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Salt Effect for Accelerating Charge Separation from 9,10-Dicyanoanthracene–Stilbene Exciplex in Dichloromethane

Bao Wen ZHANG,[†#] Yasunao KURIYAMA,[#] Yi CAO,[†] and Katsumi TOKUMARU[#*]
#Department of Chemistry, University of Tsukuba, Ibaraki 305
†Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, China

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Synopsis. On irradiation of 9,10-dicyanoanthracene (DCA) in the presence of *cis*-(CS) and *trans*-stilbene (TS) in dichloromethane, addition of tetrabutylammonium tetrafluoroborate efficiently accelerated production of the radical cations from CS and TS along with DCA radical anions.

In these several years, much interest has been paid to the isomerization of aromatic ethylenes sensitized by electron acceptors like 9,10-dicyanoanthracene (DCA).[1—8] In acetonitrile the reaction was shown to proceed through conversion of cis to trans radical cations of ethylenes by steady state irradiation[4] as well as transient absorption spectroscopy.[7,8] Recently some of the present authors found that in dichloromethane, a less polar solvent than acetonitrile, addition of tetrabutylammonium tetrafluoroborate, $Bu_4N^+BF_4^-$, (TBTF) accelerated DCA-sensitized isomerization of *cis*-(CS) to *trans*-stilbene (TS) through quenching of the exciplex between DCA and CS.[9] This finding has led us to investigate the mechanism of the above salt effect by means of transient absorption spectroscopy and fluorometry as reported below.

Experimental

Materials. DCA (Tokyo Kasei) and TS (Tokyo Kasei) were recrystallized twice from ethanol. CS (Nacalai Tesque) was chromatographed over silica gel eluting with hexane. TBTF (Nacalai Tesque) and dichloromethane (Kanto Kagaku) were used as received.

Measurement. Fluorescence was measured on a Hitachi F-4000 fluorescence spectrophotometer. Fluorescence lifetimes were determined by single photon counting on a Horiba NAES-1100 apparatus. Laser flash photolysis was performed as described elsewhere.[10] The excitation was done with 425 nm light from a Lambda Physik FL-3002 dye laser (Dye: Stilben 3, 6—7 mJ/Pulse) pumped by a 308 nm XeCl Lambda Physik LPX100 excimer laser (10 ns fwhm).

Results

Fluorescence Behavior. The fluorescence of DCA was efficiently quenched by TS and CS in aerated dichloromethane obeying the Stern–Volmer relationship (Eq. 1) with quenching constants, $k_q\tau_0$, of 173 and 170 $mol^{-1}\,dm^3$ and giving fluorescence of the resulting exciplex at $\lambda_{max}=581$ and 571 nm with lifetimes of 19.2 and 18.9 ns under air, respectively,

$$I_0/I = 1 + k_q\tau_0[Q] \qquad (1)$$

where I_0 and I stand for the fluorescence intensity of a fluorescer, DCA, in the absence and the presence of the quencher, CS or TS, k_q, the quenching rate constant, and τ_0, the lifetime of the fluorescer in the absence of the quencher. The k_q's were obtained as 1.15×10^{10} $dm^3\,mol^{-1}\,s^{-1}$ for TS and 1.13×10^{10} $dm^3\,mol^{-1}\,s^{-1}$ for CS; the latter reasonably agrees with 9.6×10^9 $dm^3\,mol^{-1}\,s^{-1}$ as previously determined for CS.[9] In dichloromethane, absorption and fluorescence spectra of DCA did not show any evidence for its charge-transfer interaction with TS or CS.

Addition of TBTF (1×10^{-3}—1×10^{-2} $mol\,dm^{-3}$) effectively quenched the intensity and the lifetime of the fluorescence from the exciplex between DCA (10^{-5} $mol\,dm^{-3}$) and CS (10^{-1} $mol\,dm^{-3}$) as previously observed[9] and that with TS (5×10^{-2} $mol\,dm^{-3}$) without shift of the emission maxima as depicted in Fig. 1 for TS. On the other hand, TBTF did not affect the fluorescence of DCA, since the fluorescence lifetime of DCA (15.0 ns in aerated dichloromethane) was essentially unaffected by addition of TBTF (10^{-3}—10^{-1} $mol\,dm^{-3}$). Quenching of the emission from the exciplex between $^1DCA^*$ and TS or CS by TBTF fits the Stern–Volmer relation as illustrated in Fig. 1, which gives the quenching rate constants as 5.9×10^9 and 5.5×10^9 $dm^3\,mol^{-1}\,s^{-1}$ for TS and CS, respectively.

Transient Absorption. Laser excitation of

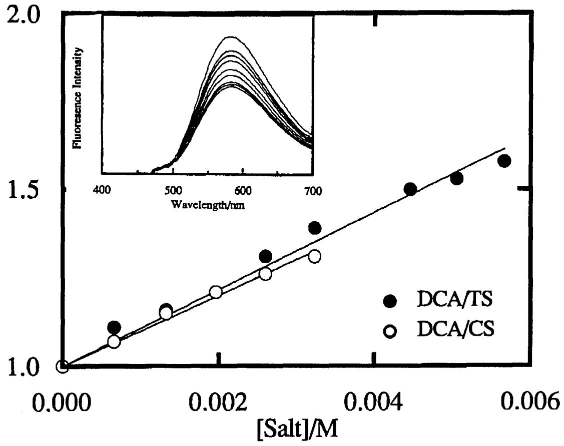

Fig. 1. Stern–Volmer plots for quenching of DCA–TS and DCA–CS exciplexes by TBTF in CH_2Cl_2. $[DCA]=10^{-5}$ $mol\,dm^{-3}$, $[TS]=0.05$ $mol\,dm^{-3}$, $[CS]=0.1$ $mol\,dm^{-3}$. Insert shows the quenching of DCA–TS exciplex by $Bu_4N^+BF_4^-$ (TBTF) in CH_2Cl_2. $[DCA]=10^{-5}$ $mol\,dm^{-3}$, $[TS]=0.05$ $mol\,dm^{-3}$.

DCA (10^{-4} mol dm^{-3}) in the presence of TS (5×10^{-2} mol dm^{-3}) and CS (5×10^{-2} mol dm^{-3}) in dichloromethane under argon at 425 nm afforded transient spectra as depicted in Figs. 2 and 3. Immediately after the laser excitation, both the emission (around 600 nm) and the $S_n \leftarrow S_0$ absorption of the exciplexes, $^1DCA^*$–TS and $^1DCA^*$–CS (around 500 nm), appeared and almost completely decayed in 200 ns (Fig. 2), to give in subsequent 0.6—50 μs the absorptions of $^3DCA^*$ (λ_{max} 440, 660, 730, and 805 nm)[11] along with weaker absorptions of DCA anion, DCA$^{-\bullet}$ (λ_{max} 640 and 705 nm),[12] and the radical cation of stilbene as observed at 480 nm for TS$^{+\bullet}$ (Fig. 3a).

Laser excitation under air reduced the absorption of $^3DCA^*$, which enabled one to observe the absorptions of TS$^{+\bullet}$ and particularly CS$^{+\bullet}$ more clearly along with the absorption of DCA$^{-\bullet}$ than under argon. In DCA–TS, TS$^{+\bullet}$ decayed by second-order kinetics with a rate constant of 3.9×10^7 dm^3 mol^{-1} s^{-1} attributable to recombination with the resulting anion radicals.

On addition of 0.1 mol dm^{-3} TBTF to DCA–TS under argon, the $^1DCA^*$–TS exciplex was not observed in the early stage but the production of TS$^{+\bullet}$ and DCA$^{-\bullet}$ was accelerated retarding the production of $^3DCA^*$. Moreover, introduction of air further suppressed the formation of $^3DCA^*$. The resulting TS$^{+\bullet}$ decayed nearly ten times more slowly than in the absence of the salt, with a second order rate constant, 2.4×10^6 dm^3 mol^{-1} s^{-1} (Fig. 3b). Likewise, in DCA–CS under air, 0.1 mol dm^{-3} TBTF increased the production of CS$^{+\bullet}$ and retarded the formation of $^3DCA^*$; however, no absorption due to TS$^{+\bullet}$ was observed in the experimental time region.

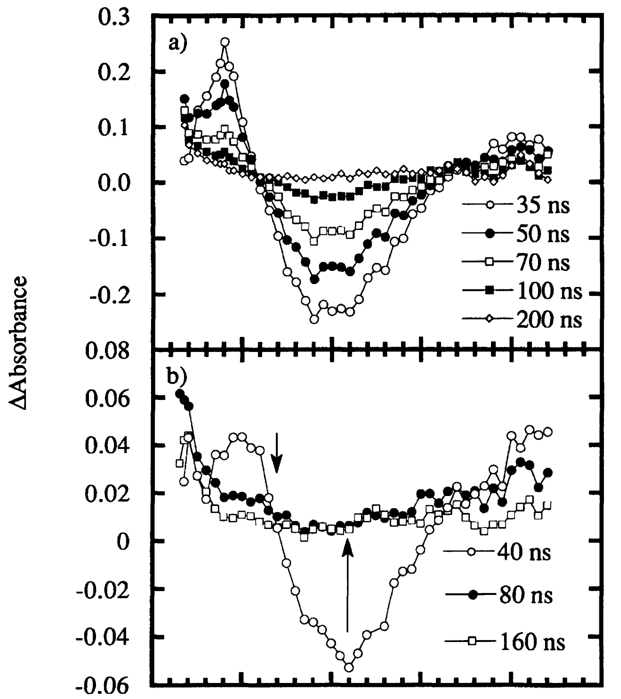

Fig. 2. Transient absorption spectra observed in nanoseconds region after the excitation of DCA (10^{-4} mol dm^{-3}) in CH_2Cl_2 under argon with 425 nm laser. a) in the presence of TS (0.05 mol dm^{-3}), b) in the presence of CS (0.05 mol dm^{-3}).

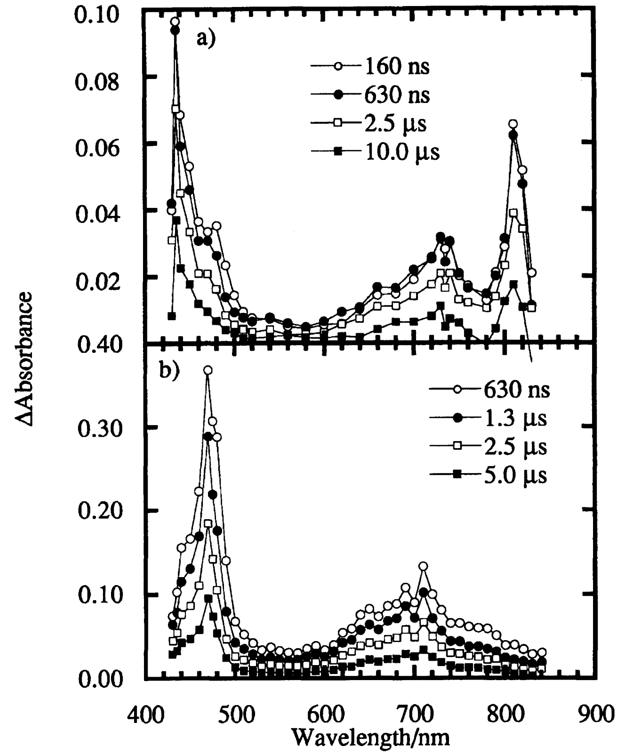

Fig. 3. Transient absorption spectra observed in microseconds region after the excitation of DCA (10^{-4} mol dm^{-3}) in the presence of TS (0.05 mol dm^{-3}) in CH_2Cl_2. a) under argon, b) under air in the presence of TBTF (0.1 mol dm^{-3}).

In both DCA–TS and DCA–CS, the addition of the salt tended to increase the yield of TS$^{+\bullet}$ and CS$^{+\bullet}$, respectively. Figure 4 plots their absorbance observed 500 ns after the laser excitation against the concentrations of TBTF. From TS, TS$^{+\bullet}$ was increased with the salt concentration, however, from CS, CS$^{+\bullet}$ was increased until [TBTF] reached to 1.5×10^{-2} mol dm^{-3}, and then saturated.

Table 1 summarized second order rate constants for the decay of TS$^{+\bullet}$ determined in DCA–TS with varying concentration of TBTF under argon and air together with the absorbance of TS$^{+\bullet}$ observed 500 ns after laser excitation.

Discussion

The electron transfer from TS and CS to $^1DCA^*$ in dichloromethane will be accompanied by reduction of Gibbs's free energy ($\Delta G^\circ < 0$) as estimated by the following equation.[13]

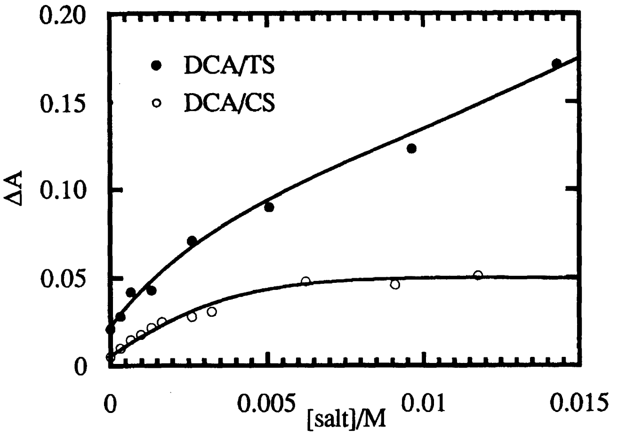

Fig. 4. The observed absorbance (ΔA) of the resulted $TS^{+\bullet}$ and $CS^{+\bullet}$ against TBTF concentration after 500 ns laser (425 nm) excitation of DCA (10^{-4} mol dm^{-3}) in the presence of TS (0.05 mol dm^{-3}) and CS (0.05 mol dm^{-3}) in CH_2Cl_2 under air.

Table 1. Effect of $Bu_4N^+BF_4^-$ Concentration on Second Order Rate Constants for Decay of $TS^{+\bullet}$ Resulted from 425 nm Laser Excitation of DCA (10^{-4} mol dm^{-3}) in the Presence of TS (0.05 mol dm^{-3}) in CH_2Cl_2 under Air and Argon

Atmosphere	Air		Ar	
Salt/M[c]	ΔA[a]	k/ε 10^6 [b]	ΔA[a]	k/ε 10^6 [b]
0	0.023	14.4	0.031	21.3
0.001	0.096	4.51	0.064	2.85
0.01	0.170	2.18	0.171	1.75
0.1	0.251	1.55	0.221	1.77

a) The initial increase of the absorbance at 480 nm corresponding to the concentration of resulting $TS^{+\bullet}$. b) Second order rate constants measured as cm s^{-1} on a transient digitizer. c) M=mol dm^{-3}.

$$\begin{aligned}\Delta G^0 = {} & E_{\mathrm{ox}}(\mathrm{TS}^{+\bullet}/\mathrm{TS}\text{ or }\mathrm{CS}^{+\bullet}/\mathrm{CS}) \\ & -E_{\mathrm{red}}(\mathrm{DCA}/\mathrm{DCA}^{-\bullet}) \\ & -E_{\mathrm{s}}(\mathrm{DCA}) - e^2/\varepsilon r + \alpha\end{aligned}$$

where E_s(DCA) denotes the singlet excitation energy of DCA, the term $e^2/\varepsilon r$ corresponds to the Coulombic energy between the resulting radical cation and anion separated by distance r in a medium with dielectric constant ε, and α is an additional term applied in not very polar solvents like dichloromethane around 0.2 eV.[13)] Based on the values of $E_{ox}(TS^{+\bullet}/TS)$, $E_{ox}(CS^{+\bullet}/CS)$, and $E_{red}(DCA/DCA^{-\bullet})$ as 1.49, 1.59, and −0.98 V vs. SCE in CH_3CN, and E_s(DCA) as 2.88 eV,[14)] addition of the first three terms of the above equation, $E_{ox}-E_{red}-E_s$, gives −0.5 and −0.39 eV for TS and CS, respectively. Further addition of the last two terms in the above equation will still keep ΔG^0 to be slightly negative for both TS and CS.

In dichloromethane, $^1DCA^*$ is quenched by TS or CS to give exciplexes, which either deactivate by the way of fluorescence emission, internal conversion and intersystem crossing as observed by formation of $^3DCA^*$, or dissociate, though not efficiently, into $TS^{+\bullet}$ or $CS^{+\bullet}$ along with $DCA^{-\bullet}$.

However, addition of TBTF leads to quenching of the exciplexes and their dissociation to $TS^{+\bullet}$, $CS^{+\bullet}$ along with $DCA^{-\bullet}$ by retarding recombination between these resulting radical ions. As Table 1 indicates, the second order decay rate constant of $TS^{+\bullet}$ is remarkably reduced on addition of 10^{-3} mol dm^{-3} TBTF, and then gradually decreased with further increase of TBTF concentration irrespective of the atmosphere. These results show that the radical cations and anions are stabilized by Coulombic interaction with BF_4^- and Bu_4N^+, respectively.

It is noteworthy that in the presence of the salt the rate constant is essentially unaffected by the atmosphere, although the rate constant is slightly higher under argon than under air in the absence of the salt. These facts are much contrasted with the recombination of the radical ions in acetonitrile; the radical ion pair between 1,4-dicyanonaphthalene anion ($DCN^{-\bullet}$) and $TS^{+\bullet}$ as well as that between $DCN^{-\bullet}$ and 1,4-dimethoxybenzene cation undergo nearly ten times and forty times slower recombination under air than under argon, which was ascribed to production of $O_2^{-\bullet}$ by electron transfer from $DCN^{-\bullet}$ to oxygen.[15)]

Therefore, in dichloromethane, a much less polar solvent than acetonitrile, $DCA^{-\bullet}$ does not efficiently undergo electron transfer to molecular oxygen particularly in the presence of the salt as observed in Fig. 3b, in which $DCA^{-\bullet}$ is still sufficiently present under air. This fact is attributed to special salt effect due to formation of contact ion pair between $DCA^{-\bullet}$ and Bu_4N^+ in dichloromethane, with smaller polarity than acetonitrile,[16—19)] which will retard the electron transfer to molecular oxygen. Likewise, $TS^{+\bullet}$ or $CS^{+\bullet}$ forms contact ion pair with BF_4^-. Formation of these contact ion pairs much stabilizes $TS^{+\bullet}$ or $CS^{+\bullet}$ and $DCA^{-\bullet}$ therefore retarding their reverse electron transfer, rotation of $CS^{+\bullet}$ to $TS^{+\bullet}$ as well as electron transfer from $DCA^{-\bullet}$ to oxygen. The rate constant for $CS^{+\bullet}$ to $TS^{+\bullet}$ may be smaller than that determined in acetonitrile, 1×10^5 s^{-1} [7)] probably due to the stabilization of $CS^{+\bullet}$ by BF_4^- which prevents this process from being observed in the present experimental time region.

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