Femtosecond–Picosecond Laser Photolysis Studies of the Ion Pair Formation Process in the Excited State of the Charge-Transfer Complex in Solution

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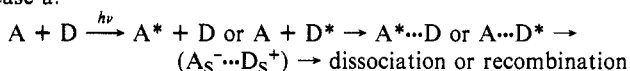*(Received: January 23, 1989)*

Femtosecond and picosecond laser photolysis and time-resolved transient absorption spectral studies have been made to directly observe the charge separation (CS) process in the excited state of the 1,2,4,5-tetracyanobenzene–toluene charge-transfer (CT) complex in toluene and in acetonitrile. Results have been compared with those of similar studies on intramolecular exciplex systems where donor and acceptor are combined with one or two $-CH_2-$ spacers and there is no donor–acceptor interaction in the ground state. It has been demonstrated that, in the case of the more strongly interacting donor–acceptor pairs in the CT complex, it takes longer time to realize the complete CS owing to the much larger rearrangement of donor–acceptor geometries and environmental configurations necessary for the CS, even in acetonitrile solution.

Introduction

Elucidation of dynamics and mechanisms of photoinduced charge transfer (CT) and/or electron transfer (ET) leading to the formation of transient ion pair (IP) states and their dynamic behaviors are the most fundamental and important problems in photochemical processes in the condensed phase.[1]

The mode of photoinduced CT and/or ET and charge separation (CS) processes in polar solution may be classified roughly into two cases:

case a:

$$A + D \xrightarrow{h\nu} A^* + D \text{ or } A + D^* \rightarrow A^* \cdots D \text{ or } A \cdots D^* \rightarrow$$
$$(A_S^- \cdots D_S^+) \rightarrow \text{dissociation or recombination}$$

case b: $(A^{-\delta}D^{+\delta}) \xrightarrow{h\nu} (A^{-\delta'}D^{+\delta'})_{FC}^* \rightarrow (A_S^- \cdots D_S^+) \rightarrow$
recombination or dissociation

(a) represents the CS at encounter and (b) the CS by excitation of the ground-state CT complex. $(A_S^- \cdots D_S^+)$ is the geminate IP, and $(A^{-\delta'} \cdots D^{+\delta'})_{FC}^*$ is the excited Franck–Condon state of the complex. In (a), the electronic interaction responsible for the ET between donor and acceptor at encounter is very weak in general, while in (b) it is much stronger in its order of magnitude. Moreover, the behaviors of the geminate IP are quite different between cases a and b even though the same A and D in the same polar solvent are used.[2] This indicates the different structure and, accordingly, different interaction between ion radicals in the pair depending on the mode of geminate IP formation. It should be noted here that, although the standard theory of ET treats the very weak or weak interaction case, photoinduced CS in actual systems can take place also when interaction is much stronger, including the excitation of the CT complex as an extreme case.

Experimental investigations with ultrafast laser spectroscopy as well as theoretical studies on weak or very weak interaction cases have been and are being made quite lively, and several aspects of the problem have been elucidated, although there are still some unsettled problems.[1,2c,3,4] Contrary to such more or less detailed studies on the systems like (a), such investigations on the excited state of the CT complexes stable in the ground state are quite scarce, although the ground-state properties of such complexes have been investigated exhaustively.[5] However, as discussed above, it is an important problem to also elucidate the dynamics of the photoinduced CS process in such more strongly interacting systems with ultrafast laser spectroscopy and compare the results with those of systems like (a), which will lead to a more complete understanding of fundamental aspects of photoinduced ET and CS phenomena.

For such a purpose, we have examined relaxation and CS processes in the excited state of the TCNB (1,2,4,5-tetracyanobenzene)–toluene complex with femtosecond and picosecond laser photolysis and transient absorption spectral measurement. More or less detailed investigations on the electronic and geometrical structures of the TCNB–toluene complex in the ground and excited states were made previously by means of fluorescence and phosphorescence measurements as well as nanosecond laser photolysis, which indicated a large structural change within the complex and also including the surrounding solvents in the course of the CS process.[1a,b,6] Although some preliminary picosecond laser photolysis studies were also made on the CS process of this complex,[1c] the exact sequence of electronic and geometrical changes involving the relative donor–acceptor geometry and environmental configurations is still unclear. For its elucidation, more direct femtosecond spectral measurements as well as accurate and more detailed picosecond spectral measurements are necessary.

In the following, we give results of femtosecond and picosecond laser photolysis and transient absorption spectral studies on the CS processes in the excited state of the TCNB–toluene complex in toluene and acetonitrile solutions with some discussions on the mechanisms of relaxation process from excited Franck–Condon state causing CS.

Experimental Section

A microcomputer-controlled picosecond laser photolysis system with a repetitive mode-locked Nd^{3+}:YAG laser was used for transient absorption spectral measurements in the 10 ps to nanosecond region.[7] The third harmonic generation (355 nm) pulse

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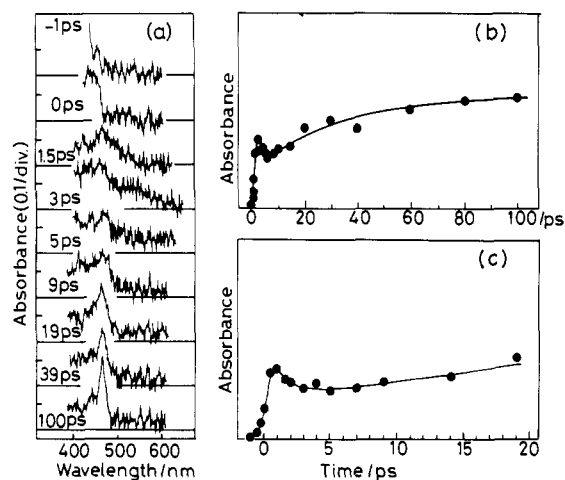
Figure 1. (a) Time-resolved transient absorption spectra of TCNB in toluene solution measured with the femtosecond laser photolysis method. [TCNB] = 6 × 10^{-3} M. (b, c) Time profiles of absorbance at 465 nm.

with 22-ps fwhm and 0.5–2-mJ output power was used for exciting the sample solution exclusively at the CT absorption band. For the measurements of time-resolved transient absorption spectra in the shorter time region, a femtosecond laser photolysis system[2d] was used. The output of a CW mode-locked Nd^{3+}:YAG laser operated at 82 MHz was compressed by a fiber-grating system, and the second harmonic generation of the compressed pulse synchronously pumped a pyridine-1 dye laser (710 nm), the output pulse (300-fs fwhm, 1 nJ) of which was amplified to 0.4 mJ/pulse by a three-stage pyridine-1 dye amplifier pumped by a frequency-doubled Q-switched Nd^{3+}:YAG laser operating at 10 Hz. The amplified pulse with typically 500-fs width was frequency doubled (355 nm) and used for exciting the sample. The rest of the fundamental pulse was focused into D$_2$O to generate a white light probe pulse. Two sets of multichannel photodiode detectors were used to observe transient absorption spectra.

Wako GR grade TCNB was recrystallized from ethanol before use, and its purity was checked by measuring the absorption spectra, CT fluorescence spectra, and decay time. Spectrograde toluene was passed through a column of silica gel before use, and spectrograde acetonitrile was used as received. Sample solutions for the measurements were deaerated by freeze–pump–thaw cycles.

Results and Discussion

TCNB in Toluene Solution. The CT interaction in the ground state of the TCNB–toluene complex is weak while it becomes stronger in the excited state causing relaxations to the equilibrium IP state, accompanied by intracomplex configurational change and solvent reorientation.

Figure 1a shows time-resolved transient absorption spectra of the TCNB–toluene system measured by the femtosecond laser photolysis method. Immediately after excitation, a rapid rise of a broad band takes place nearly within the time response of the apparatus. The absorption bands at several delay times corrected for the chirping of the monitoring white pulse are shown in Figure 2a. In Figure 1b,c, time profiles of the absorbance of corrected spectra at 465 nm are indicated. Immediately after excitation, a slight decrease of absorbance with decay time of ca. 1.5 ps, accompanied by a slight sharpening of the band shape as one can see from Figure 2a, takes place, and then the sharp TCNB anion band grows up with a rise time of 30 ps.

We have also made detailed transient absorption spectral mesurements in the 10 ps to nanosecond regions as shown in Figure 3a. In addition to the rise of the sharp TCNB anion band at 465 nm, a broad absorption that is very similar to that of the toluene dimer cation arises in the wavelength region longer than 650 nm with increase of the delay time. As indicated in Figure 3b, the rise curve of this broad absorption observed at 910 nm coincides
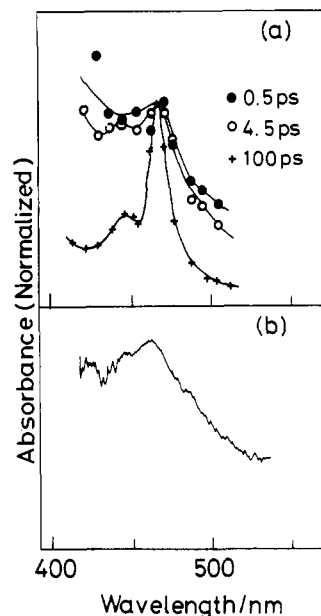
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Figure 2. (a) Transient absorption spectra at several delay times corrected for the chirping of the monitoring white pulse. The absorption intensity is normalized at 465 nm. (b) Transient absorption spectra observed at 170 K and at the delay time of 100 ps (the same system as in Figure 1).
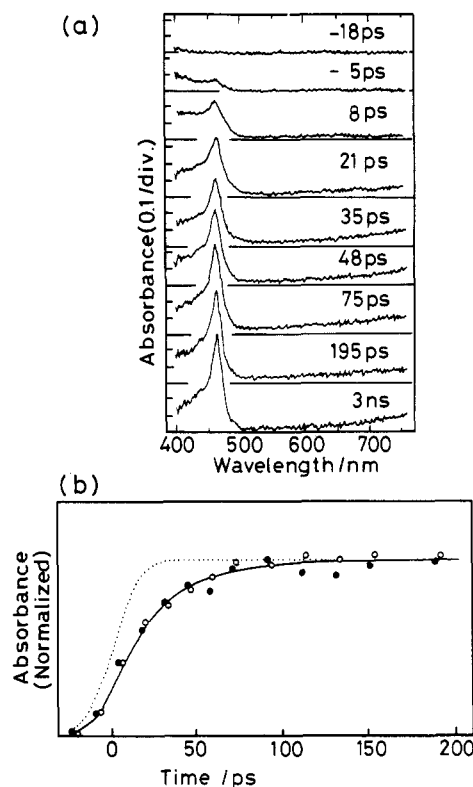

Figure 3. (a) Time-resolved transient absorption spectra measured with the picosecond laser photolysis method. (b) Time profiles of absorbance of the TCNB anion (O) and toluene dimer cation (●) bands: (···) time response of apparatus; (—) rise curve convoluted with time constant of 30 ps. [TCNB] = 3 × 10^{-3} M.

with that of the TCNB anion band. The rise time has been obtained to be 30 ps by deconvolution, which is in agreement with that obtained from Figure 1.

Previous semiempirical MO calculations[6a,d,e] on the Franck–Condon excited state of a complex such as TCNB–benzene and TCNB–toluene predicated an almost equal contribution of ET (^{1}(A$^-$·D$^+$)*) and locally excited (LE) (^{1}A*·D) structures to the wave function of the excited complex. The same theoretical calculations predicted that, in the ground state as well as in the
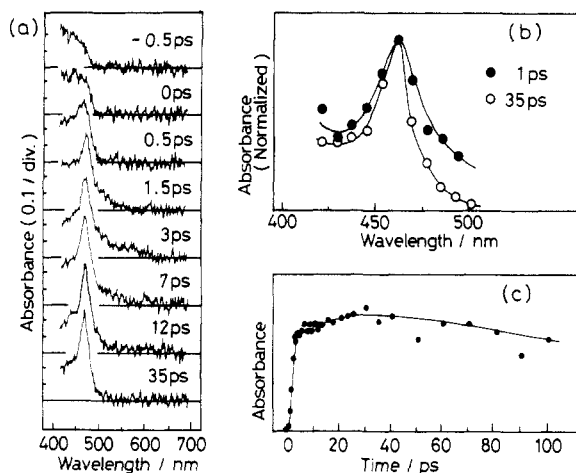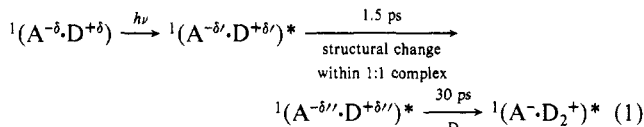
Figure 4. (a) Time-resolved transient absorption spectra of the TCNB–toluene complex in acetonitrile measured with the femtosecond laser photolysis method. Toluene concentration was 5 vol % (0.47 M). [TCNB] = 8 × 10⁻² M. (b) Transient absorption bands at several delay times corrected for the chirping of the monitoring white pulse. The intensity is normalized at 462 nm (peak wavelength in acetonitrile). (c) Time profile of absorbance of corrected spectra at 462 nm.

FC excited state, the center of one benzene ring is considerably shifted against the center of another benzene ring in the complex, while they predicted a much larger degree of CT character in the configurations where two benzene rings are overlapped symmetrically.

In view of these predictions, the absorbance decay immediately after excitation as indicated in Figure 1b,c may be ascribed to the configurational rearragement of the complex from the Franck–Condon excited state with asymmetrical configuration toward a more symmetrical overlapped configuration accompanied with a slight nonradiative deactivation in the course of the structural change. However, this structural change does not lead to the complete CS, but further interaction with toluene and structural rearrangement involving the formation of the 1:2 complex ¹(A⁻·D₂⁺)* is of crucial importance for it.

$$^1(A^{-\delta}\cdot D^{+\delta}) \xrightarrow{h\nu} {}^1(A^{-\delta'}\cdot D^{+\delta'})^* \xrightarrow[\substack{\text{structural change} \\ \text{within 1:1 complex}}]{1.5 \text{ ps}}$$

$$^1(A^{-\delta''}\cdot D^{+\delta''})^* \xrightarrow[D]{30 \text{ ps}} {}^1(A^-\cdot D_2^+)^* \quad (1)$$
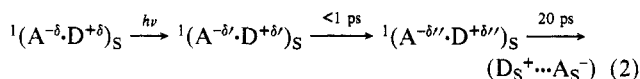
This interpretation will be supported also by the fact that the transient absorption spectrum observed at 170 K and at 100-ps delay time (Figure 2b), where the large structural change of the 1:2 complex formation seems to be difficult, is very similar to the spectrum at 4.5 ps observed at room temperature (Figure 2a).

TCNB–Toluene Complex in Acetonitrile. The time-resolved transient absorption spectra of this complex in acetonitrile solution are shown in Figure 4a. The absorption bands at different delay times are indicated in Figure 4b where the band shape is corrected for the chirping of the monitoring white pulse, and the time profile of the corrected absorbance is shown in Figure 4c.

Compared with the case of TCNB in toluene solution, the absorption band is fairly sharp already at 1 ps. Nevertheless, for the complete change to the sharp TCNB anion band, it takes ca. 20 ps as one can see from Figure 4b,c. Since we have confirmed that the rise time (20 ps) of the sharp anion band is not affected by change of added toluene concentration (from 1 vol % to several 10 vol %), the formation of the 1:2 type of the IP may not play any important role for the complete CS in acetonitrile. Therefore, in the course of the relaxation from the excited FC state, solvent reorientation and a slight intracomplex structural change will

induce CS within ca. 1 ps to a considerable extent but not completely.

The decay of the absorbance at 465 nm observed immediately after excitation in the case of TCNB in toluene solution was not clearly observed in acetonitrile solution at 462 nm (the peak position of the TCNB anion band in acetonitrile). Presumably, the extent of the intracomplex rearrangement will be smaller at the first step of the CS in acetonitrile, since the solvent reorientation assists the CS. The decay of the absorbance after its rise with rise time of 20 ps is due to the charge recombination (CR) competing with dissociation into free ions. At any rate, for the complete CS leading to the IP formation in the acetonitrile solution of the TCNB–toluene complex, further solvation and intracomplex structural change which take place with a time constant of 20 ps are necessary.

$$^1(A^{-\delta}\cdot D^{+\delta})_S \xrightarrow{h\nu} {}^1(A^{-\delta'}\cdot D^{+\delta'})_S \xrightarrow{<1 \text{ ps}} {}^1(A^{-\delta''}\cdot D^{+\delta''})_S \xrightarrow{20 \text{ ps}}$$
$$(D_S^+\cdots A_S^-) \quad (2)$$

At this point, it would be interesting to compare the present results in acetonitrile solution with those of photoinduced CS of p-(CH₃)₂N–Ph–(CH₂)ₙ–(1-pyrenyl) (P$_n$, n = 1, 2)[2d,3e,4,8] obtained by femtosecond transient absorption spectral measurements in acetonitrile solution. From the rise curve of the characteristic sharp absorption peak of the pyrene anion of the intramolecular IP state, the time constant of the CS has been obtained to be 2.6 ps for P₁ and 6 ps for P₂. The photoinduced CS of P$_n$ in acetonitrile is not exclusively regulated by the solvation time τ_s (τ_s < 1 ps for acetonitrile[3d]) but determined also by the magnitude of the electronic matrix element as well as the energy gap responsible for ET, even in the case of P₁ where the electronic matrix element may be fairly large.[2d,3e,4,8]

The first step of the CS taking place within ca. 1 ps in acetonitrile solution of the TCNB–toluene complex might be considerably facilitated by the solvent reorientation.[3] Nevertheless, CS is not completed by the first step but it takes much longer time (20 ps) compared with that of P₁ (2.6 ps) for the complete CS. On the other hand, the free energy gap $-\Delta G^\circ_{CS}$ between the partial CT state immediately after excitation and the relaxed IP state of the TCNB–toluene complex in acetonitrile estimated from the spectral and electrochemical data is about 0.7 eV while that of the pyrene–N,N-dimethylaniline system in the same solvent is ca. 0.5 eV. This means that, though the driving force for the CS may be larger in the case of the TCNB–toluene system, the actual reaction is slower, which may be ascribed to the much larger rearrangement of donor–acceptor geometries and environmental configurations necessary to realize complete CS against the electronic delocalization interaction in such pairs with stronger donor–acceptor interactions than in P₁.

Of course, the rate of the complete CS in the excited state of such CT complexes will generally depend upon the donor–acceptor geometries of the complex in the ground and excited FC states and the strength of donor–acceptor interactions as well as the nature of the environment. Results of femtosecond laser photolysis studies on the CS process as well as the femtosecond and picosecond laser photolysis studies on the CR and dissociation of produced IP of various complexes will be given shortly with some discussions on these points in forthcoming papers.

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