The Role of Solvents in the Dimerization of the 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone Anion Radical

Akihiko YAMAGISHI

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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The reversible dimerization of the anion radical of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) has been studied in water, acetonitrile (MeCN), and other organic solvents. The analysis of the thermodynamic parameters of dimerization equilibria reveals that a large negative entropy term plays a primary role in determining the equilibrium constants. The temperature-jump measurement shows that the forward rate constant in water containing 5.8 M urea is nearly a diffusion controlled one, $(1\pm0.5)\times10^8$ M^{-1} s^{-1} at −6 °C. In MeCN–water mixtures, the backward reaction rate increases with the square of the MeCN concentration. This result suggests that a dimer is effectively decomposed by the successive attacks of the two MeCN molecules.

Since the theoretical work by Hausser and Murrell, the dimerization phenomena of ion radicals have been investigated extensively.[1–6] The main attention has been focused on the interaction between unpaired electrons. In this context, the dimerization in solution was compared to the stacking of ion radicals in the crystalline state.[4]

In the present work, the dimerization phenomena is taken up from a slightly different view-point: that is, the role of solvents played in the dimerization equilibria of ion radicals. Since the attractive force in a dimer arises from the charge-transfer interaction between two fragments, it must be a short-range force.[7] Thus the slight disturbance by solvent molecules on the geometrical structure of a dimer will cause a serious effect on the interaction of unpaired electrons, and accordingly on the stability of a dimer. In this sense the role of solvents in dimerization equilibria will be completely different from that in the ion-pair formation of a simple salt. In the latter case, the dielectric continuum theory has proved to be successful in interpreting the solvent effect on the ion-pair formation.[8] In the dimerization of ion radicals, however, more specific descriptions of solvents and solvation structures are needed in order to interpret the solvent effects on the dimerization equilibria. Until now, no systematic study on this topic has been carried out except for a few examples,[2,9] probably because the ion radicals dimerize only under extreme conditions such as low temperature, or oxygen-free conditions, or concentrated acidic media.[2–6]

In this paper, the study of the dimerization of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone anion radical ($DDQ^{\overline{\cdot}}$) is presented. $DDQ^{\overline{\cdot}}$ dimerizes at room temperature in all solvents used. It is relatively stable in solution under air, although the stability depends on solvents and counter cations. The thermodynamic parameters of dimerization are obtained spectrophotometrically. The rate of dimerization is measured by a temperature-jump apparatus. From both the equilibrium and the rate data, the role of solvents in a dimerization reaction has been made clear, particularly from the view-point of the molecular processes involving radicals and solvent molecules. Some solvents are found to form a rigid solvation structure with a dimer, whereas others effectively decompose such a structure.

Experimental

The sodium (Na^+) and the tetraethylammonium (NEt_4^+) salts of DDQ were obtained by reducing DDQ with NaI and MEt_4I in acetonitrile (MeCN) respectively. MeCN, methanol (MeOH), and ethanol (EtOH) were purified as described elsewhere.[10] Acetone (Me_2CO), dimethylformamide (DMF), tetrahydrofuran (THF), and dimethoxyethane (DME) were distilled once. Water was deionized and distilled once. Tetra-*n*-propylammonium perchlorate (NPr_4ClO_4) was prepared by the reaction of NPr_4OH with $HClO_4$ in water. $NaClO_4$ of a C.P. grade was used after being dried at 130 °C.

The absorption spectra were measured with a Hitachi model EPS-3T spectrophotometer. In MeCN, Me_2CO and DMF, both $Na^+DDQ^{\overline{\cdot}}$ and $NEt_4^+DDQ^{\overline{\cdot}}$ are stable enough for the precise spectroscopic measurements. In THF and DME, $NEt_4^+DDQ^{\overline{\cdot}}$ is found more stable than $Na^+DDQ^{\overline{\cdot}}$, although both salts decompose gradually. In EtOH, MeOH, and H_2O, both $NEt_4^+DDQ^{\overline{\cdot}}$ and $Na^+DDQ^{\overline{\cdot}}$ decompose in the order of $H_2O>MeOH>EtOH$, which is inevitable even in a vacuum. The equilibrium measurements in such solvents as cause the decomposition of $M^+DDQ^{\overline{\cdot}}$ were performed by reading the absorbances at the dimer and the monomer band repeatedly within several seconds. Here we assumed that the decomposition products of $DDQ^{\overline{\cdot}}$ do not affect the dimerization equilibria. The extinction coefficients of $DDQ^{\overline{\cdot}}$ monomer ε_M in these solvents were determined from the absorbance when the 0.1 ml of the MeCN stock solution of $NEt_4^+DDQ^{\overline{\cdot}}$ (*ca.* 10^{-3} M) was dissolved into the 2.0 ml of each solvent. ε_M was calculated from the known ε_M in MeCN (6.3×10^3 at 594 nm), assuming that the presence of a small amount of MeCN does not affect the magnitude of ε_M in each solvent. The extinction coefficients of $DDQ^{\overline{\cdot}}$ dimer ε_D in all solvents except H_2O are assumed to be equal to that in MeCN. The details in determining ε_D in MeCN and water are described in the results.

The conductivity was measured with a Yanagimoto model MY-7 conductivity outfit. The temperature of a cell was maintained at 20 °C by circulating water. In THF, the concentration of $NEt_4^+DDQ^{\overline{\cdot}}$ was measured simultaneously by absorption spectra.

The rate was measured with a Union Giken temperature-jump apparatus. This appearatus instantly raises *ca.* 2 ml sample solution by 20—30 kV discharge through a co-axial cable. The cable has a length of 200 m, 0.02 μF capacitance, and 75 Ω characteristic impedance. The rise time of temperature was determined by observing the rate of a protonation reaction of phenolphthalein in H_2O at various ionic strength adjusted by NaCl. The temperature rise is attained within 2 μs when a sample solution has a conductivity higher than $10^{-3}\text{cm}^{-1}\Omega^{-1}$. For the MeCN system, NPr_4ClO_4 is used as a conducting electrolyte. The reaction was monitored by the change of the transmittance at the dimer band near 710 nm. The amount of $DDQ^{\overline{\cdot}}$ electrolyzed at discharge was concluded to be negligible since the concentration change was less than 5% after several times of discharge. The temperature of a sample solution was maintained by circulating EtOH cooled by liquid nitrogen. The temperature was measured by a thermocouple just before discharge. For the MeCN–water system, the sample solution was prepared by mixing a H_2O solvent containing 0.1 M NaCl and 6.0 M urea with the MeCN stock solution of $NEt_4^+DDQ^{\overline{\cdot}}$, both of which were pre-cooled at the desired temperature. The measurement was done about 3 minutes after preparing the solution. Thus, the concentration uncertainty of $DDQ^{\overline{\cdot}}$ was estimated to be within 10%.

Results

Dimerization Equilibria in Various Solvents. A new absorption peak appears at 710 nm when $Na^+DDQ^{\overline{\cdot}}$ is dissolved in MeCN to the concentration higher than 10^{-3} M (Fig. 1). In the concentration range of $Na^+DDQ^{\overline{\cdot}}$ from 1×10^{-3} to 5×10^{-3} M, the absorbance at 710 nm increases exactly in proportion to the square of the concentration of $Na^+DDQ^{\overline{\cdot}}$. This phenomena is compared with the facts that the anion radicals of chloranil and *p*-benzoquinone dimerize in ethanol at low temperature, showing a new peak at 670 and 585 nm, respectively.[3,4] Assuming the dimer formation for $DDQ^{\overline{\cdot}}$ ion,

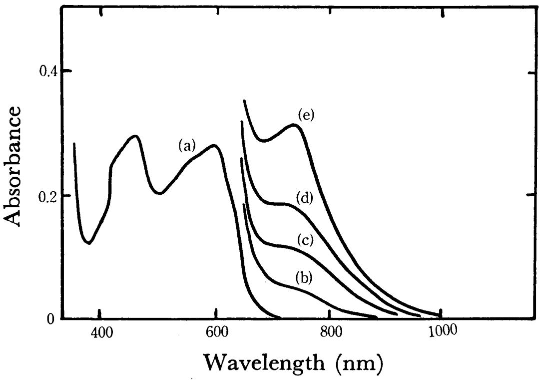


Fig. 1. The visible spectra of $Na^+DDQ^{\overline{\cdot}}$ in MeCN at various concentrations: a) 4.5×10^{-5}, b) 1.9×10^{-3}, c) 2.9×10^{-3}, d) 3.7×10^{-3} and e) 4.6×10^{-3} M at 15 °C.

$$2DDQ^{\overline{\cdot}} \rightleftharpoons (DDQ^{\overline{\cdot}})_2;\ K \tag{1}$$

the absorbance at 710 nm, A_{710}, is related to the concentration of $Na^+DDQ^{\overline{\cdot}}$, C, as follows:

$$\begin{aligned} K &= [(DDQ^{\overline{\cdot}})_2]/[DDQ^{\overline{\cdot}}]^2 \\ &= A_{710}/\varepsilon_D(1-\alpha)^2C^2 \end{aligned} \tag{2}$$

where ε_D is a molar extinction coefficient of a dimer at 710 nm and α a degree of association. In deriving this relation, $Na^+DDQ^{\overline{\cdot}}$ is assumed to dissociate completely in MeCN. This point is stated later in more detail. A_{710} would not increase linearly with C^2, since α becomes larger as C increases. The observation that A_{710} is exactly proportional to C^2 within an experimental error implies that K in the present system is too small to detect the variation of α with C. In this case, Eq. (2) reduces to

$$K = A_{710}/\varepsilon_D C^2, \tag{3}$$

$$\varepsilon_D K = (1.7\pm0.2)\times10^4\ \text{M}^{-2} \text{ at } 15^\circ\text{C}.$$

In order to obtain both K and ε_D, we first estimate ε_D in the following ways: (i) Assuming no absorption of a dimer at 594 nm where a monomer has an absorption peak, the decrease of the monomer band caused by dimerization is related to the dimer band absorption as below:

$$\Delta A_{594}/A_{710} = -2\varepsilon_M/\varepsilon_D \tag{4}$$

where ε_M is a molar extinction coefficient of a monomer at 594 nm, 6.3×10^3. (ii) The addition of NPr_4ClO_4 is found to increase the absorption at 710 nm, giving no influence to the spectral shape of a monomer band. This effect is interpreted as the displacement of the equilibrium (1) to the righthand side due to the presence of the ionic atmosphere of NPr_4^+ ions. Therefore, the decrease of the absorbance at 594 nm when NPr_4ClO_4 is added into the MeCN solution is related to the increase of the absorbance at 710 nm as follows:

$$\Delta A_{594}/\Delta A_{710} = -2\varepsilon_M/\varepsilon_D. \tag{5}$$

From relation (4), $\varepsilon_M/\varepsilon_D$ is obtained to be 1.0 ± 0.2, leading to $\varepsilon_D=(6.3\pm1)\times10^3$. From the difference spectrum of the sample solution containing 2.2×10^{-3} M $NEt_4^+DDQ^{\overline{\cdot}}$ and 0.123 M NPr_4ClO_4 with the solution of 2.2×10^{-3} M $NEt_4^+DDQ^{\overline{\cdot}}$ as reference, $\Delta A_{594}/\Delta A_{710}$ is obtained to be -2.4 ± 0.4, resulting in $\varepsilon_D=(7.2\pm2)\times10^3$. Thus the average value of ε_D is estimated to be $(7\pm1)\times10^3$ at 710 nm. Using this value, K is determined to be $2.5\pm0.5\ \text{M}^{-1}$ at 15 °C.

Similar new peaks around 710 nm are also observed, using DMF, Me_2CO, THF, DME, EtOH, and H_2O as solvents. In these solvents except for H_2O, K is calculated using the same ε_D value as obtained for MeCN and the proportional constant of A_{710} against C^2 in each solvent. For water, the K which is calculated in this way, is so large that we doubt the validity of the assumption that ε_D in H_2O is of the same magnitude as in MeCN. Thus ε_D in H_2O is determined independently by methods (i), additionally (iii) from the temperature-jump signals at the monomer and the dimer bands (Figs. 10 and 11). ε_D in H_2O is determined to be (i) $(2.5\pm0.8)\times10^4$ and (iii) $(2.4\pm0.8)\times10^4$. Taking the average of these values, ε_D is estimated to be $(2.5\pm1)\times10^4$. The large uncertainty for ε_D in H_2O arises from the gradual decomposition of $DDQ^{\overline{\cdot}}$ in H_2O. In the temperature region of 0—30 °C, a straight line is obtained by plotting log K *versus* the reciprocal of absolute temperature for all solvents, from which the enthalpy and the entropy changes in reaction (1) are determined. They are given in Table 1.

It is likely that $DDQ^{\overline{\cdot}}$ forms an ion-pair with a positive ion in solvents with small dielectric constants. Therefore, the conductivity of $Na^+DDQ^{\overline{\cdot}}$ and $NEt_4^+DDQ^{\overline{\cdot}}$ is measured in MeCN and THF. The results are shown in Fig. 2.

$$M^+DDQ^{\overline{\cdot}} \rightleftharpoons M^+ + DDQ^{\overline{\cdot}};\ K_d \tag{6}$$

In MeCN, the molar conductivity, λ, of $M^+DDQ^{\overline{\cdot}}$ ($M^+=Na^+$, NEt_4^+) is almost constant with the change

TABLE 1. THE THERMODYNAMIC PARAMETERS OF THE DIMERIZATION EQUILIBRIUM OF $\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}$ IN VARIOUS SOLVENTS

λ denotes an absorption peak of a dimer.

Solvent	K(10 °C)/ $\mathrm{M^{-1}}$	ΔH/ $\mathrm{kcal \cdot M^{-1}}$	ΔS/e.u.	λ/nm
MeCN	3.7	-9.7 ± 1.0	-29 ± 3	710
DMF	1.4	-7.0 ± 0.2	-24 ± 2	710
$\mathrm{Me_2CO}$	1.1	-7.2 ± 0.2	-25 ± 2	720
THF	17	-3.0 ± 0.2	-4.9 ± 2	710
DME	13	-3.3 ± 0.5	-6.5 ± 2	710
EtOH	5.2	-5.0 ± 1.0	-14 ± 3	715
MeOH	5.0	-3.7 ± 1.0	-11 ± 4	712
$\mathrm{H_2O}$	1300	-8.8 ± 1.0	-17 ± 2	712

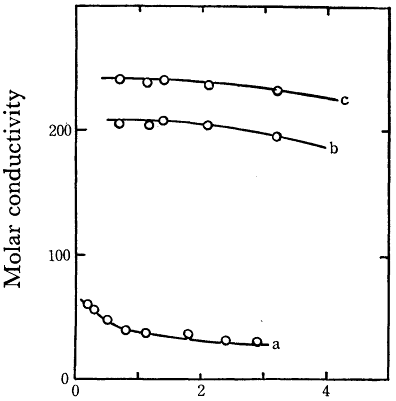


Fig. 2. The electric conductivity of $\mathrm{M^+ DDQ^{\overline{\cdot}}}$ in MeCN and THF at 20 °C. a) $\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}$ in THF, b) $\mathrm{Na^+ DDQ^{\overline{\cdot}}}$ in MeCN and c) $\mathrm{NEt_4^+ DDQ^{\overline{\cdot}}}$ in MeCN.

of the concentration. Thus, it is concluded that in MeCN, $\mathrm{M^+DDQ^{\overline{\cdot}}}$ dissociates completely to the free ions. Under this conclusion the limiting molar conductivity, λ_∞, of $\mathrm{DDQ^{\overline{\cdot}}}$ is estimated to be 150, since λ_∞ for $\mathrm{Na^+}$ and $\mathrm{NEt_4^+}$ are reported to be 70 and 86 respectively.[11] In other solvents whose dielectric constants are similar to that of MeCN, $\mathrm{M^+DDQ^{\overline{\cdot}}}$ is considered to dissociate completely. On the other hand, $\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}$ forms an ion pair at least partially in THF, because λ in THF is about 10% of that in MeCN, and increases as the decrease of the concentration. The approximate value of K_d is estimated by the equation

$$K_\mathrm{d} = C\lambda^2/\lambda_\infty^2, \tag{7}$$

where λ_∞ is determined by extrapolating the straight line of λ *versus* $\sqrt{C}$ to the infinite dilution. K_d is determined to be about 10^{-5} M at 20 °C. This means that more than 90% of $\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}$ is ion-paired at $C = 10^{-3}$ M. Thus, the dimerization equilibrium of $\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}$ in THF is almost expressed by the following equation:

$$2\mathrm{NEt_4^+DDQ^{\overline{\cdot}}} \rightleftharpoons (\mathrm{NEt_4^+DDQ^{\overline{\cdot}}})_2 \tag{8}$$

The dimerization in DME is also considered to take place between two $\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}$s.

It is likely that $\mathrm{DDQ^{\overline{\cdot}}}$ is hydrogen-bonded on the oxygen atoms with the protonic solvents like EtOH, MeOH, and $\mathrm{H_2O}$. The electronic spectra of $\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}$ monomer depend on solvents and solvent composition. The absorption peak at 594 nm in MeCN displaces to the shorter wavelength when the salt is dissolved in alcohols or water. The qualitative feature of this phenomena is displayed by plotting the change of absorbance at 600 nm, A_{600}, against the mole fraction of $\mathrm{H_2O}$ (Fig. 3). The general trend of A_{600} with $\mathrm{H_2O}$ mole fraction well corresponds to the change of the ^{13}C coupling constant for *p*-benzoquinone anion radical ($\mathrm{Q^{\overline{\cdot}}}$) in MeCN–$\mathrm{H_2O}$ mixtures recently observed by Stone and Maki.[12] In these investigations the change of the hyperfine coupling constants of carbon-13 is attributed to the specific solvation of $\mathrm{Q^{\overline{\cdot}}}$ by both MeCN and $\mathrm{H_2O}$ molecules. In the low concentration region of $\mathrm{H_2O}$, $\mathrm{Q^{\overline{\cdot}}}$ is solvated by two MeCN molecules. In the medium concentration region of $\mathrm{H_2O}$, $\mathrm{Q^{\overline{\cdot}}}$ is solvated by one MeCN and one $\mathrm{H_2O}$ molecule. In the high concentration region of $\mathrm{H_2O}$, $\mathrm{Q^{\overline{\cdot}}}$ is solvated by two $\mathrm{H_2O}$ molecules. Therefore, it is concluded that in the present system there exists a competition between $\mathrm{H_2O}$ and MeCN for solvating $\mathrm{DDQ^{\overline{\cdot}}}$ ions although no theoretical basis for the solvent effect on the electronic spectra of $\mathrm{DDQ^{\overline{\cdot}}}$ is available at present. Contrary to the $\mathrm{DDQ^{\overline{\cdot}}}$ monomer, the absorption peak of a dimer is little affected by the solvents as given in Table 1. However, the remarkably large equilibrium constant in $\mathrm{H_2O}$ may clearly be related to the hydrogen-bonding property of water. This will be treated from the kinetic point of view in a later section.

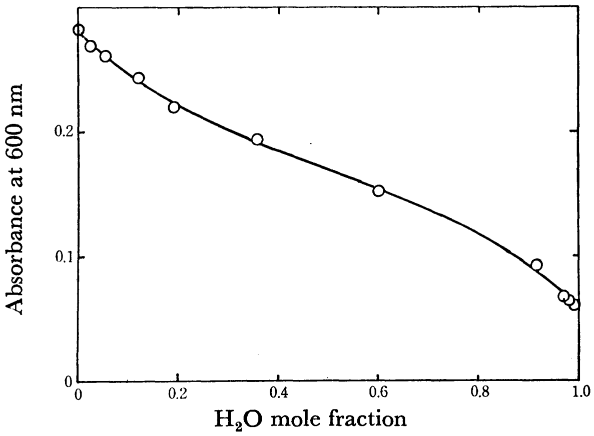


Fig. 3. The change of the absorbance of $\mathrm{DDQ^{\overline{\cdot}}}$ at 600 nm with the mole fraction of $\mathrm{H_2O}$ in an MeCN–$\mathrm{H_2O}$ mixed solvent. $[\mathrm{NEt_4^+DDQ^{\overline{\cdot}}}]$ 4.6×10^{-5} M.

The Effect of Cations on the Dimerization Equilibria. The presence of counter ions affects the dimerization equilibria remarkably. In Fig. 4, the increase of the absorbance at 710 nm is shown when $\mathrm{NaClO_4}$, $\mathrm{NEt_4ClO_4}$, and $\mathrm{NPr_4ClO_4}$ are added. Although the ion-pairing of $\mathrm{M^+DDQ^{\overline{\cdot}}}$ is neglected in MeCN in the concentration range below 10^{-3} M, $\mathrm{DDQ^{\overline{\cdot}}}$ and $(\mathrm{DDQ^{\overline{\cdot}}})_2$ probably form ion-pairs with cations in the high concentration of cation. In case of $\mathrm{NaClO_4}$, this is confirmed from the change of electronic spectra of a $\mathrm{DDQ^{\overline{\cdot}}}$ monomer and a dimer when a large amount of $\mathrm{NaClO_4}$ is present (Figs. 5 and 6). The absorption of a dimer becomes broader as $\mathrm{NaClO_4}$ is added, although the peak position is little altered. In case of a mono-

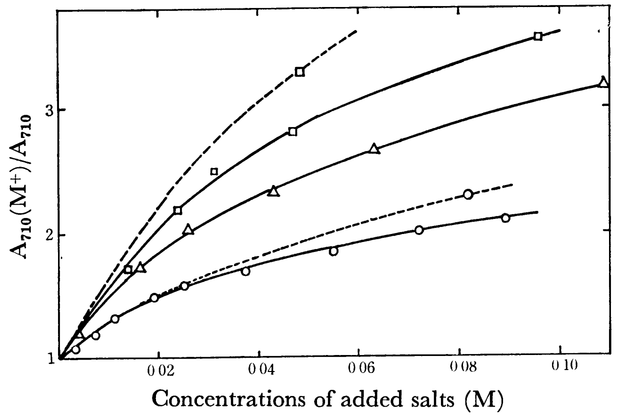


Fig. 4. The increase of the absorbance at 710 nm with the addition of various salts at 10 °C; $NaClO_4$ (□), NEt_4ClO_4 (△) and NPr_4ClO_4 (○). The dotted lines are a curve corrected against the concentration of free ions. The ordinate is taken as the ratio of the absorbace in the presence of salts, A_{710} (M^+), to that in the absence of salts, A_{710}.

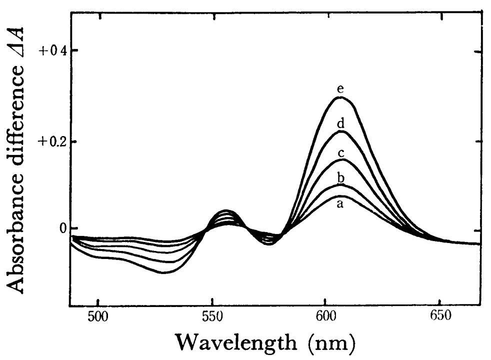


Fig. 5. The difference spectra of $DDQ^{\cdot-}$ monomer at the high concentration of $NaClO_4$ at 10 °C. The sample solution contains [$Na^+DDQ^{\cdot-}$] 2.5×10^{-4} M, the reference [$Na^+DDQ^{\cdot-}$] 2.5×10^{-4} M and [$NaClO_4$] 0.047 M (a), 0.089 M (b), 0.16 M (c), 0.30 M (d) and 0.46 M (e).

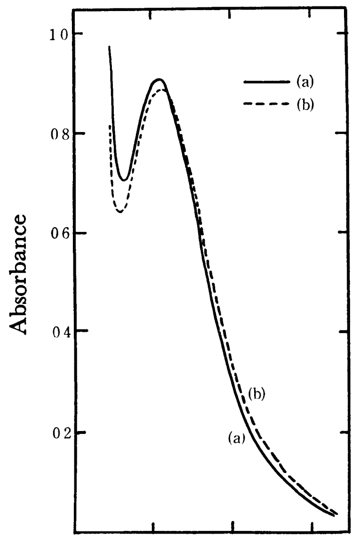


Fig. 6. The effect of $NaClO_4$ on the spectra of $DDQ^{\cdot-}$ dimer. (a) [$Na^+DDQ^{\cdot-}$] 5.6×10^{-3} M (b) [$Na^+DDQ^{\cdot-}$] 2.8×10^{-3} M and [$NaClO_4$] 0.214 M.

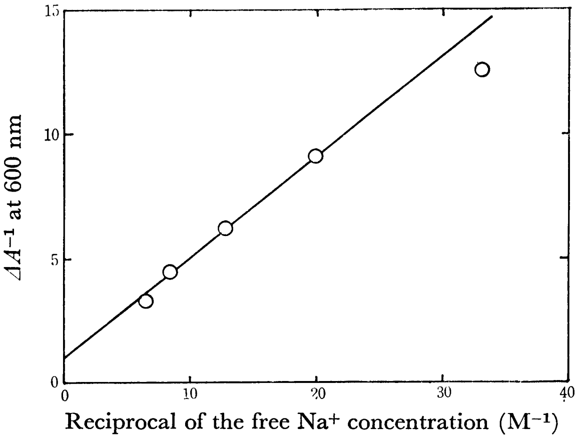


Fig. 7. The dependence of the absorbance change at 600 nm of $DDQ^{\cdot-}$ monomer on the concentration of free Na^+ ion.

mer, the presence of the isosbestic points at 581, 565, and 547 nm in Fig. 5 implies that a free $DDQ^{\cdot-}$ ion converts to another species, which is most likely to be a 1 : 1 ion-pair between Na^+ and $DDQ^{\cdot-}$. If this is correct, the change of absorbance ΔA in Fig. 5 is related to the free Na^+ concentration, $[Na^+]_f$ as follows:

$$\frac{1}{\Delta A} = \frac{1}{C(\varepsilon_1-\varepsilon_2)}\left(\frac{K_d}{[Na^+]_f}+1\right) \qquad (9)$$

where C is the total concentration of $M^+DDQ^{\cdot-}$, and ε_1, ε_2 the extinction coefficients of $DDQ^{\cdot-}$ and Na^+-$DDQ^{\cdot-}$, respectively. $[Na^+]_f$ is calculated from the conductivity results under the assumption that λ is directly proportional to the degree of the dissociation of $NaClO_4$. In Fig. 7, ΔA^{-1} at 600 nm is plotted against the reciprocal of $[Na^+]_f$. The straight line obtained from this plot confirms the formation of a 1 : 1 ion-pair between $DDQ^{\cdot-}$ and Na^+. From the intrecept and the slope of the straight line, K_d is determined to be 0.40 M at 10 °C. On the other hand, NPr_4ClO_4 enhances the dimerization, although it gives no effect on the electronic spectra of $DDQ^{\cdot-}$ monomer. This effect may be ascribed to the role of the ionic atmosphere of NPr_4^+ ions as stated previously.

Therefore, in the system containing a large amount of $NaClO_4$, the following equilibria are considered to exist:

$$DDQ^{\cdot-} + Na^+ \rightleftarrows Na^+DDQ^{\cdot-}; \qquad K_d \qquad (6)$$

$$2DDQ^{\cdot-} \rightleftarrows (DDQ^{\cdot-})_2; \qquad K \qquad (1)$$

$$(DDQ^{\cdot-})_2 + Na^+ \rightleftarrows Na^+(DDQ^{\cdot-})_2; \qquad K_1 \qquad (10)$$

$$Na^+(DDQ^{\cdot-})_2 + Na^+ \rightleftarrows (Na^+DDQ^{\cdot-})_2; \qquad K_2 \qquad (11)$$

The absorbance at 710 nm is expressed as a function of the total concentration of $Na^+DDQ^{\cdot-}$, and the concentration of free Na^+ ion as follows:

$$A_{710}(Na^+) = (\varepsilon_D K + \varepsilon_3 K K_1 [Na^+]_f + \varepsilon_4 K K_1 K_2 [Na^+]_f^2) \times (1+K_d^{-1}[Na^+]_f)^{-2} \cdot C^2 \qquad (12)$$

where ε_3 and ε_4 are the molar extinction coefficient of $Na^+(DDQ^{\cdot-})_2$ and $(Na^+DDQ^{\cdot-})_2$, respectively. K_d, K, K_1, and K_2 are all dependent on ionic strength through the interaction of the ionic atmosphere of Na^+ ions with $DDQ^{\cdot-}$ or $(DDQ^{\cdot-})_2$. As a first approximation ε_3

and ε_4 are assumed equal to ε_D. The dependence of the equilibrium constant K on ionic strength can be eliminated by taking the ratio of the absorbance in the presence of $NaClO_4$, $A_{710}(Na^+)$, to that in the presence of the same amount of free NPr_4^+, $A_{710}(NPr_4^+)$, because in the latter system, only the reaction (1) takes place.

$$A_{710}(Na^+)/A_{710}(NPr_4^+) = (1+K_1[M^+]_f+K_1K_2[M^+]_f^2)\times(1+K_d^{-1}[M^+]_f)^{-2} \qquad (13)$$

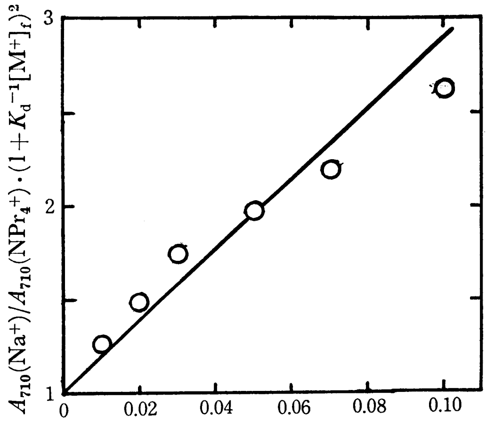


Fig. 8. The plot of A_{710} $(Na^+)/A_{710}$ $(NPr_4^+)\cdot(1+K_d^{-1}[M^+]_f)^2$ against $[M^+]_f$ at 10 °C.

In Fig. 8 $A_{710}(Na^+)/A_{710}(NPr_4^+)\cdot(1+K_d^{-1}[M^+]_f)^2$ is plotted against $[M^+]_f$. All points are roughly on a straight line with a slope of 30 M^{-1}. Thus, it is concluded that in this concentration range of Na^+, there exists no appreciable amount of $(Na^+DDQ^{\overline{\cdot}})_2$. The dimerization constant between $Na^+DDQ^{\overline{\cdot}}$ and $DDQ^{\overline{\cdot}}$,

$$Na^+DDQ^{\overline{\cdot}} + DDQ^{\overline{\cdot}} \rightleftarrows Na^+(DDQ^{\overline{\cdot}})_2;\ \tilde{K} \qquad (14)$$

is expressed as

$$\tilde{K} = KK_1K_d.$$

Since $K_1=30\ M^{-1}$ and $K_d=0.40$ M, $\tilde{K}=12\,K$ at 10 °C, that is, the presence of Na^+ ion enhances the dimerization of $DDQ^{\overline{\cdot}}$ by 12 times. The temperature dependence of the apparent dimerization constant gives that the apparent enthalpy change $-\Delta H$ decreases from 9.0 ± 1.0 to 6.5 ± 1.0 kcal M^{-1} as $[NaClO_4]$ increases from 0 to 1.14 M. This implies that the increase of the dimerization constant with the increase of Na^+ arises from the decrease of $-\Delta S$, but not from the increase of $-\Delta H$. This fact coincides with the small $-\Delta S$ observed in both THF and DME in which the dimerization occurs between ion-paired $DDQ^{\overline{\cdot}}$ ions. As a result it is concluded that the entropy change for the dimerization becomes less negative, when the charge of anion radicals is screened by the counter cation. It may be probable that the large negative entropy change accompanied with dimerization is attributed to the freezing of solvent molecules due to the stronger solvation of a dimer than monomer ions. The neutralization of the charge of a dimer by a counter cation should result in the decrease of the solvating capacity of a dimer.

Kinetic Measurements. In order to look into the significance of the remarkably large dimerization constant in H_2O, the rates of dimerization in MeCN, H_2O, and MeCN–H_2O systems were measured by the temperature-jump method. Since the dimerization reaction of $DDQ^{\overline{\cdot}}$ ions is largely exothermic, the equilibrium (1) displaces to the leftward at the sudden rise of temperature. In Fig. 9, the increase of the transmittance at 710 nm (dimer band) with time is shown for the MeCN solution of $NEt_4^+DDQ^{\overline{\cdot}}$ at −15 °C. The pseudo first-order rate constant k_{obsd} obtained from the signal is related to the forward and the backward rate constants of dimerization, $\overrightarrow{k}$ and $\overleftarrow{k}$, respectively, by Eq. (15):

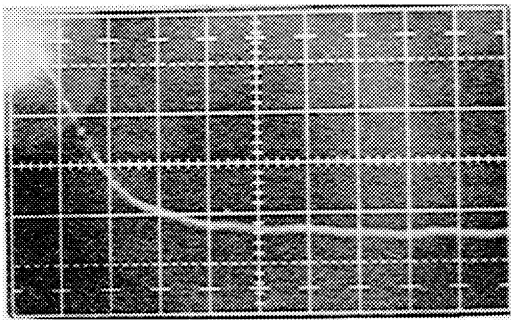


Fig. 9. The temperature-jump signal for the MeCN solution of $NEt_4^+DDQ^{\overline{\cdot}}$ at −15 °C. $[NEt_4^+DDQ^{\overline{\cdot}}]$ 5×10^{-3} M and $[NPr_4ClO_4]$ 2×10^{-2} M. Wavelength 710 nm.

$$k_{obsd} = 4\overrightarrow{k}[DDQ^{\overline{\cdot}}] + \overleftarrow{k} \qquad (15)$$

Under the conditions of $K=18.5\ M^{-1}$ at −15 °C, and $[DDQ^{\overline{\cdot}}]\cong10^{-3}$ M, the first term in Eq. (15) is neglected. That is,

$$k_{obsd} = \overleftarrow{k}. \qquad (16)$$

k_{obsd} is obtained to be $5\times10^5\ s^{-1}$ at −15 °C. However, the half-life time in Fig. 9 is almost equal to the minimum time for temperature-rise, 1.4 μs. Thus k_{obsd} is not related to $\overleftarrow{k}$ as in Eq. (16), instead it gives the lower limit of $\overleftarrow{k}$.

$$\overleftarrow{k} \geq 5\times10^5\ s^{-1} \text{ at } -15°C$$

Although the temperature of a sample solution is lowered down to −23 °C, no variation of k_{obsd} is observed. The lower limit of $\overrightarrow{k}$ is thus determined to be

$$\overrightarrow{k} = K\overleftarrow{k} \geq 2\times10^7\ M^{-1}\cdot s^{-1} \text{ at } -23°C,$$

since K at −23 °C is about 32 M^{-1}.

When H_2O containing 5.8 M urea and 1.8 M MeCN is used as a solvent, the k_{obsd} obtained at −6.0 °C is apparently smaller than the rate of the temperature-rise (Figs. 10 and 11). As expected from Eq. (15), k_{obsd} increases linearly as the increase of the concentration of free $DDQ^{\overline{\cdot}}$ (Fig. 12). The slope and the intercept of the straight line in Fig. 12 give the values of $4\,\overrightarrow{k}$ and $\overleftarrow{k}$ respectively. Thus we obtain

$$\overrightarrow{k} = (1\pm0.5)\times10^8\ M^{-1}\cdot s^{-1}$$

$$\overleftarrow{k} = (3\pm2)\times10^4\ s^{-1} \text{ at } -6°C.$$

and $K=\overrightarrow{k}/\overleftarrow{k}=(3\pm2)\times10^3\ M^{-1}$. K agrees with the

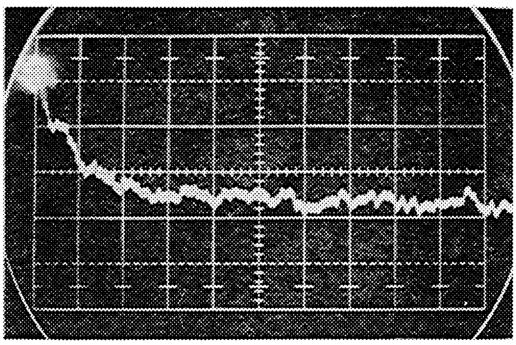


Fig. 10. The temperature-jump signal for the H_2O solution of $NEt_4^+DDQ^{\cdot-}$ at −6 °C. $[DDQ^{\cdot-}]$ 2.0×10^{-4} M. [Urea] 5.8 M. [MeCN] 1.8 M. [NaCl] 0.1 M. Wavelength 700 nm.

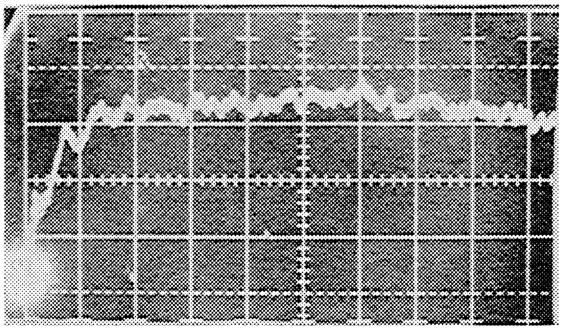


Fig. 11. The temperature-jump signal for the H_2O solution of $NEt_4^+DDQ^{\cdot-}$ at −6 °C. $[DDQ^{\cdot-}]$ 3.4×10^{-4} M. [Urea] 5.8 M. [MeCN] 1.8 M. [NaCl] 0.1 M. Wavelength 530 nm.

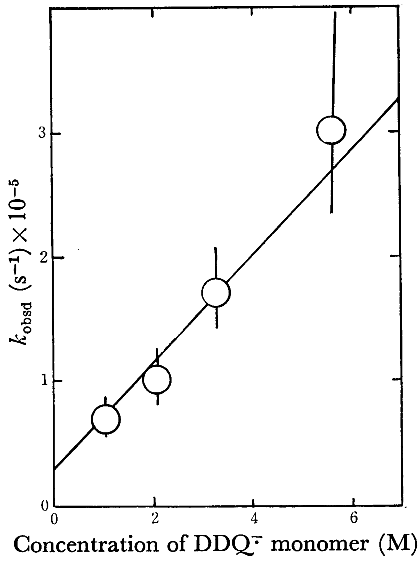


Fig. 12. The dependence of k_{obsd} on the concentration of free $DDQ^{\cdot-}$ ion in H_2O (5.8 M urea and 1.8 M MeCN) at −6 °C.

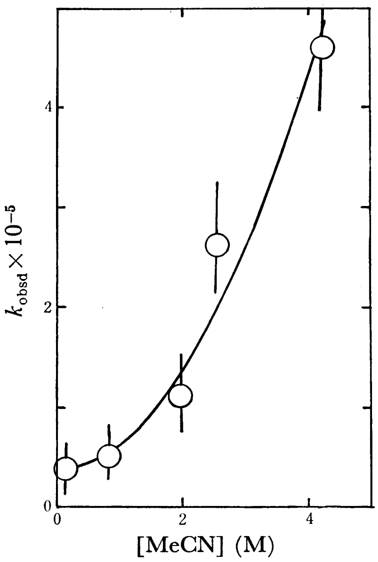


Fig. 13. The dependence of k_{obsd} on the concentration of MeCN in an MeCN/H_2O mixed solvent at −6 °C. $[NEt_4DDQ^{\cdot-}]=(1.5-3.0)\times10^{-4}$ M. [Urea] 5.8−4.8 M. [NaCl] 0.1−0.08 M.

value extrapolated from the equilibrium measurement at 0—15 °C, $K=(2\pm1)\times10^3\ M^{-1}$ at −6 °C.[13] Comparing the rate data in MeCN with those in H_2O, it is concluded that the large difference of the dimerization constants between these two solvents lies in the large difference of the decomposition rate constants of a dimer.

In Fig. 13 is shown the effect of MeCN on k_{obsd} in an MeCN–H_2O mixed solvent. k_{obsd} increases superlinearly with the MeCN concentration. The dependence of k_{obsd} on the MeCN concentration is expressed approximately as

$$k_{obsd} = k_1 + k_2[\mathrm{MeCN}]^2. \qquad (17)$$

The forward reaction rate is considered to be independent of the solvent composition from the results obtained for pure MeCN and pure H_2O solvents. Thus, the backward rate constant is expressed from Eq. (17) as below.

$$\overleftarrow{k} = k_W + k_M[\mathrm{MeCN}]^2 \qquad (18)$$

k_W is the backward reaction rate in pure H_2O, while k_M, $(2.5\pm0.6)\times10^4\ M^{-2}\ s^{-1}$ (−6 °C), corresponds to the path where a dimer is decomposed by the attacks of MeCN molecules.

Discussion

From Table 1, it is quite clear that an entropy term plays an important role in determining the dimerization constants.[9] The order of $-\Delta H$ does not follow the order of the dimerization constants. In discussing the variation of the entropy change with solvents, it is instructive to divide ΔS into three parts according to their origins.

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 \qquad (19)$$

ΔS_1 is an entropy change of the solvent molecules in the region where the solvent is considered to be a dielectric continuum and is polarized in proportion to the electrostatic field due to ion radicals. ΔS_2 is an entropy change of the solvent molecules in that region which constitues the solvation shell of the ion radicals. ΔS_3 is an entropy change accompanied with the loss of degrees of freedom of motion of ion radicals due to dimerization. ΔS_3 is considered to be almost constant for all solvents, since a dimer always gives an absosrption peak around 710 nm, indicating that the geometry of a dimer is similar in all solvents.

ΔS_1 is estimated in the electrostatic way. The free energy of solvation of an ion of radius a and charge e is

$$\Delta F_{\mathrm{I}} = -\left(1-\frac{1}{D}\right)\frac{e^2}{2a},$$

where D is a dielectric constant of a solvent. Thus, the change of free energy of solvation for the reaction of dimerization (1) is

$$\Delta F_{\mathrm{I}} = -\frac{1}{2}\left(1-\frac{1}{D}\right)\left(\frac{4e^2}{r_{\mathrm{D}}}-\frac{e^2}{r_{\mathrm{M}}}\right),$$

where r_{D} and r_{M} are the radius of a dimer and a monomer respectively. The entropy change of dimerization is thus,

$$\Delta S_{\mathrm{I}} = -\frac{\partial \Delta F_{\mathrm{I}}}{\partial T} = \frac{\partial D}{D^2 \partial T}\left(\frac{2e^2}{r_{\mathrm{D}}}-\frac{e^2}{r_{\mathrm{M}}}\right) \tag{20}$$

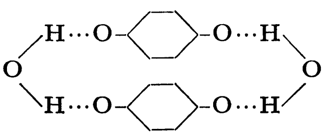
Since $\partial D/\partial T$ is negative, negative ΔS_{I} is obtained for the case of $r_{\mathrm{D}} < 2r_{\mathrm{M}}$, that is, the case that the effective radius of radicals contracts in dimerization. Taking $r_{\mathrm{M}}=4$ Å, $r_{\mathrm{D}}=6$ Å as typical values, the calculated value of ΔS_{I} in each solvent is given in Table 2. For MeCN, DMF, and Me$_2$CO, the experimentally observed ΔS is much larger than was predicted from Eq. (20). This implies that in these solvents, ΔS_2 or ΔS_3 contributes a great deal to the entropy change. Since MeCN, DMF, and Me$_2$CO are known as strong anion solvating solvents[14] it is concluded from the present results that at least a dimer is specifically solvated by MeCN solvent.

TABLE 2. THE ELECTROSTATIC ENTROPY CHANGE ΔS_1 OF DIMERIZATION REACTION CALCULATED USING Eq. (20).

Solvent	Dielectric constant at 15 °C	ΔS_1/e.u.
MeCN	38.3	−2.8
DMF	38.42	−2.8
Me$_2$CO	20.0	−6.6
EtOH	25.7	−5.8
MeOH	34.7	−4.7
H$_2$O	82.0	−1.5
THF	7.77	−17 (for Eq. (1)) 0 (for Eq. (8))

In THF and DME, both ΔH and ΔS are a little negative. As stated in the previous section, DDQ$^{\overline{\cdot}}$ associates with a counter cation and the dimerization mostly occurs between ion-paired DDQ$^{\overline{\cdot}}$ ions. Therefore, the less negative ΔS arises from the weak solvation of solvent molecules with the neutral ion-pair. ΔS_{I} is, of course, zero in these solvents. If ΔS_{I} and ΔS_2 are both zero, the observed ΔS corresponds to ΔS_3, which contains the loss of degrees of freedom of translation and rotations of monomer ions and the gain of degrees of freedom of vibrations of a dimer.

In EtOH, MeOH, and H$_2$O, both ΔH and ΔS are moderately negative. As stated previously, it is certain that these protic solvents form hydrogen-bonds with the oxygen atoms of DDQ$^{\overline{\cdot}}$ ions. It is interesting to see how the hydrogen-bonding property affects the dimerization equilibria. As the results in Table 1 show, H$_2$O gives the largest $-\Delta H$ among these protonic solvents. Since ΔH and ΔS are the difference between two monomers and a dimer, the hydrogen bonding property seems to affect monomers and a dimer equally in EtOH and MeOH, resulting in the small value of the dimerization constants. On the other hand, H$_2$O favours the dimer side drastically by making ΔH largely negative. If some speculation can be permitted at this stage, these results indicate the structure of two water molecules acting as bridges between two DDQ$^{\overline{\cdot}}$ ions, since H$_2$O is unique in having two protons in one molecule.[15]



The rate data shows the large difference of the dimerization constant between MeCN and H$_2$O lies in the large difference of the decomposition rates between these two solvents. In order to see the meaning of the forward rate constant in H$_2$O, the diffusion controlled reaction rate constant is calculated according to the equation given below:[16]

$$k = \frac{4\pi e^2 N D_{\mathrm{f}}(N/1000)}{DRT[\exp(e^2N/DRTr_{\mathrm{M}})-1]} \tag{21}$$

where N is Avogadro's number, D_{f} the diffusion coefficient of a particle, D the dielectric constant of a medium and R the gas constant. r_{M} represents the diameter of a monomer which is assumed to be a sphere. Putting in the reasonable values of $D_{\mathrm{f}}=1\times10^{-5}$ cm^2 s^{-1}, and $r_{\mathrm{M}}=4\times10^{-8}$ cm, we obtain at −6 °C,

$$k(\text{calcd}) = 1.0\times10^8\ \mathrm{M}^{-1}s^{-1}$$

k(calcd) is about one order larger than the observed $\vec{k}$. Considering that k(calcd) involves a large uncertainty in estimating D_{f} and r_{M}, it is concluded that the forward rate of dimerization in H$_2$O is nearly a diffusion controlled one.[17] This result implies that no decrease of entropy which would make the rate slower than k_{calcd} takes place until two DDQ$^{\overline{\cdot}}$ ions come into contact with each other. When two DDQ$^{\overline{\cdot}}$ ions approach each other within few angstroms, the charge-transfer interaction is considered to begin to operate.[7] This final process will result in the decrease of entropy observed in the equilibrium measurements. Thus these results support the previous conclusion from the equilibrium measurements that the large negative entropy arises from the specific solvation of a dimer ΔS_2 but not from the macroscopic entropy change of ΔS_1 or ΔS_3.

The reverse reaction rate is found to increase with the square of the MeCN concentration. This fact suggests that the main path of the decomposition of a dimer in relatively high concentration range of MeCN is the successive attacks of two MeCN molecules toward the dimer solvated by H$_2$O molecules.

$$(\mathrm{DDQ}^{\bar{\cdot}})_2 + \mathrm{MeCN} \rightleftharpoons (\mathrm{DDQ}^{\bar{\cdot}})_2(\mathrm{MeCN}) \qquad (22)$$

$$(\mathrm{DDQ}^{\bar{\cdot}})_2(\mathrm{MeCN}) + \mathrm{MeCN} \rightleftharpoons 2(\mathrm{DDQ}^{\bar{\cdot}})(\mathrm{MeCN}) \qquad (23)$$

Here reaction (23) is considered to be rate-determining. In the above scheme, $(\mathrm{DDQ}^{\bar{\cdot}})(\mathrm{MeCN})$ is introduced from the result of Fig. 3, which indicates that in the H_2O mole fraction range of 0.2—0.8, the main species of $\mathrm{DDQ}^{\bar{\cdot}}$ is the one solvated by one MeCN molecule. The reactions (21) and (22) coincide with the previous postulate that $(\mathrm{DDQ}^{\bar{\cdot}})_2$ ion combines with two H_2O molecules as bridges between two $\mathrm{DDQ}^{\bar{\cdot}}$ ions. Thus the decomposition of $\mathrm{DDQ}^{\bar{\cdot}}$ dimer is caused by the displacement of two solvated H_2O molecules by MeCN molecules.

In this way, the large solvent effect on the dimerization equilibria is understood as due to the molecular processes involving ion radicals and solvent molecules.

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