Hydrogen Atom Abstraction of *p*-Chloranil Triplet in 1,4-Dioxane in the Presence and Absence of Tetrachlorohydroquinone

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Mechanisms of hydrogen atom abstraction by triplet *p*-chloranil [CA(T)] from 1,4-dioxane (DOH) and tetrachlorohydroquinone (CAH_2) were studied in detail by means of nanosecond laser flash photolysis. A broad band around 740 nm in the transient absorption spectrum of CA in DOH was assigned to the charge-transfer band of the triplet EDA complex between CA and DOH. Efficiencies for the hydrogen atom abstraction from DOH and CAH_2 were determined to be 0.13 and 0.58, respectively. The former value indicates that the hydrogen atom abstraction from DOH is less effective than a physical process in deactivation of the triplet complex. From the latter value together with the measured value of the quenching rate constant (1.7×10^9 dm^3 mol^{-1} s^{-1}) of the triplet by CAH_2, it is inferred that the hydrogen atom abstraction of CA(T) from CAH_2 takes place competing with an efficient radiationless deactivation *via* the triplet exciplex between CA(T) and CAH_2 as a common intermediate.

In a previous work a report was given on the interaction of *p*-chloranil triplet with several vinyl monomers and solvents.[1] It was found that the hydrogen atom abstraction by CA(T) depends remarkably on the charge-transfer (CT) interaction between CA(T) and the hydrogen donors, and that CAH_2 added quenches CA(T) efficiently in company with simultaneous formation of *p*-chloranil semiquinone radical (CAH·) through the $CA(T)+CAH_2\rightarrow 2CAH\cdot$ reaction. We have carried out an extended study on the mechanism, especially on the possible existence of exciplex as an intermediate for the hydrogen atom transfer. In general, the intersystem crossing (ISC) can be enhanced as in EDA system,[2] when a remarkable CT interaction occurs. Deactivation of CA(T) may thus be considered to proceed through the triplet exciplex as a common intermediate for the hydrogen atom transfer from CAH_2 competing with physical quenching leading to the ground state. In order to confirm this the determination of efficiency of CAH· formation due to hydrogen atom transfer might be valuable. This work deals with the nanosecond laser flash photolysis of CA in DOH and the addition effect of CAH_2 on the efficiency of CAH· formation.

Experimental

The nanosecond flash photolysis at 347 nm by a ruby laser was carried out at room temperature with use of the apparatus described previously.[1] Photomultipliers HTV-1P28 and HTV-R106 were used for analysis in the wavelength ranges of ≤650 nm and 650—1000 nm, respectively, according to the low noise operation technique developed by Hunt and Thomas.[3] The intensity of the laser pulse was measured with a photodiode (HP 4220), the output being recorded digitally on a hand-made peak-hold meter[4] calibrated with a thermopile (TRG, Model 107) and a pulse generator (Anritsu, MG 411B). When the laser intensity was too high the decay of the triplet chloranil showed a considerably nonexponential feature at the initial stage owing to the triplet-triplet annihilation. In order to reduce this effect the energy of the excitation pulse was attenuated to less than 25 mJ/pulse by glass plates.

p-Chloranil (CA), tetrachlorohydroquinone (CAH_2), and benzophenone were the same as used previously.[1] 1,4-Dioxane (DOH, the letter H is used separately from others in order to emphasize a hydrogen atom which is abstracted) and benzene (Dotite spectrograde) were used without purification. The benzophenone solution in benzene was used as a reference for the determination of the extinction coefficient of CA(T). The concentrations of CA and CAH_2 were 2.5×10^{-3} mol dm^{-3} and $\leqq 2.5\times10^{-3}$ mol dm^{-3}, respectively. The sample solutions subjected to photolysis were degassed by freeze-pump-thaw cycles. Fresh solutions were used separately for time resolved spectral measurements, determination of efficiencies of CAH· formation, and measurement of extinction coefficient of CA(T), respectively.

Results and Discussion

CA–DOH System. Figure 1a shows the ground state absorption spectrum of CA in DOH. The absorption with a maximum at *ca.* 335 nm can be assigned to the CT band of the EDA complex between CA and DOH according to the linear relationship[2] between the CT band energies and ionization potentials of donors. The intensity of the CT absorption band at 347 nm is considerably higher than that of the absorption of CA in non-interacting solvent such as 1,2-dichloroethane (DCE) (Fig. 1b). The laser light for excitation is thus absorbed pracically only by the EDA complex between CA and DOH.

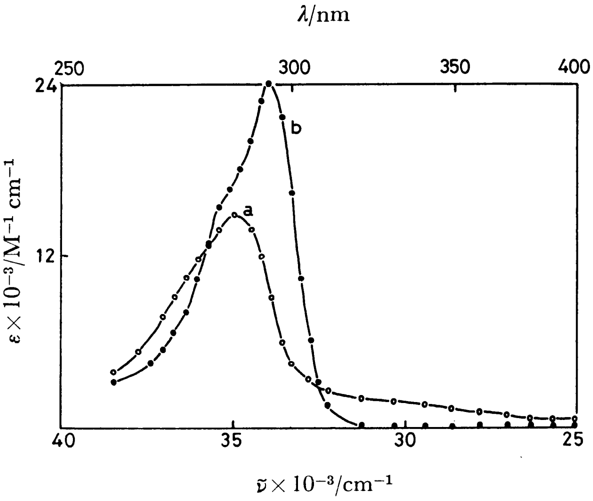


Fig. 1. Electronic absorption spectra of *p*-chloranil in 1,4-dioxane (a) and 1,2-dichloroethane (b).

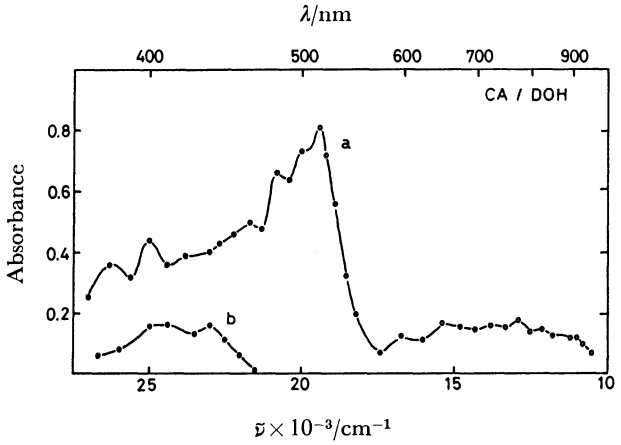


Fig. 2. Transient spectra from laser photolysis of degassed solution of CA (2.5×10^{-3} mol dm^{-3}) in DOH taken at different time after the end of excitation pulse: (a) $t=0$ and (b) $t=8$ μs.

The transient absorption spectra obtained by laser photolysis are shown in Fig. 2. The spectrum immediately after excitation (Fig. 2a) consists of a strong band with a maximum at 515 nm and a weak, broad band in the region 600—900 nm. The spectrum in the wavelength region less than 400 nm has only a qualitative significance since the ground state absorption of CA considerably overlaps in this region and the transient absorption is distorted by the recovery of CA after the photolysis. Concerning the identification of the spectrum (Fig. 2a), the following observations are noted. (1) The strong absorption band around 515 nm is very similar in wavelength position and shape to that of CA(T) in other solvent systems.[1)] The decay time of this band which obeys pseudo-first order kinetics in the time range from just after pulsing to 10 μs is obtained to be 3.4 μs. (2) The absorption in the long wavelength region has a maximum at *ca.* 740 nm, its decay profile being almost the same as that of the 515 nm band. (3) By addition of CAH_2 to the solution, the two bands were quenched efficiently, decaying with an identical time constant. (4) The transient absorption spectrum obtained on photolysis of an aerated solution of CA resembles very closely that shown in Fig. 2a. It decays rapidly keeping its whole spectral feature, no new bands appearing after complete decay.

We identified the spectrum immediately after excitation (Fig. 2a) as the one attributable to the triplet EDA complex between CA and DOH, although the band due to CA(T) free from the CT interaction with the solvent would be superposed a little. Thus, the band located around 515 nm can be assigned to the local triplet-triplet absorption in CA moiety. On the other hand, the band in the longer wavelength region may be assigned to the CT transition from DOH to CA(T) for the following reasons. Ionization potentials, 9.13 eV,[5)] of 1,4-dioxane is comparable with 9.245 eV[5)] of benzene. Both of the CT bands of CA complexes with 1,4-dioxane and benzene in the ground state are located closely together in energy *i.e.*, 3.7 and 3.6 eV,[6)] respectively. Since benzene forms a triplet complex with CA having the CT absorption band beyond 550 nm,[7)] it is expected that the triplet complex of CA–DOH also has the corresponding absorption in a similar wavelength region. By the same consideration as given by Kawai *et al.*,[7)] the CT band of the complex between CA(T) and DOH can be roughly estimated by

$$E^{T}_{CT} = E^{G}_{CT} - E_{T}$$

where E^{T}_{CT} and E^{G}_{CT} are the CT transition energies of the complex in the triplet and the ground state, respectively, and E_T is the energy of CA(T) above the ground state. When we take 3.7 eV for E^{G}_{CT} and 2.1 eV[8)] for E_T, E^{T}_{CT} is calculated to be 1.6 eV (=770 nm), in agreement with the experimental value, 1.68 eV (=740 nm). The assignment for the long wavelength band seems to be reasonable.

After the disappearance of the 515 and 740 nm bands, the relatively weak absorption with maximum at 435 nm still remains. Figure 2b shows the absorption at 8 μs after the end of the excitation pulse, the band shape resembling that of CAH· in CA–DCE system.[1)] The absorption also resembles that of CAH· produced through the $CA(T)+CAH_2\rightarrow 2CAH\cdot$ reaction. The decay of this long-lived transient was approximately of the second order. We thus identify, the transient spectrum as that of CAH·. Wong *et al.*[9)] identified the corresponding transient in the same system as CAH· which decays by the disproportionation with a second order rate as observed by means of electron spin resonance spectroscopy. It is obvious that the CAH· has been produced through the interaction of CA(T) with the solvent, since no absorption around 435 nm could be detected by the addition of a quenching species for CA(T) as in styrene[1)] or air.

If the intersystem crossing of CA from S_1 to T_1 proceeds with unit efficiency ($\Phi_{ISC}=1$) as is the case for duroquinone,[10)] the extinction coefficient of CA(T), $\varepsilon_{CA(T)}$, interacting with DOH can be determined by comparison with that of benzophenone triplet.[1)] The value of $\varepsilon_{CA(T)}$ at 515 nm was found to be $(5.8\pm0.1)\times10^3$ dm^3 mol^{-1} cm^{-1}. The extinction coefficient of CAH· in DOH, $\varepsilon_{CAH\cdot}$, is known to be 7.7×10^3 dm^3 mol^{-1} cm^{-1} at 435 nm.[9)] Using these values, we can estimate the yield (Φ^0_r) of CAH· produced from CA(T) in DOH by

$$\Phi^0_r = \frac{D_{CAH\cdot}(435)/\varepsilon_{CAH\cdot}(435)}{D_0(515)/\varepsilon_{CA(T)}(515)}$$

where $D_0(515)$ is the absorbance at 515 nm just after the cessation of the pulse and $D_{CAH\cdot}(435)$ is the residual absorbance at 435 nm at the time when CA(T) disappeared completely. A small amount of CAH· absorption decayed before this was neglected because the cecay of CAH· is considerably slower than that of CA(T). Φ^0_r was estimated to be 0.13 ± 0.03 by five runs. The error indicated is the maximum deviation from the mean. Since CAH· is considered to be produced through the reaction sequence, $CA(S_0)\cdots DOH \xrightarrow{h\nu} CA(S_1)\cdots DOH \xrightarrow{ISC} CA(T)\cdots DOH \rightarrow CAH\cdot + DO\cdot$, the efficiency ($\phi^0_r$) of CAH· formation from CA(T) interacting directly with solvent DOH is related to Φ^0_r by $\Phi^0_r=\Phi_{ISC}\phi^0_r$ where $\Phi_{ISC}=1$. We then have $\phi^0_r=0.13$. This indicates that the hydrogen atom abstraction from the solvent contributes to deactivation of CA(T) to a smaller extent than the physical quenching process. The first order rate constants of CAH· formation (k_r^0) and another deactivation process (k_d^0) of CA(T) are evaluated to be 3.8×10^4 s^{-1} by use of $k_r^0=\phi_r^0/\tau_T^0$ and 2.6×10^5 s^{-1} by use of $k_d^0=(1-\phi_r)/\tau_T^0$, respectively, where τ_T^0 is the lifetime of CA(T). Thus, the deactivation processes of CA(T) interacting with DOH [CA(T)···DOH] are expressed as follows:

$$\text{CA(T)}\cdots\text{DOH}\longrightarrow\text{CAH}\cdot+\text{DO}\cdot,\qquad k_r^0=3.8\times10^4\ \text{s}^{-1}\tag{1}$$

$$\text{CA(T)}\cdots\text{DOH}\longrightarrow\text{CA}\cdots\text{DOH},\qquad k_d^0=2.6\times10^5\ \text{s}^{-1}\tag{2}$$

CA–CAH$_2$–DOH System. The ground state absorption spectrum in CA–CAH$_2$–DOH system, which is not illustrated here, was exactly the same as that constracted by the superposition of individual spectrum of CA and CAH$_2$ in DOH up to the maximum concentration of CAH$_2$. No spectral evidence of complexation was obtained between CA and CAH$_2$ in the ground state at room temperature.

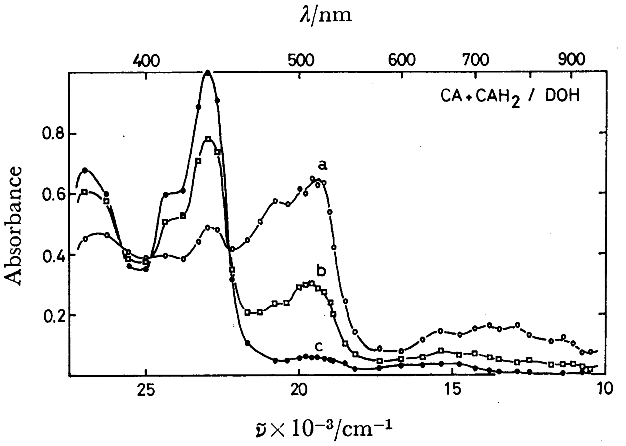


Fig. 3. Transient spectra observed in CA (2.5×10^{-3} mol dm^{-3})–CAH$_2$ (2.5×10^{-3} mol dm^{-3})–DOH system: (a) $t=0$, (b) $t=200$, and (c) $t=600$ ns after pulsing.

Figure 3 shows the transient spectra in CA–CAH$_2$–DOH system at an equal concentration of CA and CAH$_2$, 2.5×10^{-3} mol dm^{-3}. The spectrum obtained immediately after pulsing is very similar to that shown in Fig. 2a except for a small increase around the 435 nm band. With the lapse of time the triplet absorption beyond 500 nm decays rapidly and the 435 nm band grows remarkably. It is apparent that the band around 435 nm is attributed to the characteristic band of CAH· produced by the CA(T)···DOH+CAH$_2$→2CAH· reaction. This is also confirmed by the simultaneous increase of another characteristic band of CAH· at *ca.* 370 nm. There are isosbestic points at 22.3×10^3, 24.8×10^3, and 25.8×10^3 cm^{-1}. This indicates that the growing-up of CAH· absorption around 435 nm is not disturbed by any transient species formed by processes other than the CA(T)···DOH+CAH$_2$→2CAH· reaction. The CAH· absorption decays exactly according to the second order kinetics after reaching the maximum. The decay rate constant (k_t) obtained is 4.5×10^8 dm^3 mol^{-1} s^{-1}, in good agreement with the reported value, 4.1×10^8 dm^3 mol^{-1} s^{-1}.[9)]

The small peak at 435 nm (Fig. 3a) may be assumed to be due to absorption of CAH· produced within the time of excitation pulse width. This is understandable on the basis of the following observations. The 435 and 515 nm-band intensities immediately after pulsing show dependence upon the concentrations of CAH$_2$ added; increase of CAH$_2$ concentration makes the 515 nm band decrease and the 435 nm band increase. This shows that the small peak at 435 nm immediately after pulsing is due to CAH· produced within the pulse width. This is also supported by the kinetic analysis at 435 nm. After subtraction of the 435 nm absorbance presumed to be due to CAH· produced within laser excitation and the absorbance due to CA(T) contributing to 435 nm from the observed absorbance, the remaining absorbance which corresponds to that of CAH· produced gradually by the reaction between CA(T)···DOH and CAH$_2$ gives a rise time approximately equal to the decay time of the triplet monitored at 515 nm. The kinetic behavior of 435 nm absorption can thus be analyzed. Production of CAH· from the excited singlet state of CA would be rare if occurring at all. The finite difference between the 435 nm absorbances (Figs. 2a and 3a) does not indicate the existence of the triplet exciplex between CA(T) and CAH$_2$.

In general, the quenching processes of CA(T) interacting with DOH by CAH$_2$ can be represented by

$$\text{CA(T)}\cdots\text{DOH}+\text{CAH}_2\longrightarrow 2\text{CAH}\cdot+\text{DOH},\qquad k_r\tag{3}$$

$$\text{CA(T)}\cdots\text{DOH}+\text{CAH}_2\longrightarrow \text{CA}\cdots\text{DOH}+\text{CAH}_2.\qquad k_d\tag{4}$$

Reaction 3 represents the hydrogen atom abstraction from CAH$_2$ and Reaction 4 the physical quenching. The relation between the yield ($\mathit{\Phi}_r$) of CAH· generated after the cessation of pulsing and the efficiency (ϕ_r) of CAH· formation through the interaction between the triplet and CAH$_2$, is expressed by

$$\begin{aligned}\mathit{\Phi}_r &= \frac{\phi_r^0(k_r^0+k_d^0)+2\phi_r k_q[\text{CAH}_2]}{(k_r^0+k_d^0)+k_q[\text{CAH}_2]}\\ &= \{(\phi_r^0/\tau_T^0)+2\phi_r k_q[\text{CAH}_2]\}\tau_T,\end{aligned}\tag{5}$$

where, τ_T and τ_T^0 are lifetimes of CA(T) in the presence and absence of CAH$_2$, respectively, ϕ_r^0 is the efficiency of CAH· formation by the interaction with solvent (DOH in this case), $k_q(=k_r+k_d)$ is the quenching rate constant of CA(T)···DOH by CAH$_2$, and [CAH$_2$] is the molar concentration of CAH$_2$. The value of k_q was determined to be 1.7×10^9 dm^3 mol^{-1} s^{-1} from the plot corresponding to the $1/\tau_T=1/\tau_T^0+k_q[\text{CAH}_2]$ equation. Since k_q is so high as to be close to the value for diffusion control, when CAH$_2$ of adequate concentration is present, Eq. 5 can be simplified to

$$\mathit{\Phi}_r=2\phi_r(1-\tau_T/\tau_T^0)\tag{6}$$

for the case of $\phi_r^0/\tau_T^0\ll2\phi_r k_q[\text{CAH}_2]$, or

$$\mathit{\Phi}_r=2\phi_r\tag{7}$$

for the case of $\tau_T\ll\tau_T^0$. When CAH$_2$ is absent, Eq. 5 becomes $\mathit{\Phi}_r=\phi_r^0$ in accordance with $\mathit{\Phi}_r^0$. On the other hand, Φ_r is obtained experimentally from absorbance changes:

$$\Phi_r = \frac{\{D_{\mathrm{max}}(435) - \Delta D_0(435)\}/\varepsilon_{\mathrm{CAH\cdot}}(435)}{D_0(515)/\varepsilon_{\mathrm{CA(T)}}(515)} \qquad (8)$$

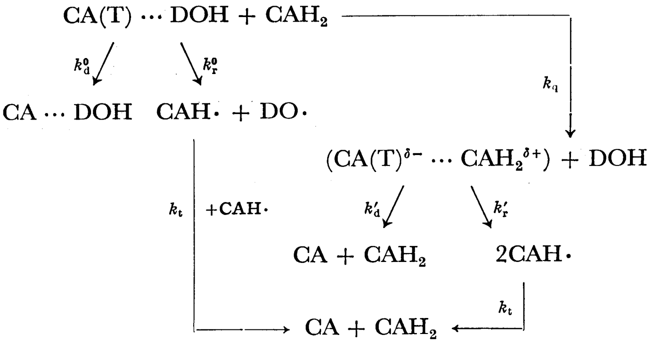
where $D_0(515)$ is the absorbance at 515 nm immediately after pulsing, $D_{\mathrm{max}}(435)$ the maximum absorbance at 435 nm, and $\Delta D_0(435)$ the absorbance at 435 nm of CAH· formed within laser excitation. $\varepsilon_{\mathrm{CA(T)}}(515)$ and $\varepsilon_{\mathrm{CAH\cdot}}(435)$ are as noted before. Hence, $\phi_r(=k_r/(k_r+k_q)=k_r/k_q)$ can be calculated by combining Eq. 5 with Eq. 8. The average value of ϕ_r was found to be 0.58 ± 0.05[11] from 15 different observations for three different concentrations of CAH_2, 2.5×10^{-3}, 2.0×10^{-3}, and 1.5×10^{-3} mol cm^{-3}. The error indicated is the standard deviation. The results are summarized in Table 1.

TABLE 1. RATE PARAMETERS AND THE EXTINCTION COEFFICIENT OBTAINED BY LASER FLASH SPECTROSCOPY IN CA–DOH AND CA–CAH_2–DOH SYSTEMS

CA(T)···DOH	CA(T)···DOH+CAH_2
$\phi_r^0=0.13$	$\phi_r=0.58$
$\tau_T^0=3.4$ μs	$k_q=1.7\times10^9$ dm^3 mol^{-1} s^{-1}
$k_r^0=0.4\times10^5$ s^{-1}	$k_r=1.0\times10^9$ dm^3 mol^{-1} s^{-1}
$k_d^0=2.5\times10^5$ s^{-1}	$k_d=0.7\times10^9$ dm^3 mol^{-1} s^{-1}
$\varepsilon_{\mathrm{CA(T)}}(515)=$ 5.8×10^3 cm^3 mol^{-1} cm^{-1}	$k_t=4.5\times10^8$ dm^3 mol^{-1} s^{-1}

In the absence of CAH_2, CA(T)···DOH decays by the hydrogen atom abstraction from DOH but mainly by the physical process of deactivation. This is similar to the previous result in DCE or acrylonitrile.[1] It is evident from k_r and k_d values that Reaction 4 is present competing with Reaction 3 in the efficient quenching (see k_q value) of CA(T)···DOH by CAH_2 and the two processes take place with almost the same probability, indicating that ISC of CA(T) is enhanced by the interaction with CAH_2. This is often observed in the excited singlet[12] and the triplet state[13] in electron transfer or charge-transfer quenching. Recently, Steiner and Winter elucidated the mechanism of the physical quenching of thionine triplet competing with radical formation by halogenated anilines.[14] Their result is explained in terms of a heavy atom effect on ISC (occurring after nearly complete electron transfer) in a triplet exciplex. In the present hydrogen atom abstraction, the existence of such an enhanced ISC also seems to favor an exciplex as an intermediate. Results suggesting the existence of exciplex are as follows. (1) A study[15] on the solvent effect of CAH· formation yield strongly suggests the CT nature of the intermediate in question; the efficiency of the hydrogen atom abstraction increases with solvent polarity. (2) In fluid media no CT band is found in the CA and CAH_2 system nor in the duroquinone and durohydroquinone system.[16] However, DOH solution of the former system shows pink coloration in the frozen state at liquid nitrogen temperature. Even *p*-benzoquinones substituted by very bulky groups such as chlorine or methyl form the quinhydrone type complexes[17] with hydroquinone in the solid state.[18] The above finding seems to be attributed to the same type of complex under restricted conditions. In the triplet state the electron affinity of CA becomes greater than in the ground state. Thus, even in fluid media, CA(T) might form a quinhydrone type complex with CAH_2 by the aid of the CT force surpassing the steric hindrance caused by bulky chlorine atoms. We may assume that the triplet exciplex between CA(T) and CAH_2 exists as a precursor for the hydrogen atom abstraction. This is essentially the same as suggested by Amouyal and Bensasson for duroquinone triplet reduction by durohydroquinone.[10]

From an unified point of view, deactivation processes of CA(T)···DOH in the absence and presence of CAH_2 are as follows:



where the ground state CA is the same as CA···DOH in the DOH solvent, $(CA(T)^{\delta-}\cdots CAH_2^{\delta+})$ represents the triplet exciplex with some charge-transfer interaction between CA(T) and CAH_2, k'_d and k'_r are the first order rate constants for the ISC and the semiquinone radical formation in the exciplex, respectively, and other rate constants having their usual meanings. If we define the quenching probability per collision as γ, k_q is replaced by γk_D where k_D is the diffusion controlled rate constant calculated by $8RT/(3000\,\eta)$. The value of γ is obtained as 0.34 in DOH at 24 °C. In other solvents γ values were found to be of the same order of magnitude.[19] The quenching reaction can be considered as a diffusion controlled reaction. The parameters given in Table 1 are related to the rate parameters in this scheme:

$$k_q = \gamma k_D$$
$$k_r = \gamma k_D\cdot k'_r/(k'_r+k'_d)$$
$$k_d = \gamma k_D\cdot k'_d/(k'_r+k'_d)$$
$$\phi_r = k'_r/(k'_r+k'_d)$$

The values of k'_r and k'_d would be so large that no exciplex absorption could be observed.

Although no absorption spectrum due to exciplex could be detected, the existence of the triplet exciplex from which the hydrogen atom abstraction takes place competing with the intersystem crossing to the ground state may be postulated in order to understand the mechanism of the hydrogen atom abstraction by CA(T) from CAH_2.

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