September, 1980] © 1980 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., **53**, 2673—2674 (1980) 2673

One-electron Reduction Potentials of Several Electron Acceptor Molecules and Cation Radicals of Donors

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(Received January 30, 1980)

Synopsis. Reversible one-electron reduction potential values of several electron acceptor molecules and cation radicals of donors were estimated by means of the equilibrium constant of electron transfer reaction between ion radicals in acetonitrile solution, and the results were compared with the observed electrochemical data.

In previous papers reports were given on a preferred electron-transfer (*i.e.*, oxidation-reduction) reaction from an anion radical to neutral electron acceptor molecule in solution.[1] The difference in reversible one-electron reduction potentials between two acceptor molecules could be estimated by measuring the equilibrium constant of the reaction spectrophotometrically. For example, the electron-transfer reaction from 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radical to neutral cyano-substituted *p*-benzoquinone in acetonitrile solution is expressed by

$$\mathrm{TCNQ}^{\bar{\cdot}} + p\text{-}\mathrm{X_2QCy_2} \rightleftharpoons \mathrm{TCNQ} + p\text{-}\mathrm{X_2QCy_2}^{\bar{\cdot}}, \tag{1}$$

where p-$\mathrm{H_2QCy_2}$ (X=H) and p-$\mathrm{Cl_2QCy_2}$ (X=Cl) stand for 2,3-dicyano-*p*-benzoquinone and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, respectively. By assuming that the activity coefficients of the solutes are unity and neglecting the effect of counter cations, the equilibrium constant of this reaction was determined spectrophotometrically to be $K=30$ at 20 ± 1 °C for X=H, while $K=(4.7\pm1.0)\times10^5$ at 15 °C for X=Cl, in acetonitrile solution.[1] By means of the Nernst equation and the estimated equilibrium constant, we obtain

$$E_0(p\text{-}\mathrm{H_2QCy_2},\ p\text{-}\mathrm{H_2QCy_2}^{\bar{\cdot}}) = E_0(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}}) + 0.09\,\mathrm{V}, \tag{2}$$

$$E_0(p\text{-}\mathrm{Cl_2QCy_2},\ p\text{-}\mathrm{Cl_2QCy_2}^{\bar{\cdot}}) = E_0(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}}) + 0.32\,\mathrm{V}, \tag{3}$$

where $E_0(\mathrm{A}, \mathrm{A}^{\bar{\cdot}})$ indicates reversible one-electron reduction potential of an acceptor, $\mathrm{A}+\mathrm{e}\rightleftharpoons\mathrm{A}^{\bar{\cdot}}$, in acetonitrile solution.

On the other hand, studies were also made on the chemical equilibrium of electron transfer reaction from neutral electron donor molecule to another cation radical molecule in acetonitrile solution.[2,3] In a similar way to that for the chemical equilibria of electron acceptor molecules, the following relations of reversible one-electron reduction potentials were obtained for the cation radicals of donor molecules of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), *N,N*-dimethyl-*p*-phenylenediamine (DMPD), *N,N,N′,N′*-tetramethylbenzidine (TMB), and tetrathiafulvalene (TTF):

$$E_0(\mathrm{DMPD}^{+\cdot},\ \mathrm{DMPD}) = E_0(\mathrm{TMPD}^{+\cdot},\ \mathrm{TMPD}) + 0.078\,\mathrm{V}, \tag{4}$$

$$E_0(\mathrm{TMB}^{+\cdot},\ \mathrm{TMB}) = E_0(\mathrm{TMPD}^{+\cdot},\ \mathrm{TMPD}) + 0.28\,\mathrm{V}, \tag{5}$$

$$E_0(\mathrm{TTF}^{+\cdot},\ \mathrm{TTF}) = E_0(\mathrm{TMPD}^{+\cdot},\ \mathrm{TMPD}) + 0.086 \pm 0.008\,\mathrm{V}, \tag{6}$$

where $E_0(\mathrm{D}^{+\cdot}, \mathrm{D})$ stands for reversible one-electron reduction potential for cation radical of a donor, $\mathrm{D}^{+\cdot}+\mathrm{e}\rightleftharpoons\mathrm{D}$, in acetonitrile solution.

So far, two series of reduction potentials have been independently obtained for the electron donor groups and the acceptor groups. In this paper, the two series are combined, for which purpose the following one-electron transfer reaction between donor TMPD and acceptor TCNQ in acetonitrile solution was considered:

$$\mathrm{TMPD} + \mathrm{TCNQ} \rightleftharpoons \mathrm{TMPD}^{+\cdot} + \mathrm{TCNQ}^{\bar{\cdot}}. \tag{7}$$

Yamagishi *et al.* examined the reaction and confirmed the occurrence of this chemical equilibrium.[4] They determined the equilibrium constant of Eq. 7 spectrophotometrically together with the enthalpy and entropy changes as

$$K = \frac{[\mathrm{TMPD}^{+\cdot}][\mathrm{TCNQ}^{\bar{\cdot}}]}{[\mathrm{TMPD}][\mathrm{TCNQ}]} = (7\pm2)\times10^{-2} \text{ at } 25\,^\circ\mathrm{C}, \tag{8}$$

$$\Delta H(\text{the enthalpy change}) = -17\pm4\,\mathrm{kJ\,mol^{-1}}, \tag{9}$$

$$\Delta S(\text{the entropy change}) = -71\pm21\,\mathrm{J\,K^{-1}\,mol^{-1}}. \tag{10}$$

Let us divide Eq. 7 into the following two reduction reactions,

$$\mathrm{TMPD}^{+\cdot} + \mathrm{e} \rightleftharpoons \mathrm{TMPD}, \tag{11}$$

$$\mathrm{TCNQ} + \mathrm{e} \rightleftharpoons \mathrm{TCNQ}^{\bar{\cdot}}. \tag{12}$$

The occurrence of the chemical equilibrium of Eq. 7 indicates that

$$E_0(\mathrm{TMPD}^{+\cdot},\ \mathrm{TMPD}) - \frac{RT}{F}\ln\frac{[\mathrm{TMPD}]}{[\mathrm{TMPD}^{+\cdot}]} = E_0(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}}) - \frac{RT}{F}\ln\frac{[\mathrm{TCNQ}^{\bar{\cdot}}]}{[\mathrm{TCNQ}]}, \tag{13}$$

where R, T, and F are the gas constant, observed temperature, and Faraday constant, respectively. Using Eq. 8, we obtain

$$E_0(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}}) = E_0(\mathrm{TMPD}^{+\cdot},\ \mathrm{TMPD}) + \frac{RT}{F}\ln K = E_0(\mathrm{TMPD}^{+\cdot},\ \mathrm{TMPD}) - 0.07\,\mathrm{V}. \tag{14}$$

The relation is important for connecting the reduction potentials of the donors with those of the acceptors. Another useful reaction is

$$\mathrm{TTF} + \mathrm{TCNQ} \rightleftharpoons \mathrm{TTF}^{+\cdot} + \mathrm{TCNQ}^{\bar{\cdot}}. \tag{15}$$

Yamagishi and Iida[3] examined the chemical equilibrium in acetonitrile solution spectrophotometrically, and determined the equilibrium constant to be $(2.8\pm0.1)\times10^{-3}$ at 11 °C. In a similar way to that for the TMPD/TCNQ system, we obtain

$$E_0(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}}) = E_0(\mathrm{TTF}^{+\cdot},\ \mathrm{TTF}) - 0.14\,\mathrm{V}. \tag{16}$$

With the aid of Eqs. 14 and 16, we can connect the reduction potential series of the acceptors (Eqs. 2 and 3) with those of the donors (Eqs. 4—6). If a standard value of reduction potential is given for $E_0(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})$ or $E_0(\mathrm{TTF}^{+\cdot}, \mathrm{TTF})$, all the other reduction potential values can be determined from the above procedure. The reversible one-electron reduction potentials thus estimated for the donors and acceptors are given in Table 1, where $E_0(\mathrm{TTF}^{+\cdot}, \mathrm{TTF})=0.30\ \mathrm{V}$ is chosen as a standard. The $E_0(\mathrm{TTF}^{+\cdot}, \mathrm{TTF})$ value was determined by Wheland and Gillson polarographically *versus* saturated calomel electrode in acetonitrile solution using tetraethylammonium perchlorate as a supporting electrolyte.[5] Since our data of reduction potentials correspond to the free energy change in pure acetonitrile, our values should be compared with standard electrode potentials measured in the same solvent. However, since no such electrode potential data are available, we compare our data with polarographic reduction potentials measured by several authors.[5—7] These values are also given in Table 1. As for the $E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\overline{\cdot}})$ value, the 0.16 V value estimated by our electron-transfer equilibrium method was in good agreement with the electrochemical value of Wheland and Gillson, 0.17 V.[5] The $E_0(p\text{-}\mathrm{H_2QCy_2}, p\text{-}\mathrm{H_2QCy_2}^{\overline{\cdot}})=0.25\ \mathrm{V}$ value estimated by our method was somewhat smaller than the half-wave potential of 0.31 V in polarography measured by Scribner,[6] but our value of $E_0(p\text{-}\mathrm{Cl_2QCy_2}, p\text{-}\mathrm{Cl_2QCy_2}^{\overline{\cdot}})=0.48\ \mathrm{V}$ was found to agree almost with the 0.51 V value measured by Peover.[7] The one-electron reduction potential of phenothiazine (PT) cation radical is also given in Table 1. The value of $E_0(\mathrm{PT}^{+\cdot}, \mathrm{PT})=0.56\ \mathrm{V}$ was estimated by our electron-transfer equilibrium method in (1:3) ethanol–water solvent, using the relation of $E_0(\mathrm{PT}^{+\cdot}, \mathrm{PT})=E_0(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})+0.34\ \mathrm{V}$,[2] the observed reduction potential of 0.58 V being the value in acetonitrile solution measured by Wheland and Gillson.[5] Although the solvents used differ from each other, a fairly good agreement was obtained between our value and that of Wheland and Gillson.

TABLE 1. ONE-ELECTRON REDUCTION POTENTIAL DATA FOR ELECTRON ACCEPTOR MOLECULES AND CATION RADICALS OF DONORS[a)]

Reduction reaction	Calcd[b)]	Obsd[c)]
$\mathrm{TCNQ} + e \rightleftharpoons \mathrm{TCNQ}^{\overline{\cdot}}$	0.16	0.17
$p\text{-}\mathrm{H_2QCy_2} + e \rightleftharpoons p\text{-}\mathrm{H_2QCy_2}^{\overline{\cdot}}$	0.25	0.31
$p\text{-}\mathrm{Cl_2QCy_2} + e \rightleftharpoons p\text{-}\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$	0.48	0.51
$\mathrm{TMPD}^{+\cdot} + e \rightleftharpoons \mathrm{TMPD}$	0.22	—
$\mathrm{TTF}^{+\cdot} + e \rightleftharpoons \mathrm{TTF}$	0.30	0.30
$\mathrm{DMPD}^{+\cdot} + e \rightleftharpoons \mathrm{DMPD}$	0.30	—
$\mathrm{TMB}^{+\cdot} + e \rightleftharpoons \mathrm{TMB}$	0.50	—
$\mathrm{PT}^{+\cdot} + e \rightleftharpoons \mathrm{PT}$	0.56[d)]	0.58

a) In unit of V *versus* saturated calomel electrode in acetonitrile solution. For abbreviations of compounds, see text. b) Values estimated by electron-transfer equilibrium method. $E_0(\mathrm{TTF}^{+\cdot}, \mathrm{TTF})=0.30\ \mathrm{V}$ is taken as a standard. c) Refs. 5—7. d) Value of phenothiazine cation radical ($\mathrm{PT}^{+\cdot}$) estimated by electron-transfer equilibrium method in (1 : 3) ethanol-water solvent. The relation of $E_0(\mathrm{PT}^{+\cdot}, \mathrm{PT})=E_0(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})+0.34\ \mathrm{V}$ was used.[2)]

For the reduction potentials of the other compounds, there are no experimental data for the purpose of comparison. However, the data obtained by our method are useful for predicting the degree of electron transfer when certain electron donor (D) and acceptor (A) molecules are mixed in acetonitrile solution. If $E_0(\mathrm{A}, \mathrm{A}^{\overline{\cdot}})-E_0(\mathrm{D}^{+\cdot}, \mathrm{D})<-RT/F$, equilibrium constant of the reaction, $\mathrm{D}+\mathrm{A}\rightleftharpoons\mathrm{D}^{+\cdot}+\mathrm{A}^{\overline{\cdot}}$, is small, and most of the chemical species in solution will be neutral D and A molecules. If $E_0(\mathrm{A}, \mathrm{A}^{\overline{\cdot}})-E_0(\mathrm{D}^{+\cdot}. \mathrm{D})>RT/F$, the equilibrium constant becomes large, so that most of the chemical species in solution will be ionized $\mathrm{D}^{+\cdot}$ and $\mathrm{A}^{\overline{\cdot}}$ radical molecules. In the case of $E_0(\mathrm{A}, \mathrm{A}^{\overline{\cdot}})-E_0(\mathrm{D}^{+\cdot}, \mathrm{D})\approx 0$, the equilibrium constant is *ca.* unity, and one can observe not only neutral D and A molecules but also ionized $\mathrm{D}^{+\cdot}$ and $\mathrm{A}^{\overline{\cdot}}$ in solution. For example, if TTF is mixed with $p\text{-}\mathrm{Cl_2QCy_2}$ in acetonitrile solution, the following reaction will take place:

$$\mathrm{TTF} + p\text{-}\mathrm{Cl_2QCy_2} \rightleftharpoons \mathrm{TTF}^{+\cdot} + p\text{-}\mathrm{Cl_2QCy_2}^{\overline{\cdot}}. \tag{17}$$

By means of the values of $E_0(\mathrm{TTF}^{+\cdot}, \mathrm{TTF})=0.30\ \mathrm{V}$ and $E_0(p\text{-}\mathrm{Cl_2QCy_2}, p\text{-}\mathrm{Cl_2QCy_2}^{\overline{\cdot}})=0.48\ \mathrm{V}$ (Table 1) and the Nernst equation, we can estimate the equilibrium constant, K, of Eq. 17 as

$$\ln K = \ln\frac{[\mathrm{TTF}^{+\cdot}][p\text{-}\mathrm{Cl_2QCy_2}^{\overline{\cdot}}]}{[\mathrm{TTF}][p\text{-}\mathrm{Cl_2QCy_2}]} = \frac{F}{RT}\{E_0(p\text{-}\mathrm{Cl_2QCy_2}, p\text{-}\mathrm{Cl_2QCy_2}^{\overline{\cdot}})-E_0(\mathrm{TTF}^{+\cdot}, \mathrm{TTF})\}. \tag{18}$$

In acetonitrile solution at 25 °C, the magnitude of K was estimated to be as great as 1.1×10^3. Thus, in this system, one electron is transferred almost completely from TTF to $p\text{-}\mathrm{Cl_2QCy_2}$, and most of the chemical species observed in acetonitrile will be ionized $\mathrm{TTF}^{+\cdot}$ and $p\text{-}\mathrm{Cl_2QCy_2}^{\overline{\cdot}}$.

References

1) Y. Iida and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **40**, 231 (1967); Y. Iida, *ibid.*, **44**, 1430 (1971); **49**, 3691 (1976); **52**, 1875 (1979).

2) Y. Iida and A. Yamagishi, *Bull. Chem. Soc. Jpn.*, **52**, 2443 (1979).

3) A. Yamagishi and Y. Iida, *Bull. Chem. Soc. Jpn.*, **53**, 1340 (1980).

4) A. Yamagishi, F. Watanabe, and T. Masui, *J. Chem. Soc., Chem. Commun.*, **1977**, 273.

5) R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98**, 3916 (1976).

6) R. M. Scribner, *J. Org. Chem.*, **31**, 3671 (1966).

7) M. E. Peover, *Trans. Faraday Soc.*, **58**, 1656 (1962).