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Journal of Photochemistry and Photobiology A: Chemistry 109 (1997) 229–236

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Spectroscopy and photochemistry of fluorene at a silica gel/air interface

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Received 3 January 1997; revised 8 April 1997; accepted 14 April 1997

Abstract

The emission spectroscopy of fluorene has been studied at a silica gel/air interface at surface loadings from 1.5% to 77.1% of a monolayer. Both monomer and excimer-like emissions are observed on the surface. The excimer-like emission, centered at 350 nm, arises from excitation of ground-state van der Waals pairs of fluorene molecules. Photolysis into the van der Waals dimers at room temperature does not lead to dissociation into constituent monomers; however, irradiation of fluorene monomers at a silica gel/air interface leads to production of 9-fluorenone as the only identifiable photoproduct in 72% yield. Fluorene triplet and cation radical are both observed at the silica gel/air interface by transient diffuse reflectance spectroscopy. Sensitization of singlet molecular oxygen by silica-sorbed methylene blue, in the presence of co-sorbed fluorene, does not lead to fluorene oxidation, thus suggesting that oxidation by direct photolysis does not involve an energy transfer mechanism. An electron transfer oxidation mechanism is proposed to account for the observed photochemical oxidation of fluorene at the silica gel/air interface. © 1997 Published by Elsevier Science S.A.

Keywords: Fluorene; Photochemistry; Silica gel; Fluorenone

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are toxic, many are carcinogenic, and the widespread occurrence of these pollutants in the environment makes the photo-oxidation of PAH a topic of current interest. Sixteen PAH have been designated as priority pollutants [1]. Small PAH (anthracene and phenanthrene) in the lower troposphere have been shown to reside primarily in the gas phase at ambient temperatures; however, as the temperature is decreased, even small PAH begin to partition onto atmospheric particulates [2]. At upper tropospheric levels, where ambient temperatures are well below those at the Earth's surface and unfiltered sunlight has a stronger UV component, photochemical transformations of PAH at the particulate/gas interface can be expected to play a role in controlling the environmental fate of these anthropogenic pollutants.

Concentrations of water-insoluble inorganic particles in the troposphere, are estimated to be in the range of 1–300 mg m^{-3} [3]. Insulators such as SiO_2, Al_2O_3, silicoaluminates and $CaCO_3$ are estimate to comprise 20–30% of inorganic atmospheric particulates [3]. One objective of our research is to understand the mechanisms of PAH photochemical transformations at interfaces which model this important class of environmental media. The highly polar surfaces of non-semiconducting inorganic oxide particulates found in the environment are simulated to a first approximation by commercial silicas and aluminas. A knowledge of the mechanisms of photochemical degradation of PAH at the solid/air interface of relatively clean silicas and aluminas provides important environmental fate data and a basis for investigating photochemical mechanisms on native environmental particulates. A second objective of our research is to elucidate the fundamental role of substrate–surface interactions in controlling the photochemistry.

Previous work in our laboratories has focused primarily on determining the products and mechanisms of the photochemical oxidation of PAH sorbed onto silicas and aluminas [4]. It has generally been found that those PAH which are good acceptors of singlet molecular oxygen (e.g. anthracene, phenanthrene, tetracene, etc.) react by an energy transfer mechanism with subsequent decomposition of thermally unstable peroxide and/or dioxetane products [4]. Several PAH that are not good acceptors of singlet molecular oxygen (e.g.

Abbreviations: PAH, polycyclic aromatic hydrocarbon; FL, fluorene; FLO, 9-fluorenone; ESR, electron spin resonance; HPLC, high performance liquid chromatography; SCE, standard calomel electrode

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PII S1010-6030(97)00148-2

naphthalene, 1-methylnaphthalene) readily undergo photolysis at the solid/air interface by what appears to be an electron transfer mechanism [4j]. The identity of the initial electron acceptor (e.g. Lewis acid site, molecular oxygen etc.) is not known; however, superoxide formed from photolysis of naphthalene at a silica gel/air interface has been directly observed by ESR [4j].

Fluorene (FL) is among the PAH which have been elevated to the status of priority pollutant [1]. When sorbed on different atmospheric particulate substrates, FL has previously been determined to have photolytic half-lives of 110 h (silica gel), 62 h (alumina), 37 h (fly ash) and >1000 h (carbon black) [5]. The role of the surface in controlling the observed differences in photolytic half-lives was unexplained in the previous work and the mechanism and products of photodegradation were not investigated. This report describes the spectroscopy and photochemistry of FL at a silica gel/air interface and is a continuation of our efforts to understand PAH photochemistry under controlled conditions which allow for mechanistic interpretation and give results that are relevant to environmental processes.

2. Experimental details

2.1. Materials

Fluorene (Aldrich Chemical Co. Inc., Milwaukee, WI; purity 99%) was recrystallized from ethanol twice before use. 9-Fluorenone (Aldrich; technical grade) was recrystallized from cyclohexane twice before use. Methylene blue (Aldrich; reagent grade) was used as received.

The physical characteristics of the silica gel used in this work are identical to those previously reported [4]. The N_2 BET surface area for the silica gel was determined (Autosorb, Quantachrome Corp.) to be 274 $m^2\ g^{-1}$ with an average pore size of 60 Å [4e]. The silica gel used in these experiments contained less than 10 ppm iron, 141.4 ppm aluminum and less than 4.9 ppm copper [4g]. The silica gel was used after activation by heating for 24 h at 200 °C under air, followed by cooling to room temperature in a desiccator charged with anhydrous $CaSO_4$ (Drierite®, Aldrich). The silica gel was loaded with FL (1.0×10^{-5} mol g^{-1}, 1.5% monolayer; 2.5×10^{-5} mol g^{-1}, 3.9% monolayer; 1.0×10^{-4} mol g^{-1}, 15.4% monolayer; and 5.0×10^{-4} mol g^{-1}, 77.1% monolayer) by adsorption from a cyclohexane (Baxter Healthcare Corp., Burdick and Jackson Division, Muskegon, MI; HPLC grade) solution following the procedure outlined in earlier papers [4]. The percent monolayer coverage is calculated as previously described [4i], assuming a fractal dimension of 2.8 for the silica gel [6], and cross-sectional areas of 16.2 $Å^2$ and 46.2 $Å^2$ for nitrogen and FL respectively. The calculation yields a surface area of 180.2 $m^2\ g^{-1}$ available to FL.

2.2. Photolysis and product analysis

Irradiation was done in quartz tubes irradiating with a 300 nm Rayonet photoreactor (irradiance of 2.68×10^{15} photons $cm^{-2}\ s^{-1}$) employing a horizontal tube orientation as previously described [4]. Photolyses were done under an atmosphere of air introduced directly into the tubes from the laboratory or under argon (Air Products Inc., Knoxville, TN; ultra high purity) introduced after evacuation of the sample to 5 μm of mercury for 10 h. Photoproducts were removed by washing the silica gel first with methylene chloride and then with methanol. Products were analyzed by GC using an internal standard method and calibration with known materials of identical chemical structure.

2.3. Spectroscopic measurements

Steady state diffuse reflectance spectra were recorded on a Cary-4 spectrophotometer equipped with an integrating sphere. Samples for emission spectra were prepared by loading FL on silica as described above and placing the dry sample in a 2 mm pathlength flat cell attached to a greaseless stopcock through an Ace-Glass® #7 fitting. The cell was attached to a vacuum line and evacuated overnight to a pressure of 5 ± 2 μmHg of mercury. The sample was back-filled with argon and the spectra were recorded immediately after removing the sample from vacuum. Baseline correction was done with a spectrum recorded from identical silica gel which had not been loaded with organics. Emission spectra were recorded from the sample front face on a Spex Fluorolog fluorimeter equipped with double monochromators in the excitation and emission paths (1.76 nm bandpass). Emission spectra are reported fully corrected.

Transient absorption spectra were recorded after excitation with 266 nm light from a Quantel YG-660A NdYAG (Continuum, Santa Clara, CA) laser (4–10 mJ per pulse of 8 ns duration). The signal was collected using an apparatus previously described [7].

3. Results

3.1. Steady-state spectroscopy

As the surface loading of FL is increased from 1×10^{-5} mol g^{-1} to 5×10^{-4} mol g^{-1} there is a continuous change in the excitation spectrum ($\lambda_{em}=330$ nm), Fig. 1. As the surface coverage is increased, the intensity of the excitation spectrum decreases and a weak band begins to appear on the red edge of the spectrum. The arrows in Fig. 1 show the change in spectral intensity with increasing surface coverage. Analogous spectral shifts are also observed in the diffuse absorption spectra at the same surface coverages. Similar absorption and excitation shifts with increasing surface coverage have previously been observed for other PAH on silica gel at comparable loadings [4,8].

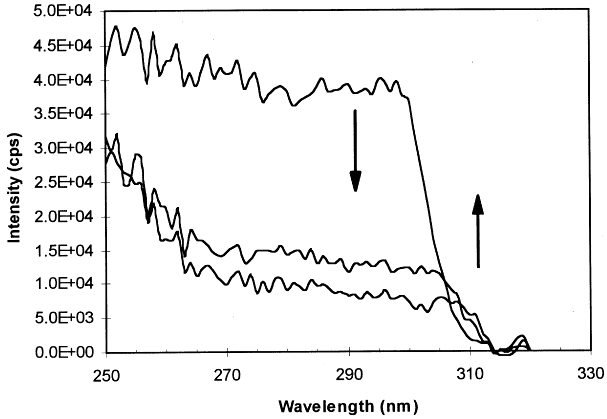


Fig. 1. Excitation spectrum (λem = 330 nm), of FL at surface loadings of 1×10^{-5}, 1×10^{-4} and 5×10^{-4} mol g^{-1}. The arrows show the direction of fluorescence intensity change with increasing surface coverage.

The fluorescence of FL at a silica gel/air interface (surface loading of 1×10^{-4} mol g^{-1}) is >95% quenched by air. This behavior is consistent with previous observations in our laboratory [4]. The fluorescence spectra (λ_{ex} = 260 nm) of FL on silica gel at surface loadings from 1×10^{-5} mol g^{-1} to 5×10^{-4} mol g^{-1} are shown in Fig. 2. These spectra reveal a dramatic shift in the emission maximum to longer wavelengths with increasing surface coverage. The increased fluorescence intensity on the red edge of the spectrum is assigned to an excimer-like emission centered at ca. 350 nm. The location of the excimer-like emission maximum closely resembles that from FL van der Waal's dimers formed in a supersonic jet (centered at 357 nm) as opposed to the excimer emission in solution (centered at 370 nm) [9]. Excimer-like emission from PAH ground-state associated pairs and higher order aggregates on silica gel surfaces have previously been observed by ourselves and others [4,8].

Fig. 3 shows the excitation spectra (λ_{em} = 375 nm) for FL on silica at surface loadings from 1×10^{-5} mol g^{-1} to 5×10^{-4} mol g^{-1}. The monitoring wavelength was chosen by virtue of the small amount of monomer emission observed at 375 nm. The spectra in Fig. 3 reveal a weak absorbance, extending to approximately 350 nm, that grows in as the surface coverage is increased (indicated by the arrow in Fig. 3). The onset of the new band is shifted red by approximately 4500 cm^{-1} relative to the monomer emission. The fluorescence (λ_{ex} = 310 nm) associated with the new absorption is also shown (Fig. 4) to intensify as the surface coverage is increased. The emission associated with the new absorption clearly corresponds to the excimer-like emission. Photolysis of a sample under argon (FL surface loading of 5×10^{-4} mol g^{-1}) at 320 nm (10 min., 8 nm bandpass, 2.47×10^{17} photons cm^{-2} s^{-1}), a wavelength where the ground state pairs absorb, does not result in any apparent change in the fluorescence spectral profile, thus demonstrating that the ground-state pairs on the surface do not readily dissociate upon excitation.

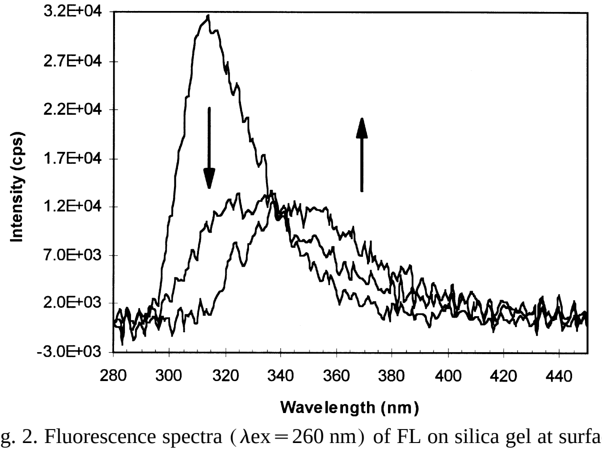


Fig. 2. Fluorescence spectra (λex = 260 nm) of FL on silica gel at surface loadings of 1×10^{-5}, 1×10^{-4} and 5×10^{-4} mol g^{-1}. The arrows show the direction of fluorescence intensity change with increasing surface coverage.

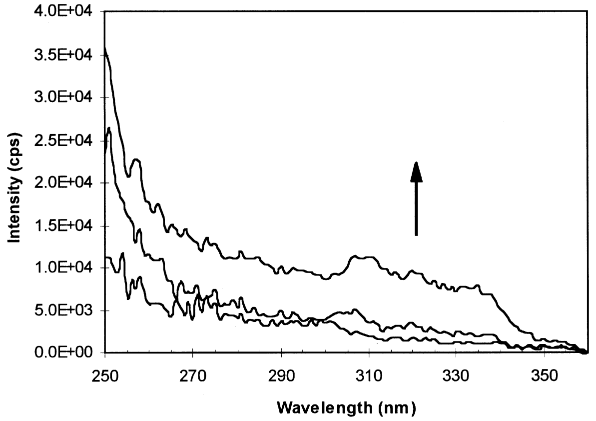


Fig. 3. Excitation spectra (λem = 375 nm) for FL on silica at surface loadings of 1×10^{-5}, 1×10^{-4} and 5×10^{-4} mol g^{-1}. The arrow shows the direction of fluorescence intensity change with increasing surface coverage.

The excitation (λ_{em} = 475 nm) and fluorescence (λ_{ex} = 310 nm) of the ground-state pairs (surface coverage of 5×10^{-4} mol g^{-1}) are shown together in Fig. 5. From these spectra we assign a 0–0 transition for the ground-state pairs to the crossing point at 320 nm (3.87 eV, 89.3 kcal-mol^{-1}) and the maximum for the excimer-like emission to 350 nm (3.54 eV, 81.7 kcal mol^{-1}). Fluorescence and exci-

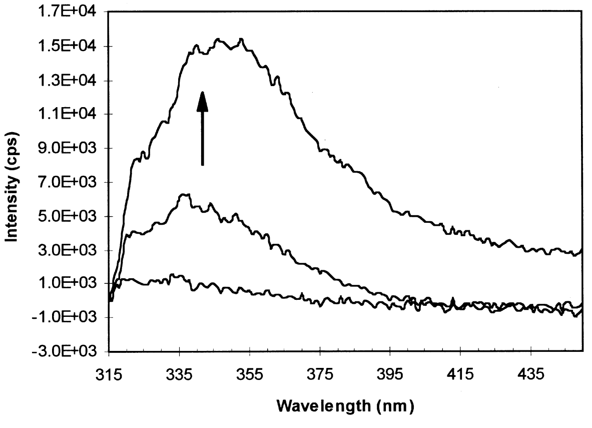


Fig. 4. The fluorescence (λex = 310 nm) associated with the new absorption at surface coverages of 1×10^{-5}, 1×10^{-4} and 5×10^{-4} mol g^{-1}. The arrow shows the direction of fluorescence intensity change with increasing surface coverage.

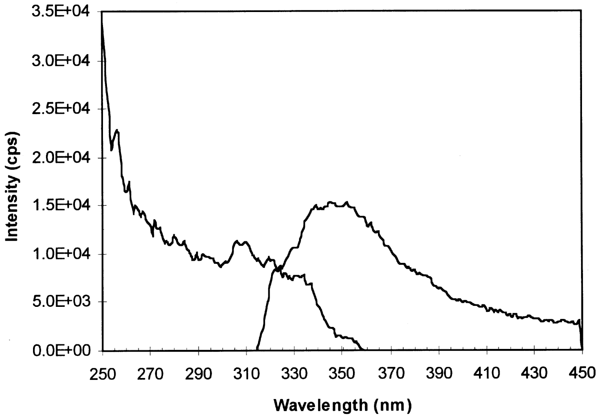


Fig. 5. The excitation (λem = 475 nm) and fluorescence (λex = 310 nm) of the ground-state pairs at a surface coverage of 5×10^{-4} mol g^{-1}.

tation spectra for FL (2.5×10^{-5} mol g^{-1}) on silica (not shown), where primarily monomeric FL is present, allow for assigning a monomer 0–0 transition at 306 nm (4.05 eV, 93.4 kcal mol^{-1}). The 0–0 value assigned to the monomer on silica is slightly red shifted relative to the value reported for FL in heptane (301 nm, 4.12 eV, 94.9 kcal mol^{-1}) [10]. The red shift in the 0–0 transition is expected for a π–π^* transition in the more polar environment of the silica surface [10].

3.2. Time resolved spectroscopy

The transient diffuse reflectance spectrum for FL at a silica gel/air interface (surface loading of 2.5×10^{-5} mol g^{-1}) is shown in Fig. 6. Absorption maxima are observed at approximately 380 nm (strong), 450 nm (weak) and 510 nm (weak). The intensity of the transient signal at 380 nm is partially quenched by oxygen; however, the transient at 450 nm is not similarly quenched, as shown in Fig. 7. The oxygen sensitivity of the 510 nm transient can not be reliably determined from our data. The 380 nm band is seen to decay in the nitrogen purged sample to a final intensity coincident with that observed in the air saturated sample. The portion of the 380 nm transient that is quenched by oxygen is assigned to the triplet of FL, as previously reported in polar solvents [11]. The observed quenching of the 380 nm band in the nitrogen purged sample is attributed to residual oxygen diffusing out of small pores where it was not removed by the nitrogen purge. We credit the decay of the triplet to oxygen quenching due to the observed lifetime being considerably shorter than the 150 μs lifetime reported for FL triplet in hexane at 300 K [11]. The portion of the transient absorption at 380 nm that is not quenched by air is assigned to the cation radical of FL, as previously reported for the cation radical in solution [12]. The origins of the 450 nm and 510 nm transients are tentatively assigned to 9-fluorenone radical anion and 9-hydroxyfluorenyl radical respectively [13].

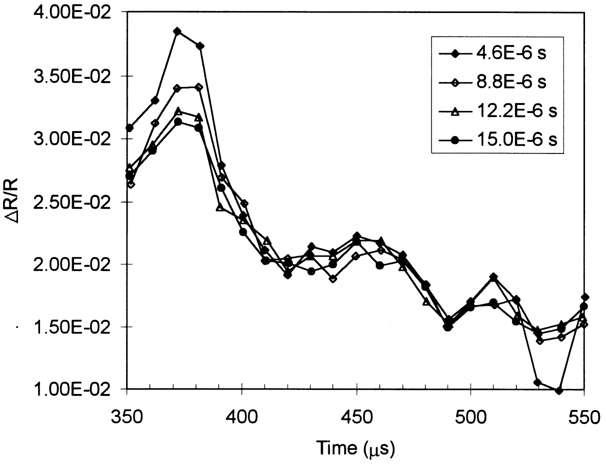


Fig. 6. The transient diffuse reflectance spectrum for FL at a silica/air interface, surface loading of 2.5×10^{-5} mol g^{-1}.

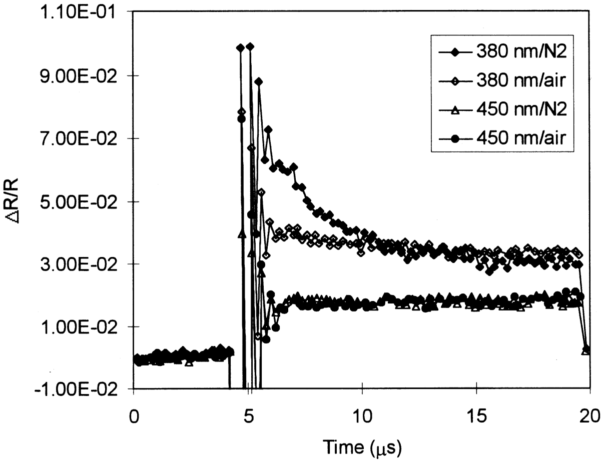


Fig. 7. Temporal profile of of the transient signal from Fig. 6 recorded at 380 and 450 nm in nitrogen purged and aerated samples.

Owing to the range of pore sizes present in the silica surface, it is possible for oxygen to diffuse into small pores which are inaccessible to larger PAH molecules. Oxygen in these smaller pores is difficult to remove, even under vacuum. Partial removal of oxygen from the larger pores results in a silica sample where the PAH and residual oxygen are segregated. Examination of the fluorescence from samples immediately after evacuation reveals strong PAH fluorescence; however, slow diffusion of oxygen out of the smaller pores gradually replenishes some of the oxygen removed from the larger cavities where the PAH resides. A slow decrease in the fluorescence intensity is observed in these samples [4]. The fluorescence is recovered by re-evacuating the sample. Fluorescence quenching in silica-sorbed PAH is more closely examined elsewhere [14].

3.3. Photochemistry

Photolysis of FL (2.5×10^{-5} mol g^{-1}) at a silica gel/air interface leads to the generation of 9-fluorenone (FLO) as the only isolable photoproduct. FLO accounts for up to 72 mol.% of the consumed FL. Some non-extractable and unidentifiable material remains on the silica after washing the surface. The FL photolysis proceeded with a 9 h half life. The half life observed on silica in this work cannot be directly compared with the values previously reported by others because of differences in light sources and differences in scattered light loss from different experimental setups. No dark reaction was observed for FL on the silica surface over a three day period. FLO does not undergo photochemical degradation when adsorbed alone on silica gel.

Likewise, photolysis (650 nm) of methylene blue (1.7×10^{-5} mol g^{-1}), a known sensitizer of singlet molecular oxygen on silica gel surfaces [15], in the presence of co-sorbed FL (2.5×10^{-5} mol g^{-1}) did not result in any detectable consumption of FL or the formation of any oxidation product. Good acceptors of singlet molecular oxygen can be readily oxidized at the silica gel/air interface using this methodology [4].

Direct photolysis (300 nm, 6 h) of FL (2.5×10^{-5} mol g^{-1}) and FLO(2.5×10^{-5} mol g^{-1}) co-sorbed on silica led to the loss of both species. The FL consumption (36%, 9.0×10^{-6} mol g^{-1}) is within experimental error of the anticipated FL loss (38%) based on the rate of photolysis in the absence of co-sorbed FLO. Moreover, the amount of consumed FLO (1.3×10^{-5} mol g^{-1}) was equivalent to 26% of the originally co-sorbed FLO in addition to all of the FLO produced from photochemical oxidation of FL (assuming a 72% yield of FLO from FL photolysis, vide supra). Additionally, direct photolysis (300 nm, 2 h) of 9-hydroxyfluorene (2.5×10^{-5} mol g^{-1}) sorbed on silica led to the formation of FLO. The surface-sorbed 9-hydroxyfluorene does not undergo any dark reaction over a period of 24 h.

4. Discussion

4.1. Stable ground state complexes

Ground-state pairing may arise as a consequence of the method of loading the PAH onto the surface by adsorption from solution. When the PAH is loaded onto the solid by adsorption from a nonpolar solvent (usually cyclohexane in our experiments), ground-state pairing is facilitated by what we have described as a solvent pooling effect [4c]. As the nonpolar solvent is removed from the polar solid, some PAH will be isolated in solvent pools and eventually left on the dry surface (these molecules give monomer emissions); however, some solvent pools will contain two or more PAH molecules and lead to ground-state pairing or clustering as the solvent is removed. This process can lead to the observation of unique excimer-like emission from solid/air interfaces. Excimer-like emission may be observed at loadings of only a few percent of a monolayer in some cases [4c].

Ground state complexes of pyrene have been well studied on silica gel, alumina and calcium fluoride and theoretical interpretation of the associated potential energy surfaces has been given [16]. It was previously suggested that pyrene interaction with surface silanols might influence the electronic polarization sufficiently to lend some stabilization to sorbed pyrene ground-state pairs [16]. The excitation spectrum associated with the pyrene ground-state pairs was shifted 800 cm^{-1} to the red of the monomer [16]. In the course of our previous work, we have observed excimer-like emission from several PAH adsorbed on silica and alumina surfaces [4]. Similar emissions have previously been observed by other researchers as well [8]. Oxygen strongly quenches PAH fluorescence at inorganic oxide/air interfaces, and it is necessary to rigorously degas samples to observe the emission spectra. Introducing solvent vapor into dry samples containing ground-state pairs is sufficient to allow molecular motion and result in the disappearance of the excimer-like emission [4c]. This experimental methodology offers the unique opportunity to study the spectroscopy and chemistry of PAH monomers and ground-state pairs (or aggregates) at a solid/air interface.

Excimer emission has been reported from the excitation of fluorene (FL) ground-state van der Waals pairs in a supersonic jet and from highly purified material in solution [9]. The dispersed fluorescence spectrum of the dimer is reported to be structureless and centered at 357 nm (28 000 cm^{-1}), while the solution excimer is reported to be centered at 370 nm (27 000 cm^{-1}) [9]. Theoretical models for the excimer estimate the inter-ring distance to be 3.5 Å [17]. In a supersonic jet expansion, ground-state van der Waals pairs dissociate upon excitation to give monomer fluorescence [9]. The red shift in excitation for the FL ground-state pairs observed on silica (4500 cm^{-1}) is much greater than the shift previously observed for pyrene. Furthermore, the excitation spectrum associated with the excimer-like emission from FL ground-state pairs on the silica surface mirrors the fluorescence and suggests that a Franck–Condon envelope exists for the surface-stabilized pair. Failure to dissociate the FL ground-state pairs upon exciting into the associated absorption band demonstrates the presence of an insurmountable barrier to photodissociation on the silica surface at room temperature. Clearly, the solution phase model for excimer formation does not explain the complex behavior observed at solid/gas interfaces. We propose that the surface provides a barrier to FL pair formation and dissociation, in addition to the previously proposed stabilization of ground-state pairs [16]. PAH diffusion on silica surfaces is known to be very slow [18].

The effect of a barrier to ground-state pair dissociation, in the case of FL on silica, is to allow for direct observation of a Franck–Condon envelope for the pair. This absorption is not normally observed in solution where a barrier sufficient to maintain the repulsive ground-state pairs does not exist. The behavior previously observed for 1-methoxynaphthalene on silica is similar to that observed for FL [4e]. In our work with 1-methoxynaphthalene, an excimer-like emission was observed at the silica gel/air interface, although an excimer emission from 1-methoxynaphthalene had not previously been observed in solution [4e]. The excimer-like emission observed on silica gel was attributed to ground-state pairing (or higher aggregation) promoted by restricted PAH mobility induced by the surface.

4.2. Photochemical oxidation

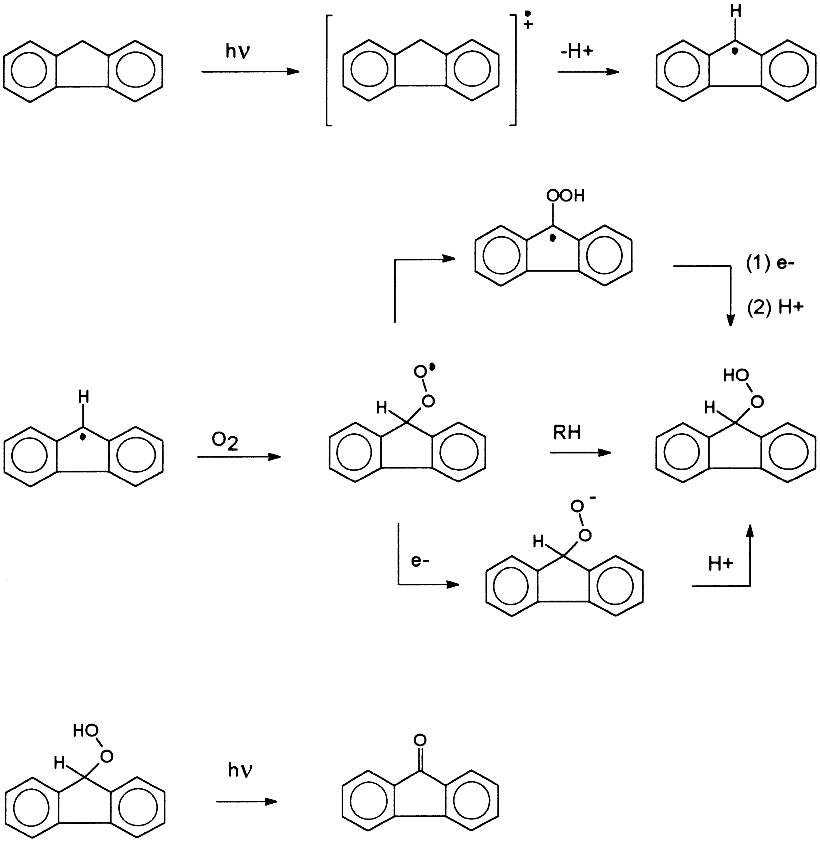
The lowest energy absorption band of FL is reported to have a 0–0 transition at 33 200 cm^{-1} (301 nm, 94.9 kcal mol^{-1}) and a fluorescence quantum yield of 0.66 in solution with a 15 ns lifetime (heptane) [10]. The lowest triplet state of FL is 68 kcal mol^{-1} above the ground-state and is approximately 26.9 kcal mol^{-1} below the lowest excited singlet state [10]. The singlet–triplet energy difference in FL is only slightly larger than the 22.5 kcal mol^{-1} required for singlet molecular oxygen generation from excited singlet state quenching by O_2 [19]. Molecular oxygen quenching of the triplet state of FL leads to the formation of singlet molecular oxygen with unit efficiency in solution [19]; however, reaction of singlet molecular oxygen with FL is reported to be quite sluggish ($k < 0.1\ M^{-1}\ s^{-1}$) [20]. The direct photolysis of FL to give FLO at a silica gel/air interface appears to proceed by a mechanism that is not mediated by singlet molecular oxygen. This conclusion is supported by the failure of FL to react with sensitized singlet molecular oxygen at the silica gel surface. Previously observed reactions of other PAH with sensitized singlet molecular oxygen on silica surfaces serve to demonstrate the effectiveness of this method [4].

Photochemical oxidation of FL in solution (acetonitrile–methanol; 9:1) activated by electron transfer catalysis (9,10-dicyanoanthracene in the presence of methyl viologen and $FeCl_2$) gives 9-fluorenone in 82–98% yield [21]. We propose a similar electron transfer mechanism for formation of FLO at the silica gel/air interface. Products attributable to electron-transfer initiated oxidation, including superoxide, have previously been observed for naphthalene, 1-methylnaphthalene and 1-methoxynaphthalene photolysis at silica gel/air interfaces with low intensity lamps [4e,j]. 1-Cyanonaphthalene, a poor singlet molecular oxygen acceptor with a relatively high oxidation potential does not undergo photolysis with any appreciable rate at a silica gel/air interface [4j]. One PAH studied in our laboratory, 1-methoxynaphthalene, notably undergoes photochemical oxidation by both a singlet molecular oxygen mediated mechanism and an electron transfer mechanisms at a silica gel/air interface [4e].

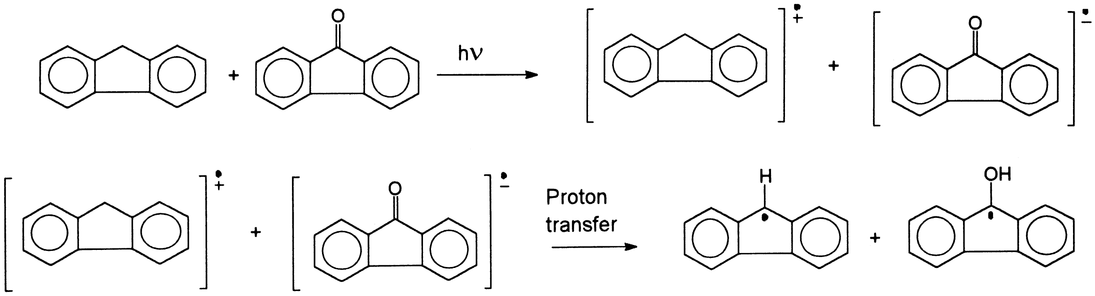
Transient spectroscopic data on silica are consistent with the formation of both FL triplet and cation radical. The proposed mechanism leading to initial FL photochemical oxidation at the silica gel/air interface is shown in Scheme 1.

Solution phase photolysis of the proposed hydroperoxide intermediates formed in the reaction is reported to require the presence of trace amounts of Fe^{2+} [21]. Trace levels of Fe^{2+} are present in the silica gel used in this study. The last step in Scheme 1 may alternatively involve intermediate formation of 9-hydroxyfluorene, which readily photolyzes on the silica surface to give FLO (vide infra).

When sorbed on silica by itself, FLO is photochemically stable; however, FLO is observed to be photochemically reac-



Scheme 1.



Scheme 2.

tive in the presence of co-sorbed FL. Photolysis of FLO in the presence of co-sorbed FL does not generate isolable photoproducts derived from FLO. A mechanism involving FLO triplet state abstraction of a benzilic hydrogen atom from a neighboring FL on the surface could account for the effect of FL on the reactivity of FLO, although the lowest triplet state of FLO has been shown to be relatively unreactive in hydrogen atom abstraction from aryl alkanes [22]. A possible mechanistic scenario, shown in Scheme 2, involves FLO as both an electron and proton scavenger in the one-electron oxidation of FL.

This reaction may also occur as FLO is formed as a product during the direct photolysis of FL, as discussed above. Tentative evidence for this reaction is seen in the transient absorption spectrum, Fig. 6, where we assign the 450 nm and 510 nm transients to 9-fluorenone radical anion and 9-hydroxyfluorenyl radical respectively. Additional transient studies of ketone and quinone oxidation of co-sorbed PAH at silica gel/air interfaces is underway in our laboratories.

The suggested mechanism in Scheme 2 does not define how the electron transfer from FL to FLO occurs. Additionally, we have not addressed the observation that co-sorbed FLO does not accelerate the photolysis of FL. The free energy change (ΔG) for an excited state electron transfer from FL to FLO (S_1 electronic state) is approximately -3 kcal mol^{-1}, as calculated by the Rehm–Weller equation [23]. This value of ΔG is calculated based on an FL oxidation potential of 1.65 V (versus SCE) [24], a FLO reduction potential of -0.87 V (versus SCE) [25] and a FLO S_1 energy of 63.2 kcal mol^{-1} [10]. The calculated ΔG is only approximate owing to neglect of the $-e^2\varepsilon^{-1}r^{-1}$ term in the Rhem–Weller equation. This term is usually small, though it is difficult to estimate the size of the term for an excited state electron transfer at a silica gel/air interface where the dielectric of the bulk silica (ε) is approximately 3.8 [26], and the donor–acceptor separation, r, is variable and not easily defined. Although electron transfer to electronically excited FLO may be thermodynamically allowed, the short S_1 lifetime of FLO (3 ns) would require a very fast excited state electron transfer. Electron transfer to the T_1 state of FLO is not as thermodynamically favored. We suggest that a mechanism whereby molecular oxygen serves as a shuttle to transport an electron from FL to FLO is more reasonable. Intermediate transfer of the electron to oxygen (reduction potential -0.87 V versus SCE) [27] from the S_1 excited state of FL ($E_{OX} = 1.65$ V versus SCE and $E(S_0–S_1) = 4.12$ eV) is calculated to have a ΔG of -1.59 eV (again the $-e^2\varepsilon^{-1}r^{-1}$ term is neglected). This process would be more thermodynamically favored than excited state electron transfer to FLO and it would account for the lack of acceleration of FL photolysis in the presence of FLO. Work to define further the role of oxygen and the silica surface in PAH photochemical oxidation at silica gel/air interfaces continues in our laboratories.

Acknowledgements

The authors gratefully acknowledge the assistance of Dr R.W. Redmond and Dr P.D. Wood (Wellman Laboratories of Photomedicine, Department of Dermatology, Harvard Medical School) for their assistance in collecting the transient diffuse reflectance data. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. and by a US DOE/EPSCoR grant DE-FGO2-94ER-75764 to the University of Puerto Rico.

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