

Surface and adsorbates effects on the photochemistry and photophysics of adsorbed perylene on unactivated silica gel and alumina

Pura Sotero, Rafael Arce*

Department of Chemistry, University of Puerto Rico, Río Piedras Campus P.O. Box 23346, San Juan, PR 00931-3346, USA

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Abstract

The effect of the nature of the surface and solvent, the presence of coadsorbed species (O_2 , Ar and H_2O) and the surface loading on some photophysical and photochemical properties of perylene (Per) are reported. Although the absorption and emission spectra of perylene adsorbed on alumina and silica gel of different average pore diameters are very similar to those observed in solution, adsorbed perylene presented spectra with broader bands, loss of vibrational structure, and a small red shift and extension to longer wavelengths. These are consequence of aggregate formation, π -stacking, and surface interactions. The nature of the environment affects also the lifetime of the first excited state, presenting a single-exponential decay when in solution and, at least, a double-exponential decay when adsorbed suggesting the adsorption on at least two major surface regions. As the average pore size increases, the emission spectra resembled more to that in solution and the photodegradation rate also increased. Sample loading causes a red shift of the bands on the emission spectrum and a change in the relative intensities of the first and second bands. Oxygen quenched significantly the fluorescence and accelerated the photodegradation. The participation of 1O_2 in the photodegradation process was confirmed as well as the participation of a perylene radical cation, identified by laser diffuse reflectance transient and EPR spectroscopy. Coadsorbed water induced the formation of a new species, probably a perylene- H_2O complex on the surface.

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1. Introduction

The polycyclic aromatic hydrocarbons (PAHs) is a family of ubiquitous organic pollutants. These are released into the atmosphere either by natural or anthropogenic processes. Natural sources include dust-rise by wind, sea spray, forest fires, volcanic dust, and some vegetation [1–3]. The major anthropogenic sources of PAHs are incomplete combustion processes including residential heating, industrial activities (e.g., aluminium production and coke manufacture), incineration, power generation [4], vehicular petrol and diesel engines. Several of the PAHs are known to be carcinogens while others act as mutagens or tumor promoters [5,6]. Once in the atmosphere, they can be transformed through thermal and/or photochemical processes into more biologically hazardous compounds.

During the past two decades, studies on PAHs have focused on the effect of the surface's characteristics on the

rate of photochemical transformations. The surface's characteristics considered on those studies were: color, carbon content, pH and porosity [7–10]. Other studies have also considered the effect of coadsorbed species [11–13], sample loading [11,13,14], and the PAH reactivity [7,15]. Results obtained from different laboratories seem to be contradictory because the reactivity depends not only on the PAH but on the surface's nature and composition, and the methodology used in the studies.

Perylene (Per) is a high molecular weight, five-ring PAH, one of the few PAHs found in nature, although it also occurs in petroleum products and it is almost exclusively associated with particulate matter in the ambient. It is phototoxic. The literature on the photosensitized and chemical oxidation of Per, and on its photodegradation in homogeneous and heterogeneous media is extremely limited. Because the products of photodegradation could be more toxic than the parent compound, it is of interest to characterize these and to understand their ultimate environmental fate. In these terms, this work focuses on the photophysics and the photochemistry of Per adsorbed on non-activated silica gel and alumina as

* Corresponding author. Tel.: +1 787 764 0000x2433.

E-mail address: rarce@goliath.cnet.clu.edu (R. Arce).

models of the atmospheric particulate matter. The purposes of this work were to study the effect of: (1) the surface's nature on the photophysical properties of Per and on the rate of photodegradation; (2) the sample loading on the rate of photodegradation; and (3) coadsorbed species (O_2 , Ar, and H_2O) on the photophysical and photochemical properties (rate of photodegradation). In this paper, we present evidence that shows that the surface's physical and chemical properties affect the photophysical and photochemical behavior of adsorbed Per by producing band broadening and shifts, changes in the lifetimes, changes in the photodegradation rates and on the initial yield and decay kinetics of the major identified reactive intermediate, the Per radical cation.

2. Experimental

2.1. Reagents

Perylene (Gold Label, 99%) was obtained from Aldrich Chemical Co. Inc., and its purity verified by HPLC. Alumina (Type F-20), Silica gel (pore size 25 Å, 100–200 mesh, water (%) = 9.1; pore size 40 Å, 35–70 mesh; pore size 60 Å, 130–270 mesh, water (%) = 7.7; pore size 150 Å, 60–200 mesh, water (%) = 4.6) were obtained from Sigma Chemical Co. and used unactivated as adsorbent models of the atmospheric particulate matter. The solvents hexane, methanol, acetone, and acetonitrile (OPTIMA grade) were obtained from Fisher Scientific.

2.2. Instrumentation

Samples were photolyzed using an Orion Xe(Hg)-Ozone Free 1000W UV Lamp with a 4-70 Corning filter. A water filter was used in front of the sample in order to minimize thermal degradation. Steady-state UV-vis diffuse reflectance measurements were carried out in a Varian Cary 1E double beam spectrophotometer with an integrating sphere. Spectra were recorded either using the substrate or the Varian Reference Plates (made of pressed polytetrafluoroethylene) as the reference. Emission and excitation spectra were obtained using an SLM 4800 Spectrofluorometer and were used to follow spectral changes during the irradiation due to destruction of Per and formation of photoproducts. The excitation wavelength used for obtaining the emission spectra was 380 nm, while the emission wavelength used for recording the excitation spectra was 470 nm. The fluorescence from solid samples was measured at 45° using excitation and emission slits set at 4 mm. Lifetime measurements were obtained using a Spex Fluorolog tau-311 spectrofluorometer. Decay times were measured using the frequency-domain or phase-modulation method. The fraction of the emission intensity observed in the usual steady-state measurement due to the i th component in the multi-exponential decay was determined by

$$f_i = \frac{\alpha_i \tau_i}{\sum_j \alpha_j \tau_j}$$

and was used to correlate the multi-exponential decay to the steady-state emission spectra of the sample. In this equation, f_i is the fractional contribution of each decay time to the steady-state intensity, α_i is a pre-exponential factor that, for a molecule displaying a complex decay, represents the fraction of chromophores in each environment, and τ_i represents the decay lifetimes. Samples were irradiated with a 450 W lamp, at an excitation wavelength of 380 nm. Glycogen was used as the scatter. Long pass cutoff filters of 400+ and 450+ were used to isolate the fluorescence emission (to eliminate scatter interference). No emission was detected from silica and alumina powders excited at 380 nm.

Transient absorption spectra and kinetic traces were recorded after excitation with 355 or 266 nm light from a Quantel YG-660A NdYAG (Continuum) laser (16–32 mJ per pulse of 8 ns duration). Data points represent the average of six measurements. Data and instrument setup for the transient spectroscopy were controlled using LabView (Ver. 5.1) from National Instruments®.

ESR measurements were made using a Bruker ER-200D spectrometer at 100 kHz modulation frequency. The modulation amplitude was 3 G, the receiver gain was 8.93×10^4 , the power level 20 mW, the attenuation 10 dB and, the sweep width 100 G. The magnetic field was calibrated with DPPH powder as a standard. Samples were irradiated using a 1000 W Xe(Hg) lamp for 15 min. The samples were contained on a quartz ESR tube which was placed in a Dewar with liquid N_2 .

2.3. Sample preparation

A stock solution of Per in hexane, 1×10^{-4} M, was prepared using Per of 99% purity and an aliquot of it was added to a weighed portion of the adsorbent (alumina or silica gel) in order to obtain the desired loading (moles of Per/g of adsorbent). The solvent was evaporated by rotoevaporation. The effect of water on the photochemistry of the Per was studied by washing the silica gel with nanopure water and evaporating it before adding an aliquot of the stock solution of Per in hexane. Chromatograms of the stock solution and/or of an extracted sample of perylene adsorbed on silica gel showed only the perylene's peak at the wavelength used in the studies.

3. Results and discussion

3.1. Ground state and excited state properties

Similar to the absorption spectra of Per solutions, the diffuse reflectance spectra of adsorbed Per on silica gel or alumina surfaces (Fig. 1) consisted of highly structured bands, consequence of the extended system of conjugated double

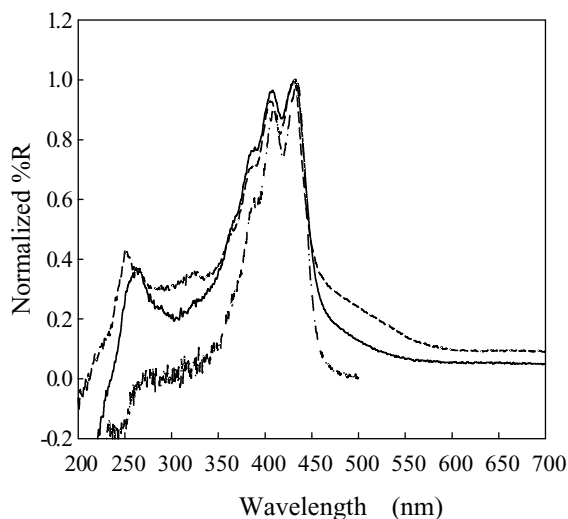


Fig. 1. Diffuse reflectance spectra of perylene adsorbed on and on silica gel 25 Å (—), silica gel 60 Å (---) and alumina (— · —).

bonds and assigned to π, π^* transitions. This indicates that adsorbed Per experiences an homogeneous environment as expected in untreated surfaces which are hydrated [16,17]. Due to the interactions of Per with these oxide surfaces the bands are broader than when in solution and present some loss of the vibronic structure. Also, a small red shift (2 nm) was observed. In addition, on a rigid environment the rotational and vibrational states of Per strongly overlap resulting in the observed broadening. The negative absorption in the wavelength region of 200–250 nm was due to light absorption by these inorganic oxides in this wavelength region.

The fluorescence emission spectra of adsorbed Per changed with surface properties (Fig. 2) and sample loading (Fig. 3). As the average pore size increases the emission spectra resembled more to those in solution in terms of

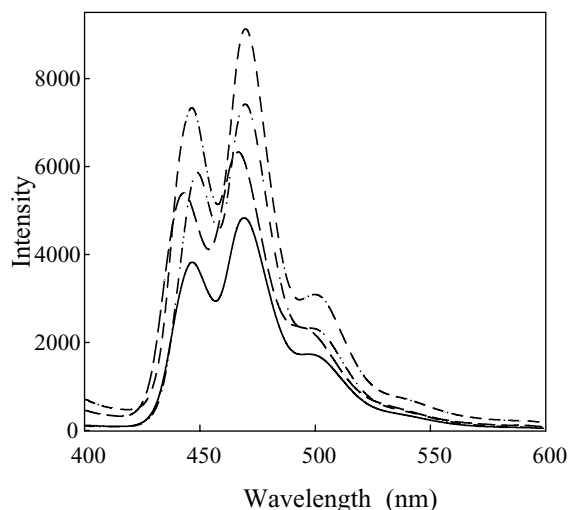


Fig. 2. Emission spectra of perylene adsorbed on alumina Type F-20 (— · —), silica gel 25 Å (— · · —), silica gel 40 Å (---), and silica gel 60 Å (—) at a sample loading of 5.0×10^{-7} mol/g. Excitation wavelength = 380 nm.

the number of bands, relative intensities and wavelength position. The surface inside the pores is more exposed to physisorbed water molecules, as the average diameter increases, thus the adsorbed Per molecules sensed an environment more solution like. De Mayo et al. [16,17] have demonstrated that untreated surfaces, such as those used in this work, are hydrated and molecules adsorbed on such surfaces experience an homogeneous environment in comparison to temperature treated dry surfaces. Nonetheless, the silica gel and alumina surfaces are complex and irregular with respect to their topography and disposition of the silanol groups active in adsorption [18,19]. In these, the binding of molecules with π -systems, such as Per, is largely through hydrogen bonding to the silanols or to physically adsorbed water molecules. Thus, depending on the silanol distribution and the local geometry (pore radius, and curvature of the surface near the adsorption site) the interaction with silanol groups may be different. Also, depending on the shape and size of the PAH, some surface areas will provide more effective binding through the overlap with more silanols, especially geminal and vecinal. Therefore, Per molecules are adsorbed in a variety of local environments subjected to different interactions, and as a consequence, the adsorbed molecules present broader absorption and emission bands than in solution.

Increasing the sample loading induced changes in the emission spectrum (Fig. 3). At loadings greater than 7×10^{-7} mol/g the spectrum extended into the 550–600 nm region and a shoulder at 521 nm on the red edge of the spectrum and a bathochromic shift were seen. Also, the emission intensity in the wavelength region of the first vibronic emission band (437 nm) decreased relative to the

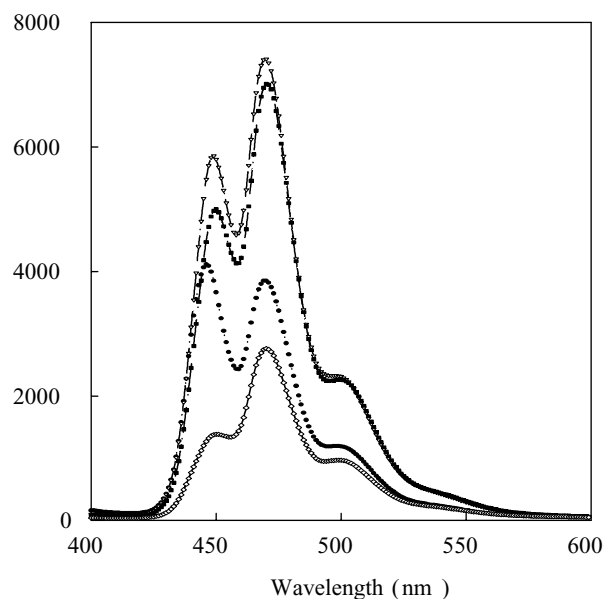


Fig. 3. Emission spectra of perylene adsorbed on silica gel 25 Å at surface loadings of 9.8×10^{-8} mol/g (\bullet), 4.9×10^{-7} mol/g (∇), 7.3×10^{-7} mol/g (\blacksquare), 4.5×10^{-6} mol/g (\diamond). Excitation wavelength = 380 nm.

second vibronic band. No appearance of an unstructured excimer band with a concomitant increase in the monomer band was seen. These spectral changes could not be explained in terms of microcrystals ($\lambda_{\text{max}} = 575 \text{ nm}$) [20,21] or excimer formation ($\lambda_{\text{max}} = 640 \text{ nm}$) [22] on the surface, previously observed for adsorbed PAHs [23]. In addition, the fluorescence excitation spectrum was the same when observed at different emission wavelengths, suggesting that only one emitting species was present. Thus, none of these species could account for the observed spectra.

The decrease in intensity observed on the short wavelength of the spectrum (Fig. 3) is due to autoabsorption effects. This is expected because the fluorescence spectrum overlaps significantly with the absorption spectrum in the wavelength region of 435 nm. This effect was not observed in dilute solutions (10^{-5} M) (data not shown). Further increase in the sample loading ($> 5 \times 10^{-7} \text{ mol/g}$) resulted in a decrease in the total fluorescence intensity, probably due to inner filter effects. Furthermore, as the loading was increased Per was forced to adsorb onto more open regions where oxygen could quench its first excited singlet state. In brief, the proximity of adsorbed Per molecules at high loadings led to aggregate formation and π -stacking interactions that could explain the observed changes in band broadening and shifts.

At the same sample loading, the intensity of the emission was stronger as the pore size of the substrate decreased. This increase is explained in terms of a larger number of Per molecules adsorbed that can absorb and emit due to an increase in the active silanol sites in the silicas of smaller pore size [24].

In the presence of an oxygen atmosphere, a decrease in the perylene's fluorescence intensity was observed suggesting the quenching of the excited singlet state. This quenching can occur by either a direct collision encounter from the gas phase or by diffusion of surface adsorbed O_2 . It was observed that as the pore size increased the fluorescence quenching was more pronounced, being 64% in alumina, 62% in silica gel 25 Å, 70% in 40 Å, and 76% in 60 Å. Similar pore size effects have been reported for the quenching reaction of O_2 and excited pyrene [25]. These have been interpreted in terms that as the pore size increases, the PAHs are adsorbed on an open or flat surface and thus are exposed more to the O_2 molecules, favoring dynamic quenching processes of the singlet state.

A new broad emission band with wavelength of maximum emission at 517 nm was observed in the presence of coadsorbed water (Fig. 4). Although water can displace Per from the active hydroxyls to the less strongly binding sites of free hydroxyls [24] with the possibility of formation of aggregates or microcrystals, the position of this band does not correspond to the reported emission of Per microcrystals [20,21] or excimer [22]. It was observed that when these samples were saturated with O_2 , the monomer emission was quenched while the band with maximum at 517 nm remained. Purging the sample with argon resulted in an increase in the intensity of the monomer emission, and the new

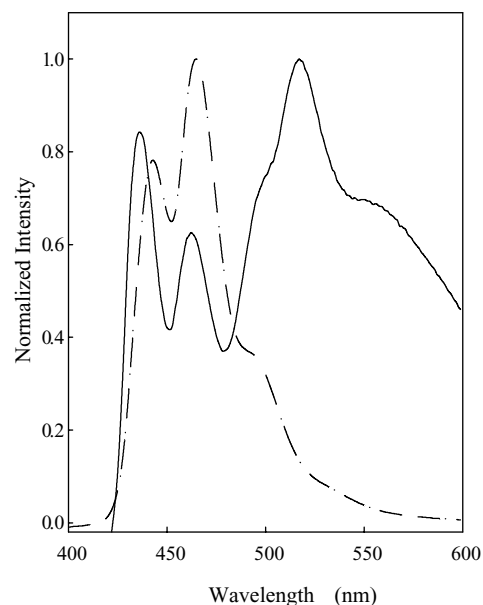


Fig. 4. Emission spectra of perylene adsorbed on silica gel 60 Å at a loading of $5 \times 10^{-7} \text{ mol/g}$ with coadsorbed water (—) and without coadsorbed water (---). Excitation wavelength = 380 nm.

band disappeared under the monomer band. These observations can be understood if the new emission band results from an emission of a weak Per–water–surface complex, that disappears when water is removed from the surface. Water containing solutions of Per in methanol or acetonitrile did not show this band, implying the necessity of a surface interaction for its formation.

As part of the photophysical studies, fluorescence lifetimes were measured for Per in solution and adsorbed on different surfaces. These lifetimes are enclosed in Table 1. In solution, perylene's fluorescence decays followed a single-exponential function. A small increment in the lifetimes was observed in going from a nonpolar, to polar aprotic to a polar protic solvent. This tendency agrees well with those reported by Ware et al. [26] Fluorescence decay curves for Per adsorbed on alumina or silica gel were multi-exponential (data not shown) due to the superposition of different exponentials arising from Per excited singlet states adsorbed at different binding sites. This type of nonexponential decay is commonly observed for adsorbed excited

Table 1

Fluorescence lifetimes of perylene on different environments (in solution or adsorbed)

Solvent or surface	τ_1 (ns)	α_1	τ_2 (ns)	α_2	f_1	f_2
Hexane	3.65	1	—	—	1	—
Acetonitrile	4.20	1	—	—	1	—
Acetone	4.27	1	—	—	1	—
Methanol	4.58	1	—	—	1	—
Alumina	1.60	0.69	4.84	0.31	0.42	0.58
Silica gel 25 Å	1.31	0.56	4.52	0.44	0.27	0.73
Silica gel 60 Å	1.37	0.90	4.82	0.10	0.72	0.28
Silica gel 150 Å	1.20	0.86	3.09	0.14	0.71	0.29

PAHs, and the most correct and accurate method to analyze these data is in terms of lifetime distributions [15,27]. In the present work, and acknowledging the limitations of the traditional method of fitting the decay curves to two or three exponentials in the sense that the exponential terms may not necessarily possess physical meaning, the observed decay curves were fitted nicely to a biexponential function. From these fits two lifetimes were obtained, one short component of 1.5 ns and a longer component of about 4.5 ns. The latter is very similar to that obtained for Per in solution. These results suggest that Per is adsorbed on at least two major different surface regions that influence its emission properties. Ware et al. [15], using a lifetime distribution to analyze the fluorescence decay data of several adsorbed PAHs, observed that in the case of Per its lifetime distributions did not show a significant change from a wet to a dry silica gel surface in comparison to other PAHs. These authors observed a bimodal lifetime distribution suggesting that there are two types of surface sites which dominate in the wet and dry surfaces. For Per, the bimodal description showed maxima around 2 and 7.8 ns, respectively, and its lifetime became slightly longer on going from solution (5–6 ns) to a wet surface (7–8 ns) as compared to a dry surface (2 ns). It was proposed [15] that this small lowering of the lifetime on going from a wet surface to a dry one, as well as the absence of a Ham effect, the solvent relaxation of the excited state and solvent stabilization of the ground state in Per are due to the 1L_a nature of its lowest excited singlet state.

An interesting observation (Table 1) is that the predominant fluorophore fraction varies with the pore size of the surface. On alumina and on silica gel of average pore size of 25 Å, the largest component that predominates was the longer lived, with a lifetime similar to that of Per in so-

lution while on silica gel surfaces of larger pore size (60 and 150 Å), the major component was the one associated to the shorter lifetime. Thus, our results are consistent with a model in which the adsorbent surface consists of two major regions. As the fraction of stronger binding sites increases, such as in the small pores where the relative concentration of active silanols to the total silanols is larger, the Per excited state is stabilized resulting in an increase in the fluorescence emission intensity and lifetime.

3.2. Photochemistry of perylene adsorbed on silica gel and alumina surfaces

The irradiation of Per on silica or alumina surfaces exposed to different atmospheres with 320–510 nm light induced its degradation. This was demonstrated by the decrease in the perylene's absorption or emission intensities (Fig. 5A and B) and by the decrease in the area of its chromatographic peak as a function of the irradiation time. From these data photodegradation rates were calculated assuming a first order kinetic process. Samples irradiated under an argon atmosphere showed a decrease in the rate of photodegradation (0.042 min^{-1}) compared to irradiated samples under oxygen (0.069 min^{-1}). Under the latter conditions, as the intensity of the perylene's emission spectrum decreased as a function of irradiation time, a broad band with maximum around 487 nm was observed. This was not seen in irradiated samples under an inert gas atmosphere. The diffuse reflectance spectra (Fig. 5B) of irradiated samples under both conditions showed the growth of bands in the UV ($\lambda_{\text{max}} = 320 \text{ nm}$) and in the visible region (650 nm). These bands were assigned to adsorbed photo-products in which electron donating groups are being incor-

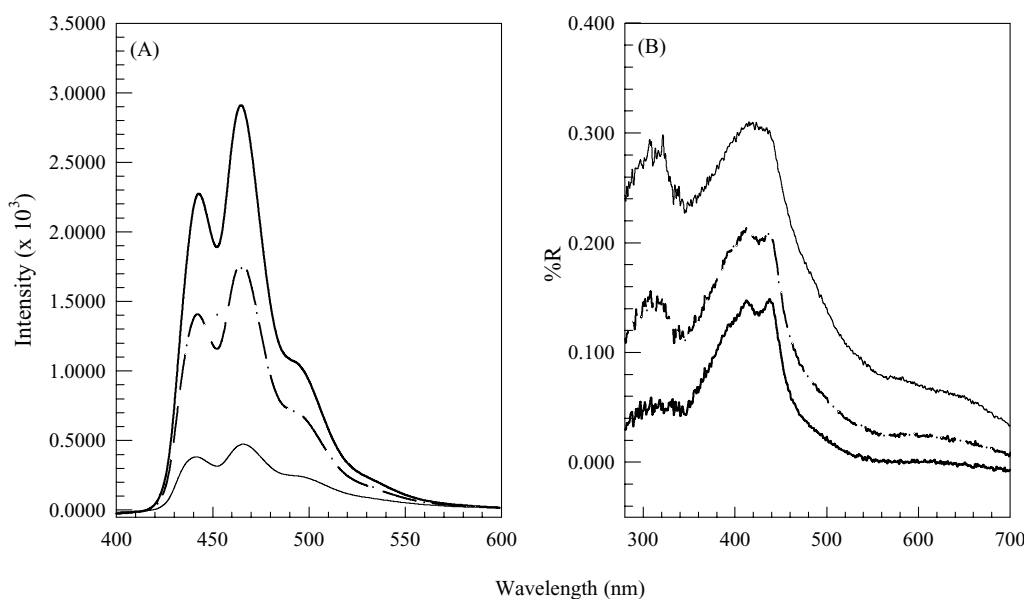


Fig. 5. (A) Emission and (B) diffuse reflectance spectra of perylene adsorbed on silica gel 60 Å at different irradiation times: 0 min (—), 2 min (---), and 15 min (· · ·). Sample loading: $5 \times 10^{-7} \text{ mol/g}$; excitation wavelength: 380 nm; argon atmosphere.

porated into the perylene's ring system. The emission and excitation spectra also showed that the products absorb in the same wavelength region as Per. Using HPLC and UV-Vis diode array and MS (APcI+) detectors several photoproducts were identified. Among these were 1,12-perylenedione and 3,10-perylenedione, another dione with m/z of 283, and perylene diols ($m/z = 285$). Their mechanism of formation and the effect of the chemical and physical properties of the surface on their yield of formation are part of another manuscript to be submitted.

The increase in the photodegradation rate and formation of different emitting and absorbing products under an oxygen atmosphere suggested a major role of oxygen reactive species in the photochemical processes in addition to the effects caused, already discussed, to the photophysical processes of adsorbed Per. Recently, the rate constants for quenching by molecular oxygen of the excited singlet and triplet state of Per in cyclohexane were reported [28]. These present values of 15×10^9 and $1.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. A value of 0.28 for the efficacy of singlet oxygen production by the excited singlet state of Per was also reported while for other 10 PAHs this was zero. These results were interpreted [28] in terms of quenching of both excited singlet and triplet states, with and without energy transfer, through a charge-transfer assisted process. In the case of excited Per, for which its intersystem crossing quantum is small in solution and on the adsorbed state, the possibility of production of singlet oxygen through a reaction of the perylene's excited singlet state and its subsequent reaction with adsorbed Per could explain the increase in the rate of photodestruction under an oxygen atmosphere.

The rate of photodegradation increased slightly with an increase in average pore size (Table 2) while it decreased by a factor of two with an increase in the sample loading from 5×10^{-7} to $15 \times 10^{-7} \text{ mol/g}$. The effect of average pore size is explained in terms that in the larger pore size samples, Per is adsorbed onto more open regions at the surface, thus increasing the possibility of oxygen not only quenching the excited singlet state but producing singlet oxygen which reacts with the adsorbed Per. This reaction was confirmed by generating singlet oxygen using methylene blue as the sensitizer in powdered samples containing Per. After irradiating methylene blue for 14 h, 93% of the Per was degraded when adsorbed on silica gel (60 Å).

Table 2

Photodegradation rate constants of perylene adsorbed on different surfaces under an air atmosphere and at a sample loading of $5 \times 10^{-7} \text{ mol/g}$, unless otherwise specified

Surface	k (min^{-1})
Alumina	0.022
Silica gel 60 Å	0.063
Silica gel 150 Å	0.069
Silica gel 60 Å, loading = $15 \times 10^{-7} \text{ mol/g}$	0.030
Silica gel 60 Å, sunlight	0.023

The decrease in the rate with an increase in the sample loading could not be explained in terms of the formation of ground state pairs or excimers with absorption bands that could act as light sinks of the incident light without inducing any photochemistry [29–31]. Thus, a possible explanation is that even if the aggregates do not absorb, self quenching reactions in the aggregates can deactivate Per resulting in a decrease in the rate of photodegradation. Coadsorbed water enhanced the photodegradation rate by 12% and the intensity of the emission band with maximum at 517 nm decreased at a similar rate as the intensity of the monomer band, suggesting that it results from a Per–water–surface complex.

3.3. Reactive intermediates

Intermediates participating in the photochemical processes were identified by electron spin resonance and diffuse reflectance laser photolysis techniques to provide information on the photodegradation mechanism and to understand the effect of the properties of the substrate, coadsorbed gases, and sample loading on the steady-state photolysis experiments. The transient diffuse reflectance spectra of laser irradiated samples of Per adsorbed on different surfaces using 266 or 355 nm photons for excitation are shown in Fig. 6B. For comparison the transient laser photolysis spectra of Per in acetonitrile purged with N_2 and exposed to air are depicted in Fig. 6A. The broad band with maximum around 540 nm was assigned to the perylene's radical cation absorption band on the basis of comparison with reported spectra for this species generated by laser flash photolysis [32,33]. In a nitrogen saturated solution of Per in acetonitrile, the transient spectra showed bands with maxima at 490 and 570 nm, assigned both to a triplet–triplet and radical anion absorptions, respectively [33]. The imperceptible presence or absence of a triplet–triplet absorption band in the transient diffuse reflectance spectra of adsorbed Per even under a nitrogen atmosphere can be rationalized in terms of a reduction in the intersystem crossing quantum yield for adsorbed Per compared to that in solution (0.009 methanol) [34]. In addition, any contribution from the triplet state to the formation of the radical ions is assumed to be negligible. In the transient spectra of adsorbed samples the shoulder around 570 nm could suggest the presence of a radical anion formed by the reaction of the ejected electron with a neutral Per.

Although the shape of the transient diffuse reflectance spectrum of the radical cation was independent of the sample loading or average pore diameter, its initial yield and decay rate presented a dependence in these parameters (data not shown). These decreased with an increase in average pore size. A similar trend was observed for the intensity of the fluorescence emission. On an alumina surface, the initial radical cation yield was smaller than on a silica gel surface and the decay was faster, suggesting that the radical cation is less stable on alumina surfaces. In general, the nonexponential decay of the radical cations presented an initial fast

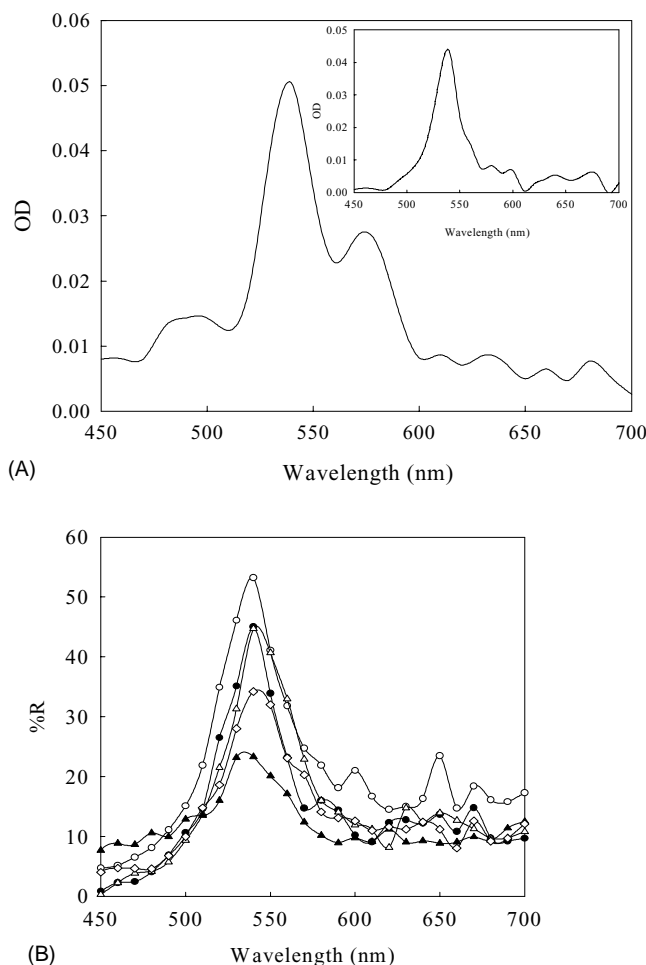


Fig. 6. (A) Laser flash photolysis spectrum of perylene in acetonitrile purged with N₂ (g) (insert in air atmosphere). (B) Diffuse reflectance laser flash photolysis spectra of perylene adsorbed on silica gel 25 Å (○), silica gel 60 Å (●), silica gel 150 Å (△) and alumina Type F-20 1 × 10⁻⁶ mol/g (▲), under an air atmosphere. The surface loading was 5 × 10⁻⁷ mol/g, unless otherwise specified. Excitation wavelength = 355 nm; laser power energy = 12 mJ.

decay followed by a slower one. This behavior has been ascribed [35,36] to the existence of the distribution of the PAH cations produced at different active sites decaying as a result of geminal recombination with the electron. The observation that the initial decay rate is affected by the average pore diameter suggests, as in the case of the fluorescence measurements, differences in the proportion of active sites in these surfaces. This observation correlates well with the fact that the photodegradation of adsorbed Per on the surfaces of smaller pore diameter was slower in comparison to the larger pore surfaces. In terms of the participation of the radical cations in the photodegradation processes, these recombine with the electron at a faster rate on the smaller pore surfaces resulting in a decrease in the probability of other reaction channels for the radical cation. This implies that in surfaces of larger pore diameters, Per cations are adsorbed on physisorption sites separated at larger distances from the electrons.

Purging the powdered samples with oxygen resulted in a decrease in the initial yield of the radical cations. These can be explained in terms that an increase in the oxygen concentration resulted in the physical and chemical quenching of the perylene's singlet excited state, thus increasing the rates of competing reactions and lowering the radical yield. Also this suggests that the precursor of the radical cation is the perylene's singlet excited state.

A decrease in the surface loading by a factor of 10 (5 × 10⁻⁷ to 5 × 10⁻⁶ mol/g), resulted in a decrease in the initial yield although an increase in the initial decay rate was observed. Similar loading effects on the initial decay rates of adsorbed PAH radical cations have been reported [35]. This increase has been explained in terms that at high loadings, electrons can combine with radical cations other than their geminate partner as the cation–cation separation distances approach cation–electron separations with an increase in the loading.

The presence of coadsorbed water caused a dramatic effect on the transient absorption spectrum. A new band was observed with maximum around 440 nm and the yield of the radical cation decreased significantly. The decay rate of the species absorbing at 440 nm was different (slower) compared to the decay of the radical cation. This species is tentatively assigned to a radical resulting from a reaction of the radical cation with water. Reactions of PAH radical cations with water to form diones, diols and alcohols have been postulated [37].

The electron spin resonance spectrum of irradiated Per adsorbed on silica gel 25 Å at 77 K (Fig. 7) is very similar to that reported by Flockhart et al. [38,39] for the Per radical cation adsorbed on activated alumina and by Kotov et al. [40] and Terenin et al. [41] for the Per radical cation adsorbed

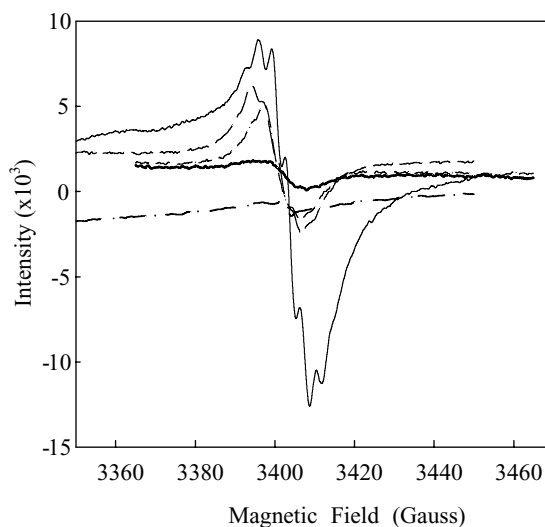


Fig. 7. E.S.R spectra of irradiated perylene adsorbed on silica gel 25 Å (—), silica gel 60 Å (— — —), silica gel 150 Å (— — — —), silica gel 150 Å + H₂O (— · — ·), alumina Type F-20 (— · — · — ·). Modulation amplitude = 3 G; receiver gain = 8.93 × 10⁴; power = 20 mW; attenuation = 10 dB; temperature = 77 K; irradiation time: 15 min.

on activated alumino-silicates. The intensity of the signal increased with irradiation time and the shape of the signal did not change when varying the microwave power from 2 to 80 mW, suggesting the presence of only one radical species. The radical cation yield decreased with an increase in pore size (Fig. 7). This behavior correlates positively with the dependence of the initial radical yield, as determined from the intensity of the band in the transient spectrum, on pore size. As discussed above, on surfaces of smaller pore diameters the number of active sites is greater than in those with larger pores, thus a greater number of Per molecules can be adsorbed per unit area. This results in greater light absorption by these samples and production of radical cations. These adsorbed radicals were very stable since warming the irradiated samples to room temperature and cooling back to 77 K produced only a small change in the intensity of the signal.

The radical spectrum showed better resolved hyperfine structure when adsorbed onto silica gel 25 Å than in the surfaces with larger pores. Because hyperfine structure can be taken as an indicator of the mobility of the radical on the surface, this surprising result suggests that the Per radical cation has more mobility on the smaller size silicas. This can be rationalized if on the silica of larger pores the Per radicals are anchored to the surface by two or more silanols reducing its mobility. Osipov et al. [42] reported that adsorption of highly polarizable organic molecules is generally accepted to involve interactions with the surface hydroxyls and it has been suggested that the vicinal silanols provide active sites for the adsorption of PAHs. Thus, based on this report and on our results, it is suggested that silicas of larger pore diameters contain a larger number of vicinal silanols. These results on the radical mobility, when adsorbed on surfaces of different pore size, followed the same trend as those observed in the transient studies for the decay rate of the radical cation, in the sense that these rates were faster on the surfaces of smaller pore diameter. In terms of the photodegradation rates, these decreased with decreasing pore diameter suggesting that on these surfaces the fast decay of the radical cation by recombining with the electron does not lead to net degradation of Per.

4. Conclusions

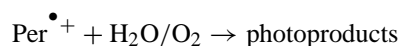
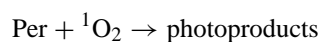
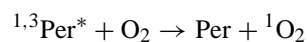
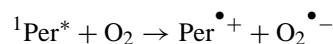
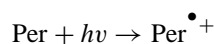
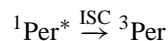
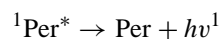
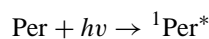
In this work we have demonstrated that the physical and chemical properties of the surface induce changes in the absorption, emission and photochemical properties of adsorbed Per. These changes can be also used to study interactions between the molecule and the surface.

The absorption and emission spectra of Per adsorbed onto alumina and silica gel of different average pore diameters were very similar to those observed for this molecule in polar solutions. As a consequence of surface interactions, aggregate formation and π -stacking, the major effects observed for adsorbed Per were broadening of the bands, loss of vi-

bronic structure, and small red shifts. On the surface, excited Per decayed emitting fluorescence with lifetimes that depended on the nature of the surface. These decays were fitted to a double-exponential function suggesting that Per was adsorbed to at least two different physisorption regions in which the fluorophores population varies according to the density of active sites in the surfaces of different average diameter.

Although in solution the first excited singlet state can intersystem cross to a triplet state that shows an absorption maximum at 490 nm, in the adsorbed state under an inert atmosphere the triplet-triplet absorption was not observed. Reactive radical cations, formed through either the direct photoionization or an electron transfer process from the excited Per to physically adsorbed O₂, were detected in all surfaces. The initial yields and decay rates of the radical cation depended also on the chemical nature of the surface and on the average pore diameter. The mobility of these radicals is affected by the way in which the molecule is anchored to the surface in the different pores rather than on the size of the pore. This was demonstrated by the changes in the hyperfine structure in the E.P.R. spectrum.

Oxygen quenched the fluorescence state and accelerated the photodegradation through the participation of oxygen reactive species, singlet oxygen. New absorption and emission bands were formed in irradiated samples containing oxygen and the incorporation of oxygen functionalities into the Per molecule was demonstrated by the identification of some of the products as diones and diols. These results are summarized in the following scheme:



Because the highly polar and non-conducting surfaces of silica gel and alumina may simulate, to a first approximation, the inorganic oxide fraction encountered in some aerosols, our results could shed some understanding on the atmospheric transformations and sinks of this PAH in the more complex environment of the atmospheric particulate matter.

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