Journal of Photochemistry, 17 (1981) 347–354

THE INDIRECT TWO-PHOTON PHOTOLYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS AND BENZENE IN RIGID MATRIXES*

J. JOUSSOT-DUBIEN, M. LAMOTTE and J. PEREYRE
Université de Bordeaux I, 33405 Talence Cédex (France)

Summary

Benzene and polycyclic aromatic hydrocarbons (PAHs) incorporated in rigid matrixes have long-lived lowest triplet states which are at the origin of the photophysical and photochemical processes that are not observed in fluid solutions. In particular, PAHs are photolysed in alkane and alcohol matrixes at 77 K, yielding the monohydrogenated radical and dihydro derivatives. For triphenylene, chosen because it gives a fluorescent dihydro photoproduct, we showed that the reaction is biphotonic and involves an upper triplet state. The overall quantum yield is very small and the efficiency of the second-photon process depends drastically on wavelength.

The data indicate a triplet energy transfer to the neighbouring alkane molecules which, in their triplet state, are dissociative, producing a hydrogen atom and a solvent radical molecule. These radicals can be trapped by the PAH molecules. Thus the photolysis of PAHs is most probably indirect. The particular case of benzene is discussed and the processes described here are related to other known reactions of PAHs in rigid matrixes.

1. Introduction

Polynuclear aromatic hydrocarbons (PAHs) constitute a fairly homogeneous series of compounds whose photophysical as well as photochemical behaviours have been intensively investigated [1]. In aerated liquid solutions the main photochemical event expected to occur is photooxidation [2], while in deaerated solutions the process which has attracted much attention, although it is limited to specific cases, is photodimerization [3].

In contrast, in rigid solutions PAHs appear to be relatively stable with respect to UV irradiation except in some very specific matrixes such as boric acid glass (see ref. 4 for a review) where, even at room temperature, they can be completely photoionized to give the radical cation. An important property of most PAHs in rigid matrixes is the long lifetime of their lowest triplet state which can be of the order of seconds. Thus large conversion to the lowest triplet state, from which a second photon can be absorbed, is easily obtained. This is why PAH molecules are useful for studying the properties of highly excited triplet states.

---

* Paper presented at the Xth International Conference on Photochemistry, Iraklion, Crete, Greece, September 6 - 12, 1981.

0047-2670/81/0000-0000/$02.50

The photochemical consequences of this biphotonic process are mainly photoionization [4] of the solute and solvent sensitization (see ref. 5 for a review). Since hardly any significant change in the aromatic concentration has been found in solvent sensitization experiments, it has been accepted that PAH molecules do not undergo any permanent photoreactions during the process [6, 7], *i.e.* the internal conversion process must be faster than any chemical reactions with the neighbouring molecules.

Contrasting with these conclusions, however, are reported observations of the photochemical degradation of certain PAHs during matrix experiments requiring high intensity irradiation [8]. We have confirmed the existence of such a photodegradation by observing the decrease in absorption spectra on UV irradiation of many PAHs in paraffinic, alcoholic and polymeric matrixes at 77 K as well as at 4.2 K, the only condition being that the solvent was able to give hydrogen atoms [9, 10].

The aim in this review is to present arguments showing that, contrary to what is admitted for the photochemistry of benzene in glasses (a one-photon mechanism from the T_1 state [11, 12]), one of the reactions identified as being responsible for the photodegradation of PAHs in rigid matrixes occurs via a two-photon mechanism with the lowest triplet state as intermediate. The efficiency of this reaction has been estimated and we discuss whether it is a new reaction of an upper triplet state or an indirect reaction after solvent sensitization.

The choice of the aromatics for studying the phenomena was guided by specific properties allowing data to be readily interpretable. For example, triphenylene proved to be the most suitable PAH to study in *in situ* photolysis since it yields a fluorescent photoproduct that is easily distinguishable from the parent emission. For isolation and identification purposes, however, phenanthrene, anthracene and naphthalene were preferred to triphenylene because of the greater stability at room temperature of the isolated photoproducts.

2. *In situ* identification of products formed from the photolysis of triphenylene in methyl cyclohexane glass

The fluorescence and absorption spectra before and after irradiation of triphenylene in methyl cyclohexane glass (MCH) with unfiltered light from a medium pressure mercury arc (HP 125 W) are shown in Fig. 1. Two systems of absorption bands appear on irradiation. Spectrum I disappears after the glass has softened; it is assigned to the monohydrogenated radical $AH_2\cdot$ [9, 10]. A different behaviour is observed for spectrum II which is left unchanged after the glass has been melted and cooled again at 77 K.

Moreover, this spectrum compares well with the excitation spectrum of the compound responsible for the new emerging fluorescence. An examination of this fluorescence reveals that it has the characteristic feature of the phenanthrene chromophore. Accordingly the new fluorescence and absorption spectra II are attributed to a reduced form of triphenylene resulting from the saturation of one C=C bond to leave a phenanthrene chromophore. A comparison of the fluorescence spectra of the photoproduct with those obtained from reduced triphenylene [9, 10] confirms that it does correspond to a dihydrotriphenylene-type com-

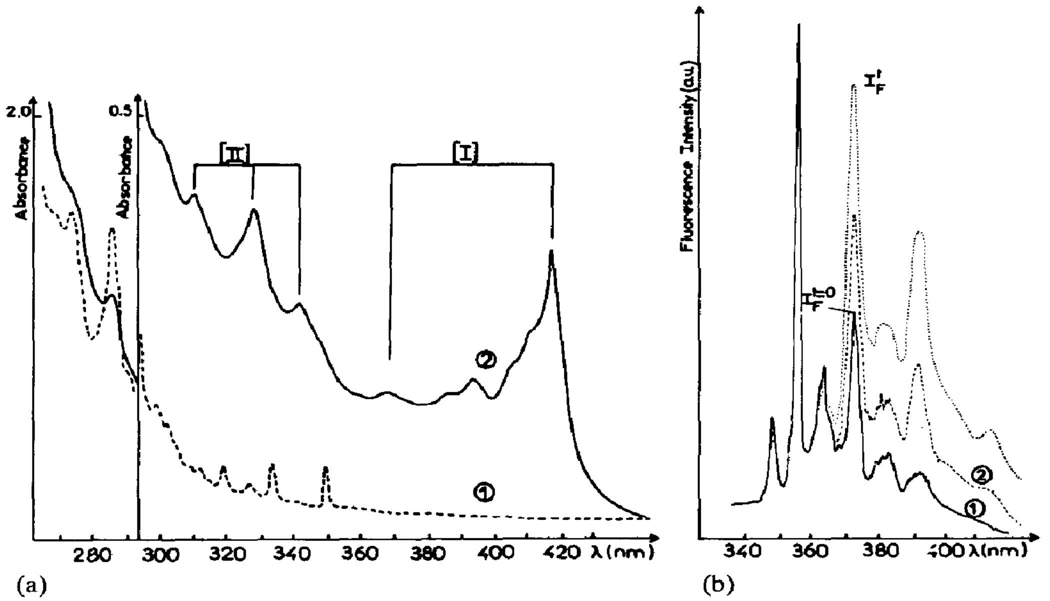
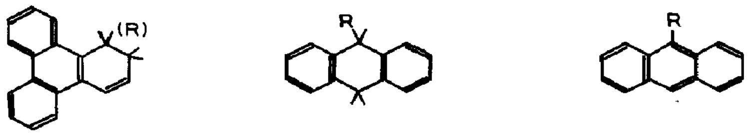


Fig. 1. Electronic spectra after irradiation of triphenylene (5×10^{-5} M) in MCH at 77 K with a medium pressure mercury lamp. (a) Absorption spectra: curve 1, before irradiation; curve 2, after 10 min of irradiation; spectrum I, $AH_2\cdot$ radical; spectrum II, addition product AH_2R. (b) Fluorescence spectra (λ_{exc} = 325 nm): curve 1, $t_{irr} = 0$; curve 2, $t_{irr} = 30$ min; curve 3, $t_{irr} = 60$ min. The relative amount of the growing photoproduct was measured from the change $I_F{}^t - I_F{}^{t=0}$ in the fluorescence intensities at 370 nm on irradiation. The intensities were normalized with the triphenylene band at 353 nm to correct for experimental irreproducibilities. Measurements were conducted for low conversion factors (less than 10%).



1 2 3

Fig. 2.

pound. Further insight has been given by experiments with polyethylene as the rigid matrix which traps the permanent photoproducts [11]. It can be concluded from these experiments that the photoproducts result most probably from the attachment of one solvent molecule RH to the triphenylene AH solute to give AH_2R **1** (Fig. 2).

3. Isolation and identification of stable photoproducts obtained by irradiation of polycyclic aromatic hydrocarbons in cyclohexane at 77 K

The preparation and identification of photoproducts was conducted using anthracene, phenanthrene and naphthalene since their dihydro derivatives are stable known compounds. Some of them were synthesized by conventional methods for identification. Owing to the low solubilities of PAHs in alkane solvents and their high extinction coefficients, the preparation of sufficient amounts of photoproducts for analysis required not only the irradiation of a large volume of the solid solution but also small sample thicknesses. The best procedure was to introduce the ground solid solution directly into liquid nitrogen and to irradiate the stirred suspension with a low pressure helicoidal mercury lamp through a clear silica Dewar [10].

After irradiation the solutions were warmed up and evaporated. The extracts were dissolved in the minimum volume of methanol and separated by high performance liquid chromatography (HPLC). Mass spectrometry (VG Micromass 16 F) was then used to analyse the fractions.

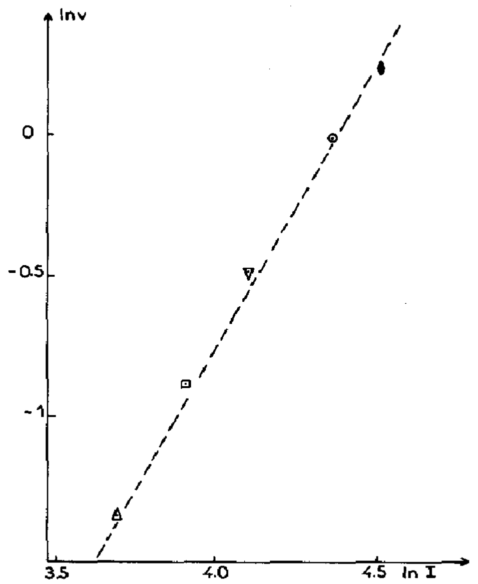
For phenanthrene [14] and anthracene [15], the analysis revealed three types of products: (1) oxidized derivatives of PAHs which eluted first; (2) cyclohexyl dihydro derivatives **2** (Fig. 2) resulting from the addition of one solvent molecule to the aromatic; (3) cyclohexyl phenanthrene and anthracene **3** (Fig. 2). Most of the compounds identified are probably formed during melting from radical oxidation or recombination. However, the presence of 9-cyclohexyl-9,10-dihydroanthracene **2** and cyclohexyl-9,10-dihydrophenanthrene confirm the attachment of one solvent molecule to the aromatic. Comparing these results with those obtained with triphenylene we may state with confidence that their formation does occur in the rigid solution.

For naphthalene, dihydrocyclohexylnaphthalene was not detected. Instead mass spectra indicate the formation of tetrahydrocyclohexylnaphthalene, dicyclohexylnaphthalene, α- and β-cyclohexylnaphthalene and naphthols (α and β forms). For benzene, apart from the occurrence of substituted hexadiene which is well known [11], we identified the formation of cyclohexylbenzene and dicyclohexylbenzene. Irradiation of perylene under the same conditions yielded no photoproduct detectable by HPLC.

4. Primary mechanism of the reaction

As already reported, the reaction does not occur in degassed solutions at room temperature. This observation indicates a reactive state whose formation is favoured by low temperature and rigidity of the medium. Accordingly a triplet state reactant seems very probable. Two types of experiment were made to check (a) that the reaction occurs via a two-photon mechanism and (b) that the second photon is absorbed by the lowest triplet state.

Details on these experiments are reported in ref. 16. They were carried out with triphenylene in MCH. The rate of formation of the photoproduct was measured by monitoring the increase in its fluorescence intensity during irradiation. A plot of the logarithm of the formation rate *versus* the logarithm of the irradiation intensity is shown in Fig. 3. The calculated slope has a value of about 1.8 which is very close to the theoretical value 2 expected for a two-photon mechanism. The identification of the intermediate state required a two-beam experiment. The first beam was provided by the fourth harmonic (λ = 265 nm) of a neodymium laser delivering 3 ns pulses of light. Since the intersystem crossing



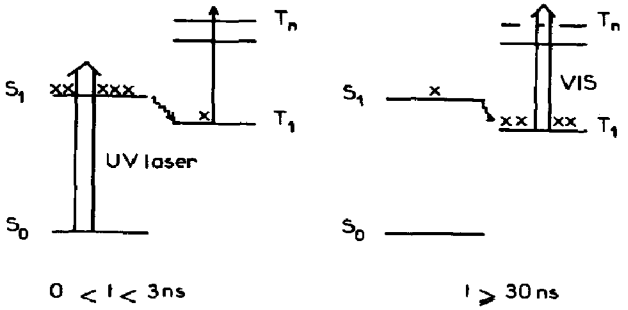


Fig. 3. Irradiation of triphenylene in MCH at 77 K (λ_{irr} = 260 nm). A plot of the rate v of photoproduct formation *vs.* the irradiation intensity I; the broken line corresponds to a slope of 2.

Fig. 4.

rate constant for triphenylene is about 50 ns [17] the triplet state is not heavily populated during the laser pulse and absorption of the laser light from this state is limited (Fig. 4).

Subsequent to the laser excitation 80% [17] of the molecules in the S_1 state relax to the lowest triplet state. Triplet molecules can then absorb the continuous light from the second beam provided by a xenon 450 W arc whose light is filtered in the visible region to allow transmission in the $T_n \rightarrow T_1$ absorption range of triphenylene [18]. This light is not absorbed by molecules in the ground state S_0.

We used 60 consecutive pulses separated by a time interval of 90 s to allow complete relaxation of the system between laser pulses. We observed that, when the solid solution was irradiated with both the laser and the visible light, more than twice the amount of photoproducts was produced than when the laser pulses alone were used. For different delays between the laser shots and the illumination of the sample by the visible light we observed that the rate of formation of the photoproduct was reduced with increasing delay time to an extent which corresponds to the phosphorescence decay rate of triphenylene (Fig. 5). Clearly the triplet state of triphenylene is the intermediate absorbing the second photon.

5. Quantum yield for the formation of the fluorescent photoproduct from the lowest triplet state

The estimation of the quantum efficiency φ_{AH_2R} of the second photon should provide valuable information to elucidate the mechanism of the reaction. Un-

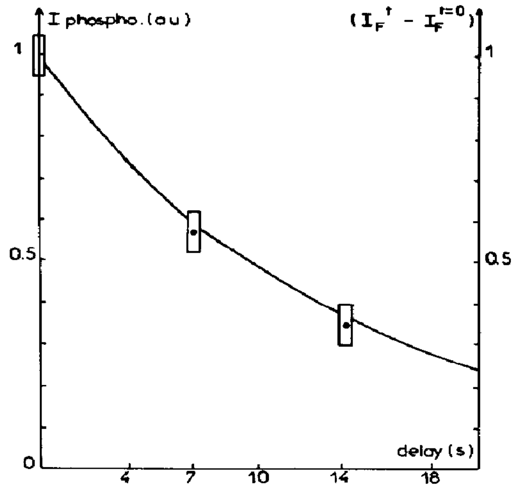


Fig. 5. A comparison of the phosphorescence decay of triphenylene (——) with the photoproduct decay rate measured for various delays ($d = 0$ s, $d = 7$ s and $d = 14$ s) between the UV laser pulses and the visible light.

fortunately the lack of data for $T_n \leftarrow T_1$ absorption in the UV range and the difficulty of determining the amount of photoproduct formed allowed only a crude estimation of φ_{AH_2R}. Details on the experiments are given in ref. 16. The amount of photoproduct formed during irradiation for 2 h was estimated from the decrease in the absorption band of triphenylene. The fluorescent photoproduct was found to represent a small part of the total amount of degraded triphenylene (less than 10%, *i.e.* less than 2% of the initial concentration). The absorption rate for visible irradiation was calculated from the $T_n \leftarrow T_1$ absorbance under the conditions of irradiation. For UV irradiation, all the photons were considered to be shared between S_0 and T_1 molecules proportionally to their populations. In this approximation we assumed similar extinction coefficients from the S_0 and T_1 states, as observed in some cases [19].

A quantum yield of 5×10^{-8} was estimated for excitation of the triplet state by visible light ($\lambda \approx 430$ nm), while the quantum yield for excitation with UV light ($\lambda \approx 260$ nm) was found to be roughly of the order of 1.5×10^{-4}. Although these estimations are very approximate, they indicate that the photochemical pathway leading to addition products with the solvent represents a very small part of the total degradation process. Moreover, it appears that UV excitation is more than 1000 times more efficient than visible light excitation.

6. Discussion

Discarding the mechanism implementing ionization of the aromatic solute since no radical cations are observed, the main event after two-photon excitation reported so far in alkane matrixes at 77 K is solvent-sensitized radical formation.

To a much smaller extent we now have clear evidence that the solute is also involved in the reaction since the monohydrogenated radical and stable addition products of the solvent with the aromatic solute were found. The question that is raised by these results is whether the solvent radicals, the radical $AH_2\cdot$ and the reduced aromatic AH_2R were formed by the same mechanism or whether a new reaction of the upper triplet aromatic should be invoked.

For many aromatic–solvent systems the quantum yields $\varphi_{R\cdot}$ for the formation of solvent radicals $R\cdot$ depend exponentially on the excess energy available in the triplet manifold [5]. The drastic increase we observed for the quantum yield φ_{AH_2R} of formation of AH_2R with triphenylene by shifting from the visible to the UV range suggests a similar wavelength dependence which might indicate that the same mechanism is at the origin of all the species detected.

In solvent sensitization, Vinogradova *et al.* [20] have established that the primary reaction is most probably cleavage of a hydrogen atom from the solvent. Observations of molecular hydrogen are consistent with such a mechanism. The most widely accepted assumption is that the dissociation of the solvent occurs after a direct energy transfer to a dissociative state of the solvent molecule [12, 20, 21]. This mechanism is somewhat analogous to mercury-photosensitized hydrogen abstraction from alkanes by mercury in the gas phase [22] and follows a pathway which has still not been determined.

Bagdasaryan has shown that $\varphi_{R\cdot}$ depends essentially on the energy of the second photon and on the ionization energy of the aromatic but is independent of the solvent. An interpretation has been made in terms of a solute intermediate state whose formation probability determines the quantum yield $\varphi_{R\cdot}$. It is described as a Rydberg state perturbed by the solvent (quasi-Rydberg state). The possibility that Rydberg states play a role in the photochemistry from highly excited states has been invoked in the photochemistry of ethylene [23] and can also be envisaged in the two-photon photochemistry of aromatics. If $AH\cdot$ radicals and AH_2R products are formed in a step after the sensitized solvent dissociation, they may result from an attack on the relaxed aromatic by an $H\cdot$ atom or an $R\cdot$ radical or both depending on the mutual orientation of the aromatic in the solvent cage. The reaction must then be considered as an indirect or secondary reaction.

Two-photon solvent sensitization is also known to occur for benzene and its derivatives [12]. Using the same procedure as for other aromatics we irradiated benzene in cyclohexane at 77 K. In addition to hexatriene formation we identified cyclohexylbenzene. However, the expected dihydro derivative, *i.e.* the cyclohexyl-1,3-cyclohexadiene $A'H_2R$, was not detected.

In the gas phase 1,3-cyclohexadiene photodecomposed easily to give mainly benzene and to a smaller extent 1,3,4-hexatriene [24]. Similar reactions are expected in the condensed phase [25]. Accordingly we can assume that the cyclohexylbenzene formed arises in part from the secondary photodecomposition of $A'H_2R$ formed by radical attack of benzene by $R\cdot$ and $H\cdot$ radicals from the solvent. We note that the secondary reaction can also produce solvent-substituted hexatriene. This product is effectively the main photoproduct known so far to be obtained by irradiation of benzene in rigid glasses [7]. However, its formation has been observed to be monophotonic [7, 12] and to proceed via the lowest T_1 state by a concerted process [26]. If we accept these conclusions, then a very small amount of hexatriene is due to the secondary photolysis of $A'H_2R$ formed by the above two-photon mechanism.

Thus for benzene in rigid matrixes two different types of photolytic reaction can occur: a direct reaction from the T_1 state and an indirect reaction after energy transfer to the solvent from a T_n state. In contrast, it seems that only the second reaction is operative for polynuclear aromatics. We have no evidence that a reaction from the T_1 state similar to that for benzene occurs, involving a ring opening.

References

1 J.B. Birks, *Photophysics of Aromatic Molecules,* Wiley, New York, 1970.
2 I. Saito, M. Imuta and T. Matsuura, *Tetrahedron, 28* (1972) 5307.
J. Rigaudy, *Pure Appl. Chem., 16* (1968) 169.
J. Rigaudy and M. Maumy, *Bull. Soc. Chim. Fr.,* (1972) 3926, and references therein.
3 H. Bouas-Laurent, A. Castellan and J.P. Desvergnes, *Pure Appl. Chem., 52* (1980) 2633, and references therein.
4 R. Lesclaux and J. Joussot-Dubien, in J.B. Birks (ed.), *Organic Molecular Photophysics,* Wiley, New York, 1973, p. 457.
5 Kh.S. Bagdasaryan, in B.M.E. Volpin (ed.), *Soviet Scientific Reviews,* 1980, p. 139.
6 S. Siegel and K. Eisenthal, *J. Chem. Phys., 42* (1965) 2494.
7 E. Migirdicyan, *J. Chem. Phys., 55* (1971) 1961.
8 R. Astier, A. Bokohza and Y. Meyer, *Proc. 20e Réunion de la Société de Chimie Physique, Paris,* in *J. Chim. Phys.,* (1969) 137.
R.E. Gerkin and P.J. Szenyi, *Chem. Phys., 50* (1969) 4095.
9 M. Lamotte, S. Risemberg, J. Pereyre and J. Joussot-Dubien, in P.W. Jones and M. Lever (eds.), *Polynuclear Aromatic Hydrocarbons,* Ann Arbor, 1979, p. 159.
10 J. Joussot-Dubien, M. Lamotte, R. Lapouyade and J. Pereyre, in R. Daudel, A. Pullman, L. Salem and A. Veillard (eds.), *Quantum Theory of Chemical Reactions,* Vol. II, Reidel, Dordrecht, 1980, p. 299.
11 E. Migirdicyan, *J. Chim. Phys., 63* (1966) 535, and references therein.
12 B. Brockelhurst, W.A. Gibbons, F.T. Lang, G. Porter and M.I. Salvadatti, *Trans. Faraday Soc., 62* (1966) 1793.
13 R.G. Harvey, *Synthesis,* (1970) 161.
14 M. Lamotte, R. Lapouyade, J. Pereyre and J. Joussot-Dubien, *C.R. Acad. Sci., Sér. C, 290* (1980) 211.
15 M. Lamotte, R. Lapouyade, J. Pereyre and J. Joussot-Dubien, *Chem. Commun.,* (1980) 725.
16 M. Lamotte, *J. Phys. Chem.,* in the press.
17 F. Wilkinson, in J.B. Birks (ed.), *Organic Molecular Photophysics,* Vol. II, Wiley, New York, 1975, p. 128.
18 G. Nouchi, *J. Chim. Phys., 66* (1969) 554.
D. Lavalette, *J. Chim. Phys., 66* (1969) 1845.
19 Kh.S. Bagdasaryan, Yu.I. Kirjukhin and Z.A. Sinitsina, *J. Photochem., 1* (1972 - 1973) 225.
20 V.G. Vinogradova, B.N. Shelimov, N.V. Fok and Voevodsky, *Dokl. Akad. Nauk S.S.S.R., 154* (1964) 188.
21 B.N. Shelimov, N.V. Fok and Voevodsky, *Dokl. Akad. Nauk S.S.S.R., 144* (1962) 596.
22 G. Marconi, G. Orlandi, G. Poggi and F. Bamgelletti, *J. Chem. Soc., Faraday Trans. II, 73* (1977) 1034, and references therein.
23 P. Kropp, *Mol. Photochem., 9* (1979) 39.
A.J. Merer and R.S. Mulliken, *Chem. Rev., 69* (1969) 639.
24 R. Srinivasan, *J. Am. Chem. Soc., 82* (1960) 5063.
25 S.I. Hirokami and R.J. Cvetanovic, *J. Phys. Chem., 78* (1974) 1254.
26 E.J. Anderton, H.T.J. Chilton and G. Porter, *Proc. Chem. Soc., London,* (1960) 352.