Bull. Chem. Soc. Jpn., 63, 1441—1446 (1990)

Heavy-Atom Effect on Decay Dynamics of Triplet-State Ion Pairs. Chloranil-Naphthalene (1:2) Termolecular Systems

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(Received December 21, 1989)

Decay kinetics of triplet-state ion pairs (^{3}IPs) have been studied for the termolecular systems consisting of the chloranil anion radical (CA$^{\cdot-}$) with the dimer cation radical of naphthalene (Np$^{\cdot+}$) or its monohalogenated derivatives (NpX$_2^{\cdot+}$) in 1,2-dichloroethane by means of laser photolysis. Marked heavy-atom (HA) effect was found on back electron transfer (back ET) but not on ionic dissociation (ID). A small effect of 1- or 2-brominated compound on ^{3}IP lifetimes was observed. Both back ET and ID processes of ^{3}(CA$^{\cdot-}$, Np$_2^{\cdot+}$) were found to be almost temperature-independent. Electron-transfer (ET) quenching of ^{3}CA leading to produce the (1 : 1) ^{3}IP was also independent on the HA substitution. For these kinetic studies, a conventional decay analysis was examined.

Dynamic properties of the triplet ion pairs (^{3}IPs) have been growing interests in relation not only to reactivity of transient intermediates in triplet-state electron-, proton- and/or hydrogen- transfer reactions[1—13] but also to important information concerning the electron transfer theory.[14] Although a study of ^{3}IP has an advantage that its lifetime can usually be observed directly by conventional nanosecond laser photolysis, back ET to the ground state involves some complicated features associated with spin conversion. Therefore, it would be valuable to study the heavy-atom (HA) effect on decay characteristics of ^{3}IP. The HA effect on ET in contact ^{3}IP or triplet exciplexes has been reported for some usual (1 : 1) systems.[15—18] However, little attention has been paid to the termolecular ^{3}IP.

In this paper, we report spectroscopic and kinetic studies of triplet-state (1 : 2) termolecular ion pairs between chloranil (CA) and naphthalene (Np) or monohalogen-substituted naphthalene (NpX) from the viewpoint of the HA effect. Furthermore, temperature variation experiments for the ^{3}(CA$^{\cdot-}$, Np$_2^{\cdot+}$) system is performed.

Experimental

Transient absorption spectra and decay traces were measured by nanosecond laser photolysis using a Nd:YAG laser system (third harmonics 355 nm, 50 mJ, pulse width 8 ns; JK lasers, HY500). The analyzing light from a pulsed Xe-lamp (150 W; Hamamatsu, L2195) was guided into an entrance slit of a monochromator (Ritsu, MC-20N), after passing an appropriate glass filter and photolyzed area of a sample solution at right angle with respect to the direction of laser beam using optical cables. Out-put from a photomultiplier (Hamamatsu Photonics, R928) was led into a digital storage oscilloscope (Iwatsu, TS-8123) combined with a microcomputer (NEC, PC-9801VX) for data acquisition. Some transient spectra were also observed by ruby laser photolysis at 347 nm as described elsewhere.[3,19]

Electrochemical oxidation potentials of naphthalenes were measured by cyclic voltammetry (CV) at room temperature under aerobic conditions. An apparatus for CV was composed of a Hokutodenko HA-301 potentio/galvanostat in conjunction with a Hokutodenko HB-104 function generator and a cell having platinum electrodes and a saturated calomel electrode as reference. Samples for CV were acetonitrile solutions of ca. 10^{-3} M (1 M=1 mol dm^{-3}) naphthalenes containing 0.1 M lithium perchlorate as a supporting electrolyte. Under these conditions, only the peak potentials (E_p) could be determined.

Chloranil (CA; Wako Chemicals) was purified by repeated recrystallizations and vacuum sublimation after passing it through a column of calcium carbonate using benzene as eluent. Scintilation-grade naphthalene (Np; Dojindo Laboratries) was zone-refined. 1-Chloro- and 1-bromonaphthalenes (1-ClNp and 1-BrNp, respectively; EP grade, Tokyo Kasei) were used as received, because ^{3}IP lifetime was unchanged in test measurements using the substance purified by vacuum distillation. 2-Chloro- and 2-bromonaphthalenes (2-ClNp and 2-BrNp respectively; GR grade, Tokyo Kasei) were used without further purification. Dotite spectrograde 1,2-dichloroethane (DCE), benzene, and acetonitrile were used as solvents. Sample solutions for the photolysis were deaerated by purging with Ar gas at room temperature or by the usual freeze-pump-thaw method for some spectral measurements. Temperature variation of a sample was performed using a cell holder made of alminium blocks by circulating water from a thermostated water bath. A Cu–constantan thermocouple sheet (Philips) was used for temperature calibration (±0.5 °C) of the cell holder. Untill just before the photolysis, a sample cell had been immersed in the water bath for a sufficiently prolonged time (more than 20 min).

Results and Discussion

The chloranil triplet ^{3}CA produced via fast intersystem crossing (ISC)[3] after excitation at 355 nm was quenched rapidly by Np, 1-ClNp, 2-ClNp, 1-BrNp, and 2-BrNp in DCE (k_q=4.9, 3.3, 1.5, 4.6, and 3.3×10^9 M^{-1} s^{-1}, respectively, at 20 °C) to yield the (1 : 1) ^{3}IP, ^{3}(CA$^{\cdot-}$, Np$^{\cdot+}$) or ^{3}(CA$^{\cdot-}$, NpX$^{\cdot+}$). At a higher concentration of the quenchers the (1 : 1) ^{3}IP was converted to the termolecular (1 : 2) ^{3}IP through a succesive reaction with the excess naphthalene molecules. In benzene, which was firstly used as a nonpolar

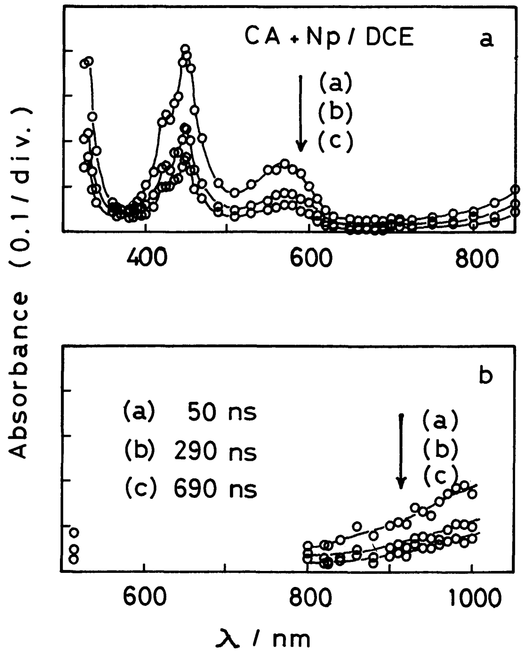

Fig. 1. Time-resolved absorption spectra measured in the system of CA (2.6×10^{-3} M) and Np (0.102 M) in DCE at 20 °C obtained by the ruby laser photolysis using the photomultipliers, a: Hamamatsu R636 and b: Hamamatsu R406. (a) 50, (b) 290, and (c) 690 ns after the beginning of laser oscillation.

solvent for preventing ionic dissociation, no ^{3}IP was produced in cases of NpX except for Np as quenchers. The observed transients in the former systems were the locally excited (LE) triplet exciplex, ^{3}CA...NpX, similar to the exciplex, ^{3}CA...mesitylene, studied previously.[20] In acetonitrile no short-lived ^{3}IP could be observed for each system studied, because the ionic dissociation took place so fast as unable to detect ^{3}IP as in the case of durene donor.[1] This is reasonable from an accepted knowledge that the ionic dissociation occurs with a rate constant of ca. $5\times10^8\ s^{-1}$ in acetonitrile.[21] Hereafter, we describe mainly the experimental results concerning the (1:2) ^{3}IPs observed in DCE.

Figures 1 and 2 show the time-resolved transient absorption spectra for the systems of CA at a high concentration of the naphthalenes in the order of Np, 1-ClNp, 2-ClNp, 1-BrNp, and 2-BrNp obtained by nanosecond laser photolysis. The band around 450 nm is all due to CA$^{\cdot-}$.[1] The band at 570 nm in Fig. 1a is assigned as that of Np$_2^{\cdot+}$ as reported for the same system in other solvents.[22,23] The tail of the charge-resonance band in Np$_2^{\cdot+}$[24,25] was additionally observed in the range 800–1000 nm by using another photomultiplier tube (Hamamatsu, R406) for detection (Fig. 1b). The other bands at 620, 600, 670, and 610 nm in Fig. 2 can also be assigned as those due to the dimer cation radicals, (1-ClNp)$_2^{\cdot+}$, (2-ClNp)$_2^{\cdot+}$, (1-BrNp)$_2^{\cdot+}$, and (2-BrNp)$_2^{\cdot+}$, respectively, from their kinetic behaviors and similarity to the spectra of the dimer cation radicals of Np or Np derivatives.[26–30] For comparison purposes, absorption bands due to a pair of the (monomer and dimer) cation radicals of 1-ClNp, 2-ClNp, 1-BrNp, and 2-BrNp were observed in acetonitrile at (ca. 750 and 620), (685 and 590), (ca. 780 and 640), and (695 and 605) nm, respectively. Each dimer band in acetonitrile resembles well the corresponding one in DCE. No absorption band due to the chloranil semiquinone radical (CAH·) at 435 nm was observed in DCE This result indicates that no proton transfer takes place from the cation radicals to CA$^{\cdot-}$ in the present systems.

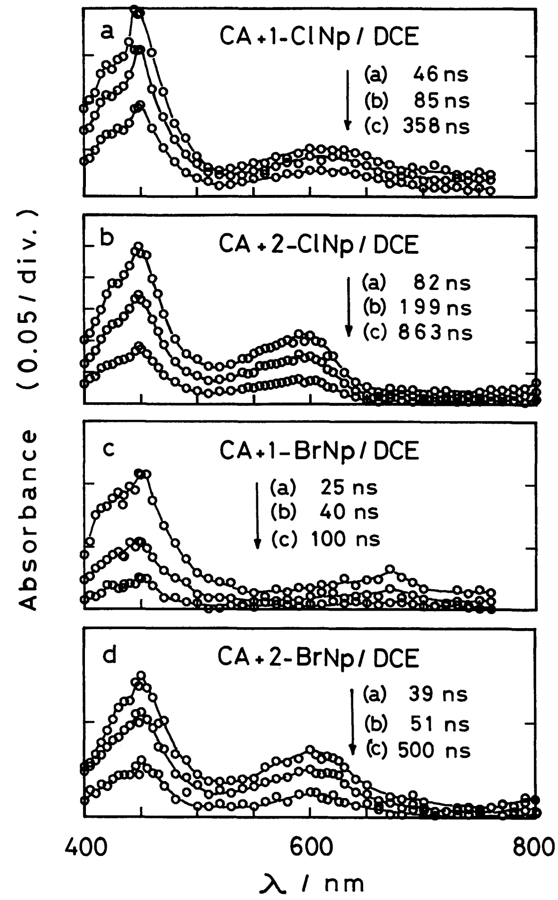

Fig. 2. Time-resolved absorption spectra measured by the Nd:YAG laser system at 20 °C. The samples are a: CA (2.1×10^{-3} M) and 1-ClNp (0.099 M), b: CA (2.0×10^{-3} M) and 2-ClNp (0.102 M), c: CA (2.1×10^{-3} M) and 1-BrNp (0.100 M), and d: CA (2.1×10^{-3} M) and 2-BrNp (0.101 M) in DCE. Time after the beginning of laser oscillation is indicated in the figure.

As can be seen from Figs. 1 and 2, the transient spectra in each system decay keeping the intial shape. Time traces of a pair of the bands due to CA$^{\cdot-}$ and Np$_2^{\cdot+}$ (or NpX$_2^{\cdot+}$) showed an identical decay pattern with two decay components. Figure 3 exemplifies the absorbance decay curves of the bands at 448 and 575 nm corresponding to the peaks of CA$^{\cdot-}$ and Np$_2^{\cdot+}$, respectively, obtained by one-shot excitation for the

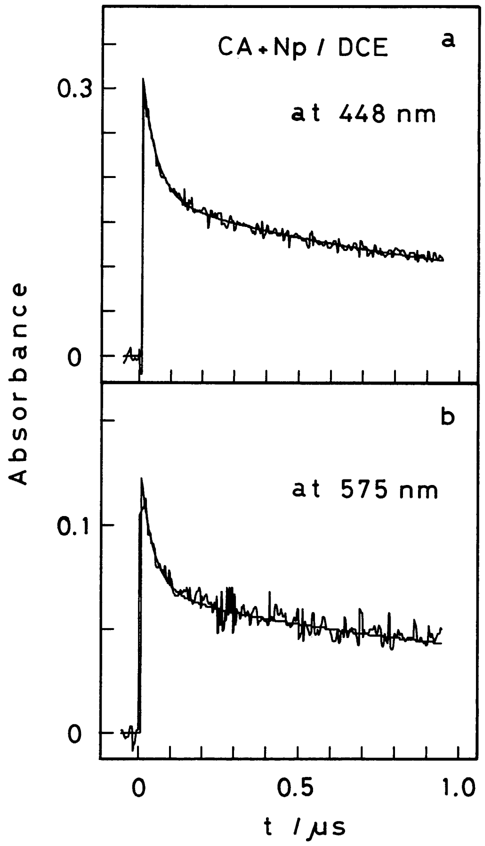

Fig. 3. Observed and calculated (smoose line) decay curves at a: 448 and b: 575 nm in the CA (2.0×10^{-3} M)–Np (0.100 M) system. Parameters for fitting are a: $k_1=2.195\times10^7$, $k_2/\varepsilon=4.019\times10^6\ \mathrm{s}^{-1}$, $\phi_i=0.5596$, $D_0=0.3063$ and b: $k_1=2.349\times10^7$, $k_2/\varepsilon=9.243\times10^6\ \mathrm{s}^{-1}$, $\phi_i=0.5517$. $D_0=0.1203$.

CA–Np system. (The smoose lines will be interpreted below.) Two curves are quite similar to each other in spite of great difference in absorbance. The long-lived component at 448 nm was confirmed to obey exactly the 2nd-order decay law in a more delayed, wide time region. After the extrapolation of this 2nd-order decay to the initial time region, the difference absorbance between the observed and extrapolated curves gave a decay of approximately single exponential. Therefore, it is plausible to suppose that in Fig. 3 the rapid decay in the initial stage corresponds to that of ^{3}IP and the slow 2nd-order decay is attributable to that of free ions. From these spectral and decay features, the reaction scheme of $^3(\mathrm{CA}^{\cdot-}, \mathrm{Np}_2^{\cdot+})$ as an example may be written as follows:

$$\begin{tikzcd}
& {}^3(\mathrm{CA}^{\cdot-}, \mathrm{Np}_2^{\cdot+}) \arrow[d, "k_d"'] \arrow[dr, "k_i"] & & \\
\mathrm{CA} + 2\mathrm{Np} & (\mathrm{CA}, \mathrm{Np}_2) \arrow[l] & \mathrm{CA}^{\cdot-} + \mathrm{Np}_2^{\cdot+} \arrow[r, "k_2"] & \mathrm{CA} + 2\mathrm{Np}\ \text{or other products}
\end{tikzcd}$$

where k_d and k_i are the rate constants for the back ET to the ground state and the ionic dissociation to free ions, respectively, and k_2 is the 2nd-order decay rate constant of the free $\mathrm{CA}^{\cdot-}$ or $\mathrm{Np}_2^{\cdot+}$. According to this scheme, the decay kinetics of ^{3}IP and the free ions (FI) are given by the following equations:

$$\mathrm{d}[^3\mathrm{IP}]/\mathrm{d}t = -(k_i + k_d)[^3\mathrm{IP}] \tag{1}$$

$$\mathrm{d}[\mathrm{FI}]/\mathrm{d}t = k_i[^3\mathrm{IP}] - k_2[\mathrm{FI}]^2 \tag{2}$$

From spectral similarity, both ^{3}IP and FI in the present systems may be approximated to have identical values of the extinction coefficient (ε) at the same wavelength (λ). In such a case, the observed absorbance (D) which is the sum of absorbances due to ^{3}IP and FI follows Eq. 3:

$$\begin{aligned}\mathrm{d}D/\mathrm{d}t = &-(1-\phi_i)k_1D_0\exp(-k_1t)\\ &-(k_2/\varepsilon)[D - D_0\exp(-k_1t)]^2\end{aligned} \tag{3}$$

where $k_1=k_i+k_d$, $\phi_i=k_i/(k_i+k_d)$ and D_0 denotes the initial value of D at $t=0$. This solution is not simple.[31]

In order to estimate the parameters, k_1, k_2/ε and ϕ_i, we adopt firstly a tentative model consisting of two species (M_1 and M_2) which decay independently with 1st- and 2nd-order kinetics, respectively:

$$\mathrm{d}[\mathrm{M}_1]/\mathrm{d}t = -k_1'[\mathrm{M}_1] \tag{4}$$

$$\mathrm{d}[\mathrm{M}_2]/\mathrm{d}t = -k_2'[\mathrm{M}_2]^2 \tag{5}$$

When two species have an equal ε at λ, the sum of absorbances due to M_1 and M_2 (D') is expressed by the following equation:

$$D' = A_1\exp(-k_1't) + 1/[(1/A_2) + (k_2'/\varepsilon)t] \tag{6}$$

where A_1 and A_2 are the respective absorbances of M_1 and M_2 at $t=0$. The differential of Eq. 6 derives Eq. 7 which is rather similar in form to Eq. 3:

$$\begin{aligned}\mathrm{d}D'/\mathrm{d}t = &-(1-\phi_i')k_1'D_0'\exp(-k_1't)\\ &-(k_2'/\varepsilon)[D' - (1-\phi_i')D_0'\exp(-k_1't)]^2\end{aligned} \tag{7}$$

where $\phi_i'=A_2/(A_1+A_2)$ and D_0' denotes the value of D' at $t=0$. We set $t=0$ at the time when the laser pulse for excitation reaches its maximum (8 ns after the start of laser oscillation). Here, we use Eq. 6 as an approximate solution of Eq. 3 and assume that ϕ_i', k_1' and k_2' correspond approximately to ϕ_i, k_1, and k_2, respectively, defined in the actual scheme. Namely, this model means that M_1 with an initial absorbance of $(1-\phi_i)D_0$ decays with the rate constant k_1' and M_2 with the partial absorbance ϕ_iD_0 at $t=0$ decays independently with the 2nd-order rate constant k_2'. Nonlinear least square fitting (Marquardt method) by use of Eq. 6 was successfully performed with small standard deviations (≦0.5%) estimated for all observed decay data within the range 97—3% of the maximum adsorbance and yielded nearly constant values of the respective parameters for the data under identical conditions. Secondly, we achieved integration of Eq. 3 by the Runge-Kutta method using the parameter values obtained by the above-mentioned fitting in order to compare the calculated curve with the observed one. Decay traces calculated by the Runge-Kutta method were found to follow approximately well the observed ones. Furthermore, we could obtain a fairly good result by simulating again after a little change (≦5%) only in the D_0 value with no change in the other parameter values. The fitting curves are overlaid by the smooth lines in Fig. 3. From the values of k_2/ε estimated at 448 and 575 nm, the ratio of the extinction coefficients, $\varepsilon(575)/\varepsilon(448)$, is calculated to be 0.43. On the other hand, $\varepsilon(575)/\varepsilon(448)=0.38$ is obtained from Fig. 1. The agreement between these two values is fairly good. Thus, the values of k_1', k_2'/ε and ϕ_i' estimated by the first procedure can be used as the reliable values for k_1, k_2/ε and ϕ_i, respectively, although more rigorous approaches have been recomended.[32,33] The most probable reason for the success of this approach would be due to the fact that the model adopted is appropriate; namely, Eq. 7 is formally close to Eq. 3 and the reassignment of the D_0 value estimated by the 1st step would contribute to decrease a difference between Eqs. 3 and 7. This method has the advantage that it can determine ϕ_i simultaneously together with k_1 and k_2/ε values from only decay traces. Therefore, even when the absorption band of a CT complex in the ground state overlaps with the band of free CA at the wavelength for excitation, the ϕ_i value for ^{3}IP can be estimated without regard to the yield of ^{3}IP formed through the ^{3}CA quenching or direct excitation of the complex. The present systems correspond to such circumstances in the high concentration region of the naphthalenes more than 0.01 M; e.g., the formation constant $K=0.8\ \mathrm{M^{-1}}$ was measured for the complex CA···Np, in DCE at 20 °C. When the extinction coefficient of ^{3}IP (ε_1) is not equal to that of FI (ε_2), Eqs. 3 and 7 are revised as Eqs. 3′ and 7′.

$$\mathrm{d}D/\mathrm{d}t = -\,[1-(\varepsilon_2/\varepsilon_1)\phi_i]k_1D_0\exp(-k_1t) - (k_2/\varepsilon_2)\,[D-D_0\exp(-k_1t)]^2 \qquad (3')$$

$$\mathrm{d}D'/\mathrm{d}t = -\,(1-\phi_i')k_1'D_0'\exp(-k_1't) - (k_2/\varepsilon_2)\,[D'-(1-\phi_i')D_0'\exp(-k_1't)]^2 \qquad (7')$$

In such a general case, therefore, if we assume that ϕ_i' defined as $A_2/(A_1+A_2)$ corresponds to $(\varepsilon_2/\varepsilon_1)\phi_i$, the present method of estimation can be utilized in the same manner as descrived above.

The lifetimes of ^{3}IP estimated by the present simple method were almost independent on the donor concentrations in the range 0.05—0.2 M for all systems examined. Therefore, it can be said that the observed lifetime of the (1:2) ^{3}IP is not affected by lifetime of the corresponding (1:1) ^{3}IP, because the equilibrium between (1:1) and (1:2) ^{3}IPs, e.g., $^3(\mathrm{CA}^{\bar{\cdot}}, \mathrm{Np}^{+})+\mathrm{Np} \longleftrightarrow {}^3(\mathrm{CA}^{\bar{\cdot}}, \mathrm{Np_2}^{\dagger})$, inclines sufficiently toward the (1:2) ^{3}IP side at the above concentrations. Table 1 lists the values of k_1, ϕ_i, k_i and k_d together with those of k_q and the peak oxidation potential (E_p). The temperature dependence of k_i and k_d was carefully examined for the ion pair, $^3(\mathrm{CA}^{\bar{\cdot}}, \mathrm{Np_2}^{\dagger})$, in the temperature range 10—45 °C. Arrhenius plots shown in Fig. 4 provide the activation energy $E_a=1.0\pm1.2\ \mathrm{kJ\,mol^{-1}}$; the frequency

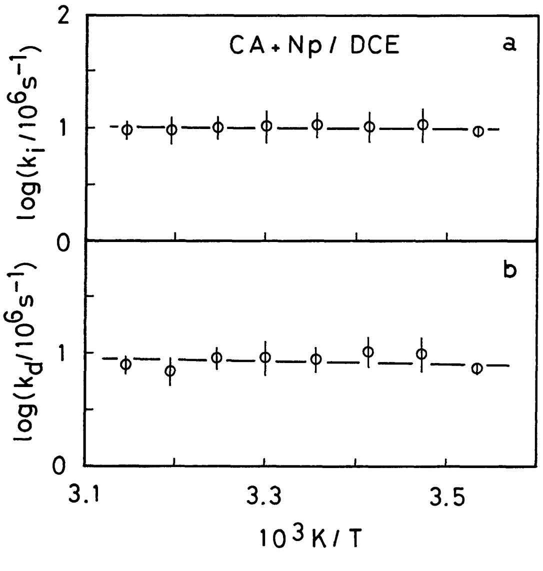

Fig. 4. Arrhenius plots for k_i and k_d of $^3(\mathrm{CA}^{\bar{\cdot}}, \mathrm{Np_2}^{\dagger})$.

Table 1. Kinetic Parameters for $^3(\mathrm{CA}^{\bar{\cdot}}, \mathrm{Np_2}^{\dagger})$ and $^3(\mathrm{CA}^{\bar{\cdot}}, \mathrm{NpX_2}^{\dagger})$ in DCE at 20°C

Donor	E_p[a)]	k_q	ϕ_i	k_1	k_i	k_d
	V	$10^9\ \mathrm{M^{-1}\,s^{-1}}$			$10^6\ \mathrm{s^{-1}}$	
Np	1.68	4.9±0.2	0.54±0.04	22±4	12±3	10±3
1-ClNp	1.73	3.3±0.2	0.52±0.02	18±2	9±1	9±1
2-ClNp	1.79	1.5±0.1	0.46±0.04	15±3	7±2	8±2
1-BrNp	1.71	4.6±0.2	0.08±0.01	75±7	6±1	69±16
2-BrNp	1.75	3.3±0.1	0.16±0.03	47±4	7±2	40±11

a) The peak oxidation potential (vs. SCE) measured in acetonitrile at the sweep rate 100 mV s^{-1}.

factor $A=10^{(7.2\pm0.2)}$ s^{-1} for k_i and $E_a=1.7\pm2.6$ kJ mol^{-1}; $A=10^{(7.2\pm0.5)}$ s^{-1} for k_d. Such small E_a values less than 3 kJ mol^{-1} and A values of the 10^6—10^7 s^{-1} order were also obtained for each rate constant in $^3[\mathrm{CA}^{\cdot-}, (2\text{-ClNp})_2^{\cdot+}]$ and in $^3[\mathrm{CA}^{\cdot-}, (2\text{-BrNp})_2^{\cdot+}]$

In Table 1, the k_q values do not depend on halogenation but tend to increase with a decrease in E_p, i.e., corresponding to the Marcus "normal" region. Since the quenching of ^{3}CA is an ET process leading to produce the (1:1) ^{3}IP, this result indicates that the spin-allowed ET is not affected by HA perturbation while depends sensitively on change in the ionization energy of the donors induced by halogen substitution. The k_i values for the ionic dissociation are nearly equal to each other and have no correlation with the halogenation. These results implies that the ionic dissociation is a diffusive separation with no respect to spin–orbit (SO) interaction. The termolecular ion pair $^3(\mathrm{CA}^{\cdot-}, \mathrm{Np}_2^{\cdot+})$ may be a loose ^{3}IP since a little activation energy ($\leqq$1.2 kJ mol^{-1}) is required for the dissociation. This supposition will be related later to a relaxation mechanism of ^{3}IP.

In contrast to k_i, the column of k_d values in Table 1 shows remarkable enhancement of the back ET in the brominated ^{3}IP. This fact gives evidence for enhancement in the triplet–singlet transition of ^{3}IP induced by SO interaction. The change in brominated positions appears to have a little effect on the enhancement of k_d, probably depending on the difference of spin density between 1- and 2-positions on the naphthalene ring of the dimer cation radical.[34] This interpretation is similar to that given by Steiner and Winter for the triplet exciplexes between thionine and monohalogenated anilines.[15] Although the effect of Cl-substitution on the cation radical part does not lead to the enhancement of k_d, it is due to the masking by coexistence of the polychlorinated anion radical ($\mathrm{CA}^{\cdot-}$) and solvent (DCE). Practically no effect of chlorination has been known also for the 2,6-diphenyl-3-chloro-*p*-benzoquinone–triphenylamine and CA–chloroanthracene systems in nonhalogenated solvent.[17,18] Hence, it is considered that perturbation by Cl-substitution is usually week and does not affect on the rapid ET in these ^{3}IPs.

If the energy level of the singlet IP, $^1(\mathrm{CA}^{\cdot-},\mathrm{Np}_2^{\cdot+})$ is considerably higher than that of the triplet one as supposed by Levin et al. for the CA–durene ($E_{1/2}=1.59$ V) system,[35] it can be considered that the back ET is the direct transition from ^{3}IP to the singlet ground state, i.e., $^3(\mathrm{CA}^{\cdot-}, \mathrm{Np}_2^{\cdot+})\rightarrow{}^1(\mathrm{CA},\mathrm{Np}_2)$, not via the $^1(\mathrm{CA}^{\cdot-}, \mathrm{Np}_2^{\cdot+})$ state as a real intermediate, because the activation energy observed for k_d is very small ($\leqq$3 kJ mol^{-1}) in the present case. This conclusion for the back ET has been also premised on elucidation of the log k_d vs. ΔG (free energy change) relation in the similar quinone–aromatic hydrocarbon and amine systems.[14] However, as mentioned above, $^3(\mathrm{CA}^{\cdot-},\mathrm{Np}_2^{\cdot+})$ observed here may be a loose ^{3}IP, e.g., "solvent separated geminate ^{3}IP", so that there is a possibility that the energy-level splitting between its singlet and triplet states is so small as to yield practically no activation energy. Even in such case, the transition $^3\mathrm{IP}\rightarrow{}^1\mathrm{IP}$ may take place efficiently with a rate of 10^7—10^8 s^{-1} (the same order as observed) and also may be enhanced by HA effect through SO interaction.[17,36] Since ^{1}IPs produced in these CT complex-forming systems are known to cause extremely rapid internal conversion returning to their ground states,[1,3] then the overall rate of an indirect route for back ET via the singlet state ($^3\mathrm{IP}\rightarrow{}^1\mathrm{IP}\rightarrow$ the ground state) may be governed by that of the first step accompaning spin inversion. Therefore, the decay mechanism of the direct transition mentioned previously may be not always valid. In this respect, further experiments including environmental effect or external magnetic field effect would be required for clear discrimination whether or not the indirect route contributes to the back ET of the present ^{3}IPs.

Summary

1) The existence of termolecular triplet ion pairs was demonstrated spectroscopically in the chloranil–naphthalene or –halonaphthalene systems.

2) The termolecular ion pair $^3(\mathrm{CA}^{\cdot-}, \mathrm{Np}_2^{\cdot+})$ is considered to be a loose ^{3}IP from the result of a very low activation barrier in the ionic dissociation; i.e., temperature dependence of k_i surves as a probe for discrimination between contact and loose ion pairs.

3) The spin-forbidden back ET of $^3(\mathrm{CA}^{\cdot-}, \mathrm{Np}_2^{\cdot+})$ is greatly enhanced by HA effect through SO interaction.

4) The ion pair $^3(\mathrm{CA}^{\cdot-}, \mathrm{Np}_2^{\cdot+})$ requires also only a little activation energy for the back ET process.

The authors are grateful to Mr. Tetsuhiro Sekiguchi for his great assistance in computer-programing and to Prof. Zenjiro Osawa of this department for facilities of cyclic voltammetry.

References

1) H. Kobashi, M. Funabashi, T. Kondo, T. Morita, T. Okada, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **57**, 3557 (1984).

2) H. Kobashi, T. Kondo, and M. Funabashi, *Bull. Chem. Soc. Jpn.*, **59**, 2347 (1986).

3) H. Kobashi, M. Funabashi, H. Shizuka, T. Okada, and N. Mataga, *Chem. Phys. Lett.*, **160**, 261 (1989).

4) V. A. Kuzmin, A. P. Darmanyan, and P. P. Levin, *Chem. Phys. Lett.*, **63**, 509 (1979).

5) P. P. Levin, T. A. Kokrashvili, and V. A. Kuzmin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **32**, 251 (1983).

6) V. A. Kuzmin and P. P. Levin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **37**, 429 (1988).

7) G. Jones, II and W. A. Haney, *J. Phys. Chem.*, **90**, 5410 (1986).

8) G. Jones, II, W. A. Haney, and X. T. Phan, *J Am.*

Chem. Soc., **110**, 1922 (1988).

9) G. Jones, II and N. Mouli, *J. Phys. Chem.*, **92**, 7174 (1988).

10) S. Arimitsu and H. Masuhara, *Chem. Phys. Lett.*, **22**, 543 (1973); S. Arimitsu, H. Masuhara, N. Mataga, and H. Tubomura, *J. Phys. Chem.*, **87**, 4855 (1983).

11) J. D. Simon and K. S. Peters, *Acc. Chem. Res.*, **17**, 277 (1984).

12) K. Hamanoue, T. Nakayama, K. Sugiura, H. Teranishi, M. Washio, S. Tagawa, and Y. Tabata, *Chem. Phys. Lett.*, **118**, 503 (1985).

13) M. Hoshino, H. Seki, and H. Shizuka, *Chem. Phys.*, **129**, 395 (1989).

14) P. P. Levin, P. F. Pluzhnikov, and V. A. Kuzmin, *Chem. Phys. Lett.*, **147**, 283 (1988); P. P. Levin, V. A. Kuzmin, and P. F. Pluzhnikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **37**, 874 (1988).

15) U. Steiner and G. Winter, *Chem. Phys. Lett.*, **55**, 368 (1978).

16) G. Winter and U. Steiner, *Ber. Bunsen-Ges. Phys. Chem.*, **84**, 1203 (1980).

17) P. P. Levin, T. A. Kokrashvili, and V. A. Kuzmin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **31**, 466 (1982).

18) P. F. Pluzhnikov, P. P. Levin, and V. A. Kuzmin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **37**, 2369 (1988).

19) H. Kobashi, H. Gyoda, and T. Morita, *Bull. Chem. Soc. Jpn.*, **50**, 1731 (1977).

20) H. Kobashi, T. Okada, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **59**, 1975 (1986); H. Kobashi, K. Hiratsuka, and K. Motegi, *Bull. Chem. Soc. Jpn.*, **61**, 298 (1988).

21) I. R. Gould, D. Ege, S. L. Mattes, and S. Farid, *J. Am. Chem. Soc.*, **109**, 3794 (1987); I. R. Gould, J. E. Moser, D. Ege, and S. Farid, *J. Am. Chem. Soc.*, **110**, 1993 (1988).

22) R. Gschwind and E. Haselbach, *Helv. Chim. Acta*, **62**, 941 (1979).

23) E. F. Hillinsky, S. V. Milton, and P. M. Rentzepis, *J. Am. Chem. Soc.*, **105**, 5193 (1983).

24) A. Kira, T. Nakamura, and M. Imamura, *J. Phys. Chem.*, **81**, 511 (1977).

25) M. Yamamoto, Y. Tsuji, and A. Tsuchida, *Chem. Phys. Lett.*, **154**, 559 (1989).

26) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2588 (1969).

27) T. Shida and S. Iwata, *J. Am. Chem. Soc.*, **95**, 3473 (1973).

28) C. K. Grätzel, A. Kira, M. Jirousek, and M. Grätzel, *J. Phys. Chem.*, **87**, 3983 (1983).

29) M. A. J. Rodgers, *J. Chem. Soc. Faraday 1*, **68**, 1278 (1972).

30) A. Tuchida, Y. Tujii, S. Ito, M. Yamamoto, and Y. Wada, *J. Phys. Chem.*, **93**, 1244 (1989).

31) J.-Y. Chien, *J. Am. Chem. Soc.*, **70**, 2256 (1948).

32) L. Andrews, J. M. Levy, and H. Linschitz, *J. Photochem.*, **6**, 355 (1976/77).

33) Y. Tang and J. A. Butcher, Jr., *J. Phys. Chem.*, **89**, 4844 (1985).

34) A. Terahara, H. Ohya-Nishiguchi, N. Hirota, and A. Oku, *J. Phys. Chem.*, **90**, 1564 (1986).

35) P. P. Levin, P. F. Pluzhnikov, and V. A. Kuzmin, *Chem. Phys. Lett.*, **152**, 409 (1988).

36) U. Steiner, *Z. Naturforsch.*, **34a**, 1093 (1979); *Chem. Phys. Lett.*, **74**, 108 (1980); T. Ulrich, U. E. Steiner, and R. E. Föll, *J. Phys. Chem.*, **87**, 1873 (1983).