Polarographic Behavior of 9-Nitroanthracene and 9,10-Dinitroanthracene in Dimethylformamide

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The polarographic behavior of 9-nitroanthracene and 9,10-dinitroanthracene has been studied in dimethylformamide. 9-Nitroanthracene shows consecutive two one-electron diffusion-controlled reduction waves followed by fast chemical reactions. 9,10-Dinitroanthracene, however, shows only one reversible two-electron diffusion-controlled wave. The effect of the supporting electrolyte cation on these reduction waves was also investigated. In alkali metal or alkaline earth metal perchlorate as a supporting electrolyte, the half-wave potentials shift to the anodic side. The relationship between the half-wave potential and the ionic potential of the cation was discussed.

A number of electrochemical and electron paramagnetic resonance studies of nitro compounds have been reported. The relationship between the structure of substituted nitrobenzene and its electrode kinetic parameter and its nitrogen hyperfine coupling constant was investigated in acetonitrile[1] and in dimethylformamide(DMF).[2,3] It was revealed that the rate constant of anion radical formation increases with the increase in resonance between the nitro groups and the remainder related to the nitrogen hyperfine coupling constant.

Recently, the ion association of radical anion or dianion produced by the reduction of organic compounds with metal cations in aprotic solvent has been investigated electrochemically for nitrobenzenes,[4,5] *p*-chloronitrobenzene,[6] quinones[7] and naphthoquinones.[8] Metal cations interact with anions but tetraalkylammonium ions are free from anions.

In this paper, we report on the reduction process of 9-nitroanthracene and 9,10-dinitroanthracene in DMF containing tetraethylammonium perchlorate (TEAP) as a supporting electrolyte and the effect of the supporting electrolyte cation on these reduction waves in the same solvent.

Experimental

DC and AC polarograms were recorded with a Yanagimoto polarograph P8 with a potentiostat. Cyclic voltammograms were recorded with a Riken Denshi F-32 X–Y recorder at a lower sweep rate and a Matsushita VP-546V oscilloscope with a Kikusui 455 function generator at a higher sweep rate. Capillary characteristics at 0 V *vs.* SCE in DMF containing 0.1 M TEAP were $m=1.52$ mg/s and $t=5.06$ s at $h=45$ cm. The area of the platinum disc electrode was calculated by chronopotentiometry for potassium ferrocyanide in 1.5 M potassium chloride and found to be 0.0665 cm^2. The reference electrode was aqueous SCE with a TEAP-DMF-methylcellulose salt bridge. All polarographic measurements were carried out at 25±0.5 °C in a dry box under a nitrogen atmosphere.

9-Nitroanthracene and 9,10-dinitroanthracene were supplied by Dr. R. Nakashima. DMF was dried over molecular sieve 3A and then distilled under reduced pressure. The content of water in DMF was found to be less than 0.01% by a gas-chromatographic method with a Porapak Q column. TEAP was prepared by neutralizing 10% tetraethylammonium hydroxide solution with 60% perchloric acid. The salt formed was recrystallized several times from water and dried *in vacuo* at 60 °C for 24 hr. Other perchlorates were dried *in vacuo* at 100 °C for 24 hr.

Results and Discussion

Polarographic Behavior of 9-Nitroanthracene and 9,10-Dinitroanthracene. The DC polarogram of 9-nitroanthracene in DMF containing 0.1 M TEAP shows two reduction waves. Its polarographic data are summarized in Table 1. The limiting current of the first wave is proportional to the concentration of 9-nitroanthracene in the range 2×10^{-4}—8×10^{-4} M, but the maximum wave appears at a concentration greater than 8×10^{-4} M. Both reduction waves are considered to be diffusion-controlled from the dependence of their wave height on the mercury column height and the current-time curve during the life of a mercury drop at the potential giving the limiting current. Comparing the diffusion current constant I and the chronoamperometric value $i\cdot t^{1/2}/C^*$, with those of *m*-nitrotoluene which is known to be a diffusion-controlled reversible one-electron process,[3] the reduction process of 9-nitroanthracene is found to be a consecutive two one-electron reduction process. In an AC polarogram under the same conditions, two waves corresponding to the waves in a DC polarogram are observed. The results are summarized in Table 1. We see that the summit potential of these waves is more cathodic than the half-wave potential of the corresponding DC polarographic reduction waves, the height of the more cathodic wave being very small. The irreversibility will be discussed in comparison with the case of 9,10-dinitroanthracene. The cyclic voltammetric behavior at a platinum disc electrode is shown in Fig. 1. Two reduction waves whose peaks correspond to the half-wave potential in the DC polarogram appear. Almost the same voltam-

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TABLE 1. SUMMARY OF POLAROGRAPHIC DATA IN DMF CONTAINING 0.1 M TEAP

	9-Nitroanthracene		9,10-Dinitroanthracene	*m*-Nitrotoluene
	1st	2nd		
DC polarography				
$I_d/\mu A \cdot mg^{-2/3} \cdot s^{1/2} \cdot mM^{-1}$	1.40	1.15	2.65	2.10
$-E_{1/2}/V$ *vs.* SCE	0.969	1.49	0.545	1.14
log plot slope/mV	44[a)]	70[a)]	33	56
AC polarography				
$E_{1/2}-E_s/mV$	50	40	17	10
$i_s/i_d \cdot \sqrt{t_d} \cdot n/\Omega^{-1}A^{-1} \cdot s^{1/2}$	38	17	130	177
$\Delta E_{s/2}/mV$	120	110	67	90
Chronoamperometry				
$i \cdot t^{1/2}/C^*/\mu A \cdot s^{1/2} \cdot mM^{-1}$	11.3	19.7	18.3	13.5

a) Nonlinear, $E_{1/4}-E_{3/4}$ value

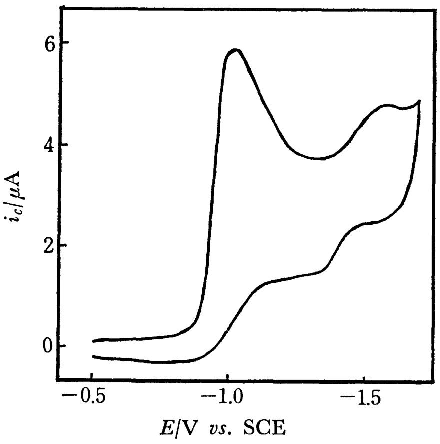

Fig. 1. Cyclic voltammogram of 0.665 mM 9-nitroanthracene at platinum disc electrode in DMF containing 0.1 M TEAP. Sweep rate: 30.3 mV/s.

mogram was obtained at a hanging mercury drop electrode. The potential difference between the cathodic peak potential and its half-peak potential for the first wave at a sweep rate of 30.3 mV/s is 60 mV which is fairly consistent with that for the reversible one-electron process[9] although the second wave shows an ill-defined curve. After reversal of the potential sweep at −1.7 V, no distinct waves corresponding to the re-oxidation of the products of the two cathodic processes appear. The first and second reduction products considered to be an anion radical and a dianion, respectively, might decompose by the following fast chemical reactions.

DC and AC polarographic and chronoamperometric results of 9,10-dinitroanthracene in DMF containing 0.1 M TEAP are also summarized in Table 1. Although most nitro aromatics show the two-step reduction process, only a single reduction wave is obtained for 9,10-dinitroanthracene. The half-wave potential is more anodic than that of the first wave for 9-nitroanthracene presumably because of the increase in coplanarity of nitro group and anthracene plane. The plot of log $(i/(i_d-i))$ against potential E gives a straight line with a slope of 33 mV, and the diffusion current constant and the chronoamperometric value are 1.3 times as large as that of *m*-nitrotoluene. Hence it appears that the reduction of 9,10-dinitroanthracene is a diffusion-controlled two-electron process, giving a dianion. The AC polarographic summit potential of the reduction wave is slightly more cathodic than the half-wave potential of the corresponding DC polarographic step. The AC wave is very high, its value of $i_s/i_d \cdot \sqrt{t_d} \cdot n$ (where $n=2$) being near that *m*-nitrotoluene which shows a reversible reduction process. In the cyclic voltammogram with a hanging mercury drop electrode at a sweep rate of 30.3 mV/s under the same conditions as above, the peak potential for the reduction is −0.560 V, the difference between the peak potential and the half-peak potential being 34 mV, which is close to the theoretical value for a two-electron transfer process.[9] The relationship between the cathodic peak current and the sweep rate, i_p *vs.* $v^{1/2}$, gives a straight line, the ratio of the cathodic to the anodic peak current being approximately 1.0 in a wide range of the sweep rate. In the case of the platinum disc electrode, the separation of the cathodic peak potential from the anodic peak potential is 147 mV at a sweep rate of 30.3 mV/s. This indicates that the electrode process of 9,10-dinitroanthracene at the platinum disc electrode is less reversible.

The electrode reaction of 9,10-dinitroanthracene is much more reversible than that of 9-nitroanthracene. Investigations of the crystal structure of 9,10-dinitroanthracene and 9-nitroanthracene show that the nitro groups are tilted 64°[10] and 85°,[11] respectively, out of the plane of the anthracene nucleus. The structures cause the decrease in resonance between the nitro groups and the aromatic π-electron. Thus, it can be said that the rate of charge transfer for 9,10-dinitroanthracene is faster than that for 9-nitroanthracene, after those which Peover and Powell developed using the Marcus theory.[3]

Many dinitro compounds have been investigated electrochemically. Most of them show two one-electron reduction process in aprotic solvent with a tetraalkylammonium salt as a supporting electrolyte. A

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[10] J. Trotter, *Acta Crystallogr.*, **12**, 232 (1959).

[11] J. Trotter, *ibid.*, **12**, 237 (1959).

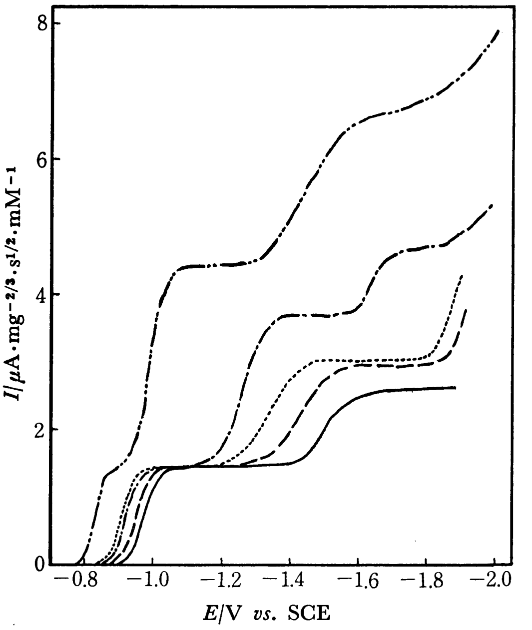

Fig. 2. DC polarograms of 9-nitroanthracene in DMF. Supporting electrolyte: 0.1 M TEAP (——), 0.1 M $KClO_4$ (----), 0.1 M $NaClO_4$ (······), 0.1 M $LiClO_4$ (—·—), 0.05 M $Mg(ClO_4)_2$ (—··—).

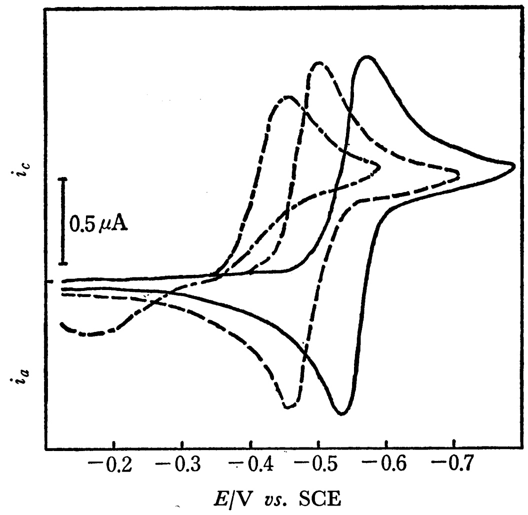

Fig. 3. Cyclic voltammograms of 0.4 mM 9, 10-dinitroanthracene at a hanging mercury drop electrode in DMF. Sweep rate: 30.3 mV/s. Supporting electrolyte: 0.1 M TEAP (——), 0.1 M $NaClO_4$ (----), 0.05 M Mg $(ClO_4)_2$ (—·—).

few dinitro compounds show only a single two-electron reduction process.[1] 9,10-Dinitroanthracene is shown to be the latter example.

Effect of the Supporting Electrolyte on the Reduction Process of 9-Nitroanthracene and 9,10-Dinitroanthracene. DC polarographic waves of 9-nitroanthracene in DMF containing 0.1 M alkali metal perchlorate or 0.05 M magnesium perchlorate are shown in Fig. 2. In 0.1 M potassium or 0.1 M sodium perchlorate, both the half-wave potential and the wave height of the first one-electron reduction process are similar to those in 0.1 M TEAP. The second wave, however, shows an anodic shift of the half-wave potential and an increase in wave height. On the other hand, in 0.1 M lithium or 0.05 M magnesium perchlorate the polarographic behavior differs from that in potassium and sodium salts. The first and the second waves shift to the anodic side, the second wave height increasing particularly in magnesium perchlorate. A new third wave appears in more cathodic potential. The value of $i_s/i_d\cdot\sqrt{t_d}\cdot n$ in 0.1 M perchlorate solution (0.05 M for magnesium perchlorate), showing the reversibility of the charge transfer, decreases in the following order for the cation of the supporting electrolyte: $Et_4N^+ > K^+ > Na^+ > Li^+ > Mg^{2+}$. This coincides with the reverse order for the anodic shift of the half-wave potential.

The effect of metal cation on the polarographic wave of 9,10-dinitroanthracene has also been examined in a similar manner in the case of 9-nitroanthracene. Cyclic voltammograms in various supporting electrolyte are shown in Fig. 3. In 0.1 M potassium, sodium, or lithium perchlorate, the half-wave potential shifts to the anodic but the DC wave height and the reversibility (AC wave height, and peak separation in cyclic voltammetry) remain unchanged in the presence of these metal cations. In 0.05 M magnesium perchlorate, however, the half-wave potential shifts to the more anodic, the AC wave height being about one third of the case of TEAP. The cyclic voltammetric peak current also decreases and the peak separation increases, which indicates the process to be less reversible.

The half-wave potential changes with cations of the supporting electrolytes. The relationship between the half-wave potential of nitroanthracenes and the ionic potential of the cation $\phi(\phi=z/r$, z; charge number, r; crystallographic radius) is plotted in Fig. 4. This gives three straight lines showing that the anodic shift of the half-wave potential increases with

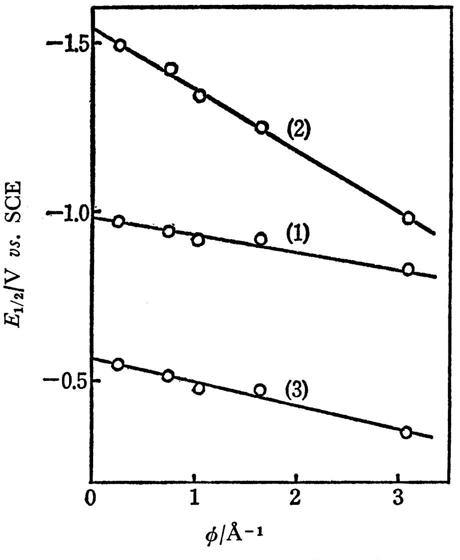

Fig. 4. Relationship between $E_{1/2}$ in 0.1 M perchlorate DMF solution and the ionic potential of the supporting electrolyte cation. From left to right, Et_4N^+, K^+, Na^+, Li^+, Mg^{2+}. 1 st (1) and 2 nd (2) wave of 9-nitroanthracene and 9, 10-dinitroanthracene (3).

the ionic potential. From the results by Krygowski *et al.*,[12] the relationship can be elucidated from the consideration that the reduction product, which may be radical anion and dianion for 9-nitroanthracene and dianion for 9,10-dinitroanthracene, forms ion pair with the metal cation of supporting electrolyte.

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