The Protonation of the TCNQ Anion Radical by Hydrogen Chloride

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The kinetics of the protonation of sodium salt of 7,7,8,8-tetracyanoquinodimethane ($Na^+TCNQ^{\overline{\cdot}}$) by hydrogen chloride in alcohols and acetonitrile was investigated, using a stopped-flow apparatus. In methanol, the protonation rate is first-order in HCl and second-order in $Na^+TCNQ^{\overline{\cdot}}$, while in ethanol, the rate is one-half-order in HCl and second-order in $Na^+TCNQ^{\overline{\cdot}}$. The protonation rate in acetonitrile is first-order in HCl, but it deviates from second-order in $Na^+TCNQ^{\overline{\cdot}}$. These results are interpreted in terms of the rapid formation of a protonated intermediate in the initial stage of the reaction, according to $TCNQ^{\overline{\cdot}}+H^+ \rightleftharpoons HTCNQ\cdot$. The reversibility of this reaction is well demonstrated by the second-order dependence of the rate on $Na^+TCNQ^{\overline{\cdot}}$. The rate is also compared with the protonation rate of semiquinones, such as sodium salts of *p*-chloranil and 2,3-dicyano-1,4-benzoquinone, from the view point of the difference in reactivity between carbon and oxygen acids.

The kinetics of the protonation of aromatic radical anions by alcohols or water has been studied by several research groups.[1-5] Radical anions are protonated according to this stoichiometry:

$$2Ar^{\overline{\cdot}} + 2ROH = ArH_2 + Ar + 2RO^- \qquad (1)$$

in which ArH_2 is the dihydroproduct of the parent hydrocarbon. On the basis of this stoichiometry, this mechanism of the protonation reaction was proposed by Paul, Lipkin, and Weissman:[6]

$$Ar^{\overline{\cdot}} + ROH \longrightarrow ArH^\cdot + RO^- \qquad (2)$$

$$ArH^\cdot + Ar^{\overline{\cdot}} \longrightarrow ArH^- + Ar \qquad (3)$$

$$ArH^- + ROH \longrightarrow ArH_2 + RO^- \qquad (4)$$

The protonation of sodium naphthalenide ($Na^+N^{\overline{\cdot}}$) by water in tetrahydrofuran (THF) was found to proceed through this mechanism.[1] It implies that the proton-transfer reaction (2) is followed by the rapid electron-transfer reaction (3) due to the electron-accepting property of $NH^\cdot$ being higher than $N^{\overline{\cdot}}$. There are, however, many aromatic radical anions whose protonations do not follow the above mechanism. Studies of the protonation of sodium perylenide ($Na^+Pe^{\overline{\cdot}}$) in THF by alcohols have revealed that the species to be protonated is a dianion, $2Na^+Pe^{2-}$, instead of $Na^+Pe^{\overline{\cdot}}$, although the dianion is present in a small amount. In the protonation of sodium and potassium anthracenides ($Na^+A^{\overline{\cdot}}$ and $K^+A^{\overline{\cdot}}$) by alcohols in THF and dimethoxyethane (DME), the nature of the ion pairs profoundly affects their reactivity of protonation.[4,5] Protonation by methanol and ethanol proceeds through the protonation of $Na^+A^{\overline{\cdot}}$ and $K^+A^{\overline{\cdot}}$. On the other hand, the participation of dianion of anthracene, $2Na^+A^{2-}$, is observed in the protonations by *t*-BuOH. In a word, the solvation and reduction states drastically affect the reactivity of the anion radicals and determine the main reaction paths.

Our work, described in this paper, is concerned with the protonation reaction of the 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radical by hydrogen chloride in alcohols and acetonitrile. $TCNQ^{\overline{\cdot}}$ is a weaker base than the ion radicals as has been mentioned above, it is stable in protonic solvents like alcohols and water. The first point we focus our attention on is the reversibility of Reaction (2). We expect that $TCNQ^{\overline{\cdot}}$ accepts a proton reversibly because of its weak basicity. The reversibility of Reaction (2) enables us to estimate the thermodynamically-defined basicity strength of $TCNQ^{\overline{\cdot}}$. The second point is to obtain the rate constant of Reaction (2) in order to compare it with the rate constants of the protonation of semiquinones. $TCNQ^{\overline{\cdot}}$ seems to accept a proton on a carbon atom,[7] while semiquinones are protonated on oxygen atoms, leading to hydroquinones. As far as diamagnetic molecules are concerned, it has been reported in several examples that the limiting rate of proton transfer to carbon acids is generally below the diffusion-controlled limit characteristic of oxygen and nitrogen acids.[8-10] We attempted to examine the validity of this rule in the scope of radical anions.

Experimental

$Na^+TCNQ^{\overline{\cdot}}$ was prepared by reducing TCNQ with NaI in acetonitrile. The salt was dried *in vacuo*. Sodium salts of *p*-chloranil (QCl_4) and 2,3-dicyano-1,4-benzoquinone ($Q(CN)_2$) were prepared in a similar way. *p*-Phenylenedimalononitrile (H_2TCNQ) was prepared from $Na^+TCNQ^{\overline{\cdot}}$ according to Method C as described by Acker and Hertler.[7] Tetraethylammonium chloride of a C.P. grade was used without purification. The methanol (MeOH) and ethanol (EtOH) were purified by distillation in the presence of CaO, using about a 30 cm distillation column. The acetonitrile (MeCN) was distilled after refluxing in the presence of P_2O_5 and K_2CO_3 successively. The water contents were determined by the Karl Fischer method; 0.5 mg/ml (MeOH), 4.3 mg/ml (EtOH) and 0.3 mg/ml (MeCN). Dried hydrogen chloride gas evolved by the reaction between concentrated sulfuric acid and concentrated hydrochloride acid was absorbed into these solvents. Stock solutions of these acid solutions (about 0.1 M) were kept in a refrigerator. The concentration of HCl was determined by titration with an 0.1 M NaOH aqueous solution.

The reaction was studied at 25 °C, utilizing a rapid-scan stopped-flow spectrophotometer, Union Giken Model 1300. The reaction was investigated under air dried by $CaCl_2$ and P_2O_5 successively. The progress of protonation was usually monitored by the absorbance at 840 nm (λ_{max} of $Na^+TCNQ^{\overline{\cdot}}$).

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Results

Stoichiometry of the Protonation Reaction. Throughout this work, we assume that $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$ dissociates completely into free ions in the solvents used. This assumption has not been verified experimentally, but it seems to be reasonable considering that the dielectric constants of these solvents are high and that these are all known as strong ion-solvating solvents. Figure 1 shows the spectral change in $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$ in MeCN when the $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$ solution is mixed with the HCl solution. With the disappearance of the absorption due to $\text{TCNQ}^{\overline{\cdot}}$, the new peaks in 340—450 nm appear, they coincide with the spectra of TCNQ.[7] When a more concentrated solution of $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$ is acidified, additional peaks are observed at 258, 264, and 270 nm. Comparing the spectra of H_2TCNQ in MeCN, these peaks are assigned to H_2TCNQ. Using the extinction coefficients of ε_{840} ($\text{TCNQ}^{\overline{\cdot}}$) 43300, ε_{395} (TCNQ) 63600,[7] and ε_{270} (H_2TCNQ) 300, which is approximately determined in this work, the initial concentration of $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$, and the final concentrations of TCNQ and H_2TCNQ were calculated (Table 1). In EtOH and MeOH similar results were obtained except that the UV absorption due to H_2TCNQ was not observed. In the experiment where H_2TCNQ is dissolved in EtOH *in vacuo*, H_2TCNQ is found to have a broad peak at 309 nm in addition to several small peaks in the 250—270 nm region. At the present stage, it is uncertain why the H_2TCNQ product is not observed in alcoholic solvents. The reason may lie in the interaction of H_2TCNQ with alcohols in an acidic medium. The number of protons consumed in the reaction was determined in MeOH, using thymol blue as the proton indicator. We obtained 1.1±0.2 as the ratio of protons consumed per $\text{TCNQ}^{\overline{\cdot}}$. Thus, the over-all stoichiometry of the reaction may be written as follows:

$$2\text{Na}^+\text{TCNQ}^{\overline{\cdot}} + 2\text{HCl} = \text{TCNQ} + \text{H}_2\text{TCNQ} + 2\text{NaCl} \qquad (5)$$

which is identical with Eq. (1).

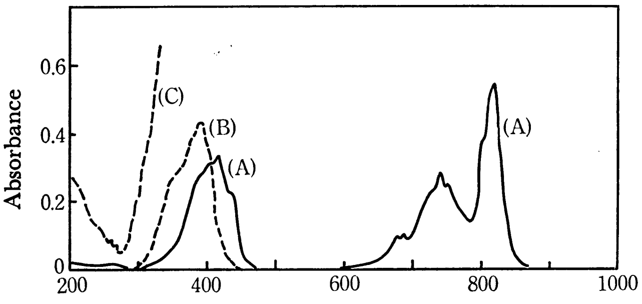


Fig. 1. Spectral change of $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$ in MeCN when mixed with HCl solution.
(A) $[\text{Na}^+\text{TCNQ}^{\overline{\cdot}}]_0 = 1.32\times10^{-5}$ M, (B) $[\text{Na}^+\text{TCNQ}^{\overline{\cdot}}]_0 = 1.32\times10^{-5}$ M, $[\text{HCl}] = 8.0\times10^{-4}$ M. (C) $[\text{Na}^+\text{TCNQ}^{\overline{\cdot}}]_0 = 4.32\times10^{-4}$ M, $[\text{HCl}] = 8.0\times10^{-3}$ M (25 °C). ——: $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$, ------: $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$+HCl

Table 1. Stoichiometry of reaction in MeCN at 25 °C

Run A)	$\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$	initial	1.32×10^{-5}M
	TCNQ	final	6.60×10^{-6}M
Run B)	$\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$	initial	4.20×10^{-4}M
	TCNQ	final	2.10×10^{-4}M
	H_2TCNQ	final	*ca.* 2×10^{-4}M

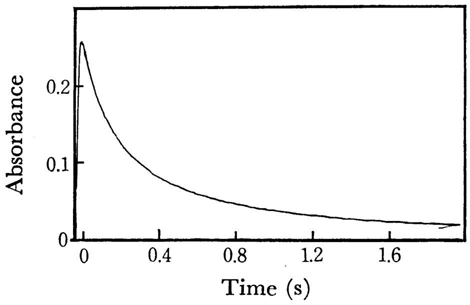


Fig. 2a. The decay of absorbance at 840 nm due to $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$ during the reaction with HCl in MeOH.

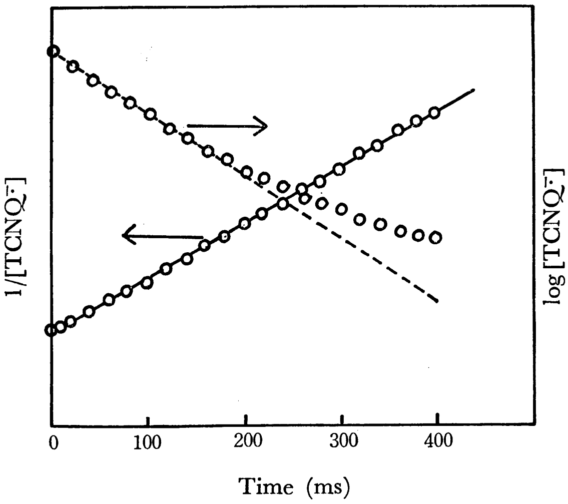


Fig. 2b. Plots of $1/[\text{TCNQ}^{\overline{\cdot}}]$ *vs.* time and $\log[\text{TCNQ}^{\overline{\cdot}}]$ *vs.* time in MeOH at 25 °C.
$[\text{Na}^+\text{TCNQ}^{\overline{\cdot}}]_0 = 7.60\times10^{-6}$ M, $[\text{HCl}] = 4.30\times10^{-4}$ M

Reaction in MeOH. The decay of $\text{TCNQ}^{\overline{\cdot}}$ was followed by mixing the MeOH solution of $\text{Na}^+\text{TCNQ}^{\overline{\cdot}}$ with the MeOH solution of HCl. Even under the $[\text{Na}^+\text{TCNQ}^{\overline{\cdot}}] \gg [\text{HCl}]$ condition (Fig. 2a), the reaction is not first-order. As is shown in Fig. 2b, the decay of $\text{TCNQ}^{\overline{\cdot}}$ is second-order with respect to $\text{TCNQ}^{\overline{\cdot}}$. The apparent second-order rate constant increases linearly with the concentration of HCl (Table 2). The rate of protonation may, therefore, be written as:

$$\frac{\mathrm{d}[\text{TCNQ}^{\overline{\cdot}}]}{\mathrm{d}t} = -k_{\text{obs}}[\text{TCNQ}^{\overline{\cdot}}]^2[\text{H}^+] \qquad (6)$$

The change in the spectra in 330—530 nm with the time (Fig. 3) shows the existence of the isosbestic point at 394 nm. This implies that the amount of intermediates accumulated in the course of the reaction, if any, is too small to give any disturbance to the condition:

TABLE 2. k_{obs} VALUES AT VARIOUS HCl CONCENTRATIONS IN MeOH AT 25 °C

$\mathrm{Na^+TCNQ^{\cdot-}}$/M	HCl/M	$k_{\mathrm{obs}}/\mathrm{M^{-2}s^{-1}}$
7.60×10^{-6}	1.08×10^{-4}	1.73×10^{8}
7.60	2.15	1.66
7.60	4.30	1.64
7.60	8.60	1.40
7.60	21.5	1.48

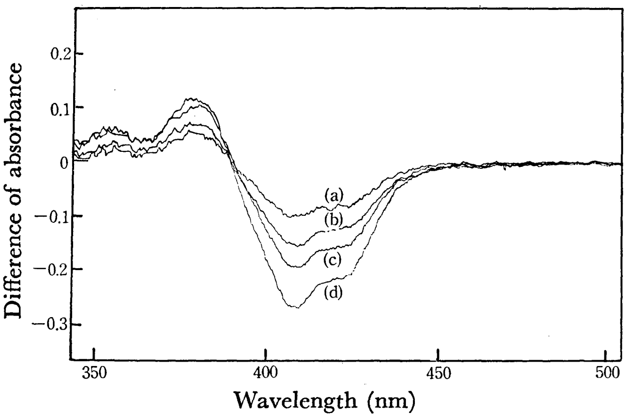


Fig. 3. Rapidly-scanned difference spectra for the system of $\mathrm{Na^+TCNQ^{\cdot-}}$ and HCl in MeOH.
(a) is the difference between the initial absorbance and the one 25 ms after mixing; (b) 50 ms after mixing; (c) 100 ms after mixing; (d) 500 ms after mixing. Scan speed 5 ms/300 nm. $[\mathrm{Na^+TCNQ^{\cdot-}}]_0$ 8.23×10^{-6} M. [HCl] 1.50×10^{-3} M.

$$[\mathrm{TCNQ^{\cdot-}}] + 2[\mathrm{TCNQ}] = [\mathrm{TCNQ^{\cdot-}}]_0$$

in which $[\mathrm{TCNQ^{\cdot-}}]_0$ is the initial concentration of $\mathrm{TCNQ^{\cdot-}}$. There are three possibilities conceivable for the origin of the second-order dependence of the rate on $\mathrm{TCNQ^{\cdot-}}$. The species to be protonated is (i) a dianion, $\mathrm{TCNQ^{2-}}$, which is produced by this reaction:

$$2\mathrm{TCNQ^{\cdot-}} \rightleftharpoons \mathrm{TCNQ} + \mathrm{TCNQ^{2-}} \tag{7}$$

(ii) a dimer anion, $(\mathrm{TCNQ^{\cdot-}})_2$, which is produced by this reaction:

$$2\mathrm{TCNQ^{\cdot-}} \rightleftharpoons (\mathrm{TCNQ^{\cdot-}})_2;\ K \tag{8}$$

or (iii) a $\mathrm{TCNQ^{\cdot-}}$, and there exists a reversible reaction to form a protonated intermediate:

$$\mathrm{TCNQ^{\cdot-}} + \mathrm{H^+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{HTCNQ^{\cdot}} \tag{9}$$

$$\mathrm{HTCNQ^{\cdot}} + \mathrm{TCNQ^{\cdot-}} \xrightarrow{k_3} \mathrm{HTCNQ^-} + \mathrm{TCNQ} \tag{10}$$

The (i) possibility can be discarded because the addition of TCNQ has no effect on the protonation rate (Table 3). If Reaction (7) worked, TCNQ would retard the reaction rate, decreasing the concentration of $\mathrm{TCNQ^{2-}}$.

TABLE 3. EFFECT OF TCNQ ON THE RATE OF PROTONATION REACTION IN MeOH AT 25 °C

$\mathrm{Na^+TCNQ^{\cdot-}}$/M	HCl/M	TCNQ/M	$k_{\mathrm{obs}}/\mathrm{M^{-2}s^{-1}}$
8.23×10^{-6}	1.50×10^{-3}	0.00×10^{-5}	1.76×10^{8}
8.23	1.50	2.27	1.83
8.23	1.50	4.54	1.76

If the (ii) assumption is correct, the k_{obs} in Eq. (6) is equal to $k \cdot K$, where k is the protonation rate of $(\mathrm{TCNQ^{\cdot-}})_2$ by the proton and where K is an equilibrium constant of (8). Using $k_{\mathrm{obs}}=1.5\times10^{8}\ \mathrm{M^{-2}\,s^{-1}}$ and $k=10^{10}\ \mathrm{M^{-1}\,s^{-1}}$, the lower limit of K is estimated to be $10^{-2}\ \mathrm{M^{-1}}$. On the other hand, assuming that the extinction coefficient of $(\mathrm{TCNQ^{\cdot-}})_2$ at 643 nm is 33600,[11] the upper limit of K may be estimated to be $10\ \mathrm{M^{-1}}$ from the electronic spectra. Therefore, the (ii) possibility can not be denied on the basis of only the kinetic results. However, in the case of sodium anthracenide, it is indicated that the $(\mathrm{A^{\cdot-}}, \mathrm{Na^+})_2$ dimer is relatively unreactive.[4] The result in MeCN also supports the (9) and (10) mechanisms, as will be mentioned later. Thus, it seems that the (iii) possibility is most plausible at the present stage. From the first-order dependence of the rate on HCl, the reaction which follows Reaction (10) to produce a stable product may be concluded to be very fast. Applying the stationary state condition to $\mathrm{HTCNQ^{\cdot}}$ in (9) and (10), we obtain the following rate equation:

$$\frac{d[\mathrm{TCNQ^{\cdot-}}]}{dt} = -\frac{2k_1k_3[\mathrm{TCNQ^{\cdot-}}]^2[\mathrm{H^+}]}{k_2+k_3[\mathrm{TCNQ^{\cdot-}}]} \tag{11}$$

in which $\mathrm{H^+}$ is introduced as a proton source instead of HCl based on the results for the EtOH system.[12] Under this condition:

$$k_2 \gg k_3[\mathrm{TCNQ^{\cdot-}}] \tag{12}$$

Eq. (11) becomes identical to the observed rate expression (6), leading to $k_{\mathrm{obs}}=2k_1k_3/k_2$. Equation (11) predicts that the rate will deviate from the second-order dependence on $\mathrm{TCNQ^{\cdot-}}$ at a sufficiently high concentration of $\mathrm{TCNQ^{\cdot-}}$. This actually happens in the MeCN system. However, no deviation from Eq. (6) was observed up to $[\mathrm{Na^+TCNQ^{\cdot-}}]=1.22\times10^{-4}$ M in MeOH, making it possible to conclude that $k_2/k_3 > 1.22\times10^{-4}$ M.

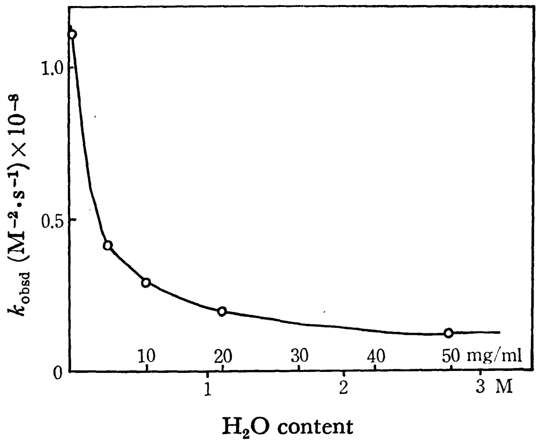


Fig. 4. Effect of $\mathrm{H_2O}$ on k_{obs} in MeOH at 25 °C. $[\mathrm{Na^+}\text{-}\mathrm{TCNQ^{\cdot-}}]_0$ 2.8×10^{-6} M, [HCl] 1.07×10^{-2} M.

The small amount of water was found to reduce the k_{obs} value to a remarkable extent, although the mechanism is not altered (Fig. 4). We may ascribe this water effect to the solvation of the proton by water molecules:

$$\mathrm{H^+(MeOH)}_n + m\mathrm{H_2O} \rightleftharpoons n\mathrm{MeOH} + \mathrm{H^+(H_2O)}_m \tag{13}$$

which results in the leftward shift of the (9) equilibrium. The solvation of H^+ by water is reported to occur even in a small amount of water.[13] Since the electron-transfer reaction (10) is thought to be diffusion-controlled and little affected by the water content, the change in the k_{obs} value with water reflects the change in the equilibrium constant of Reaction (9) with the water content.

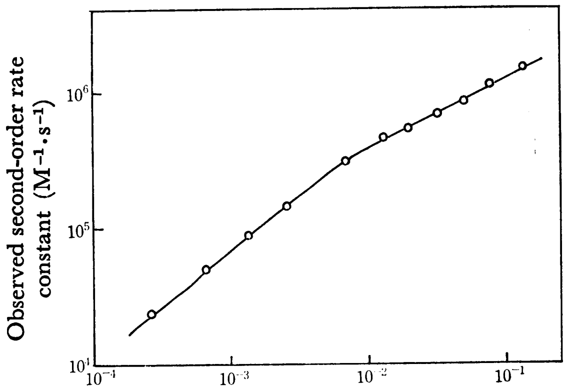


Fig. 5. Dependence of the second-order rate constant on HCl concentration in EtOH at 25 °C.
$[\mathrm{Na^+TCNQ^{\overline{\cdot}}}]_0$ 6.81×10^{-6} M.

Reaction in EtOH. The decay of $\mathrm{TCNQ^{\overline{\cdot}}}$, mixed with HCl in ethanol, is found to be second-order with respect to the $\mathrm{TCNQ^{\overline{\cdot}}}$ concentration. However, the second-order rate constant is not always linearly dependent on the HCl concentration (Fig. 5). In the range of [HCl] larger than 10^{-2} M, the rate equation is written as:

$$\frac{d[\mathrm{TCNQ^{\overline{\cdot}}}]}{dt} = -k_{obs}[\mathrm{TCNQ^{\overline{\cdot}}}]^2[\mathrm{HCl}]^{1/2} \qquad (6')$$

rather than as Eq. (6). The one-half-order dependence of the rate on the HCl concentration can best be interpreted by assuming a rapid equilibrium in EtOH:

$$\mathrm{HCl} \rightleftarrows \mathrm{H^+ + Cl^-};\ K \qquad (14)$$

and by assuming, in addition, that the dissociated proton H^+, but not HCl, is a protonating reagent. The free proton concentration is $[H^+]=K^{1/2}[\mathrm{HCl}]^{1/2}$, supposing that the degree of dissociation is very small. From the plot in Fig. 5, the k_{obs} corresponding to $2k_1k_3/k_2$ in Eq. (6) and the equilibrium constant of (14), K, are estimated to be $1\pm0.2\times10^8\ \mathrm{M^{-1}s^{-1}}$ and $2.4\pm0.8\times10^{-3}$ M respectively.[14] This conclusion is confirmed by the fact that tetraethylammonium chloride is found to suppress the protonation rate, as is shown in Table 4.[15]

TABLE 4. THE EFFECT OF TETRAETHYLAMMONIUM CHLORIDE ON THE RATE OF PROTONATION REACTION IN EtOH

$\mathrm{Na^+TCNQ^{\overline{\cdot}}}$	HCl	Tetraethyl-ammonium chloride	k_{obs}[a]
1.28×10^{-5}M	1.8×10^{-2}M	0 M	$1.86\times10^5\mathrm{M^{-1}s^{-1}}$
1.28	1.8	0.031	1.63
1.28	1.8	0.15	0.709
1.28	1.8	0.30	0.446

a) Temperature 15 °C, water content 8 mg/ml.

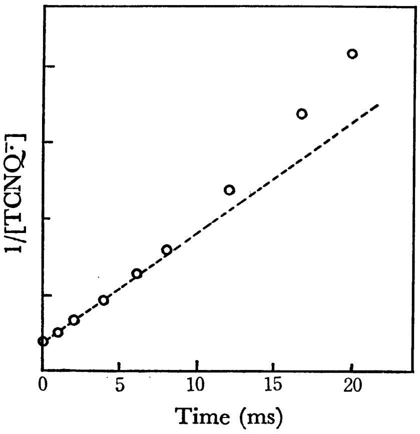


Fig. 6. Plot of $1/[\mathrm{TCNQ^{\overline{\cdot}}}]$ *vs.* time for the reaction of $\mathrm{TCNQ^{\overline{\cdot}}}$ with HCl in MeCN.
$[\mathrm{Na^+TCNQ^{\overline{\cdot}}}]_0$ 4.12×10^{-5} M, [HCl] 1.08×10^{-3} M at 25 °C.

Reaction in MeCN. We studied the protonation reaction in MeCN with the purpose of obtaining the forward rate constant, k_1, in Reaction (9) directly. Since MeCN seems to solvate H^+ less effectively than alcohols, the backward rate constant, k_2, in (9) is expected to become smaller in MeCN than in alcohols. Consequently, the observed rate expression may approach:

$$\frac{d[\mathrm{TCNQ^{\overline{\cdot}}}]}{dt} = -2k_1[\mathrm{TCNQ^{\overline{\cdot}}}][H^+]$$

This rate law has been obtained in the case of the protonation of sodium naphalenide in THF.[1] As Fig. 6 shows, the decay of $\mathrm{TCNQ^{\overline{\cdot}}}$ during the reaction with HCl is found to deviate from the second-order dependence on $\mathrm{TCNQ^{\overline{\cdot}}}$. We consider that, at least in the initial stage, $\mathrm{TCNQ^{\overline{\cdot}}}$ is protonated according to the (9) and (10) mechanism, keeping the condition of $k_2 \approx k_3$ $[\mathrm{TCNQ^{\overline{\cdot}}}]$. By integrating Eq. (11) under the condition of $[H^+] \gg [\mathrm{TCNQ^{\overline{\cdot}}}]$, we obtain:

$$\frac{1}{2k_1[H^+]}\ln\frac{[\mathrm{TCNQ^{\overline{\cdot}}}]_0}{[\mathrm{TCNQ^{\overline{\cdot}}}]} + \frac{k_2}{2k_1k_3[H^+]}\left(\frac{1}{[\mathrm{TCNQ^{\overline{\cdot}}}]} - \frac{1}{[\mathrm{TCNQ^{\overline{\cdot}}}]_0}\right) = t$$

In order to obtain k_1 and k_2/k_1k_3 from the observed decay curve, we draw a group of straight lines on the (x, y) plane as expressed by:

$$\frac{2.3}{t}\log\frac{[\mathrm{TCNQ^{\overline{\cdot}}}]_0}{[\mathrm{TCNQ^{\overline{\cdot}}}]}\cdot x + \frac{1}{t}\left(\frac{1}{[\mathrm{TCNQ^{\overline{\cdot}}}]} - \frac{1}{[\mathrm{TCNQ^{\overline{\cdot}}}]_0}\right)\cdot y = 1$$

using a pair of $\frac{2.3}{t}\log\frac{[\mathrm{TCNQ^{\overline{\cdot}}}]_0}{[\mathrm{TCNQ^{\overline{\cdot}}}]}$ and $\frac{1}{t}\left(\frac{1}{[\mathrm{TCNQ^{\overline{\cdot}}}]} - \frac{1}{[\mathrm{TCNQ^{\overline{\cdot}}}]_0}\right)$ at various values of t for a constant $[H^+]$.

The common point (x_0, y_0), through which a group of straight lines pass gives the desired values of $1/2k_1$ and $k_2/2k_1k_3$. An example is shown in Fig. 7, leading to the results tabulated in Table 5. It should be noted that, if the dimer anion mechanism (possibility (ii) in MeOH) worked, the deviation from a second-order dependence on $\mathrm{TCNQ^{\overline{\cdot}}}$ would be interpreted as the

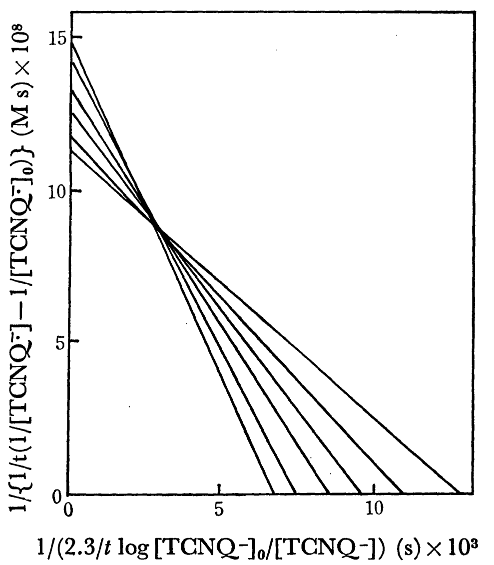


Fig. 7. Plots of a group of straight lines according to $\frac{2.3}{t}\log\frac{[\mathrm{TCNQ}^{\overline{\cdot}}]_0}{[\mathrm{TCNQ}^{\overline{\cdot}}]}\cdot x+\frac{1}{t}\left(\frac{1}{[\mathrm{TCNQ}^-]}-\frac{1}{[\mathrm{TCNQ}^-]_0}\right)\cdot y=1$ for various values of t.

Table 5. k_1 and k_1k_3/k_2 values in MeCN at 25 °C

$\mathrm{Na^+TCNQ^{\overline{\cdot}}}$/M	HCl/M	$k_1/\mathrm{M^{-1}s^{-1}}$	$k_1k_3/k_2/$ $\mathrm{M^{-2}s^{-1}}$
4.12×10^{-5}	5.40×10^{-4}	3.3×10^{5}	1.1×10^{10}
4.12	10.8	2.1	1.3
4.12	21.6	1.9	2.3
4.12	36.0	2.0	2.3

result of the participation of the direct protonation of $\mathrm{TCNQ}^{\overline{\cdot}}$ (Reaction (9)). If this were the case, the deviation from second-order would appear at lower concentrations of $\mathrm{TCNQ}^{\overline{\cdot}}$, since Reaction (8) would be predominant at higher concentrations of $\mathrm{TCNQ}^{\overline{\cdot}}$. However, the fact is that the deviation was observed at higher concentrations of $\mathrm{TCNQ}^{\overline{\cdot}}$, but not at lower concentrations. In this way, the possibility of a dimer mechanism could be dismissed. The magnitude of k_1 is about four orders below the diffusion-controlled rate constant.

In order to compare the k_1 value with the protonation rate of semiquinones, in which protonation occurs on oxygen atoms, we tried to obtain the reaction rates of protonation, $\mathrm{Na^+QCl_4^{\overline{\cdot}}}$ and $\mathrm{Na^+Q(CN)_2^{\overline{\cdot}}}$. Unfortunately, the decay of these semiquinones is too fast for us to analyse the kinetics of the protonation reaction. Therefore, the lower limits of k_1 and k_1k_2/k_3 were roughly estimated from the half-life of the decay curves of semiquinones, assuming that the decay curves are completely first-order or completely second-order respectively. The results are shown in Table 6. These values indicate that the protonation rates of semiquinones by free protons are more than one order larger than that of $\mathrm{TCNQ}^{\overline{\cdot}}$.

Table 6. The lower limit of rate constants of protonation of $\mathrm{QCl_4^{\overline{\cdot}}}$ and $\mathrm{Q(CN)_2^{\overline{\cdot}}}$ in MeCN at 25 °C

$\mathrm{Q^{\overline{\cdot}}}$/M	HCl/M	$t_{1/2}$ s	$k_1/\mathrm{M^{-1}\,s^{-1}}$	$(k_1k_2/k_3)/$ $\mathrm{M^{-2}\,s^{-1}}$
		for $\mathrm{QCl_4^{\overline{\cdot}}}$		
$5\times10^{-6\,\mathrm{a)}}$	4.10×10^{-5}	*ca.* 4×10^{-3}	$>3\times10^{6}$	$>5\times10^{11}$
2	8.10	*ca.* 2	>3	>15
2	16.1	*ca.* 0.8	>2	>20
		for $\mathrm{Q(CN)_2^{\overline{\cdot}}}$		
$5\times10^{-6\,\mathrm{b)}}$	3.60×10^{-5}	*ca.* 2×10^{-3}	$>5\times10^{6}$	$>1\times10^{12}$

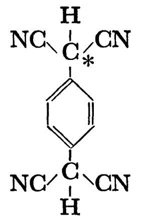
a) estimated, using $\varepsilon_{445}=9\times10^3$. b) estimated, using $\varepsilon_{465}=5\times10^3$.

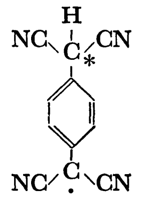
Discussion

The reversibility of the initial step of the protonation:

$$\mathrm{TCNQ}^{\overline{\cdot}}+\mathrm{H^+}\underset{k_2}{\overset{k_1}{\rightleftarrows}}\mathrm{HTCNQ^{\cdot}};\quad K_\mathrm{b} \tag{9}$$

is well demonstrated by the second-order dependence of the rate on the concentration of $\mathrm{TCNQ}^{\overline{\cdot}}$. If the backward rate of the above reaction were forbidden, the rate would be first-order in $\mathrm{TCNQ}^{\overline{\cdot}}$ as far as the decay of $\mathrm{TCNQ}^{\overline{\cdot}}$ is monitored. As the final product of the protonation of $\mathrm{TCNQ}^{\overline{\cdot}}$ is $\mathrm{H_2TCNQ}$ (I), $\mathrm{HTCNQ^{\cdot}}$ seems to have the (II) structure.


(I)


(II)

Therefore, the reversible protonation reaction (9) takes place on the carbon atom, C*. The magnitude of the equilibrium constant, K_b, can be estimated by assuming that the electron-transfer reaction (10) is diffusion-controlled. This assumption is reasonable, since Reaction (10) is more favoured from the energetic point of view than the exchange reaction:

$$\mathrm{TCNQ}^{\overline{\cdot}}+\mathrm{TCNQ}^{*}\rightleftarrows\mathrm{TCNQ}+\mathrm{TCNQ}^{*\overline{\cdot}}$$

whose rate constant is known to be about $10^9\ \mathrm{M^{-1}s^{-1}}$.[7] Table 7 gives the estimated values of K_b, assuming that $k_3=10^{10}\ \mathrm{M^{-1}\,s^{-1}}$. The variation in K_b for various kinds of solvents is interpreted consistently in terms of the proton-solvating capacity of these solvents. Alcoholic solvents give K_b values of the same order. The

Table 7. The estimated value of the equilibrium constant K_b for $\mathrm{TCNQ}^{\overline{\cdot}}+\mathrm{H^+}\leftrightarrows\mathrm{HTCNQ^{\cdot}}$ at 25 °C

Solvent	$\mathrm{H_2O}$/mg/ml	$K_\mathrm{b}/\mathrm{M^{-1}}$ a)
MeOH	0.46	7.9×10^{-3}
MeOH	5.0	2.0
MeOH	10.0	1.5
MeOH	20.0	0.97
MeOH	50.0	0.62
EtOH	4.3	5 ± 1
MeCN	0.3	1700 ± 600

a) estimated from the observed k_1k_3/k_2 values, assuming $k_3=10^{10}\mathrm{M^{-1}s^{-1}}$.

large value of the K_b in MeCN is due to the poor solvating capacity of MeCN. The water effect in MeOH implies that H_2O is the strongest solvating solvent for the proton.

A comparison of the k_1 value for the protonation of TCNQ$^{\overline{\cdot}}$ in MeCN with the lower limit of k_1 for QCl$_4^{\overline{\cdot}}$ and Q(CN)$_2^{\overline{\cdot}}$ indicates that the k_1 for TCNQ$^{\overline{\cdot}}$ is more than one order smaller than that for semiquinones. We can not conclude that the smaller k_1 value for TCNQ$^{\overline{\cdot}}$ is characteristic of the protonation on a carbon atom in ion radicals, since a comparison between carbon and oxygen acids should be made for the limiting rate of protonation, which is obtained by extrapolating the rate to the limit of an infinite K_b. However, at the present stage of investigation it is meaningful to consider what factor of TCNQ$^{\overline{\cdot}}$ makes the protonation rate smaller than for semiquinones. At least three factors must be taken into consideration as determining the rate of protonation: (i) electron density of the atom on which protonation takes place, (ii) the localization energy caused by the protonation, and (iii) the steric hindrance in the vicinity of the proton-accepting atoms. In addition, another assumption (iv) may be introduced—that, in a transition state of protonation, a proton-accepting atom has an anionic character.

TABLE 8. ELECTRON AND SPIN DENSITIES OF C* OF TCNQ$^{\overline{\cdot}}$ AND OXYGEN ATOM OF QCl$_4^{\overline{\cdot}}$.

	Electron density	Spin density	Ref.
TCNQ$^{\overline{\cdot}}$	1.17−1.24	0.29−0.24	a)
QCl$_4^{\overline{\cdot}}$		0.213±0.010	b)

a) D. A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967).
b) Y. Iida, This Bulletin, **44**, 1271 (1971).

At the initial stage of the reaction, where H^+ approaches anion radicals from an infinite distance, electostatic interaction may be predominant. The electron and spin densities of C* in TCNQ$^{\overline{\cdot}}$ are thus compared in Table 8 with those of the oxygen atom in QCl$_4^{\overline{\cdot}}$. There seems to be no remarkable difference in these quantities between TCNQ$^{\overline{\cdot}}$ and QCl$_4^{\overline{\cdot}}$. As H^+ comes closer to anion radicals, a localization of the odd π-electron takes place, together with a change in the electronic state of the C* atom into C^-. We regard the instability of the C^- state is the main factor for the protonation of TCNQ$^{\overline{\cdot}}$ being slower than that of semiquinones. In order to make this point clear, we roughly estimated the energy produced by the changes in electronic state (i) $=C< + e$ to $-C^-<$ and (ii) $=O + e$ to $-O^-$. Using the values given by Hinze and Jaffe,[16)] the energies produced for (i) and (ii) are calculated to be 1.57 and 2.01 eV respectively. Thus, the C^- state is less stable by 0.44 eV than the O^- state. Assuming a small difference in π-localization energy between TCNQ$^{\overline{\cdot}}$ and semiquinones, the slower rate for the protonation of TCNQ$^{\overline{\cdot}}$ is attributable to the unstable character of the carbon anion. This circumstance is expected to hold similarly in diamagnetic molecules.

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12) Another possibility is that HCl is an attacking agent and that in MeOH most of HCl is present as an undissociated form. This is unlikely, however, because the dissociation constants of HCl in MeOH is considered to be larger than 10^{-4} M (See Ref. 15).

13) R. G. Bates, *J. Electroanal. Chem.*, **29**, 1 (1971).

14) In this estimation, the curve in Fig. 5 is regarded as a smooth curve whose slope changes gradually from 1 to 1/2.

15) The dissociation constants of HCl in alcohols, K, recently reported are $10^{-4.26}$ M (MeOH) and $10^{-4.21}$ M (EtOH) at 25 °C (A. P. Dreshkov, V. A. Drozdov and N. A. Kolchin, *Zhur. Fiz. Khim.*, **40**, 2150 (1966)). In this work, we conclude K (MeOH) is larger than 10^{-3} M and that K (EtOH) is about $10^{-2.7}$ M. These discrepancies may arise from the presence of water in our solvents.

16) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).