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DIMERIZATION OF ANION RADICAL IN MICELLES

Akihiko YAMAGISHI and Fumiyuki WATANABE
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060

Sodium salt of 2,3-dichloro-5,6-dicyano-p-benzoquinone is found to dimerize in chloroform when it is solubilized by dodecylpyridinium chloride micelles. The enthalpy and entropy changes of dimerization equilibrium have been determined at various surfactant concentrations (0.003 - 0.07 M). The temperature-jump measurements show that the relaxation time of dimerization is less than 1.5×10^{-5} s. The results indicate that the dimerization occurs in the micelle interior.

The dynamic aspects of solubilization processes have been the subject of several research groups.[1-2] Until now, however, little is known about the interaction among solubilized species.[3] The present paper reports the dimerization of ion radicals occurring in micelles.

Sodium salt of 2,3-dichloro-5,6-dicyano-p-benzoquinone ($Na^+DDQ^{\bar{\cdot}}$) is hardly soluble in $CHCl_3$. As it is solubilized by dodecylpyridinium chloride (DPCl), a new absorption peak in electronic spectra appears at 725 nm in a high concentration range of $Na^+DDQ^{\bar{\cdot}}$.[4] Comparing this result with what was previously observed in an acetonitrile solution of $Na^+DDQ^{\bar{\cdot}}$,[5] the peak at 725 nm is assingned to the dimer of $Na^+DDQ^{\bar{\cdot}}$, $(Na^+DDQ^{\bar{\cdot}})_2$.

$$\begin{aligned} &2Na^+DDQ^{\bar{\cdot}} \rightleftharpoons (Na^+DDQ^{\bar{\cdot}})_2 \\ &K_d = [(Na^+DDQ^{\bar{\cdot}})_2]/[Na^+DDQ^{\bar{\cdot}}]^2 \end{aligned} \qquad (1)$$

The equilibrium constant K_d is expressed in terms of a degree of dimerization, α, as below.

$$K_d = \alpha/(1 - 2\alpha)^2 C \quad \text{with} \quad A_{725} = \varepsilon_d \alpha C,$$

in which C is the total concentration of $Na^+DDQ^{\bar{\cdot}}$, A_{725} the absorbance at 725 nm and ε_d the molar extinction coeffecient of a dimer at this wavelength, respectively. Transforming the equation above with α^2 terms neglected, A_{725} is related to C as below.

$$C/A_{725} = 1/\varepsilon_d(1/K_dC + 4)$$

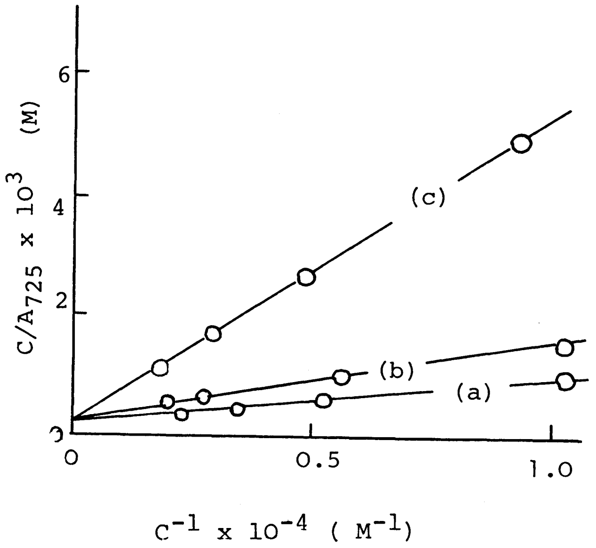

Fig. 1. Plot of C/A_{725} against C^{-1} at $[\mathrm{DPCl}] = 3.25 \times 10^{-3}$ M (a), 1.54×10^{-2} M (b) and 6.50×10^{-2} M (c). T = 22.5 °C.

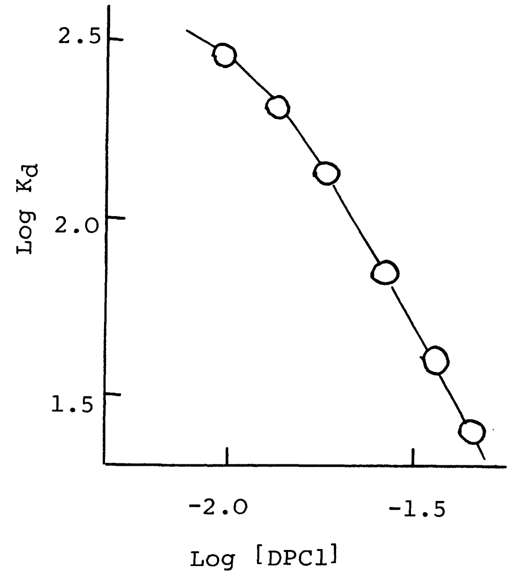

Fig. 2. The dependence of K_d on [DPCl] at 22.5 °C.

In Fig. 1, C/A_{725} is plotted against C^{-1} at the constant DPCl concentrations. Straight lines in the figure indicate the validity of the method of analysis based on a dimerization mechanism. From the slopes and intercepts, K_d and ε_d are determined at various DPCl concentrations (Table 1). Table 1 also includes the enthalpy and entropy changes of dimerization, which are obtained from the linear dependence of log K_d on T^{-1} (K^{-1}) in the temperature range of 9 - 39 °C. It is noteworthy that $\Delta H°$ and $\Delta S°$ obtained are both largely negative. These values are similar to those obtained in water and acetonitrile rather than in tetrahydrofuran. As pointed out previously,$^{5)}$ a large negative entropy term in water and acetonitrile arises from the stronger solvation of a doubly charged dimer, $(\mathrm{DDQ}^{\bar{\cdot}})_2$, whereas such solvation process is not present in tetrahydrofuran, since dimerization occurs between ion-paired monomers, $\mathrm{Na}^{+}\mathrm{DDQ}^{\bar{\cdot}}$. It is concluded, therefore, that the dimerization process in the present system is expressed as

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

instead of (1). Since the micelle interior is a polar medium due to the positively charged pyridinium groups, the above conclusion supports the view that the equilibrium (2) takes place inside the micelles. Figure 2 shows the dependence of K_d on [DPCl]. K_d decreases with the increase of [DPCl]. This result suggests the possibility that a dimer decomposes into monomers by the collision between an empty micelle (S) and a micelle containing a dimer ($\mathrm{S}/(\mathrm{DDQ}^{\bar{\cdot}})_2$).

$$\mathrm{S} + \mathrm{S}/(\mathrm{DDQ}^{\bar{\cdot}})_2 \rightleftharpoons \mathrm{S}/\mathrm{DDQ}^{\bar{\cdot}} + \mathrm{S}/\mathrm{DDQ}^{\bar{\cdot}} \qquad (3)$$

Table 1. The thermodynamic parameters of $Na^+DDQ^{\overline{\cdot}}$ dimerizations in $CHCl_3$

Solvent	[DPCl]/M	K_d/M^{-1}	ε_d	ΔH°/Kcal $mole^{-1}$	ΔS°/e.u.
$CHCl_3$	3.25×10^{-3}	$448^{b)}$	2.5×10^4	-9.2 ± 1.0	-18 ± 3
$CHCl_3$	1.54×10^{-2}	$317^{b)}$	2.5×10^4	-8.7 ± 1.0	-17 ± 3
$CHCl_3$	6.50×10^{-2}	$44.8^{b)}$	2.5×10^4	-7.4 ± 1.0	-16 ± 4
$CH_3CN^{a)}$	0	$3.7^{c)}$	7.2×10^3	-9.7 ± 1.0	-29 ± 3
$H_2O^{a)}$	0	$1300^{c)}$	2.5×10^4	-8.8 ± 1.0	-17 ± 2
Tetrahydrofuran$^{a)}$	0	$17^{c)}$		-3.3 ± 0.2	-4.9 ± 2

a) From ref. (5); b) at 22 5 °C; c) at 10 °C

A temperature-jump measurement is performed with a Union-Giken temperature-jump apparatus having a coaxial cable of 200 m length as capacitor.$^{5)}$ No concentration change is observed at 585 nm (a monomer peak) for the solution containing 7.0×10^{-5} M $Na^+DDQ^{\overline{\cdot}}$ and 0.220 M DPCl, in which no dimer is present. At the higher concentration of $Na^+DDQ^{\overline{\cdot}}$, the rapid decrease of the dimer is observed at 725 nm as shown in Fig. 3. The synchronous increase of the monomer is observed at 585 nm, indicating that the observed relaxation is due to the dissociation of the dimer. The relaxation time is estimated to be 1.5×10^{-5} s, which is close to the rise time of temperature, 1×10^{-5} s.$^{6)}$ Thus the true relaxation time of dimerization equilibrium is concluded to be less than 1.5 $\times 10^{-5}$ s. This fast relaxation may represent the dimerization-dissociation processes occurring in micelles. No slower relaxation is observed in the time range of 10^{-4} - 10^{-1} s, beyond which the elevated temperature is not maintained.

A stopped-flow measurement is performed with a Union-Giken Rapid Scan stopped-flow spectrophotometer. The solution containing 1.40×10^{-3} M $Na^+DDQ^{\overline{\cdot}}$ and 1.30×10^{-3} M DPCl is mixed with the solution containing 1.30×10^{-3} M DPCl. A transient change can not be followed at 725 nm, although the decrease of the dimer concentration takes place at the mixing. This result implies that the redistribution processes of $DDQ^{\overline{\cdot}}$ and $(DDQ^{\overline{\cdot}})_2$ into empty micelles (eq. (3)) are completed within the dead time of the apparatus, ca. 1×10^{-3} s.

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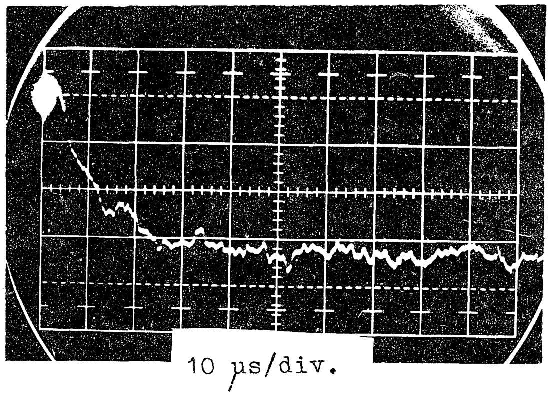

Fig. 3. A temperature-jump signal observed at 725 nm; $[Na^+DDQ^-]$ 3.20×10^{-3} M and [DPCl] 0.220 M.

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4) The cmc of DPCl is estimated to be 1.0×10^{-4} M on the basis of the deviation of an electronic spectra from the Beer's Law.

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6) The sample in Fig. 3 has the conductivity of $2.4 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The rise-time of temperature for the aqueous solution with this conductivity is determined to be 1×10^{-5} s by following the protonation reaction of phenolphthalein.

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