

Oxidation-Reduction Equilibrium between Anion Radicals

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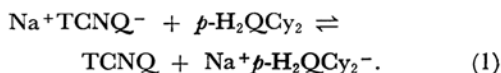
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(Received June 1, 1966)

Preferred 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*-H₂QCy₂)

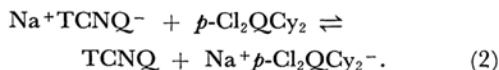
is added into the acetonitrile solution of sodium salt of tetracyanoquinodimethane (TCNQ) anion radical, the green color due to TCNQ⁻ changes into red. By observing the absorption spectra, one can find, on adding *p*-H₂QCy₂, the decrease in the optical density of Na⁺TCNQ⁻ and the increase in those of TCNQ and Na⁺*p*-H₂QCy₂⁻. This reaction is expressed by the following oxidation-reduction equilibrium;



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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 $842\text{ m}\mu$, which is not interfered by other molecular species. Assuming that ions in the solution are free and their activity coefficients be unity, the equilibrium constant at $20\pm 1^\circ\text{C}$ was estimated as $K=30$ in acetonitrile. Similar behavior was observed with 2,3-dicyano-5,6-dichloro-*p*-benzoquinone ($p\text{-Cl}_2\text{QC}_2\text{Y}_2$), which can be expressed as



The equilibrium constant was obtained as $K \geq 2 \times 10^3$ at $20\pm 1^\circ\text{C}$.

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



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

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

where $\Delta \Delta G^\circ_{\text{soln}}(\text{R}, \text{R}^-)$ 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

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

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

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

where D_{R} and D_{R^-} are the diffusion constants of R and R^- respectively, and 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 $p\text{-X}_2\text{QC}_2\text{Y}_2$, where $\text{X}=\text{H}$ or Cl , the observed equilibrium constant is related

with ΔG° 's,

$$\begin{aligned} -RT \ln K &= \Delta G^\circ_{\text{TCNQ}} - \Delta G^\circ_{p\text{-X}_2\text{QC}_2\text{Y}_2} \\ &= E_{\text{A}}(\text{TCNQ}) - E_{\text{A}}(p\text{-X}_2\text{QC}_2\text{Y}_2) \\ &\quad + \Delta \Delta G^\circ_{\text{soln}}(\text{TCNQ}, \text{TCNQ}^-) \\ &\quad - \Delta \Delta G^\circ_{\text{soln}}(p\text{-X}_2\text{QC}_2\text{Y}_2, p\text{-X}_2\text{QC}_2\text{Y}_2^-) \\ &\doteq F[\varepsilon_{1/2}(\text{TCNQ}) - \varepsilon_{1/2}(p\text{-X}_2\text{QC}_2\text{Y}_2)]. \quad (7) \end{aligned}$$

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

$$\begin{aligned} \Delta \Delta G^\circ_{\text{soln}}(\text{TCNQ}, \text{TCNQ}^-) \\ - \Delta \Delta G^\circ_{\text{soln}}(p\text{-X}_2\text{QC}_2\text{Y}_2, p\text{-X}_2\text{QC}_2\text{Y}_2^-) = 0, \quad (8) \end{aligned}$$

one can obtain

$$-RT \ln K = E_{\text{A}}(\text{TCNQ}) - E_{\text{A}}(p\text{-X}_2\text{QC}_2\text{Y}_2). \quad (9)$$

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

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

Acceptor molecule	K	$\varepsilon_{1/2}(\text{V vs. SCE})$		E_{A}, eV	
		Calcd.	Obs. ^{2,3)}	Calcd.	Obs. ⁴⁾
TCNQ	—	—	0.19	—	1.7
<i>p</i> -H ₂ QC ₂ Y ₂	30	0.28	—	1.79	1.7
<i>p</i> -Cl ₂ QC ₂ Y ₂	$\geq 2 \times 10^3$	≥ 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.

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).