Terplex Formation in the Excited Triplet State. The Chloranil and Mesitylene System

Harumichi KOBASHI,* Ken-ichi HIRATSUKA, and Kazuaki MOTEGI
Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376
(Received July 1, 1987)

Synopsis. The enthalpy and entropy changes have been estimated for the formation of a triplet-state (1:2) terplex as well as an ordinary (1:1) exciplex between triplet chloranil (^{3}CA) and mesitylene (M) in carbon tetrachloride. Results indicate that the terplex is energetically less stable than the bimolecular exciplex, while the stabilization of the terplex is compensated by the positive entropy change associated with transformation from the exciplex to the terplex.

There are many reports on the formation of a ternary component exciplex (terplex) in the excited singlet state of electron donor–acceptor systems.[1-4] On the other hand, only little is known the terplex formation in the excited triplet state.[5] In addition, it was reported recently that not only termolecular interaction but also the existence of an ordinary triplet exciplex could not be reconfirmed for some systems such as the zinc etioporphyrin I and *p*-nitrotoluene system, which had been believed for a long time as a representative of a locally excited (LE-type) triplet exciplex.[6] Under these circumstances, it will be very important to study a triplet-state terplex as well as ordinary (1:1) exciplex and the contribution of the terplex to a dynamic behavior of the exciplex.

In a previous paper,[7] one of us reported both spectroscopic and kinetic results concerning the formation of the LE-type triplet exciplex between ^{3}CA and M, ^{3}(CA–M), which is an intermediate for the hydrogen atom transfer from M to ^{3}CA in 1,2-dichloroethane (DCE). During the course of our study concerning solvent effects on the reactivity of this triplet exciplex,[8] we have found that a termolecular interaction occurs between the exciplex and the exess donor M in less polar solvents.[9]

In this paper, we describe results of thermodynamic and kinetic properties of the terplex ^{3}(CA–M_2) as well as the exciplex ^{3}(CA–M) in the nonpolar solvent CCl_4. This is, to our knowledge, the first report presenting thermodynamic data of a terplex formed in the excited triplet state. After this work had been completed, we knew a report concerning the (1:1) exciplex formation for the same system in CCl_4.[10] However, there was no information concerning the terplex formation.

Experimental

A nanosecond laser photolysis was carried out using the same ruby laser as used previously.[7] A transient signal was memorized to a strage oscilloscope (Iwatu, TS-8123) and displayed on a recorder (Rikadenki, RW-11T). Temperature was varied in the range 5—55 °C by circulating water into a sample cell holder using a thermostat (Taitec, Jr-80) combined with a cooling pipe (Taitec, 150L). Chloranil (tetrachloro-*p*-benzoquinone) and mesitylene (1,3,5-trimethylbenzene) were purified by the same methods as used before.[7,11] Carbon tetrachloride (*Cica*-Merk, Uvasol) as a solvent was fractionally distilled after purification through an alumina column. All samples were carefully degassed by the usual freeze-pump-thaw method.

Results and Discussion

Figure 1 shows transient absorption spectra observed for a CCl_4 solution of CA (0.0025 mol dm^{-3}) and M (0.030 mol dm^{-3}). A broad band in the wavelength region longer than 800 nm is attributed to the CT band of the LE-type triplet exciplex ^{3}(CA–M).[7] The relative intensity of this band to the band at 510 nm increased apparently for the case [M]=0.60 mol dm^{-3}, although no other new band was observed. The band around 510 nm, which is due to both free ^{3}CA and ^{3}(CA–M), decays rapidly and the bands attributable to chloranil semiquinone radical (CAH·) emerge at 427.5 and 360 nm. The rise time of CAH· followed at 427.5 nm was identical to the decay time of the triplet species monitored at 510 nm as well as at 1000 nm. These spectral features are quite similar to those observed in DCE. Namely, the hydrogen atom transfer from M to ^{3}CA proceeds through the exciplex;

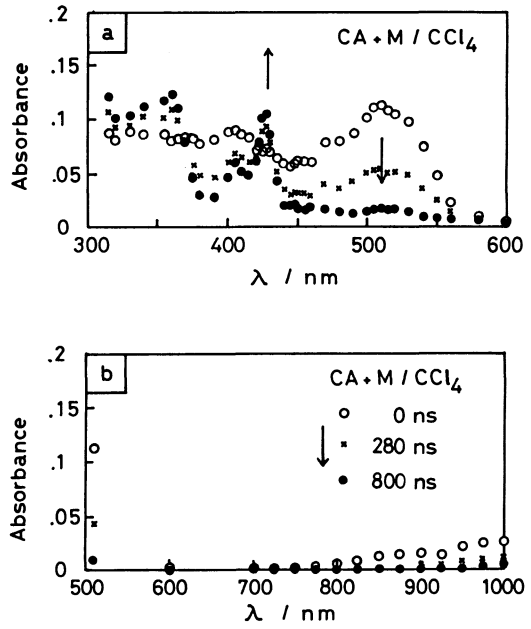

Fig. 1. Transient absorption spectra for the CCl_4 solution containing CA(0.0025 mol dm^{-3}) and M(0.030 mol dm^{-3}) in the wevelength regions of (a) 320—600 nm measured using an R636 photomultiplier and (b) 510—1000 nm measured using an R406 photomultiplier. Time after the pulsing: (○) 0, (×) 280, and (●) 800 ns. The absorbances of the 0 ns spectra in (a) and (b) were normalized to each other at 510 nm.

the same mechanism as revealed previously in DCE.[7]

Figure 2 shows the dependence of the decay rate (τ^{-1}) at the 510 nm band on [M] ranging from 0.0025 to 1.2 mol dm^{-3}. The decay rates were not dependent on the laser power for excitation (ca. 3—15 mJ). In the low concentration region of [M] less than ca. 0.1 mol dm^{-3}, the quenching curve bends downward with an increase of [M], while in the more concentrated region the decay rate becomes slow gradually passing through the maximum value with increasing [M]. The decay features can not be interpreted only by taking into account the (1:1) exciplex formation. This finding suggests that there exists the interaction between the exciplex and another M molecule. Since the triplet species at 510 nm decays exactly with a single exponential function, it is reasonable to consider that a dynamic equilibrium may be established rapidly among triplet species including a terplex under the present experimental conditions. The reaction scheme is written as follows:

$$\begin{array}{ccccc} & & K_1 & & K_2 \\ & & & & +M \\ {}^3CA + M & \rightleftharpoons & {}^3(CA^{\delta-} - M^{\delta+}) & \rightleftharpoons & {}^3(CA^{\delta'-} - M_2^{\delta'+}) \\ & & & & -M \\ & & \downarrow k_0 & & \downarrow k_1 \qquad \downarrow k_2 \end{array}$$

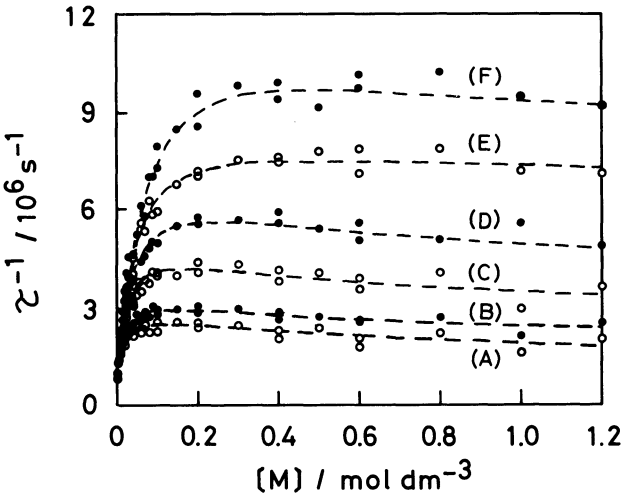

Fig. 2. Relations of τ^{-1} vs. [M] ranging from 0.0025 to 1.2 mol dm^{-3} at several temperatures: (○) and (●) Observed values measured at (A) 10, (B) 15, (C) 25, (D), 35, (E) 45, and (F) 55 °C. (----) Calculated curves.

In this case, the decay rate of ^{3}CA can be expressed by the following Eq. 1.

$$\tau^{-1} = \frac{k_0 + k_1K_1[M] + k_2K_1K_2[M]^2}{1 + K_1[M] + K_1K_2[M]^2} \quad (1)$$

where k_0, k_1, and k_2 are the decay rate parameters of free ^{3}CA, ordinary exciplex ^{3}(CA–M) and terplex ^{3}(CA–M$_2$), respectively, and K_1 and K_2 are the equilibrium constants for formation of the exciplex and terplex, respectively.

As exemplified in Fig. 2, the calculated curve according to Eq. 1 reproduces well the experimental values. Then, five parameters k_0, k_1, k_2, K_1, and K_2 can be estimated by a nonlinear least-square regression analysis using a combination of damping Gauss-Newton and Marquardt methods for 32 experimental points. Results are listed in Table 1. The k_1 and K_1 values are obtained with a good accuracy at each temperature. The corresponding parameters for the terplex, k_2 and K_2, are also estimated although the errors are relatively large. The k_0 values have large errors in the present 5-parameters fitting and tend to be estimated somewhat largely; e.g., the decay rate of ^{3}CA in the absence of M is ca. 0.1×10^6 s^{-1} at 25 °C. The van't Hoff plots for K_1 and K_2 values in Table 1 yield the enthalpy (ΔH) and entropy (ΔS) changes for the formation of both (1:1) and (1:2) exciplexes. These thermodynamic parameters together with equilibrium constants (K_e) and lifetimes (τ_e) of both exciplexes are summarized in Table 2.

The noticeable results in Table 2 are the positive enthalpy and entropy changes for the terplex formation. That is, the terplex formation from the

Table 2. Properties of Triplet Exciplexes in CCl_4

	Exciplex	
	(1:1)	(1:2)
K_e/dm^3 mol^{-1} [a]	49±1	1.7±1.3
ΔG/kJ mol^{-1} [a,b]	−9.6±0.1	$-1.3\pm^{1.4}_{3.6}$
ΔH/kJ mol^{-1} [c]	−32±3	15±3
ΔS/J K^{-1} mol^{-1} [c]	−74±11	52±9
τ_e/ns [a]	197±4	391±121

a) At 25 °C. b) Calculated using the relation $\Delta G = -RT\ln K_e$. c) The errors were estimated by a linear least-square regression treatment of the relation of $\ln K_e$ vs. $1/T$ including the experimental deviations of K_e as weight.

Table 1. Results of 5-Parameters Fitting by Nonlinear Least-Square Regression Analysis

T	k_0	k_1	k_2	K_1	K_2
°C	10^6 s^{-1}			dm^3 mol^{-1}	
10	0.78±0.81	2.8±0.5	0.8±1.0	90±1	0.9±0.6
15	0.63±0.69	3.3±0.4	1.5±0.8	80±1	0.9±0.5
25	0.34±0.12	5.1±0.1	2.6±0.8	49±1	1.7±1.3
35	0.59±0.08	7.0±0.1	3.6±1.2	29±1	1.4±1.2
45	0.65±0.29	8.7±0.5	6.6±1.6	23±5	1.5±3.1
55	1.04±0.10	13.0±0.4	8.0±0.6	11±1	2.1±1.0

bimolecular exciplex is energetically unfavorable but the positive entropy change contributes largely to decreasing the free energy change. The latter result may be attributed to an increase in entropy of solvation on going from the exciplex state to the terplex state or attributed to a conformational change between ^{3}(CA–M) and ^{3}(CA–M_2) accompanied by a solvent reorientation. A similar discussion about such contribution of entropy has been given for the stabilization of an ordinary (1:1) triplet exciplex[12] and the conformational change has been suggested for a terplex formed in the excited singlet state.[2]

Other results are summarized as follows: 1) The triplet-state terplex formation becomes significant in a concentrated solution of M over ca. 0.2 mol dm^{-3}, although no distinct absorption due to the terplex was observed. 2) The deactivation rate of the terplex is smaller than that of the ordinary exciplex. This fact suggests that H-atom transfer in the terplex takes place more slowly than that in the exciplex, because it is considered that the reaction rate of H-atom transfer must depend on the mutual orientation between ^{3}CA and M in each exciplex but a competing deactivation, i.e., intersystem crossing, would be relatively unaffected. 3) The thermodynamic quantities for the (1:1) exciplex are similar to those for an usual electron donor–acceptor complex in the ground state.[13] 4) The lifetime of ^{3}(CA–M) in CCl_4 is considerably longer than that in DCE (32 ns at 25 °C).[7] It is presumed from this result that the solvent polarity affects significantly on the H-atom transfer reaction.

This work was financially supported in part by the Gunma University Foundation for Science and Technology. The authors also thank to Professor Haruo Shizuka for his interest and manuscript reading.

References

1) H. Beens and A. Weller, *Chem. Phys. Lett.*, **2**, 140 (1968).

2) K. H. Grellmann and U. Suckow, *Chem. Phys. Lett.*, **32**, 250 (1975).

3) T. Mimura and M. Itoh, *J. Am. Chem. Soc.*, **98**, 1095 (1976); *Bull. Chem. Soc. Jpn.*, **50**, 1739 (1977); T. Mimura, M. Itoh, T. Ohta, and T. Okamoto, *ibid.*, **50**, 1665 (1977); M. Itoh, N. Takita, and M. Matsumoto, *J. Am. Chem. Soc.*, **101**, 7363 (1979).

4) R. A. Beecroft, R. S. Davidson, and D. Goodwin, *Tetrahedron*, **41**, 3853 (1985).

5) J. K. Roy, F. A. Carroll, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 6349 (1974).

6) I. V. Renge, V. A. Kuzmin, and Yu. E. Borsevich, *J. Photochem.*, **31**, 67 (1985).

7) H. Kobashi, T. Okada, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **59**, 1975 (1986).

8) H. Kobashi, K. Motegi, and H. Shizuka, Preprint for the 52nd Annual Meeting of Chem. Soc. Jpn. (Kyoto, April 1986), Abstr. No. I-2F31; H. Kobashi, K. Hiratsuka, and H. Shizuka, Symposium on Molecular Structure (Osaka, October 1986), Abstr. No. 2B05.

9) Partly presented in the 54th Annual Meeting of Chem. Soc. Jpn. (Tokyo, April 1987), Abstr. No. I-3IIIQ11.

10) P. P. Levin and V. A. Kuzmin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **35**, 1303 (1986).

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

12) E. I. Kapinus, M. M. Aleksankina, and I. I. Dilung, *Chem. Phys. Lett.*, **114**, 507 (1985).

13) G. Briegleb, "Elektron-Donor-Acceptor-Komplexe," Springer-Verlag, Berlin (1962).