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Rate of Protonation of TCNQ Anion Radical in Water

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Synopsis. The protonation of TCNQ anion radical has been studied with an oxygen-free stopped-flow apparatus. The protonation rate is proportional to the square of $\mathrm{TCNQ}^{\overline{\cdot}}$ concentration, being independent of the proton concentration. It is suggested that there exists an intramolecular step in which the electronic structure of $\mathrm{TCNQ}^{\overline{\cdot}}$ changes into another one ready to accept a proton.

In the previous work, the protonation of 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radical was investigated in methanol, ethanol and acetonitrile.[1] On the basis of kinetic results, it was confirmed that the first attack of H^+ on $\mathrm{TCNQ}^{\overline{\cdot}}$ was reversible according to $\mathrm{TCNQ}^{\overline{\cdot}}+H^+ \rightleftharpoons \mathrm{TCNQH}^{\cdot}$.

This paper reports the protonation of $\mathrm{TCNQ}^{\overline{\cdot}}$ in water. It was intended to examine the effect of a dimer species on the reaction rate, since $\mathrm{TCNQ}^{\overline{\cdot}}$ is known to dimerize in water.[2] The rate was determined using an oxygen-free stopped-flow apparatus in order to avoid the decomposition of $\mathrm{TCNQ}^{\overline{\cdot}}$ under air.

Experimental

$\mathrm{Li^+TCNQ}^{\overline{\cdot}}$ was prepared by reducing TCNQ with LiI in acetonitrile. $HClO_4$ of reagent grade was used as proton source. The concentration of proton was equated to the proton activity at the investigated ionic strength (10^{-4}—10^{-2} M).

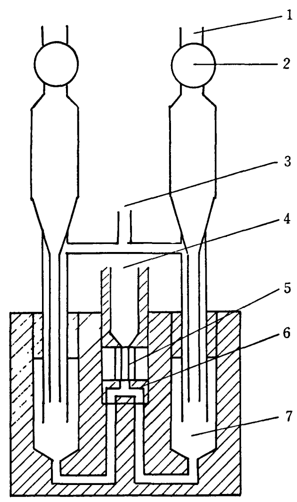


Fig. 1. A mixing part free from oxygen contamination; (1) to a vaccum line, (2) a gleaseless valve, (3) to a He tank, (4) to a rotary pump, (5) a quartz cell, (6) a mixer and (7) the reservoir of a sample solution.

The rate was measured with a Union Giken rapid scan stopped-flow spectrophotometer RA 1300. A mixing part free from oxygen contamination was newly constructed (Fig. 1).[3] The whole part was made of Teflon and Pyrex glass sealed by O-rings. About 10^{-3} mmHg vacuum was attainable under pumping. The sample solutions were directly drived by He gas pressure (*ca.* 0.5 kg/cm^2) without pistons. Thus the decomposition due to oxygen arose mainly from He gas impurity (nominal purity 99.9%). The samples were prepared in a vacuum line. The rate was followed by the absorbance change at 743 nm (a peak of $\mathrm{TCNQ}^{\overline{\cdot}}$ monomer).

Results and Discussion

All measurements were performed under the condition that the initial concentration of $\mathrm{TCNQ}^{\overline{\cdot}}$ was less than 10^{-5} M. At this concentration range, the contribution of a dimer to the total amount of $\mathrm{TCNQ}^{\overline{\cdot}}$ is less than 5%. Thus the protonation rate is given by the decrease of a monomer species per unit time, $-d[\mathrm{TCNQ}^{\overline{\cdot}}]/dt$, with a good approximation. The reactivity of a dimer may reflect on the observed rate through the rapid equilibrium below.[4]

$$2\mathrm{TCNQ}^{\overline{\cdot}} \rightleftharpoons (\mathrm{TCNQ}^{\overline{\cdot}})_2 \qquad (1)$$

At the constant proton concentration, which is in large excess compared with $[\mathrm{TCNQ}^{\overline{\cdot}}]$, the rate is expressed as below (Fig. 2).

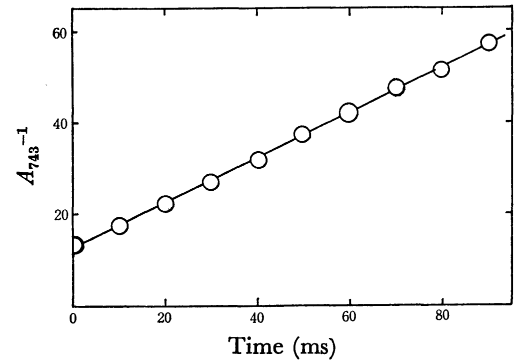


Fig. 2. Second-order plot of the disappearance of $\mathrm{TCNQ}^{\overline{\cdot}}$; $[\mathrm{TCNQ}^{\overline{\cdot}}]_0$ 3.9×10^{-6} M, and $[HClO_4]$ 3.98×10^{-3} M at 25±2 °C. The vertical scale is the reciprocal of the absorbance at 743 nm and the horizontal scale 20 ms/div.

$$-d[\mathrm{TCNQ}^{\overline{\cdot}}]/dt = k[\mathrm{TCNQ}^{\overline{\cdot}}]^2. \qquad (2)$$

k is found to be independent of the proton concentration for $[HClO_4]=(2.34$—$13.0)\times10^{-3}$ M. $k=(8.9\pm1.0)\times10^6$ M^{-1}s^{-1} at 25±2 °C. From the temperature dependence of k between 14.5—35.0 °C, the apparent activation enthalpy is determined to be $\Delta H^{\neq}=10.1\pm0.3$ kcal mole^{-1}.

The second-order dependence of the rate on $[\mathrm{TCNQ}^{\overline{\cdot}}]$ (Eq. 2) may seem to suggest the mechanism that the protonation takes place only by way of a dimer form, $(\mathrm{TCNQ}^{\overline{\cdot}})_2$. This possibility is, however, discarded on the following ground. If the dimer is an active species for protonation, k is expressed by

$$k = k_0 K_D$$

in which k_0 and K_D are the protonation rate of a dimer and the equilibrium constant of reaction (1), respectively. Since k is independent of the proton concentration, k_0 may be the rate constant of some intramolecular step at which a dimer is activated. Taking $K_D = 2.5 \times 10^3\ M^{-1}$,[2] k_0 is obtained to be $3.6 \times 10^3\ s^{-1}$. Expressing k_0 as $\nu \exp(-\Delta H_0^{\neq}/RT)$, and equating $\Delta H_0^{\neq} = \Delta H^{\neq} - \Delta H_D$, in which ΔH_D is the enthalpy change of reaction (1), -10.4 kcal mol^{-1},[2] $\Delta H_0^{\neq}$ is obtained to be 20.5 kcal mol^{-1}. Substituting this value for the above expression of k_0, the frequentry factor, ν, is determined to be $3 \times 10^{18}\ s^{-1}$. ν exceeds the electronic vibration. It is very improbable to assume the presence of an activating mode with such a high frequency.

Therefore it is concluded that the second-order dependence of k on $[\mathrm{TCNQ}^{\overline{\cdot}}]$ arises from the same mechanism as observed previously in methanol, ethanol and acetonitrile. That is, the disproportionation takes place between protonated $\mathrm{TCNQ}^{\overline{\cdot}}$, or $\mathrm{HTCNQ}^{\cdot}$, and $\mathrm{TCNQ}^{\overline{\cdot}}$.

$$\mathrm{TCNQ}^{\overline{\cdot}} + \mathrm{H}^+ \rightleftharpoons \mathrm{HTCNQ}^{\cdot} \tag{3}$$

$$\mathrm{HTCNQ}^{\cdot} + \mathrm{TCNQ}^{\overline{\cdot}} \longrightarrow \mathrm{HTCNQ}^- + \mathrm{TCNQ} \tag{4}$$

$$\mathrm{HTCNQ}^- + \mathrm{H}^+ \longrightarrow \mathrm{H_2TCNQ} \tag{5}$$

The fact that k is independent of $[\mathrm{H}^+]$ suggests the presence of the intramolecular step in which $\mathrm{TCNQ}^{\overline{\cdot}}$ is activated into a more basic species.

$$\mathrm{TCNQ}^{\overline{\cdot}} \rightleftharpoons \mathrm{TCNQ}^{\overline{\cdot}*} \tag{6}$$

Assuming the stationary conditions for both $\mathrm{TCNQ}^{\overline{\cdot}*}$ and $\mathrm{HTCNQ}^{\cdot}$, k is expressed by

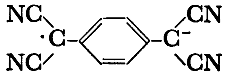
$$k = \frac{k_6 k_3 k_4 [\mathrm{H}^+]}{(k_{-6} + k_3[\mathrm{H}^+])k_{-3}}$$

Under the condition that $k_{-6} \ll k_3[\mathrm{H}^+]$, k is reduced to

$$k = k_6 k_4 / k_{-3}$$

which is independent of the proton concentration as observed in Eq. 2.

One of the possibilities for the nature of the intramolecular step (6) is that $\mathrm{TCNQ}^{\overline{\cdot}}$ transforms electronically into another species which accepts more readily a proton. For example, one of the carbon atoms in $\mathrm{TCNQ}^{\overline{\cdot}}$ may become carbon anion, C^-, by destructing partially the solvation structures by water molecules.



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

3) The author expresses thanks to Mr. Toshihiko Nagamura of Union Giken Co. Ltd. for constructing the mixing part.

4) A. Yamagishi, Y. Iida, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **45**, 3482 (1972).