3208 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (11), 3208—3212 (1979) [Vol. 52, No. 11

Anodic Oxidation of 2-Aminofluorene at a Platinum Electrode in Acetonitrile Solutions

Kazuo Yasukouchi, Isao Taniguchi,* Hiroko Yamaguchi,
Katsuji Miyaguchi, and Koji Horie

Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University,
2-39-1, Kurokami, Kumamoto 860

(Received April 16, 1979)

Anodic oxidation of 2-aminofluorene in acetonitrile solutions at a Pt electrode was investigated by using electrochemical techniques and by preparative-scale electrolyses. The cyclic voltammogram of 2-aminofluorene exhibited two anodic waves, which had peak potentials at 0.45 V (I_a) and 1.15 V (II_a) *vs.* Ag/0.01 M $AgClO_4$. Wave II_a was due to oxidation of protonated 2-aminofluorene. In the voltammogram of repetitive sweeps, another redox couple (III_a/III_c) was observed at 0.13 V for III_a and 0.06 V for III_c, respectively. This indicates that at wave I_a, a species which is more easily oxidized than 2-aminofluorene was produced by follow-up chemical steps. By controlled-potential electrolysis at 0.5 V of a 2-aminofluorene solution containing pyridine as a proton acceptor, a dark green product, 3-(2-fluorenylimino)-2,3-dihydro-2-fluorenimine (**5**) (or 1-(2-fluorenylimino)-1,2-dihydro-1-fluorenimine (**5′**)), precipitated as the main product in more than 70% yield. The oxidation pathway of 2-aminofluorene (Eqs. 1—4) has been proposed on the bases of the following results: (i) The apparent *n*-value was 1.95, (ii) two protons/molecule of 2-aminofluorene were released in the follow-up chemical steps, and (iii) the peak potential for oxidation of 2′-amino-2,3′-difluorenylamine (**3**) (or 2-amino-1,2′-difluorenylamine (**3′**)) was in good agreement with that of wave III_a, and the anodic oxidation of **3** (or **3′**) gave the same product as that obtained by oxidation of 2-aminofluorene.

Anodic oxidation of aromatic amines has been extensively studied in both aqueous and nonaqueous solutions, and some general rules for reaction pathways have been obtained for mononuclear aromatic amines.1—5) For polynuclear aromatic amines, however, little is known about the oxidation pathway. This is partially because in many cases the oxidation products film the electrode surface and no product could be isolated. Most investigations of these compounds have been limited to the measurement of the oxidation half-wave potentials which are correlated with the HMO energies of the highest occupied molecular orbitals.6,7) Recently, however, electrochemical pathways of polynuclear aromatic amines have become increasingly important biologically. This is because, (i) since these compounds are typical carcinogens and their azo and/or hydrazo derivatives are important metabolic intermediates of the carcinogens,8,9) information which elucidates the carcinogenic mechanism may be obtained, and (ii) an electrochemical technique for the synthesis of biologically important compounds can be developed. Furthermore, it would be worthwhile to study the oxidation of polynuclear aromatic amines to examine whether or not the general rules for the oxidation mechanism proposed for mononuclear aromatic amines can be applicable for polynuclear ones.

In the present study, anodic oxidation of 2-aminofluorene, whose reaction pathway has not yet been reported, was investigated.

Experimental

Reagents were analytical GR grade and used without further purification unless otherwise noted. Sodium perchlorate was recrystallized twice from ethanol, dried overnight under a reduced pressure (400 Pa), and stored over silica gel. Acetonitrile was purified by distillation with P_2O_5 and with K_2CO_3, and then twice by slow fractional distillation. The MeCN was used within two weeks after purification. The water concentration of the test solution was determined to be less than 0.2 wt% by the Karl-Fischer titration.

The cyclic voltammograms were measured at a Pt disk electrode (2.0×10^{-3} cm^2) using a Yanaco P8 polarograph. The electrode was polished with an oil stone before each measurement. Rotating disk electrode (RDE) voltammetry was carried out using a commercially available instrument constructed by Nikko Keisoku. The kinematic viscosity (ν) of the solution used was 0.00441 $cm^2\,s^{-1}$. The diffusion coefficient (D) of 2-aminofluorene was estimated to be 1.55×10^{-5} $cm^2\,s^{-1}$ by the Levich equation.

Controlled-potential electrolysis was undertaken using a Nikko Keisoku NPGS 301 potentiostat. A two-compartment cell with a fine glass frit was used. The working (50 cm^2) and the counter electrodes were Pt plates. During electrolysis, cyclic voltammograms of the solution were measured to check the change of the composition of the solution. The working electrode for preparative-scale electrolysis was reactivated, when necessary, by burning, because the product which adhered on the electrode surface caused a steep decrease in current. In the time scale for voltammetric measurements, however, no serious adsorption of the product was observed.

An Ag/0.01 M $AgClO_4$ couple in MeCN was used as the reference electrode and potentials appearing in this paper are referred to this electrode. All electrochemical experiments were carried out at 25±0.5 °C under an atmosphere of nitrogen. Throughout this paper, 1 M = 1 mol dm^{-3}.

After exhaustive electrolysis of 2-aminofluorene, the solution was concentrated and water was added to precipitate a dark green product. The precipitate was separated by centrifugation and filtered off. The crude product was washed more than six times with each 10 ml of water to remove trace amounts of 2-aminofluorene which remained unreacted, and then recrystallized from either aqueous methanol or aqueous *N,N*-dimethylformamide. Thus, for example, 19 mg of the product (I) was obtained by electrolysis of 27 mg of 2-aminofluorene (150 ml of 1 mM solution); the yield is more than 70%. The product I was then chromatographed on both silica gel (Wako B-10) and alumina (Wako B-10) with either benzene, acetone, or ethanol, and detected with iodine. In each case only a single spot was observed. The analytical data on the product I are: mp> 300 °C; UV-Vis$_{max}$ (MeCN) 277 (log ε 4.3) and 660 nm (log ε 3.4); NMR (C_5D_5N) δ=3.76 (4H, s, CH_2) and 6.9—7.8 (13H, m, Ar-H); IR (KBr) 3370 (ν N-H) and 1610 cm^{-1} (ν C=N). Found: C, 87.2; H, 5.4; N, 7.4%; M^+, 358. Calcd for $C_{26}H_{18}N_2$: C, 87.1; H, 5.1; N, 7.8%; M, 358.4. The product I was easily soluble in *N,N*-dimethylformamide, fairly soluble in pyridine, soluble in MeCN, methanol, and ethanol, but almost insoluble in water.

Acetylation of I was performed by a method similar to that described by Bridger *et al.*[10] In the IR spectrum of the acetylated product, the absorption of N-H stretching at 3370 cm^{-1} disappeared, and those of C=O stretching and C-CH_3 bending appeared at 1720 and 1370 cm^{-1}, respectively (=NH→=N-C(=O)-CH_3). The number of NH groups was estimated to be one by the ratios of the number of methyl protons introduced by acetylation to those of methylene protons and aromatic protons of the fluorene ring in the NMR spectrum of the acetylated product.

2′-Amino-2,3′-difluorenylamine (**3**) was prepared according to the literature,[11] where it had not been determined whether the compound was **3** or 2-amino-1,2′-difluorenylamine (**3′**). No data for distinguishing between **3** and **3′** were obtained in the present study; we denote this compound as **3** just for convenience. Oxidation of **3** was carried out electrochemically by a method similar to that used for the oxidation of 2-aminofluorene, except for the applied potential.

The IR and UV spectra were obtained using a Hitachi 125-G (using KBr pellet technique) and a Hitachi 200-10 spectrophotometer, respectively. The NMR spectra were measured using a JEOL MH-100 spectrometer in either pyridine-d_5 or $CDCl_3$ containing TMS as an internal standard. The mass spectra were recorded using a JEOL JMS D-100 spectrometer.

Results and Discussion

The cyclic voltammogram of 2-aminofluorene showed two anodic waves having peak potentials, E_p, of 0.45 (I_a) and 1.15 (II_a) (Fig. 1a). Wave II_a was due to oxidation of protonated 2-aminofluorene. When the concentration of proton added was equal to that of 2-aminofluorene, only this wave was observed (Fig. 1b). Further increase in proton concentration did not cause appreciable change in the shape or height of the wave. On the other hand, the height of wave I_a increased with increasing amounts of pyridine added. Finally, in the solution containing twice as much pyridine as the concentration of 2-aminofluorene, the peak current of I_a became twice the value observed in the solution with no pyridine, whereas wave II_a disappeared and a wave due to oxidation of pyridine at E_p=0.95 V was observed (Fig. 1c). These cyclic voltammetric data show that 2-aminofluorene acted as a base in the follow-up chemical steps, but pyridine replaced 2-aminofluorene as a proton acceptor.

By controlled-potential electrolysis of 1 mM 2-aminofluorene solution with no pyridine, the *n*-value (electrons consumed/molecule of the starting amine) observed was 0.5—0.6, and a dark green precipitate and protonated 2-aminofluorene were produced. During electrolysis, the color of the solution turned green and then reddish purple. The latter color was due to protonated species of the dark green product, because an acetonitrile solution of the green product changed from green to reddish purple when perchloric acid was added to the solution. Thus, in order to reduce the complication caused by the protonation of both the starting amine and the product, preparative-scale electrolyses at 0.5 V of 1 mM 2-aminofluorene solution containing 2—5 mM pyridine were carried out. During electrolysis, the dark green product was generated as the main product in a yield of more than 70%, and the *n*-value of 1.95 was obtained by coulometry. The color of the solution became dark green and no further change to reddish purple was observed even at the end of the electrolysis. In the cyclic voltammograms of the solution during electrolysis, the peak current of I_a decreased and a new reduction wave (IV_c) due to reduction of protonated pyridine appeared (Fig. 2). The peak current of wave IV_c observed at the end of the electrolysis indicates that two protons per molecule of 2-aminofluorene were released in the follow-up chemical steps. No appreciable change in the results was observed by varying the concentration of pyridine (2—5 mM).

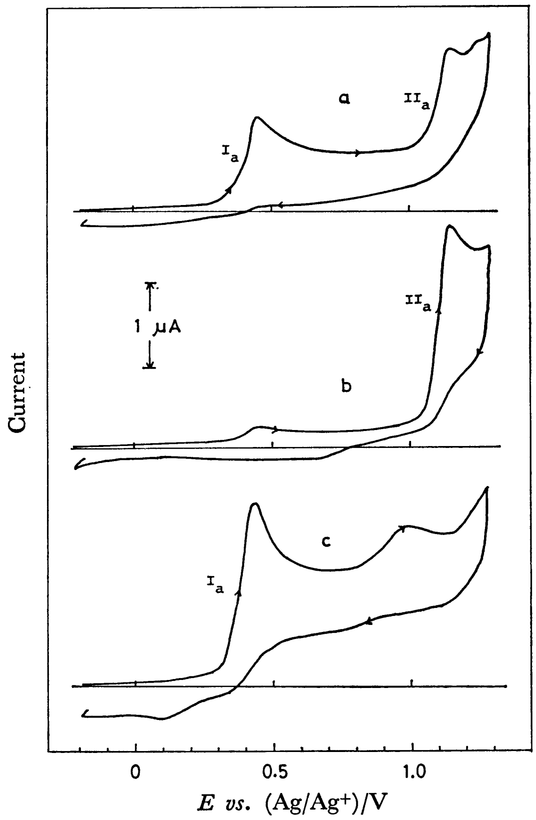


Fig. 1. Cyclic voltammograms of 1 mM 2-aminofluorene in 0.1 M $NaClO_4$–MeCN at the scan rate of 0.2 V s^{-1}. a; With no additive, b; with 1 mM $HClO_4$, and c; with 2 mM pyridine. The direction of the potential sweep is shown by arrows on the voltammograms.

Oxidation Product. The structure of the dark green product is now considered in detail. In general, anodic oxidation of aromatic amine gives three types of compounds, namely, azo type (which is formed by N–N coupling of the intermediates), ortho-semidine type (by ortho C–N coupling), and benzidine type

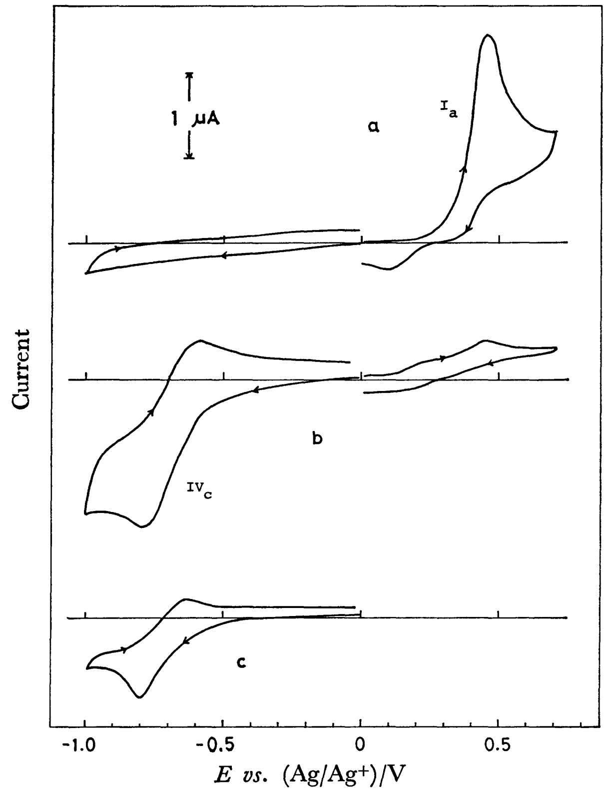
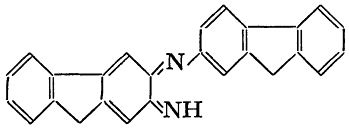


Fig. 2. Cyclic voltammograms of 1 mM 2-aminofluorene in 0.1 M $NaClO_4$–MeCN containing 3 mM pyridine (a and b), and of 1 mM protonated pyridine (c) in 0.1 M $NaClO_4$–MeCN. a; Before, and b; after exhaustive oxidation at 0.5 V. c; 1 mM pyridine solution containing 1 mM $HClO_4$. Scan rate: 0.2 V s^{-1}.

compounds (by C–C coupling). For product I, 2,2′-azofluorene must be rejected because no appreciable UV absorption for 2,2′-azofluorene or 2,2′-hydrazofluorene[12] was observed. A benzidine type compound may also be unlikely because of the structural hindrance of 2-aminofluorene. Thus, an ortho-semidine type is most probable, and 2′-amino-2,3′-difluorenylamine (**3**), which seems to be an intermediate in the present reaction, was synthesized according to the literature[11] (see experimental section).

By anodic oxidation of **3** at 0.3 V, the slightly orange-colored solution turned green and a product was obtained, which was identical with that obtained by oxidation of 2-aminofluorene, judging from their NMR, IR, and UV spectra. Thus, the following structure, **5**, is suggested for product I:



5

To further clarify the structure, the product was analyzed by several methods (see experimental section). The following analytical data support the structure **5**: (i) In the IR spectrum of I, N–H stretching absorptions for 2-aminofluorene at 3360 and 3450 cm^{-1} changed to a single band at 3370 cm^{-1} and a C=N stretching absorption at 1610 cm^{-1} was observed ($-NH_2 \rightarrow \rangle C=NH$). (ii) Acetylation of I took place, and the number of N–H groups per molecule of I was estimated to be one from the NMR spectrum of the acetylated product. (iii) Results of elementary analysis and molecular weight (=358) are in good agreement with those calculated for **5**. (iv) The NMR spectrum showed that the number of aromatic protons and that of methylene protons are reasonably explained in terms of the structure of **5**, though no appreciable peak for N–H protons was observed.

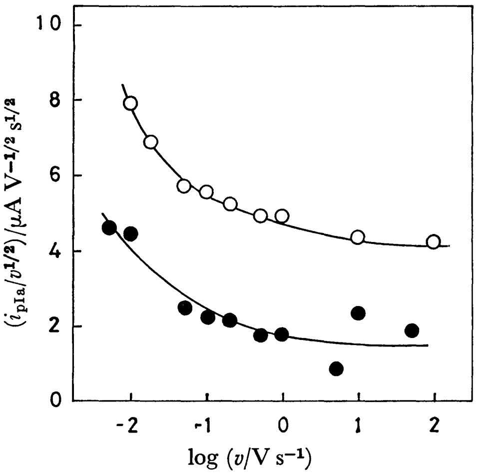


Fig. 3. The ratio of the peak current for wave I_a of 1 mM 2-aminofluorene solution to the square root of the scan rate, $i_{pIa}/v^{1/2}$, as a function of the scan rate in 0.1 M $NaClO_4$–MeCN. (○); With 2 mM pyridine, and (●); without.

Oxidation Pathway. To clarify the mechanism for the formation of **5**, further cyclic voltammetric investigations were carried out. The ratio of the peak current of wave I_a to the square root of the scan rate of the potential, $i_{pIa}/v^{1/2}$, decreased with an increase in the scan rate (Fig. 3). In repetitive cyclic voltammograms, a couple of waves (III_a/III_c) at potentials less anodic than that of wave I_a were observed (Fig. 4). These results indicate that for oxidation at wave I_a a primary one-electron transfer occurred to form a cation radical, and then a species which is more easily oxidized than the starting amine was produced by a chemical reaction and was further oxidized; this would be like a so-called ECE mechanism. Wave III_a in the cyclic voltammogram of 2-aminofluorene was in good agreement with the oxidation wave of **3** in both the peak potential and the wave shape (Fig. 4). The differences in shape and the peak potential observed between wave III_c and the corresponding re-reduction wave of **3** are probably because the oxidation product adsorbed on the electrode shifts the re-reduction wave of **3** to more negative potentials (Fig. 4c). During controlled-potential electrolysis of **3** at 0.3 V, two electrons per molecule of **3** were consumed, and the number of protons liberated was estimated to be two from the peak current for the reduction of protonated pyridine.

Thus, taking into account the results that (i) the over-all *n*-value for oxidation of 2-aminofluorene was two, and (ii) two protons with respect to the starting

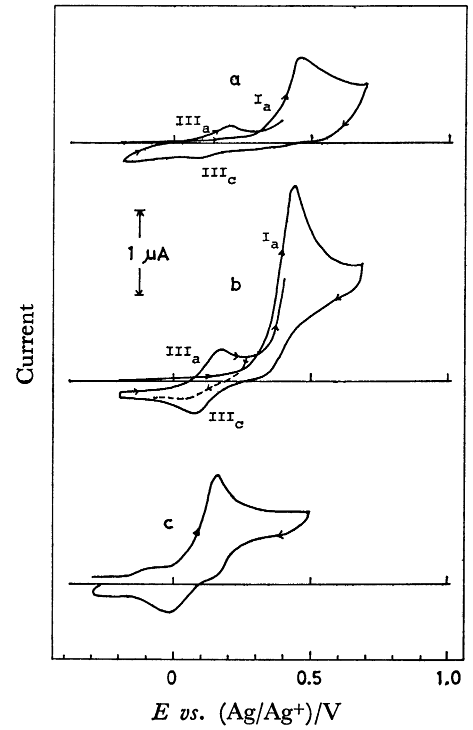
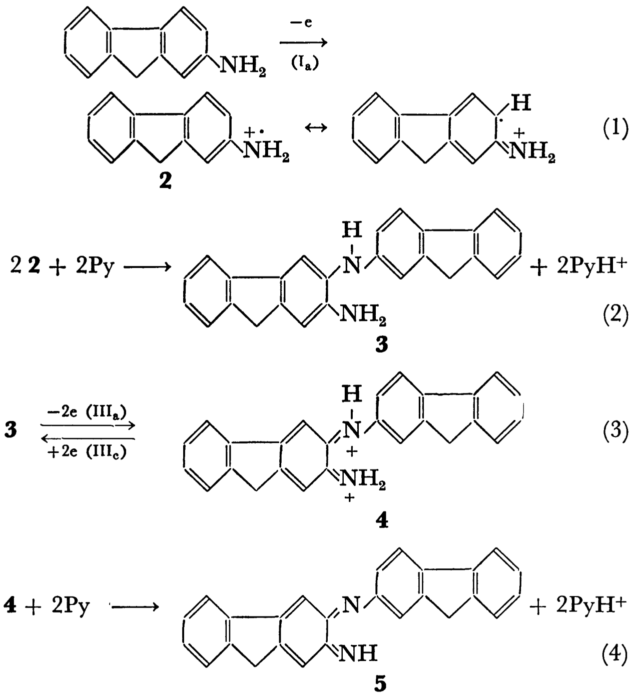


Fig. 4. Repetitive cyclic voltammograms of 1 mM 2-aminofluorene (a and b), and of 0.5 mM of **3** (c) in 0.1 M $NaClO_4$–MeCN containing a; 0 mM, b; 2 mM, and c; 5 mM pyridine. Scan rate: 0.2 V s^{-1}.

amine were released in the follow-up chemical steps to produce **5**, we propose that **5** is formed by the following reactions in a solution containing pyridine (Py):

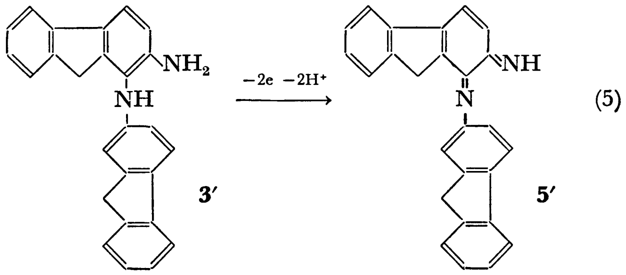


where the formation of **5′**, an isomer of **5**, is also possible *via* similar reactions. In the present experiment, no data for distinguishing between **5** and **5′** have yet been obtained; to determine the correct structure of the product I, further experiments, for example ^{13}C NMR measurements, are required, and some investigations are now in progress.

Table 1. RDE[a)] data for oxidation of 2-aminofluorene in 0.1 M $NaClO_4$-MeCN

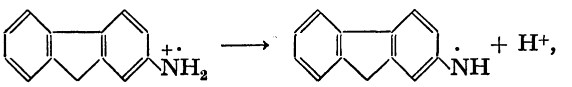
Concn mM	ω rad s^{-1}	$i_l\omega^{-1/2}$ [b)] µA rad$^{-1/2}$ $s^{1/2}$	n_{app}	k [c)] s^{-1}
0.6	20.7	3.99	1.05	0.20
	30.4	3.94	1.04	0.22
	40.3	3.87	1.02	0.16
	49.8	3.83	1.01	—
	61.3	3.79	1.00	—
	mean[d)]	3.79	1.00	—
0.8	20.7	5.46	1.05	0.19
	30.2	5.41	1.04	0.23
	40.2	5.36	1.03	0.23
	50.0	5.29	1.02	0.16
	61.4	5.19	0.998	—
	mean[d)]	5.20	1.00	—
1.0	11.0	6.99	1.07	0.15
	20.7	6.77	1.04	0.15
	30.6	6.71	1.03	0.17
	40.2	6.64	1.02	0.15
	50.3	6.56	1.01	—
	mean[d)]	6.51	1.00	—
1.2	20.7	8.68	1.05	0.20
	30.4	8.51	1.03	0.17
	40.4	8.45	1.02	0.17
	50.2	8.43	1.02	0.19
	mean[d)]	8.26	1.00	—
			Av.	0.18

a) The area of the electrode was 0.0707 cm^2. b) The values adopted are the average of more than five independent experiments. c) The values of k were estimated using Eq. 7 of Ref. 14, where $D=1.55\times10^{-5}$ cm^2 s^{-1} and $\nu=0.00441$ cm^2 s^{-1}. d) The mean of the values obtained at $83.8<\omega<314.2$ rad s^{-1}.



Since the potentials for the waves III_a/III_c and I_a were not affected by the presence of pyridine, similar reactions to those described above (Eqs. 1—4) also occurred in the solution with no pyridine, except that the protonations of the starting amine and of the product **5** occurred in this solution. The proposed reactions for 2-aminofluorene are similar to those usually observed for mononuclear aromatic amines. However, the predominant formation of the ortho-semidine type dimer should be noted because several compounds involving polymers are usually formed for mononuclear amines. This probably results from the structures of 2-aminofluorene and its generated cation radical.

Preliminary Information for the Chemical Steps. Due to protonations of both 2-aminofluorene and the product, it appears difficult to measure kinetic data on the chemical steps. However, some preliminary information on the rate of chemical steps may be obtained. Since the peak current of the wave III_c increased when pyridine was added, the deprotonation in Eq. 2 was accelerated by pyridine, whereas the deprotonation in Eq. 4 was probably slow and the addition of pyridine did not affect the rate. Thus, in the solution with no pyridine, the step of deprotonation of the cation radical generated by the primary electron transfer,


(6)

becomes a rate-determining step for oxidation at wave I_a. To confirm this consideration, RDE voltammetry was applied for 2-aminofluorene solution with no pyridine. The value of $i_l/\omega^{1/2}$, where i_l is the limiting current at an RDE and ω is the rotation speed of the electrode, decreased to a limiting value (I_{lim}) with an increase in the rotation speed (Table 1). The limiting value, I_{lim}, corresponds to the initial one-electron oxidation. The values of n_{app} ($=i_l\omega^{-1/2}/I_{lim}$) for lower rotation speeds depend on the rotation speed but are independent of the concentration of 2-aminofluorene. This is explained in terms of a first-order reaction for the chemical step,[13,14] namely, deprotonation. The rate constant of the deprotonation in Eq. 6 was thus estimated to be about 0.2 s^{-1} using Eq. 7 of Ref. 14 (Table 1).

This work was supported in part by the Asahi Glass Foundation for the Contribution to Industrial Technology.

References

1) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York (1969), pp. 327—363.

2) S. D. Ross, M. Finkelstein, and E. J. Rudd, "Anodic Oxidation," Academic Press, New York (1975), Chap. 8.

3) R. F. Nelson, "Technique of Electroorganic Synthesis," ed by N. L. Weinberg, Interscience, New York (1974), Part I, Chap. 5.

4) R. L. Hand and R. F. Nelson, *J. Electrochem. Soc.*, **125**, 1059 (1978).

5) P. Berkenkotter and R. F. Nelson, *J. Electrochem. Soc.*, **120**, 346 (1973).

6) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

7) C. Parkanyi and R. Zahradnik, *Collect. Czech. Chem. Commun.*, **30**, 4287 (1965).

8) M. J. Namkung and T. L. Fletcher, *J. Chem. Soc., Chem. Commun.*, **1969**, 1052.

9) H. Pan and T. L. Fletcher, *J. Med. Chem.*, **13**, 567 (1970).

10) R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, **33**, 4329 (1968).

11) F. E. Cislak, I. M. Eastman, and J. K. Senior, *J. Am. Chem. Soc.*, **49**, 2318 (1927).

12) T. L. Fletcher and M. J. Numkung, *J. Org. Chem.*, **35**, 4231 (1970).

13) L. S. Marcoux, R. N. Adams, and S. W. Feldberg, *J. Phys. Chem.*, **73**, 2611 (1969).

14) P. A. Malachesky, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, **70**, 4068 (1966).