Photochemistry of Pyrene on Unactivated and Activated Silica Surfaces

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Photolysis of pyrene at the solid/air interface of unactivated and activated silica gel proceeds slowly to give mainly oxidized pyrene products. We have identified 1-hydroxypyrene, 1,6-pyrenedione, and 1,8-pyrenedione among the main reaction products. The remaining minor products show molecular weights and spectral properties consistent with oxygenated pyrenes. Furthermore, small amounts of 1,1'bipyrene dimer are also formed at higher surface coverages $(2 \times 10^{-5} \text{ mol/q})$. When photolysis is carried out at 5 \times 10^{-5} mol/g pyrene, photodegradation rate drops sharply and pyrene loss becomes insignificant. No significant change in the product distribution is observed when the photolysis is carried out on unactivated or activated silica. Photodegradation rate is slightly faster on activated silica compared to unactivated silica. Mechanistic studies indicate that the precursor to photoproduct formation is pyrene cation radical which is postulated to be formed by electron transfer from pyrene excited state to oxygen (type I) or by photoionization of pyrene. The cation radical reacts with physisorbed water on silica to give the observed oxidation products.

Introduction

Analyses of airborne particulate matter have shown significant mutagenic and/or carcinogenic activity. This is ascribed not only to the primary pollutants but also to their degradation products (1-5). Although only at trace levels, the organic fraction of a particulate represents a real danger to humans because its assimilation and possibilities of transformation increases once in the body. Polycyclic aromatic hydrocarbons (PAHs), an important class of pollutants present in air, are released into the atmosphere by the incomplete combustion of fossil fuels. Many of these PAHs have been classified as priority pollutants by the EPA (6). Thus, the study of PAHs and their possible phototransformations in the atmosphere is important owing to the carcinogenic nature of some of

these molecules and the threat they pose when present in respirable ambient particles (2, 7, δ).

Marine and lacustrine sediments are among the ultimate environmental sinks for PAHs (9). Small PAHs have been shown to reside mainly in the gas phase when present in the atmosphere (10). Insulators such as silica, alumina, silicoaluminates, and calcium carbonate are believed to constitute up to 20-30% of inorganic particulates present in the atmosphere (11). The use of silica as a model substrate in this work is the continuation of our effort in the area of PAH photochemistry under controlled conditions, to gain a better understanding of PAH photodegradation mechanism that are relevant to environmental processes occurring on similar materials.

Photodegradation studies of pyrene and other PAHs on particulate matter have focused on the effect of surface's chemical and physical properties such as color, carbon content, surface area, particle porosity and size, and surface pH on the rate of phototransformation (12-15). Photolytic half-lives for pyrene and 17 other PAHs adsorbed on different substrates such as alumina, silica, fly ash, and carbon black have been determined (14).

Mamantov et al. (*15*) have reported that pyrene was least photoreactive when adsorbed on the carbonaceous subfraction of coal stack ash but showed high reactivity when adsorbed on mineral subfraction, silica or alumina. An early report on the photodegradation of pyrene adsorbed on garden soil identified five of the eight photoproducts as 1,1'-bipyrene, 1,6- and 1,8-pyrenedione, and 1,6- and 1,8-dihydroxypyrene (*16*).

The formation of excited singlet and triplet states of pyrene on silica (17-24) and alumina (25-27) have been reported. The nature and dynamics of these states have been used as probes to provide information about the surface properties and adsorption sites. Using diffuse reflectance laser flash photolysis technique, the formation and kinetics of pyrene excited triplet state and cation radical on alumina have been studied (26). More recently, Thomas and Mao (28) investigated the photochemical behavior of pyrene adsorbed on active sites of activated γ -alumina and silica–alumina (T > 350 °C) and reported that the main photoproducts of this reaction were mono- and dihydroxypyrene. They also reported that pyrene adsorbed on these surfaces forms pyrene-adsorbate charge-transfer complexes and pyrene radical cation via a photoinduced process as revealed by EPR and diffuse reflectance spectroscopy (28). The study further states that photolysis of pyrene adsorbed on nonactivated surfaces proceeds via a similar radical process to give only one detectable product.

Previous reports on photochemistry of a number of PAHs adsorbed on silica, alumina, and other surfaces have focused on determining the photoproducts and mechanism of their formation (12-15, 29-38). In this study, we report the photochemical reaction of pyrene adsorbed on activated and unactivated silica under (a) simulated laboratory irradiation conditions and (b) solar irradiation in order to mimic the atmospheric particulate photolysis conditions. Photodegradation of pyrene with time was followed directly on the adsorbent by front face emission and diffuse reflectance absorption spectroscopy. Mechanistic studies indicate that the intermediate leading to photoproducts is pyrene radical cation which may be generated by electron transfer from excited triplet state of pyrene to oxygen (type I) or by photoionization. No evidence of singlet oxygen involvement in the photooxidation process is observed.

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Materials and Methods

Chemicals. Pyrene (Supelco, 99.9%) was recrystallized from ethanol before use. All solvents used were HPLC grade. Silica-60 (EM Reagents) particle size 0.04-0.06 mm and surface area of 550-675 m²g⁻¹ as reported by the manufacturer was used as received (unactivated). The physical characteristics of activated silica (J. T. Baker, Phillipsburg, PA; reagent grade, 60-200 mesh) used in this work have been reported previously (*34*). The N₂ BET surface area for the activated silica was determined to be 274 m² g⁻¹ with an average pore radius of 60 Å. The silica was activated by heating for a minimum of 24 h at 200 °C in air.

Synthesis of 1,6- and 1,8-Dihydroxypyrene. 1,6- and 1,8pyrenediones were first synthesized by a method described previously (*39, 40*). Photoreduction of both diones to the corresponding diols was carried out in 2-propanol (*41*). A degassed solution of 1,8-pyrenedione (0.2 g) in 50 mL of 2-propanol was irradiated with visible light ($\lambda_{ex} > 400$ nm, Oriel 200-W Xe–Hg lamp using cutoff filter) for 1 h. Removal of solvent afforded 1,8-dihydroxypyrene (90% yield). The air sensitive 1,8-dihydroxypyrene could not be purified and as a result was used without further purification. Photoreduction of 1,6-pyrenedione (0.2 g) in degassed 2-propanol (50 mL) yielded a mixture of 1,6-dihydroxypyrene (50% yield) and unreacted dione. Because 1,6-dihydroxypyrene was very oxygen sensitive, it could not be purified and thus was used in its impure form.

Methods. Adsorption of pyrene onto unactivated silica was achieved by adding the silica to a hexane solution of pyrene and allowing it to equilibrate for 30 min. Removal of the solvent carried out by any of the following methods rotary evaporation, nitrogen flow, or desiccation (avoiding the use of heat)—leads to efficient loss of solvent. Pyrene surface coverage was determined by extracting pyrene from the silica surface (a known weight of silica in a known volume of solvent) and injecting a measured volume of the extracted pyrene solution into HPLC. Using a pyrene calibration curve (determined by HPLC from known solutions), the concentration of pyrene in extracted solution and thus on silica surface was calculated.

Adsorption of pyrene onto activated silica (several different surface coverages were employed as described in the text) from a cyclohexane solution was achieved in a similar manner described before (29-38).

Photolysis of pyrene adsorbed on unactivated silica was carried out using a Xe–Hg 1000W Oriel light source (Oriel Corp.) equipped with a 10 cm long cylindrical tube for water circulation to absorb the IR radiation. A Corning 7-51 bandpass filter was used to isolate the 320-420 nm wavelength region that overlaps well with the absorption bands of pyrene. The samples were irradiated in a rotatory cell (*12*), where the powder is tumbled during irradiation. The loss of pyrene with time upon photolysis studies were carried out in a 1 mm flat optical cell. The cells were placed on an optical bench at a distance of 35 cm from the lamp housing. An irradiance of 66 Wm⁻² was measured at this distance using K₃Fe₂(C₂O₄) as chemical actinometer (*42*). A similar value was obtained with a radiometer (IL1700 International light) using a SD033 #2585 detector.

For sunlight radiation studies, the samples were placed on Petri dishes, sealed with Teflon tape, and then exposed to solar radiation on the roof of the College of Natural Sciences building in Rio Piedras, Puerto Rico. For background correction, a similar sample was covered with aluminum foil to protect it from light, and a second sample containing an equal weight of silica without adsorbed pyrene was exposed to sunlight for the same period of time. After irradiation, the unreacted pyrene and photoproducts were extracted from the silica surface by adding the powder to 20 mL of methanol followed by sonication in an ice bath for 10 min. The solution was then centrifuged for 5 min to remove any suspended particles and preconcentrated to 1-2 mL under a soft flow of nitrogen for HPLC analysis.

Separation of photoproducts was achieved by HPLC using a C-18 reverse phase column (Supelco, 10 mm diameter) on a Waters (501 and 600 A pumps, 994 diode array and 470 fluorescence detectors) or Shimadzu LC-6A system. Optimum product separation for 25 μ L injections was obtained using a gradient mode starting with methanol/water (70:30, v/v) at a flow rate of 1 mL/min and changing the ratio linearly to 85:15 in 15 min during the run. The extracts and the collected chromatographic fractions were analyzed by GC-FID and GC-MS (Hewlett-Packard 5890 and 5995A) using a SPB-5 (Supelco 30 mm × 0.032 mm id) GC column. The injected sample volume was 3 μ L with a 3 min solvent delay at an initial oven temperature of 100 °C during the first 3 min which was ramped to 250 °C at a rate of 15 °C/min.

Photolysis of pyrene on activated silica was carried out in quartz tubes in a Rayonet photoreactor using 300 nm light bulbs (2.68×10^{15} photons cm⁻² s⁻¹ measured irradiance) in a horizontal orientation as described previously (29-38). Extraction of the unreacted pyrene and photoproducts from the surface for HPLC analysis (HP 1090, C-18 reverse phase column, 2.1 mm diameter, 0.21 mL/min flow rate and 35:65 by volume acetonitrile:water isocratic changing to 100% acetonitrile between 20 and 30 min into the run) was performed in a similar fashion reported earlier (*32*).

Steady state diffuse reflectance spectra of samples prepared on activated silica were recorded on a Cary-4 (Varian) spectrophotometer equipped with an integrating sphere. A Cary 1E (Varian) spectrophotometer was used to follow the progress of the reaction by taking the absorption spectra of extracts from samples of pyrene on unactivated silica irradiated at different time intervals. Emission and excitation spectra of pyrene adsorbed on unactivated silica before and after irradiation were obtained in front face mode on an SLM/Aminco 4800S spectrofluorimeter. Emission spectra for pyrene adsorbed on activated silica were recorded on a Spex Fluorolog II spectrofluorimeter and are reported fully corrected for silica background.

Time-resolved fluorescence studies of pyrene on activated silica were carried out in a diffuse reflective mode using 355 nm excitation beam of a Minilite II Nd:YAG laser (Continuum) with a 5 ns pulse width and energies less than 9 mJ/pulse. Diffusely reflected emission was refocused with a lens onto the entrance slit of a polychromator (EG&G PARC-1226). The light from the exit port of the polychromator was then directed to the front entrance port of a gated intensified charge coupled detector (InstaSpec IV, Andor Technology). Data acquisition was performed at ≥ 5 ns time intervals after the excitation using manufacturer software (Andor Technology) which was integrated with a DG355 Digital Delay Generator (Stanford Research System, Inc.) to control the gate width and delay times through a GPIB board. Emission traces recorded at different time intervals were exported as ASCI files to Origin 4.0 software program (Microcal) and fitted using standard procedures to obtain the kinetic information.

Transient absorption spectra for pyrene adsorbed on unactivated silica were recorded after excitation with 266 nm light from a Quantel YG-660A/ND-YAG (Continuum, Santa Clara, CA) laser (4–10 mJ/pulse of 8 ns duration). The signal was recorded and analyzed as described previously (*36, 38*).

Results and Discussions

Spectroscopic Evidence for Photodegradation of Pyrene on Unactivated Silica. The loss of adsorbed pyrene on unactivated silica $(1 \times 10^{-6} \text{ mol/g})$ due to photodegradation process was monitored by emission spectroscopy. The



FIGURE 1. Decrease in the emission intensity of pyrene band at 393 nm with time for the photolyzed samples of pyrene adsorbed on unactivated silica (1×10^{-6} mol/g) and purged with argon (- \bullet -) and oxygen (-• \bullet -).



FIGURE 2. Fluorescence spectra of photoproducts in methanol obtained from an irradiated sample of pyrene adsorbed on unactivated silica (1 \times 10⁻⁶ mol/g) under an oxygen atmosphere at different irradiation times (- Φ - 0 h, ... 1 h, -2 h).

decrease in the emission intensity of pyrene bands suggests that the molecule is undergoing photodegradation as irradiation proceeds. Accordingly, the sample developed a yellow color with time indicative of pyrene phototransformation. No color change was observed in samples that were kept in the dark or when pure silica was irradiated under similar conditions. The photodegradation rate of pyrene adsorbed on unactivated silica decreased by 30% when photolysis was carried out on silica containing residual solvent (left on silica as a result of incomplete removal of solvent from the surface during the adsorption process). The decrease in photodegradation rate in the presence of residual solvent is not too surprising since the solvent molecules could replace loosely held pyrene molecules from the surface to cover the sites. This in turn could result in an increase in collisional deactivation rate of excited pyrenes (e.g. excimer formation) and lead to less photoproduct formation. Pyrene diffusion on silica and other surfaces has been reported to increase in the presence of coadsorbed solvent leading to dynamic excimer formation (43). The photodegradation rates for air saturated or oxygen purged samples of pyrene adsorbed on unactivated silica were similar. However, under an atmosphere of argon, the photodegradation rate dropped by a factor of 2 (Figure 1).

Figure 2 shows the changes in emission spectra of photoproduct mixtures (in methanol) extracted from the surface at different time intervals after irradiation. The decrease in the emission intensity of pyrene bands is accompanied by the appearance of new bands at 405, 430,



FIGURE 3. Absorption spectra of photoproducts in methanol obtained from an irradiated sample of pyrene adsorbed on unactivated silica $(1 \times 10^{-6} \text{ mol/g})$ under an oxygen atmosphere at different irradiation times (-0 h, ... 1 h, -A- 2 h).



FIGURE 4. Representative chromatogram of photoproducts for a sample of pyrene adsorbed on unactivated silica $(1 \times 10^{-6} \text{ mol/g})$ that was irradiated for 3 h (a) absorption and (b) fluorescence (excitation wavelength 280 nm, emission at 405 nm during the first 25 min, excitation wavelength 334 nm, and emission wavelength 393 nm during the next 10 min).

and 455 nm due to photoproducts. Changes in the absorption spectra of pyrene with irradiation time are shown in Figure 3. The new red-shifted bands between 350 and 500 nm, which appear as irradiation proceeds, are attributed to the observed photoproducts. Similar spectral changes were also observed when samples of pyrene adsorbed on unactivated silica were exposed to sunlight (not shown).

HPLC analysis of extracted photoproducts shows a total of 16 components (Figure 4). Assuming similar absorptivities at the monitoring wavelength, there are three major products (F6, F7, and F8) and the remaining 13 account for minor products. Except for fractions F1–F4, all the other fractions show structured absorption and emission spectra consistent with that of pyrene (parent compound) implying that these products are substituted pyrenes. The main difference between the absorption and emission spectra of these products and the parent compound pyrene is a bathochromic displacement and the presence of a broad visible band with maxima around 450–470 nm.

Photoproduct identification by GC-MS using co-injection of authentic samples identified three of the products as 1,6pyrenedione (F6, major), 1,8-pyrenedione (F7, major), and 1-hydroxypyrene (minor). The fragmentation patterns of the MS spectra show consistent loss of fragments corresponding to m/z (mass-to-charge ratio) values of 28 (-CO) and 29 (-COH) in good agreement with the oxygenated nature of these pyrene derivatives. Although the molecular mass corresponding to F8 (236) is consistent with pyrenedihydrodiols, its MS and absorption spectrum are different from those reported for 4,5-pyrenedihydrodiol (44-46). It is conceivable that other pyrenedihydrodiols or dihydrodihydroxypyrene (e.g. reduced forms of 1,6- and 1,8-pyrenediones) could form.

The GC/MS analysis of F4 revealed presence of two isomers with m/z equal to 208. Although 1,6- and 1,8dioxapyrenes (47, 48) have a molecular formula of C14H8O2 and a mass of 208, the observed MS fragmentation pattern and absorption spectrum for F4 do not allow its assignment as either of the two species. Fraction F5 shows an absorption spectrum resembling substituted phenanthrene and a MS fragmentation pattern indicating loss of -COH and -CO₂H. Although its molecular weight suggests a molecular formula of C₁₅H₁₂O₃, based on the available data we cannot assign a definitive structure to this fraction. Fraction F10 (m/z = 220) exhibits a MS and absorption spectrum similar to that of 4-oxapyrene-5-one (C15H8O2, a strong mutagen found in diesel fuel) first identified by Pitts et al. (49). The MS fragmentation pattern for F4, F5, and F10 contains ions with m/z values of 45 (-COOH), 29 (-COH), and 28 (-CO), respectively, suggesting presence of oxygen functionality in these fractions. We cannot assign molecular formulas to the remaining minor products based on our available absorption and mass spectral data.

Photoproduct yields were compared for samples irradiated up to 30% conversion (pyrene loss) under argon, air, and oxygen. The yield of fraction F1 was unaffected while those of F10, F11, and F12 dropped to almost zero in the absence of oxygen. A 4-fold increase in the yield of pyrenediones (fraction F6 and F7) and a 2-fold increase in fraction F3 was observed when oxygen purged samples were photolyzed. Fraction F12 disappeared in the presence of oxygen, while the yield of F11 dropped by about 50%. In general, except for F1, F11, and F12, the yield of all the other fractions increased in the presence of oxygen suggesting that they are formed via photooxidation processes.

Photolysis of Pyrene Adsorbed on Activated Silica. When photolysis ($\lambda_{ex} = 300$ nm) of pyrene was carried out on activated silica (2 \times 10⁻⁶ mol/g), the same number of photoproducts was observed. In addition, a small amount of 1,1'-bipyrene (identified by matching its absorption, emission, and HPLC retention time with an authentic sample) was also observed. A decrease in the rate of pyrene loss was observed as the surface coverage increased from 2×10^{-6} to 5×10^{-5} mol/g. The photodegradation rate was extremely slow at 5×10^{-5} mol/g. This drop in the photodegradaion rate of pyrene can be attributed to the presence of groundstate pairs and/or aggregates (formed as surface loading is increased) which can act as a light sink to absorb the incident light without inducing any photochemistry. We have observed a similar behavior with other PAHs reported previously (32-38). This notion was further supported by our steady state and time-resolved fluorescence studies (vida infra).



FIGURE 5. Time-resolved fluorescence spectra of degassed 2 \times 10⁻⁶ mol/g (a) and 5 \times 10⁻⁵ mol/g (b) pyrene adsorbed on activated silica. A 5 ns pulse of an Nd:YAG laser (355 nm) was used for excitation. Curves E, J, and R shown in the top figure (a) are the emission profiles obtained at 20, 40, and 60 ns after the laser pulse. Curves D, I, and P shown in the bottom figure (b) are the emission profiles obtained at 20, 40, and 60 ns after the laser pulse.

Time-Resolved Fluorescence Studies. Our time-resolved fluorescence data indicated that the emission of samples became predominantly excimer-like as the surface loading was increased from 2×10^{-6} to 5×10^{-5} mol/g (Figure 5). Time-resolved fluorescence studies of the degassed samples provided additional information that substantiated the presence of monomers as the main species at low surface coverage (2×10^{-6} mol/g, Figure 5a) and ground-state pairs and/or aggregates at higher surface coverage (5×10^{-5} mol/g, Figure 5b). For both surface coverages, the fluorescence decay curves fitted best to a biexponential fit at the wavelengths of monomer ($\lambda = 384$, 404, 427 nm) or excimer ($\lambda = 482$ nm) emission. The lifetimes of these species are of the order of 160 ± 10 and 60 ± 5 ns in good agreement with those reported by Bauer et al. (*20*) on various silica surfaces.

Photoproducts of Pyrene Photolysis on Activated Silica. Analysis of photoproducts on activated silica revealed that the yield of 1,6- and 1,8-pyrenediones decreased significantly relative to unactivated silica. Furthermore, no better than 60% mass balance could be obtained despite our repeated attempts to account for 100% loss of pyrene. Since activation of silica through heat treatment initially induces the loss of physisorbed water followed by subsequent dehydration of silanol groups (20), we decided to assess the role of physisorbed water in the observed phenomenon. Identical samples of pyrene (2 \times 10⁻⁶ mol/g) adsorbed on unactivated silica, activated silica, and silica containing \geq one monolayer of physisorbed water were prepared, photolyzed in parallel, and analyzed for pyrene loss and photoproducts formation. Although the photolysis rate was slower for unactivated silica and silica containing physisorbed water relative to activated silica, the yield of both 1,6- and 1,8-pyrenedione were higher for unactivated and wet silica samples. The 1-hydroxypyrene,



on the other hand, did not show any significant change in its yield in the presence of physisorbed water. When photolysis of pyrene adsorbed on activated silica was carried out in air or oxygen, no significant change in the photodegradation rate was observed. However, the yield of 1,6and 1,8-pyrenedione in oxygen purged sample were increased by a factor of 5 and 3, respectively, while that of 1-hydroxypyrene decreased by a factor of 2. Similar increases were also observed for other products.

These results clearly indicate that (a) water plays a significant role in the formation of pyrenediones and (b) the precursors to these diones are air sensitive and readily oxidized (*vida infra*). Although dihydroxypyrenes have been reported to form during photolysis of pyrene on activated γ -alumina and silica–alumina (28), we observed no significant amount of either 1,6- or 1,8-dihydroxypyrene in the reaction mixture. Lack of significant accumulation of either diol on silica, compared to γ -alumina and silica–alumina (28), suggests that these species are unstable and undergo facile air oxidation to the corresponding diones. This is not too surprising in view of the fact that catechols are known to readily air oxidize to the more stable quinones.

To examine this possibility, we followed the change in absorption spectra of both 1,6- and 1,8-dihydroxypyrene (in air saturated acetonitrile) with time in the dark. Absorption spectral results revealed (not shown) that both diols were very unstable and readily oxidized to the corresponding diones. When the solutions were purged with oxygen, oxidation proceeded much more rapidly. Based on these findings and the fact that no significant amounts of these diols are found in the reaction products isolated from photolyzed pyrene on silica, it can be concluded that 1,6and 1,8-dihydroxypyrene may be the precursor to 1,6- and 1,8-pyrenediones. These results are in good agreement with the proposed mechanism of pyrene photolysis in water (*50*). The major products observed during photolysis of pyrene in water were 1,6- and 1,8-pyrenediones and 1-hydroxypyrene with only trace amounts of the corresponding diols.

A type I (electron transfer) mechanism where pyrene cation radical is produced by electron transfer from its excited state to oxygen was postulated to explain photodegradation of pyrene in water (*50*). It appears that a similar mechanism may be operating on silica as well. Initial formation of pyrene cation radical and its subsequent reaction with physisorbed water can lead to 1-hydroxypyrene. The 1-hydroxypyrene can undergo secondary photolysis by a similar mechanism to form 1,6- and 1,8- dihydroxypyrene as well as other pyrene oxidation products. Unstable 1,6- and 1,8-dihydroxypyrene can air oxidize (or possibly undergo photolytic transformation) to form the corresponding diones.

When an aerated sample of 1-hydroxypyrene adsorbed on silica $(4.3 \times 10^{-7} \text{ mol/g})$ was photolyzed at 300 nm, about 80% of it was lost during the same irradiation period as the time used for photolyzing a pyrene/silica sample. Conversion of 1-hydroxypyrene to the corresponding diones in aerated water upon photolysis has also been reported in our previous work (*50*). These findings further support the notion that initial formation of 1-hydroxypyrene and its subsequent photodegradation on silica may account for the observed photochemistry of pyrene.



FIGURE 6. Transient diffuse reflectance spectra of pyrene adsorbed on unactivated silica under an atmosphere of air (a) and nitrogen (b) recorded 9.6 us after the laser pulse.

To determine whether singlet molecular oxygen played a role in photodegradation of pyrene by a type II mechanism, a methylene blue sensitized reaction of pyrene adsorbed on silica was carried out. No oxidation product(s) of pyrene or any significant loss of pyrene was observed when methylene blue (a sensitizer of singlet oxygen) coadsorbed with pyrene on silica was excited (650 nm) directly for days. Based on these findings, photodegradation of pyrene appears to proceed exclusively by a type I mechanism, and significant involvement of singlet oxygen can be ruled out.

Excited-State Transients of Pyrene on Unactivated Silica. The 266 nm laser excitation of pyrene adsorbed on unactivated air saturated silica gel produces the radical cation and excited triplet transients (Figure 6). Similar bands have been observed using an excimer laser to excite pyrene adsorbed on activated alumina (26-28). The reported spectra are similar to the published absorption spectra of pyrene's triplet state (51) and the radical cation in solution (52).

Oxygen quenches excited singlet (*26*, *53*) and triplet states and not the radical cation of pyrene on activated and unactivated silica surfaces (*27*). In polar solvents, energy transfer from the excited triplet state of pyrene to molecular oxygen leads to the formation of singlet molecular oxygen with a quantum efficiency of 0.65-0.74 (*54*). It has also been proposed that adsorbed oxygen serves as an electron trap forming superoxide radical anion, $O_2^{\bullet-}$ (*29*, *53*). Although mononphotonic and biphotonic processes have been postulated for the photoionization of pyrene on solid surfaces (*27*), the low photon flux used in our studies rule out the involvement of a biphotonic process in the formation of cation radical.

Mechanism of Pyrene Photolysis. Pyrene radical cation can form either by energy transfer from excited pyrene to molecular oxygen or by photoionization of adsorbed pyrene. The reaction of radical cation with physisorbed water on silica surface can lead to the formation of 1-hydroxypyrene. It is postulated that 1-hydroxypyrene can undergo secondary photolysis to dihydroxypyrenes (which can air oxidize to diones) and other oxidation products of pyrene. Scheme 1 depicts a plausible mechanism for the formation of products upon photolysis of pyrene on silica.

In summary, our photochemical studies of pyrene on unactivated and activated silica have revealed that (a) photodegradation proceeds efficiently at low surface coverages to give mainly 1,6- and 1,8-pyrenediones, small amounts of 1-hydroxypyrene, and some other oxidation products, (b) photodegradation rate drops significantly at higher surface coverages as a result of ground-state pair and/or aggregation believed to be responsible for the observed formation of 1,1'-bipyrene dimer, (c) photooxidation of pyrene proceeds predominantly by type I (electron transfer) mechanism and does not involve singlet molecular oxygen (type II) as an intermediate, and (d) photodegradation rate drops in the presence of physisorbed water.

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