

THE PHOTOLYSIS OF PYRENE AND PERYLENE IN CYCLOHEXANE LIQUID SOLUTION FROM HIGHLY EXCITED ELECTRONIC STATES

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(Received October 18, 1986)

Summary

The photolysis of pyrene and perylene using the 185 nm and/or the 254 nm mercury line has been studied in liquid cyclohexane. Different photochemical processes, which depend on whether the excitation takes place from highly excited singlet or triplet states, are shown to be involved. Contrary to excitation into highly excited triplet states, charged species are shown to play a major role in the photodegradation of the aromatics (Ar) when they are excited into upper singlet states just above their ionization threshold.

Analysis of the photoproducts resulting from the photolysis of perylene provides evidence for the formation of dihydrocyclohexenylperylene. It is suggested that the formation of this product can be traced to the previously postulated sensitized formation of a cyclohexyl cation (Cy^+) which is then rapidly converted into a cyclohexenyl cation. The possibility for the formation of ion pairs ($Cy^+ \cdots Ar^-$), as first proposed by Warman, is discussed.

However, as we failed to detect these ion pairs using picosecond spectroscopy, we did not obtain experimental evidence to sustain this hypothesis.

1. Introduction

The photochemistry of polar substituted aromatic hydrocarbons in polar and non-polar solvents has been extensively studied and is still the subject of frequent investigations as evidenced by the large number of studies published every year on this subject [1]. In contrast, the photo-reactivity of unsubstituted polycyclic aromatic hydrocarbons (PAHs) in non-polar solvents such as alkanes is much less well documented.

Besides isomerization, which occurs in certain cases [2 - 4], three main processes are known to take place following electronic excitation of PAHs: (i) photo-oxidation [1, 5]; (ii) photoionization [6]; (iii) sensitized solvent dissociation [7]. The last process, which produces solvent radicals ($R\cdot$), has been mainly studied in frozen solvents and proceeds essentially from excita-

tion into highly excited triplet states [7 - 10]. Besides radical formation, which has been known for some time [8 - 10], subsequent photochemical reactions may also arise [11] and we have recently shown that stable aromatic photoproducts are also formed [12, 13]. These have been identified as substituted or dihydrosubstituted aromatic derivatives resulting from the attachment of solvent molecules to the aromatic rings.

Interestingly, the same types of compounds were identified in the photolysis of naphthalene in liquid alkanes under high pressure conditions by Yin and Nicol [14]. In fact, the reaction appears to be quite general and is also found to take place in liquid solutions [14, 15] or in micelles under normal conditions [16] provided a sufficiently high concentration of the T_1 state can be produced by the excitation.

The experimental data that we have obtained, which included the quantum yield [12] and the nature of the products [13], can be accounted for by an energy transfer from an aromatic upper T_n state to a dissociative alkane triplet state. Even when energy in excess of the ionization threshold is deposited, the energy transfer process appears to dominate over the ionization pathway in forming photoproducts when excitation takes place in the triplet manifold.

In contrast, the outcome of electronic excitation into highly excited singlet states of PAHs in non-polar solvents has not yet been elucidated. The photochemical degradation of PAHs from highly excited singlet states in non-polar solvents has been reported from time to time [17] but to our knowledge the mechanism of this process and the nature of the photoproducts have not yet been thoroughly investigated.

In this paper we report a study of the photochemical behaviour of pyrene following excitation into highly excited S_n and T_n states. We used either the 254 nm mercury line to excite the molecules to a high triplet state by a two-photon two-step process via the T_1 state or the 185 nm mercury line for providing excitation directly into a high S_n state above the ionization threshold in solution (in which case the contribution from the T_1 state is negligible).

We also report our analysis of the products resulting from the photolysis of perylene using the 185 nm mercury line in liquid alkanes at room temperature. In this case, because of the very low triplet yield of perylene ($\phi_T \approx 0.02$), a two-photon stepwise excitation of the molecule to a highly excited T_n state is quite inefficient and the reaction is expected to proceed essentially from a highly excited S_n state.

Previously published results, obtained from resonance laser excitation [17, 18] and conductivity measurements [17, 19, 20], indicate that aromatic ionization, charge carrier formation and their subsequent recombination play an important role in the degradation of aromatics from excitation into the singlet manifold. The case with cyclohexane as the solvent, which is known to exhibit unusual conductivity behaviour [21] with abnormal ion mobility, is of particular importance. We have tentatively interpreted our results on the basis of the ionic species which could have been formed

[17, 22, 23] subsequent to the excitation of the aromatic into highly excited singlet states.

2. Experimental details

UV irradiation of deaerated alkane solutions of pyrene, perylene and naphthalene was performed with a helicoidal low pressure mercury lamp at room temperature. For irradiation with $\lambda \geq 185$ nm, a continuous flow of dry nitrogen gas was maintained through the inner part of the lamp coil where a fused silica cell (path length, 1 cm) containing the solution was located. A Vycor glass tube was used as a filter around the cell for irradiation with $\lambda \geq 240$ nm. The reaction was monitored by recording the decrease in intensity of the absorption bands of the aromatic.

For high performance liquid chromatography (HPLC) and mass analysis of the photoproducts, large volumes of irradiated solutions were needed. In this case, about 50 ml of the solution was introduced into the annular space (thickness, 4 mm) between two fused silica envelopes of a dewar-like flask. Absorbances at 185 nm were measured with a Cary 219 spectrophotometer thoroughly purged with dry nitrogen gas.

Cyclohexane was of spectroscopic grade (Fluka). It was washed with sulphuric acid, distilled and kept over molecular sieves. Its absorbance at 185 nm was less than 0.2 through a path length of 1 mm.

Perfluorohexane (pFH) (Fluka purum) was used as an electron scavenger.

The aromatic concentrations were set to about 5×10^{-5} M for perylene, 3.5×10^{-4} M for naphthalene and 3.6×10^{-5} M for pyrene, giving an aromatic absorbance of about 0.5 at 185 nm for a light path length of 1 mm.

HPLC analysis of the photoproducts resulting from the 185 nm irradiation of perylene in cyclohexane was performed using cyclohexane as eluant after having concentrated the irradiated solution (ratio 1:300) by evaporating the solvent.

The column (Licrosorb Si 60-5, $L = 250$ mm, $\phi = 4.6$ mm) was used in conjunction with a UV absorbance detector (Pye Unicam) set at 275 nm. The collected fractions were reconcentrated and analysed by mass spectrometry using a direct injection mode.

3. Results and discussion

3.1. Photolysis of pyrene in liquid cyclohexane for excitation into highly excited S_n or T_n states

Figure 1 displays the disappearance of pyrene at two different irradiation wavelengths in the presence and in the absence of the electron scavenger pFH ($[pFH] = 10^{-1}$ M).

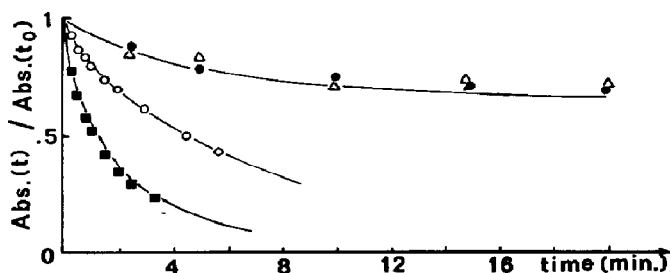


Fig. 1. Effect of pFH on the photolysis rate of pyrene in cyclohexane ($[pFH] = 3.5 \times 10^{-5} \text{ M}$) for different wavelengths of irradiation: $\lambda_{exc} > 240 \text{ nm}$ in the presence (●) and in the absence (Δ) of pFH; $\lambda_{exc} > 180 \text{ nm}$ in the presence (■) and in the absence (○) of pFH.

The slowest decay corresponds to irradiation through the Vycor filter, *i.e.* with wavelengths longer than 240 nm ($E_{exc} \leq 5.1 \text{ eV}$). Under these conditions, direct excitation into the singlet manifold is not sufficiently energetic to induce ionization (I_{11q} for pyrene is about 6.2 eV) [24] and other photochemical events, if any, are thought to be very inefficient. Reactive highly excited triplet states, however, may be reached via a sequential two-photon mechanism with the T_1 state as an intermediate. Such a mechanism has been found to be responsible for the rapid disappearance of pyrene in frozen alkanes leading to 1-alkyl-substituted pyrene [15]. No difference is observed for the disappearance rate of pyrene whether pFH is present or not in the solution. This observation points to the fact that charge carriers are probably not involved in the degradation mechanism of pyrene from high triplet states, in agreement with a previously proposed radical attack by \dot{R} radicals formed from a triplet-triplet energy transfer from the aromatic to the solvent molecule [12].

This behaviour is in contrast to that observed when the Vycor filter was removed, allowing the 185 nm line of the mercury lamp to irradiate the solution. Compared with the irradiation with only the 254 nm line, a more efficient photolysis together with a large accelerating effect of pFH occurs. This latter observation indicates that, contrary to what happens for excitation into the triplet manifold, ionization and charge carrier generation could be an important pathway for the degradation of PAHs in non-polar solvents when the excitation is carried into the singlet manifold. This result is in agreement with data obtained by Sauer *et al.* [17] from repetitive multiphoton laser pulse excitation at 248 nm (full width at half-maximum, 20 ns) of a solution of anthracene in cyclohexane in the presence of SF_6 . Besides obtaining evidence for efficient charge carrier generation, as measured by conductimetry, these workers also reported on the disappearance of anthracene. Since laser multiphoton processes or direct excitation by the 185 nm mercury line promote the aromatic molecules to comparable highly excited singlet states, the subsequent processes leading to PAH degradation are likely to be the same.

Photolysis of PAHs is also known to occur from highly excited singlet states in polar solvents [25]. However, although the mechanism also involves

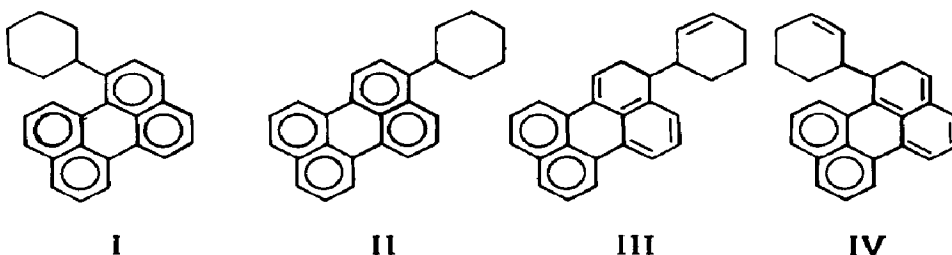
charge carriers, we have no evidence that they are the same as in non-polar solvents.

3.2. Photolysis of perylene in liquid cyclohexane with $\lambda \geq 185$ nm: analysis of the photoproducts

Figure 2 displays the change in the absorption spectra of a solution of perylene in cyclohexane ($c = 5 \times 10^{-5}$ M) during irradiation with the unfiltered low pressure mercury lamp ($\lambda_{\text{exc}} \geq 185$ nm; $E_{\text{exc}} \leq 6.7$ eV).

The absorption bands of perylene disappear rapidly and new bands grow in the range 270 - 360 nm. Comparison of the emerging spectrum with the absorption spectrum obtained on electrochemical reduction of perylene [26] indicates that it is likely that these bands can be assigned to hydroperylene derivatives. Analysis by HPLC and mass spectrometry gave further indications as to the nature of these compounds.

A typical chromatogram obtained on irradiation of a perylene solution in cyclohexane for 20 min is shown in Fig. 3. Obviously the reaction leads to a large variety of photoproducts. Typically, mass spectrometry analysis indicates the formation of 1- and 3-cyclohexylperylene (I and II) and of dihydrocyclohexenylperylene (III and/or IV).



The structures of I and of II were ascertained by comparison of their fluorescence spectra with those of synthesized 1- and 3-cyclohexylperylene. Intense peaks in the chromatogram correspond to perylene molecules with two or more cyclohexyl or cyclohexenyl groups attached (polycyclohexyls and polyhydrocyclohexenyls).

The most striking result is the attachment of a cyclohexenyl group to perylene, which implies the loss of two hydrogen atoms (or one hydrogen molecule) from cyclohexane.

In the photolyses of phenanthrene, anthracene and pyrene that we carried out in cyclohexane with $\lambda \geq 254$ nm (two-photon mechanism via the T_1 state) [13, 16, 27], no cyclohexenyl derivatives were identified among the photoproducts. Thus the presence of such a group appears to be characteristic of the irradiation of the aromatic into highly excited singlet states.

As in the 185 nm irradiation of pyrene, the disappearance rate of perylene increases drastically in the presence of pFH (10^{-1} M), pointing to the involvement of charged species in the reaction mechanism. Since the ionization threshold of perylene in alkane solution has been estimated to be

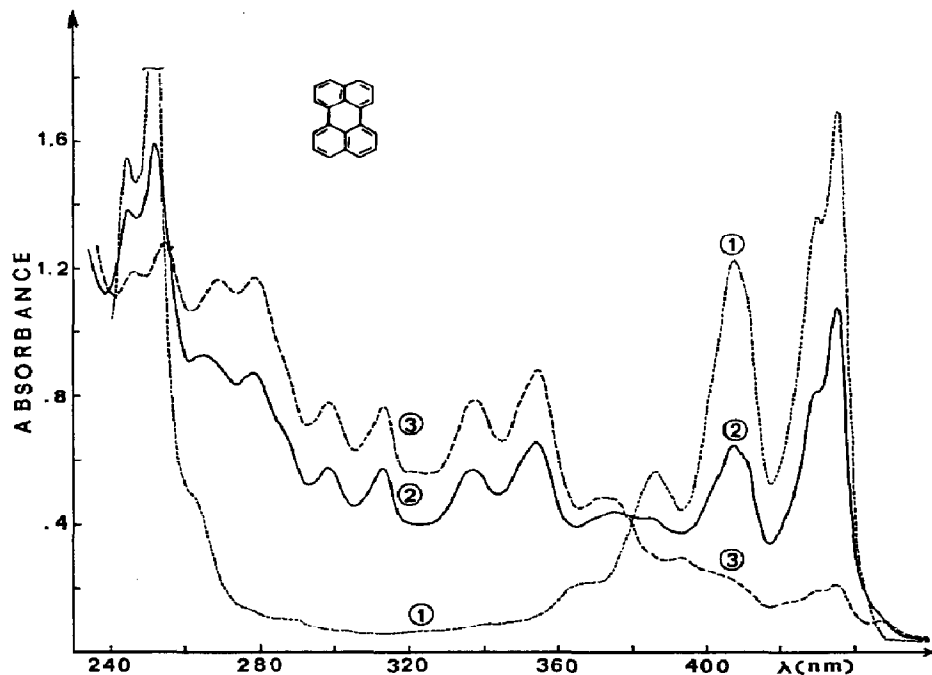


Fig. 2. Spectral changes observed during the 185 nm photolysis of a deaerated liquid solution of perylene (5×10^{-5} M) in cyclohexane. Curve 1, before irradiation; curves 2 and 3, after respectively 10 min and 20 min of irradiation.

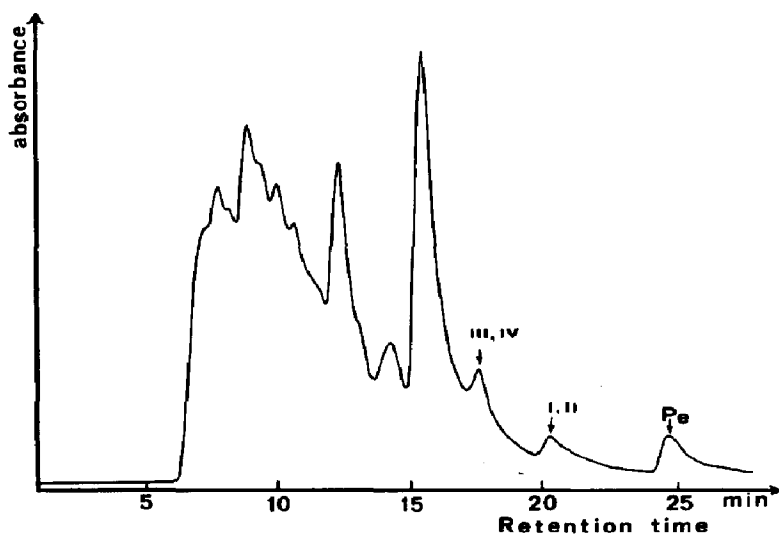


Fig. 3. Chromatogram obtained from a perylene solution in cyclohexane irradiated for 20 min with $\lambda > 185$ nm. The arrows indicate the fractions in which photoproducts I, II, III and/or IV were identified by mass spectrometry.

about 5.78 eV [24], irradiation with the 185 nm line (about 6.7 eV) is energetically sufficient to produce the perylene cation radical PeH^{\ddagger} . However, in alkane solutions, geminate recombination is very efficient and it has been estimated that the lifetime of the cation does not exceed 10 ps [20]. This could explain why aromatic cations have not, up to now, been detected by their characteristic absorption spectra in these non-polar solvents following direct or multiphoton excitation of the aromatic solute. An exception is the observation of the pyrene cation in iso-octane by Hirota and Mataga [28]; however, this species was associated with the biphenyl anion as an ion pair.

Fast electron recombination with the aromatic cation could be a source of photoproducts, but the increase in the irradiation efficiency in the presence of pFH is indicative that this is not the major process. This fact plus the very short lifetime of the aromatic cation allows one to infer that this species is most probably not directly involved in the mechanism for the disappearance of these aromatics.

A possible ionic species to be considered is the cyclohexane cation radical $\text{C}_6\text{H}_{12}^{\ddagger}$. The production of such a cation has been postulated by Warman [22] and by Sauer *et al.* [17] in order to interpret the intense conductivity signal following the laser multiphotonic ionization of anthracene in alkane solvents.

It is suspected that the cation radical of cyclohexane is unstable and decomposes either monomolecularly or photochemically to yield the cyclohexyl cation $\text{C}_6\text{H}_{10}^+$ [29, 30]. The possible involvement of this cation may then constitute a clue for the production of dihydrocyclohexenyl-*perylene*s (III and/or IV). Accordingly, the formation of these photoproducts can be interpreted through the following sequence of reactions, the first step being the formation of the cyclohexyl cation radical (reaction (1)):



Also, consecutive to reaction (1), the formation of photoproducts I and II may be accounted for by the three following possible mechanisms.

(i) Photodetachment of an electron from PeH^- followed by the formation of the cyclohexyl radical $\text{C}_6\text{H}_{11}^{\cdot}$ through electron recombination and the radical attack of perylene:



(ii) Proton transfer to a neutral cyclohexane molecule leading to a cyclohexyl radical



followed by reaction (6).

(iii) Decomposition of $C_6H_{12}^{\ddagger}$ to yield $C_6H_{11}^+$ followed by recombination with a perylene anion:



The low quantum yield of the electron photodetachment of perylene on the one hand [31] and the fact that the presence of an electron scavenger (pFH) does not reduce the photodegradation efficiency on the other hand indicates that mechanism (i) is not a major route in forming substituted photoproducts I and/or II.

Mechanisms (ii) and (iii) involve two non-radical cationic species ($C_6H_{13}^+$ and $C_6H_{11}^+$) which are difficult to detect either by electronic absorption or by electron spin resonance methods. Trifunac *et al.* have suggested that they may be good candidates for the highly mobile positive ions encountered in cyclohexane radiolysis [23]. Moreover, Klassen and Teather have proposed that reaction (7) can explain the fast decay of initial cations which is thought to occur in irradiated neat alkanes [32]. Accordingly, although at the present we have no experimental evidence that all of these mechanisms really operate, they offer a possible explanation for the formation of the identified photoproducts.

The mechanisms we propose are based on the process expressed by reaction (1). To our knowledge such a process has not yet received any experimental support. It corresponds to an electron transfer from solvent to solute, and has been described as a "hole injection" by Warman [22]. A similar process has also been invoked by Konuk *et al.* [33] in interpreting the photoionization of perylene in polar solvents.

We may question, however, whether such a process is energetically possible. We have made a rough estimation of the energy needed to produce a cyclohexane cation-aromatic anion pair (Cy^+/Ar^-) by using the expression

$$E(Cy^+/Ar^-) = I_{liq}(Cy) - A(Ar) + P(Ar^-) + C$$

where $I_{liq}(Cy)$ is the ionization threshold for liquid cyclohexane, $A(Ar)$ is the electron affinity of the aromatic molecule, $P(Ar^-)$ is the polarization energy of the medium by the aromatic anion and C is the coulombic interaction energy of the ion pair. $P(Ar^-)$ can be calculated using the usual Born expression:

$$P(Ar^-) = \frac{e^2}{2r_a^-} \left(1 - \frac{1}{\epsilon} \right)$$

The aromatic anion radius r_a^- has been approximated either by taking the effective cation radius (r_a^+) [34], or by taking the radius calculated from the molar volume (r_m). $I_{liq}(Cy) = 8.43$ eV was taken from ref. [35] and for the electron affinities we used a mean value derived from data found in the literature [36 - 38].

The coulombic interaction C has been omitted because of the large uncertainty of the structure of such a pair. As this term is expected to bring

TABLE 1

Results of the energy calculations for the cyclohexane cation–aromatic anion pairs

	$A(\text{Ar})$ (eV)	r_a^+ (Å)	r_m (Å)	$-P(\text{Ar}^-)$ (eV)		$E(\text{Cy}^+/\text{Ar}^-)$ (eV)	
				A	B	A	B
Pyrene	0.5	2.5	4.0	1.45	0.91	6.5	7.0
Perylene	0.9	2.9	4.2	1.23	0.87	6.3	6.6
Naphthalene	0.1	~2	3.5	1.75	1.0	6.8	7.3
Anthracene	0.6	2.6	3.8	1.38	0.96	6.4	6.8

A, calculated with $r_a^- = r_a^+$; B, calculated with $r_a^- = r_m$.

in a stability energy, an upper limit will be given for the estimated energy to form the Cy^+/Ar^- pair. The results are given in Table 1 for perylene, pyrene, naphthalene and anthracene using the approximated values for r_a^- .

They strongly suggest that the 6.7 eV energy provided by the 185 nm radiation is sufficient to produce the Cy^+/Ar^- pair from a highly excited S_n state in the case of perylene, pyrene and anthracene. For naphthalene, the energy at 185 nm is just at the limit for the required energy.

The photolysis of these aromatic compounds was carried out at 185 nm in cyclohexane using similar conditions of absorbance at 185 nm. Figure 4 displays the curves for the disappearance of each compound during irradiation.

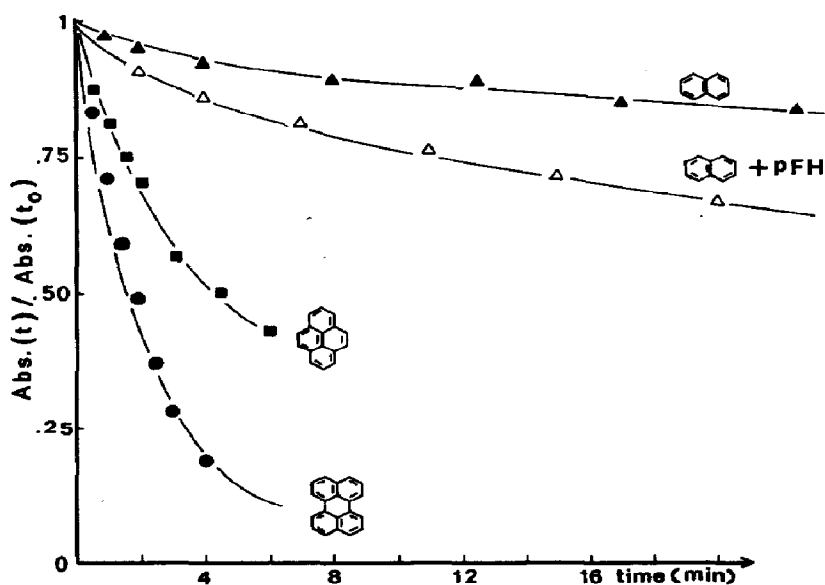


Fig. 4. Relative photolysis rate of naphthalene (▲), pyrene (■) and perylene (●) in liquid cyclohexane irradiated at $\lambda > 185$ nm. Δ , case of naphthalene in the presence of pFH.

Interestingly, a correlation is observed between the photolysis rate and the estimated energy for Cy^+/Ar^- pair formation. Perylene, for which the pair energy is the lowest, has the largest photolysis rate, while naphthalene decomposes most slowly.

The two main experimental results which we are reporting in this paper, namely the identification of cyclohexenylperylene derivatives and the correlation of the aromatic photolysis rate with the energy for Cy^+/Ar^- pair formation in cyclohexane solution, conform with Warman's hypothesis of reaction (1). Nevertheless, they do not prove formally that this pair is effectively formed during photoionization of aromatics in cyclohexane. Definitive proof would require unambiguous spectroscopic detection and identification of the species involved. However, the pair is suspected to have a very short lifetime and until now there have been few attempts to perform such an experiment on the picosecond time scale.

According to Warman [22], one such experiment has been performed by Braun and another study was announced by McDonald and Sauer [39]. More recently, we have also tried to study transient absorption from a cyclohexane solution of perylene using two 20 ps pulses at 266 nm [40].

Superimposed on the $S_1 \rightarrow S_n$ absorption bands, we detected a weak transient absorption at 700 nm whose decay time was less than 100 ps. However, although the position of the absorption is what we may have expected [41] we could not make a choice between this assignment and other possibilities such as relaxing $S_m \rightarrow S_n$ transitions [42]. Moreover, no absorption band assignable to the Pe^- radical ($\lambda_{\text{max}} \approx 580$ nm) was detected (Fig. 5).

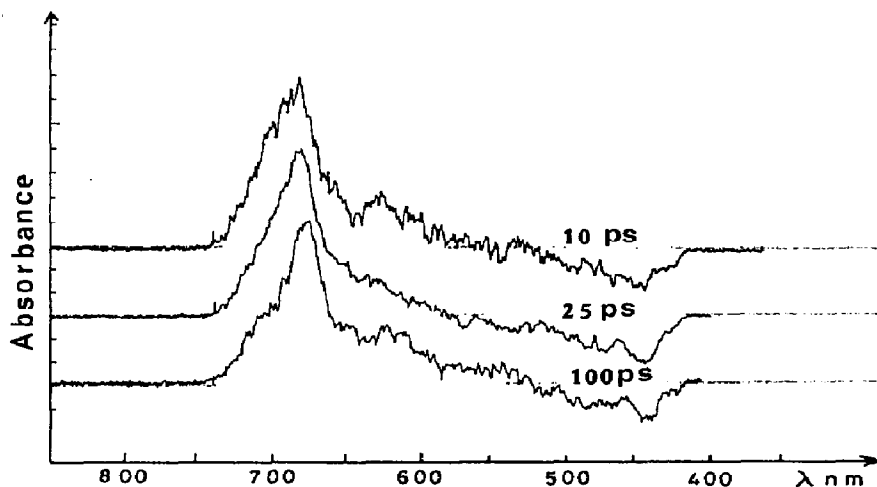


Fig. 5. Transient absorption spectra obtained from a 5×10^{-5} M solution of perylene in cyclohexane in the presence of pFH (10^{-1} M) by a two-pulse excitation with the fourth harmonic of a picosecond Nd^{3+} :YAG laser [40]. The delay times after excitation with the second pulse are indicated in the figure. The spectra are normalized at the maximum.

4. Conclusions

The insensitivity of the photolysis of PAHs to the presence of perfluorohexane (pFH) when the excitation is performed into highly excited triplet states is in contrast to the large effect observed when the molecules are excited into highly excited singlet states. These results clearly demonstrate that the photodegradation of PAHs in non-polar solvents proceeds quite differently depending on whether highly excited triplet or singlet states are concerned.

Although charged species appear to be involved in the PAH degradation from highly excited singlet states their definitive identification is not yet clearly established.

The analysis of the photoproducts in the case of perylene in cyclohexane appears to conform with the mechanism involving the initial formation of the cyclohexyl radical cation-perylene anion pair as postulated by Warman and Trifunac *et al.* Unfortunately we could not confirm unambiguously the formation of these species in a pulse laser experiment on the picosecond time scale. Obviously, other intermediate charged species may be generated and further laser investigations with even better time resolutions need to be carried out.

Acknowledgments

We are grateful to Dr. D. Grand for her assistance in the estimation of the energy of the ion pairs and also express our thanks to C. Rullière for giving us the opportunity to perform picosecond experiments and to K. McAdam for having carefully read the manuscript.

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