BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1058—1065 (1967)

# Studies of the Electrolytic Reduction Mechanism of Anthracene, Benzophenone and Anthraquinone by the Use of Polarography and Electron Spin Resonance Spectroscopy

Kisaburo UMEMOTO

*Chemistry Institute, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto*

(Received October 1, 1966)

The electrochemical reduction mechanism of anthracene, benzophenone and anthraquinone was studied in *N, N'*-dimethylformamide (DMF) and/or its water mixture by means of polarography and electron spin resonance spectroscopy (ESR). The polarograms of these compounds consisted of two well-defined waves in anhydrous DMF: the first wave corresponds to the formation of the anion radical and the second wave to the reduction of the anion radical to the dinegative anion. When water was added, the limiting current of the first wave increased at the expense of the second wave. In order to elucidate the reduction mechanism of these molecules in DMF-water mixture, the kinetic behavior of the anion radical was studied by the ESR method. It has been found that the reduction of anthracene is understood by the protonation mechanism, but that of anthraquinone is not explained by the protonation mechanism at all; the disproportionation of the anion radical must be considered. For the reduction of benzophenone both the protonation and the disproportionation mechanism must be taken into consideration.

Electrochemical reduction of organic molecules has been studied by several groups of workers in recent years. Most contemporary effort has been concerned with studies of the reduction mechanism in solvents of low proton availability in the presence or in the absence of the proton donor.[1-5]

---

[1] G. J. Hoijtink and J. van Schooten, *Rec. trav. chim.*, **71**, 1089 (1952); G. J. Hoijtink, J. van Schooten, E. de Boer and W. I. J. Aalbersberg, *ibid.*, **73**, 355 (1954).

[2] S. Wawzoneck, R. Berkey, E. W. Blaha and M. E. Runner, J. *Electrochem. Soc.*, **103**, 456 (1956).

[3] P. H. Given, M. E. Peover and J. Schoen, *J. Chem. Soc.*, **1958**, 2674.

[4] P. H. Given and M. E. Peover, *ibid.*, **1960**, 385.

[5] S. Wawzoneck and A. Gundersen, *J. Electrochem. Soc.*, **107**, 537 (1960).

It was shown by means of polarography that aromatic hydrocarbons,[1,4] ketones[4,5] and quinones[2,4] were reduced stepwise to give two one-electron waves in solvents of low proton availability such as 96% dioxan-water mixture,[1] *N, N'*-dimethylformamide (DMF)[2,4,5] or acetonitrile[2,5]. It was found that in the presence of high concentration of water[1,2,5] or a small amount of hydrogen iodide,[1] phenol,[4] or benzoic acid,[4] the first wave increased in height at the expense of the second wave. In order to explain this phenomenon the protonation mechanism was proposed: the increase of the first wave is due to the protonated radical which is formed from the anion radical by protonation.[1,4]

The present study was undertaken to elucidate the reduction mechanism of anthracene, benzophenone and anthraquinone in DMF and/or its water mixture at the mercury electrode, using polarography and electron spin resonance spectroscopy (ESR). As the results of the kinetic investigation, it has been found that the disproportionation of the anion radicals has to be considered together with the protonation mechanism in the course of the reduction of these organic molecules.

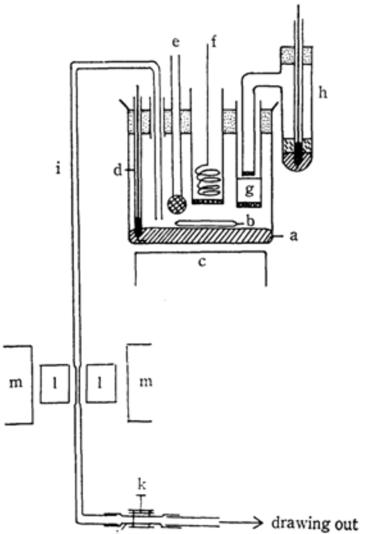


Fig. 1. Electrolysis cell for the ESR measurement.

- a) Mercury pool cathode
- b) Magnetic bar
- c) Magnetic stirrer
- d) Contact to mercury cathode
- e) Nitrogen gas inlet
- f) Pt anode
- g) Agar bridge
- h) Reference electrode (SCE)
- i) Glass capillary through which the solution is introduced into the microwave resonance cavity
- j) Rubber tube
- k) Screw cock which controls the flow of the solution
- l) ESR microwave resonance cavity
- m) Magnet

## Experimental

**Materials.** All organic materials were obtained commercially. Anthracene was purified by recrystallization from toluene and anthraquinone from ethyl alcohol. Benzophenone was G. R. grade and was used without further purification.

Tetraethylammonium perchlorate (TEP), used as the supporting electrolyte, was prepared from perchloric acid and tetraethylammonium iodide which was synthesized according to the prescription of Given and Peover.[3] The salt was recrystallized from hot water for several times. The pure TEP showed no polarographic wave in DMF solution in the range of +0.4 and −2.8 V *vs.* aqueous saturated caromel electrode (SCE).

The solvent was *N, N'*-dimethylformamide (DMF), which was purified by the usual manner: the commercial DMF was dried over anhydrous $K_2CO_3$ and $Na_2SO_4$ for a few days and then distilled twice under reduced nitrogen atmosphere. The water content of the solvent was determined as 0.05% by the Karl Fischer titration.

**Polarography.** The solution, which contained $1.0 \times 10^{-3}$ M of reducible substance ($1.0 \times 10^{-4}$ M in the case of anthraquinone because of its low solubility in DMF-water mixture) and 0.1 N of TEP as the supporting electrolyte, was taken in an H-type cell, each compartment of which was separated with a sintered glass disk, and it was deaerated by bubbling pure nitrogen gas for 20 min. The polarogram was recorded against the aqueous SCE which was connected to the electrolysis

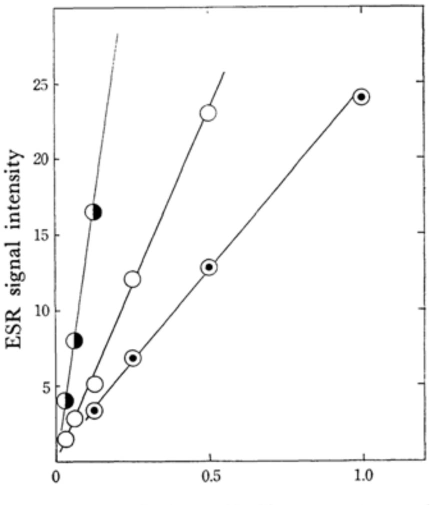


Fig. 2. The relationship between the ESR signal intensity and the concentration of the anion radical.

Solutions of nitrosodisulfonate anion radical were used as known concentration samples. The ESR signal intensity was measured by the peak height of the derivative absorption curve.

○ Gain 30 ◑ Gain 21 ⊙ Gain 35

solution through a 60% DMF - 40% $H_2O$ agar salt bridge satulated with TEP to prevent the contamination of water from the SCE into the solution.

The correction of the liquid junction potential was not carried out. The temperature was kept at 20°C. The polarograph used was Yanagimoto model PA-102.

**ESR Method.** The solution, which was $1\times10^{-3}$—$5\times10^{-3}$ M in reducible substance ($1$—$2\times10^{-4}$ M in anthraquinone) and 0.1 N in TEP, was taken in a beaker type electrolysis cell as shown in Fig. 1 and it was deaerated by bubbling pure nitrogen gas for one hour. It was then electrolyzed at the constant potential which was a little more negative than that of the first wave of the polarogram. In order to observe the ESR spectrum of the anion radical, the solution was introduced through a capillary into the microwave resonance cavity as shown in Fig. 1. The changes of the ESR signal intensity with time were recorded after the flow solution was stopped. In order to treat the ESR results quantitatively, calibration curves were prepared as shown in Fig. 2: a series of the solution of nitrosodisulfonate anion radical were used as known concentration samples. The straight lines show that there exists a good linear relation between the ESR signal intensity and the concentration of the anion radical in the range of $1\times10^{-3}$—$1\times10^{-5}$ M. The ESR measurements

TABLE 1. POLAROGRAPHIC RESULTS

(a) Anthracene

| | D. c. polarography | | | | | | A. c. polarography | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O$, % | $-E_{1/2}$ | | $i_d$ | | $I_d$ | | $-E_p$ | | $i_p$ | |
| | I | II | I | II | I | II | I | II | I | II |
| 0 | 1.93 | 2.45 | 2.48 | 1.60 | 2.68 | 1.92 | 1.95 | 2.52 | 0.35 | 0.04 |
| 5 | 1.96 | 2.35 | 2.26 | 1.78 | 2.45 | 2.08 | | | | |
| 10 | 1.96 | 2.29 | 2.20 | 1.46 | 2.38 | 1.68 | 1.97 | 2.37 | 0.29 | 0.03 |
| 15 | 1.97 | 2.28 | 2.64 | 0.96 | 2.86 | 1.10 | 1.98 | 2.34 | 0.26 | 0.02 |
| 20 | 1.98 | 2.29 | 3.04 | 0.27 | 3.30 | 0.31 | 1.99 | 2.32 | 0.20 | 0.02 |
| 30 | 1.99 | | 2.92 | | 3.18 | | 2.00 | 2.30 | 0.10 | 0.01 |
| 40 | 1.95 | | 2.62 | | 2.85 | | 2.01 | | 0.06 | |

(b) Benzophenone

| | D. c. polarography | | | | | | A. c. polarography | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O$, % | $-E_{1/2}$ | | $i_d$ | | $I_d$ | | $-E_p$ | | $i_p$ | |
| | I | II | I | II | I | II | I | II | I | II |
| 0 | 1.75 | 2.06 | 2.52 | 1.99 | 2.61 | 2.13 | 1.71 | 2.12 | 0.31 | $0.04_0$ |
| 3 | 1.72 | 1.90 | 2.74 | 1.68 | 2.84 | 1.76 | 1.70 | 2.04 | 0.36 | $0.03_6$ |
| 5 | 1.70 | 1.87 | 2.88 | 1.56 | 2.87 | 1.63 | 1.69 | 1.93 | 0.35 | $0.03_2$ |
| 10 | 1.65 | 1.86 | 3.08 | 0.92 | 3.17 | 0.96 | 1.65 | 1.88 | 0.30 | $0.02_8$ |
| 20 | 1.59 | 1.80 | 2.56 | 0.76 | 2.61 | 0.79 | 1.60 | 1.84 | 0.18 | $0.02_0$ |
| 30 | 1.53 | 1.75 | 2.40 | 0.58 | 2.42 | 0.60 | 1.57 | 1.81 | 0.10 | $0.00_4$ |
| 40 | 1.49 | 1.75 | 2.56 | 0.42 | 2.58 | 0.43 | 1.54 | 1.78 | 0.09 | 0.00 |
| 50 | 1.45 | 1.73 | 2.70 | 0.26 | 2.71 | 0.27 | 1.50 | | 0.08 | |

(c) Anthraquinone

| | D. c. polarography | | | | | | A. c. polarography | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O$, % | $-E_{1/2}$ | | $i_d$ | | $I_d$ | | $-E_p$ | | $i_p$ | |
| | I | II | I | II | I | II | I | II | I | II |
| 0 | 0.85 | 1.43 | 0.27 | 0.26 | 2.76 | 2.74 | 0.84 | 1.50 | 0.057 | 0.040 |
| 10 | 0.77 | 1.08 | 0.22 | 0.17 | 2.24 | 1.75 | 0.77 | 1.10 | 0.037 | 0.020 |
| 20 | 0.73 | 0.95 | 0.18 | 0.15 | 1.82 | 1.48 | 0.73 | 0.97 | 0.032 | 0.015 |
| 30 | 0.70 | 0.86 | 0.19 | 0.10 | 1.92 | 1.02 | 0.71 | 0.88 | 0.032 | 0.014 |
| 40 | 0.72 | 0.81 | 0.21 | 0.07 | 2.12 | 0.71 | 0.71 | 0.85 | 0.035 | 0.011 |
| 50 | 0.68 | | 0.28 | | 0.69 | | 0.72 | | 0.065 | |

$E_{1/2}$ and $E_p$ are in V *vs.* SCE, $i_d$ the instantaneous limiting current in $\mu$A, $I_d$ the diffusion current constant, and $i_p$ the peak current in m℧.

were carried out at room temperature which was exactly kept at 20°C. The ESR spectrometer was the same as that used previously.⁶⁾

## Experimental Results

In direct current (d. c.) polarography, all the substances studied gave well defined waves in anhydrous DMF. The results are given in Table 1. Logarithmic wave analysis of the first waves gave good straight lines of slopes of 0.06—0.07 V and the second waves gave lines of slopes of 0.07—0.08 V. From the results of alternating current (a. c.) polarography and ESR method, it was found that the first wave is a reversible one-electron wave corresponding to the formation of the corresponding anion radical and the second wave corresponds to the reduction of the anion radical to the dinegative anion. The polarographic results in anhydrous DMF can be explained by the well known mechanism¹,²,⁴⁾ as,

$$R + e \rightleftarrows R^{\overline{\cdot}} \qquad \text{(the 1st wave)} \qquad (1)$$

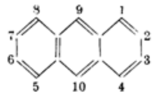
$$R^{\overline{\cdot}} + e \rightleftarrows R^{=} \qquad \text{(the 2nd wave)} \qquad (2)$$

$$R^{=} + 2H^{+} \rightleftarrows RH_2 \qquad (3)$$

The intermediate anion radicals were found to be very stable and the ESR spectra were easily recorded. The results are given in Table 2.

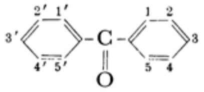
TABLE 2. OBSERVED COUPLING CONSTANTS*

(a) Anthracene



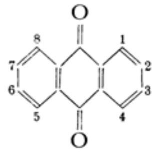
| $H_2O$, % | $a_{H_i}$, gauss | | |
|---|---|---|---|
| | $i$: 9, 10 | $i$: 1, 4, 5, 8 | $i$: 2, 3, 6, 7 |
| 0 | 5.35 | 2.68 | 1.52 |
| 2.0 | 5.40 | 2.70 | 1.53 |

(b) Benzophenone



| $H_2O$, % | $a_{H_i}$, gauss | | |
|---|---|---|---|
| | $i$: 1, 5, 1′, 5′ | $i$: 2, 4, 2′, 4′ | $i$: 3, 3′ |
| 0 | 2.56 | 0.84 | 3.46 |

(c) Anthraquinone



| $H_2O$, % | $a_{H_i}$, gauss | |
|---|---|---|
| | $i$: 1, 4, 5, 8 | $i$: 2, 3, 6, 7 |
| 0 | 1.01 | 0.29 |
| 10 | 1.00 | 0.41 |
| 20 | 0.94 | 0.45 |
| 30 | 0.99 | 0.51 |
| 40 | 1.01 | 0.53 |
| 50 | 1.00 | 0.56 |

* For all measurements of the coupling constants, the spectrum of nitrosodisulfonate anion radical, which shows three lines with a 13.0 gauss separation due to nitrogen splitting, was referred to as the standard.

In the presence of high concentration of water in DMF, both the polarographic behavior and the ESR spectra were different from those in anhydrous DMF.

**Anthracene.** When water was added in DMF, the half wave potential of the first wave

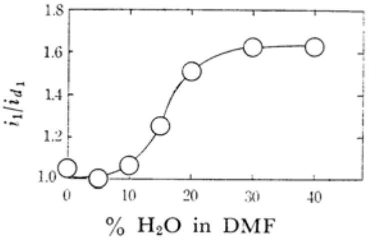


Fig. 3(a).

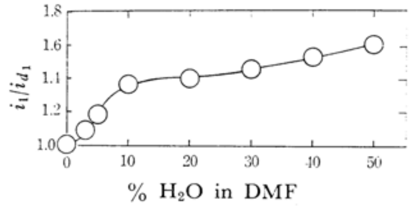


Fig. 3(b).

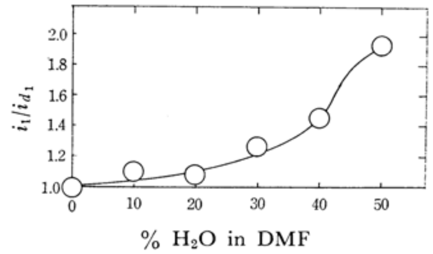


Fig. 3(c).

Fig. 3. Effect of added water in DMF on the limiting current on the first wave.
a) anthracene b) benzophenone c) anthraquinone
$i_1$ is the limiting current on the first wave in DMF water mixture and $i_{d_1}$ is that in anhydrous DMF.

---

6) K. Umemoto, Y. Deguchi and T. Fujinaga, This Bulletin, **36**, 1539 (1963); T. Fujinaga, Y. Deguchi and K. Umemoto, *ibid.*, **37**, 822 (1964).

remained almost unchanged but that of the second wave shifted to a little less negative potential (Table 1a), and the first wave increased in height at the expense of the second wave as shown in Fig. 3a. It was found that the reversible peak of the first wave in a. c. polarogram decreased remarkably by the addition of a small amount of water (Table 1a). This result indicates that the anion radical will be considerably reactive with water. The reactivity of anthracene anion radical with water was studied by observing the changes of the ESR signal intensity with time. It was found that the rate of the decrease of the ESR signal intensity with time was faster in the solution of higher concentration of water and the anion radical is very reactive with water. These results seem to be explained by the protonation mechanism[1]: the anion radical $R^{\overline{\cdot}}$ formed at the potential of the first wave takes a proton from water to form a protonated radical $RH\cdot$, which is further reduced at the same potential or accepts an electron from another anion radical to form $RH^-$ in the solution. The possibility of this reaction may be explained by the fact that the electron affinity of $RH\cdot$ is greater than that of the parent molecule as predicted from the molecular orbital calculation.[1] This mechanism is, therefore, formulated as follows:

At the electrode[1,4]

$$R + e \rightleftarrows R^{\overline{\cdot}} \tag{4}$$

$$R^{\overline{\cdot}} + H_2O \rightleftarrows RH\cdot + OH^- \tag{5}$$

$$RH\cdot + e \rightleftarrows RH^- \tag{6}$$

$$RH^- + H_2O \rightleftarrows RH_2 + OH^- \tag{7}$$

and in the solution[7]

$$R^{\overline{\cdot}} + H_2O \rightleftarrows RH\cdot + OH^- \tag{8}$$

$$RH\cdot + R^{\overline{\cdot}} \rightleftarrows RH^- + R \tag{9}$$

$$RH^- + H_2O \rightleftarrows RH_2 + OH^- \tag{10}$$

where Eq. (5) is the same to Eq. (8). If the reactions (8)—(10) are only reactions occurring in the solution, the change of the concentration of the anion radical with time are given by the following relation as shown in Appendix 1,

$$\frac{d[R^{\overline{\cdot}}]}{dt} = -2k'[H_2O][R^{\overline{\cdot}}] \tag{11}$$

According to Eq. (11), the reaction of the anion radical with water will follow a first-order reaction with regard to the anion radical when the concentration of water is much greater than that of the anion radical, and the apparent rate constant will increase linearly to the water content. In order to examine this relation the change of the ESR signal intensity with time was measured and some of the curves are given in Fig. 4. From the analysis of these curves, it was found that the ESR signal intensity of anthracene anion radical decreased in accordance with a first-order reaction as was expected from Eq. (11). Therefore, the reaction of anthracene anion radical is well explained by the protonation mechanism. The rate constants are given in Table 3a. Contrary to Eq. (11) the rate constant does not increase

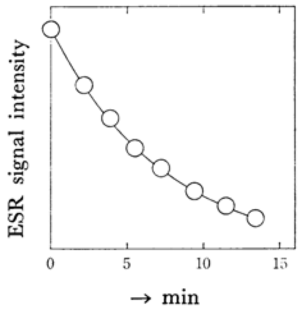


Fig. 4(a).

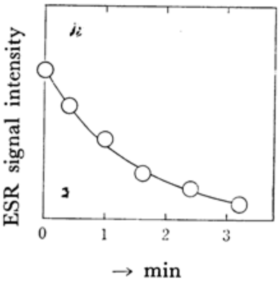


Fig. 4(b).

Fig. 4. The change of the ESR signal intensity with time of anthracene anion radical.
a) in 3.0% $H_2O$-DMF b) in 5.0% $H_2O$-DMF

TABLE 3. OBSERVED RATE CONSTANTS

(a) Anthracene

| $H_2O$, % | $k$, $sec^{-1}$ |
|---|---|
| 0 | — |
| 1.0 | $2\times10^{-4}$ |
| 2.0 | $8.5\times10^{-4}$ |
| 3.0 | $2.3\times10^{-3}$ |
| 4.0 | $5.8\times10^{-3}$ |
| 5.0 | $1.2\times10^{-2}$ |
| 6.0 | $6\times10^{-2}$ |

(b) Benzophenone

| $H_2O$, % | $k_1$, $sec^{-1}$ | $k_2$, $l\ mol^{-1}\ sec^{-1}$ |
|---|---|---|
| 0.19 | $1.9\times10^{-4}$ | — |
| 0.53 | $2.3\times10^{-4}$ | 2 |
| 1.80 | $4.8\times10^{-4}$ | 5 |
| 4.0 | $1.1\times10^{-3}$ | 10 |
| 6.0 | — | $8\times10^2$ |
| 7.5 | — | $1\times10^3$ |

---

[7] D. E. G. Austen, P. H. Given, D. J. E. Ingram and M. E. Peover, *Nature,* **182**, 1784 (1958).

linearly to the water content. This result will be due to the solvent effect on the reaction rate in a DMF-water mixture, because in a mixed solvent the reaction rate is much influenced by its composition.⁸⁾

**Benzophenone.** Both the first and the second wave of the d. c. polarogram shifted to less negative potential by the addition of water (Table 1b) and the first wave increased in height at the expense of the second wave (Fig. 3b). From the results of a. c. polarography, it was found that in the presence of a small amount of water the second wave was irreversible but the first wave was still reversible (Table 1b). These results show that the proton affinity of benzophenone anion radical will be much smaller than that of the dinegative anion. The reactivity of the anion radical was studied by means of the ESR method. Some of the curves which show the change of the ESR signal intensity with time are given in Fig. 5. From the analysis of these curves it was found that there were involved two pathways in the reaction: one was a first-order and the other, a second-order reaction with regard to benzophenone anion radical. In the range of a small amount of water the decay curve follows mainly the first-order reaction, which is replaced by the second-order reaction in the presence of much water. The first-order rate constant $k_1$ and the second-order rate constant $k_2$ were obtained by the method as shown in Appendix 2. The results are summarized in Table 3b. The presence of a second-order reaction in the presence of much water suggests that the reaction of benzophenone anion radical can not be explained simply by the protonation mechanism, being different from the case of anthracene anion radical.

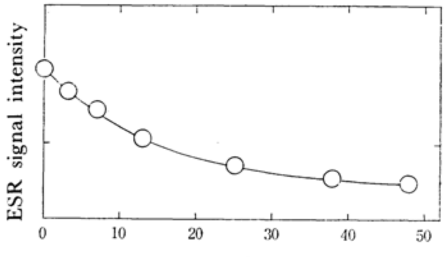


Fig. 5(a).

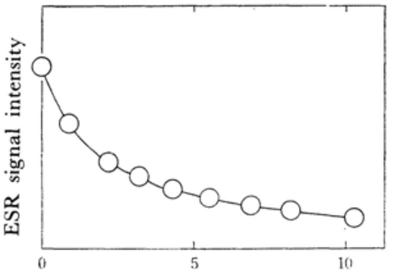


Fig. 5(b).

Fig. 5. The change of the ESR signal intensity with time of benzophenone anion radical.

a) in 1.0% $H_2O$-DMF b) in 5.0% $H_2O$-DMF

**Anthraquinone.** Both the two waves of the d. c. polarogram shifted to less negative potential by the addition of water (Table 1c) and the first wave increased in height at the expense of the second wave, finally coalesced to one wave as shown in Fig. 3c. However, the reversible peak height of the a. c. polarographic waves was proportional to the height of the corresponding d. c. polarographic step and therefore the reversibility of the electrode reaction of both the waves was little affected by the addition of water. This result indicates that both the anion radical and the dinegative anion of anthraquinone will react very little with water, being different from the cases of anthracene and benzophenone. The reactivity of anthraquinone anion radical was examined also by means of the ESR method. The ESR signal did not show any remarkable decrease even with 50%$H_2O$-DMF mixture. The fact again shows that anthraquinone anion radical does not react with water, being different from the cases of anthracene and benzophenone anion radical. From the results obtained by both polarography and the ESR method, the protonation mechanism would not be applied in the case of the reduction of anthraquinone.

## Discussion

It has been shown above that the reduction of anthracene can be explained by the protonation mechanism but that of benzophenone and anthraquinone can not fully be explained by this mechanism. Therefore, not only the protonation but also other reactions must be taken into consideration for the complete interpretation of the reduction mechanism of these molecules.

The reduction mechanism of anthracene can also be examined by the kinetic theory of polarography. If the protonation is the only reaction in the solution, the rate constant $k$ obtained by the polarographic method will agree with that obtained by the ESR method. The former constant was calculated by the method developed by Koutecky.⁹⁾ The relation between the rate constant $k$ and the ratio of the first waves $i_1/i_{d1}$, where $i_1$ is the limiting current in DMF-water mixture and $i_{d1}$ is that in

---

8) J. Parker, *Quart. Rev.*, **16**, 163 (1962).

9) J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **18**, 311, 597 (1953).

anhydrous DMF, is shown in Fig. 6.*1 Interpolating the $i_1/i_{d_1}$ value obtained with anthracene (Fig. 3a) into the relation (Fig. 6), the value of $k$ of less than or at most 0.1 $\mathrm{sec}^{-1}$ could be found in the range of 0—10% $H_2O$ content in DMF. On the other hand, the value of $k$ obtained from the ESR method was found to be about 0.01 and 0.06 $\mathrm{sec}^{-1}$ in 5% and 6% $H_2O$ - DMF mixture respectively. Therefore, the value of $k$ obtained by the polarographic method is in the same order with that obtained by the ESR method, and the protonation mechanism seems reasonable for the reduction of anthracene.

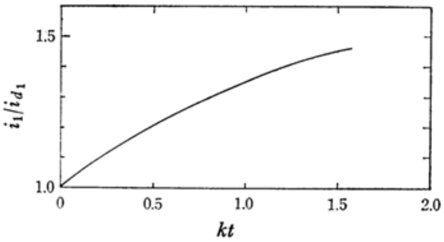


Fig. 6. The dependency of the limiting current of the first wave upon the protonation reaction rate constant.
$k$ is the rate constant of the protonation reaction in $\mathrm{sec}^{-1}$, and $t$ is the drop time of the dropping mercury electrode in sec.

Similar treatments were carried out with benzophenone comparing the data shown in Fig. 3b with those of Fig. 6. It was found that the $k_1$ obtained by the polarographic method gave values of about one hundred times greater than those obtained by the ESR method. Therefore, the polarographic behavior of benzophenone can not be explained by the protonation mechanism. The most probable mechanism which includes the second-order reaction of the anion radical and gives the reversible first wave is the disproportionation of the anion radicals as shown below,

$$\mathrm{R}^{\overline{\cdot}} + \mathrm{R}^{\overline{\cdot}} \rightleftarrows \mathrm{R} + \mathrm{R}^{=} \qquad (12)$$

$$\mathrm{R}^{=} + 2\mathrm{H_2O} \rightleftarrows \mathrm{RH_2} + 2\mathrm{OH}^{-} \qquad (13)$$

The equilibrium of Eq. (12) will shift to right-hand side as the dinegative anion is consumed by the reaction with water. As the dinegative anion is more reactive with water than the anion radical, the decrease of the anion radical with time follows a second-order reaction as shown by the ESR study. The reaction which gives the polarographic kinetic current is the forward reaction of Eq. (12). The enhancement of the limiting current of the first wave is attributed to the regenerated parent molecule. Therefore, in contrast to the case of anthracene, the first wave of the polarogram of benzophenone is still reversible even when the first wave increased in height by the addition of water.

The reduction of anthraquinone was found understandable by the disproportionation mechanism after the quantitative treatment of the results of polarography and the ESR method. In this case, as both the anion radical and the dinegative anion does not react with water, the equilibrium of Eq. (12) does not shift to the right-hand side in the solution and therefore the ESR signal intensity does not show any remarkable decrease for long standing. The increase of the limiting current of the first wave is attributed to the regenerated parent molecule as in the case of benzophenone.

The disproportionation mechanism, however, has been considered not to be feasible from the energetic viewpoint.[11] The disproportionation does not take place so far as the energy difference between $\mathrm{R}^{\overline{\cdot}}$ and $\mathrm{R}^{2-}$ is large. But in the case of the reduction in a DMF-water mixture the hydrogen bonding solvation of water to carbonyl group[12,13] will lower the energy levels of these ions resulting in the decrease of the energy difference between $\mathrm{R}^{\overline{\cdot}}$ and $\mathrm{R}^{2-}$. The fact that the two waves of anthraquinone approach each other by the addition of water keeping the reversibility of the electrode reaction as shown by a. c. polarography will support the consideration; as the electrode reaction of both waves is reversible, the approach of the half wave potential of the second to the first wave shows the decrease of the energy difference between $\mathrm{R}^{\overline{\cdot}}$ and $\mathrm{R}^{2-}$. The fact would suggest the possibility of the disproportionation in the reduction of anthraquinone (and probably of benzophenone). The possibility of the disproportionation of para-phenylenediamine cation[14] and aromatic quinone in DMF-ethyl alcohol[15] were also reported lately. In contrast to carbonyl compounds, hydrocarbon anion radicals are little solvated with water.[16] Therefore, in the case of anthracene the energy difference between $\mathrm{R}^{\overline{\cdot}}$ and $\mathrm{R}^{2-}$ is not so much altered as the disproportionation to occur. The forward reaction of Eq. (12) is not promoted by the addition of water and the consumption of the anion radical is caused by the reaction with water

---

[*1] This result was shown at the 12th symposium of polarography at Kyoto in November, 1965. Quite recently, Nicholson *et al.*[10] solved, in the study of the reduction of *p*-nitrosophenol, the same kinetic problem as discussed in this work and obtained similar results as shown in Fig. 6.

10) R. S. Nicholson, J. M. Wilson and M. L. Olmstead, *Anal. Chem.*, **38**, 542 (1966).

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

12) E. W. Stone and A. H. Maki, *ibid.*, **36**, 1944 (1962).

13) J. Gendell, J. H. Freed and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962).

14) P. Ludwig and R. N. Adams, *Anal. Chem.*, **34**, 917 (1962).

15) Y. Sakai, *Denki Kagaku*, **34**, 90 (1966).

16) P. Ludwig, T. Layloff and R. N. Adams, *J. Am. Chem. Soc.*, **86**, 4568 (1964).

which follows a first-order reaction. This consideration explains the experimental results very well.

The author wishes to express his grateful acknowledgment to Professor Taitiro Fujinaga for his kind guidance and constant encouragement throughout the course of this work. The author is also indebted to Dr. Kosuke Izutsu for his many helpful advices and discussions for the kinetic study of polarography. Thanks are also due to Dr. Yasuo Deguchi for his useful advice in ESR study.

## Appendix 1

*The Rate of the Concentration Change of the Protonation Mechanism.* The rate of the concentration change of the anion radical is represented by the following equations

$$-\frac{\mathrm{d}[\mathrm{R}^{\cdot-}]}{\mathrm{d}t} = k'[\mathrm{R}^{\cdot-}][\mathrm{H_2O}] - k''[\mathrm{RH}^{\cdot}][\mathrm{OH}^-] + l'[\mathrm{RH}^{\cdot}][\mathrm{R}^{\cdot-}] - l''[\mathrm{RH}^-][\mathrm{R}] \tag{14}$$

$$\frac{\mathrm{d}[\mathrm{RH}^{\cdot}]}{\mathrm{d}t} = k'[\mathrm{R}^{\cdot-}][\mathrm{H_2O}] - k''[\mathrm{RH}^{\cdot}][\mathrm{OH}^-] - l'[\mathrm{RH}^{\cdot}][\mathrm{R}^{\cdot-}] + l''[\mathrm{RH}^-][\mathrm{R}] \tag{15}$$

where $k'$ and $k''$ are the rate constants of the forward and the backward reaction of Eq. (8) respectively, and $l'$ and $l''$ are those of Eq. (9). From the ESR study it was verified that only the anion radical $\mathrm{R}^{\cdot-}$ exists at a measurable extent. If the radical $\mathrm{RH}^{\cdot}$ exists at a measurable extent, it will cause a drastic change in the ESR spectrum because of the new splittings of the added proton. Actually, however, such a change was not observed and therefore the radical $\mathrm{RH}^{\cdot}$ was not considered to exist so much as to be measured. It seems that the radical $\mathrm{RH}^{\cdot}$ is very reactive and accepts an electron from another anion radical to form $\mathrm{RH}^-$ immediately, and therefore,

$$\frac{\mathrm{d}[\mathrm{RH}^{\cdot}]}{\mathrm{d}t} = 0 \tag{16}$$

Then, Eq. (14) is written as,

$$\frac{\mathrm{d}[\mathrm{R}^{\cdot-}]}{\mathrm{d}t} = -2k'[\mathrm{H_2O}][\mathrm{R}^{\cdot-}] + 2k''[\mathrm{RH}^{\cdot}][\mathrm{OH}^-] \tag{17}$$

The forward and the backward reaction of Eq. (8) needs activation energy but not in the electron transfer reaction of Eq. (9). Therefore, the latter reaction proceeds very fast and the backward reaction of Eq. (8) will be neglected against the forward reaction. Now, Eq. (17) is written simply as,

$$\frac{\mathrm{d}[\mathrm{R}^{\cdot}]}{\mathrm{d}t} = -2k'[\mathrm{H_2O}][\mathrm{R}^{\cdot-}] \tag{11}$$

## Appendix 2

*Analysis of the Curves in Fig. 5.* When a first-order and a second-order chemical reaction are involved, the rate of the concentration change of the anion radical is written as,

$$\frac{\mathrm{d}b}{\mathrm{d}t} = -k_1 b - k_2 b^2 \tag{18}$$

where $k_1$ and $k_2$ represent the rate constants of the first-order and the second-order reaction respectively, and $b$ is the concentration of the anion radical. This equation can be solved and the following result is obtained,

$$b = b_0 \frac{\rho e^{-k_1 t}}{1 + \rho - e^{-k_1 t}} \tag{19}$$

where $b_0$ is the initial concentration of $\mathrm{R}^{\cdot-}$ and $\rho$ is defined as,

$$\rho = \frac{k_1}{k_2 b_0} \tag{20}$$

Kastening[17] obtained the same equation but he did not apply it to the analysis of the curves which showed the change of the polarographic diffusion current with time. Eq. (19) can be written as follows by rearrangement,

$$e^{-k_1 t} = \frac{b(1+\rho)}{b + b_0\rho} \tag{21}$$

Now, by taking the logarithm,

$$-k_1 t = 2.303 \log \frac{b(1+\rho)}{b + b_0\rho} \tag{22}$$

At $t=t_1$,

$$-k_1 t_1 = 2.303 \log \frac{b_1(1+\rho)}{b_1 + b_0\rho} \tag{23}$$

and at $t=t_2=2t_1$

$$-k_1 t_2 = -2k_1 t_1 = 2.303 \log \frac{b_2(1+\rho)}{b_2 + b_0\rho} \tag{24}$$

By comparing Eq. (23) with Eq. (24)

$$\rho = \frac{2b_1 b_2 b_0 - b_1^2 b_0 - b_1^2 b_2}{b_1^2 b_0 - b_2 b_0^2} \tag{25}$$

As $b_0$, $b_1$ and $b_2$ are known from the experimental results, $\rho$ can be obtained from Eq. (25) and then $k_1$ can be calculated from Eq. (23) as,

$$k_1 = -\frac{2.303}{t_1} \log \frac{b_1(1+\rho)}{b_1 + b_0\rho} \tag{26}$$

and from the definition of $\rho$, $k_2$ is obtained from Eq. (20) as,

$$k_2 = \frac{k_1}{b_0\rho} \tag{27}$$

From Eqs. (25), (26) and (27), $k_1$ and $k_2$ are determined from the curves in Fig. 5.

---

17) B. Kastening, *Electrochimica Acta*, **9**, 241 (1964); *Collection Czechoslov. Chem. Commun.*, **30**, 4033 (1965).