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Evidence for nonemissive exciplexes in the singlet quenching of polycyclic aromatic hydrocarbons by polychlorobenzenes in cyclohexane

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Abstract

The quenching of the singlet excited state of several polycyclic aromatic hydrocarbons (PAH) by polychlorobenzenes was investigated in cyclohexane by static and time-resolved fluorescence measurements. Intensity Stern–Volmer plots were linear, while the corresponding τ_0/τ plots presented a downward curvature. Laser flash photolysis experiments indicated that the only intermediate formed in the quenching process is the triplet state of the PAH. The efficiency of the triplet formation was determined and it was found to be near unity in several cases. These results were interpreted with a mechanism involving the intermediacy of an exciplex formed by the excited singlet of the PAH as an electron donor and the chlorobenzene as an electron acceptor. Bimolecular quenching rate constants were obtained from the intensity Stern–Volmer plots or from the initial slope of the lifetime plots. They could be satisfactorily correlated with the energy of the charge transfer state by using the exciplex model. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Polycyclic aromatic hydrocarbons; Polychlorobenzenes; Cyclohexane

1. Introduction

The collisional deactivation of excited states of organic molecules in homogeneous solution may occur by several different mechanisms depending on the photophysical and ground state properties of the reactive pair. In many cases the mechanism can be clearly demonstrated by combining several experimental techniques with well-established free energy correlations of the rate constants. However, in many circumstances the clear determination of the deactivation pathway remains elusive. In these cases it is customary to postulate the intermediacy of an excited state complex or exciplex. However, when there is no direct evidence for the exciplex, such as a new emission band, it is difficult to establish its presence as an entity clearly distinct of the precursor complex. Nevertheless, in some cases an adequate analysis of the kinetic behaviour of the system may be useful to establish the exciplex intermediacy and determine some of its properties. In this paper we present a treatment of this kind for the deactivation of the excited singlet state of polycyclic aromatic hydrocarbons by chlorobenzenes. The interaction of chloroaromatics with excited states of organic molecules and/or semiconductors is of great interest because of its possible relation to photochemical decontamination processes. From this point of view, it is important to have a clear understanding of the quenching mechanisms of excited states by chloroaromatics.

The quenching of excited states of organic molecules by chlorobenzenes (CBs) has been a subject of interest in our group during the last years [1–4]. We have found that both the excited singlet and triplet states of aromatic amines are quenched by an electron transfer process [1–3]. In these cases the dechlorination of the quencher takes place with high efficiency.

On the other hand, the quenching of the excited singlet of polycyclic aromatic hydrocarbons (PAHs) by CBs in acetonitrile did not afford dechlorination products, even when the overall Gibbs energy change for the reaction

$$^1\mathrm{PAH}^* + \mathrm{CB} \rightarrow \mathrm{PAH}^{+\bullet} + \mathrm{CB}^{-\bullet}$$

is negative for the more efficient quenchers [4]. Moreover, transient absorption spectra taken after the quenching event, did not present evidence for the presence of radical ions. The only transient species observed was the triplet state of the PAH. We found that the bimolecular quenching rate constants increase with the number of chlorine atoms, being near diffusion controlled for hexachlorobenzene. In spite that direct evidence for an electron transfer was absent, the rate constants obey a Rehm–Weller type correlation when the overall Gibbs energy change is negative. In the ender-

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gonic region, on the other hand, the rate constants are higher than those expected from the model. The results were rationalized in terms of an exciplex that decays to the triplet or ground state [4]. Since the polychlorobenzenes may act as electron acceptors towards the excited singlet of the PAHs, the electron–donor–acceptor structure may be advanced for the exciplex, thus explaining the free energy correlation observed. However the fluorescence spectra taken with a high quencher concentration do not present evidence of an emissive exciplex, but this is not unexpected in a polar solvent. Later on, we observed that the quenching rate constants are practically independent of the solvent polarity. Thus, the rate constant for the quenching of naphthalene by 1,2,3-trichlorobenzene is (in units of M^{-1} s^{-1}) 3.9×10^7 in acetonitrile, 3.3×10^7 in ethanol and 3.4×10^7 in cyclohexane.

The solvent effect on the fluorescence quenching of singlet excited states was previously investigated by several research groups. Chen et al. [5] investigated the reductive quenching of phenanthrene derivatives and naphthalene by a series of electron donors and acceptors in acetonitrile, dimethylformamide and cyclohexane. They found that in the two polar solvents the bimolecular rate constants are very similar while they decrease markedly in the nonpolar medium. We have also observed that, for electron transfer reactions, the rate constants markedly decrease with the solvent polarity [6]. On the other hand, other researchers [7] found that in the quenching of excited singlet 9,10-dicyanoanthracene the rate constants do not differ by more than one order of magnitude on going from hexane to acetonitrile. Nevertheless, in this case two different Rehm–Weller plots are obtained for π or n-donors [7].

In order to confirm these elusive exciplexes we decided to undertake a more detailed study of the quenching process in low polarity solvents. In this paper we present an investigation of the quenching of the excited singlet state of several PAHs by polychlorobenzenes in cyclohexane. Stationary and dynamic fluorescence measurements were performed, and laser flash photolysis experiments were done to try to reveal the nature of the quenching process. For a given PAH the rate constants correlate with the reduction potential of the chloroaromatic. However we could not find a general correlation with the excited state properties of the PAHs. Transient absorption spectral measurements show that in all cases the triplet state is produced in the quenching reaction. The mechanism of the induced intersystem crossing is discussed.

2. Experimental

Naphthalene (Fluka) was purified by sublimation. Pyrene (Aldrich) was recrystallized from ethanol. Phenanthrene (Aldrich, zone refined, 99.5%), 2-methylnaphthalene (Aldrich, 98%), chrysene, 1,2-benzanthracene and 1,2,5,6-dibenzanthracene from Sigma were used as received. Cyclohexane was Sintorgan HPLC grade and it was used without further purification. Chlorobenzene (CB) was purified by fractional distillation. 1,2-Dichlorobenzene (12DCB) (Aldrich, "Gold Label"; purity better than 99%), 1,3-dichlorobenzene (13DCB) (Fluka, 99%), 1,2,3-trichlorobenzene (123TCB) (Aldrich, purity 99%), 1,2,4-trichlorobenzene (124TCB) (Aldrich "Gold Label"; purity better than 99%), 1,3,5-trichlorobenzene (135TCB) (Fluka; purity better than 99%), 1,2,4,5-tetrachlorobenzene (tetraCB) (Aldrich, 98%) were used without further purification. Pentachlorobenzene (pentaCB) (Aldrich, 98%) was recrystallized from acetonitrile. Hexachlorobenzene (hexaCB) (Aldrich 99%) was used as received.

Stationary fluorescence quenching experiments were carried out with a Spex Fluoromax spectrofluorometer. Transient absorption measurements were performed by excitation with the third harmonic of a Spectron Nd-YAG laser (18 ns FWHM and 25 mJ per pulse at 355 nm) or with a Laseroptics nitrogen laser (7 ns FWHM and 5 mJ per pulse at 337 nm). For fluorescence measurements the sample was placed in a TRW 75A filter fluorometer with appropriate filters for the emission. The excitation was carried out with the nitrogen laser highly attenuated. Naphthalene lifetimes were determined by excitation at 280 nm using an interference filter and a nanolamp (Xenon Corporation) or by excitation at 266 nm with the fourth harmonic of the Nd-YAG laser. The signal was acquired by a digitizing scope where it was averaged and then transferred to a computer.

Bimolecular quenching rate constants were determined from the slopes of Stern–Volmer (SV) plots of fluorescence intensity measurements or by measuring the decay of the fluorescence of the PAH as a function of the CB concentration. Replicate runs produced values that were within ±5%. The observed decays were monoexponential in all cases. All measurements were performed in deaerated solutions at 298 K.

3. Results

The fluorescence of PAHs in cyclohexane is quenched by chlorobenzenes with an efficiency that increases with the number of chlorine atoms on the ring. The absorption spectra of the PAHs were undistorted by the presence of the CBs, except for hexachlorobenzene at high concentration. For the latter the quenching experiments were carried out at low concentrations where ground state interactions are unobserved.

Stern–Volmer (SV) plots from fluorescence intensity measurements are linear, while those from lifetime measurements present a downward curvature at high quencher concentration for the less efficient quenchers. Typical SV plots are shown in Figs. 1–4 for quenchers of diverse efficiency. It can be seen that in the case of a poor quencher, 14DCB or 124TCB, the deviation from linearity in τ_0/τ plot is clearly present,. On the other hand, for the efficient

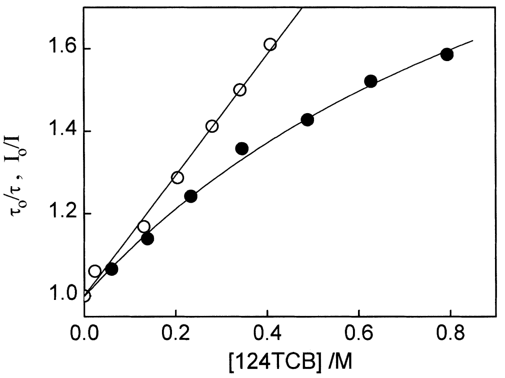


Fig. 1. Quenching of 1,2-Benzanthracene by 124TCB in cylcohexane. (O) I_0/I, (●) τ_0/τ.

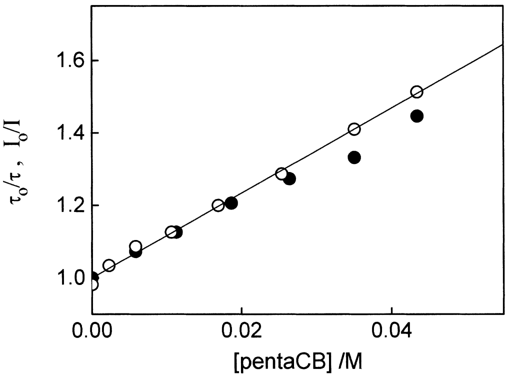


Fig. 2. Quenching of 1,2-Benzanthracene by pentaCB in cylcohexane. (O) I_0/I, (●) τ_0/τ.

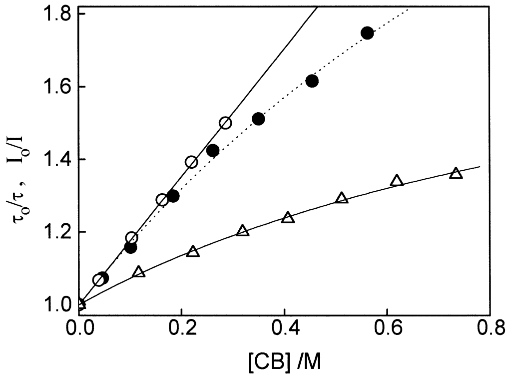


Fig. 3. Quenching of chrysene by 124TCB (O) I_0/I, (●) τ_0/τ and of pyrene by 14DCB (Δ)τ_0/τ.

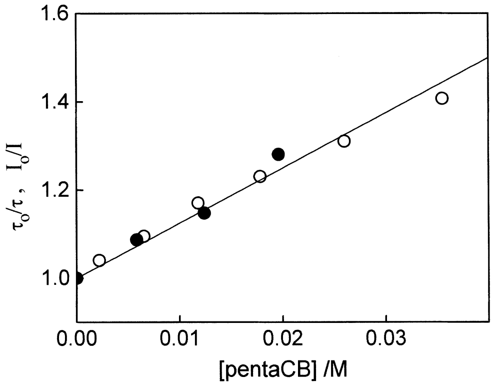


Fig. 4. Quenching of chrysene by pentaCB in cylcohexane. (O) I_0/I, (●) τ_0/τ.

quencher pentaCB the τ_0/τ plots are almost linear and coincide with the I_0/I plots. For quenchers of moderate or high efficiency, bimolecular quenching rate constants k_q, were determined at 298 K from the slopes of the I_0/I plots and/or from the initial slopes of lifetime plots. The results of both methods are coincident within the experimental error. For the low efficiency quenchers the initial slopes of the lifetime plots are lower than those of the I_0/I plots. In this case the rate constants were obtained from the stationary experiment. The values are collected in Table 1.

The negative deviation from linearity in the τ_0/τ plots may be taken as an evidence for an exciplex quenching mechanism [8–10]. However, the fluorescence spectra taken with a high quencher concentration do not present evidence of an emissive exciplex. They were identical in the absence and the presence of the quencher, except for the reduction in

Table 1
Singlet quenching rate constants in cyclohexane at 298 K

PCB (EA/eV)[a]	PAH						
	2-methyl-naphthalene	naphthalene	pyrene	phenanthrene	chrysene	1,2-benz-anthracene	1,2:5,6-dibenz-anthracene
CB (−0.14)	3.0×10^6	5.4×10^6	2.9×10^5	1.3×10^6		7.0×10^5	
12DCB (0.08)	8.6×10^6	1.3×10^7	5.6×10^5	3.8×10^6			
14DCB (0.10)			1.6×10^6				
124TCB (0.30)	5.4×10^7	5.0×10^7	5.3×10^6	1.9×10^7	3.5×10^7	2.3×10^7	2.7×10^7
135TCB (0.32)		6.4×10^7	6.1×10^6	2.4×10^7			
123TCB (0.34)		3.4×10^7	2.5×10^6	1.3×10^7			
tetraCB (0.49)		2.5×10^8	3.2×10^7	1.0×10^8			
pentaCB(0.73)		3.0×10^9	1.2×10^8	2.1×10^8	3.4×10^8	2.1×10^8	2.3×10^8
hexaCB (0.98)	6.8×10^9	6.8×10^9	7.7×10^8	5.7×10^8			

[a] Electron affinity from J.R. Wiley, E.C.M. Chen, E.S.D. Chen, P. Richardson, W.R. Reed and W.E. Wentworth, J. Electroanal. Chem. 307 (1991) 169.

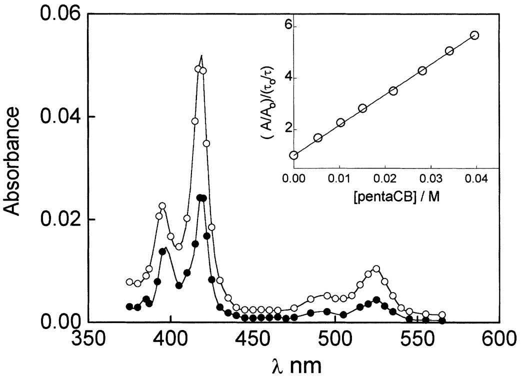


Fig. 5. Transient absorption spectrum of the system pyrene-pentaCB at 1 μs after the laser pulse. (●) in the absence and (o) in the presence of penta CB 0.095 M. Inset: Plot according to Eq. (1) for the system pyrene–pentaCB in cyclohexane.

intensity. Moreover, the spectra in neat chlorobenzene were practically the same as those in benzene. In this case the position of the bands was unchanged with respect to cyclohexane, but a slight broadening was observed.

In order to obtain information on the nature of the quenching process, laser flash photolysis experiments were performed by excitation of the PAH at 337 or 355 nm. Fig. 5 shows the transient absorption spectrum taken 1 μs after the laser pulse for the system pyrene–pentaCB in cyclohexane. In the absence of the chloro compound the spectrum corresponds to that of the triplet state of pyrene. In the presence of pentaCB 0.095 M more than 75% of the excited singlets are quenched, yet it can be seen that the triplet yield increases. Similar experiments with the other PAHs point to the triplet state as the only product of the quenching reaction.

The fraction of the quenching events leading to the triplet state of the PAH was determined with the aid of Eq. (1)[4]

$$\left(\frac{A^{\mathrm{T}}}{A_0^{\mathrm{T}}}\right)\left(\frac{\tau_0}{\tau}\right) = 1 + \frac{k_{\mathrm{q}}}{k_{\mathrm{isc}}}[Q] \qquad (1)$$

where A_0^{T} and A^{T} are the absorbances measured at the maximum of the T–T absorption, determined by laser flash photolysis, immediately after the laser pulse in the absence and the presence of the chloroaromatic, respectively. τ_0 and τ are the singlet lifetimes of the PAH under the same conditions than the flash photolysis experiments. k_{isc} is the rate constant for intersystem crossing of the PAH in the absence of the quencher, and η_{isc} is the fraction of quenching events leading to the triplet state, that is the intersystem crossing efficiency in the quenching process. A typical plot according to Eq. (1) is presented in the inset in Fig. 5. From the slopes of these plots, and with the aid of literature values [8,11] for k_{isc}, the values of η_{isc} in Table 2 were obtained. The quantities in the table are compared with those previously determined in acetonitrile [4]. Clearly in the less polar solvent the induced intersystem crossing is favoured. Similarly, Löhmannsröben et al. [12] found that in the quenching of the excited singlet of 1,6-diphenylhexa-1,3,5-triene by *p*-dicyanobenzene the efficiency of triplet state formation in the quenching process increases when the solvent polarity decreases.

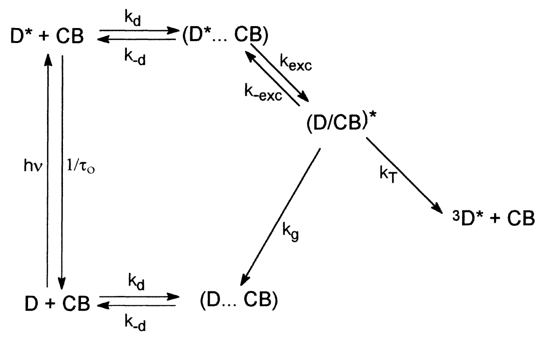
Table 2
Induced intersystem crossing efficiency

PAH	Chlorobenzene	Cyclohexane	Acetonitrile
Pyrene	124TCB	0.99	1.0
	TetraCB	1.0	0.8
	PentaCB	0.91	<0.01
	HexaCB	0.61	0.01
Phenanthrene	124TCB	0.58	0.6
	PentaCB	0.65	–
1,2,5,6-Dibenzanthracene	PentaCB	1.0	–
	124TCB	1.0	–
1,2,-Benzanthracene	124TCB	0.12	–
	pentaCB	0.62	–
Chrysene	124TCB	0.40	–
	pentaCB	0.54	–

4. Discussion

From an inspection of the rate constants in Table 1 it is clear that they increase with the number of chlorine atoms on the quencher. However for a given CB they present a very low sensitivity to the excited state properties of the PAH. Thus they are practically independent of the excited singlet energy level. As stated before the negative curvature of the τ_0/τ (plots suggests a quenching mechanism involving an exciplex in dynamic equilibrium, whose main decay route is intersystem crossing to the triplet state of the PAH. The stability of the exciplex, and accordingly the rate constants, will depend on several factors. These factors will vary in a way not clearly predictable when the structure of the PAH is changed. Even the symmetry of the quencher and quenchee may affect the stability of the excited state complex [13–15]. However, if the parameters that control the exciplex stability are assumed to remain constant for a series of systems comprising a common PAH, a free energy type correlation of the rate constants may be attempted.

Accordingly the detailed quenching mechanism, including the diffusion steps for forming the encounter complex, may be written as in the Scheme 1.



Scheme 1.

Here D stands for the PAH and CB is the chlorobenzene. In the scheme $(D^{*}\ldots CB)$ represents the encounter complex in the solvent cage. In this stage the excitation energy resides in the PAH and it may be considered as a localised excited state. The exciplex is represented by $(D/CB)^{*}$.

If the exciplex is in a dynamic equilibrium with the excited state D^{*} and the precursor complex that is,

$$k_{exc} \gg 1/\tau_0 \text{ and } k_{-exc} \gg 1/\tau_0' \text{ with } \tau_0' = (k_g + k_t)^{-1} = k_p^{-1}$$

it may be shown that both the exciplex and D^{*} decay exponentially with a common lifetime, and the τ_0/τ plots are given by [8,9]

$$\frac{\tau_0}{\tau} = \frac{1 + (\tau_0/\tau_0')K[\mathrm{CB}]}{1 + K[\mathrm{CB}]} \tag{2}$$

where

$$K = \frac{k_d k_{exc}}{k_{-d} k_{-exc}} = \frac{k_d}{k_{-d}} K_{exc} \tag{3}$$

Eq. (2) explains the negative curvature of the τ_0/τ plots and it is in agreement with the high efficiency for induced intersystem crossing, since in this case k_p would be spin forbidden and the condition of dynamic equilibrium in the exciplex could be attained. This curvature is present when the quencher is of low efficiency, cf. Figs. 1 and 3. In principle, from the τ_0/τ plots both τ_0' and K could be obtained. However, if the condition of equilibrium is not fully reached, i.e. when $k_p \approx k_{-exc}$ the values obtained of K may be wrong by more than one order of magnitude. Nevertheless, in this situation the lifetime plots may still present negative curvature. Since it is impossible to discern if the equilibrium approximation is valid for the treatment of the data, we prefer to discuss the results in terms of the dependence of the rate constants on the electron donor–acceptor properties of the PAH excited state and the CBs in a general way, trying to confirm the exciplex intermediacy in the quenching mechanism.

For the more efficient quenchers monoexponential decay is also observed. However, in these cases linear SV plots based on lifetime measurements are obtained and the τ_0/τ and I_0/I plots coincide, Figs. 2 and 4. The same mechanism applies, but now with $k_p \gg k_{-exc}$.

The rate constants in Table 1 are the result of intensity quenching experiments (or lifetime measurements in the case where initial slopes coincide). Therefore, they may be analyzed in terms of the Scheme 1 by application of the steady state treatment. The result for k_q is

$$k_q = \frac{k_d}{1 + (k_{-d}/K_{exc}k_p) + (k_{-d}/k_{exc})} \tag{4}$$

In order to apply Eq. (4) to the experimental results the following values where taken: k_d was set to $7 \times 10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ from the experimental results for the quenching of naphthalene and 2-methylnaphthalene by hexachlorobenzene. This coincides with the theoretical diffusion limit [11] in cyclohexane. The cage escape rate constant can be expressed as a function of the solvent viscosity by Eq. (5)[16]

$$k_{-d} = \frac{RT}{2\pi N_A \sigma^3 \eta} \tag{5}$$

where σ is the intermolecular distance in the encounter complex and η is the solvent viscosity. With a judicious value of 0.8 nm for σ a value of $1 \times 10^{10}\ \mathrm{s^{-1}}$ results for k_{-d}.

A method to estimate K_{exc} and k_{exc} is necessary. The equilibrium constant for the exciplex may be written as

$$K_{exc} = \frac{k_{exc}}{k_{-exc}} = A \exp\left(\frac{-\Delta H_{exc}}{RT}\right) \tag{6}$$

The enthalpy change ΔH_{exc} may be calculated with a two-state model variational treatment [9,17]. The two states are the local excited state, whose energy level corresponds to the first excited singlet of the PAH, and the hypothetical total charge transfer state $(D^{+\bullet}/CB^{-\bullet})$. The energy level of the latter may be estimated from the ionization energy of the PAH and the electron affinity of the CB.

From the variational treatment the following expression results [9,17] for the enthalpy change

$$\Delta H_{exc} = \frac{\Delta H_{CT}}{2} - \sqrt{\left(\frac{\Delta H_{CT}}{2}\right)^2 + \beta^2} \tag{7}$$

where β is the resonance integral between the locally excited and the charge transfer states. ΔH_{CT} is the enthalpy change of forming the total charge transfer state from the locally excited state, and it is given by

$$\Delta H_{CT} = IP - E_s - EA - C \tag{8}$$

where E_S is excited state energy level of the PAH, IP and EA are the ionization energy of the PAH and the electron affinity of the CB respectively, and C is a Coulombic interaction term. Beens and Weller [18] theoretically estimate the quantity C for several exciplexes of aromatic molecules. The mean result of their calculation was 3.5 eV and this is the value that we adopt here. The other quantities used in Eq. (8) for the calculations are given in Tables 1 and 3. The pre-exponential factor A in Eq. (6) is related to the entropy change on forming the exciplex, $A = \exp(\Delta S_{exc}/R)$. From the experimental data for the entropy change of exciplex

Table 3
Photophysical properties and ionization energies of the PAHs

PAH	τ (ns) [a]	E_s (eV) [b]	IP (eV) [b]
Naphthalene	110	3.99	8.14
Phenanthrene	57	3.59	7.86
Pyrene	410	3.34	7.41
2-Methylnaphthalene	60	3.88	7.80
chrysene	44.7	3.43	7.59
1,2-benzanthracene	44.1	3.23	7.43
1,2,5,6-dibenzanthracene	37	3.15	7.38

[a] Singlet lifetime in cyclohexane deoxygenated solutions.

[b] Excited singlet energy and adiabatic ionization energies from [9].

formation a mean value of ca. −20 cal/K can be estimated for ΔS_{exc} [19]. With this 5×10^{-5} resulted for A, and this figure was used for all the systems. From the plots of τ_0/τ vs. [CB] that present a downward curvature experimental values for K and τ_0/τ_0' can be obtained by a nonlinear square fitting of the data to Eq. (2). From the values of τ_0/τ_0' the exciplex decay rate constant k_{p} was obtained. It was assumed to be the same for a given series of rate constants corresponding to the quenching of the same PAH by the chlorobenzenes. We are aware that this is a simplification of the problem, since τ_0' is expected to vary with the CB.

An estimate for the forward rate constant for the exciplex formation k_{exc} is also needed. To this end an empirical relation of the type of Marcus free energy correlation was used

$$k_{\mathrm{exc}} = \upsilon \exp(-\Delta H^*/RT) \tag{9}$$

$$\Delta H^* = \frac{\lambda}{4}\left(1 + \frac{\Delta H_{\mathrm{exc}}}{\lambda}\right)^2 \tag{10}$$

where υ is the frequency factor and λ is an empirical reorganization energy.

When the rate constants are plotted as $\log(k_{\mathrm{q}})$ vs. ΔH_{CT} it can be seen that they follow a different correlation for each PAH, Figs. 6 and 7. A sigmoidal curve is apparent. This is similar to the trend observed for exciplex mediated quenching in polar solvents [9,20]. The lines in the plots are the result of the fitting of the data with Eq. (4) with the rate constants and K_{exc} obtained as described above, using only β, υ and λ as adjustable parameters. The rate constants k_{d} and $k_{-\mathrm{d}}$ and the pre-exponential factor in Eq. (8) were the same for all the systems as discussed before. The other parameters employed in the fitting are shown in Table 4.

It can be seen in Fig. 6 that a very good agreement of the calculated rate constant with the experimental data is obtained for naphthalene, while the points for 2-methylnaphthalene follow a similar correlation but with a slightly different value of the β parameter. Fig. 7 shows that the data for the quenching of pyrene and phenanthrene are equally well described by the exciplex model. For the quenching of benzanthracene, dibenzanthracene and chrysene a similar analysis was not effected due to the few experimental points. However, from the values of the rate constants in Table 1 and the curvature of the plots in Figs. 1 and 3, a similar operating mechanism may be anticipated for these systems.

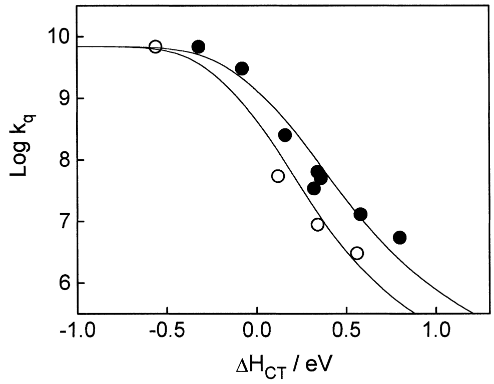


Fig. 6. Rate constants correlation with the enthalpy change of forming the total charge transfer state from the locally excited state, ΔH_{CT}, for the quenching of naphthalene (●) and 2-methylnaphthalene (o) by polychlorobenzenes according to the exciplex model.

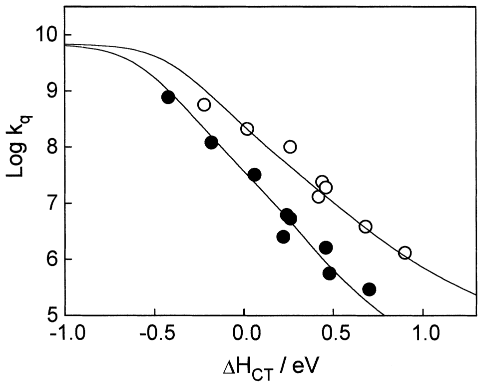


Fig. 7. Rate constants correlation with the enthalpy change of forming the total charge transfer state from the locally excited state, ΔH_{CT}, for the quenching of pyrene (o) and phenanthrene (●) by polychlorobenzenes according to the exciplex model.

With regard to the fitting parameters in Table 4 one must be cautious with the meaning of the values in the table. The quantity β was taken as a constant for a given PAH while clearly its value for each PAH-CB pair must be different. The β given in the table must be understood as a mean value for each series. The decay rate constant of the exciplex, k_{p} was assumed to be constant for each series. However, these constants were estimated from the curvature of SV plots for only one or two low efficiency quenchers, and there is no reason a priori to suppose that they are the same for all the systems in a series. Finally, it is obvious that considering the number of adjustable parameters in the model, there is not a unique set of values that adjust the model to the experimental data. However we think that the values in Table 4 are very judicious in the context of the quantities that normally are involved for exciplexes in nonpolar solvents. The most important conclusion is that the unconventional dependence of the quenching rate constants on the driving force may be explained with a relatively simple kinetic model.

In summary, the quenching of the singlet excited state of PAHs by chlorobenzenes is characterized by τ_0/τ plots that present negative curvature and by sigmoidal $\log k_{\mathrm{q}}$ vs. ΔH_{CT}

Table 4
Fitting parameters for the exciplex model

	Naphthalene	2-Methylnaphtalene	Phenanthrene	Pyrene
β (eV)	0.45	0.37	0.45	0.4
υ (s^{-1})	7×10^{12}	7×10^{12}	1×10^{12}	5×10^{11}
λ (eV)	1.6	1.6	1.6	1.65
k_{p} (s^{-1})	3×10^7	5.3×10^7	3.4×10^7	5×10^6

plots. This features confirm the exciplex mechanism in this case. If the energetics of the system is analyzed assuming the mixing of the locally excited and charge transfer states, the structural dependency of the rate constants may be explained.

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