Singlet and triplet energy splitting in the radical ion pairs generated by photoinduced electron-transfer reactions*

Shozo Tero-Kubota

Institute for Chemical Reaction Science, Tohoku University, Sendai 980-8577, Japan

Abstract: Chemically induced dynamic electron polarization (CIDEP) spectra generated by photoinduced electron-transfer reactions have been studied using continuous-wave time-resolved EPR and FTEPR spectroscopy. It has been suggested that the energy difference (ΔE_{ST}) between the singlet and triplet states of radical ion pairs (RIPs) is dependent on the charge recombination free energy ($-\Delta G_{CR}$) and reorganization energy (λ). The result is interpreted in terms of the spin-selective stabilization or destabilization of RIP states by electronic coupling with the S_0 and locally excited triplet states of the donor–acceptor pair at equilibrium distance in the reaction coordinate. It has been verified that a charge transfer-type exchange interaction governs the ΔE_{ST}. Magnitudes as well as the sign of ΔE_{ST} can be predicted at the distance of the solvent-separated RIP based on ΔG_{CR} and λ values.

INTRODUCTION

The energy difference (ΔE_{ST}) between the singlet (E_S) and triplet (E_T) states of a radical pair (RP), corresponding to the so-called exchange interaction (J), is described by eq. 1.

$$\Delta E_{ST} = 2\, J(r) = E_S - E_T \tag{1}$$

In neutral RPs, the singlet state usually lies below the triplet state because the singlet state is stabilized by bond formation (Fig. 1a). This fact is verified by the observation of electron spin polarization due to a radical pair mechanism (RPM), which is one of the fundamental chemically induced dynamic electron polarization (CIDEP) mechanisms [1–3]. The multiplet polarization pattern due to RPM depends on electron spin multiplicity of the precursor (μ) and the sign of J.

$$\Gamma_{me} = \mu\, \text{sign}(J) \tag{2}$$

The spin multiplicity factor μ is assigned +1 for triplet precursors and –1 for singlet precursors. The sign of Γ_{me} determines whether the CIDEP spectrum appears with low-field half in emission and high-field half in absorption (E/A, $\Gamma_{me} = -1$) or vice versa (A/E, $\Gamma_{me} = +1$). Therefore, we can easily determine the sign of J from the RPM-CIDEP spectra when the spin multiplicity of the precursor is known. In contrast to the neutral RPs, some radical ion pairs (RIPs) seem to have a positive J, indicating a triplet state lower than the singlet state (Fig. 1b). Recently, we proposed that the ΔE_{ST} in RIPs generated by photoinduced electron transfer is dependent upon charge recombination free energy ($-\Delta G_{CR}$) and reorganization energy (λ) [4–7]. This paper describes the important role that spin-selective, charge transfer-type exchange interactions play in determining ΔE_{ST} in donor and acceptor pair systems.
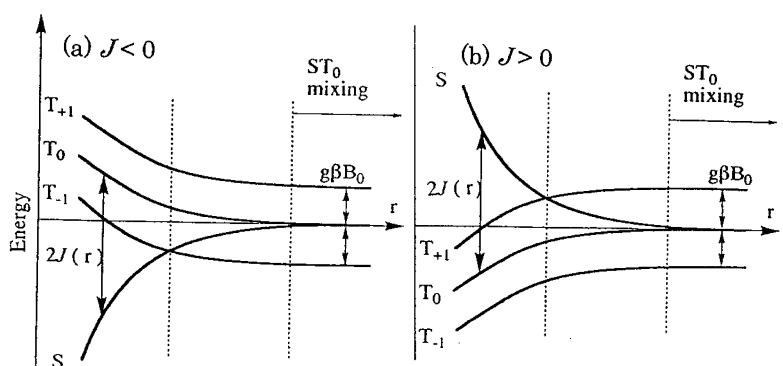

Fig. 1 Energy diagram of the spin states of radical pairs with $J < 0$ (a) and $J > 0$ (b).

MARCUS FREE-ENERGY DEPENDENCE OF THE SIGN OF J IN TRIPLET PRECURSOR GENERATED RIPS

To verify the exchange interaction mechanism in RIPs, we measured CIDEP spectra for various photo-induced electron-transfer systems. The phase of the observed RPM versus ΔG_{CR} and triplet energy (ET) of the sensitizers are plotted (Fig. 2). The ΔG_{CR} values were estimated from redox potentials of acceptors and donors [8,9].

$$-\Delta G_{CR} = E_{1/2}{}^{ox} - E_{1/2}{}^{red} - C. \tag{3}$$

Where $E_{1/2}{}^{ox}$ and $E_{1/2}{}^{red}$ are donor and acceptor oxidation and reduction potentials, respectively. The correction term for Coulomb interaction between pair radical ions (C) is neglected in polar solvents. As shown in Fig. 2, the sign of J is dependent upon the ΔG_{CR} value but independent of the E_T value. The sign of J inverts at $-\Delta G_{CR} \sim 1.8$ eV in these reaction systems. Because free energy of ca. 1.8 eV corresponds to the boundary between normal and inverted regions of the back electron-transfer reactions, the level crossing between potential surfaces of the RIP state and ground state is a key factor. Figures 3a and 3b show the reaction coordinate dependence of potential surfaces of the collision complex of the donor and the excited acceptor (^{3}*AD), the singlet and triplet RIPs (^{1,3}A⁻D⁺), and the ground state. When the potential surface of the RIP crosses with the ground state at the normal region in the triplet
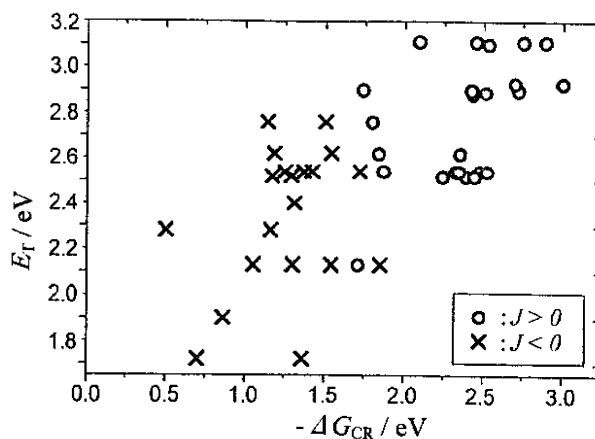

Fig. 2 Plots of the sign of J versus $-\Delta G_{CR}$ and E_T of the sensitizers.
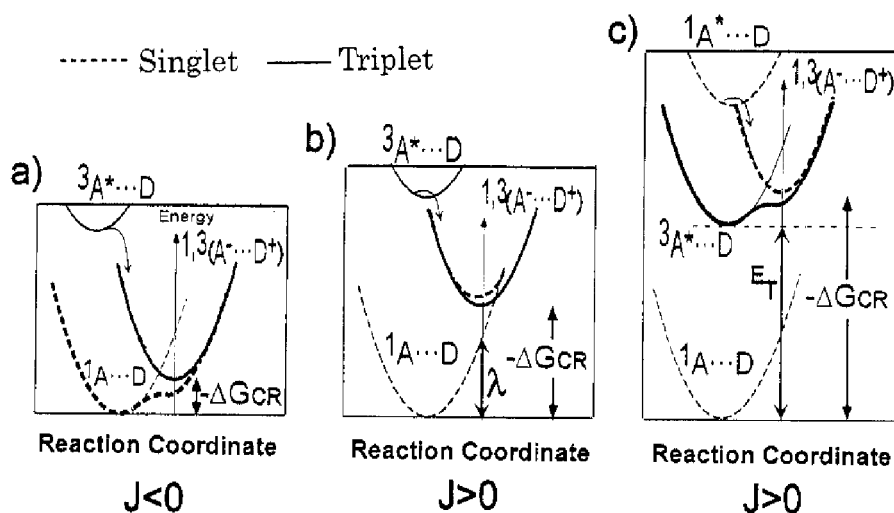
Fig. 3 Schematic free-energy diagram for the photoinduced electron-transfer reactions depicted versus solvent coordinate for the triplet precursor systems (a, b) and singlet precursor systems (c).

precursor system, the charge transfer-type interaction leads to singlet state stabilization compared to the triplet state in energy. On the other hand, avoided crossing of the RIP and ground-state potentials at the Marcus inverted region destabilizes the singlet RIP state compared with the triplet RIP one, resulting in a positive J.

THE SIGN OF J IN SINGLET PRECURSOR GENERATED RIPS

We also measured CIDEP spectra produced from various singlet precursor reaction systems, involving fluoranthene, coronene, anthracene, dibenzo[a,h]anthracene, and pyrene as acceptors. These systems showed E/A type CIDEP spectra. It was confirmed that the observed multiplet effects were produced via a singlet reaction process. The lifetime of the S_1 state and electron-transfer rate determined by Stern–Volmer plot of the CIDEP signal rise agree well with fluorescence quenching experiment results. Therefore, a positive J was determined for these RIPs. In these systems, locally excited triplet state energies are smaller than $-\Delta G_{CR}$ values. Therefore, in singlet precursor electron-transfer systems, the sign of J is determined by spin-selective, charge transfer-type interactions between RIP potential surfaces and locally excited triplet state at the normal region (Fig. 3c). If the RIP potential surface crosses with the locally excited triplet state at the inverted region, a negative J is expected.

CHARGE TRANSFER-TYPE EXCHANGE INTERACTION IN RIPS

As denoted above, ΔE_{ST} in RIPs is explained by a spin-selective stabilization or destabilization of RIP states caused by perturbation due to electronic coupling with the S_0 state and the locally excited triplet state of the donor–acceptor pair at equilibrium distance in the nuclear coordinate. From a simple perturbation treatment, the charge transfer-type exchange interaction between the RIP state and the ground state or the locally excited triplet state is described as the function of distance-dependent electronic coupling matrix element $H_{el}(r)$, reorganization energy (λ), and ΔG_{CR} as follows,

$$J(r) = H_{el}(r)^2/(\lambda + \Delta G_{CR}) \tag{4}$$

$$H_{el}(r) = H_0 \exp\{ -\beta (r - d)\}. \tag{5}$$

Where H_0 denotes the electronic coupling matrix element at the contact separation of d. The reorganization λ is the energy required to reorganize the system to the optimum configuration for electron transfer, and consists of a component associated with donor and acceptor molecules (intramolecular reorganization energy, λ_V) and a solvent component (solvent reorganization energy, λ_S). The Marcus relation represents the solvent reorganization energy in a polar solvent as

$$\lambda_s = \frac{e^2}{2}\left(\frac{1}{r_A} + \frac{1}{r_D} - \frac{2}{r_{AD}}\right)\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right) \tag{6}$$

where r_D and r_A are radii of reactants and r_{AD} is the distance between the donor and acceptor. The refractive index and dielectric constant of solvents are represented by n and ε, respectively. Thus, magnitudes and the sign of ΔE_{ST} can be predicted at the distance of the solvent-separated RIP. Equation 4 suggests that the sign of J switches at $-\Delta G_{CR} = \lambda$. The present model explains almost all experimental results and indicates that the ΔE_{ST}(RIP) value is dependent upon solvent polarity.

SOLVENT POLARITY DEPENDENCE ON THE SIGN OF *J*

Figure 4 shows CIDEP spectra generated from the photoinduced electron transfer from MPTZ (3 mM) to phenazine (3 mM) in DMSO and DMSO-glycerol (3:1). The CIDEP spectra assigned to MPTZ$^{\bullet+}$ and phenazine$^{\bullet-}$ were well simulated with normal RPM theory. It is obvious that CIDEP spectra differ from each other in the phase. Observed in DMSO was A/E type polarization, while E/A polarization was seen in DMSO-glycerol (3:1). Because the electron-transfer reactions originate in the excited triplet state of MPTZ in both systems, the CIDEP spectra indicate sign inversion of J by solvent polarity. Present results suggest that $-\Delta G_{CR} > \lambda$ in DMSO while $-\Delta G_{CR} < \lambda$ in DMSO-glycerol (3:1) in the MPTA-phenazine system. Specific solvent effects due to hydrogen bonding would decrease the $-\Delta G_{CR}$ value, resulting in the switching J sign. Theoretical analysis for prediction of J was also performed while considering explicitly the solute-solvent interactions and the solute's vibrational excitation. Calculations well reproduced experimental results [10].
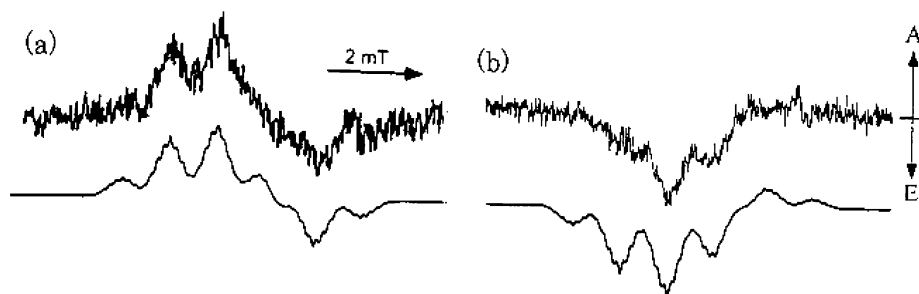

Fig. 4 CIDEP spectra generated from the photoinduced electron transfer of methylphenothiazine (3 mM)-phenazine (3 mM) system in DMSO (a) and (3:1) DMSO-glycerol (b).

ACKNOWLEDGMENTS

REFERENCES

1. F. J. Adrian. *J. Chem. Phys*. **54**, 3918 (1971).
2. J. B. Pedersen and J. H. Freed. *J. Chem. Phys*. **58**, 2746 (1973).
3. F. J. Adrian. *Rev. Chem. Intermed*. **3**, 3 (1979).
4. S. Sekiguchi, K. Akiyama, S. Tero-Kubota. *Chem. Phys. Lett*. **263**, 161 (1996).
5. S. Sekiguchi, Y. Kobori, K. Akiyama, S. Tero-Kubota. *J. Am. Chem. Soc.* **120**, 1325 (1998).
6. Y. Kobori, S. Sekiguchi, K. Akiyama, S. Tero-Kubota. Proceedings of the Joint 29th AMPERE— 13th ISMAR International Conference on Magnetic Resonance and Related Phenomena; Vol. II, p. 929 (1998).
7. Y. Kobori, S. Sekiguchi, K. Akiyama, S. Tero-Kubota. *J. Phys. Chem. A,* **103,** 5416 (1999).
8. H. Siegman. In "Technique of Electroorganic Synthesis", Technique of Chemistry Vol. 5, Part II, N. L. Weinberg (Ed.), Wiley, New York (1975).
9. Y. Kawanishi, N. Kitahama, S. Tazuke. *J. Phys. Chem*. **90**, 2469 (1986).
10. Y. Kobori, K. Akiyama, S. Tero-Kubota. *J. Chem. Phys.* **113**, 465 (2000).