BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1496—1503 (1971)

The Protonation of Aromatic Hydrocarbon Radical Anions. I. A Comparison of Methods and a Study of the Mechanism[1]

Shigeo HAYANO and Masamichi FUJIHIRA
Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo

(Received November 30, 1970)

The protonation mechanism of the aromatic hydrocarbon radical anions, such as biphenyl, naphthalene, phenanthrene, anthracene, 1,2-benzanthracene, and pyrene, in dimethylformamide (DMF) and water mixtures was studied. Three methods of measuring the concentration of the radical anions, *i.e.* polarography and ESR and UV absorption spectroscopy, were compared with each other by making simultaneous measurements of the same anthraquinone radical anion solution. A good linear relation of the polarographic anodic diffusion current to the UV absorbance was found, while the ESR signal intensity had linear relations with neither of the others in the system which contained an excessive number of parent molecules, 2×10^{-3} M. The change in the visible absorption spectra of the aromatic hydrocarbon radical anions as a function of the time suggested that all the aromatic hydrocarbon radical anions decay by a first-order reaction. As a result, the radical anions were considered to decay through the following sequence:

$$R^{\overline{\cdot}} + H_2O \xrightarrow{k} RH\cdot + OH^-,\ RH\cdot + R^{\overline{\cdot}} \rightleftarrows RH^- + R, \text{ and } RH^- + H_2O \xrightarrow{k'} RH_2 + OH^-.$$

The electrochemical reduction of aromatic hydrocarbons in aprotic solvents has been the subject of a number of studies.[2,3] These investigations have elucidated the mechanism of the reduction and the correlation between the polarographic half-wave potentials with electron affinities, ultraviolet absorption frequencies, or parameters of Hückel molecular orbital (HMO) calculations.[2-6] In such aprotic media, aromatic hydrocarbons[7,8] undergo reversible one-electron transfers at cathodes, yielding radical anions. Most radical anions undergo further reduction, at potentials half a volt more negative, to dianions, which are then usually rapidly protonated to carbanions, which themselves may then be protonated to the dihydro compounds. That is, the aromatic hydrocarbons usually give two one-electron waves in their polarograms. It was found, however, that on the addition of proton donors such as water,[7] hydrogen iodide,[7] and phenol,[8] the first wave increased in height at the expense of the second wave. Hoijtink[7] was the first to show that this phenomenon could be explained by means of the HMO theory; that is, for alternant aromatic hydrocarbons the radical, $RH\cdot$, formed by the protonation of the radical anion, $R^{\overline{\cdot}}$, has a higher electron affinity than the parent molecule. The $RH\cdot$ radical can, therefore, be reduced without the necessity of further change in the electrode potential. Although the mechanisms have been studied extensively by polarography, very few investigations[9,10] have made direct measurements of the mechanism and kinetics of protonations of radical anions.

The aims of this investigation were to examine the methods of measuring the radical anion concentrations and then to study the mechanism of the protonation of aromatic hydrocarbon radical anions in dimethylformamide (DMF) and water mixtures where radical anions were electrochemically generated by controlled potential electrolysis.

Experimental

Materials. All the organic reagents were obtained commercially. E.P.-grade anthraquinone, phenanthrene,

---

[1] Parts of this work were presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970, and at the 16th Symposium of Polarography, Kyoto, Oct., 1970.

[2] M. E. Peover, "Electroanalytical Chemistry," Vol. 2, ed. by A. J. Bard, Marcel Dekker, Inc., New York, N. Y. (1967), p. 1.

[3] G. J. Hoijtink, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 7, ed. by P. Delahay and C. W. Tobias, Interscience Publishers, New York, N. Y. (1970), p. 221.

[4] A. Maccoll, *Nature*, **163**, 178 (1949).

[5] F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956).

[6] G. J. Hoijtink, *Rec. Trav. Chim.*, **74**, 1525 (1955).

[7] G. J. Hoijtink, J. van Schooten, E. de Boer, and W. Y. Aalbersberg, *Rec. Trav. Chim.*, **73**, 355 (1954).

[8] P. H. Given and M. E. Peover, *J. Chem. Soc.*, **1960**, 385.

[9] K. Umemoto, This Bulletin, **40**, 1058 (1967).

[10] T. Fujinaga, K. Izutsu, K. Umemoto, T. Arai, and K. Takaoka, *Nippon Kagaku Zasshi*, **89**, 105 (1968).

and naphthalene were purified by recrystallization from ethanol, ethanol, and methanol respectively. E.P.-grade anthracene was purified by sublimation. G.R.-grade pyrene and 1,2-benzanthracene were used without further purification. E.P.-grade biphenyl was also used without further purification.

Tetraethylammonium iodide (TEAI) and tetraethylammonium perchlorate (TEAP) were prepared according to the methods of Given *et al.*[11] and Fujinaga[12] *et al.*; these reagents showed no polarographic wave in a DMF solution in their accessible potential ranges of -0.6 V to -2.8 V and $+0.4$ V to -2.8 V, respectively, *vs.* SCE. Commercially-available G.R.-grade tetraethylammonium bromide (TEAB) was wet because of its deliquescent property and was consequently purified by recrystallization[13] from ethanol; then it was dried at 100°C for 12 hr in a vacuum and stored in a desiccator over silica gel. The TEAB also showed no polarographic wave in DMF in its accessible potential range, -0.5 V to -2.8 V *vs.* SCE.

The solvents used were purified in the usual manner,[12] the commercial, G.R. grade dimethylformamide (DMF) was dried over anhydrous K_2CO_3 for a few days with occasional shaking and then vacuum-distilled twice under nitrogen gas, and the water content of the DMF was determined to be 0.02% by Karl Fischer titration.

Polarography. An aqueous saturated calomel electrode was connected to the cell by a 1 N KNO_3-agar bridge[14] or a 1 N TEAB-agar bridge, the outlet of which was positioned just above the dropping mercury electrode. The 1 N KNO_3-agar bridge is adapted for measurements of the potential range of $+0.4$ V to -2.0 V *vs.* SCE, as in the case of anthraquinone, while the 1 N TEAB-agar bridge is adapted for measurements of the potential range of -0.5 V to -2.8 V *vs.* SCE, which was used for aromatic hydrocarbons; the bridges prevent the contamination of bromide or potassium ions from the TEAB- and KNO_3-bridges respectively. In order to lower the contamination of water from the bridge, one end of the bridge was aged in an aliquot of the supporting electrolyte solution for at least a day. The solution which contained a small amount of a depolarizer and 0.1 N of a supporting electrolyte was deaerated by bubbling pure nitrogen gas[15] for 15—20 min. No correction for the liquid-junction potential was taken into account. All the measurements were carried out at 25°C. The polarograph used was a Yokogawa Denki model POL-11.

The Simultaneous Measurements of Polarograms and UV and ESR Spectra of Anthraquinone Radical Anions. A solution containing 2×10^{-3} M of anthraquinone and 0.1 N of TEAP as the supporting electrolyte was placed in the electrolysis cell, as is shown in Fig. 1, and was deaerated for 20—30 min by bubbling pure nitrogen gas, which came through a flow-type 10-mm quartz cell for the absorption spectra and which came through a glass capillary for the ESR measurements. Then the bubbling was stopped and the nitrogen gas overflowed the catholyte by means of the cock, C_1, in Fig. 1; the DC polarogram of the base solution was recorded against the SCE (RE), which was also used in the controlled potential electrolysis as the reference electrode. Again, nitrogen bubbling was started and the solution was electrolyzed at the constant potential on the first plateau of the polarogram. The concentration of the radical anion could be controlled roughly by the length of the electrolysis time. After the electrolysis, the nitrogen gas again overflowed the catholyte, the solution in the center and in the anodic chamber was removed to prevent backflow, and then a DC polarogram was recorded. After that, the solution was introduced into the 10-mm quartz cell used for the UV spectrometry and the glass capillary used for the ESR spectrometry.

All the measurements were carried out at 20°C. A Japan Electron Optics Laboratory ESR spectrometer model JES-ME-3X, a Shimadzu recording spectrophotometer model MPS-50L, a Shimadzu polarograph model RP-50, and a Hokuto Denko potentiostat model PS-500B, were used.

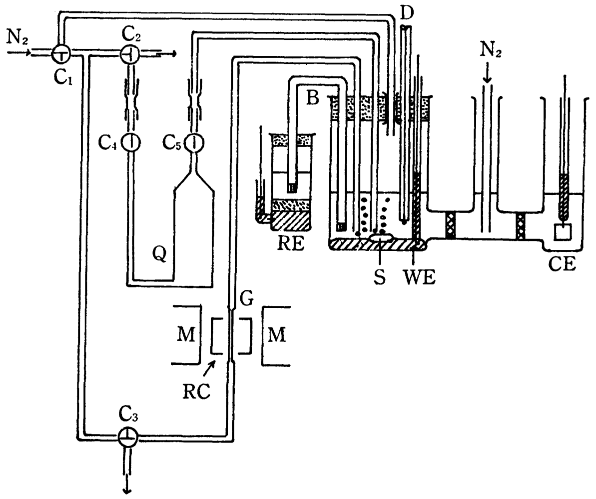

Fig. 1. Apparatus for simultaneous measurements of radical anions. N_2, pure nitrogen; C, cock; Q, UV quartz cell; M, magnet; G, glass capillary for ESR measurements; RC, resonant cavity; B, agar bridge; S, magnetic stirrer; RE, reference electrode (SCE); WE, mercury pool cathode; CE, Pt anode; D, d. m. e.

Visible Absorption Spectroscopy of Aromatic Hydrocarbon Radical Anions. The apparatus was almost identical with that used for the simultaneous measurements described above (Fig. 1). The following improvements were made, however: the 10-mm quartz cell and the electrolysis cell were kept at a constant temperature by means of a thermostat in order to make it possible to change the temperature. One more electrolysis cell, in which a DMF solution containing 5×10^{-3} M of the same aromatic hydrocarbon as was measured and 0.1 N of TEAB was placed, was connected to the line before the cock, C_1, in Fig. 1. After pure nitrogen had been bubbled in for 10—15 min, the solution in this cell was electrolyzed at the potential on the first diffusion plateau and the electrolysis was continued throughout each experiment. By this procedure, pure nitrogen gas was purified much more; the reduction potentials of the aromatic hydrocarbons are so negative that the oxygen is practically completely absorbed by the reaction with the radical anion.[16–18]

---

11) P. H. Given, M. E. Peover, and J. Schoen, *J. Chem. Soc.*, **1958**, 2674.

12) T. Fujinaga, K. Izutsu, and K. Takaoka, *J. Electroanal. Chem.*, **12**, 203 (1966).

13) C. K. Mann, "Electroanalytical Chemistry," Vol. 3, ed. by A. J. Bard, Marcel Dekker, Inc., New York, N. Y. (1969), p. 132.

14) M. E. Peover and J. D. Davies, *J. Electroanal. Chem.*, **6**, 46 (1963).

15) Pure nitrogen is purified by passing it through four alkaline pyrogallol solutions, concentrated sulfuric acid, and sodium hydroxide.

16) D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, **37**, 1562 (1965).

17) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **88**, 2669 (1966).

18) D. L. Maricle, *Anal. Chem.*, **35**, 683 (1963).

The main electrolysis was started after the nitrogen bubbling had continued for 45 min, and it was continued for 10 min. When the water content was small, the decay was slow enough to record the change in the spectra, but in the case of fast decay by the addition of considerable water, the absorbance against time must be recorded at the absorption maximum of the radical anions.

Results and Discussion

Controlled-Potential Electrolysis of Anthraquinone and Polarography of the Radical Anion of Anthraquinone. The polarographic reduction of anthraquinone (AQ) in DMF showed two well-defined waves with half-wave potentials of −0.90 V and −1.54 V *vs.* SCE (Fig. 2); these waves correspond to the formation of radical anions and dianions respectively:

$$\mathrm{AQ} + \mathrm{e} \rightleftarrows \mathrm{AQ}^{\cdot-} \qquad \text{1st wave} \qquad (1)$$

$$\mathrm{AQ}^{\cdot-} + \mathrm{e} \rightleftarrows \mathrm{AQ}^{2-} \qquad \text{2nd wave} \qquad (2)$$

However, the controlled potential electrolysis of anthraquinone at the potential (B), which was a little more negative than that of the second wave, gave radical anions as in the electrolysis at the potential (A) on the diffusion plateau of the first wave, but the rate of formation of the radical anions was double that of the latter. This is because a dianion, AQ^{2-}, reacts with a neutral AQ in solution to give two radical anions, as is shown below:

$$\mathrm{AQ}^{2-} + \mathrm{AQ} \rightleftarrows 2\mathrm{AQ}^{\cdot-} \qquad (3)$$

The equilibrium constant of this reaction:

$$K = \frac{[\mathrm{AQ}^{\cdot-}]^2}{[\mathrm{AQ}^{2-}][\mathrm{AQ}]} \qquad (4)$$

is obtained[19] from Eq. (5):

$$E_{1/2}(\text{1st}) - E_{1/2}(\text{2nd}) = \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln K \qquad (5)$$

where $E_{1/2}$(1st) and $E_{1/2}$(2nd) are the half-wave potentials of the first and second waves respectively, where $\boldsymbol{R}$ is the gas constant, where T is the absolute temperature, and where $\boldsymbol{F}$ is the Faraday constant. The value of K is calculated to be 10^{11}; therefore, the equilibrium of Reaction (3) lies almost completely to the right. Thus, we can obtain the various concentrations of the radical anions of anthraquinone by changing the length of the electrolysis time of the controlled potential electrolysis at the potential on the first palteau (A), and when we want to generate the radical anions rapidly and in large quantities, electrolysis at the potential on the second plateau (B) is useful.

The polarogram (Fig. 2) for the solution containing $\mathrm{AQ}^{\cdot-}$ which was prepared by the controlled potential electrolysis at either the potential on the first (A) or the second plateau (B) described above, shows an anodic wave with a large maximum (C) which suddenly drops at −0.4 V *vs.* SCE and which has a diffusion plateau at more positive potential (D). The shape of this anodic wave is very similar to that found by Santhanam and Bard[17] for the anodic oxidation of 9,10-diphenylanthracene radical anions, and it probably can be explained by a similar mechanism. The base currents before electrolysis and anodic currents after electrolysis were measured with the various heads of the dropping mercury electrode (d.m.e.). From these data, we obtained the anodic currents, i_d, of $\mathrm{AQ}^{\cdot-}$ in the anodic plateau (D) with the various heads of the d.m.e.; we found that this anodic current, i_d, varied as the square-root of the head of the d.m.e. (Fig. 3). Therefore, this anodic current may be diffusion-controlled and may be proportional to the concentration of $\mathrm{AQ}^{\cdot-}$. Furthermore, this anodic diffusion current showed no change with time; *i.e.*, the radical anion $\mathrm{AQ}^{\cdot-}$ was found to be stable[9,10,20] in DMF.

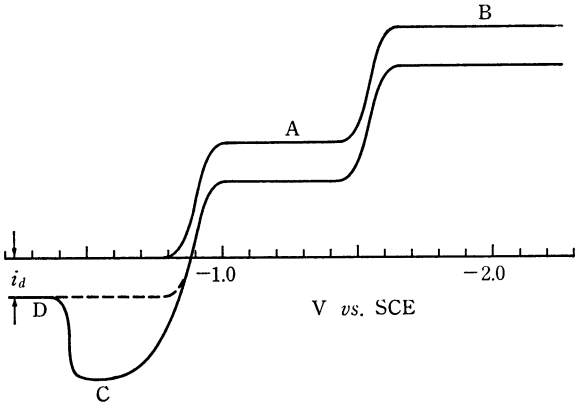

Fig. 2. DC polarograms of anthraquinone.

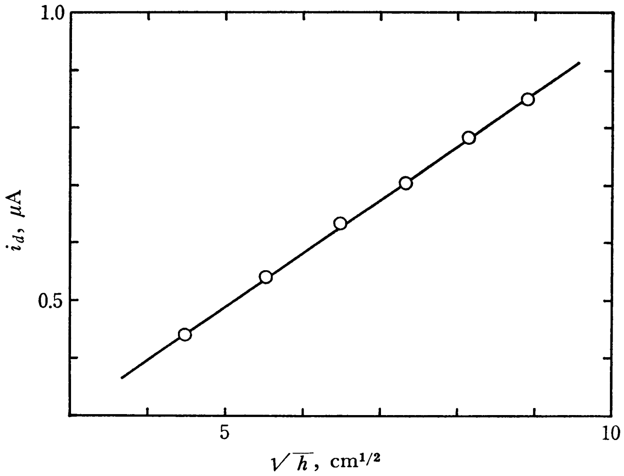

Fig. 3. Dependence of anodic current i_d on the square-root of the mercury head.

UV Absorption Spectra. The UV absorption spectra of radical anions and dianions of anthraquinone will be reported in detail in this Bulletin. The parent molecule, AQ, has an absorption band at the $\lambda_{\max}$ of 325 mμ in DMF, which itself has strong absorptions at wavelengths shorter than 270 mμ. The catholyte by controlled potential electrolysis had absorption bands at the $\lambda_{\max}$ of 390, 410, and 553 mμ in the visible region; these results are consistent with the absorption spectra of the anthraquinone radical anion reported

---

[19] J. Heyrovsky and J. Kuta, "Principle of Polarography," Academic Press, New York, N. Y. (1966), p. 181.

[20] W. Sakai, I. Matsuo, K. Miyata, and F. Hori, *Denki Kagaku*, **37**, 618 (1969).

by other authors.[10,21,22] The intensity of the maxima showed no change with time. As a result of this observations, the $AQ^{\overline{\cdot}}$ radical anion was found to be not only stable in DMF, but also completely free from oxygen in the UV cell.

ESR Spectra. The ESR spectra of anthraquinone radical anions in DMF solutions containing 1×10^{-4} M, 2×10^{-3} M, and 5×10^{-3} M of anthraquinone before controlled potential electrolysis, which were carried out at -1.20 V *vs.* SCE for 15 min, 45 sec, and 30 sec respectively, are given in Fig. 4. The hyperfine coupling constants obtained from the ESR spectrum of the solution containing 1×10^{-4} M of anthraquinone before electrolysis are $a_{H_1}=0.3$ gauss and $a_{H_2}=1.0$ gauss; these values almost agree with those in the literature.[9,21,23] As is shown in Fig. 4, the more parent molecules were present, the broader were the spectra obtained. This behavior can be explained as a result of rapid intermolecular electron-exchange[24] between the parent anthraquinone molecules and the radical anions:

$$AQ^{\overline{\cdot}} + AQ \rightleftarrows AQ + AQ^{\overline{\cdot}} \tag{6}$$

It can be said also that the radical anions were free from the oxygen throughout the measurements, for the ESR spectra showed no change with time.

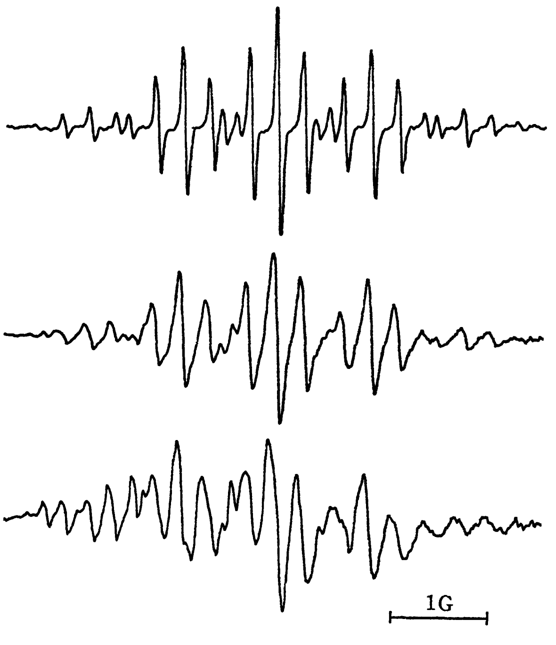

Fig. 4. ESR spectra of anthraquinone radical anions in DMF: above, 1×10^{-4} M; center, 2×10^{-3} M; below, 5×10^{-3} M of anthraquinone contained before partial reduction.

Comparison of Methods. It has been shown above from the measurements of polarograms and the UV and ESR spectra, that anthraquinone radical anions are stable in DMF and are free from oxygen. Therefore, the anthraquinone radical anions are suitable for the simultaneous measurements of the same solution by the three different methods; this can make clear the correlation of the measured quantities. The correlation between the anodic diffusion current, i_d, the absorbance, A, and the ESR signal intensity, I, of the derivative absorption curve are shown in Fig. 5. There exist a good linear relation between the diffusion currents and the absorbance, while the ESR signal intensity has no linear relation either with the diffusion currents or the absorbance. As the diffusion currents and the absorbance are usually proportional to the concentration, the above result leads to the conclusion that the ESR signal intensity of anthraquinone radical anions has no linear dependence on the concentration.

As the diffusion coefficients of the radical anion and the parent molecule are assumed to be approximately equal, the concentration of radical anions in Fig. 5 could be estimated from the i_d values to vary over the range of $2\times10^{-5}-2\times10^{-4}$ M; therefore, the molar extinction coefficient (at 553 mμ) of anthraquinone radical anions may be 1.2×10^4 M^{-1} cm^{-1}.

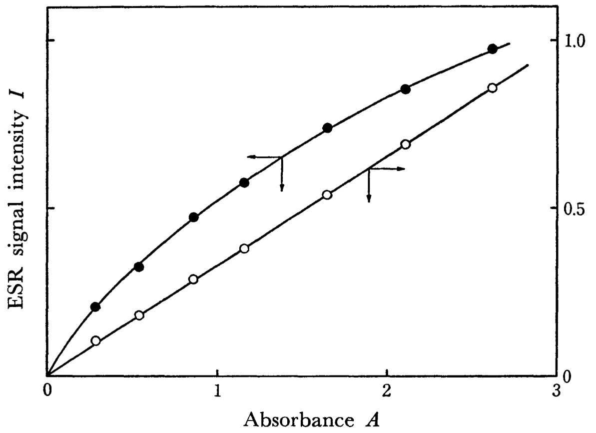

Fig. 5. Correlation between anodic diffusion current i_d, absorbance A and ESR signal intensity of the derivative absorption spectra I.

In the present system, it can be assumed, according to Weissman,[24] that the lines of ESR are close to Lorentzian and that the contributions to the line width from individual broadening mechanisms are additive. Then the line width of a line can be written as follows:

$$\begin{aligned}\Delta H_{p-p} &= \Delta H_0 + \Delta H_e + \Delta H_s \\ &= \Delta H_0 + h_e[\mathrm{R}] + h_s[\mathrm{R}^{\overline{\cdot}}]\end{aligned} \tag{7}$$

where ΔH_{p-p} is the line width as measured between points of extreme slope, *i.e.*, from peak to peak of the derivative spectrum, where ΔH_e is the contribution to the width from the electron-exchange reaction with the parent molecule, where ΔH_s is the contribution to the width from the intermolecular spin exchange reaction, and where ΔH_0 is the width in the absence of these two contributions, or when there is little such contributions. As is written in Eq. (7), these two contributions are known[24,25] to be proportional to the concentration of the parent molecule and the radical

---

[21] W. Sakai, K. Miyata, and F. Hori, *ibid.*, **37**, 688 (1969).

[22] T. Osa and T. Kuwana, *J. Electroanal. Chem.*, **22**, 389 (1969).

[23] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

[24] R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957).

[25] A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

anions respectively. Furthermore, the rate constants of these reactions are related to the line brodening by $k_e = 1.52 \times 10^7\, h_e\, \text{M}^{-1}\,\text{sec}^{-1}$ or $k_s = 1.52 \times 10^7\, h_s\, \text{M}^{-1}\,\text{sec}^{-1}$. The sum of the concentrations of the parent molecules and the radical anions were kept constant, 2×10^{-3} M, in the above experiment. Hence:

$$\Delta H_{p-p} = (h_s - h_e)[\text{AQ}^{\cdot-}] + \text{const.}$$

The plot of ΔH_{p-p} against $[\text{AQ}^{\cdot-}]$ gave a straight line (Fig. 6). The direct measurements of ΔH_{p-p} from the ESR spectra are not so accurate. Therefore, ΔH_{p-p} was determined from $\sqrt{[\text{AQ}^{\cdot-}]/I}$, since $I \times (\Delta H_{p-p})^2$ is proportional to the concentration of the radical anions.[26] The value of $(h_s - h_e)$ was determined from the slope of the straight line and was 140± 10 gauss M^{-1}. Similarly, the value of h_e could be determined from experiments where the concentrations of the radical anions were kept constant and where only the concentrations of parent molecules were varied; it was 10±5 gauss M^{-1} and the rate constants, k_e and k_s, were $(1.5 \pm 0.8) \times 10^8\ \text{M}^{-1}\,\text{sec}^{-1}$ and $(2.3 \pm 0.2) \times 10^9\ \text{M}^{-1}\,\text{sec}^{-1}$ respectively. These values are comparable to those of others.[25]

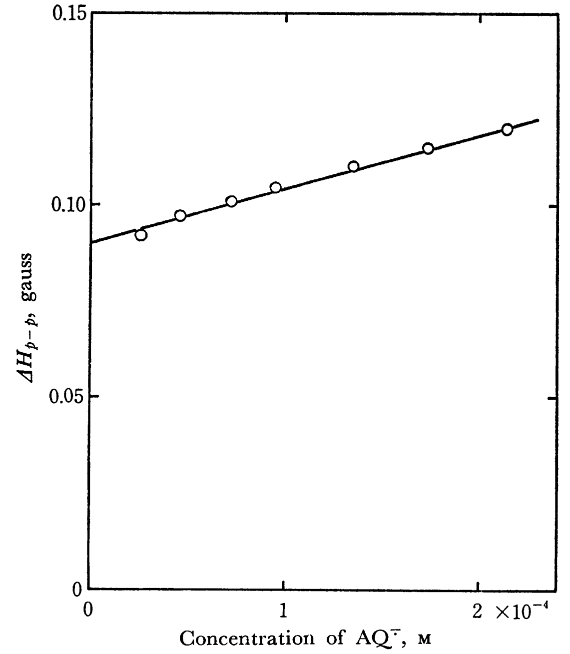

Fig. 6. Dependence of ΔH_{p-p} on $[\text{AQ}^{\cdot-}]$ where the sum of the concentrations of parent molecules and radical anions were kept constant, 2×10^{-3} M.

As has been described above, the nonlinear dependence of the ESR signal intensity on the concentration of the radical anions was found to be due to the broadening caused by the rapid intermolecular spin exchange, even if the concentration of the parent molecule is constant. However, the ESR measurement is very useful for studying the mechanism of the protonation of radical anions, because it can detect only radicals. As the quantitative method, UV absorption spectroscopy is more appropriate than polarography because of its accuracy and simplicity, unless the absorption maxima of the radical anions overlap those of the parent molecule and other compounds produced during the reaction.

The Decay of Aromatic Hydrocarbon Radical Anions in DMF-Water Mixtures. The radical anions of aromatic hydrocarbons in a DMF solution which contains small amounts of water are considered to decay by this protonation mechanism:

$$\text{R}^{\cdot-} + \text{H}_2\text{O} \xrightarrow{k} \text{RH}\cdot + \text{OH}^- \qquad (8)$$

$$\text{RH}\cdot + \text{R}^{\cdot-} \overset{k_{12}}{\rightleftharpoons} \text{RH}^- + \text{R} \qquad (9)$$

$$\text{RH}^- + \text{H}_2\text{O} \xrightarrow{k'} \text{RH}_2 + \text{OH}^- \qquad (10)$$

If the radical anions decay only through the sequence described above, the changes of the concentration of the radical anions with time are as given by Umemoto[9]:

$$\frac{\text{d}[\text{R}^{\cdot-}]}{\text{d}t} = -2k[\text{H}_2\text{O}][\text{R}^{\cdot-}] \qquad (11)$$

Equation(11) can be deduced from the facts that the reaction of Eq. (8) is slow, but the electron transfer reaction of Eq. (9) is very fast, and that, furthermore, the equilibrium of Eq. (9) lies completely to the right.[27]

---

[26] However, the proportional constant must be determined from at least one direct measurement.

[27] These facts are confirmed as follows. The equilibrium constant of Eq. (9) can be estimated by Eq. (14) if the half-wave potentials of Eq. (12) and Eq. (13) are known:

$$\text{R} + \text{e} \rightleftharpoons \text{R}^{\cdot-} \qquad (12)$$

$$\text{RH}\cdot + \text{e} \rightleftharpoons \text{RH}^- \qquad (13)$$

$$E_{1/2}(\text{RH}\cdot \rightarrow \text{RH}^-) - E_{1/2}(\text{R} \rightarrow \text{R}^{\cdot-}) = \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln K \qquad (14)$$

The Hückel theory predicts that the protonated radicals, RH·, derived from alternant hydrocarbons should have the same half-wave potentials, about −1.1 V *vs.* SCE, since the highest occupied orbital into which a further electron is uptaken is the non-bonding molecular orbital. This fact was ascertained experimentally by Dietz and Peover[28] using rapid sweep cyclic voltammetry at a platinum electrode. Among the aromatic hydrocarbons used in the present work, anthracene shows the lowest half-wave potential; its value is −1.95 V *vs.* SCE. Therefore, the equilibrium constant of Eq. (9) is greater than 10^{14} in the present study.

The rate constants of such a rapid intermolecular electron exchange of aromatic hydrocarbon radical anions as Eq. (15) have been determined by studying the line broadening of the ESR spectra[29,30]:

$$\text{R}^{\cdot-} + \text{R} \overset{k_{11}}{\rightleftharpoons} \text{R} + \text{R}^{\cdot-} \qquad (15)$$

they are about $10^8\ \text{M}^{-1}\,\text{sec}^{-1}$ in DMF and $10^7\ \text{M}^{-1}\,\text{sec}^{-1}$ in DMF containing 10% of water.[29] The rate constants of Eq. (16) may also be the same order as Reactions (6) and (15):

$$\text{RH}^- + \text{RH}\cdot \overset{k_{22}}{\rightleftharpoons} \text{RH}\cdot + \text{RH}^- \qquad (16)$$

According to Marcus,[31] the rate constant of the forward reaction of Eq. (9) can be estimated as follows:

$$k_{12} \simeq (k_{11}k_{22}Kf)^{1/2} \qquad (17)$$

where:

$$\ln f = (\ln K)^2/4 \ln (k_{11}k_{22}/Z^2) \qquad (18)$$

In the present system, k_{12} is calculated to be $10^{10.94}\ \text{M}^{-1}\,\text{sec}^{-1}$ when k_{11} and k_{22} are $10^7\ \text{M}^{-1}\text{sec}^{-1}$, Z is $10^{11}\ \text{M}^{-1}\,\text{sec}^{-1}$ and K is 10^{14}. Thus, the k_{12} is nearly equal to the collision frequency of the hypothetical uncharged species in solution, Z.

[28] R. Dietz and M. E. Peover, *Trans. Faraday Soc.*, **62**, 3535 (1966).

[29] T. P. Layloff, T. Miller, R. N. Adams, H. Fäh, A. Horsfield, and W. G. Proctor, *Nature*, **205**, 382 (1965).

[30] M. T. Jones and S. I. Weissman, *J. Amer. Chem. Soc.*, **84**, 4269 (1962). P. J. Zandstra and S. I. Weissman, *ibid.*, **84**, 4408 (1962).

[31] R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

Table 1. The visible absorption spectra of aromatic hydrocarbon radical anions

Hydrocarbon anion	a) in mμ	b) in mμ	c) in mμ	d) in mμ
(Biphenyl)$^{\overline{\cdot}}$	407	405	402	
	610	617	625	
	648	637		
(Naphthalene)$^{\overline{\cdot}}$	368	366	366	369
	437	437	433	437
	466	465	463	
	775	735		735
(Phenanthrene)$^{\overline{\cdot}}$	383	395	379	392
	421	415	415	417
	452	444	446	444
	665	654	637	649
(Anthracene)$^{\overline{\cdot}}$	364**	369		
	400**	401	403	400
	510			513
	548	549	546	546
	595	599	595	595
	638		637	
	656	662	654	662
	693		694	
	725	714	725	719
(1,2-Benz-anthracene)$^{\overline{\cdot}}$	**			388
	**			397
	415			422
	475			
	505			503
	538			541
	588			592
	758			
	792			
(Pyrene)$^{\overline{\cdot}}$	365	366	364	
	385	385	383	385
	450	455	450	455
	496	493	490	493
	742	719	735	730

a) Our results. b) See Ref. 32. c) See Ref. 33.
d) See Ref. 34.
** The parent molecules have absorption bands in the same region.

Equation (11) suggests that the radical anions will decay by a first-order reaction when the concentration of water is much greater than that of the radical anions. These predictions can be confirmed by a study of the change in the absorbance of the radical anions with time. The positions of the electronic absorption bands of the aromatic hydrocarbon radical anions obtained are given in Table 1, where the spectra of other authors[32–34] are compared with our results. These results show a fairly good agreement, though the measurements were carried out with different solvents.

The parent molecules, R, used, except for anthracene and 1,2-benzanthracene and their dihydroderivatives, RH_2, have no strong absorption bands in the range of 350—750 mμ, but the carbanions, RH^-, formed by Eq. (9) or by the monoprotonation of the dianions Eq. (20) have absorption maxima in a visible region.[35,36] Furthermore, the spectra of the RH^- carbanion were found to be similar to that of the carbonium ion, RH^+.[37]

However, the spectra corresponding to the RH^- carbanion were not found during the decay of the radical anions. These results mean that the rate constant of the protonation of RH^- in Eq. (10) is much greater than that of $R^{\overline{\cdot}}$ in Eq. (8). The absorbances of all the radical anions in the present study decayed exponentially with time; that is, the log A against time plots gave straight lines, which means a first-order decay of the radical anions as expected from Eq. (11).

Now that the radical anions of the aromatic hydrocarbons investigated in this study have been shown to decay through the Eq. (8)—Eq. (10) sequence, let us consider the reason why the aromatic hydrocarbon radical anions do not decay through this sequence:

$$2R^{\overline{\cdot}} \rightleftarrows R^{2-} + R \qquad (19)$$

$$R^{2-} + H_2O \xrightarrow{k''} RH^- + OH^- \qquad (20)$$

$$RH^- + H_2O \xrightarrow{k'} RH_2 + OH^- \qquad (10)$$

First, let us consider the case in which the disproportionation reaction Eq. (19) is the rate-determining step. The rate constants are assumed to be given approximately by the theory of Marcus[38] even in a system where the standard free energy of the reaction, ΔG°, is very large, as follows:

$$k = Z\exp(-\Delta G^*/\boldsymbol{R}T) \qquad (21)$$

where Z is the collision number in the solution and where ΔG^* is as given by Eqs. (22)—(24):

$$\Delta G^* = e_1{}^*e_2{}^*/D_sr + m^2\lambda \qquad (22)$$

where:

$$2m + 1 = -[\Delta G^\circ + (e_1e_2 - e_1{}^*e_2{}^*)/D_sr]/\lambda \qquad (23)$$

and:

$$\lambda = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)(\Delta e)^2 \qquad (24)$$

In these equations, the notations are the same as those of Marcus.[38] In a disproportionation reaction such as Eq. (19), the work of bringing reactants tagether, $e_1{}^*e_2{}^*/D_sr$, is not neglected, but the work for the products, e_1e_2/D_sr, is neglected, since one product is uncharged. The solvent reorganization parameter, λ, is assumed to be almost the same as that of the reaction of Eq. (15), and λ=13.1 kcal/mol, obtained from

---

[32] P. Balk, G. J. Hoijtink and W. H. Schreurs, *Rec. Trav. Chim.*, **76**, 813 (1957).

[33] E. de Boer and S. I. Weissman, *ibid.*, **76**, 824 (1957).

[34] A. G. Evans and B. J. Tabner, *J. Chem. Soc.*, **1963**, 5560.

[35] C. N. R. Rao, V. Kalyanaraman, and M. V. George, "Applied Spectroscopy Reviews," Vol. 3, ed. by E. G. Brame, Jr., Marcel Dekker, Inc., New York, N. Y. (1970), p. 153.

[36] N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, **87**, 4529 (1965).

[37] H. H. Perkampus, "Advances in Physical Organic Chemistry," Vol. 4, ed. by V. Gold, Academic Press, New York, N.Y. (1966), p. 195.

[38] R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

TABLE 2. HALF-WAVE POTENTIAL DIFFERENCES, STANDARD FREE ENERGIES AND RATE CONSTANTS OF DISPROPORTIONATION REACTION

Hydrocarbon	$-E_{1/2}$ (1st) V *vs.* SCE	$-E_{1/2}$ (2nd) V *vs.* SCE	$\Delta E_{1/2}$ V	ΔG° kcal/mol	ΔG^* kcal/mol	k_d $\mathrm{M^{-1}\,sec^{-1}}$
1,2-Benzanthracene	2.02	2.42	0.40	9.3	9.7	6.2×10^3
Pyrene	2.08	2.57	0.49	11.3	11.4	3.1×10^2
Anthracene	1.95	2.45	0.50	11.6	11.7	1.9×10^2
Biphenyl	2.60					
Naphthalene	2.54					
Phenanthrene	2.47					
Benzophenone[a]	1.75	2.06	0.31	7.2	8.1	9.3×10^4

a) See Ref. 9.

Eq. (24) by taking $a_1=a_2=6\text{Å}$, was used for the calculation of k_d.

The standard free energy of the disproportionation reaction, ΔG°, is also determined from the experimental results, the half-wave potentials of the first and second waves of aromatic hydrocarbons, by the following equation:

$$E_{1/2}(\mathrm{R}^{\bar{}} \to \mathrm{R}^{2-}) - E_{1/2}(\mathrm{R} \to \mathrm{R}^{\bar{}}) = \frac{RT}{F}\ln K \qquad (25)$$

which is an inverse of Eq. (5). The difference in the half-wave potentials, $\Delta E_{1/2}$, the standard free energy, ΔG°, and the calculated values of the rate constants, k_d, of the disproportionation reaction are given in Table 2. The differences in the half-wave potentials of biphenyl, naphthalene, and phenanthrene can not be obtained, since these compounds do not give the second wave in the accessible potential region. These differences, however, may not be smaller than those of the others obtained, because the electrostatic repulsion of the pair of electrons in the antibonding orbital, ϕ_{n+1}:

$$E_{\mathrm{rep}} = \iint \phi_{n+1}(1)\phi_{n+1}(2)\frac{e^2}{r}\phi_{n+1}(1)\phi_{n+1}(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

is larger in the case of smaller molecules, such as biphenyl, naphthalene and phenanthrene[39]; furthermore, the values of $\Delta E_{1/2}$ were found[40] to have a linear dependence on E_{rep}.

Hence, if the forward reaction of Eq. (19) is rate-determining, the decay of the radical anion by the sequence of Eqs. (19), (20), and (10) is given by:

$$\frac{\mathrm{d}[\mathrm{R}^{\bar{}}]}{\mathrm{d}t} = -k_d[\mathrm{R}^{\bar{}}]^2$$

As the concentrations of the radical anions are of the order of 10^{-4} M in the initial period, the products, $k_d[\mathrm{R}^{\bar{}}]$, are $10^{-1}-10^{-2}\,\mathrm{sec^{-1}}$ and are comparable to the apparent first-order rate constants, $2k[\mathrm{H_2O}]$, in Eq. (11), the values of which are $10^{-1}-10^{-3}\,\mathrm{sec^{-1}}$ in the present system.

As the present work has shown that the radical anion obeys the first-order decay, the rate-determining reaction may be the protonation reaction of dianions, Eq. (20), if the calculated order for k_d is correct.

At present, however, k_d is not obtained experimentally; furthermore, attempts to test the theory of Marcus for the dependence of ΔG^* on ΔG° have beem made[41,42] for the system, where ΔG° is not so large, 2—3 kcal/mol, but have never been made for the system where ΔG° is as large as 10 kcal/mol in the aromatic hydrocarbon radical anion disproportionation reaction. The values of ΔG° calculated from $\Delta E_{1/2}$ as Table 2 shows, are, however, possibly smaller than the true values, because $E_{1/2}$ (2nd) may be shifted to a positive potential by the rapid protonation of dianions, as is ascertained from the fact that AC polarography almost did not give the second wave. For the calculation of k_d, $10^{11}\,\mathrm{M^{-1}\,sec^{-1}}$ was used as the value of Z, but 10^9—$10^{10}\,\mathrm{M^{-1}\,sec^{-1}}$ may be more appropriate as the collision number between radical anions in solution, because the rate constants of spin exchange described before are considered[25] to be diffusion-controlled. Considering these factors, the disproportionation reaction itself is possibly slower than the protonation reaction of radical anions, Eq. (8), in the present system.

It is very interesting that the decay of benzophenone radical anions is known[9] to consist of the contributions of a first- and second-order reaction for radical anion concentrations. This is explained by the smaller ΔG° of benzophenone (in Table 2), as has been discussed by Fujinaga *et al.*[9,10]

The protonation reactions through either the Eqs. (8), (9), and (10) sequence or the Eqs. (19), (20), and (10) sequence lead to an increase in the first wave height at the expense of the second wave, because the reducible substance, *i.e.*, RH or R, is regenerated at the potential of the first plateau by these sequences, which are examples of ECE mechanisms. However, the radical anion and dianion of anthraquinone are not protonated in the DMF-alkaline water system.[43] Therefore, by the addition of water, no increase in the first wave height is found, although the second wave shifts to the positive potential and the two waves approach each other. This is because the strong solvation of the dianion by hydrogen bonding with water lowers the standard free energy of disproportionation

---

[39] N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

[40] Y. Matsui and Y. Date, presented at the 16th Symposium of Polarography, Kyoto, Oct., 1970.

[41] L. M. Dorfman, *Accounts Chem. Res.*, **3**, 224 (1970).

[42] K. Suga and S. Aoyagi, presented at the 9th Symposium of ESR, Tokyo, Oct., 1970.

[43] S. Hayano and M. Fujihira, presented at the 15th Symposium of Polarography, Sendai, Oct., 1969.

reaction, $\Delta G°$. As a result, R is reproduced to some extent and may be reduced at the potential of the first plateau, but at the same time R^{2-} is generated equally. The latter may be oxidized and may compensate for the reduction of neutral species.

The authors wish to thank Dr. M. Senō, Dr. T. Osa and Dr. M. Sukigara for their helpful discussions. The authors also wish to thank Mr. H. Saito and Mr. I. Yamashita for their assistance in the simultaneous measurements.