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Effects of Quinones on the Protonation Reaction of TCNQ Anion Radical; The Role of a Protonated Quinone as a Strong Electron Acceptor

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Various kinds of substituted *p*-benzoquinones (Q) have been found to accelerate the rate of the reaction between 7,7,8,8-tetracyanoquinodimethane(TCNQ) anion radical and hydrogen chloride in acetonitrile. The stoichiometry of the reaction is altered by the presence of Q from $2\mathrm{TCNQ}^{\cdot-}+2\mathrm{H}^+=\mathrm{TCNQ}+\mathrm{H_2TCNQ}$ to $2\mathrm{TCNQ}^{\cdot-}+2\mathrm{H}^++\mathrm{Q}=2\mathrm{TCNQ}+\mathrm{QH_2}$. In case of *p*-benzoquinone, the rate of the disappearance of $\mathrm{TCNQ}^{\cdot-}$ is expressed by $v=k[\mathrm{TCNQ}^{\cdot-}]\,[\mathrm{Q}]\,[\mathrm{H}^+]$, where $k=3.0\times10^8\ \mathrm{M^{-2}\,s^{-1}}$ at 8 °C. From these results, it is concluded that a protonated quinone QH^+ is an active species which accepts an electron from $\mathrm{TCNQ}^{\cdot-}$.

In the previous paper, the protonation reaction of 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radical by hydrogen chloride was investigated in various organic solvents.[1] Comparing the protonation rate of $\mathrm{TCNQ}^{\cdot-}$ with that of semiquinone ion ($\mathrm{Q}^{\cdot-}$), it was revealed that $\mathrm{TCNQ}^{\cdot-}$ reacts with a proton with the rate more than one order slower than $\mathrm{Q}^{\cdot-}$ does.

From these results it is expected that the reaction of $\mathrm{TCNQ}^{\cdot-}$ with HCl is accelerated by Q, when Q rapidly accepts an electron from $\mathrm{TCNQ}^{\cdot-}$ and is protonated to hydroquinone.

$$\mathrm{TCNQ}^{\cdot-}+\mathrm{Q}\rightleftharpoons\mathrm{TCNQ}+\mathrm{Q}^{\cdot-} \tag{1}$$

$$2\mathrm{Q}^{\cdot-}+2\mathrm{H}^+\rightarrow\mathrm{QH_2}+\mathrm{Q} \tag{2}$$

Reaction paths (1) and (2) may proceed faster than the direct protonation of $\mathrm{TCNQ}^{\cdot-}$, as far as a sufficient amount of $\mathrm{Q}^{\cdot-}$ is produced rapidly by reaction (1).[2]

Based on the above expectation, the effects of quinone on the protonation reaction of $\mathrm{TCNQ}^{\cdot-}$ have been investigated using acetonitrile as a solvent. The present result may provide a new aspect as to the function of quinones in oxidation-reduction reactions especially in the acidic aprotic medium.

Experimental

p-Chloranil, *p*-benzoquinone, 1,4-naphthoquinone and di-*t*-butyl-*p*-benzoquinone were sublimed once. Chloro-*p*-benzoquinone was synthesized according to Levy and Schultz.[3] The product was identified with IR spectra.[4] Other reagents were prepared as described previously.[1]

The visible spectra were measured with a Hitachi EPS-3T spectrophotometer. The rate was measured in acetonitrile with a Union Giken RA-1300 rapid scan stopped-flow spectrophotometer. The rate was obtained by mixing the solution containing $\mathrm{Na^+TCNQ}^{\cdot-}$ and quinone with HCl. All measurements were performed at 8 °C. A Union Giken temperature-jump apparatus was used to try to detect a protonated quinone.

Results

As a preliminary experiment, the rate of the disappearance of $\mathrm{TCNQ}^{\cdot-}$ is measured by mixing the solution of HCl with the solution containing both $\mathrm{Na^+TCNQ}^{\cdot-}$ and a quinone. The kinetic results are summarized in Table 1. All quinones except di-*t*-butyl-*p*-benzoquinone are found to accelerate the rate of the reaction. The accelerating capacity of quinone is expressed by the quantity, $\ln 2/\{t_{1/2}[\mathrm{Q}][\mathrm{HCl}]\}$, where [Q] is the concentration of quinone, [HCl] the initial concentration of HCl and $t_{1/2}$ the half-life of the reaction, although the decay of $\mathrm{TCNQ}^{\cdot-}$ with time is either exponential or non-exponential, depending on the kind of quinone.

The detailed study of the kinetics of the reaction has

TABLE 1. THE EFFECT OF SUBSTITUTED *p*-BENZOQUINONES ON THE REACTION RATE OF $\mathrm{Na^+TCNQ}^{\cdot-}$ WITH HCl

[Q]/M	[HCl]/M	$k_{\mathrm{obsd}}/\mathrm{s^{-1}}$	$k_{\mathrm{obsd}}/[\mathrm{HCl}][\mathrm{Q}]/\mathrm{M^{-2}\,s^{-1}}$	$k_1/\mathrm{M^{-1}\,s^{-1}}$ a)
No quinone b)	1.0×10^{-4}	7.5		
p-Chloranil (1.45×10^{-4}) c)	1.0×10^{-4}	1.0×10^{2}	6.9×10^{9}	6.0×10^{7}
	1.9×10^{-4}	1.6×10^{2}	5.8×10^{9}	
	2.9×10^{-4}	2.9×10^{2}	6.9×10^{9}	
	4.8×10^{-4}	3.8×10^{2}	5.4×10^{9}	
Chloro-*p*-benzoquinone (3.5×10^{-3}) c)	2.0×10^{-4}	5.8×10^{2}	1.5×10^{8}	35
p-Benzoquinone (9.12×10^{-3}) c)	1.0×10^{-4}	3.0×10^{2}	3.2×10^{8}	3.2×10^{-2}
1,4-Naphthoquinone (5.6×10^{-2}) b)	3.0×10^{-5}	3.4	2.0×10^{6}	8.5×10^{-6}
	1.2×10^{-4}	12	1.8×10^{6}	
	4.0×10^{-4}	69	3.0×10^{6}	
Di-*t*-butyl-*p*-benzoquinone (1.6×10^{-2}) b)	3.0×10^{-4}	1.2		3.7×10^{-6}
	1.2×10^{-4}	4.4		
	4.0×10^{-4}	5.8		

a) The forward rate constant of the reaction (1) according to the Eq. (7). ΔF^0 is calculated from the half-wave reduction potential reported by Peover.[7] b) The decay of $\mathrm{TCNQ}^{\cdot-}$ is non-exponential with time. c) The decay of $\mathrm{TCNQ}^{\cdot-}$ is almost exponential with time.

TABLE 2. THE STOICHIOMETRY OF THE REACTION OF $\mathrm{Na^+TCNQ^{\cdot-}}$ WITH HCl IN PRESENCE OF *p*-BENZOQUINONE

$[\mathrm{Na^+TCNQ^{\cdot-}}]_0$/M	[HCl]/M	[Q]/M	[TCNQ]/M
6.58×10^{-6}	1.0×10^{-5}	0	3.43×10^{-6}
6.58×10^{-6}	1.0×10^{-5}	3.36×10^{-2}	6.48×10^{-6}
6.58×10^{-6}	5.0×10^{-5}	3.36×10^{-2}	6.48×10^{-6}

been performed in the case of *p*-benzoquinone. In Table 2, the stoichiometry of the reaction is presented. In the absence of quinone, the overall stoichiometry is expressed by

$$2\mathrm{TCNQ^{\cdot-}} + 2\mathrm{H^+} = \mathrm{TCNQ} + \mathrm{H_2TCNQ}, \qquad (3)$$

where $\mathrm{H_2TCNQ}$ denotes *p*-phenylenedimalononitrile.[1] On the other hand, when *p*-benzoquinone is present, almost 100% of $\mathrm{Na^+TCNQ^{\cdot-}}$ is converted to TCNQ. The same result is obtained for *p*-chloranil where the decrease of *p*-chloranil is found to be equal to 44% of the initial amount of $\mathrm{Na^+TCNQ^{\cdot-}}$. Therefore, the stoichiometry of the reaction in the presence of quinone is expressed as below.

$$2\mathrm{TCNQ^{\cdot-}} + \mathrm{Q} + 2\mathrm{H^+} = 2\mathrm{TCNQ} + \mathrm{H_2Q} \qquad (4)$$

This stoichiometry suggests that $\mathrm{TCNQ^{\cdot-}}$ is oxidized to TCNQ by Q instead of being protonated and that it is $\mathrm{Q^{\cdot-}}$ that is protonated.

The decay of $\mathrm{TCNQ^{\cdot-}}$ with time is shown in Fig. 1. In the absence of Q, $\mathrm{TCNQ^{\cdot-}}$ decreases according to the following equation as established previously.[1]

$$-\mathrm{d}[\mathrm{TCNQ^{\cdot-}}]/\mathrm{d}t = k[\mathrm{TCNQ^{\cdot-}}]^2[\mathrm{H^+}], \qquad (5)$$

in which the initial concentration of $\mathrm{TCNQ^{\cdot-}}$ is less than 10^{-5} M. On the other hand, $\mathrm{TCNQ^{\cdot-}}$ decreases exponentially in the presence of a large excess of Q. The pseudo first-order rate constant k_{obsd} is linearly dependent on both the concentrations of *p*-benzoquinone and of HCl (Figs. 2 and 3). k_{obsd} is independent of both the concentrations of $\mathrm{Na^+TCNQ^{\cdot-}}$ and TCNQ (Figs. 4 and 5). Thus the decay rate is expressed as

$$-\mathrm{d}[\mathrm{TCNQ^{\cdot-}}]/\mathrm{d}t = k_{\mathrm{ap}}[\mathrm{TCNQ^{\cdot-}}][\mathrm{Q}][\mathrm{H^+}], \qquad (6)$$

and

$$k_{\mathrm{ap}} = 3.0\times10^8\ \mathrm{M^{-2}\,s^{-1}} \text{ at } 8\ ^\circ\mathrm{C},$$

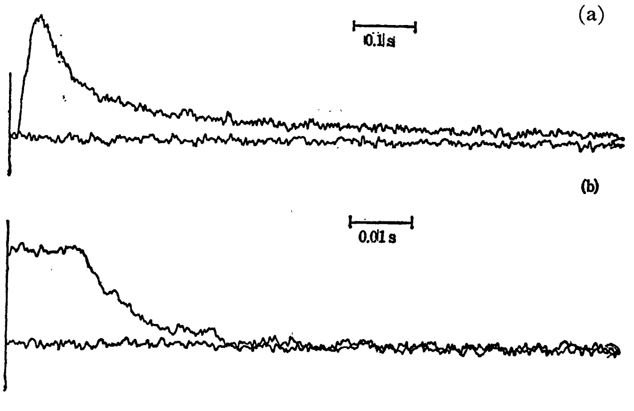

Fig. 1. (a) The decay of $\mathrm{TCNQ^{\cdot-}}$ for the reaction of $\mathrm{Na^+TCNQ^{\cdot-}}$ with HCl; $[\mathrm{Na^+TCNQ^{\cdot-}}]_0$ 3.0×10^{-6} M and $[\mathrm{HCl}]_0$ 4.9×10^{-5} M. At 840 nm. (b) The decay of $\mathrm{TCNQ^{\cdot-}}$ in the presence of 9.1×10^{-3} M *p*-benzoquinone; other experimental conditions are the same as in Fig. 1. (a).

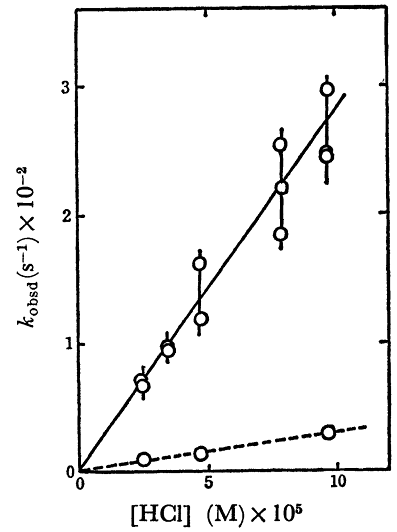

Fig. 2. The dependence of the pseudo first-order rate constant k_{obsd} on [HCl] in the absence (--O--) and in the presence of *p*-benzoquinone (—O—). $[\mathrm{Na^+TCNQ^{\cdot-}}]_0$ 3.0×10^{-6} M and [*p*-benzoquinone] 9.1×10^{-3} M for the solid line.

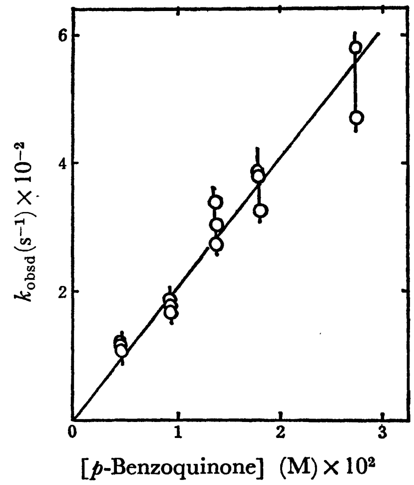

Fig. 3. The dependence of k_{obsd} on [*p*-benzoquinone]. $[\mathrm{Na^+TCNQ^{\cdot-}}]_0$ 3.0×10^{-6} M and $[\mathrm{HCl}]_0$ 6.2×10^{-5} M.

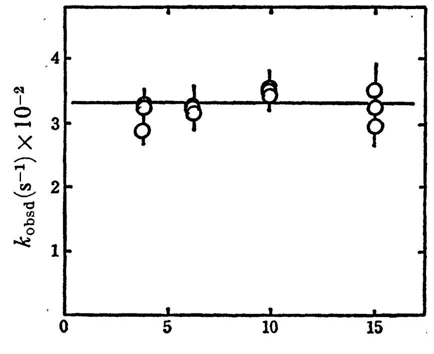

Fig. 4. The dependence of k_{obsd} on $[\mathrm{Na^+TCNQ^{\cdot-}}]_0$. $[\mathrm{HCl}]_0$ 1.1×10^{-4} M and [*p*-benzoquinone] 9.1×10^{-3} M.

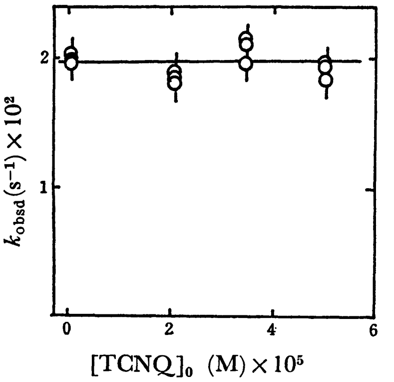

Fig. 5. The dependence of k_{obsd} on $[\mathrm{TCNQ}]_0$. $[\mathrm{Na^+TCNQ^{\dot{-}}}]$ 3.0×10^{-6} M, $[\mathrm{HCl}]_0$ 6.2×10^{-3} M and [*p*-benzoquinone] 9.1×10^{-3} M.

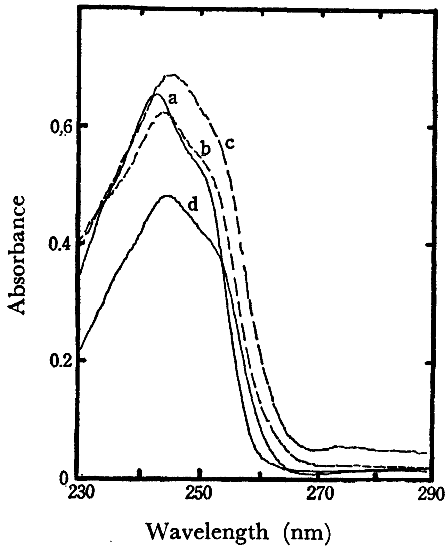

Fig. 6. The electronic spectra of *p*-benzoquinone in the following media; (a) acetonitrile, (b) acetonitrile contaning 20 vol% of concentrated $\mathrm{HClO_4}$, (c) acetonitrile containing 40 vol% of concentrated $\mathrm{HClO_4}$, and (d) acetonitrile containing 40 vol% of $\mathrm{H_2O}$. [*p*-Benzoquinone] 3.3×10^{-5} M.

where HCl is considered to dissociate completely in acetonitrile.

In order to detect a protonated species of quinone, the ultraviolet spectra of *p*-benzoquinone are measured in the acetonitrile containing concentrated $\mathrm{HClO_4}$ (Fig. 6). As $\mathrm{HClO_4}$ is added, the peak at 243 nm is displaced by several nanometers to the longer wavelength. No new peak at 358 nm is detected contrary to the observation by Eggins and Chambers.[5] Comparing the present result with the red shift of the absorption peak at 245 nm of acetophenone in concentrated sulfuric acid due to the protonation of a carbonyl group,[6] this observation is considered to support the protonation of *p*-benzoquinone. It should be noted, however, that the observed change of electronic spectra may also include the change of medium properties, since the peak at 243 nm in acetonitrile displaces to 245 nm when acetonitrile contains 40 volume % of water. Although the temperature-jump measurements are performed for the solution containing *p*-benzoquinone and concentrated $\mathrm{HClO_4}$, no change of the transmittance is detected at the temperature-jump in the wavelength region of 255—280 nm.

Discussion

The most striking feature of the present result is that quinones of low electron affinity like *p*-benzoquinone have an effect to accelerate the protonation rate of $\mathrm{TCNQ}^{\dot{-}}$.

At first, the accelerating effect by quinones seems to be ascribed to reaction paths (1) and (2). This may be true at least partially with *p*-chloranil and chloro-*p*-benzoquinone. In case of *p*-benzoquinone and other quinones, however, the participation of reaction (1) is negligible, since the forward rate of this reaction is too slow to give any effect on the reaction mechanism. The forward reaction rate constant k_1 is evaluated according to the following equation.[2]

$$k_1 = Z\exp\left(-\Delta F^\circ/RT\right) \quad \text{for } \Delta F^\circ > 0 \tag{7}$$

where Z is $10^{11}\ \mathrm{M^{-1}\,s^{-1}}$ and ΔF° the change of the free energy of reaction (1). Assuming ΔF° to be the difference of the half-wave reduction potential between TCNQ and Q, k_1 thus estimated is given in the last column in Table 1.[7] Evidently k_1 except for *p*-chloranil is too small to explain the observed acceleration effect by quinones. To overcome this difficulty, two possible mechanisms are postulated by noticing the $[\mathrm{H^+}]$ dependence of the overall rate (Eq. (6)).

As a first possibility, it is assumed that there exists a pre-equilibrium of the protonation of $\mathrm{TCNQ}^{\dot{-}}$ (8), which is followed by the oxidation reaction by Q either through electron-transfer or through hydrogen atom transfer, (9) or (9)′.

$$\mathrm{TCNQ}^{\dot{-}} + \mathrm{H^+} \rightleftharpoons \mathrm{HTCNQ}\cdot \tag{8}$$

$$\mathrm{HTCNQ}\cdot + \mathrm{Q} \rightarrow \mathrm{HTCNQ}^{\dot{+}} + \mathrm{Q}^{\dot{-}} \tag{9}$$

or

$$\mathrm{HTCNQ}\cdot + \mathrm{Q} \rightarrow \mathrm{TCNQ} + \mathrm{QH}\cdot \tag{9$'$}$$

The $[\mathrm{H^+}]$ dependence of the rate may arise from reaction (8) which constitutes a pre-equilibrium in the overall reaction mechanisms. As K_8 was determined to be about $1.7\pm0.6\ \mathrm{M^{-1}}$,[1] k_9 or $k_{9'}$ becomes about $2\times10^8\ \mathrm{M^{-1}\,s^{-1}}$. It is very unlikely, however, that reaction (9) or (9)′ proceeds with such a large rate constant, considering that the oxidation of $\mathrm{HTCNQ}\cdot$ is less favoured than that of $\mathrm{TCNQ}^{\dot{-}}$ itself from an energetic point of view.[1]

As a second possibility, it is assumed that there exists a pre-equilibrium where Q is protonated to $\mathrm{QH^+}$, followed by the oxidation of $\mathrm{TCNQ}^{\dot{-}}$ by $\mathrm{QH^+}$.

$$\mathrm{Q} + \mathrm{H^+} \rightleftharpoons \mathrm{QH^+};\ K_{10} \tag{10}$$

$$\mathrm{TCNQ}^{\dot{-}} + \mathrm{QH^+} \rightarrow \mathrm{TCNQ} + \mathrm{QH}\cdot \tag{11}$$

The $[\mathrm{H^+}]$ dependence arises from reaction (10) under the condition that reaction (11) is rate-determining. If this is the case, k_{ap} in Eq. (6) is equated to

$$k_{\mathrm{ap}} = K_{10}k_{11}, \tag{12}$$

where K_{10} and k_{11} are the equilibrium constant of reaction (10) and the forward rate constant of reaction

(11), respectively. The fact that the rate is independent of the TCNQ concentration is also consistent with this mechanism. Thus at the present stage of the investigation, it is concluded that protonated quinones $\mathrm{QH^+}$ accelerate the protonation rate of $\mathrm{TCNQ}^{\dot{-}}$ by accepting an electron from $\mathrm{TCNQ}^{\dot{-}}$.

The validity of this conclusion is supported by the fact that $\mathrm{QH^+}$ is a stronger electron-acceptor than Q itself. This fact is confirmed by evaluating the electron affinity of $\mathrm{QH^+}$ as follows.

$$\mathrm{QH^+} + \mathrm{e} \rightleftharpoons \mathrm{QH}\cdot \tag{13}$$

$$\mathrm{Q} + \mathrm{e} \rightleftharpoons \mathrm{Q}^{\dot{-}} \tag{14}$$

The free energy change of reaction (13), ΔF_{13}, is related to the free energy change of reaction (14), ΔF_{14}, as below.

$$\Delta F_{13} - \Delta F_{14} = RT\ln K_{10} - RT\ln K_{16} \tag{15}$$

in which K_{10} and K_{16} are the equilibrium constants of the protonations of Q and $\mathrm{Q}^{\dot{-}}$, respectively.

$$\mathrm{Q} + \mathrm{H^+} \rightleftharpoons \mathrm{QH^+} \tag{10}$$

$$\mathrm{Q}^{\dot{-}} + \mathrm{H^+} \rightleftharpoons \mathrm{QH}\cdot \tag{16}$$

Using the values reported in Refs. 8 and 9, $K_{10}=10^{-1.0}\,\mathrm{M^{-1}}$ in water and $K_{16}=10^{4.1}\,\mathrm{M^{-1}}$ in water containing excess acetone and 2-propanol, $\Delta F_{13}-\Delta F_{14}$ is approximately estimated to be −6.6 kcal at 8 °C. If protonated *p*-benzoquinone $\mathrm{QH^+}$ increases its electron affinity by this amount, $\mathrm{QH^+}$ is as strong an electron acceptor as 2,5- or 2,6-dichloro-*p*-benzoquinone.

In the field of electrochemistry, it has been noted that the electrochemical reduction of quinone in the presence of proton donors displays the additional irreversible reduction wave at the less negative potential.[5,10] This additional wave indicates the existence of the more easily reducible species than neutral quinone. This species was suspected to be a protonated quinone.[5] The present conclusion that protonated quinone becomes a stronger electron-acceptor in homogeneous reaction is completely consistent with these electrochemical results, and confirms the above proposal.

Baxendale *et al.* studied the oxidation of Fe(II) by *p*-benzoquinone in aqueous solution.[11] In their study it is observed that the oxidation rate is independent of proton concentration from 0.35 to 0.15 M. This seems to contradict with the present results. However, since a proton in water is more stably solvated than in acetonitrile, K_{10} in aqueous solution is considered to be too small to produce the sufficient concentration of $\mathrm{QH^+}$. Therefore, the present finding as to the high reactivity of $\mathrm{QH^+}$ is important only in aprotic solvents where unstable proton leads to the large value of K_{10}.

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