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# Reaction Rates in the Monomer-Dimer Equilibrium of TCNQ Anion Radicals as Studied by the Temperature-Jump Method

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In spite of electrostatic repulsion, various ion-radical molecules are known to dimerize in solution. There have been a number of investigations concerning the equilibrium constants and the heats of dimerization in the reversible monomer-dimer equilibria of ion radicals.[1-5] Up to now, however, no attempt has been made to measure the reaction rate constants for such systems.

Boyd and Phillips found a reversible monomer-dimer equilibrium of the 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radicals in an aqueous solution. The equilibrium constant for dimerization at 25°C and the heat of dimerization were determined to be $2.5\times10^3\text{M}^{-1}$ and $-10.4$ kcal/mol·dimer respectively.[2] In the present paper, the temperature-jump technique was applied to this equilibrium in order to investigate the kinetics of the formation and dissociation of the TCNQ anion radical dimers. The intermolecular interaction between the ion radicals in solution will be discussed on the basis of these experimental results.

## Experimental

The kinetic measurements were performed on a temperature-jump apparatus, Messanlagen Studiengesellschaft. A Teflon cell was constructed so that the measurements could be made under deaerated conditions. The temperature rise was attained by Joule heating. For this cell, the time constant of the abrupt temperature rise was estimated by using

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1) K. Uemura, S. Nakayama, Y. Seo, K. Suzuki, and Y. Ooshika, This Bulletin, **39**, 1348 (1966).

2) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

3) K. Kimura, H. Yamada, and H. Tsubomura, *ibid.*, **48**, 440 (1968).

4) N. Sakai, I. Shirotani, and S. Minomura, This Bulletin, **44**, 675 (1971).

5) T. Yamazaki and K. Kimura, *ibid.*, **44**, 298 (1971).

the acid hydrolysis of $p$-nitrophenol, in which the rate constant is of the order of $10^{10}$ M$^{-1}$ sec$^{-1}$.⁶⁾ In its aqueous solution with an ionic strength of 0.23, the time constant required for a 90% rise of about 2°C was found to be 4 $\mu$sec at a 30 kV discharge. An aqueous solution of $Li^+$ $TCNQ^-$ containing 0.2 M $LiClO_4$ as a supporting electrolyte was prepared *in vacuo* and was then admitted into the cell without any exposure to air. The measurements were made after nitrogen gas (1 atm) had been introduced into the cell.

## Results and Discussion

First, the monomer-dimer equilibrium of the TCNQ anion radicals in 0.2 M aqueous $LiClO_4$ solution, as expressed by Eq. (1), was examined by measuring the absorption spectrum and its concentration dependence:

$$2TCNQ^- \rightleftharpoons (TCNQ^-)_2. \tag{1}$$

The concentrations of the monomer, $[TCNQ^-]$, and the dimer, $[(TCNQ^-)_2]$, in the equilibrium state were determined by using the values for their molar extinction coefficients at 660 and 740 nm respectively in a pure aqueous solution reported by Boyd and Phillips.²⁾ The equilibrium constant:

$$K = \frac{[(TCNQ^-)_2]}{[TCNQ^-]^2} \tag{2}$$

was thus estimated to be $1.2\times10^4$ M$^{-1}$ at 14°C in a 0.2 M $LiClO_4$ aqueous solution. This value was found to be rather larger than that of $4.9\times10^3$ M$^{-1}$ at 14°C in a pure aqueous solution reported by Boyd and Phillips.²⁾ This means that the ionic atmosphere of the solvent favors the dimer form in the equilibrium of Eq. (1).

For the equilibrium of Eq. (1) in a 0.2 M $LiClO_4$ aqueous solution at 14°C, the temperature-jump relaxation measurements were made by observing the time dependence of the optical absorption and its concentration dependence. When the temperature was abruptly raised, we found a decrease in the absorbance in the region of 450—540 nm, where the dimer of the TCNQ anion radicals mostly absorbs.²⁾ The observed decrease in the absorbance is, then, attributable to the decrease in the dimer concentration in Eq. (1); that is, the equilibrium expressed by Eq. (1) is shifted to the left when the temperature is raised. For example, the solution of $[TCNQ^-]=5.7\times10^{-5}$ M at 20°C is given in Fig. 1. Figure 2 shows experimental plots of the reciprocal value of the observed relaxation time, $\tau^{-1}$, *versus* the concentration of $[TCNQ^-]$ for various solutions.

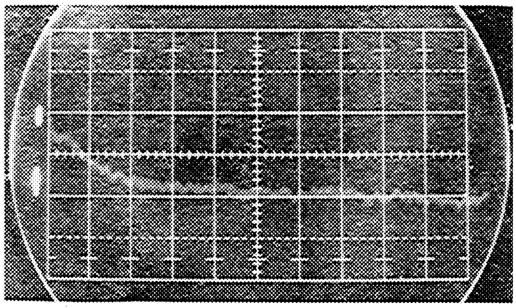

Fig. 1. The decrease of the absorbance observed by the temperature-jump method in the monomer-dimer equilibrium of Eq. (1) at 20°C; $\lambda=525$ nm, 5 $\mu$sec/division, $[TCNQ^-]=5.7\times10^{-5}$ M.

In the monomer-dimer equilibrium of Eq. (1) let the rate constants for the dimerization and the dissociation be $\overrightarrow{k}$ and $\overleftarrow{k}$ respectively. In this case, we have the following relation:

$$\tau^{-1} = 4\overrightarrow{k}[TCNQ^-] + \overleftarrow{k}. \tag{3}$$

If we put the average $\tau$ value in the experimental results into this equation, we obtain the following values for $\overrightarrow{k}$ and $\overleftarrow{k}$:

$$\overrightarrow{k} = 3.5\times10^8 \text{ M}^{-1} \text{ sec}^{-1}, \tag{4}$$

$$\overleftarrow{k} = 9\times10^4 \text{ sec}^{-1}. \tag{5}$$

We can relate these values to the monomer-dimer equilibrium constant as $K=\overrightarrow{k}/\overleftarrow{k}$. The $K$ value thus estimated, $4\times10^3$ M$^{-1}$, is consistent with that previously estimated from the static measurement of the absorption spectra. The $\tau$ value, however, may be almost independent of $[TCNQ^-]$, because the observed $\tau$ values in Fig. 2 include some uncertainty. In this case, the observed $\tau$ values practically coincide with the cell constant of the apparatus, and the $\overrightarrow{k}$ and $\overleftarrow{k}$ values may be larger than those for Eqs. (4) and (5) respectively. Although more accurate measurements are desirable for the determination of the $\tau$ values, we can consider, at present, that the values in Eqs. (4) and (5) give the lower limits of the intrinsic $\overrightarrow{k}$ and $\overleftarrow{k}$ values respectively.

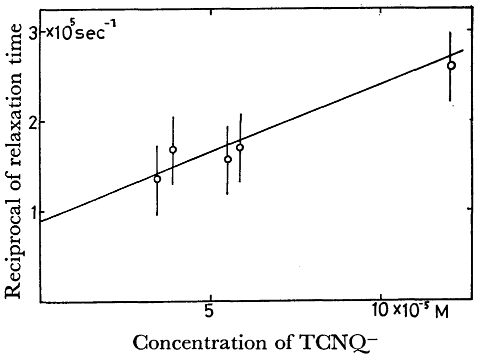

Fig. 2. The dependence of a relaxation time $\tau^{-1}$ on $[TCNQ^-]$ in the monomer-dimer equilibrium of Eq. (1) at 15°C.

On the other hand, if the reaction rate for the dimerization of the TCNQ anion radicals in an aqueous solution can be described by a diffusion-controlled process for charged particles, the theoretical reaction rate at the temperature, $T$, can be represented by:⁷⁾

$$\overrightarrow{k}(\text{calc}) = \frac{4\pi q^2 ND(N/1000)}{\varepsilon \boldsymbol{R}T[\exp(q^2N/\varepsilon \boldsymbol{R}T\sigma)-1]} \tag{6}$$

where $q$ is the charge of a particle; $\boldsymbol{N}$, Avogadro's number; $D$, the diffusion coefficient of a particle; $\varepsilon$, the dielectric constant of a medium, and $\boldsymbol{R}$, the gas constant. $\sigma$ represents the diameter of a particle, which is assumed to be a sphere. Putting the reasonable values of $D=1.8\times10^{-5}$ cm$^2$ sec$^{-1}$ and $\sigma=4.0\times$

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6) M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, **82**, 5952 (1960).

7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York (1961), p. 271.

$10^{-8}$ cm into Eq. (6), we obtain, at 15°C:

$$\vec{k}(\text{calc}) = 1.8\times 10^{9}\,\text{M}^{-1}\,\text{sec}^{-1}. \tag{7}$$

The observed $\vec{k}$ value in Eq. (4) was found to agree with the $\vec{k}$(calc) value. Therefore, the reaction rate for the dimerization of the TCNQ anion radicals in an aqueous solution can be understood in terms of the diffusion-controlled process.