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Oxidation-reduction Equilibrium between Anion Radicals. Electron-accepting Property of 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

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Synopsis. The electron affinity and the oxidation-reduction potential of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were estimated by means of the equilibrium constant of the preferred electron transfer reaction between anion radicals in acetonitrile solution.

It is known that 7,7,8,8-tetracyanoquinodimethane (TCNQ) and cyano-substituted *p*-benzoquinone molecules are strong electron acceptors, forming stable anion radical salts with some diamagnetic counter cations.[1-6)]

A method was worked out for determining the electron affinity values of electron acceptor molecules by means of preferred electron transfer reaction between anion radicals in solution.[1)] By measuring the equilibrium constant of such a reaction, we can estimate the difference of the electron-accepting strengths between two acceptor molecules. The method was applied to the following electron-transfer (oxidation-reduction) reaction in acetonitrile solution:

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

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. The equilibrium constant K of this reaction is given by

$$K = \frac{[\mathrm{TCNQ}][p\text{-}\mathrm{X_2QCy_2}^{\bar{\cdot}}]}{[\mathrm{TCNQ}^{\bar{\cdot}}][p\text{-}\mathrm{X_2QCy_2}]}. \tag{2}$$

Chemical equilibrium was easily observable in the reaction between $\mathrm{TCNQ}^{\bar{\cdot}}$ and p-$\mathrm{H_2QCy_2}$, when p-$\mathrm{H_2QCy_2}$ was added to an acetonitrile solution of the sodium salt of TCNQ anion radical. The effect of cations was neglected, the activity coefficients of the solutes being assumed to be unity since their concentrations were of the order 10^{-5} mol/l. The concentrations of $[\mathrm{TCNQ}^{\bar{\cdot}}]$ and $[p\text{-}\mathrm{H_2QCy_2}^{\bar{\cdot}}]$ in the equilibrium state were easily estimated spectrophotometrically, the K value in acetonitrile being determined as $K=30$ at 20 ± 1 °C.

In the reaction between $\mathrm{TCNQ}^{\bar{\cdot}}$ and p-$\mathrm{Cl_2QCy_2}$, however, the chemical equilibrium was not easily observed when p-$\mathrm{Cl_2QCy_2}$ was added to an acetonitrile solution of TCNQ anion radical. An unpaired electron of TCNQ anion radical is transferred almost completely to p-$\mathrm{Cl_2QCy_2}$, the equilibrium constant K being so great that we can hardly determine the $[\mathrm{TCNQ}^{\bar{\cdot}}]$ concentration in the equilibrium state by the usual spectrophotometric method. We could determine only the lower limit of K as $K\geq2\times10^3$ in acetonitrile solution at 20 ± 1 °C. This hampered the quantitative estimation of the electron affinity and the oxidation-reduction potential of p-$\mathrm{Cl_2QCy_2}$. Yamagishi overcame the above difficulty and succeeded in determining the K value for the reaction between $\mathrm{TCNQ}^{\bar{\cdot}}$ and p-$\mathrm{Cl_2QCy_2}$.[4)] By adding p-$\mathrm{Cl_2QCy_2}$ to an acetonitrile solution containing the TCNQ anion radical in the presence of large excess of TCNQ and p-$\mathrm{Cl_2QCy_2}^{\bar{\cdot}}$, the equilibrium concentration of $[\mathrm{TCNQ}^{\bar{\cdot}}]$ can be estimated spectrophotometrically. The equilibrium constant of Eq. 2 for the case of X=Cl was then determined to be $K=(4.7\pm1.0)\times10^5$ at 15 °C in acetonitrile solution.[4)]

First, we estimate the oxidation-reduction potential of p-$\mathrm{Cl_2QCy_2}$ by the use of the K value obtained and the equation

$$\begin{aligned} &E_0(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}}) - \frac{RT}{F}\ln\frac{[\mathrm{TCNQ}^{\bar{\cdot}}]}{[\mathrm{TCNQ}]} \\ &\quad = E_0(p\text{-}\mathrm{Cl_2QCy_2},\ p\text{-}\mathrm{Cl_2QCy_2}^{\bar{\cdot}}) \\ &\qquad - \frac{RT}{F}\ln\frac{[p\text{-}\mathrm{Cl_2QCy_2}^{\bar{\cdot}}]}{[p\text{-}\mathrm{Cl_2QCy_2}]}, \end{aligned} \tag{3}$$

where R, T, and F are the gas constant, the observed temperature and the Faraday constant, respectively, E_0 $(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}})$ and E_0 $(p\text{-}\mathrm{Cl_2QCy_2},\ p\text{-}\mathrm{Cl_2QCy_2}^{\bar{\cdot}})$ representing the standard oxidation-reduction potentials in the formation of the anion radicals of $\mathrm{TCNQ}+\mathrm{e}\rightleftarrows\mathrm{TCNQ}^{\bar{\cdot}}$ and $p\text{-}\mathrm{Cl_2QCy_2}+\mathrm{e}\rightleftarrows p\text{-}\mathrm{Cl_2QCy_2}^{\bar{\cdot}}$, respectively. These reactions are assumed to be reversible electrode reactions in acetonitrile solution. When the value of $K=(4.7\pm1.0)\times10^5$ determined spectrophotometrically is put into Eq. 3, we have

$$\begin{aligned} &E_0(p\text{-}\mathrm{Cl_2QCy_2},\ p\text{-}\mathrm{Cl_2QCy_2}^{\bar{\cdot}}) \\ &\quad = E_0(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}}) + 0.32\ \mathrm{V}. \end{aligned} \tag{4}$$

The oxidation-reduction potential in the formation of p-$\mathrm{H_2QCy_2}$ anion radical was obtained as E_0 $(p\text{-}\mathrm{H_2QCy_2},\ p\text{-}\mathrm{H_2QCy_2}^{\bar{\cdot}})=E_0$ $(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}})+0.09$ V in acetonitrile solution. Thus, the value of E_0 $(p\text{-}\mathrm{Cl_2QCy_2},\ p\text{-}\mathrm{Cl_2QCy_2}^{\bar{\cdot}})$ is larger than E_0 $(p\text{-}\mathrm{H_2QCy_2},\ p\text{-}\mathrm{H_2QCy_2}^{\bar{\cdot}})$ by 0.23 V. The increase in the E_0 $(p\text{-}\mathrm{Cl_2QCy_2},\ p\text{-}\mathrm{Cl_2QCy_2}^{\bar{\cdot}})$ value is caused by the introduction of two chlorine substituents into 2,3-dicyano-*p*-benzoquinone. In view of the magnitudes of these oxidation-reduction potentials, the electron-accepting strengths of acceptor molecules lie in the range $\mathrm{TCNQ}<p\text{-}\mathrm{H_2QCy_2}<p\text{-}\mathrm{Cl_2QCy_2}$.

Next, we examine the electron affinities of these acceptors. The observed equilibrium constant of Eq. 2 is related to electron affinity by

$$\begin{aligned} -RT\ln K &= E_\mathrm{A}(\mathrm{TCNQ}) - E_\mathrm{A}(p\text{-}\mathrm{X_2QCy_2}) \\ &\quad + \Delta\Delta G^\circ_\mathrm{solv}(\mathrm{TCNQ},\ \mathrm{TCNQ}^{\bar{\cdot}}) \\ &\quad - \Delta\Delta G^\circ_\mathrm{solv}(p\text{-}\mathrm{X_2QCy_2},\ p\text{-}\mathrm{X_2QCy_2}^{\bar{\cdot}}), \end{aligned} \tag{5}$$

where $E_\mathrm{A}(\mathrm{M})$ is the electron affinity of neutral acceptor molecule M, and $\Delta\Delta G^\circ_\mathrm{solv}$ $(\mathrm{M},\ \mathrm{M}^{\bar{\cdot}})$ the difference in the free energy of solvation between the molecule and its anion radical. As long as the molecular sizes and shapes of the acceptors are similar, we can reasonably assume $\Delta\Delta G^{\circ}_{\mathrm{solv}}$ (TCNQ, $\mathrm{TCNQ}^{\overline{\cdot}}$)$\approx\Delta\Delta G^{\circ}_{\mathrm{solv}}$ (p-$\mathrm{X_2QCy_2}$, p-$\mathrm{X_2QCy_2}^{\overline{\cdot}}$), and we have

$$-RT\ln K = E_{\mathrm{A}}(\mathrm{TCNQ}) - E_{\mathrm{A}}(p\text{-}\mathrm{X_2QCy_2}). \qquad (6)$$

Thus, the absolute values of E_{A} (p-$\mathrm{X_2QCy_2}$), (X=H or Cl), will be determined from this relation if the value is once given for E_{A} (TCNQ). So far, Briegleb's value of E_{A} (TCNQ)=1.7 eV has been taken as a reference,[2,5] but the value appears to be underestimated. Farragher and Page measured the E_{A} (TCNQ) value by magnetron method and proposed E_{A} (TCNQ)=2.88 eV as a standard.[6] Their value is considered to be more reliable. If we take E_{A} (TCNQ)=2.88 eV, we can estimate the values of E_{A} (p-$\mathrm{H_2QCy_2}$) and E_{A} (p-$\mathrm{Cl_2QCy_2}$) by Eq. 6 to be 2.97 eV and 3.20 eV, respectively. The electron-accepting strength of p-$\mathrm{Cl_2QCy_2}$ is very strong but somewhat weaker than that of hexacyanobutadiene; Farragher and Page reported the electron affinity of the latter compound to be 3.30 eV.[6]

It is of interest to compare the E_{A} (p-$\mathrm{X_2QCy_2}$)$-E_{\mathrm{A}}$ (TCNQ), (X=H or Cl), values obtained from Eq. 6 with those estimated from the charge-transfer absorption spectra. The acceptors of TCNQ, p-$\mathrm{H_2QCy_2}$, and p-$\mathrm{Cl_2QCy_2}$ form charge-transfer complexes with various electron donors in solution. For a common donor, D, the energy difference of the charge-transfer bands, $h\nu_{\mathrm{CT}}$ (D, TCNQ)$-h\nu_{\mathrm{CT}}$ (D, p-$\mathrm{X_2QCy_2}$), (X=H or Cl), can be approximately written as

$$h\nu_{\mathrm{CT}}(\mathrm{D},\ \mathrm{TCNQ}) - h\nu_{\mathrm{CT}}(\mathrm{D},\ p\text{-}\mathrm{X_2QCy_2}) = E_{\mathrm{A}}(p\text{-}\mathrm{X_2QCy_2}) - E_{\mathrm{A}}(\mathrm{TCNQ}). \qquad (7)$$

The charge-transfer complexes with various donor molecules of polycyclic aromatic hydrocarbons were examined in 1,2-dichloroethane. By observing the charge-transfer absorptions, together with Eq. 7, E_{A} (p-$\mathrm{X_2QCy_2}$)$-E_{\mathrm{A}}$ (TCNQ), (X=H or Cl), was evaluated for each common donor. For five donors, the average value of E_{A} (p-$\mathrm{H_2QCy_2}$)$-E_{\mathrm{A}}$ (TCNQ) was 0.05±0.05 eV, while that of E_{A} (p-$\mathrm{Cl_2QCy_2}$)$-E_{\mathrm{A}}$ (TCNQ) was 0.29±0.05 eV. On the other hand, from Eq. 6, the experimental results of oxidation-reduction equilibrium give E_{A} (p-$\mathrm{H_2QCy_2}$)$-E_{\mathrm{A}}$ (TCNQ)=0.09 eV and E_{A} (p-$\mathrm{Cl_2QCy})_2-E_{\mathrm{A}}$ (TCNQ)=0.32 eV. The values agree, within experimental error, with those estimated from the charge-transfer absorptions, respectively. This, in return, supports the assumption $\Delta\Delta G^{\circ}_{\mathrm{solv}}$ (TCNQ, $\mathrm{TCNQ}^{\overline{\cdot}}$)$\approx\Delta\Delta G^{\circ}_{\mathrm{solv}}$ (p-$\mathrm{X_2QCy_2}$, p-$\mathrm{X_2QCy_2}^{\overline{\cdot}}$), (X=H or Cl), in deriving Eq. 6.

In conclusion, the present technique of oxidation-reduction equilibrium between anion radicals is useful for determining the electron affinity values of electron acceptor molecules as well as the oxidation-reduction potentials in the formation of anion radicals of these acceptors.

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