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Investigation of Photoinduced Electron Transfer of the Model Vitamin E−Duroquinone System by Means of Femtosecond Spectroscopy

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Abstract: Photoinduced electron transfer (ET) of the model vitamin E−duroquinone system (MVE-D) has been investigated by means of femtosecond spectroscopy. The interaction between the vitamin E and duroquinone moieties is not extensive in the ground state, and the charge-transfer band is not clearly seen in the absorption spectrum. The bonding of vitamin E to duroquinone largely reduces the lifetime of the lowest excited singlet state (S_1 state) of duroquinone owing to ET from the vitamin E moiety to the duroquinone moiety. Since the S_1 state [(n,π*) state] of duroquinone is regarded as a model for the peroxyl radical, the reduction of the lifetime is direct microscopic observation of the initial stage in the corresponding part of the antioxidant process of vitamin E. It is considered that the photoinduced ET of MVE-D corresponds to the inverted regime. The vibrational modes of the product reduce the lifetime by opening ET vibronic channels which have small barriers.

Introduction

The study of electron transfer (ET) processes is at the forefront of the revolution in the molecular level understanding of chemical reaction in liquid.[1−3] It is a chemically very simple process, which is readily accessible to both accurate measurements and quantitative theoretical analyses. Furthermore, the ET processes play a central role in various practical areas.

Important examples of ET are also found in biochemistry. Vitamin E (α-, β-, γ-, and δ-tocopherols) inhibits autoxidation of organic molecules and acts as an antioxidant.[4,5] The antioxidant reaction system includes

$$\mathrm{LOO^\bullet + TocH \rightarrow LOOH + Toc^\bullet} \qquad (1)$$

where LOO$^\bullet$, TocH, LOOH, and Toc$^\bullet$ stand for a peroxyl radical, a tocopherol, the hydroperoxide, and the tocopheroxyl radical, respectively. In previous papers,[6,7] S.N. and co-workers concluded that ET plays an important role in the initial stage of reaction 1. Their explanation can be widely applicable to many similar reactions in addition to the corresponding parts of the antioxidant and prooxidant reactions of TocH.[6−8] However, details of the reaction mechanism have not necessarily been elucidated so far. Especially, direct microscopic observation of the initial stage of reaction 1 has not been reported so far.

In order to directly observe the initial stage of reaction 1, it is desirable to synthesize a bridged system of TocH and a precursor of LOO$^\bullet$, to produce TocH−LOO$^\bullet$ with a laser pulse, and to initiate reaction 1. However, since it is difficult to synthesize such a precursor, we have sought a model for LOO$^\bullet$ instead.

For the following reason, the lowest excited singlet state (S_1 state) of benzoquinones [(n,π*) type] can be regarded as a model for LOO$^\bullet$. In the S_1 state of benzoquinones, a nonbonding electron is promoted to a delocalized π* orbital with another electron in the nonbonding orbital. The S_1 state tends to undergo various photoreactions. The postulate that a half-filled n orbital of the ^{1}(n,π*) state dominates the electronics of the photoreaction suggests that the S_1 state is a suitable model for alkoxyl radical; the usefulness of such a model is now widely recognized.[9] Since the reactivity pattern of TocH for reaction 1 does not depend on the type of oxyradicals,[10] it seems reasonable to use the S_1 state as a model for LOO$^\bullet$.

Thus, we have synthesized a model vitamin E−duroquinone system (2-[3-(3,4-dihydro-6-hydroxy-5,7,8-trimethyl-2*H*-1,3-benzoxazinyl)]methyl-3,5,6-trimethyl-2,5-cyclohexadiene-1,4-dione, abbreviated hereafter as MVE-D). To facilitate the organic synthesis, we have used duroquinone as the precursor of the model for LOO$^\bullet$. Then, we have investigated the dynamic process following photoexcitation of the duroquinone moiety of MVE-D by means of femtosecond spectroscopy. As described above, the process following photoexcitation of the duroquinone moiety of MVE-D corresponds to the initial stage of reaction 1.

On the other hand, ubiquinone and plastoquinone are well-known as typical biological quinones. The function common to these quinones in biology is to act as the redox component of transmembrane electron transport systems. However, aromatic ketones such as these molecules are also effective photoinitiators of lipid peroxidation,[11] and TocH's may directly

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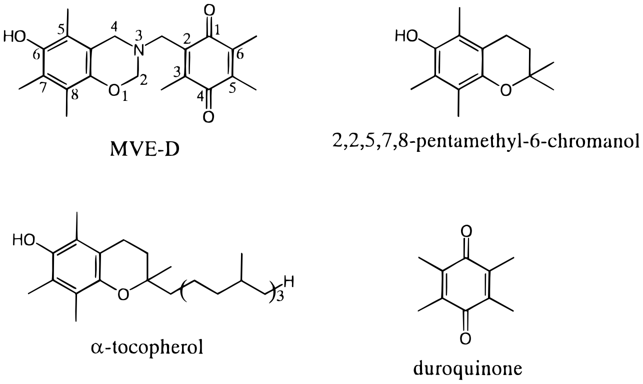
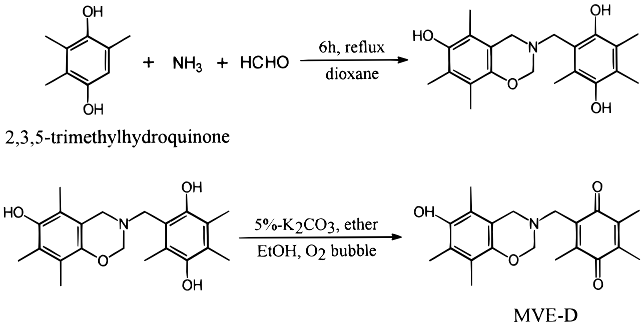


Figure 1. Molecular structures of MVE-D, α-TocH, TocHM, and duroquinone and the numbering system for the atoms of MVE-D used in the present work.

Scheme 1



prevent the light-induced initiation of peroxidation by these molecules. The process following photoexcitation of the duroquinone moiety of MVE-D can also be regarded as the initial stage of such an antioxidant reaction.

From the experimental results of MVE-D obtained by means of femtosecond spectroscopy, the detailed mechanism of these antioxidant reactions is discussed in the present paper. The structures of molecules studied in this work are shown in Figure 1, together with the numbering system for the atoms of MVE-D.

Experimental Section

Sample Preparation. MVE-D was synthesized according to Scheme 1 for the first time for the sake of this study. Experimental details for the preparation and characterization of MVE-D are available as supporting information. In order to obtain deuterated MVE-D (MVE-D-d_1), MVE-D was dissolved in ethyl alcohol-*d* and the solution was refluxed. Replacement of the hydrogen atom of the OH group of MVE-D by a deuteron was verified by proton NMR.

In the present study, experimental results of MVE-D are compared with those of 2,2,5,7,8-pentamethyl-6-chromanol (TocHM) and duroquinone. Since TocHM has no phytyl side chain at the 2-position as well as MVE-D, TocHM is used instead of α-TocH in the present study. TocHM was prepared according to the method of Nilsson et al.[12] Commercially obtained duroquinone was used without further purification.

Methanol (MeOH), methyl-d_3 alcohol-*d* (MeOD), ethanol (EtOH), 1-propanol (PrOH), 1-butanol (BuOH), 1-octanol (OcOH), acetonitrile (ACN), propionitrile (PrCN), acetone, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) used in the spectroscopic measurements were all of spectroscopic grade or guaranteed grade, and were used without further purifications.

Measurements. All the experiments were made at room temperature. Steady-state absorption spectra were obtained with a Shimadzu UV-2100S spectrometer.

The femtosecond transient absorption apparatus was described in detail previously.[13] Briefly, a Ti:sapphire oscillator (Clark NJA-2) pumped by 3.7 W from an Ar^+ laser (Spectra Physics 2060) produced about 90-fs pulses[14] which were amplified utilizing a chirped-pulse-amplification scheme.[15] The femtosecond pulses from the oscillator were temporally stretched to 130 ps and seeded into a Ti:sapphire regenerative amplifier pumped by a Nd:YLF laser (527 nm, 6.2 W, 2 kHz, Quantronix 117). After amplification and recompression, the output consisted of 130-fs, 780-nm, 180-μJ pulses at a repetition rate of 2 kHz. Next 45% of the amplifier output was frequency doubled in β-BBO to produce 25-μJ pulses at 390 nm, which were used to excite MVE-D to the $^1(n,\pi^*)$ state. The remaining light was used to generate a white-light continuum by focusing it into a fused-silica flat. The probe pulse was obtained by wavelength selection of this continuum using interference filters (Corion, 10 nm bandwidth). A half-wave plate in the pump beam was adjusted to obtain magic-angle polarization between the pump and probe beams. The change in optical density (ΔOD) following the photoexcitation was monitored with a temporally delayed probe pulse.

Pump and probe pulses were focused, but the sample was not placed at the focus of the pump pulse, making the beam larger than the $\approx$200 μm spot size of the probe beam. The pump and probe pulses passed through the same lens (10 cm focal length) before the sample, but the spot size of the pump beam could be independently varied by adjusting a telescope in this beam. The pump beam was enlarged to the point at which it did not generate continuum in the sample.

The transient thus obtained was fit to a sum of exponentials convolved with the instrument-response function. The transients obtained by probing at various wavelengths were combined to yield the transient absorption spectrum (ΔOD spectrum as a function of probe wavelength).

Freshly prepared solutions were used in the measurements of femtosecond transients. The concentrations of samples were 10^{-4} to 10^{-2} M. A rectangular quartz cell (2 mm in light-path length) or a quartz flow cell (1 mm in light-path length) was used in the measurements. The sample solution in the rectangular cell was changed repeatedly to minimize accumulation of unwanted chemical species.

Results and Discussion

Steady-State Absorption Spectrum. Figures 2a–c show the steady-state absorption spectra of MVE-D, TocHM, and duroquinone in MeOH, respectively. The absorption spectrum of MVE-D can substantially be made up by the superposition of those of TocHM and duroquinone. From these results, it is considered that the interaction between the vitamin E and duroquinone moieties is not extensive in the ground state (S_0 state). Bridged methoxyphenol–benzoquinone systems (monomethyl ethers of *syn*- and *anti*-[3.3]paracyclophan-quinhydrone) show the charge-transfer band around 390 nm and its absorption coefficient is large (a few thousand).[16] Although MVE-D is close in molecular constituent (methoxyphenol and benzoquinone derivatives) to these systems, the charge-transfer band is not clearly seen in the absorption spectrum of MVE-D.

From analogy with duroquinone and TocHM, the absorption bands of MVE-D (Figure 2a) can be assigned in the following way. The absorption bands above 310 nm are due to those of the duroquinone moiety. The lowest and second excited singlet states (S_1 and S_2 states) of MVE-D correspond to the S_1 and S_2 states of (n,π^*) type in the duroquinone moiety, respectively. The $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of MVE-D show broad absorption bands around 460 and 340 nm, respectively, as in the case of duroquinone. The absorption band located at 295

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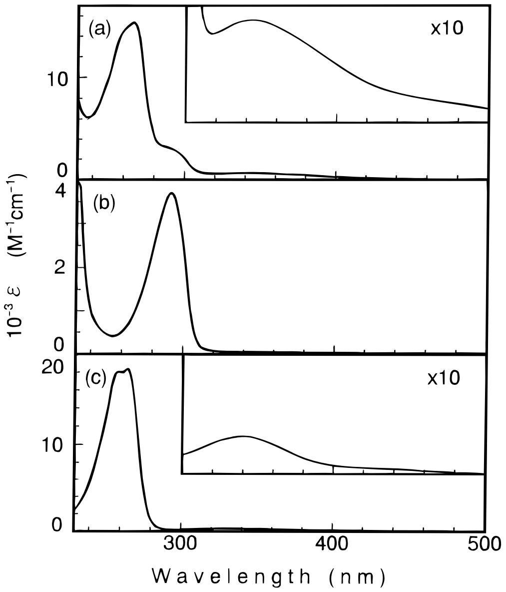

Figure 2. Steady-state absorption spectra of MVE-D (a), TocHM (b), and duroquinone (c) in MeOH. The spectra shown in the upper right-hand corners in parts a and c show the absorption spectra in the range 300−500 nm in which the vertical scales are enlarged ten times.

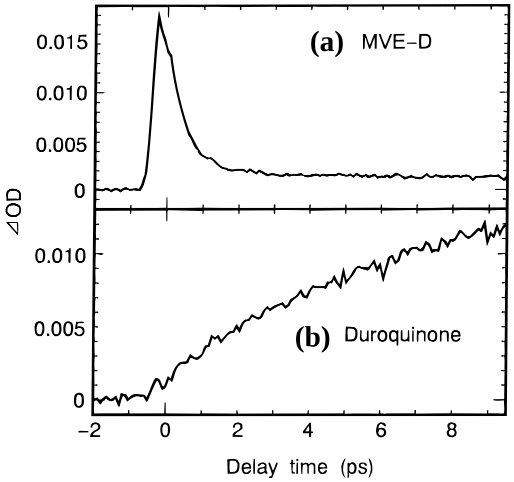

Figure 3. Femtosecond pump-probe transients of MVE-D (a) and duroquinone (b) in MeOH. The probe wavelengths for MVE-D and duroquinone are 430 and 480 nm, respectively. A rectangular cell was used in the measurements.

nm arises from the transition to the third excited singlet state (S_3 state) of MVE-D and is assigned to the S_1 state of (π,π*) type in the vitamin E moiety.

Femtosecond Spectroscopy. Figures 3a and 3b show the pump-and-probe absorption transients after photoexcitation to the S_2 states [(n,π*) type] of MVE-D and duroquinone in MeOH, respectively. The absorption transient of MVE-D is very different from that of duroquinone.

In duroquinone, the transient is well-characterized by an exponential rise and a plateau (see supporting information, too). The rise time is obtained to be 5.7 ps and is considered to correspond to the lifetime of the S_1 state when the rate of the $S_2 \rightarrow S_1$ internal conversion is assumed to be very fast. The plateau is due to the T−T absorption.[17−20]

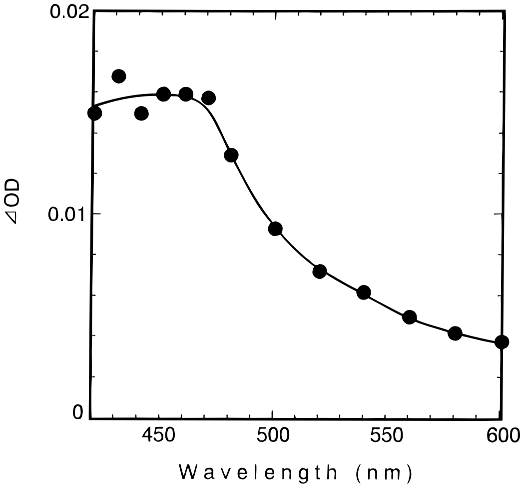

Figure 4. Transient absorption spectrum for the fast component of MVE-D in MeOH. A rectangular cell was used in the measurements of the transient absorption. The amplitude of the fast component in the double-exponential fit was used to construct this spectrum. The curve was drawn only as an eye guide.

In MVE-D, the transient is well-characterized by a double-exponential decay. The decay times (the weights) in MeOH are 490 fs (91 %) and about 27 ps (9%); the small signal intensity of the slow component leads to serious errors in estimation of its decay time. From Figures 3a and 3b, the relaxation process following photoexcitation of the duroquinone moiety in MVE-D is considered to be very different from that of duroquinone.

When a rectangular cell is used in the measurements, the proportion of the slow component in the pump-probe transient of MVE-D is large. However, when a flow cell is used, it is small. From these results, the slow component is likely due to the transient absorption of the photoproduct. When a stale solution is used, the proportion of the slow component is also large. At present, we cannot make an unambiguous assignment of the species with the 27-ps lifetime. In this paper, we confine our attention to the fast component. Since the pump-laser power dependence of the amplitude of the fast component is linear, multiphoton excitation is unlikely to play a role in the dynamics of the fast component. The decay time of the fast component (τ_f) is independent of the concentration of MVE-D throughout the concentration range studied.

In order to assign the species corresponding to the fast component of MVE-D, its transient absorption spectrum in MeOH has been reconstructed from the absorption transients (Figure 4). The spectrum has a plateau or peak between 420 and 470 nm and a gradually decreasing absorption from 470 to 600 nm. Since the spectrum is close to the $S_1 \rightarrow S_m$ ($m \geq 4$) absorption spectrum of *p*-benzoquinone,[21] it is assigned to the $S_1 \rightarrow S_m$ absorption spectrum of the duroquinone moiety of MVE-D. The rate of the $S_2 \rightarrow S_1$ internal conversion is likely to occur within the lifetime of the pump light pulse (130 fs).

We have critically examined other possibilities in the assignment of the transient absorption spectrum of MVE-D (Figure 4). The transient absorption spectrum is similar to neither the steady-state absorption spectrum of durosemiquinone neutral radical nor that of duroquinone anion radical; the former has a sharp peak and a shoulder around 410 nm and the latter sharp peaks at 415 and 438 nm.[17,22] The spectrum of MVE-D is not

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Table 1. τ_f, ϵ_r, n, η, and $\langle\tau_s\rangle$

solvent	τ_f,[a] fs	ϵ_r[b]	n[b]	η,[b] cP	$\langle\tau_s\rangle$,[c] ps	$E_T(30)$,[d] kcal/mol
MeOH	490	32.70	1.33057	0.5506	3.3−6.21	55.5
MeOD[e]	550	32.70[f]	1.33057[f]	0.5506[f]	3.3−6.21[f]	55.5[f]
EtOH	640	24.58	1.3614	1.078	17	51.9
PrOH	760	20.33	1.38556	2.256	17−100	50.7
BuOH	770	17.51	1.3993	2.948	17−100	50.2
OcOH	930	10.34	1.4295	10.640		48.3
ACN	340	37.5	1.34411	0.345	0.21−0.89	46.0
PrCN	470	27.2	1.3658	0.454	0.70−1.42	43.7
acetone	490	20.7	1.35868	0.304	0.29−0.83	42.2
CH_2Cl_2	740	8.931[g]	1.42416	0.449		41.1
$CHCl_3$	1040	4.806	1.4459	0.58		39.1
CCl_4	1930[h]	2.238	1.4601	0.969		32.5

[a] The probe wavelength is 430 nm. [b] References 23 and 24. [c] References 25−27. [d] References 28−30. [e] MVE-D-d_1. [f] ϵ_r, n, η, $\langle\tau_s\rangle$, and $E_T(30)$ of MeOD were assumed to be the same as those of MeOH. [g] The value in ref 23 (0.893) is not correct. [h] Some photoproducts attached to the cell lead to difficulty in the measurements. Those lead to errors in estimation of τ_f. The photoproduct is likely to be a polar molecule and to be insoluble in CCl_4.

similar to the absorption spectrum of bridged methoxyphenol−benzoquinone systems, either, which shows a strong charge-transfer band around 390 nm.[16] The T−T absorption spectrum of duroquinone has a broad peak around 490 nm,[17−20] and is not similar to the transient absorption spectrum of MVE-D, which has a gradually decreasing absorption above 470 nm. From these facts, it is concluded that the transient absorption spectrum of MVE-D (Figure 4) is assigned to the $S_1 \rightarrow S_m$ absorption spectrum of the duroquinone moiety.

Thus, τ_f (490 fs in MeOH) corresponds to the lifetime of the S_1 state [(n,π*) type] of the duroquinone moiety in MVE-D. τ_f is much less than the lifetime of the S_1 state [(n,π*) type] of duroquinone (5.7 ps in MeOH). The bonding of vitamin E to duroquinone largely reduces the lifetime of the S_1 state of duroquinone. In MVE-D, a new relaxation route is considered to be open through the interaction between the two moieties.

τ_f's obtained in various solvents are given in Table 1 together with the dielectric constants (ϵ_r's), refractive indexes (n's), viscosities (η's) of the solvents,[23,24] the average solvation times ($\langle\tau_s\rangle$'s) extracted from the data reported previously,[25−27] and the empirical parameters of solvent polarity [$E_T(30)$'s].[28−30] τ_f decreases as ϵ_r increases (Figure 5); τ_f decreases as $E_T(30)$ increases in a series of hydrogen-bonding solvents and in a series of non-hydrogen-bonding solvents; the vitamin E moiety (a methoxyphenol derivative) and the duroquinone moiety (a benzoquinone derivative) have electron-donating and -accepting properties, respectively.[16] These facts suggest that an element of intramolecular ET from the vitamin E moiety to the duroquinone moiety is involved in the decay from the S_1 state of the duroquinone moiety.

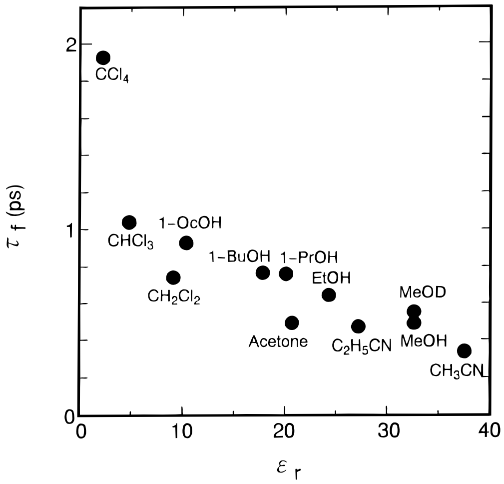

Figure 5. Plot of τ_f obtained by probing the transient at 430 nm vs ϵ_r.

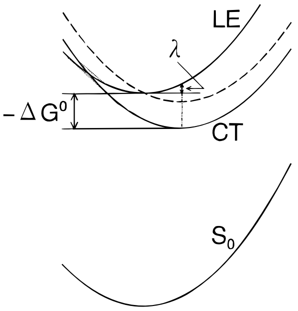

Figure 6. Schematic potential energy surfaces of MVE-D. The solid and dotted curves around the crossing point of the potential curves of the LE and CT states correspond to the non-adiabatic and adiabatic cases, respectively. The dashed curve represents a vibrationally excited level of the CT state.

Since τ_f is dependent on η only very slightly, internal motions of MVE-D are unlikely to be important in the relaxation (for example, see ref 31). Since the situation of decay obtained in carbon tetrachloride having no hydrogen atom is similar to that in other solvents, the hydrogen abstraction from the solvent will not be very important in the decay. τ_f of MVE-D-d_1 is close to that of MVE-D, and deuteration of the OH group of the vitamin E moiety does not affect τ_f very much. Although proton tunneling from TocH to $LOO^{\bullet}$ plays an important role in reaction 1,[6] proton transfer or hydrogen atom transfer is unlikely to occur yet in MVE-D in the time range studied. Hydrogen bonding between MVE-D and (a) solvent molecule(s) seems to increase τ_f.

It should be noted that τ_f is even less than $\langle\tau_s\rangle$ in some solvents. Such a result has not been observed for barrierless and normal regime ET reactions.[1,32]

Electron Transfer. As mentioned above, it is considered that the vitamin E and duroquinone moieties of MVE-D are an electron donor (D) and an electron acceptor (A) in the excited state, respectively. Historically, the precursor and product of ET are denoted by LE and CT, respectively.[33] The S_0, LE, and CT states are signified by D−A, D−A*, and D^+-A^-, respectively. The CT state of MVE-D might be signified more properly by $D^{\delta+}-A^{\delta+}$.

When the electronic interaction between D and A* is large enough, the transition probability from LE to CT is unity at the crossing point of the potential curves of the LE and CT states (see the dotted curves in Figure 6, adiabatic process). Theory and experiment have shown that for approximate models for

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ET in the adiabatic limit, $1/\tau_f$ can be directly proportional to the inverse of $\langle\tau_s\rangle$.[33]

$$1/\tau_f \approx (1/\langle\tau_s\rangle)\exp(-\Delta^{\ddagger}G/RT) \qquad (2)$$

Here, $\Delta^{\ddagger}G$ is the activation energy. In the limit of $\Delta^{\ddagger}G = 0$ (i.e., the barrierless case), $\tau_f \approx \langle\tau_s\rangle$.

However, τ_f of MVE-D is even less than $\langle\tau_s\rangle$ in some solvents. Similar results were obtained for ET of betaine[34] and 4-(9-anthryl)-*N*,*N*′-dimethylaniline.[33] From analogy with these cases, it is considered that the photoinduced ET of MVE-D corresponds to the inverted regime (Figure 6), and that the vibrational modes of the CT state reduce τ_f by opening ET vibronic channels which have small barriers (see the dashed curve in Figure 6). The high-frequency vibrational modes of the CT state apparently act as the accepting modes for the energy in the inverted regime ET process.

There is a decrease in τ_f as solvent polarity increases (Table 1). At first glance, this is opposite to our expectations for the inverted regime ET, because, as the solvent polarity increases, the standard free energy change ($-\Delta G°$) should become more exothermic; this should drive the system further into the inverted regime and should increase $\Delta^{\ddagger}G$ and τ_f. However, a result similar to that of MVE-D was also obtained for the inverted regime ET of betaine,[34] in which $-\Delta G°$ is not dependent largely on the solvent dielectric properties (Table III of ref 34). If the dependence of τ_f of MVE-D on the solvent dielectric properties is assumed to be also governed not by $-\Delta G°$ etc. but by the reorganization energy (λ), the solvent dependence of τ_f can be explained in the following way.

In Marcus theory,[35,36] $\Delta^{\ddagger}G$ in eq 2 can be expressed as

$$\Delta^{\ddagger}G = (\lambda/4)(1 + \Delta G^{\circ\prime}/\lambda)^2 \qquad (3)$$

$$\Delta G^{\circ\prime} = \Delta G^{\circ} + \omega_p \qquad (4)$$

$$\lambda = \delta^2 e^2(1/n^2 - 1/\epsilon_r)(1/2r_D + 1/2r_A - 1/r_{DA}) + \lambda_i \qquad (5)$$

Here, δ is the charge change on each of D and A* and e is the charge on the electron. ω_p refers to the work required to form a complex from the product with the solvent in dielectric equilibrium throughout the process; in the complex, the center-to-center distance between D and A* during ET is r_{DA}. r_D and r_A are radii of D and A*, respectively. λ_i refers to the work required to change the dimensions of reactants and is essentially the potential energy of a vibrational displacement. The work required to form the complex from the reactant is negligible in MVE-D since D and A* are uncharged.

The dependence of the ET rates on the solvent dielectric properties has been studied by plotting the logarithm of the rate constant as a function of $(1/n^2 - 1/\epsilon_r)$.[36−40] When ϵ_r equals n^2, the solvent is completely nonpolar. The slope of the plot (S) is expressed as

$$S = \delta^2 e^2(1/2r_D + 1/2r_A - 1/r_{DA})[(\Delta G^{\circ\prime}/\lambda)^2 - 1]/9.212RT \qquad (6)$$

Since $\delta^2 e^2(1/2r_D + 1/2r_A - 1/r_{DA})/9.212RT$ and λ are positive, S is negative in the normal ($|\Delta G^{\circ\prime}| < \lambda$) regime, as reported previously,[36−39] and positive in the inverted regime ($|\Delta G^{\circ\prime}| > \lambda$).

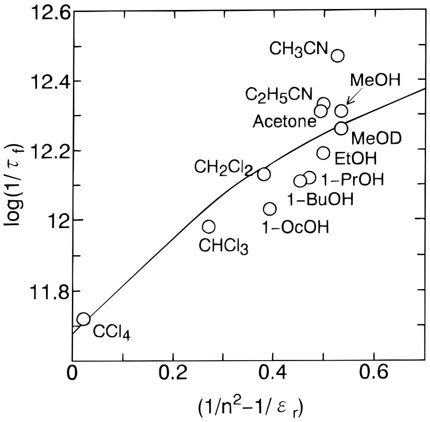

Figure 7. Plots of $\log(1/\tau_f)$ vs $(1/n^2 - 1/\epsilon_r)$. The curve was calculated from eqs 2−5 with $\log(1/\langle\tau_s\rangle) = 12.60$, $\Delta G^{\circ\prime} = -8.5$ kcal/mol, $\delta = 0.25$, $r_{DA} = r_D + r_A$, $r_D = r_A = 4.0$ Å, and $\lambda_i = 4.0$ kcal/mol.

Figure 7 shows a plot of $\log(1/\tau_f)$ vs $(1/n^2 - 1/\epsilon_r)$ in MVE-D. The positive S is consistent with our view that the photoinduced ET of MVE-D corresponds to the inverted regime (Figure 6). The curve shown in Figure 7 was calculated from eqs 2−5 with $\log(1/\langle\tau_s\rangle) = 12.60$, $\Delta G^{\circ\prime} = -8.5$ kcal/mol, $\delta = 0.25$, $r_{DA} = r_D + r_A$, $r_D = r_A = 4.0$ Å, and $\lambda_i = 4.0$ kcal/mol. Since λ_i is not negligible in the simulation, the vibrational modes are likely to play important roles in ET of MVE-D. The experimental points for the solvents with small $\langle\tau_s\rangle$ (non-hydrogen-bonding solvents) are located almost above the simulation curve in Figure 7 and those with large $\langle\tau_s\rangle$ (hydrogen-bonding solvents) below it.

Although the photoinduced ET of MVE-D corresponds to the inverted regime as described above, ET in reaction 1 corresponds to the normal regime.[6] The reason for this difference can be found in the fact that the one-electron reduction potential of duroquinone in the S_1 state (2.22 V vs SCE, see refs 41 and 42 and Figure 2) is expected to be much larger than that of LOO•.[6] The large reduction potential of duroquinone in the S_1 state makes the system more exothermic and drives it into the inverted regime.

Comparison with Results for Reactions of Excited Triplet Duroquinone with α-TocH. While this paper was in preparation, a paper by Bisby and Parker on the reactions of excited triplet duroquinone with α-TocH appeared.[43] They investigated the reactions by means of nanosecond laser flash photolysis and time-resolved resonance Raman spectroscopy. One of their conclusions was that the reaction of excited triplet duroquinone with α-TocH occurs by hydrogen atom transfer rather than by electron transfer. On the contrary, we consider from the present results of MVE-D with femtosecond spectroscopy that the reaction of excited singlet duroquinone with α-TocH involves an initial electron transfer. Two research groups have suggested two different mechanisms for similar reactions.

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Previously, Burton et al.[44] and Mukai et al.[45] discussed a similar subject; although Burton et al. suggested that the hydrogen atom transfer from TocH to LOO$^•$ is rate controlling in reaction 1, Mukai et al. suggested that the mechanism of reaction 1 can be explained in terms of the electron transfer from TocH to LOO$^•$. In conclusion, S.N. and co-workers[6,7] showed that both the electron transfer and the hydrogen atom transfer (proton tunneling) play important roles in reaction 1; the electron transfer and the hydrogen atom transfer (proton tunneling) could be different sides of the same coin, and it seems unsound to present them as conflicting models.

From analogy with reaction 1, it is considered that the most probable mechanism of the reaction of excited duroquinone and α-TocH is as follows. In the initial stage of the reaction, excited duroquinone and α-TocH approach each other and their electron clouds begin to overlap. The excited duroquinone and α-TocH are relatively susceptible to accepting and donating an electron, respectively. Thus, the final goal of this process is the transition state which has the property of the ET species (duroquinone$^-$- - -TocH$^+$). In reality, when the excited duroquinone and α-TocH approach each other to some extent (duroquinone$^{\delta-}$- - -TocH$^{\delta+}$), the proton tunneling takes place below the transition state. The tunneling allows the proton to cut a corner on the potential energy surface. Finally, the duroquinone and Toc$^•$ separate from each other. Since the lifetime of the species duroquinone$^{\delta-}$- - -TocH$^{\delta+}$ is so short, it cannot be detected by means of nanosecond spectroscopy.

Critical Check of Results and Discussion

Next we will critically check our results and discussion. MVE-D contains a tertiary amine group as well as the phenolic group of the vitamin E moiety. The tertiary amine group could act as an electron donor; such intramolecular electron transfers from a tertiary amine are known from earlier works.[46,47] Although a molecule containing both electron donor and acceptor with an unreactive spacer would obviously have been preferred, many difficulties would arise in the synthesis of such a molecule. We have thus used MVE-D which can be synthesized without great difficulty. However, the electron-transfer rate from a tertiary amine amounts to about 10^{-8}–10^{-10} s^{-1} and is much slower than that of MVE-D (10^{-12}–10^{-13} s^{-1}).[46,47] Accordingly, it seems reasonable to attribute the very rapid decay of the excited duroquinone moiety of MVE-D to the interaction from the vitamin E moiety. Furthermore, the results of PM3 molecular-orbital calculations that the CT state of MVE-D has the character of electron transfer from the vitamin E moiety to the duroquinone moiety[48] also support our view.

The use of the S_1 state [(n,π*) state] of the duroquinone moiety as a model for LOO$^•$ is an important assumption. However, our conclusions are based mainly on the kinetic solvent effect, which is independent of the nature of the radicals in the case of vitamin E;[49,50] the S_1 state of the duroquinone moiety is a model for the alkoxyl radical.[9] Furthermore, the reactivity pattern of TocH for reaction 1 does not depend on the type of oxyradicals,[10] as described in the Introduction. From these facts, it seems reasonable to use the S_1 state as a model for LOO$^•$.

Reaction 1 proceeds by partial electron transfer and a transient species appearing during the reaction is not a fully electron-transferred species (LOO$^{•-}$- - -TocH$^+$) but a partially electron-transferred species (LOO$^{•\delta-}$- - -TocH$^{\delta+}$).[6,7] Accordingly, it is reasonable that transient absorption bands of a phenolic cation radical (TocH$^+$), a duroquinone anion radical (duroquinone$^-$), and/or a fully electron-transferred species (duroquinone$^-$- - -TocH$^+$) are not observed in MVE-D. The bands of the partially electron-transferred species of MVE-D will be shifted from those of the fully electron-transferred species and the lifetime and absorption coefficient of such a species are unknown. Further investigations on the transient spectra after the decay of the singlet-duroquinone excited state are clearly needed.

Conclusions

The photoinduced ET of MVE-D has been investigated by means of femtosecond spectroscopy. The interaction between the vitamin E and duroquinone moieties is not extensive in the S_0 state, and the charge-transfer band is not clearly seen in the absorption spectrum.

The bonding of vitamin E to duroquinone largely reduces τ_f owing to ET from the vitamin E moiety to the duroquinone moiety. Since the S_1 state [(n,π*) state] of duroquinone is regarded as a model for peroxyl radical, the reduction of τ_f is direct microscopic observation of the initial stage in the corresponding part of the antioxidant process of vitamin E. It is considered that the photoinduced ET of MVE-D corresponds to the inverted regime. The vibrational modes of the CT state reduce τ_f by opening ET vibronic channels which have small barriers.

The present results support the view that ET from TocH to LOO$^•$ occurs in the initial stage of reaction 1.[6,7]

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Supporting Information Available: Femtosecond pump-probe transient of duroquinone in MeOH obtained with the delay-time range −10 to 100 ps (Figure 8), transient absorption spectra of MVE-D in ACN and dichloromethane (Figures 9 and 10, respectively), a plot of τ_f obtained by probing the transient at 480 nm vs ϵ_r (Figure 11), and experimental details for the preparation and characterization of MVE-D (18 pages). See any current masthead page for ordering and Internet access instructions.

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