Oxidation-Reduction Equilibrium between Anion Radicals

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Prefered electron transfer from an anion radical to another acceptor molecule has been reported by Ishitani and Nagakura.[1] The oxidation-reduction can take place simply through one electron transfer between anion radicals in solution, and in some cases the equilibrium of the reaction is observable.

When 2, 3-dicyano-*p*-benzoquinone (p-H_2QCy_2) is added into the acetonitrile solution of sodium salt of tetracyanoquinodimethane (TCNQ) anion radical, the green color due to $TCNQ^-$ changes into red. By observing the absorption spectra, one can find, on adding p-H_2QCy_2, the decrease in the optical density of Na^+TCNQ^- and the increase in those of TCNQ and Na^+p-$H_2QCy_2^-$. This reaction is expressed by the following oxidation-reduction equilibrium;

$$Na^+TCNQ^- + p\text{-}H_2QCy_2 \rightleftharpoons TCNQ + Na^+p\text{-}H_2QCy_2^-. \qquad (1)$$

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1) A. Ishitani and S. Nagakura, This Bulletin, **38**, 367 (1965).

The concentration of Na^+TCNQ^- in the equilibrium state was measured by the optical density at 842 $m\mu$, which is not interferred by other molecular species. Assuming that ions in the solution are free and their activity coefficients be unity, the equilibrium constant at 20±1°C was estimated as $K=30$ in acetonitrile. Similar behavior was observed with 2, 3-dicyano-5, 6-dichloro-*p*-benzoquinone ($p\text{-Cl}_2\text{QCy}_2$), which can be expressed as

$$\text{Na}^+\text{TCNQ}^- + p\text{-Cl}_2\text{QCy}_2 \rightleftharpoons \text{TCNQ} + \text{Na}^+p\text{-Cl}_2\text{QCy}_2{}^-. \tag{2}$$

The equilibrium constant was obtained as $K \geqslant 2\times10^3$ at 20±1°C.

In a reversible one electron abstraction from an anion radical R^- in the solution,

$$R^- \rightleftharpoons R + e, \tag{3}$$

the free-energy change represented by the half-wave potential in polarography is

$$\Delta G^\circ_{\text{R}} = (G^\circ_{\text{R}})_{\text{gas}} - (G^\circ_{\text{R}^-})_{\text{gas}} + (G^\circ_{\text{electron}})_{\text{Hg}} + \Delta\Delta G^\circ_{\text{solv}}(\text{R}, \text{R}^-), \tag{4}$$

where $\Delta\Delta G^\circ_{\text{solv}}(\text{R}, \text{R}^-)$ is the difference in free-energy of solvation of the molecule and its anion. In the absence of entropy effects, we may write Eq. (4) as

$$\Delta G^\circ_{\text{R}} = E_{\text{A}}(\text{R}) + (G^\circ_{\text{electron}})_{\text{Hg}} + \Delta\Delta G^\circ_{\text{solv}}(\text{R}, \text{R}^-), \tag{5}$$

where $E_{\text{A}}(\text{R})$ is the electron affinity of the molecule. The half-wave potential, $\varepsilon_{1/2}$, is given by

$$\varepsilon_{1/2}(\text{R}) = \frac{\Delta G^\circ_{\text{R}}}{\boldsymbol{F}} - \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{D_{\text{R}}}{D_{\text{R}^-}}, \tag{6}$$

where D_{R} and D_{R^-} are the diffusion constants of R and R^- respectively, and $\boldsymbol{F}$ is the Faraday constant. The term involving the diffusion constants will be small, because D_{R} and D_{R^-} are nearly same for the molecules conceived.

In the case of oxidation-reduction equilibrium between TCNQ and $p\text{-X}_2\text{QCy}_2$, where X=H or Cl, the observed equilibrium constant is related with ΔG°'s,

$$\begin{aligned} -\boldsymbol{RT}\ln K &= \Delta G^\circ_{\text{TCNQ}} - \Delta G^\circ_{p\text{-X}_2\text{QCy}_2} \\ &= E_{\text{A}}(\text{TCNQ}) - E_{\text{A}}(p\text{-}X_2\text{QCy}_2) \\ &\quad + \Delta\Delta G^\circ_{\text{solv}}(\text{TCNQ}, \text{TCNQ}^-) \\ &\quad - \Delta\Delta G^\circ_{\text{solv}}(p\text{-X}_2\text{QCy}_2, p\text{-X}_2\text{QCy}_2{}^-) \\ &\doteqdot F[\varepsilon_{1/2}(\text{TCNQ}) - \varepsilon_{1/2}(p\text{-X}_2\text{QCy}_2)]. \end{aligned} \tag{7}$$

Therefore, from the observed equilibrium constant one can estimate the difference of half-wave potentials between two acceptor molecules. Referring to $\varepsilon_{1/2}(\text{TCNQ})=0.19$ V (*vs.* SCE) in acetonitrile,[2] $\varepsilon_{1/2}(p\text{-X}_2\text{QCy}_2)$, where X=H or Cl, is calculated as shown in Table 1. Assuming

$$\Delta\Delta G^\circ_{\text{solv}}(\text{TCNQ}, \text{TCNQ}^-) - \Delta\Delta G^\circ_{\text{solv}}(p\text{-X}_2\text{QCy}_2, p\text{-X}_2\text{QCy}_2{}^-) = 0, \tag{8}$$

one can obtain

$$-\boldsymbol{RT}\ln K = E_{\text{A}}(\text{TCNQ}) - E_{\text{A}}(p\text{-X}_2\text{QCy}_2). \tag{9}$$

Taking $E_{\text{A}}(\text{TCNQ})=1.7$ eV[4] as a reference, $E_{\text{A}}(p\text{-X}_2\text{QCy}_2)$ is obtained as shown in Table 1.

TABLE 1. CALCULATED AND OBSERVED VALUES OF $\varepsilon_{1/2}$ AND E_{A}

Acceptor molecule	K	$\varepsilon_{1/2}$(V *vs.* SCE)		E_{A}, eV	
		Calcd.	Obs.[2,3]	Calcd.	Obs.[4]
TCNQ	—	—	0.19	—	1.7
$p\text{-H}_2\text{QCy}_2$	30	0.28	—	1.79	1.7
$p\text{-Cl}_2\text{QCy}_2$	$\geq 2\times10^3$	≥ 0.38	0.51	≥ 1.89	1.9_5

The calculated values of $\varepsilon_{1/2}$ and E_{A} are in coincidence quite well with observed ones respectively. In conclusion, the dominating factor of the oxidation-reduction equilibrium between anion radicals is the electron affinities of those molecules.

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[2] M. E. Peover, *Trans. Faraday Soc.*, **58**, 2370 (1962).

[3] M. E. Peover, *ibid.*, **58**, 1656 (1962).

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