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Hydrogen Atom Transfer Reaction through Partial Charge-Transfer Triplet Complex. Chloranil and Mesitylene System

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Mechanism and kinetics of hydrogen atom transfer reaction from mesitylene (M) to triplet chloranil (^{3}CA) in 1,2-dichloroethane (DCE) at room temperature have been studied by means of picosecond (ps) and nanosecond (ns) laser flash photolysis techniques. It was found that the hydrogen transfer resulting in the formation of chloranil semiquinone radical (CAH·) proceeded through a partial charge-transfer (CT) triplet complex between ^{3}CA and M as an intermediate. No ion-pair formation was observed. The triplet complex showed transient absorption bands in the visible and near infrared regions. The association constant ($K_T=28\,\mathrm{dm^3\,mol^{-1}}$) and lifetime ($\tau_C=32$ ns) of the complex were estimated from a kinetic analysis for ^{3}CA quenching. From these results, combined with those of the quantum yield of CAH· formation, the first order rate constants for the hydrogen transfer and intersystem crossing in the triplet complex were estimated to be (1.7 and 1.4)$\times 10^7\,\mathrm{s^{-1}}$, respectively.

Photoinduced H atom abstraction reactions of quinones exhibit very complicated features depending on properties of H donors and solvents. Although many investigations have suggested the participation of a triplet exciplex as an intermediate, detailed studies by direct observation of short lived triplet exciplexes are still rather scarce[1–4] and desirable to elucidate the reaction mechanisms.

In a previous paper we reported the intermediation of a triplet ion pair (or exciplex with complete CT) between chloranil radical anion ($\mathrm{CA}^{\bar{\cdot}}$) and durene radical cation (DH^{+}) in the course of H atom transfer from durene (DH) to ^{3}CA in DCE; i.e., a two-step mechanism via the ion pair.[1] Simultaneously, we showed the existence of a fast H atom transfer competing with the ion-pair formation. The mechanism of the fast transfer was suggested to be, substantially, also a two-step mechanism via transitory electron transfer immediately followed by a proton transfer in a collision complex with a geometrical conformation favorable to cause the fast transfer. In relation to this, it is of interest whether such a fast H atom transfer can take place commonly for the case of CA (acceptor) and other methylated benzene (donor) systems where a complete electron transfer does not occur between the donor and acceptor. Since M has an ionization potential ($I_P=8.4$ eV)[5] higher than that of DH ($I_P=8.03$ eV),[5] it is expected that such a complete electron transfer does not take place between ^{3}CA and M.

This paper describes a laser photolysis study of H abstraction for the system of CA and M in DCE. Results indicate that the production of CAH· proceeds through the partial CT triplet complex between ^{3}CA and M, $^3(\mathrm{CA}^{\delta-}\cdots\mathrm{M}^{\delta+})$, but not an ion pair, and that no fast H transfer competes with the complex formation. The first-order rate constants for the H transfer and intersystem crossing in the triplet complex have been estimated by kinetic analysis.

Experimental

Transient absorption spectra were measured by the same ps and ns ruby laser photolysis systems as used previously.[1] The R636 and R406 (Hamamatsu Photonics) photomultipliers were used for the ns photolysis in the 320—825 and 500—1000 nm regions, respectively. The ground state absorption spectra were measured with a Hitachi Model 200 spectrophotometer. Chloranil (CA: Tetrachloro-*p*-benzoquinone) was the same material as purified previously.[1] The GR grade mesitylene (M: 1,3,5-trimethylbenzene) was distilled under vacuum after dried with calcium hydride or Zeolite 4A. 1,2-Dichloroethane (DCE) as a solvent was purified by the usual method. Sample solutions for ns laser photolysis were degassed by freeze-pump-thaw cycles and those for ps laser photolysis were purged with dry nitrogen gas. Transient absorption measurements were carried out at 25 °C unless otherwise stated.

Results

Ground State Complex Formation. It is well-known that the present donor-acceptor pair forms an electron donor-acceptor (EDA) complex, CA···M, in the ground state.[6] We have confirmed this in DCE by means of the electronic absorption spectroscopy. Since a large part of the CT band of the complex overlapped the absorption band of free CA in the 350—450 nm range, we determined the values of the complex formation constant ($K_G=0.31\pm0.08\,\mathrm{dm^3\,mol^{-1}}$) and the extinction coefficient of the CT band at 410 nm ($\varepsilon_{410}=3270\pm930\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) at 20 °C by the Rose-Drago's method.[7] This K_G value for the M donor is smaller than that for the DH donor ($0.89\,\mathrm{dm^3\,mol^{-1}}$)[1] as expected from the difference in their ionization potentials.

Quenching Curve of ^{3}CA. The T_n—T_1 absorption of ^{3}CA was quenched efficiently by added M. The decay kinetics monitored at 510 nm obeyed the first-order rate law throughout all concentrations (1.4×10^{-3}—0.32 mol dm^{-3}) of M examined. The plot of observed decay

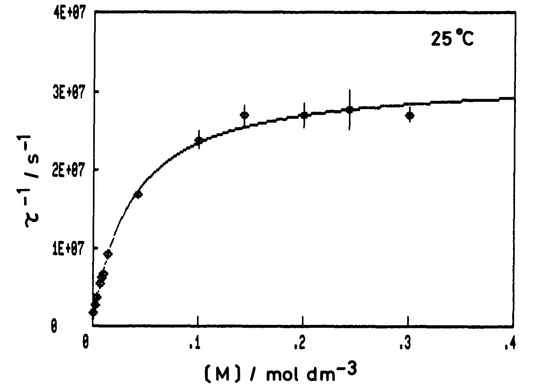


Fig. 1. A plot of the inverse lifetime τ^{-1} of ^{3}CA against the concentration of M at 25 °C. ϕ: The observed value with error bar, ——: the calculated curve with K_T=27.89 dm^{3}mol^{-1}, τ_c=31.55 ns, and τ_0=4.325 μs obeying Eq. 5.

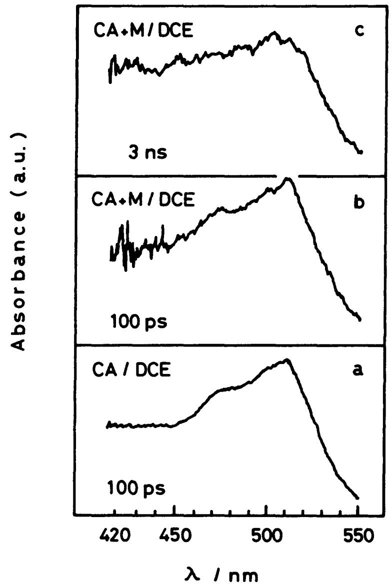


Fig. 2. Transient absorption spectra obtained by the ps laser photolysis for the solutions of CA (5.5×10^{-3} mol dm^{-3}) alone (a) and CA (5.5×10^{-3} mol dm^{-3}) plus M (0.32 mol dm^{-3}) (b and c) in DCE. Delay times: (a) 100 ps, (b) 100 ps, and (c) 3 ns. The absorbance is not corrected for the shot to shot variations of the excitation pulse intensity.

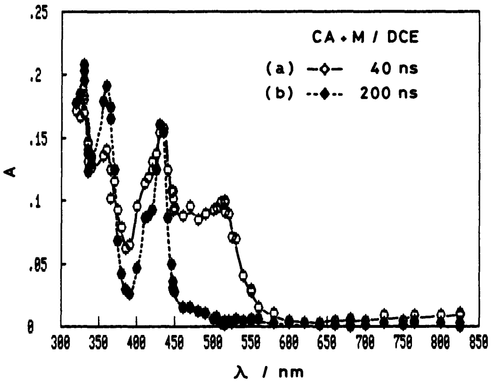


Fig. 3. Time-resolved absorption spectra obtained by the ns laser photolysis for the CA (3.0×10^{-3} mol dm^{-3}) and M (0.30 mol dm^{-3}) system in DCE. Delay times: (a) 40 ns and (b) 200 ns after the start of laser oscillation.

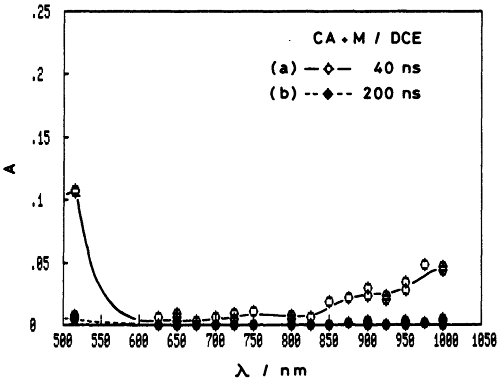


Fig. 4. Transient absorption spectra for the CA–M–DCE system in the long wavelength region. Delay times and concentrations of CA and M are the same as those in Fig. 3.

rate (τ^{-1}: the inverse of the lifetime) as a function of [M] is given in Fig. 1. The quenching curve tends to approach an asymptotic value on going to higher [M], which suggests the existence of a reverse process from a reaction intermediate such as exciplex.[8]

Picosecond Laser Photolysis. Figure 2 illustrates transient absorption spectra obtained by the ps laser photolysis. The spectrum observed for the solution of CA alone at 100 ps delay time (Fig. 2a) shows the band peaking at 510 nm, which is very similar to that of ^{3}CA obtained previously by the ns laser photolysis.[9] Since the intersystem crossing from the lowest excited singlet to the triplet state is very rapid,[1,10] the spectrum of Fig. 2a is assigned to the absorption band due to ^{3}CA. In the presence of M (0.32 mol dm^{-3}), the spectrum observed at 100 ps (Fig. 2b) resembles quite well with that of ^{3}CA (Fig. 2a). The spectrum at 3 ns (Fig. 2c) is also similar to that of Fig. 2a, although it shows slightly different features; the lack of vibrational structure and a slightly high absorbance in the 420—450 nm region relative to that at 510 nm. It should be noted that no absorption peaks were observed at 435 and 448 nm, which correspond to the characteristic bands of CAH· and CA$^{\overline{\cdot}}$, respectively.

Nanosecond Laser Photolysis. Time resolved absorption spectra obtained by the ns laser photolysis is given in Fig. 3. The spectrum immediately after excitation (Fig. 3a) shows an absorption band similar to that of Fig. 2c, in the 450—550 nm region. After the passage of time, this band around 510 nm disappears and strong absorption bands at 435, 360, and 325 nm, which are partly observed already in Fig. 3a, become remarkable (Fig. 3b). Among these bands, the 435 and 360 nm bands can be ascribed to CAH· produced by the H abstraction reaction by comparing them with those of CAH· observed previously in the CA and DH system[1] as well as in other related systems.[2,9] The sharp band around 325 nm may be assigned to 3,5-dimethylbenzyl (M·) radical[11] produced by an H atom release from M, which is analogous to the formation of the benzyl-type 2,4,5-trimethylbenzyl (D·) radical observed in the CA–DH system.[1]

Figure 4 shows the transient spectra in the VIS and near IR region observed by using the R406 photomultiplier. The absorption from 800 to 1000 nm is clearly observed in the early stage after excitation, which was not detected in the absence of M. This long wavelength band disappears simultaneously with the band around 510 nm. The decay times observed at 975 as well as 1000 nm agree with that measured at 510 nm ($\tau=38\pm3$ ns at 25 °C).

The decay kinetics of long lived CAH· was second-order; plot of the inverse of absorbance at 435 nm against time gave a straight line with the slope of $1.76\times10^6\,\mathrm{s}^{-1}$. Using this value together with those of the molar extinction coefficient of CAH· at 435 nm ($\varepsilon_{\mathrm{CAH}\cdot}(435)=1.0\times10^4\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$)[1] and the effective length of optical path (l=0.90 cm), the second-order decay rate constant of CAH· is estimated to be $1.6\times10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ at 25 °C. This value is approximately equal to that of CAH· ($1.4\times10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) estimated previously in the CA–CAH$_2$ (tetrachlorohydroquinone)–DCE system.[9]

Determination of CAH· Yield. Under the condition of a constant laser intensity, the yield of CAH· (Φ_h) generated from ^{3}CA can be related to the following equation.

$$\Phi_\mathrm{h} = \frac{A_{\mathrm{CAH}\cdot}(435)/\varepsilon_{\mathrm{CAH}\cdot}(435)}{A_{^3\mathrm{CA}}(510)/\varepsilon_{^3\mathrm{CA}}(510)} \qquad (1)$$

where $A_{^3\mathrm{CA}}(510)$ and $A_{\mathrm{CAH}\cdot}(435)$ are the absorbance at 510 nm of ^{3}CA initially excited and that at 435 nm of produced CAH·, respectively, in a mixed solution of CA and M. $\varepsilon_{^3\mathrm{CA}}(510)$ is the molar extinction coefficient of ^{3}CA at 510 nm; $\varepsilon_{^3\mathrm{CA}}(510)=7.3\times10^3\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$.[1] On the addition of M of the concentration less than $2\times10^{-2}\,\mathrm{mol\,dm^{-3}}$, the solution of CA ($2.0\times10^{-3}$ mol dm^{-3}) showed only little change (<3%) in the absorbance at 347 nm in the ground state, corresponding to little contribution of the ground state complex formation (<1%). Therefore, no correction for a small change in the concentration of the initially excited ^{3}CA was made in the photolysis at 347 nm for solutions involving a constant concentration of CA (2.0×10^{-3} mol dm^{-3}) regardless of the presence and absence of M when [M] was less than 2×10^{-2} mol dm^{-3}. At a relatively higher concentration of M in this concentration range, however, the quenching of ^{3}CA could not be neglected even at the time immediately after excitation by the laser pulse of ca. 25 ns fwhm. It was then necessary to estimate the true $A_{^3\mathrm{CA}}(510)$ value using a separate solution as a reference. Since the absorbance change at 347 nm by the mixing of CA and M was negligible, a solution of CA alone containing the equal concentration to those of the mixed solutions could be used as a reference solution. Therefore, $A_{^3\mathrm{CA}}(510)$ for the mixed solution can be replaced by the absorbance of ^{3}CA at 510 nm observed immediately after the excitation of the reference solution. $A_{\mathrm{CAH}\cdot}(435)$ was obtained by observing the absorbance at 435 nm immediately after the decay of ^{3}CA in the mixed solution. CAH· did not show decay practically in the time range required for this estimation. Thus, Φ_h values were estimated to be 0.54 and 0.53 for the solutions of [CA]=2.0×10^{-3} mol dm^{-3} with [M]=4.0×10^{-3} and 1.6×10^{-2} mol dm^{-3}, respectively.

Discussion

Formation of a Partial CT Triplet Complex. As is shown in Figs. 2(b, c) and 3, no appreciable absorption band characteristic to CA$^{\bar{\cdot}}$ was found around 450 nm both in ps and ns time regions. This result indicates clearly that an ion pair between CA$^{\bar{\cdot}}$ and M^{+} (mesitylene radical cation) is not formed in the present system,[12] contrary to the case of the CA–DH system[1] where dominant ion-pair formation takes place in the early stage after excitation. The reaction between ^{3}CA and M apparently leads to the formation of neutral radicals CAH· and M· as a result of H atom transfer from M to ^{3}CA (Fig. 3b).

The existence of intermediate complex which was suggested from the profile of quenching curve (Fig. 1) is supported also by the following results. It is expected that an EDA complex between CA and M is produced more efficiently in the triplet state than in the ground state, since ^{3}CA has a higher electron affinity than CA by the energy required for excitation from the ground to the triplet state; i.e., generally

$$E_\mathrm{A}(^3A) = E_\mathrm{A}(^1A) + E_\mathrm{T} \qquad (2)$$

where $E_\mathrm{A}(^3A)$ is the electron affinity of the triplet state acceptor ^3A, $E_\mathrm{A}(^1A)$ corresponds to that of the ground state acceptor ^1A, and E_T is the excitation energy to the triplet state. Combining Eq. 2 with the approximate relation,[13]

$$h\nu_\mathrm{CT} = \mathrm{const.} - E_\mathrm{A}(^1A), \qquad (3)$$

we can derive the following approximate equation,[2,14] assuming the same value for const.

$$h\nu_{^3\mathrm{CT}} = h\nu_\mathrm{CT} - E_\mathrm{T}. \qquad (4)$$

In Eqs. 3 and 4, $h\nu_\mathrm{CT}$ and $h\nu_{^3\mathrm{CT}}$ denote the transition energies of CT band of the ground and triplet state EDA complexes, respectively. When we use the values of E_T=2.13 eV for ^{3}CA[15] and $h\nu_\mathrm{CT}$=3.02 eV (corresponding to the CT band of CA···M at 410 nm) in Eq. 4, the CT band of the triplet complex can be estimated to lie around ca. 1380 nm. The broad absorption band observed in the 800—1000 nm region (Fig. 4a), which would have an absorption maximum beyond 1000 nm, may correspond to the CT band estimated above.

In view of the above results, we analyze the quenching data given in Fig. 1 on the basis of complex formation. Since the observed decay curves were exponential, the so called "dynamic equilibrium" would be established under the present experimental conditions.[16] In the equilibrium state, one can derive the following relation;[8,16]

$$\tau^{-1} = (\tau_0^{-1}+K_T[M]\tau_c^{-1})/(1+K_T[M]) \qquad (5)$$

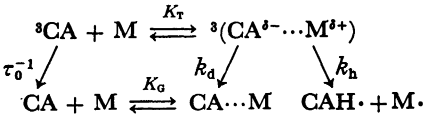
where K_T is the formation constant of the triplet complex, τ and τ_0 are the decay times of ^{3}CA in the presence and absence of M, and τ_c is the lifetime of the complex. As is illustrated in Fig. 1, the experimental values of τ^{-1} are reproduced satisfactorily by the curve calculated with Eq. 5 employing the values, $K_T=27.89$ dm^3 mol^{-1}, $\tau_0=4.325$ μs, and $\tau_c=31.55$ ns which are determined by the least square method. The value of τ_0 (4.3 μs) is close to the observed one (5.6 μs) of pseudo first-order decay time of ^{3}CA in the absence of M.[9] The K_T value (28 dm^3 mol^{-1}) is significantly larger than the K_G value (0.31 dm^3 mol^{-1}), indicating that in the triplet state the complex formation is more favorable than in the ground state. This result agrees with the expectation from the larger electron affinity of ^{3}CA than CA mentioned above. Thus, the complex formation in the triplet state has been rationalized from the kinetic analysis as well as the detection of CT band.

We can estimate using the K_T value that in the equilibrium state 89% of ^{3}CA molecules are present as the triplet complex in the solution containing 0.30 mol dm^{-3} M. Hence, the intensity of absorption band around 510 nm in Fig. 3a (the spectrum at 40 ns) may be attributed mainly to the complex. That is, the triplet complex should have the absorption band around 510 nm as well as that in the near IR region. Since the absorption band around 510 nm is characteristic of ^{3}CA unit, the observed spectra in the presence of M may be assigned to the locally excited (LE) triplet state with a partial CT character; $^3(CA^{\delta-}\cdots M^{\delta+})$.

Reaction Mechanism of H Atom Transfer. In the solution of [CA]=5.5×10^{-3} and [M]=0.32 mol dm^{-3} submitted to the ps laser photolysis experiments, the absorbance due to the ground state complex reaches 38% of the total absorbance at 347 nm for the laser excitation, although CA is present by only 9% as the complex in the ground state. Under these conditions, therefore, the excellent similarity between Figs. 2a and 2b appears to indicate that a direct excitation of the ground state complex does not lead to the fast formation of CAH· as well as the ion pair.[17]

A rate constant for the formation of an outer complex can be usually approximated to be a diffusion controlled one (8.4×10^9 dm^3 mol^{-1} s^{-1} at 25 °C), so that ^{3}CA would collide with M of 0.32 mol dm^{-3} frequently enough to establish the equilibrium concerning the triplet complex formation during 3 ns delay time. Because the equilibrium in the triplet state shifts largely to the side of the complex formation (90% mole fraction), the spectrum at 3 ns (Fig. 2c) may be regarded mainly as that of the triplet complex. In addition, Fig. 2c can not be reproduced by the superposition of spectra of ^{3}CA (Fig. 2a) and CAH·. It is then implied that no CAH· is produced simultaneously with the triplet complex, if the spectrum of the triplet complex is almost the same as that of free ^{3}CA. Therefore, the fast H atom transfer competing with the formation of the triplet complex does not occur and CAH· is formed concomitantly with decrease of the triplet complex (Fig. 3).

Thus, a combination of ps and ns laser photolysis results allows us to conclude that the H atom transfer reaction proceeds via the triplet complex formation followed by H atom transfer from M to ^{3}CA in the complex. The reaction scheme may be written as follows.



where τ_0 is the lifetime of ^{3}CA in the absence of M, k_d, and k_h are the rate constants for the intersystem crossing and H atom transfer processes in the triplet complex, respectively, and K_T and K_G are the equilibrium constants, respectively, as defined before.[18] The present mechanism of H abstraction is in a striking contrast with that for the case of CA and DH system where the H transfer proceeds mainly through the ion pair $CA^{\overline{\cdot}}\cdots DH^+$ formation followed by proton transfer and partly through the fast H transfer taking place competing with the ion-pair formation.[1] This difference in the mechanism seems to result from the level inversion between the zeroth order LE and CT states in the triplet complexes; i.e., the former state is lower than the latter one for the case of M donor and vice versa for the case of DH donor.

Estimation of k_h and k_d. Under the dynamic equilibrium condition between species A and B, in general, the mean rate parameter $\bar{k}$ for a certain process is given by the weighted mean of the corresponding rate parameters of A (k_A) and B (k_B) as follows:[16]

$$\bar{k} = k_A\chi_A + k_B\chi_B \qquad (6)$$

where χ_A and χ_B are the mole fractions of A and B respectively. When A and B correspond respectively to ^{3}CA and $^3(CA^{\delta-}\cdots M^{\delta+})$, we can put $\bar{k}=\Phi_h/\tau$, $k_A=\phi_0/\tau_0$, $k_B=\phi_h/\tau_c$, $\chi_A=1/(1+K_T[M])$, and $\chi_B=K_T[M]/(1+K_T[M])$ for the H abstraction by ^{3}CA, so that Eq. 6 yields the following expression:

$$\Phi_h = \left(\frac{1}{1+K_T[M]}\cdot\frac{\phi_0}{\tau_0} + \frac{K_T[M]}{1+K_T[M]}\cdot\frac{\phi_h}{\tau_c}\right)\cdot\tau \qquad (7)$$

Table 1. The Estimated Efficiencies (ϕ_h) of Hydrogen Transfer in the Triplet Complex along with the Observed Lifetimes (τ) of 510 nm Absorption and Yields (Φ_h) of CAH·

[CA] 10^{-3} mol dm^{-3}	[M] 10^{-3} mol dm^{-3}	τ ns	Φ_h	ϕ_h
2.0	4.0	297	0.54	0.56
2.0	16	103	0.53	0.54
				av. 0.55

where ϕ_0 is the efficiency of CAH· production by H abstraction of ^{3}CA from the solvent DCE, ϕ_h is the efficiency of CAH· formation from $^3(CA^{\delta-}\cdots M^{\delta+})$, and other parameters are the same as defined in Eqs. 1 and 5. According to Eq. 7, ϕ_h at each [M] can be estimated as far as Eq. 5 holds. Using the values of K_T=28 dm^3 mol^{-1}, τ_c=32 ns, τ_0=4.3 μs, and ϕ_0=0.19,[9] we obtained an average value ϕ_h=0.55 corresponding to the Φ_h values, 0.54 and 0.53, at [M]=4.0×10^{-3} and 1.6×10^{-2} mol dm^{-3}, respectively. Results are listed in Table 1. From these results, k_h=1.7×10^7 s^{-1} and k_d=1.4×10^7 s^{-1} are estimated. The k_h value is larger than the proton transfer rate constant k_p (2×10^6 s^{-1} at 20 °C) of the reaction $CA^{\overline{\cdot}}\cdots DH^+ \rightarrow CAH\cdot + D\cdot$, although the k_d value is the same order of magnitude as a corresponding rate constant k_d (1.3×10^7 s^{-1} at 20 °C) of the ion pair.

Above results show clearly that the difference in nature of the intermediate complexes; i.e., the partial CT and the complete CT triplet complexes, is reflected in the rate constant of the hydrogen atom transfer between electron donor and acceptor pairs. It would be worthwhile to note that the difference by only one in the number of methyl group in the homologeous series of methylated benzene donors caused a drastic change in the mechanism of the quenching of ^{3}CA.

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12) In Fig. 3b, a weak absorption band in the 450—500 nm region remains as a tail of the strong absorption band of CAH· which has no absorption band in this wavelength region.[1] The time dependence of absorbance at 448 nm showed a small rise following a fast partial decay and then decayed slowly with nearly identical behavior to that of CAH·; i.e., the second-order decay. Since the spectral profile of this band is rather similar to that of $CA^{\overline{\cdot}}$, we attempted to measure a transient photocurrent by the same way as described previously.[1] The weak current was observed in the solution containing CA (3.0×10^{-3} mol dm^{-3}) and M (0.30 mol dm^{-3}). Its decay followed exactly the second-order kinetics but its rise time (ca. 49 ns) longer than the decay time of the triplet complex did not coincide with the rise time (ca. 0.9 μs) of the 448 nm absorption band. A similar absorption band was also observed with a long life in ethyl acetate as a solvent while the transient photocurrent did not flow at all. These results indicate that the absorption band decaying slowly with approximate second-order kinetics is not due to the ion pair $CA^{\overline{\cdot}}\cdots M^+$ produced from, or in the equilibrium with, the triplet complex. If $CA^{\overline{\cdot}}\cdots M^+$ was present, the decay time of $CA^{\overline{\cdot}}\cdots M^+$ would be short as supposed from similarity with the lifetime (49 ns) of the ion pair $CA^{\overline{\cdot}}\cdots D^+$.[1] Therefore, it may be plausible to consider that the weak band gives no evidence for the formation of $CA^{\overline{\cdot}}\cdots M^+$, although the origins of this band and the photocurrent in DCE are not clear at the present stage of investigation.

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17) This result suggests that the excited singlet state of the complex which should be produced by the direct excitation undergoes an immediate relaxation to the $^3(CA^{\delta-}\cdots M^{\delta+})$ and/or CA···M state through ISC and/or IC. It is not clear whether the direct excitation of the EDA complex affords no triplet complex. At the present stage, however, it is sufficient to note that no CAH· forms immediately after the excitation of the EDA complex.

18) The process of a relatively slow H abstraction from the solvent DCE by ^{3}CA[9] is omitted in the scheme, but for a quantitative purpose one must take this process into consideration as being included in the relaxation process of ^{3}CA with the rate constant τ_0^{-1}.