Effects of Lewis acid on the sign of exchange interaction of photogenerated radical ion pairs

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FTEPR study shows that the sign of the exchange interaction of the radical ion pair including the 4,4′-dimethoxybenzophenone radical anion and 1,4-diazabicyclo[2,2,2]octane (DABCO) radical cation changes from positive to negative by addition of BF_3.

It is well known that radical pairs usually have a negative exchange interaction (J), *i.e.* where the singlet radical pair is the lower in energy. However, there have been reports that J is positive in some radical ion pairs.[1–4] A conflicting mechanism has also been proposed.[5] Recently, we showed unambiguous evidence of a positive J for the radical ion pairs including the radical anions of benzophenone and its derivatives with DABCO$^{\cdot+}$.[4] Note that the neutral radical pairs generated under the same conditions have a negative J. The factors involved in determining the sign of J are unclear. We have studied the effects of Lewis acid on the sign of J of the radical ion pair, since the charge of the radical pair seems to be an important factor in the interradical interactions. It is expected that a Lewis acid can form a weak complex with the photogenerated radical anion, leading to partial shielding of the charge.

4,4′-Dimethoxybenzophenone (DMBP, Tokyo Kasei Chemicals) was recrystallized from ethanol. DABCO (Ncalai Tesque) was purified by sublimation. Dimethyl sulfoxide (DMSO, Ncalai Tesque) was used as received. The complexes of DABCO·$(BF_3)_2$ and DABCO·BF_3 were prepared by the interchange reaction of BF_3–diethyl etherate (Wako Chemicals) with DABCO in benzene according to the method reported in the literature.[6] The precipitated complex was evaporated and dried under vacuum. FTEPR measurements were carried out using a Bruker ESP 380E EPR spectrometer. The pulse sequence and detection method were reported in previous papers.[4,7] The nanosecond laser photolysis spectra were recorded using a multichannel analyzer equipped with a diode array (Princeton Instruments, IRY-700). A Nd:YAG laser (355 nm) was used as the light source. All measurements were performed at room temperature.

Figs. 1(*a*) and 1(*a*′) show the parts of the FTEPR spectrum observed at a delay time of 200 ns after the pulsed laser excitation of DMBP (3×10^{-3} mol dm^{-3}) in the presence of DABCO (0.06 mol dm^{-3}) in DMSO at room temperature. The spectra were measured separately because the excitation bandwidth of the microwave pulse was too narrow to excite the whole spectrum. The external magnetic fields were set to the regions of a part of the lower [Fig. 1(*a*)] and higher [Fig. 1(*a*′)] fields of the DABCO$^{\cdot+}$ spectrum. The E/E* (E + A/E) polarization observed indicates the contribution of the net E-polarization due to triplet mechanism (TM) and weak A/E-radical pair mechanism (RPM), where E and A denote emission and absorption of microwave radiation, respectively. Since the A/E-RPM is generated from the triplet reaction process, we can conclude that the present radical ion pair has a positive J as reported previously.[4]

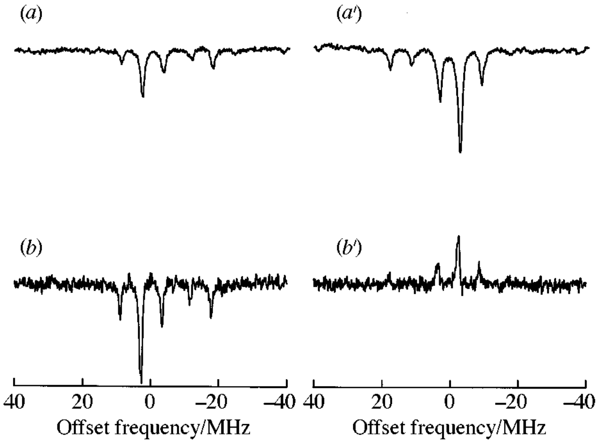

Fig. 1 Symmetrically located portions (*a*, *b*: the low magnetic field lines; *a*′, *b*′: the high field lines) of the echo detected FTEPR spectra observed at the delay time of 200 ns after the laser pulse excitation of DMBP (3×10^{-3} mol dm^{-3}) in the presence of 0.06 mol dm^{-3} DABCO (*a*) and DABCO·$(BF_3)_2$ (*b*) in DMSO

Addition of a Lewis acid into the above system induced a drastic change in the CIDEP pattern, while the hyperfine splitting constants obtained are completely identical to those of free DABCO$^{\cdot+}$. Figs. 1(*b*) and 1(*b*′) depict the parts of the FTEPR spectrum obtained from the laser excitation of DMBP (3×10^{-3} mol dm^{-3}) in the presence of 0.06 mol dm^{-3} DABCO·$(BF_3)_2$ complex in DMSO. The FTEPR spectrum shows that the photoinduced electron transfer definitely occurs to produce free DABCO$^{\cdot+}$. The E*/A-polarized spectrum due to DABCO$^{\cdot+}$ is easily interpreted by the contribution of the E-TM and E/A-RPM. These facts suggest that J is negative for this radical ion pair.

The time profiles of the RPM polarization are shown in Fig. 2. The RPM components were obtained from the difference between the signal amplitudes of $-m_I$ and $+m_I$ hyperfine lines. In the DMBP–DABCO and DMBP–DABCO·$(BF_3)_2$ systems, their A/E and E/A RPM phases were unchanged during the observation. On the other hand, the polarization inversion was observed in the DMBP–DABCO·BF_3 system. The A/E-polarization changed to the E/A one at 550 ns, indicating the existence of two kinds of radial ion pairs in this system. The growth and decay curves were analyzed by the sum of exponential functions. The curve fitting shown in Fig. 2 gave a decay time constant of 560 ns for the A/E-polarization. On the other hand, a relatively long time constant (910 ns) was obtained for the decay of E/A-polarization.

In order to clarify the structure and dynamics of the reaction intermediates, we measured transient absorption spectra. The excitation of DMBP without the electron donor gave the transient spectrum having a peak maximum at 550 nm and a broad band with an absorption tail up to 750 nm. The spectrum is attributed to the T–T absorption of DMBP. A lifetime of 130 ns was obtained. As shown in Fig. 3(*a*), the T–T absorption was

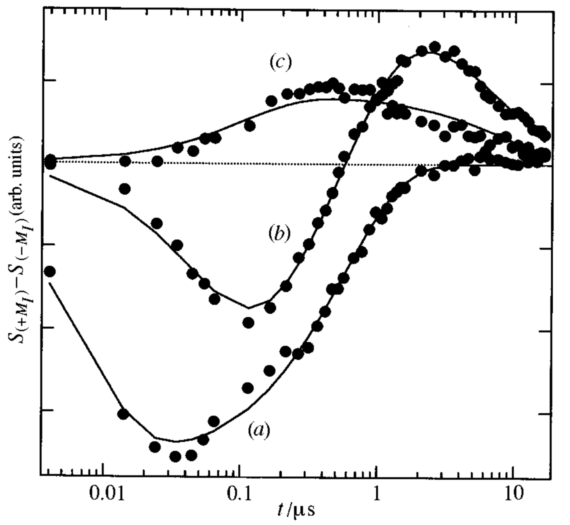

Fig. 2 Time variations in the RPM component of the CIDEP spectra calculated by the subtraction of low and high field lines of $DABCO^{\cdot+}$ generated from the laser photolysis of DMBP (3×10^{-3} mol dm^{-3}) in the presence of 0.06 mol dm^{-3} DABCO (*a*), DABCO·BF_3 (*b*) and DABCO·$(BF_3)_2$ (*c*) in DMSO

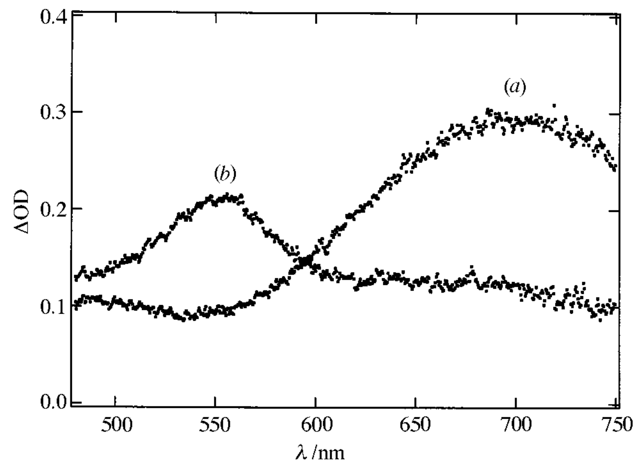

Fig. 3 Transient absorption spectra observed immediately after the laser photolysis of DMBP (3×10^{-3} mol dm^{-3}) in the presence of 0.06 mol dm^{-3} DABCO (*a*) and DABCO·$(BF_3)_2$ (*b*) in DMSO

quenched by the addition of DABCO and resulted in a band at 700 nm. This is easily assigned to $DMBP^{\cdot-}$.[8] The absorption of $DABCO^{\cdot+}$ would be observed in the wavelength region below 500 nm.[9,10] The band at 700 nm decays with a lifetime of 590 ns, which agrees well with the decay time constant of A/E-polarization in the FTEPR spectrum. It can be deduced that the back electron transfer reaction governs the decay rate of the radicals in the DMBP–DABCO system.

Fig. 3(*b*) shows the transient absorption spectrum observed immediately after laser excitation of the DMBP–DABCO·$(BF_3)_2$ system. The spectrum completely coincides with the T–T absorption of DMBP, indicating very low quenching rate by DABCO·$(BF_3)_2$. This is probably due to the high oxidation potential of the complex. The slow buildup and small contribution of the TM observed in the FTEPR spectra supported this speculation. No absorption due to free $DMBP^{\cdot-}$ was observed after the disappearance of the triplet signal, while the FTEPR experiments indicated that photoinduced electron transfer clearly occurred. Since BF_3 is a strong electrophilic reagent, a $DMBP^{\cdot-}$·BF_3 complex would be formed after photolysis, leading to a blue shift of the absorption compared with that of free $DMBP^{\cdot-}$. It can be deduced that the complex formation weakens the Coulomb interaction between the ion radicals and serves to slow down the back electron transfer rate.

The present study clearly shows that the radical ion pair including $DMBP^{\cdot-}$ and $DABCO^{\cdot+}$ has a positive *J* and the addition of BF_3 induces the inversion of the sign of *J*.

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