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Time-Resolved ESR Study on the Photochemistry of Naphthoquinones Included in Cyclodextrins

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The photochemical reactions of 1,4-naphthoquinones included in α-, β- and γ-cyclodextrins (CDs) are studied using a time-resolved ESR method. The CIDEP (chemically induced dynamic electron polarization) spectra observed in the case of 1,4-naphthoquinone (NQ) in α- and γ-CDs show the main formation of the NQ anion radical, contrary to the case of β-CD that shows the naphthosemiquinone neutral radical. The carbon-centered radicals of the CDs are also identified in all the cases. The spin polarization patterns of these species prove that the reaction takes place via the excited triplet state of NQ, and the NQ neutral and anion radicals are ejected from the CD cavity. The initial reaction of these systems is the hydrogen abstraction from the CD framework and some NQ neutral radicals lose the proton to form the anion radical. In the case of 2-methyl-1,4-naphthoquinone in CDs, similar results are obtained. As for β-CD both NQ and MNQ systems show the appearance of a broad emissive spectrum immediately after photolysis. This is tentatively assigned to a strongly coupled radical pair formed inside of the β-CD cavity. Accordingly, the initial photochemical reaction takes place inside of the CD cavities and the NQ and MNQ radicals are ejected to the aqueous phase.

Introduction

Cyclodextrins (CDs) are very attractive inclusion compounds that can be used for a practical use, and they occasionally compose supermolecules having special functions.[1] The specific inclusion property and the dynamic behavior of CDs attract many interests chemically and physically, and have been reported by many groups. Some photochemical reactions in CD cavity have also been reported.[3−5] Although great amounts of publications have been done, only a few reports of the dynamic behavior of the transient paramagnetic species produced in the photochemical reaction in CD cavities are available.[5−8] The ESR is very powerful tool to assign the species and investigate the dynamics and/or chemical behavior of the radicals included in CDs. In low-temperature time-resolved ESR (tr-ESR) studies of CD systems have proved the included conditions of the excited triplet states of aromatic compounds.[8] The energy transfer accompanied by the spin polarization transfer between the included molecules has also been studied.[9] In these reports, the spin polarization transfer and the dipole−dipole interaction were the sources of the information. As for the photochemistry, ordinary solutions of general CD complex at room temperature may interest many photochemists. There are a few reports of the tr-ESR study of this kind of works. One of the reports showed the spectrum of the dipole−dipole interaction of the transient radical−ion pair included in a CD cavity even at the room temperature, probably because of the CD aggregation formation which blocks the free tumbling of the complex in the solution.[5] Recent tr-ESR report of the photolysis of benzoin included in CDs showed the ejection of the photodecomposed fragments from the CD cavity.[7] The photoejection of the transient species is quite attractive phenomenon in the aspect of the controlling of the chemical reaction in inclusion compounds.

In the present report, the photochemical reaction of 1,4-naphthoquinone (NQ) and 2-methyl-1,4-naphthoquinone (MNQ) included in three different CDs are investigated using a tr-ESR method. The main reaction pathway of the hydrogen abstraction from the CD molecule and the ejection of the transient radicals of NQs are shown. Each CD molecule shows the different property concerning the chemical and physical point of view.

Experimental Section

Guaranteed reagents of NQ (Wako Pure Chemical) and MNQ (Tokyo Kasei) were purified by repeated recrystallization by dry ethanol followed by sublimation in a vacuum. Commercially available α-, β-, and γ-CDs (Wako Pure Chemical) were used as received. Water as the solvent was purified by the distillation after processing by $KMnO_4$. The concentrations of CDs were controlled among 0.5 mM ($M = mol\ dm^{-3}$) and 40 mM (0.5 and 15 mM in the case of β-CD) for tr-ESR studies. The concentrations of NQ and MNQ in the aqueous solution with CDs were controlled among 0.5 and 2.5 mM.

We used an ESR spectrometer (BRUKER esp-380E) with a slight modification for the X-band tr-ESR observation.[10] A pulsed excimer laser (Lumonics EX-600, XeCl 308 nm, 10 Hz) was used to excite the sample inside the ESR resonator. The sample was deoxygenated by bubbling with nitrogen gas and flowed through a flat quartz cell with 0.3 mm optical path length. All the experiments of NQ and MNQ in α- and β-CDs were carried out at room temperature (ca. 25 °C) and those in γ-CD were done at 40 °C to get better solubility. For the measurements of optical absorption spectra, SHIMAZU UV-1600PC photometer was used. As for the fluorescence measurements, SHIMAZU RF-5300PC spectrophotofluorometer was used. Observation of NMR spectra of the present system was performed by the 500 MHz JEOL α-500 operated in the Instrumental Analysis Center for Chemistry of Tohoku University.

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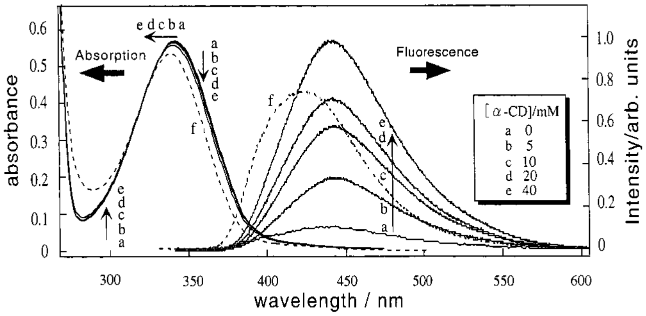

Figure 1. CD-concentration dependence of absorbance and fluorescence of NQ (2.0 mM) in α-CD. Broken lines show the data of NQ (2.0 mM) in *β*-CD (15 mM). All the concentrations given in parentheses in the figure captions are those used for the preparation of the aqueous solutions.

Results and Discussion

Optical Absorption and NMR Observations. The optical absorption spectra of NQ and MNQ showed a slight shift of the peak position and decrease of the absorbance by the addition of CDs as shown in Figure 1. This implies the formation of the inclusion complex of these systems,[11] but this is not enough to prove it. The enhancement of the fluorescence intensity in the conditions of the inclusion of the solute molecule in the CD cavity has been reported.[12,13] Typical fluorescence spectra observed in different α-CD concentrations with a constant concentration of NQ are given in Figure 1. The wavelength of 308 nm that was used for the tr-ESR measurements was used for the excitation. The α-CD concentration dependence of the fluorescence intensity apparently shows that NQ molecule is effectively included in the α-CD cavity. This situation may be expressed by the equilibrium equation, assuming 1:1 complex formation.

$$\mathrm{NQ} + \mathrm{CD} \leftrightarrow \mathrm{NQ/CD} \tag{1}$$

Here NQ/CD shows the NQ included in a CD cavity. Assuming that the extinction coefficient of NQ and included NQ is very close, the intensity of the emitting fluorescence is expressed as

$$I_f \propto [{}^1\mathrm{NQ}^*] + \gamma[{}^1\mathrm{NQ}^*/\mathrm{CD}] \tag{2}$$

where $[{}^1\mathrm{NQ}^*]$ and $[{}^1\mathrm{NQ}^*/\mathrm{CD}]$ represent the concentration of the excited NQ and included excited NQ, respectively. The coefficient γ shows the enhancement factor, namely, increase of the efficiency of the emitting fluorescence intensity in the CD cavity. A roughly estimated equilibrium (association) constant (K) by the concentration change of α-CD (0−40 mM) keeping that of NQ (2 mM) is ca. 5×10 M^{-1}, and the efficiency of the fluorescence emission in α-CD was ca. 13 times larger ($\gamma \approx 13$) than that of free NQ in aqueous solution. This equilibrium constant shows that approximately two-thirds of NQ molecules are included in α-CD in the solution employed for the tr-ESR experiments. In the case of the other CDs, the data were scattered and not always quantitative, but similar trends were observed. For example, K was about 2×10^2 M^{-1} and $\gamma \approx 12$ for NQ in *β*-CD. These fluorescence data suggest efficient formation of the inclusion complex in the systems of NQ and MNQ in CDs.

For the purpose of further direct confirmation of the equilibrium conditions of the inclusion, NMR spectra of NQ protons in the solution of α-CD (and *β*-CD) were observed in D_2O. The observation of the nuclear polarization of protons in NQ induced by the nuclear Overhauser effects by pumping the protons of the α-CD and *β*-CD directly showed the existence of the inclusion complex. The observation of the chemical shifts of the proton signals of NQ by the concentration change of α-CD (0−120 mM) keeping that of NQ constant (2 mM) provides the equilibrium constant of the present system as 7 M^{-1}. Although the conditions of the solvent (H_2O and D_2O) are different, the difference of the equilibrium constants is too large to be explained solely by the experimental error. The NMR method showed that about a quarter of NQ molecules are included in α-CD in equilibrium under the conditions of the present tr-ESR observation. Since the concentration range is much larger than that of the fluorescence method, the simple assumption of 1:1 complex formation in all the conditions is doubtful. Anyway, large amounts of NQ molecule are included in CDs in the present tr-ESR observation.

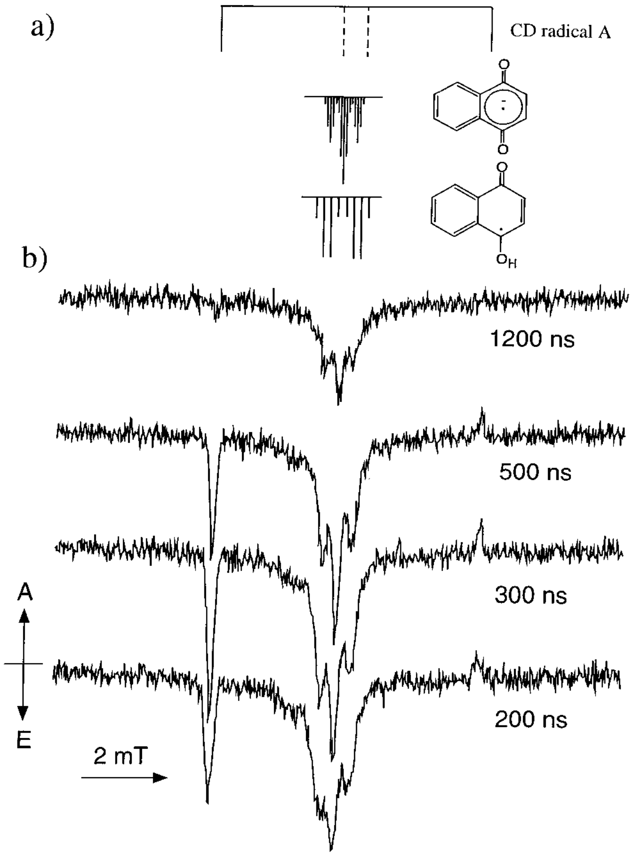

Figure 2. Time-resolved ESR spectra observed in the photolysis of NQ (2.5 mM) in α-CD (40 mM) (b), and the simulated stick spectra of NQ radicals and CD radical A (a).

Tr-ESR Observation of NQ in α-CbfbfD. Figure 2 shows the tr-ESR spectra observed in the photolysis of NQ in α-CD. The signal grows up within 300 ns and then decays slowly. The spectra were analyzed to be composed of at least two paramagnetic species that will be shown later. The spectral pattern is emissive with a slight E/A pattern (emission in low field and absorption in high field); namely, E*/A. The emission implies that reaction takes place by way of the excited triplet state of NQ in α-CD, and this is called the triplet mechanism (TM), because the TM polarization of the photoreaction of NQ has been known to be emissive.[14−18] The $S-T_{-1}$ mixing under the conditions of a large exchange interaction (J) and long time interaction in the intermediate radical pair may also induce emissive TM-like polarization. The contribution of this mechanism cannot be excluded. The E/A pattern is due to the triplet precursor radical pair mechanism, which proves that the intermediate radical pair formed in the photolysis of NQ in

TABLE 1: HFC Constants

quinone radicals	number/positions of H	HFCC (mT)
$NQH^{\bullet}$	1/H(2)	0.694[a]
	2/H(5,7)	0.165
	1/H(4/OH)	0.165
$NQ^{-\bullet}$	2/H(2,3)	0.320[b]
	2/H(5,8)	0.066
	2/H(6.7)	0.066
$MNQH^{\bullet}$	3/H(2/CH3)	0.684[a]
	1/H(3)	0.059
	2/H(5,7)	0.155
	1/H(4/OH)	0.155
$MNQ^{-\bullet}$	3/H(2/CH3)	0.302[c]
	1/H(3)	0.237
	4/H(5.6.7.8)	0.066
CD radicals		
A (α- & β-CD)	2/H(β−protons)	3.03 (∼ +0.5)[d]
		3.03 (∼ −0.5)
B (β- & γ-CD)	3/H(β−protons)	3.35[d]
		1.08
		0.66
C (γ-CD)	2/H(α- or β-protons)	2.77 (∼ +0.5)[d]
		2.77 (∼ −0.5)

[a] Reference 21. [b] Reference 20. [c] Reference 24. [d] This work.

α-CD diffuses away from the included conditions and the radicals reencounter to induce the RPM polarization.

Another important result is the CD concentration effect. The concentration change of CD did not show any significant change of the spectral shape such as the ratio of the TM and RPM in α-CD and also in the other CD systems. The system of MNQ in CDs also showed concentration independent spectral pattern. If the reaction is initiated by the free collision by diffusive motion between the excited NQs and CD molecules, the spectral shape is dependent on the concentration of CD, because the intensity of the TM polarization in free diffusion is dependent on the reaction rate with CD, while the RPM polarization is independent of the initial reaction rate. Therefore, the independence of the CD concentration implies that the reaction takes place efficiently only in the included complex. The low reactivity of the excited NQs in aqueous phase may be due to the property of the lowest excited triplet state because the excited triplet state of para-quinones is sensitive to its environment.[19] In highly polar media such as H_2O, the $^3n\pi^*$ state of NQ shifts energetically higher than that of $^3\pi\pi^*$. That makes the reactivity of the lowest excited-state such as the hydrogen atom abstraction low.

Figure 2a shows the simulated stick spectra of NQ anion radical ($NQ^{\bullet-}$)[20] and NQ neutral (semiquinone/$NQH^{\bullet}$) radical[21] (see Table 1) for the assignment of the center portion of the spectrum. According to the comparison with the simulated stick spectra it is apparent that the $NQ^{\bullet-}$ radical is mainly formed in this system. By careful analysis we concluded that here existed a weak contribution of the $NQH^{\bullet-}$ radical. The two-line spectrum with E*/A pattern observed at the both side of the center spectrum is assumed to be the part of the triplet one or both side lines of the doublet of doublet, and center line(s) may be superimposed on those from NQ. In that case the hyperfine coupling constant (HFCC) of this species, the triplet or the average of two HFCCs, is 3.03 mT. This value seems to be a bit larger than that of the ordinary isotropic HFCC of a carbon centered radicals in liquid phase.

This spectrum with a large HFCC is assigned to the α-CD carbon centered radical (CD radical A) due to the following analysis. At this stage we should remember that we are handling a huge CD molecules having rather rigid frameworks. Although there exist 6 sites having hydrogen atom(s) in one glucopyranose unit (hydroxy groups are not counted) where a hydrogen atom can be abstracted, four reaction sites, which give the HF splitting of two protons of the radical formed, become the candidates of this spectrum. Because of the large HFCC, it is easily assumed that two β-protons are not freely rotating around the molecular axes which connect with the radical center carbon. The HFCCs of two protons provide the estimate of the angle (θ), which is the twist between the p-orbital of the radical center carbon and the plane containing the β-proton C−H bond. The angle dependence of HFCC is given by the following equation:

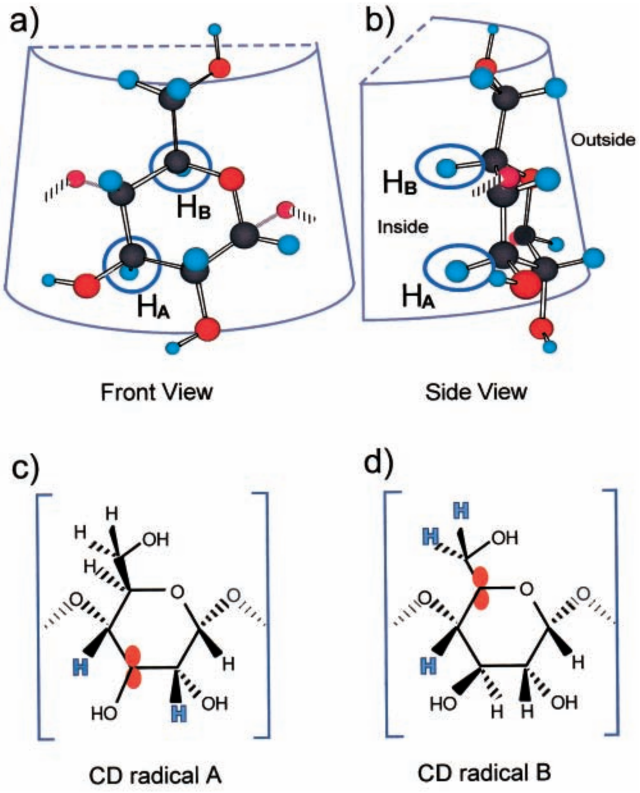

Figure 3. The front (a) and side (b) views of a CD structure showing a unit glucopyranose molecule. Here, H_A and H_B show the most actively reacted protons in the present systems (see text). Chemical equations, (c) and (d), are the assigned structure of CD radical A and B, respectively.

$$a(\theta) = B_0 + B_2 \cos^2 \theta \qquad (3)$$

where the spin is assumed to be localized on the p-orbital and the values of $B_0 = 0.32$ mT and $B_2 = 4.35$ mT are used.[22] The center line(s) are superimposed on the spectra of the radical(s) from NQ showing the width of about 1 mT. This gives some allowable possibility of two angles as 38° (if equivalent) or $\theta_1 = 38 - \alpha$ and $\theta_2 = 38 + \alpha$ where α is less than 7° (unless equivalent). These HFCCs excluded the methylene hydrogen of the hydroxymethyl group as the possible reaction site because the α-proton should show much smaller value (2.4 mT or less). Therefore, three sites remain as the candidates of the reaction site. Furthermore, one proton is extruded into the CD cavity (H_A in Figure 3) and two outside as shown in Figure 3. If the reaction takes place exclusively inside of α-CD, we may determine the molecular structure of the α-CD radical and may visualize the photochemical reaction of NQ included in α-CD. If a C−H bond where the hydrogen atom can be abstracted directs into the α-CD cavity and two β-protons which equivalently or slight differently configured to the p-orbital of the

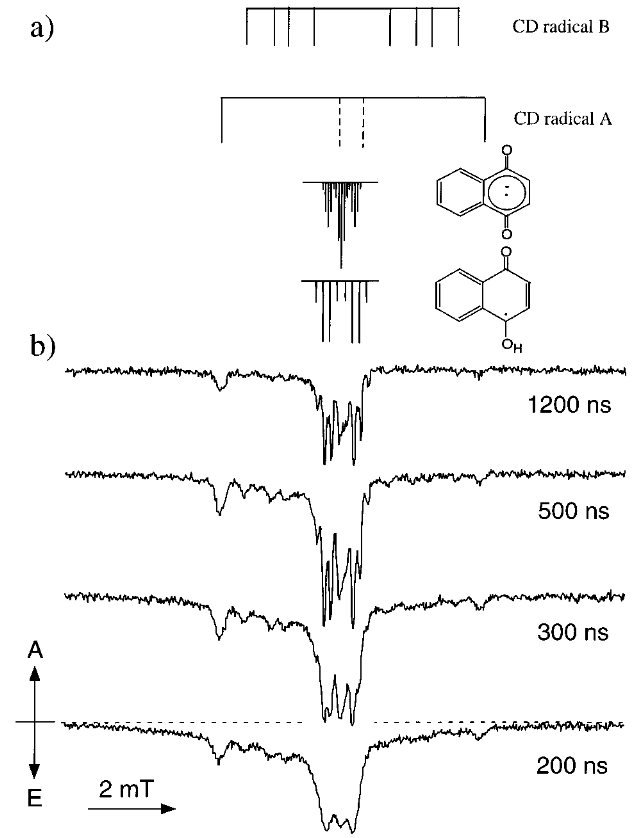

Figure 4. Time-resolved ESR spectra observed in the photolysis of NQ (2.5 mM) in β-CD (15 mM) (b), and the simulated stick spectra of NQ radicals and CD radical A and B (a).

radical center formed by the reaction, only one structure of the α-CD radical becomes a candidate that is illustrated in Figure 3c.

According to the above results and assignment of the radical species, there arises one question about the formation of $NQ^{\bullet -}$ radical contrary to the hydrogen abstraction from the α-CD molecule. It is easily assumed that the initial reaction takes place inside of the CD and the neutral $NQH^\bullet$ radical is formed by the hydrogen abstraction reaction immediately after laser irradiation. The $NQH^\bullet$ radical is converted to the anion radical by the deprotonation process that is controlled by α-CD cavity and escapes from the cavity to be a free anion radical.

$$^3NQ^*/\alpha\text{-CD} \rightarrow NQ^{\bullet -} + \alpha\text{-CD}^\bullet + H^+ \qquad (4)$$

Direct formation of the NQ anion radical by the electron transfer from the glucopyranose unit is unlikely, because of no appearance of the cation radical as the counter radical of this reaction. Furthermore, the formation of the carbon center radical of CD by the deprotonation of CH parts of glucopyranose unit cation cannot be acceptable. As for the reaction of excited free NQ molecule with CD in the solution, every CD showed different CD radicals having different radical center(s) in the CD frame, as we will mention in the following section. This also suggests that the reaction from outside of CD is unlikely, because all the CDs have the same glucopyranose CH bonds projected to the outside of their CD framework in the same manner and the same CD radical(s) can be expected to appear.

Tr-ESR Observation of NQ in β-CD. Figure 4 shows the tr-ESR spectra observed in the photolysis of the system of NQ in β-CD. The spectra are similar to those obtained in the system of NQ in α-CD, but several differences are recognized clearly. First of all, immediately after laser excitation there appears a reproducible broad emissive spectrum, which decays quickly and the other radical species grow up slowly. This spectrum seems to be shifted to the lower field or asymmetrically distorted. Second, the center portion of the spectrum consists mainly of the neutral $NQH^\bullet$ radical by comparing with the stick spectra as shown in Figure 4a. Third, the spectrum with several HF lines of much smaller HFCCs appears along with that with large HFCCs. The polarization pattern of these radical species is emissive with slight E/A distortion. The broad short-lived species must be a kind of precursor state of the finally formed radicals. One candidate is the excited triplet state of NQ included in the β-CD cavity. Another possibility is the observation of the precursor radical pair showing the dipole−dipole and/or exchange interaction. The former possibility may be excluded because of the fast reactivity and the fast spin−lattice relaxation time of the excited triplet state at room temperature in general. In fact this broad spectrum was not recognized in aqueous solution without CDs and this spectrum was not apparently observed in α- and γ-CD systems employed in the present experiments. The observation of the radical pair in β-CD is the most probable explanation. The totally emissive pattern of the spectrum may be rationalized by the spin polarization transferred from the excited triplet NQ to the radical pair formed by the reaction. The asymmetrical distortion of this spectrum may be explained by the imperfect random distribution of the principal axes of the radical pair[5,9,23] compared with those in the excited triplet state of NQ in slowly tumbling β-CD. The slow rise of the spectra of free radical species is explained by the delayed dissociation of the trapped radical pair in the case of NQ in β-CD.

$$^3NQ^*/\beta\text{-CD} \rightarrow (^3NQH^\bullet/\beta\text{-CD}^\bullet) \rightarrow NQH^\bullet + \beta\text{-CD}^\bullet \qquad (5)$$

The observation of the neutral $NQH^\bullet$ radical as being the mainly contributed species in this system seems to be very consistent, because the primary reaction is believed to be the hydrogen atom abstraction from the β-CD molecule. This also supports the reaction pathway assumed in the case of NQ in α-CD where $NQ^{\bullet -}$ radical is predominantly formed by the deprotonation after the hydrogen abstraction reaction. The difference between α- and β-CDs may be rationalized by the environment and/or the size of those inclusion compounds. Since the cavity size in α-CD is much smaller than that in β-CD, the environment of $NQH^\bullet$ radical is much more polar than that in β-CD as known in general. This suggests that deprotonation of the $NQH^\bullet$ radical to form $NQ^{\bullet -}$ takes place in the cavity of α-CD efficiently when the radical pair dissociates to the free radicals.

As for the carbon centered radicals observed when β-CD is used, there are two different kinds of radicals. One of the radicals showing the largest HFCC has an almost identical structure to that observed in α-CD (CD radical A) except the line width. The broadened line width of this spectrum observed in β-CD may be due to the short spin−spin relaxation time (T_2) by the slow molecular motion of a large β-CD framework. The other extra lines are assigned to a different hydrogen abstracted β-CD radical with different molecular structure from that of the large HFCC one. This radical has three nonequivalent β-protons having the HFCCs of 3.35, 1.08, and 0.66 mT (CD radical B). From the analysis as used before, the angles from the direction of p-orbital of the radical center are 34, 65, and 74°. For this reason only one site is the candidate of the reaction site as shown in Figure 3 where the reactive hydrogen atom (H_B) is projected inside of the cavity. The formation of CD radical B may be

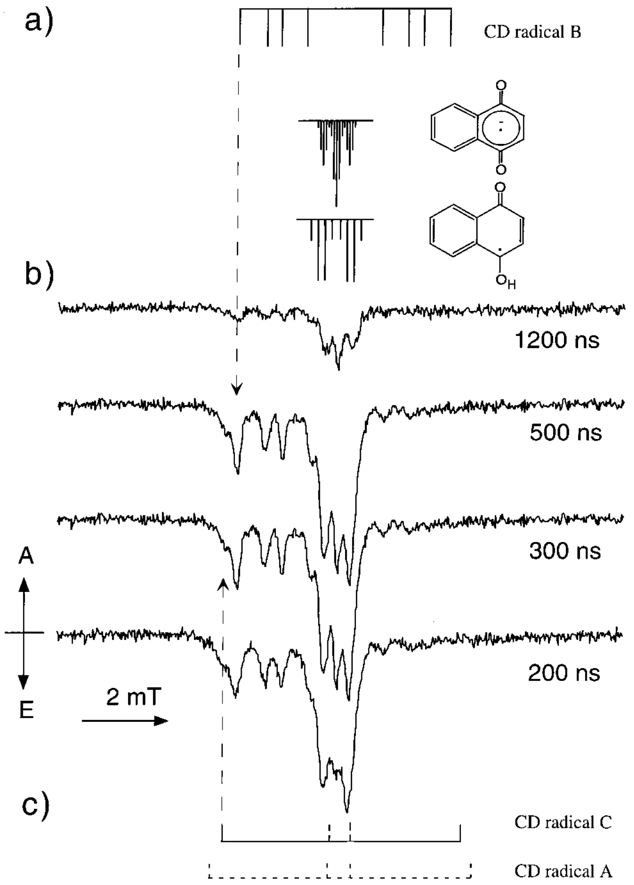

Figure 5. Time-resolved ESR spectra observed in the photolysis of NQ (2.0 mM) in γ-CD (20 mM) (b), and the simulated stick spectra of NQ radicals and CD radical B (a). The stick spectrum of CD radical C is given along with that of A (c). The vertical arrows with broken lines indicate the lowest field positions of B and C.

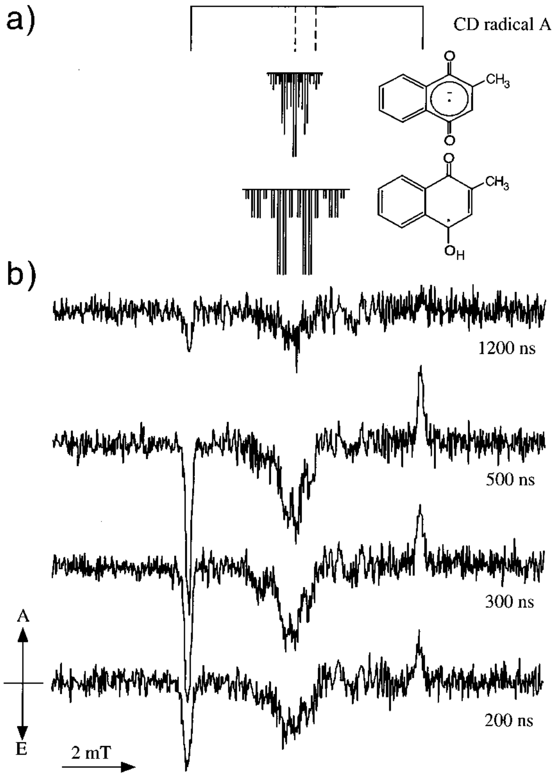

Figure 6. Time-resolved ESR spectra observed in the photolysis of MNQ (2.0 mM) in α-CD (40 mM) (b), and the simulated stick spectra of MNQ radicals and CD radical A.

due to the large cavity sized β-CD where the guest molecule can locate deep inside of the cavity.

Tr-ESR Observation of NQ in γ-CD. In the case of NQ in γ-CD, The observed spectrum is a bit different from previously presented two cases as shown in Figure 5. The center portion is not easily analyzed by the superposition of the spectra of more than two radicals, but it is mainly due to the $NQ^{\bullet-}$ radical when the spectrum at later time is analyzed. There exist at least two different γ-CD radicals. The main radical showing many HF lines is assigned to three proton radicals that is nearly identical to that observed in β-CD (CD radical B). Another very weak signal may be due to a two proton radical (CD radical C). This radical is different from the large HF one (CD radical A) observed in the systems of α- and β-CDs, because of their smaller HFCCs. One possibility is the observation of a distorted unit glucopyranose radical (CD radical A) due to the large frame structure of γ-CD, but appearance of such a frame distortion only in γ-CD is questionable. Another possibility is the hydrogen abstraction reaction by the deeply included photoexcited NQ from the methylene group which is connected with the hydroxy group, namely, the formation of a radical with one α- and one β-protons. However these mechanisms have not been clarified, the reaction by the free diffusion of the excited NQ with γ-CD is unlikely, because the other CDs do not show this spectrum.

These data suggest that the hydrogen abstraction reaction from γ-CD also takes place and the deprotonation of $NQH^{\bullet}$ occurred like the case of α-CD. The different CD radical formation may be due to the much larger and flexible cavity size of γ-CD, but the deprotonation in γ-CD is not easily rationalized. One explanation is the inclusion of two NQ molecules in the cavity that makes the environment of NQ more polar-like conditions or $NQH^{\bullet}$ radical interacts with the ground-state NQ in the cavity. The main apparent reaction in γ-CD is

$$^{3}NQ^{*}/\gamma\text{-CD} \rightarrow NQ^{\bullet-} + \gamma\text{-CD}^{\bullet} + H^{+} \tag{6}$$

The accurate comparison of the system of γ -CD with the other CD ones is difficult, because all the experiments about γ -CD system were performed at 40 degree Celsius to increase the solubility.

Tr-ESR Observation of MNQ in CDs. As for the MNQ, the tr-ESR spectra observed in α-, β-, and γ-CDs are shown in Figures 6, 7, and 8, respectively. The results were very similar to those observed in the NQ systems. The simulated stick spectra of $MNQH^{\bullet}$ and $MNQ^{\bullet-}$ radicals[21,24] using the reported HFCCs are given in Figures 6a, 7a, and 8a. According to these results, we can safely conclude that the main radical species from MNQ are $MNQ^{\bullet-}$ radical in α-CD. and $MNQH^{\bullet}$ neutral radical in β-CD. The cause of this difference is due to the cavity size of the respective CDs like the systems of NQ in these CDs. The HFCCs of the CD radicals were almost identical to those obtained in the case of NQ system, namely, CD radical A in α-CD and both radicals A and B in β-CD.

$$^{3}MNQ^{*}/\alpha\text{-CD} \rightarrow MNQ^{\bullet-} + \alpha\text{-CD}^{\bullet} + H^{+} \tag{7}$$

$$^{3}MNQ^{*}/\beta\text{-CD} \rightarrow (^{3}MNQH^{\bullet}/\beta\text{-CD}^{\bullet}) \rightarrow + MNQH^{\bullet} + \beta\text{-CD}^{\bullet} \tag{8}$$

A broadened spectrum with an emissive character also appeared in the system of MNQ in β-CD immediately after laser excitation (Figure 7). This may be due to the intermediate radical pair confined in the β-CD cavity as explained in the case of

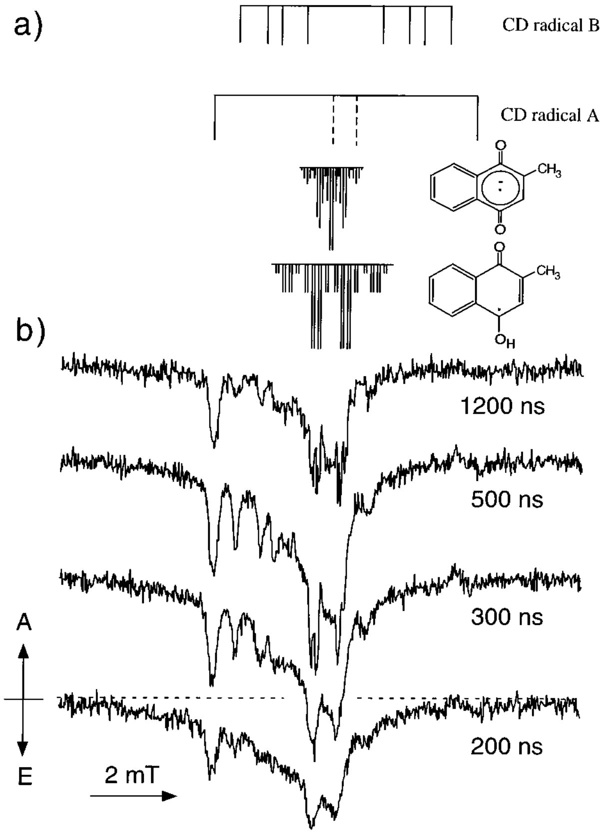

Figure 7. Time-resolved ESR spectra observed in the photolysis of MNQ (2.0 mM) in β-CD (15 mM) (b), and the simulated stick spectra of MNQ radicals and CD radical A and B (a).

NQ in β-CD. This pair may dissociate to free radicals in the time scale of a few hundreds of nanoseconds.

In the system of MNQ in γ-CD, the results of the spin polarization and the spectra from γ-CD radicals were also very similar to those observed in the system of NQ (CD radical B and C) but the intensity of CD radical C was a little enhanced. The center portion is mainly composed of the spectrum of the $\text{MNQH}^\bullet$ contrary to the $\text{NQ}^{\bullet -}$ in the system of NQ in γ-CD.

$$^3\text{MNQ}^*/\gamma\text{-CD} \rightarrow \text{MNQH}^\bullet + \gamma\text{-CD}^\bullet \qquad (9)$$

The respective observation of the $\text{NQ}^{\bullet -}$ and $\text{MNQH}^\bullet$ radicals in the systems of NQ and MNQ in γ-CD cannot be rationalized at this stage, but some delicate condition change, such as the number of the NQs included in the cavity and their mobility, may affect the deprotonation process in γ-CD.

Conclusion

NQ and MNQ included in three different CDs were photolyzed in aqueous solution, and the tr-ESR spectra of the intermediate paramagnetic species were studied to investigate the photochemistry of these inclusion systems. All the systems showed the CIDEP spectra which were explained by the hydrogen abstraction reaction from the inside of the framework of CDs at the initial step. In the case of α-CD, the anion radicals of NQ and MNQ mainly appeared which were concluded to be produced by way of deprotonation of the neutral semiquinone radicals initially formed in the CD cavity. In the case of β-CD, the neutral semiquinone radicals from NQ and MNQ were mainly appeared. γ-CD showed different main species, anion radicals in the case of NQ and semiquinone in the case of MNQ. The difference of the appearance of these species may be due to the environment of NQs in different CD cavities such as the polarity. The E/A type CIDEP spectra indicate that the radical species eject from the CD cavity after its birth. The spectra of CD radicals show the most reactive site of the frame of CDs. When larger sized CDs (β- and γ-) were used, two different CD radicals were observed. This indicates that the reactive site increases in larger and more flexible CD cavity conditions. Furthermore, the observation of broad spectra in the systems of NQs in β-CD showed the existence of the long-lived transient radical pair strongly coupled and stabilized in the β-CD cavity. The observation of common carbon center radicals in three CDs indicates that the molecular frame of the glucopyranose unit is rigid and not heavily distorted by the size of CDs.

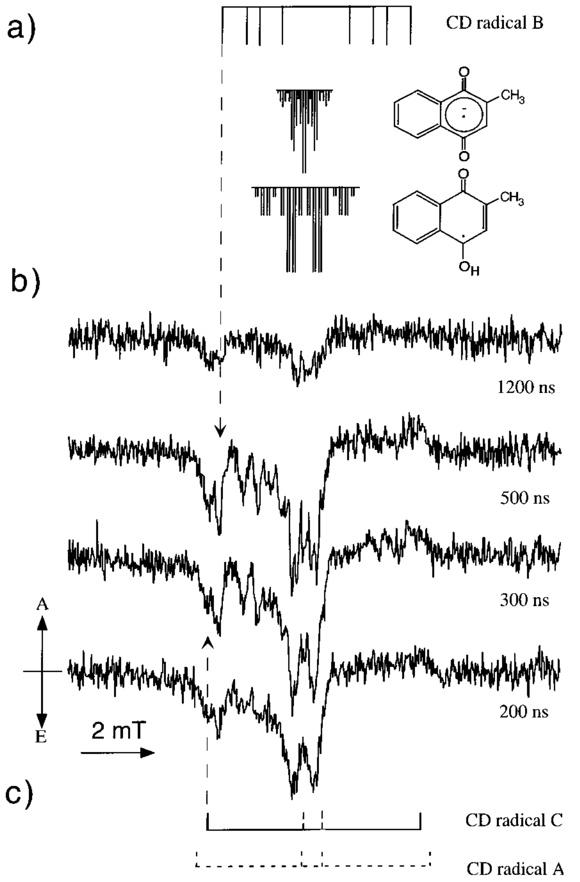

Figure 8. Time-resolved ESR spectra observed in the photolysis of MNQ (2.0 mM) in γ-CD (40 mM) (b), and the simulated stick spectra of MNQ radicals and CD radical B (a). The stick spectrum of CD radical C is given along with that of A (c). The vertical arrows with broken lines indicate the lowest field positions of B and C.

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