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Formation and dynamics of intermolecular charge transfer (CT) intermediates. A study with photo-excited all-*trans*-1,6-diphenylhexa-1,3,5-triene and *p*-dicyanobenzene

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Abstract

Photoinduced electron transfer reactions between singlet excited all-*trans*-1,6-diphenylhexa-1,3,5-triene (^{1}DPH*) and *p*-dicyanobenzene (*p*-DCB) were investigated by electrochemical methods, stationary and time-resolved fluorescence and absorption measurements and charge transfer (CT) emission spectral fitting in five solvents of different polarity. Rate constants of triplet DPH (^{3}DPH*) formation, fluorescence (CT emission), and radiationless deactivation (charge recombination, CR) of the respective CT intermediates (solvent-separated ion pairs or exciplexes) and the free energy changes of the corresponding processes were determined. The S_1–S_n absorption spectra of the CT intermediates in the less polar solvents provided solid evidence that the CT intermediates can be approximately described by pure CT states with negligible contributions of locally excited states. A bandshape analysis of the CT emission spectra (CT emission spectral fitting) was employed to determine the Franck–Condon factors which depend, among other parameters, on the vibrational and solvent reorganization energies (λ_i, λ_o), on the electronic matrix coupling element (V_{CR}) and on the free energy change (ΔG^G_{CR}). With the experimental values for λ_i, λ_o, ΔG^G_{CR}, and V_{CR}, rate constants of the charge recombination reaction of the CT intermediates were calculated in the framework of non-adiabatic electron transfer theory, and the results were found to be in good agreement with experimental rate constants. © 1997 Elsevier Science S.A.

Keywords: Intermolecular charge transfer intermediates; All-*trans*-1,6-diphenylhexa-1,3,5-triene; *p*-dicyanobenzene

1. Introduction

The elucidation of the dynamics and mechanisms of intermolecular photoinduced electron transfer (ElT) reactions is among the most important fundamental challenges in photophysical research, and a particular research objective in ElT studies has always been the determination of the quantities which govern ElT reaction rates, such as, e.g., the standard free energy change ΔG, the solvent and vibrational reorganization energies λ_o and λ_i, the characteristic vibrational mode energy of the product state $h\nu_v$, and the electronic matrix coupling element V.

We have studied photoinduced ElT reactions between singlet excited all-*trans*-1,6-diphenylhexa-1,3,5-triene (^{1}DPH*) and *p*-dicyanobenzene (*p*-DCB) in five solvents (toluene, diethyl ether, ethyl acetate, 1,2-dichloroethane and acetonitrile) by using electrochemical methods, stationary and time-resolved absorption and fluorescence spectroscopy, and charge transfer (CT) emission spectral fitting.

The remarkable interest that all-*trans*-1,6-diphenylhexa-1,3,5-triene (DPH) has received in the photophysical literature during the last two decades arises from its strongly solvent-dependent fluorescence properties [1–3] and from the fact that DPH has become one of the most widely applied fluorescent probe chromophores for investigations of, e.g., viscosities and polarities in microheterogenous systems [4–6].

Although numerous studies have been addressed to the photophysical properties and photoinduced intramolecular processes of DPH, no systematic investigation of bimolecular reactions involving ^{1}DPH* seems to be available in the literature. In a previous publication we reported the results of our investigations of intermolecular deactivation processes of ^{1}DPH* induced by external heavy atom perturbers and by organic electron acceptor molecules [7]. In extension of these studies, we have investigated the formation and dynam-

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ics of CT intermediates formed between ^{1}DPH* and *p*-DCB in five solvents having different polarities. Whereas the details of the kinetic analysis through combination of the results from stationary and time-resolved absorption and fluorescence measurements are presented and discussed elsewhere [8], special emphasis in this communication is placed on the dependence of charge recombination (CR) rate constants on free energy changes and solvent polarity and on the elucidation of the applicability of the theory of non-adiabatic electron transfer reactions in this context.

2. Experimental details

DPH (Fluka, >99%) was used as received; *p*-DCB (Aldrich) was sublimed in vacuo and recrystallized three times from ethyl acetate prior to use. The solvents toluene (Aldrich), diethyl ether (Fluka), ethyl acetate (Aldrich), 1,2-dichloroethane (Fluka), and acetonitrile (Aldrich) were of spectroscopic grade and were used without purification.

All samples were prepared in 1 × 1 cm cuvettes except for laser flash measurements in acetonitrile, which were carried out in a flow system to prevent excessive formation of DPH isomers. The DPH concentrations were in the range $(0.5–1)\times10^{-5}$ M. In the cuvettes, the samples were deoxygenated by bubbling purified nitrogen through the solutions and sealed off.

The fluorescence decay functions were determined by the technique of time-correlated single photon counting with a nitrogen-filled nanosecond flash lamp (Edinburgh Instruments) as described previously [9]. The transient absorption measurements were carried out with an apparatus already described [10]. The S_1–S_n spectra of the exciplexes were measured using the pump-and-probe technique with a 308 nm excimer pump laser and a dye laser probe (Lambda Physik). Stationary fluorescence measurements were performed with a quantum-corrected Perkin Elmer MPF-44 fluorescence spectrometer. Electrochemical methods are described elsewhere [7,8].

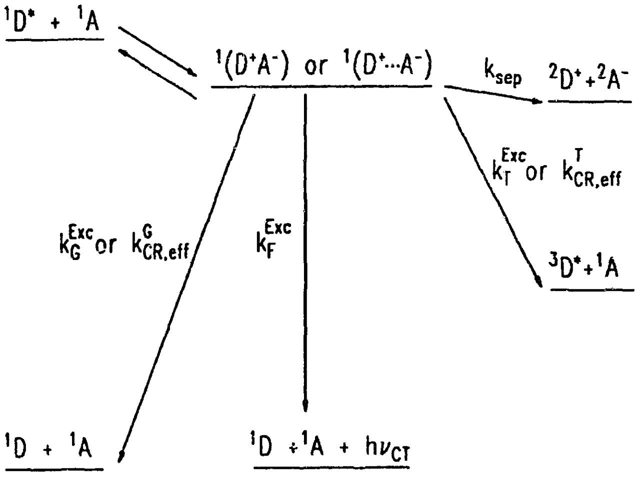
3. Results and discussion

3.1. Kinetics of intermolecular electron transfer in solution and experimental strategy of investigation

In this section, before discussing our experimental results, a more general and brief description of the kinetics underlying electron transfer reactions in solvents of different polarity is given.

The quenching process of a singlet excited molecule ^{1}D* which acts as both energy and electron donor by an electron acceptor molecule ^{1}A in solution in the absence of heavy atom perturbers can be described by the following kinetic scheme (Scheme 1).

From simple energetic considerations, it is anticipated that in polar solvents the structure of the CT intermediate can be described by a solvent-separated ion pair [SSIP, denoted in Scheme 1 as $^1(D^+\cdots A^-)$], whereas in less polar solvents the structure can be better approximated by an exciplex [$^1(D^+A^-)$] [11]. The switch-over between more exciplex-like and more SSIP-like structures is reported to take place in the solvent polarity range of dielectric constant $\epsilon=7–20$ depending on the system [12].



Scheme 1.

As the experimental determination of rate constants followed different routes for the SSIPs and for the exciplexes, the deactivation rate constants for the SSIPs and the exciplexes (superscipt Exc) are denoted separately. Scheme 1 encompasses the following deactivation processes of the CT intermediates: separation into free ions (rate constant k_{sep}), exciplex fluorescence (CT emission, k_F^{Exc}), formation of triplet state donor molecules $^3D^*$ (k_T^{Exc} or $k_{CR,eff}^T$, respectively), and radiationless CR reaction leading to ground states of donor and acceptor molecules (k_G^{Exc} or $k_{CR,eff}^G$).

The overall CR reactions of the SSIPs given in Scheme 1 are a combination of spin evolution and genuine CR reactions. Therefore, the rate constants $k_{CR,eff}^T$ and $k_{CR,eff}^G$ depicted in Scheme 1 are denoted as effective rate constants. It was shown previously that the experimental value of $k_{CR,eff}^G$ describes approximately the pure spin-allowed CR process leading to the ground states of DPH and *p*-DCB, whereas the spin evolution process is probably essentially described by the value of $k_{CR,eff}^T$ [7].

As the radiative deactivation process of the CT intermediates (CT emission) can be regarded as radiative CR reaction, investigations of this process allow the determination of electron transfer parameters governing the radiationless CR reactions. Our investigations of the quenching process of ^{1}DPH* as electron donor ^{1}D* by *p*-DCB as electron acceptor ^{1}A included the following techniques and procedures.

(i) Analysis of DPH fluorescence decay in presence of *p*-DCB allowed the determination of rate constants of exciplex formation, of reverse population of the educts from the exciplex, of exciplex deactivation and of standard free energy changes for exciplex formation (ΔG_{Exc}) in the less polar solvents (see below).

(ii) Electrochemical methods were employed to determine halfwave oxidation and reduction potentials of DPH and p-DCB, respectively, which were used to calculate the standard free energy changes for formation of the SSIPs (ΔG_{CS}) in polar solvents with the Weller equation.

(iii) Stationary fluorescence measurements delivered the rate constants of DPH fluorescence quenching and, together with results from time-resolved measurements, the efficiencies of exciplex fluorescence.

(iv) Excited state absorption spectroscopy was employed to determine the efficiencies of triplet (^{3}DPH*) and cationic DPH (^{2}DPH$^+$) formation and to characterize the exciplexes through their S_1–S_n absorption spectra.

(v) CT emission spectral fitting of the exciplex emission spectra was used to determine solvent reorganization energies λ_o for the CR reactions of the CT intermediates.

(vi) Experimental electron transfer parameters and free energy changes were used to calculate rate constants for the radiationless CR reaction of CT intermediates in the framework of non-adiabatic electron transfer theory in order to elucidate whether a consistent description of the experimental results with the theoretical approach is possible.

3.2. *Deactivation processes of CT intermediates: rate constants and free energy changes*

The solvent dependence of the quenching reaction between ^{1}DPH* and p-DCB can be characterized by the following observations. (i) In every solvent employed, the rate constants of fluorescence quenching k_q^F approached the rate constant of diffusion k_d, and the ratio k_q^F/k_d varied between 0.5 and 0.9 without any significant trend (see Table 1). (ii) In polar solvents (acetonitrile and 1,2-dichloroethane) the formation of ^{2}DPH$^+$ and monoexponential fluorescence decay of DPH in presence of p-DCB was observed. (iii) In less polar solvents (ethyl acetate, diethyl ether, and toluene) no formation of free ions was evident, and an additional emission band in the fluorescence spectrum and a biexponential fluorescence decay of DPH in the presence of p-DCB were discernible. The dependence of the fluorescence decay curves on the detection wavelength and on the p-DCB concentration exhibited the behaviour typical for exciplex-forming systems [13,14]. These observations and the remarkable consistency of the kinetic parameters computed from the fluorescence decay curves with the k_q^F values derived from stationary fluorescence measurements provided solid evidence for the reversible formation of a fluorescent exciplex between ^{1}DPH* and p-DCB in the given solvents [8]. Fitting the fluorescence decay curves to the kinetic equations derived from the usual reaction scheme for reversible exciplex formation allowed computation of the rate constants of exciplex formation, of reverse population of the educts from the exciplex, and of exciplex deactivation. The analysis of biexponential fluorescence decay allowed the experimental determination of the standard free energy change of exciplex formation, ΔG_{Exc}, independent of electrochemical measurements, which are particularly difficult in less polar solvents. (iv) In every solvent employed, formation of ^{3}DPH* occurred from the quenching reaction.

Fig. 1 shows a plot of the efficiencies of ^{3}DPH* (η_T) and ^{2}DPH$^+$ (η_K) formation and of exciplex fluorescence (η_F) vs. the solvent dielectric constant ϵ. η_T, η_K and η_F denote the fractions of quenching events that result in ^{3}DPH* and ^{2}DPH$^+$ formation and exciplex fluorescence. In the inset of Fig. 1, the absorption spectra of ^{3}DPH* and ^{2}DPH$^+$ in acetonitrile are shown. The high extinction coefficients (extinction coefficient of ^{3}DPH* $\epsilon_T = 119\,000$ M^{-1} cm^{-1} at 417 nm and of ^{2}DPH$^+$ $\epsilon_K = 143\,500$ M^{-1} cm^{-1} at 590 nm in acetonitrile [7]) and the spectral separation of the spectra ensured measurements with high sensitivity.

Seemingly, the efficiencies of product formation from the quenching reaction exhibited severe solvent dependence, whereas no significant influence of the solvent on the k_q^F values was discernible. The observations that in less polar solvents ($\epsilon < 10$) the efficiency of ^{2}DPH$^+$ formation ($\eta_K < 0.005$) and in the polar solvents ($\epsilon > 10$) the efficiency of exciplex fluorescence ($\eta_F < 0.01$) was not detectable strongly support the assumption that in less polar solvents exciplex formation and in polar solvents SSIP formation is energetically favoured.

Fig. 2 shows a plot of the rate constants for the individual deactivation processes of the CT intermediates vs. solvent dielectric constant ϵ. In Table 1 the results are summarized. The rate constants of exciplex fluorescence k_F^{Exc} in toluene and diethyl ether were the same within experimental uncertainty, whereas k_F^{Exc} in ethyl acetate was about half that in the other two solvents. The experimental values for k_F^{Exc} allow the estimation of electronic matrix coupling elements V_{CR} of the CR reaction (see below). The rate constants of ^{3}DPH* formation (k_T^{Exc}) from the exciplex exhibited only a minor solvent dependence, if any. The respective rate constants for the SSIPs ($k_{CR,eff}^T$) were somewhat larger, which might reflect a change of the underlying mechanism of singlet-to-triplet state intersystem crossing (ISC). This is consistent with earlier observations that ISC within exciplexes is governed by spin–orbit coupling, whereas hyperfine interaction is the more important ISC mechanism within SSIPs [12].

The spin-allowed CR rate constants (k_G^{Exc} and $k_{CR,eff}^G$, respectively), exhibited the strongest solvent dependence. The rate constant $k_{CR,eff}^G$ was, e.g., in acetonitrile solution ≈ 300 times larger than k_G^{Exc} in toluene solution. The standard free energy changes for the CR process of the CT intermediates (ΔG_{CR}^G) is shown in the lower part of Fig. 2. $-\Delta G_{CR}^G$ decreased with increasing solvent polarity and increasing CR rate constant. This is the well-known behaviour of CR rate constants in the Marcus inverted region of electron transfer.

3.3. *Radiative charge recombination of CT intermediates: electronic coupling and CT emission spectral fitting*

It is well known that radiative and radiationless transitions between two states are closely related [16]. This analogy has

Table 1
Kinetic and thermodynamic parameters of the quenching reaction reaction of ^{1}DPH* by *p*-DCB and of the deactivation processes of the respective CT intermediates formed in various solvents at 298 K

	Solvent				
	Toluene	Diethyl ether	Ethyl acetate	1,2-Dichloroethane	Acetonitrile
ϵ [a]	2.4	4.3	6.0	10.4	37.5
$k_d/10^9\ M^{-1}\ s^{-1}$ [b]	12	31	16	9	20
$k_q^F/10^9\ M^{-1}\ s^{-1}$ [c]	9.7 ± 1.0	14.0 ± 1.0	9.9 ± 1.0	7.9 ± 0.8	13 ± 1
$k_F^{Exc}/10^6\ s^{-1}$	3.4 ± 0.6	3.8 ± 0.7	1.7 ± 0.3	–	–
k_T^{Exc} [d] or $k_{CR,eff}^T$ [e] $/10^6\ s^{-1}$	19 ± 3	14 ± 2	12 ± 2	70 ± 36	170 ± 40
k_G^{Exc} [d] or $k_{CR,eff}^G$ [e] $/10^6\ s^{-1}$	6 ± 4	7 ± 4	53 ± 7	420 ± 280	1700 ± 400
ΔG_{Exc} [f] or ΔG_{CS} [g] /eV	-0.19 ± 0.02	-0.20 ± 0.05	-0.22 ± 0.02	-0.36	-0.47
ΔG_{CR}^G/eV [h]	-2.92 ± 0.02 (-2.92 [m])	-2.91 ± 0.05 (-3.07 [m])	-2.89 ± 0.02 (-3.01 [m])	-2.74	-2.64
V_{CR}/eV [i]	0.11	0.13	0.09	0.00322 [k]	0.00322 [k]
λ_o/eV	0.27 ± 0.02 [l] (0.28 [m])	0.30 ± 0.05 [l] (0.45 [m])	0.46 ± 0.02 [l] (0.58 [m])	1.20 [k]	1.20 [k]
$k_{CR}/10^6\ s^{-1}$ [n]	5	11	53	632	1249

[a] Solvent dielectric constant.

[b] Calculated from k_u in acetonitrile with the viscosity relationship.

[c] From stationary fluorescence measurements.

[d] For toluene, diethyl ether and ethyl acetate.

[e] For 1,2-dichloroethane and acetonitrile under the assumption $k_{sep} = 1 \times 10^7$ and $1 \times 10^9\ s^{-1}$, respectively.

[f] From (biexponential) DPH fluorescence decay analysis.

[g] Calculated from the Weller equation without work term.

[h] $\Delta G_{CR}^G = -E(^1DPH^*) - \Delta G_{Exc}$ (for toluene, diethyl ether and ethyl acetate) or $\Delta G_{CR}^G = -E(^1DPH^*) - \Delta G_{CS}$ (for 1,2-dichloroethane and acetonitrile with the energy of ^{1}DPH* $E(^1DPH^*) = 3.11 \pm 0.01$ eV [26] (measured in EPA glass matrix at 77 K). From solvent effects on the fluorescence spectrum of DPH it can be deduced that $E(^1DPH^*)$ differs in the solvents considered by not more than 0.01 eV [27].

[i] Calculated from k_F^{Exc} under the assumption of $\Delta\mu = 15$ D.

[k] Taken from [10].

[l] Optimum value from two-parameter spectral fitting.

[m] Optimum value from one-parameter spectral fitting.

[n] Calculated by Eq. (2) with ΔG_{CR}^G, V_{CR} and λ_o given in the table and with $\lambda_i = 0.30$ eV and $h\nu_v = 1600\ cm^{-1}$.

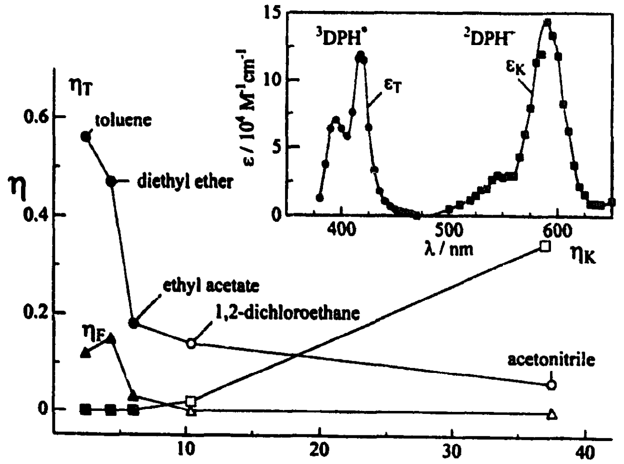


Fig. 1. Plot of the efficiencies of ^{3}DPH* (η_T, ● and ○) and ^{2}DPH$^+$ (η_K, ■ and □) formation and of fluorescence (η_F, ▲ and △) of the CT intermediates formed between ^{1}DPH* and *p*-DCB vs. solvent dielectric constant at room temperature. The open symbols refer to SSIPs and the filled symbols to exciplexes. Inset: absorption spectra of ^{3}DPH* (ϵ_T) and ^{2}DPH$^+$ (ϵ_K) in acetonitrile.

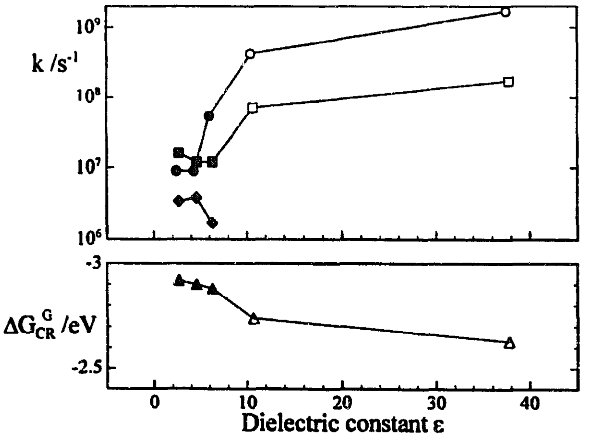


Fig. 2. Upper part: plot of the rate constants of ^{3}DPH* formation (k_T^{Exc}, ■, and $k_{CR,eff}^T$, □) of fluorescence (k_F^{Exc}, ◇), and of CR leading to the ground states of DPH and *p*-DCB (k_G^{Exc}, ●, and $k_{CR,eff}^G$, ○) from the CT intermediates formed between ^{1}DPH* and *p*-DCB vs. solvent dielectric constant ϵ at 298 K (same *x*-axis as in the lower part). Lower part: plot of the standard free energy change for the CR reaction of the CT intermediates (ΔG_{CR}^G, ◆ and ◇) vs. solvent dielectric constant ϵ at 298 K. The open symbols refer to the SSIPs and the filled symbols to the exciplexes. The lines are included only to illustrate the trend of the results.

been used by several groups to determine Franck–Condon factors and extract electron transfer parameters from CT emission spectra [15,17–19].

The frequency distribution of a CT emission spectrum $I(\nu_{CT})$ depends among the Franck–Condon weighted density of states $F(\nu_{CT})$ and other parameters on the transition dipole moment $M(\nu_{CT})$. Only in the case of negligible electronic coupling between the CT state $^1(D^+A^-)$ and the locally excited state $^1(D^*A)$ is $M(\nu_{CT})$ a simple function of ν_{CT}

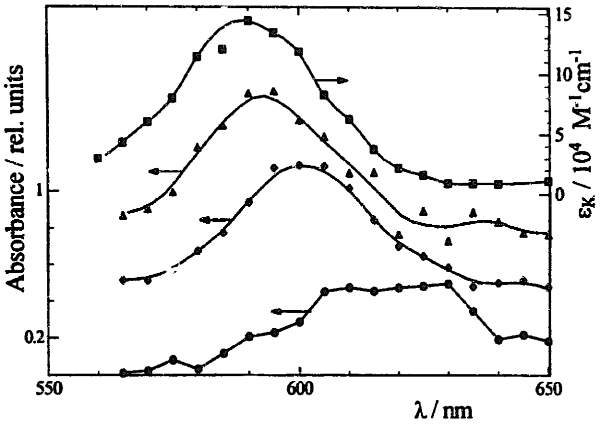


Fig. 3. Absorption spectra of ^{2}DPH$^+$ in acetonitrile (ϵ_K, ■), and relative S_1–S_n absorption spectra (for clarity displaced vertically) of the DPH/p-DCB exciplexes in ethyl acetate (▲), diethyl ether (◆), and toluene (●) at room temperature.

[i.e. $M(\nu_{CT}) \propto 1/\nu_{CT}$), whereas in the case of considerable electronic coupling between $^1(D^+A^-)$ and $^1(D^*A)$ the frequency dependence of $M(\nu_{CT})$ becomes more complicate [19]. It is therefore of crucial importance to address the question of the CT character of the exciplexes experimentally in order to derive the appropriate frequency distribution $I(\nu_{CT})$ for the system under investigation.

In Fig. 3 the exciplex absorption spectra measured 2–3 ns after photoexcitation of DPH in the presence of p-DCB and the absorption spectrum of ^{2}DPH$^+$ in acetonitrile are shown. Only one absorption band was observed in the spectral region between 550 and 650 nm in the less polar solvents.

At longer times after the photoexcitation, the formation of ^{3}DPH* from the exciplexes could be observed. The spectral shape and the solvent shift of the exciplex absorption were very similar to those of the ^{2}DPH$^+$ absorption (wavelengths of maximum absorption λ_{max} = 590, 606, and 635 nm in acetonitrile [20–22], 1,2-dichloroethane [23], and cyclohexane [21], respectively). It is thus very likely that the exciplexes can be approximately described by pure CT states with negligible electronic coupling to locally excited states. The exciplex emission can therefore be treated as essentially pure CT emission.

Under the assumption, that the difference in the dipole moments of the exciplexes and the ground states of DPH and p-DCB ($\Delta\mu$) equals 15 D, and using average emission frequencies obtained from the exciplex emission spectra, V_{CR} can be estimated from the rate constants of exciplex fluorescence k_F^{Exc} (cf. [15]). The results are listed in Table 1. They are in agreement with previous results obtained from radiative rate constants for excited CT complexes [15] and are considerably higher than values determined for SSIPs [24].

The emission spectra were analysed by comparing experimental spectra with spectra generated using Eq. (1), which accounts for the appropriate frequency dependence of $M(\nu_{CT})$ [15]

$$I/\nu_{CT} = I'F(\nu_{CT}) \qquad (1)$$

with

$$F(\nu_{CT}) = \frac{1}{\sqrt{4\pi\lambda_o k_B T}} \sum_{j=0}^{\infty} \frac{e^{-S}S^j}{j!} \times \exp\left[-\frac{(\lambda_o + \Delta G_{CR}^G + h\nu_{CT} + jh\nu_v)^2}{4\lambda_o k_B T}\right]$$

and

$$S = \frac{\lambda_i}{h\nu_v}$$

where I is the emission intensity in photons per time per unit spectral energy, ν_{CT} is the CT emission frequency, I' is a proportionality factor, $F(\nu_{CT})$ is the Franck–Condon weighted density of states, k_B is the Boltzmann constant, T is the absolute temperature, and h is Planck's constant).

This equation expresses the frequency dependence of the emission intensity in terms of the CR reaction back to the ground states with four parameters ΔG_{CR}^G, λ_o, λ_i, and $h\nu_v$.

I' can be calculated from the integral of the experimental spectrum I/ν_{CT} and the integral of $F(\nu_{CT})$, but treating I' as a free fit parameter did not significantly influence the results. With the assumed values of $\lambda_i = 0.30$ eV and $h\nu_v = 1600$ cm^{-1} (cf. [15,17,19]) and the experimentally determined values for ΔG_{Exc}, only λ_o needed to be fitted in the analysis of the spectra. This experimental strategy avoids one particular problem connected with CT emission spectral fitting procedures. As was recently pointed out by Cortés et al., the CT emission spectral fitting allows estimation of the sum of ΔG_{CR}^0 and λ_o but may not sufficiently discriminate between them [19]. This is because the maximum of the CT emission band is approximately given by $h\nu_{CT}^{max} \approx -(\Delta G_{CR}^G + \lambda_o + \lambda_i)$, whereas the full width at half maximum ($h\Delta\nu_{CT}^{1/2}$) of the band is essentially determined by $h\Delta\nu_{CT}^{1/2} \approx \text{const.}\sqrt{\lambda_i h\nu_v}$ with negligible contribution of λ_o.

In Fig. 4 the experimental emission spectra and the best fits to the spectra using Eq. (1) are shown. The results for λ_o (cf. Table 1) are in good agreement with published data obtained with CT emission spectral fitting procedures of similar systems, which are the subject of current discussions because they cannot be explained with common continuum-solvent dipole models [15,17,19].

Fitting both λ_o and ΔG_{CR}^G led to somewhat improved fits, and it is noted that the sum of ΔG_{CR}^G and λ_o remained equal to the results of the one-parameter fits. However, in diethyl ether and ethyl acetate slight changes in the individual ΔG_{CR}^G and λ_o values were found. Wether this discrepancy may be related to the experimental quality of our spectra, the inapplicability of the physical model which accounts only for one average vibrational mode of the product state, or the general inability of spectral fitting procedures to yield reliable results for both λ_o and ΔG_{CR}^G [19] must be the subject of further studies. It is therefore of particular relevance that the independent determination of ΔG_{CR}^G from fluorescence decay analysis and of λ_o from CT emission spectral fitting, as

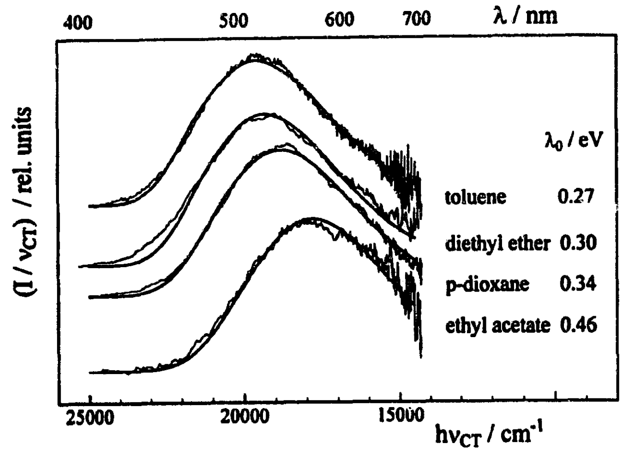


Fig. 4. CT emission spectra of the DPH/*p*-DCB exciplexes in various solvents at room temperature, and best fits to the spectra calculated with Eq. (1) with the parameters given in the text. The λ_o values given in the inset were obtained from one-parameter spectral fitting with the exception of the result for λ_o in *p*-dioxane, which was obtained with $\Delta G^{G}_{CR} = -2.89$ eV from two-parameter spectral fitting. The experimental spectra were corrected by subtraction of residual DPH fluorescence and displaced vertically for clarity.

demonstrated in this work, avoids the ambiguities of multiparameter spectral fitting procedures.

3.4. Radiationless charge recombination of CT intermediates: calculation of rate constants

According to the theory of non-adiabatic electron transfer reactions, the CR reaction rate constant depends among other parameters on λ_o, λ_i, $h\nu_v$, V_{CR}, and ΔG^{G}_{CR} [25]

$$k_{CR} = \frac{2\pi}{\hbar} V^2_{CR} F \tag{2}$$

with

$$F = \frac{1}{\sqrt{4\pi\lambda_s k_B T}} \sum_{j=0}^{\infty} \frac{e^{-S} S^j}{j!} \exp\left[-\frac{(\lambda_o + \Delta G_{CR} + jh\nu_v)^2}{4\lambda_o k_B T} \right]$$

and

$$S = \frac{\lambda_i}{h\nu_v}$$

Comparison of Eq. (1) with Eq. (2) shows the close relationship of the two expressions.

It was shown recently that, for a CR rate constant of excited CT complexes in the Marcus inverted region, Eq. (2) still holds true even if V_{CR} exceeds the non-adiabatic limit of $k_B T$ as in the present case [24].

With the values for λ_o, ΔG^{G}_{CR} and V_{CR} in hand and with the assumptions that $\lambda_i = 0.30$ eV and $h\nu_v = 1600$ cm^{-1}, we can now calculate CR rate constants with Eq. (2) in every solvent employed in order to elucidate whether a consistent description of the experimental results with Eq. (2) is possible. For acetonitrile and 1,2-dichloroethane, parameters from previous investigations of CR reactions of SSIPs in acetonitrile were used: $\lambda_o = 1.20$ eV and $V_{CR} = 0.00322$ eV [10].

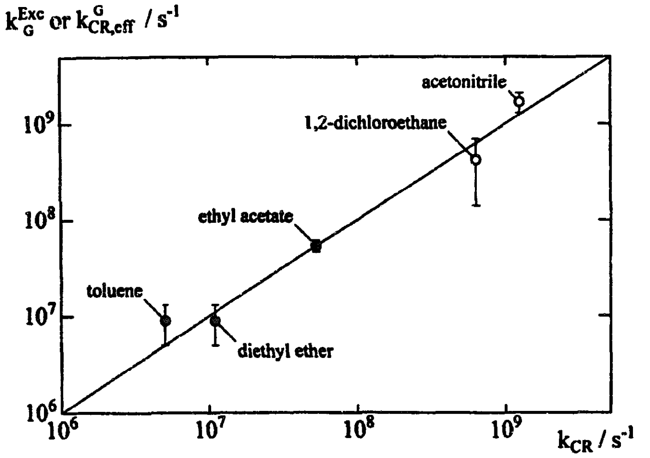


Fig. 5. Plot of the experimental CR rate constants $k^{G}_{CR,eff}$ (○) and k^{Exc}_{G} (●) vs. CR rate constants k_{CR} calculated with Eq. (2) with parameters given in Table 1.

Fig. 5 shows a plot of the experimental rate constants $k^{G}_{CR,eff}$ and k^{Exc}_{G} vs. the rate constants k_{CR} calculated with Eq. (2). It is obvious from Fig. 5 that the calculated rate constant k_{CR} can reproduce the experimental rate constants $k^{G}_{CR,eff}$ and k^{Exc}_{G} in every solvent employed within the experimental accuracy.

4. Conclusions

The investigation of CT intermediates formed between all-*trans*-1,6-diphenylhexa-1,3,5-triene and *p*-dicyanobenzene with stationary and time-resolved absorption and fluorescence measurements and CT emission spectral fitting allowed a comprehensive description of the formation and deactivation processes and the determination of kinetic, thermodynamic, and electron transfer parameters. With experimental values for the solvent reorganization energies λ_o, standard free energy changes ΔG^{G}_{CR}, and for the electronic matrix coupling element V_{CR}, rate constants of the charge recombination reaction of the CT intermediates were calculated in the framework of non-adiabatic electron transfer theory, and the results were found to be in good agreement with experimental rate constants. This outcome shows that the theory of non-adiabatic electron transfer can deliver with experimental electron transfer parameters a good approximation of CR rate constants in the Marcus inverted region, even in cases where the electronic coupling is relatively high, as in exciplexes and contact ion pairs.

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