 - e^- \longrightarrow C_6H_5\overset{\cdot+}{N}H_2 \qquad (1)$$

Moreover, the B peak may be assumed to correspond to the anodic oxidation of *p*-amino-diphenylamine, the intermediate product. Mohilner and his co-workers[7] have already observed this phenomenon at *ca.* 0.1 V (*vs.* SCE) in dilute sulfuric acid containing aniline.

Anodic Oxidation of Aniline at a Controlled Potential. As has previously been mentioned, the initial electrochemical reaction corresponded to the A peak in Fig. 1. In this potential range, a Tafel relation was observed when the current was measured 1 min later after setting the potential; the relation between the current and the concentration of aniline was found to be as is shown in Fig. 2. The electrochemical reaction order was found to be one from the slope of the line in Fig. 3.

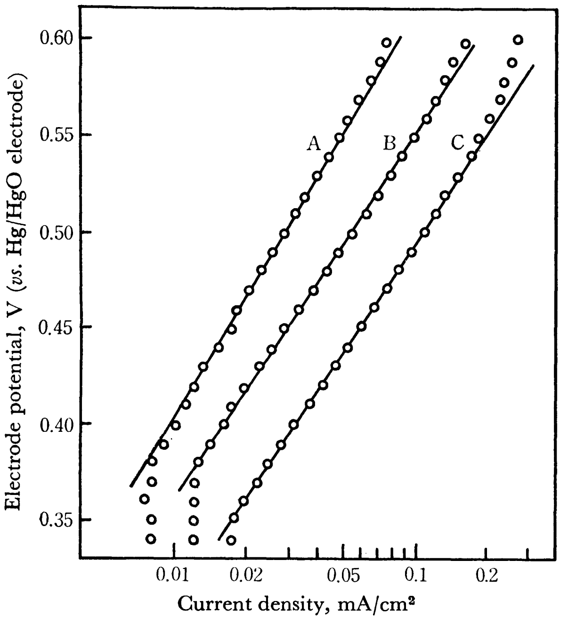


Fig. 2. Tafel lines for anodic oxidation of aniline in aqueous KOH solution.
Under stationary state, Electrode: platinum plate, 30°C
A: 1N KOH+1×10^{-3}M aniline
B: 1N KOH+2.5×10^{-3}M aniline
C: 1N KOH+5×10^{-3}M aniline

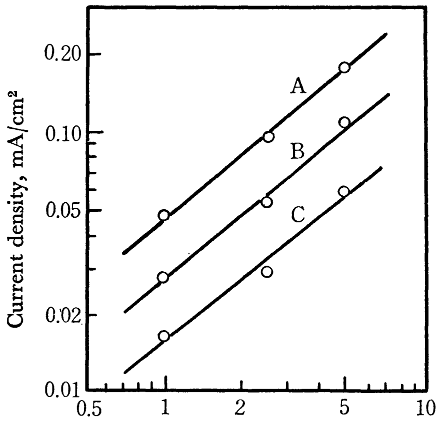
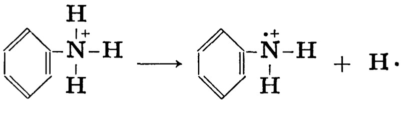


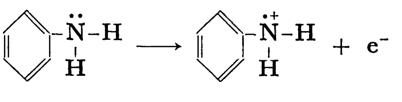
Fig. 3. Relation between current density and concentration of aniline for anodic oxidation of aniline in aqueous KOH solution.
Electrode: platinum plate, 30°C
A: 550 mV (*vs.* Hg/HgO electrode)
B: 500 mV (*vs.* Hg/HgO electrode)
C: 450 mV (*vs.* Hg/HgO electrode)

Mohilner and his co-workers[7] reported that the initial anodic reaction of aniline in an acidic solution was the formation of the cation radical, shown in Eq. (1). Other reports[3–5] on the anodic oxidation of aromatic amines in nonaqueous solvents have pointed out mechanisms similar to Eq. (1). For Eq. (1) to proceed in an acidic solution, a protonated aniline molecule must be de-hydrogenated, as in Eq. (2), because aniline in an acidic solution is usually protonated:



(2)

However, in an alkaline solution, an aniline molecule is only to be de-electronated as in Eq. (3), which is the same as Eq. (1), because aniline is a free amine in an aqueous alkaline solution:



(3)

If we compare the two mechanisms, the reaction shown by Eq. (3) should be easier than the reaction shown by Eq. (2) because the de-electronation is usually easier than the de-hydrogenation. At the same time, the reaction order, one, suggests that the reaction shown by Eq. (1) is the initial anodic reaction.

Furthermore, this process is the rate-determining process for the anodic oxidation in an aqueous alkaline solution, because a Tafel relation was observed at the potential for the current peak A in Fig. 1.

Materials for the Anode. By using carbon, nickel, and lead electrodes, cyclic voltammetric measurements were made at the alkaline solution containing aniline. The current peak potentials corresponding to the A peak in Fig. 1 for these systems are shown in Table 1. This table also shows the slopes of the Tafel lines which were measured by the procedures described in the previous section.

The potential of the current peak and the slope of

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[7] D. M. Mohilner, R. N. Adams, and W. J. Argersinger, Jr., *J. Amer. Chem. Soc.*, **84**, 3618 (1962).

Table 1. Peak potentials and slopes of Tafel lines on various electrodes

Electrode	Peak potentials corresponding to the peak A in Fig. 1 (*vs.* Hg/HgO electrode)	Slope of Tafel line V/log *i*
Ni	0.52 V	0.100
C	0.55	0.131
Pt	0.71	0.188
Pb	0.73	0.501

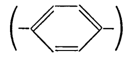
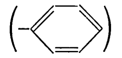
Tafel line give measures of the electrochemical reaction rate, and nickel is the most active electrode in an aqueous alkaline solution for the initial anodic reaction of aniline corresponding to the A peak in Fig. 1, with carbon and platinum following next. From the data in Table 1, the lead electrode can be said to be the most inactive electrode among them.

Characterization of the Deposit (film) on the Anode. The anodic oxidation of aniline was made by using nickel electrode (3×4 cm^2) and a beaker-type electrolytic cell. The anode potential was $+0.5$ V (*vs.* Hg/HgO electrode), the electrolyte solution was an aqueous solution of 1 N potassium hydroxide with 10^{-2}M aniline, and the temperature was 30°C±0.1°C. The samples for UV and NMR spectrometries, the measurement of the molecular weight, the elementary analysis, and thin-layer chromatography were obtained by the extraction of the film on the electrode with benzene.

After the electrolysis, the IR spectrum of the film on the anode was taken with a polarized IR spectrometer.

Table 2. Analytical results by IR spectrometry for deposit on the electrode

(Nickel anode potential: $+500$ mV *vs.* Hg/HgO/1 N KOH, Polarized reflective IR spectrum)

1560—1580 cm^{-1}	(–C=C–, –C=N– conjugate)
1480 cm^{-1}	(–N=N–)
830 cm^{-1}	
750 cm^{-1}, 690 cm^{-1}	

There was no absorption corresponding to –NH$_2$ or –NH– in the range of 3200—3500 cm^{-1}.

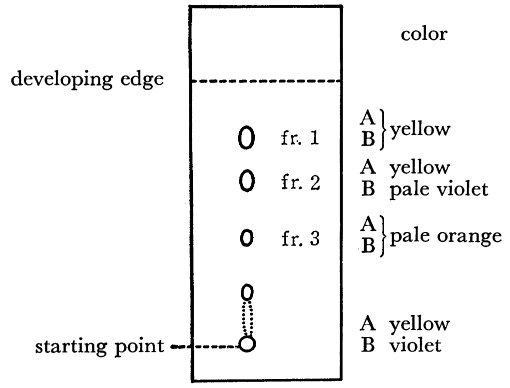
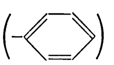


Fig. 4. Thin layer chromatogram of the deposit on the electrode.
A: Colour during the development,
B: Colour after spraying dilute H$_2$SO$_4$.

The results are shown in Table 2. The absorption band at 1560—1580 cm^{-1} was found to correspond to the –C=C– and –C=N– bonds with a quinoid structure, while that at 1480 cm^{-1}, and, those at 750 and 690 cm^{-1}, were caused by the –N=N– group of azobenzene and the mono-substituted phenyl ring respectively. Moreover, the absorption at 830 cm^{-1} was probably due to the disubstituted phenyl ring.

The results of thin-layer chromatography are shown in Fig. 4. The thin-layer consisted of silica gel, and the developing agent was benzene. As is shown in Fig. 4, two different groups were detected when the sample was developed and sulfuric acid was sprayed on the chromatogram. The R$_f$ values of fraction 1 were identical with those of the authentic sample.

Table 3. Analytical results through column chromatography for the deposit on the electrode

Fraction 1 (eluted with hexane)
IR: 1480 cm^{-1} (–N=N–)
780 cm^{-1}, 690 cm^{-1} 
UV: 450 mμ, 320 mμ
mp: 65.5—67 °C
agreed with the mp of authentic sample of azobenzene
Yield: 30%

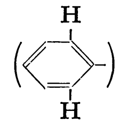
Fraction 1′ (eluted with benzene)
UV: 450 mμ, 365 mμ, 310 mμ

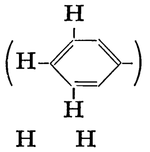
Fraction 2 (eluted with benzene)
UV: 375 mμ, 298mμ (–C=N–)
cf. UV: 288 mμ Ph$_2$NH
292 mμ PhNHNHPh

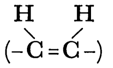
Furthermore, the sample of the film was divided into 3 fractions by column chromatography, and these fractions were analysed by UV spectrometry. These results are shown in Table 3. When the fraction 1 was

Table 4. Analytical results of the fraction by benzene extraction of the deposit on the electrode

Mean molecular weight: 440 (V.P.O. -benzene)

NMR: 2.0—2.4ppm 

2.5—2.8ppm 

2.7—3.4ppm 
$(\text{-}\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}\text{-})$

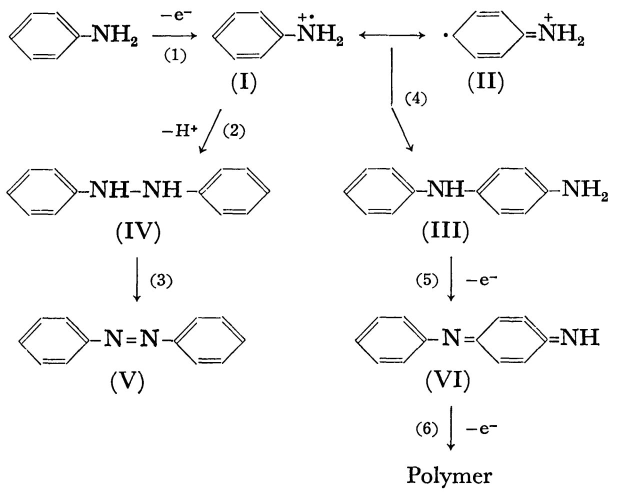
Elementary analysis:

	C	H	N	
Found	76.99	5.25	14.03	C$_{12.2}$H$_{10}$N$_{1.9}$
Calculated				
for aniline	77.38	7.58	15.04	
for azobenzene	79.09	5.53	15.38	

eluted with hexane, reddish-orange crystals were isolated. The IR and UV spectra and the melting point agreed with those of the authentic sample of azobenzene. The fraction 1′ was the first fraction with a benzene eluant; this fraction was determined by UV spectrometry to be a mixture of a substance containing an azo group and a quinoid structure. For the fraction 2, the UV spectrum showed λ_{max} at 375 mμ and 298 mμ corresponding to the n-π^* transition of the –C=N– group in the quinoid structure and the n-π^* transition of –N–H respectively; this fraction was assumed to consist of polymers with a quinoid structure and an N–H group.

The mean molecular weight of the film was 440, as is shown in Table 4. Because the azo-benzene content in the film, which was separated by column chromatography, was about 30%, the mean molecular weight of the residual polymer should be about 1100; this was assumed to be the dodecamer of the aniline.

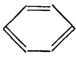
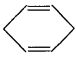
The results of NMR spectrometry are shown in Table 4. The signals of the NMR spectrum were observed at τ 2.0—2.4, 2.5—2.8, and 2.7—3.4. These signals were identified as the signals of protons at the ortho position of azo benzene, the protons at the *meta* and *para* positions of azo benzene, and the protons at the quinoid ring respectively.



Scheme 1

From the results presented above, it seems that the film was formed on the anode during the electrolysis of aniline in the aqueous alkaline solution; its composition consisted of azo benzene and of polymers with a quinoid structure, but its structure was not clear in detail.

Reaction Mechanism. The reaction mechanism of the anodic oxidation of aniline in an aqueous alkaline solution is assumed to be as in Scheme 1.

At first, the de-electronation of lone-pair electrons of the nitrogen atom in the aniline molecule caused the production of the radical cation, $\overset{+\cdot}{N}H_2$; this process is the rate-determining step. Some of the radical cations are coupled together and form azobenzene *via* hydrazobenzene. The other radical cations led to *p*-amino-diphenylamine by head-to-tail coupling between the radical cation and its resonance form, =$\overset{+}{N}H_2$; this product is de-electronated again and changed to the polymer step by step. The formation of phenyl-hydroxylamine may be considered in this reaction between the radical cation and hydroxyl ion. However, it is not probable, because the current-potential curve of phenyl-hydroxylamine was quite different from that of aniline in cyclic voltammetry. There are many radical cations on the electrode, and so the probability for the coupling is high and paths (2) and (4) in Scheme 1 must proceed simultaneously. In view of other experiments in which hydrazobenzene oxidized easily to azobenzene with air or alkali, the path (3) must proceed chemically.

On the anodic oxidation of aniline in an acidic solution, the formation of the octamer, emeraldine, had been reported by Mohilner and his co-workers.⁷⁾ However, in the anodic oxidation of aniline in an alkaline solution, the mechanism was different from that in an acidic solution, and the products were azo benzene and the polymer with a quinoid structure.