BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (12), 3691—3692 (1976)

Oxidation-Reduction Potentials in the Formation of Anion Radicals

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(Received May 15, 1976)

Synopsis. The oxidation-reduction potentials in the formation of anion radicals were determined by using the equilibrium constant of the preferred electron transfer reaction between anion radicals in acetonitrile solution.

The 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3-dicyano-*p*-benzoquinone (p-$\mathrm{H_2QCy_2}$) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (p-$\mathrm{Cl_2QCy_2}$) molecules are known to be strong electron acceptors and to form stable anion radical salts with some diamagnetic counter cations.[1–3]

Several years ago,[4] we reported on the preferred electron transfer reaction between anion radicals in solution. When p-$\mathrm{X_2QCy_2}$ (X=H or Cl) was added to an acetonitrile solution of the sodium salt of the TCNQ anion radical, the oxidation-reduction reaction was found to take place simply through a one-electron transfer from the TCNQ anion radical to p-$\mathrm{X_2QCy_2}$. This reaction was expressed by the following oxidation-reduction equilibrium:

$$\mathrm{TCNQ}^{\cdot-} + p\text{-}\mathrm{X_2QCy_2} \rightleftharpoons \mathrm{TCNQ} + p\text{-}\mathrm{X_2QCy_2}^{\cdot-}, \qquad (1)$$

where X=H or Cl. It was assumed that the activity coefficients of the solutes were unity, since their concentrations were as dilute as 10^{-5} mol/l. In this case, the equilibrium constant, K, of this reaction was simply expressed by

$$K = \frac{[\mathrm{TCNQ}][p\text{-}\mathrm{X_2QCy_2}^{\cdot-}]}{[\mathrm{TCNQ}^{\cdot-}][p\text{-}\mathrm{X_2QCy_2}]}. \qquad (2)$$

The value of K in acetonitrile solution at 20 ± 1 °C was determined spectrophotometrically as $K=30$ for the case of X=H, while it was $K \geq 2\times10^3$ for the case of X=Cl.[4] At that time, we related the values of K to the half-wave potentials in polarography or to the electron affinities of the neutral p-$\mathrm{X_2QCy_2}$ molecules. In the present paper, we obtained oxidation-reduction potentials in the formation of anion radicals, because attempts have scarcely been made to obtained such values.

The occurence of the equilibrium of Eq. 1 means that[5]

$$E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-}) - \frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln\frac{[\mathrm{TCNQ}^{\cdot-}]}{[\mathrm{TCNQ}]}$$
$$= E_0(p\text{-}\mathrm{X_2QCy_2}, p\text{-}\mathrm{X_2QCy_2}^{\cdot-}) - \frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln\frac{[p\text{-}\mathrm{X_2QCy_2}^{\cdot-}]}{[p\text{-}\mathrm{X_2QCy_2}]}, \qquad (3)$$

where $E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-})$ and $E_0(p\text{-}\mathrm{X_2QCy_2}, p\text{-}\mathrm{X_2QCy_2}^{\cdot-})$ represent the standard oxidation-reduction potentials of

$$\mathrm{TCNQ} + e \rightleftharpoons \mathrm{TCNQ}^{\cdot-}, \qquad (4)$$

$$p\text{-}\mathrm{X_2QCy_2} + e \rightleftharpoons p\text{-}\mathrm{X_2QCy_2}^{\cdot-}. \qquad (5)$$

They were assumed to be reversible electrode reactions in acetonitrile solution. In Eq. 3, $\boldsymbol{R}$, T, and $\boldsymbol{F}$ are the gas constant, the observed temperature and the Faraday constant, respectively. Eq. 3 leads to

$$E_0(p\text{-}\mathrm{X_2QCy_2}, p\text{-}\mathrm{X_2QCy_2}^{\cdot-}) - E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-})$$
$$= \frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln K. \qquad (6)$$

When the spectrophotometrically determined values of K are put into Eq. 6, we have

$$E_0(p\text{-}\mathrm{H_2QCy_2}, p\text{-}\mathrm{H_2QCy_2}^{\cdot-}) = E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-}) + 0.09\ \mathrm{V}, \qquad (7)$$

$$E_0(p\text{-}\mathrm{Cl_2QCy_2}, p\text{-}\mathrm{Cl_2QCy_2}^{\cdot-}) \geq E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-}) + 0.19\ \mathrm{V}. \qquad (8)$$

The absolute values of $E_0(p\text{-}\mathrm{X_2QCy_2}, p\text{-}\mathrm{X_2QCy_2}^{\cdot-})$, (X=H or Cl), will be determined from these relations if the value is once given for $E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-})$. Although no definite value has been determined for $E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-})$, we obtained, in a previous paper,[6] the relationship of Eq. 9 by analyzing spectrophotometrically the oxidation-reduction reaction between TCNQ and iodide ion in acetonitrile solution:

$$E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-}) = E_0(\mathrm{I_2}, 2\mathrm{I}^-) + 0.045 \pm 0.004\ \mathrm{V}, \qquad (9)$$

where $E_0(\mathrm{I_2}, 2\mathrm{I}^-)$ represents the standard oxidation-reduction potential for the following reversible electrode reaction in acetonitrile solution:

$$\mathrm{I_2} + 2e \rightleftharpoons 2\mathrm{I}^-. \qquad (10)$$

Therefore, by using Eqs. 7, 8, and 9, the values for $E_0(p\text{-}\mathrm{X_2QCy_2}, p{=}\mathrm{X_2QCy_2}^{\cdot-})$, (X=H or Cl), versus $E_0(\mathrm{I_2}, 2\mathrm{I}^-)$ are obtained as is shown in Table 1.

TABLE 1. THE DATA ON THE OXIDATION-REDUCTION POTENTIALS IN THE FORMATION OF THE TCNQ, p-$\mathrm{H_2QCy_2}$, AND p-$\mathrm{Cl_2QCy_2}$ ANION RADICALS IN ACETONITRILE SOLUTION

Oxidation-reduction system	Oxidation-reduction potential, V
$\mathrm{I_2} + 2e \rightleftharpoons 2\mathrm{I}^-$	$E_0(\mathrm{I_2}, 2\mathrm{I}^-)$
$\mathrm{TCNQ} + e \rightleftharpoons \mathrm{TCNQ}^{\cdot-}$	$E_0(\mathrm{I_2}, 2\mathrm{I}^-) + 0.045 \pm 0.004$
$p\text{-}\mathrm{H_2QCy_2} + e \rightleftharpoons p\text{-}\mathrm{H_2QCy_2}^{\cdot-}$	$E_0(\mathrm{I_2}, 2\mathrm{I}^-) + 0.14$
$p\text{-}\mathrm{Cl_2QCy_2} + e \rightleftharpoons p\text{-}\mathrm{Cl_2QCy_2}^{\cdot-}$	$\geq E_0(\mathrm{I_2}, 2\mathrm{I}^-) + 0.24$

The oxidation-reduction potentials in acetonitrile solution are found to range, with increasing the electron-accepting strength, as $E_0(\mathrm{I_2}, 2\mathrm{I}^-) < E_0(\mathrm{TCNQ}, \mathrm{TCNQ}^{\cdot-}) < E_0(p\text{-}\mathrm{H_2QCy_2}, p\text{-}\mathrm{H_2QCy_2}^{\cdot-}) < E_0(p\text{-}\mathrm{Cl_2QCy_2}, p\text{-}\mathrm{Cl_2}$-

$QCy_2^{\cdot-}$). These oxidation-reduction potentials in the formation of ion radicals are important not only for the electrochemical study, but also for the investigation on the mechanism of certain chemical reactions involving ion radical molecules. The values of the oxidation-reduction potentials in the present paper were obtained by analyzing spectrophotometrically the oxidation-reduction reaction between anion radicals in solution, but an attempt is currently under way to measure those values of E_0 (TCNQ, $TCNQ^{\cdot-}$), E_0(p-X_2QCy_2, p-$X_2QCy_2^{\cdot-}$), (X=H or Cl), directly by electrochemical method.

References

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5) See, for example, I. M. Kolthoff, and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," MacMillan Co., New York (1952), p. 463.

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