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Determination of Electron-Transfer Reorganization Energy in Nanometer-Separated Radical Ion Pair by Time-Resolved EPR Spectroscopy

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The reorganization energy (λ) plays an important role to control the efficiency of the electron transfer (ET) reaction between the electron donor (D) and acceptor (A) molecules, as predicted by Marcus theory.[1] As for the charge-recombination (CR) reactions of the solvent-separated radical ion pairs (RIP), the solvent reorganization (λ_S) and the solute intramolecular reorganization energies (λ_V) have been estimated by fitting the Marcus plots of the energy gap ($-\Delta G_{CR}$) dependences of the CR rates, which have been obtained by the transient absorption spectroscopy.[2] The characteristic λ value for the *individual* D–A system is quite significant to understand the solute–solvent interaction in the ET process. Thus far, no studies have determined the individual λ value in the flexibly nanometer-separated bimolecular ET systems. In this Communication, we have precisely determined the λ values for 1,2,4-trimethoxybenzene (TMB) cation and duroquinone (DQ) anion RIP separated at ~1.2 nm produced from the triplet precursor photoinduced bimolecular charge separation (CS), by observing the temperature dependence of the time-resolved electron paramagnetic resonance (TREPR) spectra in polar solvents.

For the purpose of the determination of the λ ($= \lambda_S + \lambda_V$), we probed the chemically induced dynamic electron polarization (CIDEP)[3,4] produced through the interaction of the singlet–triplet energy splitting (J) in the RIP. Recently, it has clearly been demonstrated that the J in the RIPs is governed by the charge-transfer interaction (J_{CT}), which is created by the electronic coupling (V) perturbation from the charge-recombined D–A configurations.[5–7] The radical pair mechanism (RPM) CIDEP is generated by the singlet–triplet (S–T$_0$) mixing during the diffusive separation and by the possible subsequent reencounter in the RIPs.[3,4] The RPM polarization pattern provides the information of the sign of the J at the flexibly separated center-to-center D–A distance (r), where the J is comparable to the hyperfine interaction.[3,4,7] From the J_{CT} mechanism, when the $-\Delta G_{CR}$ is smaller than the λ, the J is negative (the singlet energy is lower than the triplet energy), while in the case of $-\Delta G_{CR} > \lambda$, the J is positive in the triplet precursor reaction systems.[6,7]

Figure 1 shows the temperature dependence of the TREPR spectra obtained at 0.5 μs after the 355 nm laser excitations of DQ in the presence of TMB in *N,N*-dimethylformamide (DMF).[8] The sharp peaks were assigned to the DQ anion radical (DQ$^{-\bullet}$) from the g value ($g = 2.0049$) and the hyperfine coupling constants.[9,10] The CIDEP pattern is interpreted by the superposition of the net microwave emission due to the triplet mechanism (TM)[3] and the RPM. In Figure 1a, the emission signal intensity (indicated by the arrow) of DQ$^{-\bullet}$ is weaker at the lower magnetic field than the intensity at the higher field. This denotes the RPM phase is the microwave absorption (*A*) in the lower field and the emission (*E*) in the higher field (*A/E*-type polarization),[3,4] representing the positive J at 285 K, while in Figure 1c, the *E/A*-type polarization shows the negative J at 236 K (Supporting Information). At 258 K, the RPM polarization was hardly observed, resulting in $J \approx 0$ in Figure 1b. The temperature dependences of the reduction and oxidation potentials ($E_{1/2}^{red}$ and $E_{1/2}^{ox}$) of DQ and TMB were respectively measured by the cyclic voltammetry (CV) method in DMF vs SCE (Supporting Information). The $-\Delta G_{CR}$ obtained by $-\Delta G_{CR} = E_{1/2}^{ox} - E_{1/2}^{red}$ was decreased with decreasing temperature as shown in Table 1. The $-\Delta G_{CR}$ dependence of the sign of the J is well explained by the J_{CT} model described above.

On the basis of the J_{CT} mechanism, the RPM electron spin polarization (P_{RPM}) was calculated by the numerical analysis of the stochastic-Liouville equation (SLE).[7] In the analysis, the following effects were included; the S–T$_0$ mixing rate ($Q = 7 \times 10^7$ rad/s) due to the g factors and the hyperfine coupling, temperature-dependent solute diffusion motion (mutual diffusion coefficient: D)[11,12] within the RIP, r-dependent CR reaction from the singlet RIP and the J_{CT} (Supporting Information). The r dependence of the λ_S was taken into account by the Marcus equation[1,13] for the calculation of the J_{CT},[7]

$$\lambda_S(r) = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{2d_A} + \frac{1}{2d_D} - \frac{1}{r}\right)\left(\frac{1}{n_D^2} - \frac{1}{\epsilon}\right) \qquad (1)$$

The λ_V values[14] of $\lambda_V^{TMB} = 0.32$ eV and $\lambda_V^{DQ} = 0.25$ eV for

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(14) The geometry optimizations of the ion radicals and neutral ground states were performed from the UB3LYP density functional ab initio molecular orbital calculations with the 6-31G* basis set. At the optimized geometries for the ion radicals, the energies in the neutral states were obtained by the single-point calculations. The λ_V values were determined from the energy differences between the two different geometries obtained in the neutral states.
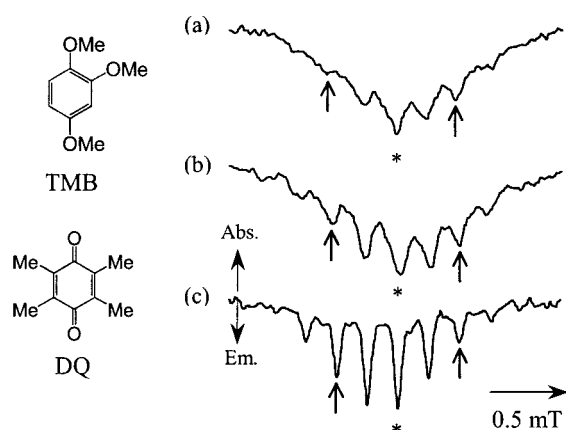
Figure 1. Temperature effect on the time-resolved EPR spectra in the TMB-DQ electron donor−acceptor system in DMF, showing the positive J at 285 K in (a), $J \approx 0$ at 258 K in (b) and the negative J at 236 K in (c) in the radical ion pairs. The asterisks indicate the center of the hyperfine structure of the DQ anion radicals.

Table 1. Temperature (T) Dependences of the Sign of the J, the Energy Gap ($-\Delta G_{CR}$) for the Charge Recombination and the RPM Polarization in the RIP of 1,2,4-Trimethoxybenznene−Duroquinone in *N,N*-Dimethylformamide

T/K	$E_{1/2}^{ox}$/V	$E_{1/2}^{red}$/V	$-\Delta G_{CR}$/eV	sign of J	$P_{RPM}/P_{eq}{}^a$
	TMB	DQ			
285	+1.13	−0.73	1.86	positive	+0.57
258	+1.12	−0.71	1.83	$J \approx 0$	−0.08
236	+1.10	−0.69	1.79	negative	−1.42

a The calculated magnitude of the RPM polarization by the SLE analysis in the units of the thermal equilibrium electron spin polarization P_{eq} at room temperature (see text for discussion).

TMB and DQ were respectively used for the J_{CT} calculation.[7] Calculated P_{RPM} values were listed in Table 1. The positive P_{RPM} denotes the A/E-type RPM polarization, indicating the positive J at the effective RPM generation region, while the negative P_{RPM} the E/A-type polarization, indicating the negative J. The good agreement between the experimental results and the model calculations indicates that the $P_{RPM} = 0$ gives rise to $-\Delta G_{CR} = \lambda$ at $r \sim 1.2$ nm.[7,15] From the $-\Delta G_{CR}$ value under the condition of $J \approx 0$ at 258 K, the total reorganization energy of λ is determined to be $\lambda = 1.83(\pm0.02)$ eV as the individual value for the TMB-DQ system in DMF. The λ is the sum of the λ_S and λ_V values; $\lambda = \lambda_S + \lambda_V^{TMB} + \lambda_V^{DQ}$.[2,7] Therefore, the λ_S was determined as $\lambda_S = 1.26$ eV. The obtained λ_S value is well consistent with the calculated by eq 1 at $r = 1.2$ nm in DMF, suggesting the validity of the λ and λ_S as the individual values for the $\sim$1.2 nm-separated TMB-DQ molecular system in DMF (see Table 2).

It should be interesting to examine the solvent effect on the λ_S for the nanometer-separated RIP in the same D−A molecular system. We also determined the λ and λ_S for the TMB-DQ system in butyronitrile (BuN). As was observed in DMF, the sign of the J was inverted from positive to negative with decreasing tem-

Table 2. Electron-Transfer Reorganization Energies (in eV) Determined in the $\sim$1.2 nm-Separated 1,2,4-Trimethoxybenznene−Duroquinone RIP System

solvent	λ	λ_S	λ_S (calc)^a
N,N-dimethylformamide	1.83($\pm$0.02)	1.26	1.28
butyronitrile	1.92($\pm$0.02)	1.35	1.33

a Calculated by eq 1 with $r = 1.2$ nm. The other parameters are described in ref 13.

perature. From the $-\Delta G_{CR}$ value (= 1.92 eV)[16] under the condition of $J \approx 0$ obtained at 249 K in BuN, the λ was determined to be $\lambda = 1.92$ ($\pm$0.02) eV and $\lambda_S = 1.35$ eV was obtained with the same procedure as determined in DMF. Table 2 summarizes the solvent effect on the λ and λ_S obtained in the TMB-DQ system. The λ_S(calc) denotes the calculated values from eq 1 with $r = 1.2$ nm and with the solvent parameters in DMF and BuN, respectively.[13] Both of the determined λ_S values are well consistent with the calculated ones, and the solvent effect on the λ_S is obviously explained by the differences in the dielectric parameters in eq 1. The results demonstrated that, concerning the solvents and solutes used in this study, the dielectric character is well held in the solvent−solute interaction for the nanometer-separated D−A molecular system. This is well consistent with the theoretical predictions based on the realistic molecular models. Ando[17] suggested from the molecular dynamics simulations that the solvent−solute potential energy surface is approximately parabolic along the solvation coordinate and that the dielectric effect is dominant in the *N,N*-dimethyianiline-anthracene solvent separated D−A system in acetonitrile.

In conclusion, we were successful in determining the individual reorganization energies for the ET reactions in the $\sim$1.2 nanometer flexibly separated 1,2,4-trimethoxybenzene cation and duroquinone anion RIPs by the time-resolved EPR spectroscopy. This method provides the specific reorganization property for the individual D−A molecular system, and will be quite useful to clarify the detailed mechanism of the solvent and solute molecular behavior during the ET reactions in the solvent-separated RIPs.

Supporting Information Available: Pulsed EPR investigations, details of the cyclic voltammetry measurements, theoretical analysis of the singlet−triplet energy splitting, and the RPM electron spin polarization calculation are described (PDF). This information is available free charge via the Internet at http://pubs.acs.org.

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(15) In the numerical analysis, the separation of r_{RPM} for the effective RPM generation is dependent on the parameters of the electronic coupling V. In this study, we used as follows: $\beta = 1.0$ Å^{-1}, $V_0 = 600$ cm^{-1} and $d = 3.5$ Å (ref 2c) in $V(r)^2 = V_0^2 \exp\{-\beta(r - d)\}$, and obtained $r_{RPM} = 1.2$ nm.

(16) The value of $-\Delta G_{CR}$ =1.92 eV was obtained from $E_{1/2}^{ox}$ = + 1.09 V and $E_{1/2}^{red}$ = −0.83 V vs SCE in BuN by the CV measurements. The solvent effect on the $-\Delta G_{CR}$ is explained by the difference in the dielectric constant between DMF and BuN (ref 13).

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