Electronic Structure and Dynamics of the Excited State in CT Microcrystals As Revealed by Femtosecond Diffuse Reflectance Spectroscopy

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Transient absorption spectra of charge-transfer (CT) crystals between methyl- or methoxy-substituted benzene derivatives and pyromellitic dianhydride (PMDA) were measured by femtosecond diffuse reflectance spectroscopy, and the electronic structure and dynamics of the excited state depending on the nature of the electron donor (D) are discussed. For such weak CT complexes, it was confirmed that excitation energy is localized in one donor−acceptor pair and the mixing of CT and locally excited (LE) configurations is important in the excited CT singlet state. The CT degree of the excited state depends on the oxidation potential of D and on the mutual configuration of D and electron acceptor (A) molecules. The second-order decay constant of the excited state was observed under usual photolysis conditions, from which a motion-limited diffusion was considered. A first-order decay of the transient absorption was obtained, when the excitation intensity was weak, and ascribed to charge recombination to the ground state. The energy gap ($-\Delta G$) dependence of the charge recombination rate constant (k_{CR}) was confirmed to give a linear relationship between $\ln(k_{CR})$ and $|-\Delta G|$.

Introduction

CT interaction in excited states plays fundamental and important roles in a number of photochemical and photophysical processes in condensed phases such as electron and proton transfer, hydrogen abstraction, photoinduced charge transport of organic molecular crystals and amorphous polymer films, and so on,[1] and it has been investigated for various kinds of D−A systems. Among them, the ground-state CT complexes of weak π-electron D−A pairs, such as methyl-substituted benzene−1,2,4,5-tetracyanobenzene (TCNB) and −PMDA complexes, have been studied as representative systems.[2−7]

The ground-state absorption spectra and the fluorescence spectra of such CT complexes have been studied thoroughly in solution.[1a−c] Quantum mechanical calculations in the framework of PPP approximation were conducted for analyzing the spectral bands and for elucidating their electronic structures by Nagakura et al.[2,3,6] and by us.[4,5] A more direct confirmation of the CT character in the excited singlet state is to measure the absorption spectra of the excited state, which was first made possible by nanosecond laser photolysis technique.[4−6] Moreover, recent developments of picosecond and femtosecond transient absorption spectroscopy made possible the direct observation and analysis of the very fast charge separation processes following photoexcitation of the ground-state CT complexes.[7,8]

The wave function of the CT complex in the ground state consists mainly of nonbonded structure (DA) and partially of CT structure (D^+A^-), while that of the excited singlet state is mainly composed of the CT structure according to Mulliken theory.[9] However, the degree of CT is less than unity in the Franck−Condon (FC) excited state of such weak CT complexes as toluene−TCNB and −PMDA.[2−8] Previous quantum mechanical calculations on the excited state of the toluene−TCNB complex predicted that CT and LE configurations contribute almost equally to the FC excited state, in which the center of the benzene ring of toluene is shifted against the center of that of TCNB.[2−6] It was also shown that the high CT degree is attained in the geometrical conformation where two rings are symmetrically overlapped.[2−5] A geometrical and electronic structural change from the FC excited state to the equilibrium one, including solvation by surrounding solvent molecules, should take place. This relaxation was considered in details by picosecond and femtosecond transient absorption spectroscopic methods.[7,8b] A full CT state (or a contact ion pair) is generated within several tens picosecond after excitation, whose dynamics depends on the nature of D and A and on the solvent polarity. In polar solvents, the contact ion pair is followed by dissociation into free ion radicals, competing with charge recombination to the ground state.[7,8,10−12]

The similar electronic structure and dynamics of the CT excited state were revealed for the solid crystals composed of weak π-electron D and A molecules by picosecond and femtosecond diffuse reflectance spectroscopy.[13−15] This spectroscopic technique[16] for opaque microcrystalline powder samples is useful for transient absorption spectroscopic studies of CT crystals, because it does not need a large and transparent sample as required for experiments using transmittance mode absorption spectroscopy. The ionic character of the excited state has been directly proved for several kinds of CT crystals; hence, it is considered to be an ionic D−A pair generated in an infinite quasi-one-dimensional array with co-facial alternating stacking of neutral D and A. It was also confirmed for durene−PMDA CT crystal that the ion-pair-like state was formed within a few picoseconds after excitation and was localized in a D−A pair.[15] The electronic coupling of CT and LE configurations is of importance even in the relaxed excited state, and large geometrical changes accompanied with the relaxation process from

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the FC excited state to the relaxed excited state, which is appreciable in solutions, should be strongly restricted. These results clearly demonstrate that the relaxation dynamics and the resultant electronic structure of the equilibrium excited state differ from those of the same D−A pair in solution.

In the present work, we have prepared a series of CT crystals of various methyl- or methoxy-substituted benzene derivatives and PMDA and have measured the transient absorption spectra with excitation of the CT absorption band by femtosecond diffuse reflectance spectroscopy. By changing D in a series of the PMDA CT crystals, their crystalline form, i.e., local geometrical conformation between D and A, may change from one to another. Also, the energy level of the CT configuration varies with the oxidation potential of D. From these viewpoints, transient absorption spectral data were examined. Interesting features of the transient absorption spectra and the dynamics, depending on the nature of D, are presented and discussed.

Experimental Section

Samples. PMDA (GR grade, Tokyo Kasei) was recrystallized several times from ethyl acetate. Durene, 1,3,5-trimethoxybenzene (135TMB) (GR grade, Tokyo Kasei), and *p*-dimethoxybenzene (pDMB) (GR grade, Nacalai tesque) were purified by recrystallization from ethanol. 1,2,4-Trimethoxybenzene (124TMB), hydroquinone (HQ) (GR grade, Nacalai tesque), and hexamethylbenzene (HMB) (zone refined, Tokyo Kasei) were used as received. CT crystals were grown from their acetonitrile or methyl ethyl ketone solution containing equimolar amounts of benzene derivative and PMDA by slowly evaporating the solvent or by slowly cooling the hot solution. In the cases of durene−, pDMB−, and HQ−PMDA complexes, rather large crystals were grown from the acetonitrile solutions. In other cases, only microcrystals of the CT complexes were obtained. Durene and pDMB microcrystals doped a little with PMDA were prepared by heating their mixture at 90 °C under deaerated conditions, followed by rapidly cooling the molten mixture. The concentration of PMDA was diluted to about 10^{-4} and 10^{-3} M for durene and pDMB mixtures, respectively.

All transient absorption spectra were obtained for the microcrystals prepared by grinding the crystals in a mortar and were contained in a quartz cell (2-mm thickness). Their particle sizes ranged over several micrometers as estimated with an optical microscope. In order to check the effect of the grinding procedure upon transient absorption spectral data, we examined microcrystals with different sizes (several 10 to 100 μm). As no clear size dependence was obtained, we concluded that the surfaces of the small microcrystals and some defects in the crystal, which may be generated by grinding the crystals, do not affect the results appreciably.

Transient Diffuse Reflectance Spectra. The details of a femtosecond diffuse reflectance spectroscopic system have been reported elsewhere.[15] Briefly, an excitation light source consists of a cw self-mode-locked Ti:sapphire laser (Mira 900 Basic, Coherent), pumped by an Ar^+ laser (Innova 310, Coherent), and a Ti:sapphire regenerative amplifier system (TR70, Continuum) with a Q-switched Nd:YAG laser (Surelight I, Continuum). The fundamental output from the regenerative amplifier (780 nm, 3−4 mJ/pulse, 170-fs fwhm, 10 Hz) was frequency doubled (390 nm) and used as an excitation light source. The residual of the fundamental output was focused into a quartz cell (1-cm path length) containing H_2O to generate a white-light continuum as the probe beam.

Transient absorption intensity was displayed as the percentage absorption given by

$$\%\ \text{absorption} = 100(1 - R/R_0)$$

where R and R_0 represent intensities of the diffuse-reflected white-light continuum of the probe pulse with and without excitation, respectively.[16] Typically, the spectral data were averaged over 300 measurements. It is well-known that the value of % absorption is not proportional to the concentration of transients species for the high values of % absorption.[16] We examined a linearity of the value against excitation intensity and a transient absorption spectral deformation under high excitation conditions for some powders. In the case of durene−PMDA crystal, for a representative example, a saturation tendency in % absorption was observed above 25%. In this region, the transient absorption spectral shape became much broader than those in the weak intensity region. Therefore, we adjusted the excitation intensity so that the maximum % absorption was less than 25% in the measurements; typically, the excitation intensity was less than 0.5 mJ cm^{-2}.

Time-Resolved Fluorescence Spectra and Fluorescence Decay Curves. Fluorescence decay curves were measured by a picosecond 2-D streak camera (C4334, Hamamatsu). A femtosecond pulse train (76 MHz, 1 W, 150-fs fwhm) from a cw self-mode-locked Ti:sapphire laser (Mira 900, Coherent), which was pumped by an Ar^+ laser (Innova 310, Coherent), was dumped to a 4-MHz train by a pulse picker (Model 9200, Coherent). The obtained laser pulse was frequency doubled and used as an excitation light source. The excitation wavelength was about 390 nm and its intensity was less than 1 nJ/pulse.

Ground-State Absorption Spectra. Absorption spectra of the ground-state CT crystals were estimated by the Kubelka−Munk reemission function.[17] Diffuse reflectance spectra were measured using MgO powder (GR grade, Tokyo Kasei) as a standard, which was recorded with two synchronously driven monochromators of a fluorescence spectrophotometer (F4500, Hitachi). For this measurement, CT crystals were diluted to about 5 vol % with MgO powder.

Results and Discussion

Electronic Structure of the CT Excited State. The transient absorption spectra of durene−, HMB−, and pDMB−PMDA crystals at 10 ps after excitation are shown in Figure 1. With the excitation of the ground-state CT absorption, we observed transient absorption spectra with an absorption maximum around 700 nm which are more or less similar to the absorption band of PMDA anion radical.[8,18] Compared to the anion radical in solution, the bandwidth of the crystals is broader and the peak position shifts to the longer wavelength. All the transient absorption spectra increased within the temporal response of the spectroscopic system (a few picoseconds) and monotonously decayed without any appreciable spectral change. Moreover, when the excitation intensity was low, the decay behavior was approximately the same as that of CT fluorescence measured by a streak camera as shown in Table 1. Therefore, it is concluded that the absorption spectra are due to the relaxed excited singlet state (the fluorescence state) and not to other ionic species.

The S_n-S_1 absorption spectral shape depending on D is not due to the spectral overlap of the absorption band eventually ascribed to the countercation of D, since the cation radicals of durene, HMB, and pDMB do not have any absorption band in the wavelength range from 600 to 900 nm.[18] This is clearly confirmed by the transient absorption spectra of these CT complexes in solution. As shown in Figure 1B, their transient

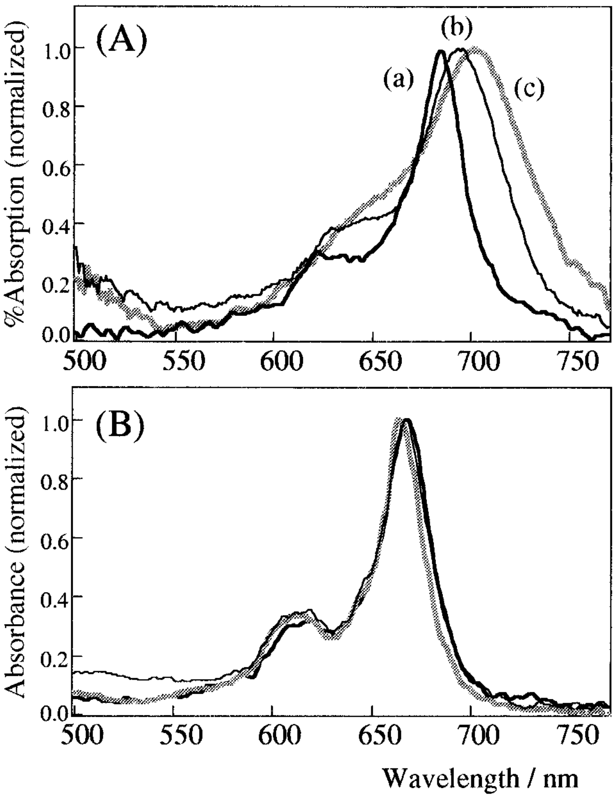

Figure 1. (A) Transient absorption spectra of CT microcrystals of (a) pDMB−PMDA, (b) HMB−PMDA, and (c) durene−PMDA at 10 ps after 390-nm excitation and (B) those in ethyl acetate solution.

TABLE 1: Energetic and Dynamic Properties of the Excited States of the CT Crystals of Methyl- or Methoxy-Substituted Benzene Derivatives and PMDA

				spectral data of PMDA anion-like band			
donors	E_{ox},[a] eV	$h\nu^{\mathrm{a}}_{\mathrm{max}}$,[b] 10^3 cm^{-1}	$h\nu^{\mathrm{f}}_{\mathrm{max}}$,[c] 10^3 cm^{-1}	peak, nm	width,[d] 10^3 cm^{-1}	τ_{ta},[e] ps	τ_{fluo},[f] ps
HQ		17.2	h	698	0.38	1.5	h
124TMB	1.12	17.5	h	688	0.32	6	h
pDMB	1.34	18.5	∼14	688	0.31	15	<20
135TMB	1.49	22.7	16.7	678	0.39	900	800
HMB	1.59	21.3	18.3	693	0.50	4300	5500
durene	1.78	21.7	18.7	703	0.58	4500	4500
ion pair[g]				667	0.3		

[a] Oxidation potential of donors *vs* SCE from ref 19. [b] The energy of the CT absorption maximum of the ground state. [c] The energy of the CT fluorescence maximum. [d] The absorption spectral width (hwhm) of the PMDA anion band with a peak around 700 nm. [e,f] The lifetime of the CT excited state obtained by transient absorption and fluorescence decay measurements, respectively. [g] A contact ion pair in acetonitrile. [h] No fluorescence was observed.

absorption spectral shape in ethyl acetate solution is almost independent of D.

The difference of the S_n-S_1 absorption spectra between these PMDA complexes is ascribed to the geometrical conformation of D and A and to the electronic nature of D. Namely, the CT degree of the excited PMDA complexes is determined by the crystal structure and the oxidation potential of D. The electronic interaction of D and A can be discussed for the fixed D and A geometry. Before going on with the detailed discussion, we have to mention whether the excited state is delocalized over many or several D and A moieties in the crystals as an exciton or localized on one D−A pair. Hochstrasser et al. and Haarer et al. considered that CT excited states of molecular crystals of weak D−A complexes are rather localized (self-trapped), because of its alternating molecular stacks, strong electron−phonon coupling, and also an appreciable Coulomb interaction between generated highly ionic component molecules.[20,21] Recently, we compared the transient absorption spectrum of a 1:1 CT crystal of durene−PMDA and that of 10^{-3} M PMDA-doped durene crystal and found good agreement between the spectra.[15] Here, we have further diluted PMDA to 10^{-4} M in the durene crystal, but its transient absorption spectrum was still in accordance with that of the 1:1 CT crystal. Namely, the absorption band which is broad and red-shifted compared to PMDA anion radical was observed independent of the concentration ratio of D and A. A similar result was also observed for the pDMB−PMDA complex. Consequently, we can conclude that the electronic excitation is localized in one D−A pair and the electronic interactions between the pair and neighboring neutral molecules are quite small. Therefore, we can treat surrounding ground-state D and A molecules as the solvent (an oriented-gas model) and consider the excited electronic structure of the CT crystals in terms of a D−A pair.

As absorption spectra of the excited state are not identical with the absorption bands of D cation and A anion, we should consider the contribution of the LE and the nonbonded ground-state configurations. This was first theoretically shown by Nagakura et al.[3,4] and later experimentally demonstrated in solution as mentioned above. The wave function of a weak CT complex is given by

$$\Psi_{\mathrm{complex}} = C_1\Psi_{\mathrm{g}} + C_2\Psi_{\mathrm{CT}} + C_3\Psi_{\mathrm{LE}}$$

where Ψ_{g}, Ψ_{CT}, and Ψ_{LE} represent the electronic wave functions for the nonbonded ground state, the full CT state, and the LE states of D or A, respectively.[3−5] In general, the configuration interactions among them depend on their energy levels as well as the mutual geometry of D and A. When the LE configuration has an energy level close to that of the CT configuration, the former configuration is involved to a great extent in the excited state, reducing its CT degree. Since we examined a series of PMDA CT crystals of methyl- and methoxy-substituted benzene derivatives, the energy level of the LE configuration is almost constant for each crystal. Therefore, it is predicted that the CT degree varies with the CT energy level, i.e., the oxidation potential of D.

In Table 1, the peak wavelengths and the widths of the excited-state absorption spectra of the CT crystals are listed. They become close to those of a contact ion pair in solution with decreasing of the oxidation potential of D and with lowering of the peak energy of the CT absorption of the ground state. Namely, the electronic structure of the PMDA complexes changes to be more ionic and the CT degree becomes higher in the excited state for the crystals of D with lower oxidation potential. For the crystal of pDMB, the width is almost the same as that of the contact ion pair in solution; hence, the LE configuration is negligibly small, and a full CT state should be attained. On the other hand, the absorption peak wavelength of the pDMB−PMDA crystal is still longer than that of the contact ion pair. This may be ascribed to the difference of the surrounding environmental conditions. In the case of the HQ complex, the peak is red-shifted and the width is broader conversely, although the CT absorption band of the ground state is located in the lowest energy for the crystals examined here. Some contribution of the ground-state configuration appears to be involved as further lowering of the energy level of the CT configuration.

Generally, the electronic structure of the relaxed excited state of a weak CT complex in solution as well as the solid state has been considered, to the first approximation, as one electron transferred state from D to A. However, the present results

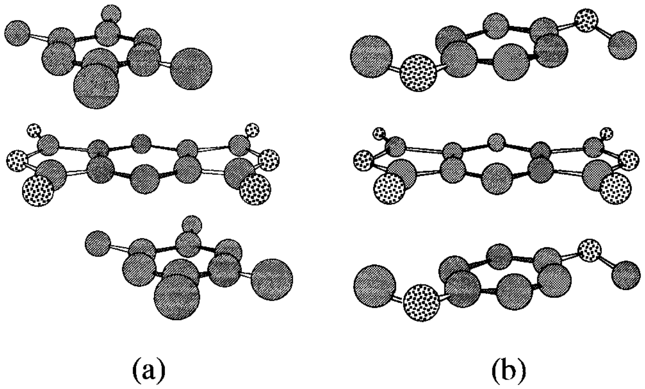

Figure 2. Crystal structures of CT complexes of (a) durene−PMDA and (b) pDMB−PMDA according to the crystallographic data.[22] The geometry of the two benzene rings of D and A in the HQ−PMDA crystal is similar to that in the pDMB−PMDA crystal. Durene−PMDA crystal: monoclinic; $C2$; $a = 10.734$ Å, $b = 10.566$ Å, $c = 15.562$ Å, $\beta = 93.84°$; $V = 1771.1$ Å^3; $Z = 4$. pDMB−PMDA crystal: monoclinic; $P2_1$; $a = 6.068$ Å, $b = 7.765$ Å, $c = 16.751$ Å, $\beta = 93.42°$; $V = 787.8$ Å^3; $Z = 2$. HQ−PMDA crystal: monoclinic; $P2_1$; $a = 7.411$ Å, $b = 6.057$ Å, $c = 14.978$ Å, $\beta = 96.13°$; $V = 668.5$ Å^3; $Z = 2$.

and discussion clearly indicate that the excited singlet state of weak CT crystals is not always a full CT even in the equilibrium state, and the electronic interaction among the ground, CT, and LE configurations is still important, leading to the dependence of the CT degree on the oxidation potential of D.

The above discussion on the CT character holds well, assuming that their crystalline structure is common to the relevant complexes. Some differences in the geometrical structure were estimated by X-ray crystallographic analysis, which can be related to the electronic structure of the excited state. We compare here three crystals of durene−, pDMB−, and HQ−PMDA, the details of which will be published separately. These complexes are crystallized in a similar fashion to form a cofacial alternating stack of D and A. The geometry of two benzene rings of D and A is slightly different but with almost the same distance of about 0.35 nm,[22] as shown in Figure 2. These benzene rings are fully overlapped in the case of the crystals of pDMB and HQ, while they are shifted to each other in the case of durene−PMDA. The relation between the CT degree and the geometrical structure indicates that a high CT degree in the excited state is attained in the geometry where two benzene rings overlapped symmetrically. This is consistent with the prediction of some MO calculations on the excited state of toluene− and benzene−TCNB complexes[2−4] as described in the Introduction.

Decay Dynamics of the CT Excited State. As mentioned above, the transient absorption decay of all the crystals examined here is approximately represented by a single-exponential function under low excitation conditions. For the crystal of HMB−PMDA and durene−PMDA, the lifetime of which is several nanoseconds, an additional fast decay component was observed when increasing the intensity of the excitation pulse as shown in Figure 3. Because the fast decay depends on the excitation intensity, it is considered that a bimolecular annihilation of the excited state is involved. In this case, the decay kinetics can be described by

$$\frac{\mathrm{d}n(t)}{\mathrm{d}t} = -k_1 n(t) - \gamma n(t)^2 \tag{1}$$

where k_1 is the rate constant of unimolecular decay and γ is that of the bimolecular annihilation process. Integration of eq 1 gives the population density of the excited state ($n(t)$) as a function of time:

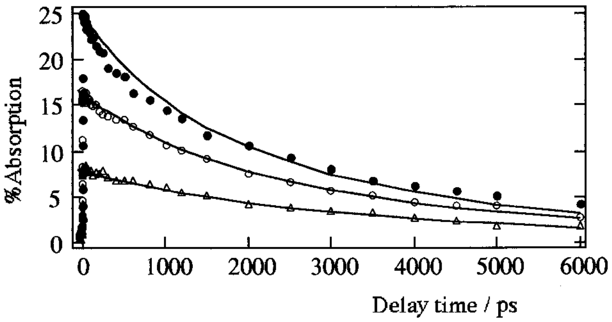

Figure 3. Observed time profiles of the transient absorption of durene−PMDA microcrystals at three excitation intensities (●, 470 μJ cm^{-2}; ○, 310 μJ cm^{-2}; △, 150 μJ cm^{-2}). The excitation wavelength and probe wavelength are 390 and 704 nm, respectively. Solid lines are curves calculated by eq 2 with the parameters $\tau_0 = 4.5$ ns and $(n_0\gamma)^{-1} = 3.3 \times 10^8$ s^{-1}, 2.1×10^8 s^{-1}, and 1.0×10^8 s^{-1} (top to bottom).

$$n(t) = \frac{n_0 \exp(-t/\tau_0)}{1 + n_0\gamma\tau_0(1 - \exp(-t/\tau_0))} \tag{2}$$

where n_0 is its initial density and $\tau_0 = k_1^{-1}$. Fitting this equation to the data on the assumption that n_0 was proportional to the excitation intensity yielded the solid lines in Figure 3 with the parameters of $(n_0\gamma)^{-1}$ and τ_0 in the figure caption. The value of τ_0 was estimated from the fluorescence decay measurements under the low-excitation intensity. When the intensity is 470 μJ cm^{-2}, n_0 was calculated to be 1×10^{19} cm^{-3} by using 1000 M^{-1} cm^{-1} as the molecular extinction coefficient of the ground state at the excitation wavelength. From the values of n_0 and $(n_0\gamma)^{-1}$, γ was estimated to be 3×10^{-11} cm^3 s^{-1}. Since the density of D−A units is estimated to be approximately 2.4×10^{21} cm^{-3} from the lattice parameter of the durene−PMDA crystal, the density of the excited state (1×10^{19} cm^{-3}) corresponds to the condition in which 1 CT excited state is created in every 240 D−A units.

Singlet−singlet exciton annihilation in crystalline anthracene has been studied extensively.[23] The bimolecular rate constant was reported to be 1×10^{-8} cm^3 s^{-1} from measurements of fluorescence quantum yields under the nanosecond laser pulse illumination[23b] and from photoconductivity measurements.[23c] The rate constant for the CT crystal is much smaller than that in the anthracene crystal, which suggests that in the CT crystal the singlet excited state migrates quite slowly or it diffuses in a motion-limited manner. The motion-limited diffusion of the excited state will be consistent with its crystalline form with quasi-one-dimensional stacks of alternate D and A. The diffusion motion along the stack axis is more efficient than that which crosses the stacks. In such a case, the bimolecular annihilation decay has to be analyzed by using a time-dependent rate instead of the constant rate. However, quite similar results were obtained for other CT crystals such as naphthalene−, pyrene−, and anthracene−PMDA; then, the details on the annihilation mechanism in the CT crystals are discussed separately elsewhere.[24]

The lifetime of the exited state is drastically changed with D as shown in Table 1. It decreases with the lowering of the CT energy level. When the excitation intensity is not so high or when the unimolecular decay rate is short, the decay can be ascribed to nonradiative charge recombination to the ground state. In Figure 4, the values of k_{CR} ($=\tau_0^{-1}$) are plotted against $-\Delta G$ between the excited and ground states, which was estimated from the peak energy of the CT absorption band ($h\nu^{\mathrm{a}}_{\max}$) and of CT fluorescence band ($h\nu^{\mathrm{f}}_{\max}$) by

$$-\Delta G = h\nu^{\mathrm{a}}_{\max} - \Delta h\nu/2 \tag{3}$$

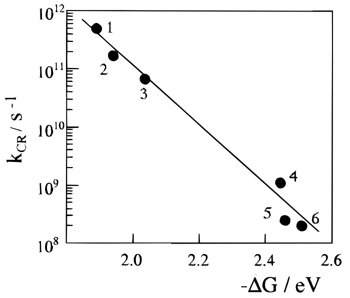

Figure 4. k_{CR} *vs* $-\Delta G$ relation of the CT excited state in CT crystals. Donors are (1) HQ, (2) 124TMB, (3) pDMB, (4) 135TMB, (5) HMB, and (6) durene.

where $\Delta h\nu$ represents the Stokes shift ($= h\nu^{a}_{max} - h\nu^{f}_{max}$). The values of the $\Delta h\nu$ of the 124TMB−PMDA and HQ−PMDA crystals were assumed to be the same as that of the pDMB−PMDA crystal, because the former two crystals were nonfluorescent. The observed dependence can be well represented by

$$\ln k_{CR} = \alpha - \beta|-\Delta G| \qquad (4)$$

A similar relationship was already reported for the charge recombination of contact ion-pair states in homogeneous solution[8,25] and in heterogeneous environments.[27] Recently, a study on the energy gap law for the CT excited state of arene−TCNB and −methylviologen CT crystals has been reported by Hubig et al. by using picosecond diffuse reflectance spectroscopy, and a similar linear dependence was also observed.[14] These results suggest that the linear relation of k_{CR} *vs* $|-\Delta G|$ is general for the contact ion-pair state or the CT excited state generated by photoexcitation of weak CT complexes.

At the present stage of investigation, we consider that the linear relation can be qualitatively interpreted in terms of "the weak coupling limit" in the radiationless transition.[28] This was first suggested in the nanosecond laser photolysis studies on ionic photodissociation of representative D−A pairs in polar solution.[29] The dominant contribution of the high-frequency quantum mode (intramolecular vibration) as an accepting one is considered to be important for the relaxation process. It should be noted that the slope β ($\partial \ln(k_{CR})/\partial|-\Delta G|$) obtained here is quite different from that for contact ion pairs in solution; the former is about 3 times larger than the latter. This discrepancy will be related to the rigidity of D and A molecules in the crystal state and also to the lattice vibrational modes coupled with the charge recombination. A more detail investigation including other PMDA CT crystals and the temperature effects is now in progress.

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