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Electron-accepting Properties of 2,3-Dicyano-1,4-benzoquinone and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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Various methods are available for determining the electron affinities of electron-acceptor molecules.[1] The 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3-dicyano-1,4-benzoquinone (p-H$_2$QCy$_2$), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (p-Cl$_2$QCy$_2$) molecules are known to be strong electron acceptors and to form stable anion radical salts with some diamagnetic counter cations.

Several years ago, we reported on the preferred electron transfer reaction between anion radicals in solution.[2] When p-X$_2$QCy$_2$, (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-X$_2$QCy$_2$. This reaction was expressed by the following oxidation-reduction equilibrium:

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

where X=H or Cl. The equilibrium constant in acetonitrile at 20±1°C was determined spectroscopically as $K=30$ for the case of X=H, while it was $K \geq 2\times10^3$ for the case of X=Cl. As for this oxidation-reduction equilibrium, the observed equilibrium constant at temperature, T, is expressed as:

$$\begin{aligned} -RT\ln K = {} & E(\mathrm{TCNQ}) - E(p\text{-}\mathrm{X_2QCy_2}) \\ & + \Delta\Delta G^0_{\mathrm{solv}}(\mathrm{TCNQ},\ \mathrm{TCNQ^-}) \\ & - \Delta\Delta G^0_{\mathrm{solv}}(p\text{-}\mathrm{X_2QCy_2},\ p\text{-}\mathrm{X_2QCy_2}^-), \end{aligned} \qquad (2)$$

where E(A) is the electron affinity of the neutral A molecule and $\Delta\Delta G^0_{\mathrm{solv}}(\mathrm{A,A^-})$, the difference in the free energy of solvation between the molecule and its anion radical. Therefore, if one assumes $\Delta\Delta G^0_{\mathrm{solv}}(\mathrm{TCNQ},\ \mathrm{TCNQ^-}) \approx \Delta\Delta G^0_{\mathrm{solv}}(p\text{-}\mathrm{X_2QCy_2},\ p\text{-}\mathrm{X_2QCy_2}^-)$, one can obtain:

$$-RT\ln K = E(\mathrm{TCNQ}) - E(p\text{-}\mathrm{X_2QCy_2}). \qquad (3)$$

From the observed values of K, the difference in the electron affinities between TCNQ and p-H$_2$QCy$_2$ was estimated to be $E(p\text{-}\mathrm{H_2QCy_2})-E(\mathrm{TCNQ})=0.09$ eV, while that between TCNQ and p-Cl$_2$QCy$_2$ was $E(p\text{-}\mathrm{Cl_2QCy_2})-E(\mathrm{TCNQ})\geq 0.19$ eV.

On the other hand, TCNQ, p-H$_2$QCy$_2$, and p-Cl$_2$QCy$_2$ form charge-transfer complexes with many electron donor molecules in solution. It has been known, in general, that the energy of the charge-transfer band of a molecular complex, $h\nu_{\mathrm{CT}}$ (D,A), can be described as:

$$h\nu_{\mathrm{CT}}(\mathrm{D,\ A}) = I(\mathrm{D}) - E(\mathrm{A}) - C + P, \qquad (4)$$

where I(D) is the ionization potential of the donor, D, and E(A), the electron affinity of the acceptor, A; C is the coulombic energy of the dative-bond structure, and P is the difference between all the other energy quantities in the dative-bond and no-bond structures with both partners at their equilibrium internuclear separation in the complex.[3] This relation has often been used for the estimation of the electron affinity.[1] In the present paper, the difference in the electron affinities, $E(p\text{-}\mathrm{X_2QCy_2})-E(\mathrm{TCNQ})$, where X=H or Cl, was estimated from the difference in the charge-transfer energies between $h\nu_{\mathrm{CT}}$ (D, p-X$_2$QCy$_2$) and $h\nu_{\mathrm{CT}}$ (D, TCNQ). We shall examine how these values of $E(p\text{-}\mathrm{X_2QCy_2})-E(\mathrm{TCNQ})$ correspond to those evaluated previously from the oxidation-reduction equilibria.

The charge-transfer complexes of TCNQ, p-H$_2$QCy$_2$, and p-Cl$_2$QCy$_2$ were examined in an ethylene dichloride solution. Various aromatic hydrocarbons were employed as the electron donors. The charge-transfer spectra were measured by means of a Beckman DK-2A spectrophotometer. Table 1 shows the observed maximum positions of the charge-transfer absorptions under investigation.[4].

As for the complexes containing TCNQ, p-H$_2$QCy$_2$, or p-Cl$_2$QCy$_2$ as an acceptor, the I(D) value is constant for a common donor. In these cases, the great variation will occur in E(A). It is assumed that the other quantities are more or less constant, since the molecular sizes and the shapes of the acceptors are all similar. In this case, the energy difference of the charge-transfer bands, $h\nu_{\mathrm{CT}}$ (D, TCNQ)-$h\nu_{\mathrm{CT}}$ (D, p-X$_2$QCy$_2$), where X=H or Cl, can be approximately written as:

$$h\nu_{\mathrm{CT}}(\mathrm{D,\ TCNQ}) - h\nu_{\mathrm{CT}}(\mathrm{D},\ p\text{-}\mathrm{X_2QCy_2}) = E(p\text{-}\mathrm{X_2QCy_2}) - E(\mathrm{TCNQ}). \qquad (5)$$

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[1] G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

[2] Y. Iida and H. Akamatu, This Bulletin, **40**, 231 (1967).

[3] S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958); G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin-Göttingen-Heidelberg (1961).

[4] Two charge-transfer bands were observed for the complex containing naphthalene, 2,3-dimethylnaphthalene, acenaphthene or pyrene as a donor, and p-H$_2$QCy$_2$ or p-Cl$_2$QCy$_2$ as an acceptor. We can see that the energy difference of the complex between the first and the second charge-transfer bands remains nearly constant for a given donor; the value of this energy difference was found to be $(5.05\pm0.15)\times10^3\ \mathrm{cm^{-1}}$ for the naphthalene complexes, $(3.95\pm0.05)\times10^3\ \mathrm{cm^{-1}}$ for the 2,3-dimethylnaphthalene complexes, $(7.45\pm0.05)\times10^3\ \mathrm{cm^{-1}}$ for the acenaphthene complexes, and $(6.75\pm0.15)\times10^3\ \mathrm{cm^{-1}}$ for the pyrene complexes. This means that these two charge-transfer bands can be attributed to the transitions from the highest and the next occupied orbitals of the donor to the lowest vacant orbital of the acceptor. The energy difference between the highest and the next occupied orbitals of the donor is approximated by that between the first and the second charge-transfer bands. See, for example, H. Kuroda, T. Kunii, S. Hiroma, and H. Akamatu, *J. Mol. Spectrosc.*, **22**, 60 (1967).

TABLE 1. THE DATA ON THE MAXIMUM POSITIONS OF THE CHARGE-TRANSFER BANDS (in unit of 10^3 cm^{-1})a)

Donor	Acceptor		
	TCNQ	p-H_2QCy_2	p-Cl_2QCy_2
Benzene	—	25.9	24.2
Toluene	—	24.1	22.5
p-Xylene	—	21.1	19.4
Naphthalene	18.6	17.9	15.9
		22.8	21.1
2,3-Dimethylnaphthalene	17.0	16.8	14.7
		20.7	18.7
Acenaphthene	15.4	14.9	13.2
		22.4	20.6
Phenanthrene	19.5	19.0	17.1
Pyrene	13.7	13.7	11.8
		20.6	18.4

a) They were measured in ethylene dichloride solution at room temperature, although benzene, toluene, or *p*-xylene was used as a solvent as well as a donor.

When the complexes showed two charge-transfer absorptions, the maximum positions of the first charge-transfer bands were employed for $h\nu_{CT}(D, A)$. Unfortunately, the maximum positions for the complexes of TCNQ with benzene, toluene, and *p*-xylene were not determined, because the absorption due to TCNQ hindered the observation of their charge-transfer bands. Therefore, the data on the charge-transfer bands for the complexes of p-H_2QCy_2 or p-Cl_2QCy_2 with the same donor molecules were not available for comparison. We used, then, the values of $h\nu_{CT}(D, A)$, where D is naphthalene, 2,3-dimethylnaphthalene, acenaphthene, phenanthrene, or pyrene, and where A is TCNQ, p-H_2QCy_2, or p-Cl_2QCy_2. These values were taken from Table 1. By the use of Eq. (5), $E(p\text{-}X_2QCy_2) - E(\text{TCNQ})$, where X=H or Cl, was evaluated for each common donor. For the above five donors, the average value of $E(p\text{-}H_2QCy_2) - E(\text{TCNQ})$ was estimated to be $(0.4 \pm 0.4) \times 10^3$ cm^{-1} (*i.e.*, 0.05 ± 0.05eV), while that of $E(p\text{-}Cl_2QCy_2) - E(\text{TCNQ})$ was estimated to be $(2.3 \pm 0.4) \times 10^3$ cm^{-1} (*i.e.*, 0.29 ± 0.05 eV). If the standard value is once given to the electron affinity for TCNQ, $E(p\text{-}H_2QCy_2)$ and $E(p\text{-}Cl_2QCy_2)$ will be determined from these relations. When $E(\text{TCNQ}) = 1.7$ eV is taken as a reference,5) $E(p\text{-}H_2QCy_2)$ and $E(p\text{-}Cl_2QCy_2)$ are estimated to be 1.75 ± 0.05 eV and 1.99 ± 0.05 eV respectively. These values are found to be in good accordance with $E(p\text{-}H_2QCy_2) = 1.79$ eV and $E(p\text{-}lC_2QCy_2) \geq 1.89$ eV respectively; these latter values were determined from the method of the oxidation-reduction equilibrium between the anion radicals by using the same standard value of $E(\text{TCNQ}) = 1.7$ eV.2) It is interesting to note that the introduction of the chlorine substituents into p-H_2QCy_2 increases the value of the electron affinity by at least 0.1—0.2 eV.

Judging from these results, the previous estimation of the $E(p\text{-}H_2QCy_2)$ and $E(p\text{-}Cl_2QCy_2)$ values from the method of oxidation-reduction equilibrium is strongly supported by the present method of the charge-transfer spectra. Therefore, it may be concluded that the application of the oxidation-reduction equilibrium between anion radicals in solution is a new method for determining the electron affinities of acceptor molecules generally. However, we should keep in mind that, in this method, the $E(A)$ values include some uncertainties, since the $\Delta\Delta G^0_{solv}(A, A^-)$ value does not remain constant for each of the acceptor molecules.

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5) Although Briegleb reported $E(\text{TCNQ}) = 1.7$ eV,1) no definite value has yet been determined for $E(\text{TCNQ})$.