July, 1986] © *1986 The Chemical Society of Japan* **NOTES** *Bull. Chem. Soc. Jpn., 59, 2347—2348 (1986)*

Solvent Effect on Lifetime of Triplet Exciplex between Chloranil and Durene

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(Received January 9, 1986)

Synopsis. The triplet exciplex between chloranil (CA) and durene (DH) shows a decay which is associated with solvent viscosity rather than polarity, in spite of having a full charge-transfer (CT) character.

A strong dependence of the photophysical and photochemical processes of exciplexes upon solvent polarity is well-known for singlet states. However, solvent effects on the dynamic behavior of triplet exciplexes have not yet been fully investigated. The triplet exciplex with a nearly complete CT nature (CT-type triplet exciplex) or an ion pair between CA and DH has previously been reported by us for the solvent 1,2-dichloroethane (DCE).[1] Here, we report on the lifetimes of this triplet exciplex in various solvents, while paying attention to the effects of the solvent polarity and viscosity.

Experimental

The transient spectra and lifetimes of the exciplex were measured by means of nanosecond laser photolysis using a Q-switched frequency-doubled ruby laser at room temperature (20±1 °C).[1] The method used for photocurrent measurements was the same as that used before.[1] Solvents used were 1,4-dioxane (DO), benzene (BZ), diethyl ether (EE), ethyl acetate (EAC), dichloromethane (DCM), acetone (ACT), and acetonitrile (ACN). DCM was purified as follows: shaken with concd. H_2SO_4, water, aq 5% NaOH, and again water, it was then distilled twice over P_2O_5 after being pre-dried with $CaCl_2$ and stored in a brown bottle with molecular sieves (Zeolite 4A). After these treatments, it was fractionally distilled just before use. Other solvents of spectrograde (Dotite) were distilled after being dried with Zeolite 4A.

Results and Discussion

In DO, BZ, EE, EAC, and DCM (nonpolar and moderately polar solvents) the quenching of triplet chloranil (^{3}CA) by DH led to the formation of a short-lived triplet exciplex, $^3(CA^{\cdot-}\cdots DH^{\cdot+})$, having an absorption band around 450 nm, similar to that in DCE.[1] After a lapse of time, a long-lived chloranil semiquinone radical (CAH·) was observed at 435 and 365 nm in these solvents as well as in DCE.[1] Figure 1 shows the transient spectra observed in DCM as a representative of such spectral features. The first-order decay rate constants of $^3(CA^{\cdot-}\cdots DH^{\cdot+})$ were analyzed at 448 nm in the same manner as that used for the case of a DCE solution.[1]

In ACT and ACN (polar solvents) ^{3}CA quenching also led to a rapid appearance of an absorption band around 450 nm due to a $CA^{\cdot-}$ unit. However, its decay was very slow and did not obey first- or second-order kinetics. Figure 2 gives an example of the spectral change together with an oscillogram of the absorption band at 448 nm observed in ACN. Absorbance at a later stage of the time trace decays with a second-order kinetics resulting from a recombination between free $CA^{\cdot-}$ and $DH^{\cdot+}$ produced through the ionic dissociation of a relaxed and/or nonrelaxed exciplex. A fast formation of free ions and their decays (obeying second-order kinetics) were also observed through transient photocurrent measurements.[2] The decay curve at 448 nm consists of at least two components, first- and second-order decays in both solvents. However, a further detailed analysis of the decay in the polar solvents was not performed during the present stage of the investigation.

Table 1 summarized the data for the lifetimes of the triplet exciplex in various solvents. The values of $\tau_{1/e}$ in ACT and ACN are the apparent decay times of both ion pairs and free ions superposing each other. These values have only qualitative meanings for a comparison purpose with those of true exciplexes in

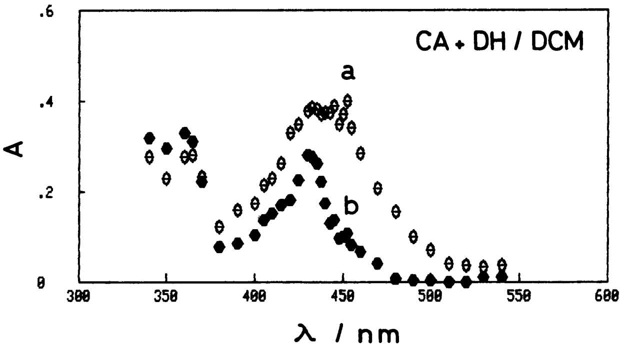

Fig. 1. Transient absorption spectra for the system of CA (2.0×10^{-3} mol dm^{-3}) and DH (0.20 mol dm^{-3}) in DCM. The delay time after the start of laser oscillation. a): 60 ns, b): 540 ns.

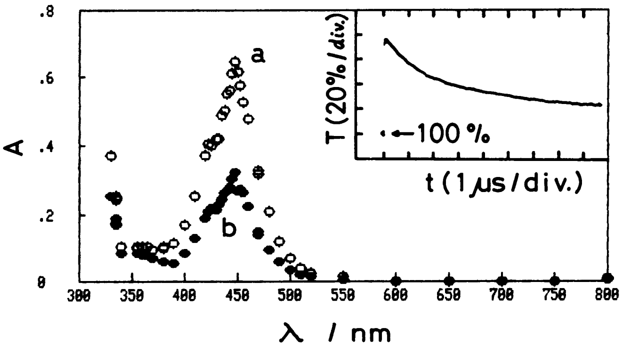

Fig. 2. Transient absorption spectra for the system of CA (2.5×10^{-3} mol cm^{-3}) and DH (0.19 mol dm^{-3}) in ACN. The delay time. a): 60 ns, b): 1.54 μs.

Table 1. Lifetimes of the Triplet Exciplex τ (in ns) in Various Solvents of Dielectric Constant ε and Viscosity Coefficient η (in cp; $1\text{cp}=10^{-3}$ Pas)

Solvent	ε	η	τ[a]
DO	2.3	1.31	60
BZ	2.3	0.64	45
EE	4.3	0.24	25
EAC	6.4	0.45	47
DCM	9.1	0.43	47
DCE	10.7	0.83	49[b]
ACT	21.4	0.32	(1250)[c]
ACN	37.5	0.36	(2600)[c]

a) Experimental errors were within 6% in the standard deviation. b) Ref. 1. c) The apparent decay time ($\tau_{1/e}$) of the band at 448 nm on changing from the initial absorbance (ca. 0.6) to $1/e$ of it.

other solvents. It has been found that the lifetime of ${}^3(\mathrm{CA}^{\bar{\cdot}}\cdots\mathrm{DH}^{\dot{+}})$ does not depend on the polarity of the solvent in a range of ε from 2.3 to 10.7, while it depends weakly upon the viscosity of the solvent. A linear correlation (factor $\gamma=0.87$) between the decay rate τ^{-1} and the parameter T/η (here, $T=293$ K) of the diffusion coefficient seems to indicate that τ^{-1} is affected by the easiness of the vibrational and/or reorientational motion of the exciplex associated with solvent molecules. It is known that the escape probability of the triplet exciplex, between fluorenone and 1,4-diazabicyclo[2.2.2]octane, into dissociated ions depends on the solvent viscosity.[3] In our case, however, the ionic dissociation is not involved in the exciplex decay since no transient photocurrent was gained in DO, BZ, EE, and EAC.[4] Kuz'min et al. have reported that the lifetimes of the triplet exciplexes of 2,6-diphenyl-*p*-benzoquinone with diphenylamine and triphenylamine tend to decrease with increasing ε, ranging from 2.4 to 7.3.[5] The polarity dependence of the present exciplex differs from those of the exciplexes cited above, though they are exciplexes of quinones with a full CT character. This difference in decay behavior can be attributed to a difference in the chemical species constructing the exciplex. Although there is a small difference, such a small (or no) effect of the solvent polarity seems to be consistent with the result that the intersystem crossing (ISC) or back electron transfer of CT-type triplet exciplexes is only weakly dependent on the polarity of the medium.[6]

The relaxation of our exciplex consists of two processes, ISC and a proton transfer, except for cases involving a slight ionic dissociation.[4] Then, if the rate constant of ISC can be regarded as almost constant while changing ε,[7] the dependence on η in the present exciplex might mainly reflect a change in the rate of the proton transfer (k_p). This expectation would not contradict the supposition that ${}^3(\mathrm{CA}^{\bar{\cdot}}\cdots\mathrm{DH}^{\dot{+}})$ is necessary for changing its conformation through a diffusive movement upon going from the relaxed state to a state favorable for causing a proton transfer.[1] Recently, Manring and Peters have also pointed out the requirement of molecular reorientation in a triplet ion pair prior to causing a proton transfer (k_p) for the benzophenone and *N*-methyldiphenylamine system.[8] They have additionally shown in the same system that the rate constant corresponding to k_p decreases upon increasing the solvent polarity. Thus, the decay behavior of triplet exciplexes exhibits various dependences on solvents. A further study of the solvent effect on the single process of a proton transfer in our exicplex is in progress now.

We with to thank Prof. Haruo Shizuka for his interest and encouragement.

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2) An example of photocurrent for the system in ACN has been given in Fig. 11 of Ref. 1.

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4) A weak photocurrent was observed in DCM as well as in DCE.[1] Accordingly, ionic dissociation contributes a little to the decay of ${}^3(\mathrm{CA}^{\bar{\cdot}}\cdots\mathrm{DH}^{\dot{+}})$ in these two solvents.

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