J. Am. Chem. Soc. **1998,** *120,* 1325−1326

Communications to the Editor

Marcus Free Energy Dependence of the Sign of Exchange Interactions in Radical Ion Pairs Generated by Photoinduced Electron Transfer Reactions

Shinji Sekiguchi, Yasuhiro Kobori, Kimio Akiyama, and
Shozo Tero-Kubota*

Institute for Chemical Reaction Science
Tohoku University
Katahira 2-1-1, Aobaku, Sendai 980-77, Japan

Received July 28, 1997
Revised Manuscript Received December 9, 1997

There has been considerable interest on radical ion pairs (RIPs), because they are fundamental intermediates in the photoinduced electron-transfer reactions.[1−5] The exchange interaction (*J*) in RIPs is expected to be quite different from that of neutral radical pairs (RPs), since solvent−solute interactions have characteristic features. Electron spin polarization observed in the transient free radicals has been increasingly useful to understand the chemistry of transient intermediates. The pattern of radical pair mechanism (RPM), which is one of the important mechanism for generating chemically induced dynamic electron polarization (CIDEP), depends on the spin multiplicity as well as the sign of the J of radical pair precursors.[6] The *J* is defined by the energy separation between singlet (E_S) and triplet (E_T) radical ion pairs: $2J(r) = E_S - E_T$. It has been well-known that the sign of *J* is normally negative in neutral radical pairs, indicating the lower energy of the singlet state compared with the triplet state. In contrast, recent studies suggest that some radical ion pairs have a positive *J*.[7−10] In the present work, we investigated the CIDEP spectra generated by photoinduced electron-transfer reactions and found that the sign of *J* depends on the charge recombination free energy. A new mechanism for the sign of *J* has been proposed on the basis of Marcus theory.[11]

Xanthone (XN), duroquinone (DQ), and 2,3-dimethoxy-5-methylbenzoquinone (CoQ$_0$) were used as the acceptors.[12] Triphenylamine (TPA) and *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMBD) were used as the donors.[12] The continuous wave time-resolved EPR (TREPR) spectroscopy used was described in a previous paper.[13] A Nd:YAG laser (355 nm) was utilized as the light source.

Figure 1 shows the CIDEP spectra of the acceptor anion radicals of XN, DQ, and CoQ$_0$ generated by the photoinduced electron-transfer reactions with the donors TPA and TMBD, respectively. The cation radicals of the donors did not give well-resolved EPR spectra because of the complicated signals.

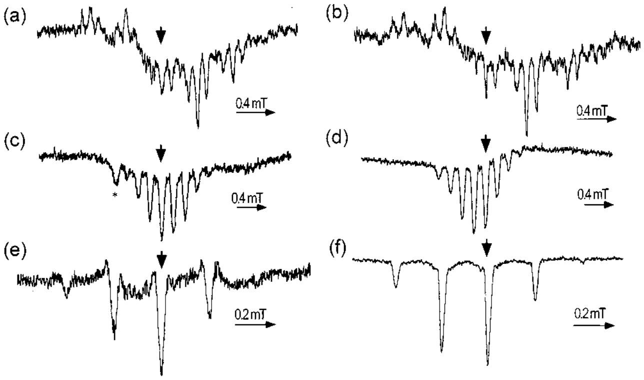

Figure 1. CIDEP spectra of the anion radicals generated by the photoinduced electron transfer in the systems of (a) 5 mM XN−3 mM TPA in DMSO/cyclohexanol (1:1, v/v), (b) 5 mM XN−3 mM TMBD in DMSO/cyclohexanol (1:1, v/v), (c) 5 mM DQ−2 mM TPA in DMSO, (d) 5 mM DQ−2 mM TMBD in DMSO, (e) 2 mM CoQ$_0$−2 mM TPA in DMSO, and (f) 2 mM CoQ$_0$−2 mM TMBD in DMSO at room temperature. The arrow indicates the center of the CIDEP spectrum due to the corresponding anion radical. The asterisk indicates the impurity signal.

The CIDEP spectra with the *A*/*E** (*A*/*E* + *E*) pattern were observed for XN$^{\bullet-}$, where *A*/*E* and *E* are enhanced absorption on the low-field side and emission on the high-field side, and the net emission of microwave, respectively. For CoQ$_0^{\bullet-}$, the CIDEP pattern was *E**/*E* (*E*/*A* + *E*). Since the net *E* polarization is ascribable to the triplet mechanism (TM), the RPM patterns are *A*/*E* and *E*/*A* for XN$^{\bullet-}$ and CoQ$_0^{\bullet-}$, respectively. In contrast, the RPM patterns of DQ$^{\bullet-}$ were dependent on the donor; *A*/*E* and *E*/*A* patterns were observed in the presence of TPA and TMBD. A Δg effect in the S−T$_0$ mixing of the RPM cannot explain these results, since the *g* values of the acceptor anion radicals are larger than those of the countercation radicals in the present systems.[14] The intersystem crossing rates from the S$_1$ to T$_1$ in the carbonyl molecules used are much higher than the bimolecular electron-transfer rates in the present concentrations.[10] Therefore, the photoinduced electron-transfer reactions occur through the excited triplet states, yielding the triplet RIPs as the reaction intermediate. The observation of E-TM supports the triplet reaction process. We can, therefore, conclude from the RPM pattern that the RIPs of XN$^{\bullet-}$−TPA$^{\bullet+}$, XN$^{\bullet-}$−TMBD$^{\bullet+}$, and DQ$^{\bullet-}$−TPA$^{\bullet+}$ have a positive *J*, while the RIPs of DQ$^{\bullet-}$−TMBD$^{\bullet+}$, CoQ$_0^{\bullet-}$−TPA$^{\bullet+}$, and CoQ$_0^{\bullet-}$−TMBD$^{\bullet+}$ have a negative *J*.

The present results are summarized in Table 1 together with those previously reported for the systems of 4,4′-dimethoxybenzophenone (DMBP)−diazabicyclo[2,2,2]octane (DABCO) and benzophenone (BP)−DABCO.[10] The values of the charge recombination free energy, ΔG_{CR}, are also listed. The values are approximately obtained from the redox potentials of the parent donor, $E_{1/2}^{\mathrm{ox(D)}}$, and acceptor, $E_{1/2}^{\mathrm{red(A)}}$; $\Delta G_{CR} = E_{1/2}^{\mathrm{red(A)}} - E_{1/2}^{\mathrm{ox(D)}}$.

---

(1) (a) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, D.; Weller, *Isr. J. Chem.* **1970,** *8*, 259. (c) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *130*, 129.

(2) (a) Masuhara, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312. (b) Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255.

(3) Mauzerall, D.; Ballard, S. G. *Annu. Rev. Phys. Chem.* **1982**, *33*, 377.

(4) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(5) Gould, I. R.: Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522.

(6) (a) Adrian, F. J. *J. Chem. Phys.* **1971**, *54*, 3918. (b) Monchick, L.; Adrian, F. J. *J. Chem. Phys.* **1978**, *63*, 4376.

(7) Murai, H.; Kuwata, K. *Chem. Phys. Lett.* **1989**, *164*, 567.

(8) Batchelor, S. N.; Heikkila, H.; Kay, C. W. M.; McLauchlan, K. A.; Shkrob, I. A. *Chem. Phys.* **1992**, *162*, 29.

(9) Jeevarajan, A. S.; Fessenden, R. W. *J. Phys. Chem.* **1992**, *96*, 1520.

(10) Sekiguchi, S.; Akiyama, K.; Tero-Kubota, S. *Chem. Phys. Lett.* **1996**, *263*, 161.

(11) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(12) XN (Tokyo Kasei), TPA (Nacalai Tesque), and TMBD (Tokyo Kasei) were recrystallized from ethanol. CoQ$_0$ (Tokyo Kasei) was used as received. DQ was carefully sublimed in the dark. All solvents were specially prepared reagent grade (Nacalai Tesque). The sample solutions were degassed by argon bubbling and flowed into a quartz flat cell in the EPR resonator. Measurements were performed on the solutions with concentration of 2−5 mM donors and acceptors at room temperature.

(13) Tero-Kubota, S.; Akiyama, K.; Ikoma, T.: Ikegami, Y. *J. Phys. Chem.* **1991**, *95*, 766.

(14) The *g* values: XN$^{\bullet-}$, 2.0032; DQ$^{\bullet-}$, 2.0047; CoQ$_0^{\bullet-}$, 2.0041; TPA$^{\bullet+}$, 2.0028;[14a] TMBD$^{\bullet+}$, 2.0029. (a) Neugebauer, F. A.; Bamberger, S.; Groh, W. R. *Chem. Ber.* **1975**, *108*, 2406.

S0002-7863(97)02533-X CCC: $15.00

Table 1. Correlation between the Sign of J and the Thermodynamic Parameters

	$E_{1/2}{}^{red}$ (eV)		$E_{1/2}{}^{ox}$ (eV)	ΔG_{CR} (eV)	sign of J
XN	−1.77[a]	TPA	0.98[e]	−2.75	positive
DMBP	−2.02[b]	DABCO	0.68[f]	−2.70	positive[h]
BP	−1.83[b]	DABCO	0.68[f]	−2.51	positive[h]
XN	−1.77[a]	TMBD	0.43[g]	−2.20	positive
DQ	−0.73[c]	TPA	0.98[e]	−1.71	positive
		TMBD	0.43[g]	−1.16	negative
CoQ$_0$	−0.13[d]	TPA	0.98[e]	−1.11	negative
		TMBD	0.43[g]	−0.56	negative

[a] Reference 15. [b] Reference 20. [c] Reference 16. [d] Reference 17. [e] Reference 18. [f] Reference 21. [g] Reference 19. [h] Reference 10.

Table 1 clearly indicates that the sign of J in RIPs depends on the ΔG_{CR} values. Inversion of the sign of J seems to occur at about ΔG_{CR} of −1.5 eV. Neither the mixing of the highly excited donor−acceptor state[22] nor the long-range electron spin dipole−dipole interactions[23,24] explain this.

The level crossing between the potential surfaces of the RIP state and ground state is a key factor because the ΔG_{CR} of −1.5 eV corresponds to the boundary between the normal and inverted regions of the back electron-transfer reactions as reported by Mataga et al.[25] Figure 2 shows the solvent coordinate dependence of the potential surfaces of the collision complex of the donor and the excited acceptor (^{3}A*D), the singlet and triplet RIPs ($^{1,3}A^-D^+$) and the ground state (^{1}AD). When the $-\Delta G_{CR}$ value is smaller than 1.5 eV, the potential surface of the RIP state crosses with the ground state at the normal region. The charge-transfer interaction between the ^{1}RIP and S$_0$ states leads to the stabilization of the ^{1}RIP potential as compared to the ^{3}RIP one by avoided crossing (Figure 2). Thus, a negative J is indicated in the RIPs, when the level crossing occurs at the normal region.

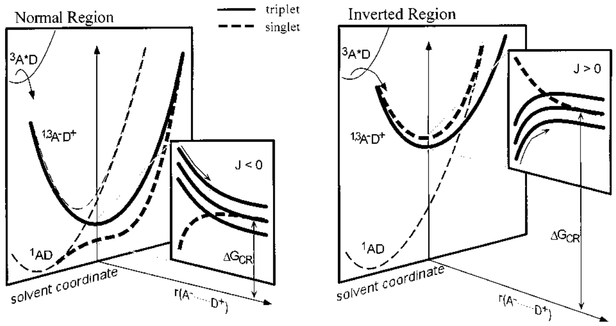

Figure 2. Free energy diagram for the photoinduced electron-transfer reactions depicted versus solvent coordinate and the energies of the singlet and triplet RIP states versus the distance between the ion radicals. Level crossings of the singlet RIP state with the S$_0$ state (a) at the normal region, $J < 0$, and (b) at the inverted region, $J > 0$.

On the other hand, when the $-\Delta G_{CR}$ value is larger than 1.5 eV, the potential surfaces of the RIP and S$_0$ states cross at the Marcus inverted region. Avoided crossing at the inverted region induces the destabilization of the ^{1}RIP state compared with the ^{3}RIP state, resulting in a positive J.

However, one would not expect such an inversion of the sign of J in the case of neutral RPs which form a new covalent bond in the recombination process. The present work suggests that the exchange interaction in RIPs would be governed by charge-transfer interactions rather than covalent bonding interactions. A positive J in the RIPs produced from the singlet precursor[8] is also explained by the charge-transfer exchange interaction. When the ^{3}RIP state crosses with the locally excited triplet donor−acceptor pair state at the Marcus normal region, the state of ^{3}RIP is selectively stabilized due to the charge-transfer interaction, leading to a positive J.

Acknowledgment. The present research was supported in part by a Grant-in-Aid for Scientific Research No. 070404040 from the Ministry of Education, Science, Sports and Culture, Japan.

JA972533M

---

(15) Streitwieser, A., Jr.; Schwager, I. *J. Phys. Chem.* **1962**, *66*, 2316.

(16) Kolthoff, I. M.; Reddy, T. B. *J. Electrochem. Soc.* **1961**, *108*, 980.

(17) Wahab, H. A.; Khalil, S. M.; Shanshal, M. *Stud. Biophys.* **1987**, *118*, 75.

(18) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(19) Siegman, H. In *Technique of Electroorganic Synthesis; Technique of Chemistry*; Weinberg, N. L., Ed.; John Wiley: New York, 1975; Vol. 5, Part II, pp 667−1056.

(20) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

(21) McKinney, T. M.; Geske, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 3013.

(22) Adrian, F. J. *Res. Chem. Intermed.* **1979**, *3*, 3.

(23) Shushin, A. I. *Chem. Phys. Lett.* **1991**, *183*, 321.

(24) Shkrob, I. A. *Chem. Phys. Lett.* **1996**, *264*, 417.

(25) Mataga, N.; Asahi, Y.; Kanda, Y.; Okada, T. *Chem. Phys.* **1988**, *127*, 249.