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Photochemical Oxidation of Phenanthrene Sorbed on Silica Gel

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There have been relatively few detailed studies of PAH photochemical degradation mechanisms and products at solid/air interfaces under controlled conditions. Results from mechanistic studies on particulate simulants are important in understanding the fates of PAH sorbed on similar materials in natural settings. In this study, the photolysis of phenanthrene (PH) on silica gel, in the presence of air, has been carefully examined. Once sorbed onto the silica surface, PH is not observed to repartition into the gas phase, even under vacuum, and dark reactions of PH are not observed at the silica/air interface. Photolysis (254 nm) of PH leads to the formation of 2,2′-biformylbiphenyl (**1**), 9,10-phenanthrenequinone (**2**), *cis*-9,10-dihydrodihydroxyphenanthrene (**3**), benzocoumarin (**4**), 2,2′-biphenyldicarboxylic acid (**5**), 2-formyl-2′-biphenylcarboxylic acid (**6**), 2-formylbiphenyl (**7**), 1,2-naphthalenedicarboxylic acid (**8**), and phthalic acid (**9**). These products account for 85−90% of the reacted PH. The photoproducts are independent of excitation wavelength (254 and 350 nm), and the reaction proceeds entirely through an initial step involving the addition of singlet molecular oxygen to the ground state of phenanthrene with subsequent thermal and/or photochemical reactions of the initially formed product. Singlet molecular oxygen is produced through quenching of the lowest triplet state of PH at the silica gel/air interface. The high material balance and detailed mechanistic information provided by this study serve as a standard for comparisons with the products and mechanism of PH photochemical oxidation on environmentally derived inorganic oxide particulates.

Introduction

The photochemical oxidation of polycyclic aromatic hydrocarbons (PAH) is a topic of current interest. These substances are toxic and many are carcinogenic. The Environmental Protection Agency (EPA) has included 16 PAH in their list of priority pollutants (*1*). PAH are found in coal tar and on fly ash and other atmospheric particulates, and when washed by rain, they contaminate the soil and water. Many PAH have been shown to have photolytic half-lives that are dependent on the nature of the substrate to which they are sorbed (*2*). It has been found that photolytic half-lives for PAH on silica, alumina, and fly ash are generally much shorter than the half-lives on carbon black (*2*); however, information concerning the products or the photochemical mechanisms on these surfaces are scarce. It has also been reported that some PAH are photolytically stable on coal fly ash, although those with benzylic hydrogens are prone to thermal oxidation (*3*). Previous work in our laboratories has focused on determining the photoproducts and mechanisms of photochemical oxidation of PAH sorbed onto silicas and aluminas where structural dependence of the photolytic half-life has been observed (*2, 4*). For example, the photochemical oxidation of anthracene at a silica gel/air interface was shown to occur entirely by a singlet oxygen-mediated pathway (*4a*); however, naphthalene and 1-methylnaphthalene were shown to react by an apparent electron transfer mechanism (*4h*). Photochemical oxidation of 1-methoxynaphthalene was shown to occur by both singlet oxygen- and electron transfer-mediated pathways, giving two distinct sets of products (*4c*). Studies of other PAH have also shown one or both of these mechanisms to be operative (*4*).

The work detailed in this paper is a continuation of our efforts to understand PAH photochemistry under controlled conditions, which allow for mechanistic interpretations and give results that are relevant to environmental processes occurring on similar materials. Considerable amounts of water-insoluble solid inorganic particles are found in the atmosphere (*5*). Tropospheric concentrations of these particulates are estimated to be in the range of 1−300 μg m^{-3} (*5*). As much as 20−30% of inorganic atmospheric particulates have been estimated to be oxides, including insulators such as SiO_2, Al_2O_3, silicoaluminates, and $CaCO_3$ (*5*). The highly polar and non-semiconducting surfaces of commercial silicas and aluminas may simulate, to a first approximation, inorganic oxide particulates found in the environment. Evaluating commercial silicas and aluminas as simulants of environmentally derived inorganic oxide particulates requires detailed mechanistic studies on both commerically available and naturally occurring materials.

An understanding of the PAH structural dependence observed for photolytic degradation rates and mechanisms on silica gel and alumina will assist in understanding and predicting the fates of PAH at similar interfaces. Studies of the photochemical oxidation of small PAH at solid/air interfaces also afford the opportunity to rigorously identify and quantitate products derived from members of this important class of pollutant. This information forms an experimental basis for predicting reactivity paterns in much larger PAH having similar structural features and physical properties (e.g., combinations of K-, L-, and bay-regions, oxidation potentials, reactivity toward singlet molecular oxygen, etc.) but where independent synthesis of the

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oxidation products is much more difficult. For these reasons, it is important to generate a detailed mechanistic understanding of photolytic transformations occurring in small PAH sorbed to substrates of environmental relevance. The topic of this paper is the products and mechanism of the photochemical oxidation of phenanthrene (PH) on silica surfaces.

PH is reported to have a low vapor pressure and a sizable organic carbon−water partition coefficient, log $K_{OC} \cong 4.2$ (*6*). PH is one of the 16 PAH on the EPA list of priority pollutants (*1*). In solution, PH has been shown to undergo dye-sensitized photooxidation, and the potentially carcinogenic oxirane 9,10-epoxy-9,10-dihydrophenanthrene has been suggested as a possible intermediate (*7*). Sorbed on different atmospheric particulate substrates and/or substrate simulants, PH has been determined to have photolytic half-lives of 150 (silica gel), 45 (alumina), 49 (fly ash), and greater than 1000 h (carbon black) (*2*). The differences in the reported half-lives on various supports are unexplained for PH, as they are for other PAH, and will remain as such until detailed mechanistic information is available for a range of PAH on a series of substrates.

Marine and lacustrine sediments have been said to be the ultimate environmental sinks for PAH (*2*). In the atmosphere, PH and other small PAH have been shown to reside mostly in the gas phase (*8*). The half-life for PH in the gas phase has been determined to be less than 1 day (*9*). Failure of PH to repartition from the sorbed state into the gas phase in our experimnets (vide infra) coupled with sluggish photolytic degradation observed by ourselves and others (*2*) suggest that particulate materials may serve as a sink for PH in the atmosphere.

Experimental Section

The SiO_2 used in this work has characteristics identical to those previously reported (*4c*). The N_2 BET surface area for the SiO_2 was determined to be 274 $m^2\,g^{-1}$ with an average pore size of 60 Å (*4c*). The SiO_2 was loaded with PH (2.5×10^{-5} mol g^{-1}, 5.9% monolayer; 1.0×10^{-4} mol g^{-1}, 23.8% monolayer; and 1.0×10^{-3} mol g^{-1}, 238% monolayer) by adsorption from cyclohexane following the procedure outlined in earlier papers (*4*). Cyclohexane was removed under aspirator vacuum, and final traces were removed at a vacuum of 5−15 μm of mercury. Photolysis was done in quartz tubes irradiating in a Rayonet photoreactor (254 nm, 3.4×10^{16} photons $cm^{-2}\,s^{-1}$ or 350 nm, 1.23×10^{16} photons $cm^{-2}\,s^{-1}$) using a horizontal tube orientation as previously described (*4*). Photolysis was done under an atmosphere of air introduced directly from the laboratory or under argon (ultra-high purity, Air Products Inc.) introduced after evacuation (5 μm of mercury for 10 h).

Photoproducts were removed by washing the SiO_2 first with acetone and then with methanol. Identification of the photoproducts was initially done by GC/MS, and the initial assignments were confirmed by spiking product mixtures with authentic materials where possible. The non-acid products were quantitated on a GC (Hewlett Packard 5890) fitted with a cross-linked methyl silicone colum (HP-1, 12 m, 0.2 mm i.d., 0.33 μm film thickness, Hewlett Packard) and a flame ionization detector (FID). Analysis was done using an internal standard method and calibration with known materials. Organic acid products were analyzed by GC/FID as their respective methyl esters following reaction of the product mixture with diazomethane. The diazomethane was generated following a standard procedure (*10*). Similarly, calibration standards were prepared by esterification of organic acids by diazomethane following the same procedure.

GC/FID analysis of **1** was performed using **2** (Aldrich Chemical Co., Milwaukee, WI) as a calibration standard. Quantitative analysis of **3** was done with the isomeric *trans*-9,10-dihydrodihydroxyphenanthrene, which was prepared by reduction of **2** with $LiAlH_4$, as previously described (*11*). Reduction of **2** with $LiAlH_4$ produced both *trans*-9,10-dihydrodihydroxyphenanthrene and **3** in a ratio of approximately 90:1, as determined by GC and GC/MS. The stereochemistry of the major product from the reduction (the *trans* isomer) was assigned on the basis of previous results (*11*). The formation of both isomers from the reduction of **2** allows us to assign the stereochemistry of the photochemically derived diol, **3**, as *cis*. Analysis of **4** was done using methyl *o*-phenylbenzoate as a calibration standard. Methyl *o*-phenylbenzoate was prepared from *o*-phenylbenzoic acid (Aldrich Chemical Co.). Quantitation of **6** was done using the response factor determined for the dimethyl ester of **5** (Aldrich Chemical Co.), which has the same number of carbon atoms. Similarly, the response determined for 9-fluorenone (Aldrich Chemical Co.) was used to quantitate **7**. The dimethyl esters of 2,3-naphthalenedicarboxylic acid (Aldrich Chemical Co.) and phthalic acid (Aldrich Chemical Co.) were used to quantitate **8** and **9**, respectively.

For the purposes of product identification, **4** was prepared by the thermal decomposition of *tert*-butylperoxy *o*-phenylbenzoate, as previously described (*12*). The final product was analyzed by mass spectrometry; *m/z* (%) = 196 (100), 168 (48), 139 (52).

EPR measurements were made at room temperature on an instrument that has been described elsewhere (*13*). Diffuse reflectance spectra were recorded on a Cary-4 spectrophotometer equipped with an integrating sphere. Baseline correction was done with the spectrum recorded from a sample of SiO_2 that had not been loaded with organics. Emission spectra were recorded on a Spex Fluorolog fluorimeter and are reported fully corrected. Singlet molecular oxygen luminescence was recorded on an instrument that has previously been described (*4a,e*).

Results and Discussion

Spectroscopic Analysis of Phenanthrene Sorbed onto Silica. The diffuse reflectance spectra of PH on silica gel at surface loadings of 1×10^{-5} mol g^{-1} (curve A), 2.5×10^{-5} mol g^{-1} (curve B), and 1×10^{-4} mol g^{-1}(curve C) are shown in Figure 1. The spectra show no sign of ground-state pair formation as previously observed for some silica-sorbed PAH (*4*). Ground-state pairs previously observed on silica exhibited a red-shifted absorption profile in the diffuse reflectance spectra. Similarly, the fluorescence spectra recorded at PH loadings of 1×10^{-5} mol g^{-1} (curve A) and 1×10^{-4} mol g^{-1}(curve B), Figure 2, do not reveal contributions from excimer or excimer-like emissions, although the spectrum recorded at the higher loading (curve B) does have some added intensity on the red-edge of the spectrum.

Ground-state association of sorbed PAH on silicas has previously been detected by the presence of excimer-like emission (*4*). In the case of sorbed 1-methoxynaphthalene, restricted diffusion of the PAH on the surface allowed the observation of excimer-like emission, although an excimer emission has not been reported for 1-methoxynaphthalene

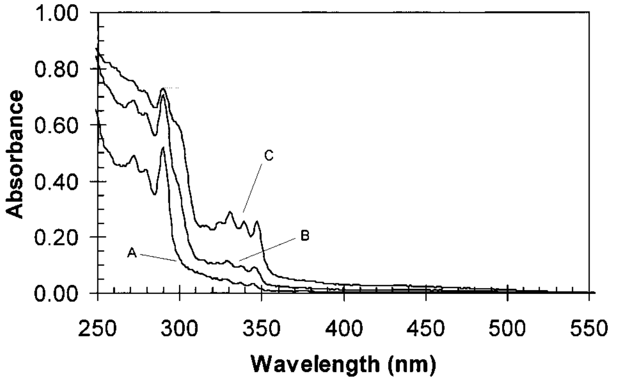


FIGURE 1. Diffuse reflectance spectra of phenanthrene on silica gel at (A) 1 × 10^{-5} mol g^{-1}, (B) 2.5 × 10^{-5} mol g^{-1}, and (C) 1 × 10^{-4} mol g^{-1} surface loading.

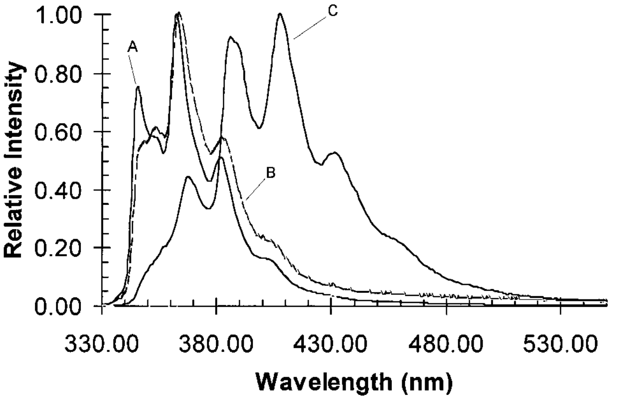


FIGURE 2. Fluorescence of phenanthrene on silica gel at (A) 1 × 10^{-5} mol g^{-1}, (B) 1 × 10^{-4} mol g^{-1}, and (C) 1 × 10^{-3} mol g^{-1} loadings. All samples were excited at 291 nm.

in solution (*4c*). Excimer emission from PH has previously been observed centered at 430 nm in an ethanol/isopentane/diethyl ether solvent at subambient temperatures; however, no excimer fluorescence was observed at room temperature in the mixed solvent system (*14*). These results indicate a very weak stabilization of the PH excimers in solution. The absence of excimer-like emission from sorbed PH on silica suggests the absence of ground-state pairs; however, the existence of ground-state pairs is not rigorously excluded on this basis.

The fluorescence spectrum of PH at a surface loading of 1 × 10^{-3} mol g^{-1} (curve C) in Figure 2 is identical to the fluorescence observed in our laboratory for crystalline PH. The fluorescence and excitation spectra of PH on silica at 1 × 10^{-3} mol g^{-1} loading are shown in Figure 3. The excitation spectrum clearly shows strong transitions at greater than 350 nm that should be visible in the diffuse reflectance spectra in Figure 1 if microcrystalline PH were present on the surface at lower loadings. Both the diffuse reflectance and fluorescence spectra indicate that under the conditions where we have studied the photochemistry of PH on silica, at loadings less than or equal to 1 × 10^{-4} mol g^{-1}, microcrystalline PH is not present. Our interest is in the photochemistry of monomeric PH sorbed onto the surface; therefore, no studies of the photochemistry were conducted at a surface coverage of 1 × 10^{-3} mol g^{-1}.

Emission from singlet molecular oxygen, generated by direct excitation of PH on the silica surface, was directly observed, although the signal was weak. Singlet molecular oxygen emission was also observed from sorbed 9,10-phenanthrenequinone, a product from PH photolysis on silica (*vide infra*). We were unable to detect signals due to superoxide or PH cation radical formation in photolyzed samples (by electron paramagnetic resonance spectroscopy) as were previously observed for other PAH (*4g,i*).

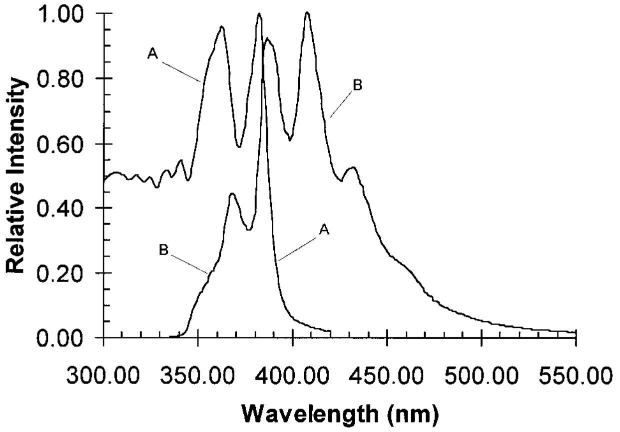
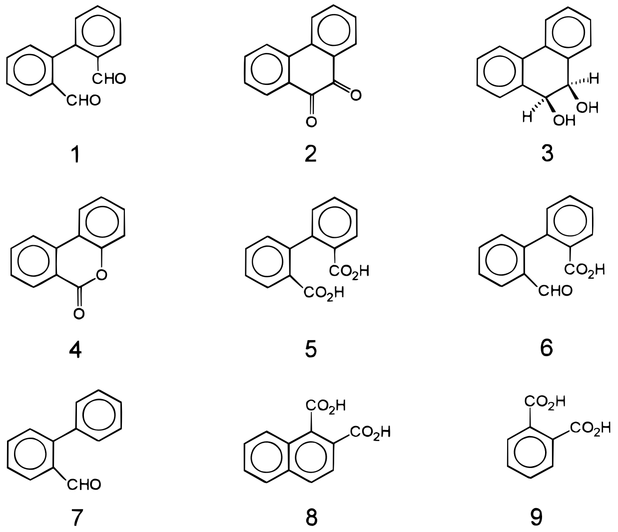


FIGURE 3. Excitation (curve A, λ_{em} = 450 nm) and emission (curve B, λ_{ex} = 291 nm) spectra of phenanthrene (1 × 10^{-3} mol g^{-1}) on silica.

SCHEME 1



Photochemistry of Phenanthrene Sorbed onto Silica. Samples of PH on silica (2.5 × 10^{-5} mol g^{-1} and 1.0 × 10^{-4} mol g^{-1}) photolyzed slowly at 254 nm ($t_{1/2}$ = 15.1 h at 2.5 × 10−5 mol g^{-1} loading) to yield 2,2′-biformylbiphenyl (**1**), 9,10-phenanthrenequinone (**2**), *cis*-9,10-dihydrodihydroxyphenanthrene (**3**), benzocoumarin (**4**), 2,2′-biphenyldicarboxylic acid (**5**), 2-formyl-2′-biphenylcarboxylic acid (**6**), 2-formylbiphenyl (**7**), 1,2-naphthalenedicarboxylic acid (**8**), and phthalic acid (**9**). A direct comparison between the half-life observed in our work (15.1 h) and the previously reported value of 150 h on silica (*2*) cannot be made due to differences in light source photon flux and other experimental parameters. The structural formulas for the products are shown in Scheme 1, and the yields (mole percent of reacted PH) obtained at the two surface loadings (2.5 × 10^{-5} mol g^{-1} and 1 × 10^{-4} mol g^{-1}) are given in Table 1. As shown in Table 1, approximately 90% of the reacted PH is accounted for as photoproducts. The high material balance reported here reveals tht once PH is sorbed onto the silica surface it does not repartition to the gas phase, even under vacuum (*vide supra*). The product yields from photolysis at 254 nm in Table 1 reveal that the surface

TABLE 1

Product Yields (in mol %) from PH Photolysis on Silica

product	surface loading 2.5×10^{-5} mol g^{-1a}	 1×10^{-4} mol g^{-1b}
1	36	37
2	30	31
3	7.4	10
4	7.6	8.2
5	3.8	0.7
6	1.1	*c*
7	2.1	*c*
8	0.6	*c*
9	1.4	*c*
total	90.0	86.9

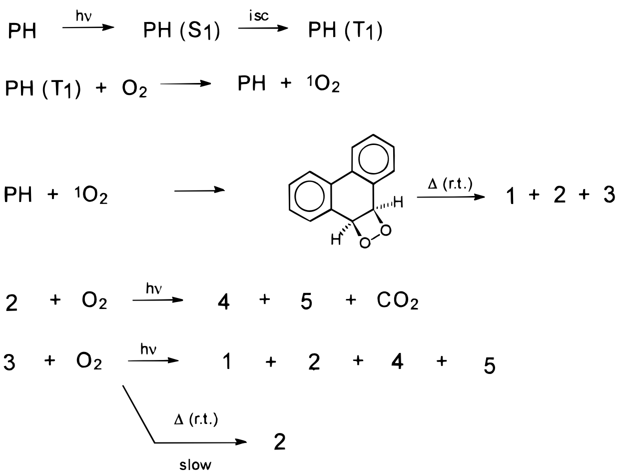
[a] Photolysis time of 3 h, 15% conversion. [b] Photolysis time of 4 h, 6% conversion. [c] Trace of material present, less than 0.5 mol %.

loading has only minimal effect on the product distribution. Control experiments showed no oxidation of PH/silica samples that were not exposed to light for a period of 4 days. The photolysis of PH on silica in the presence of cosorbed 2,5-dimethylfuran, a known singlet oxygen scavenger (*15*), resulted in the formation of products derived only from the furan, and no oxidation products from PH were observed. When methylene blue, a good singlet oxygen sensitizer, was cosorbed on silica with PH and photolyzed at 650 nm (photolysis into the absorption band for methylene blue), major products **1**, **2**, and **3** and minor products **5** and **6** were produced, as in the nonsensitized photolysis. These results indicate that oxidation of PH by singlet molecular oxygen is the major reaction pathway in the photooxidation on silica surfaces.

Photolysis was also done at 350 nm (65 h), and the major products were substantially unchanged from those produced by irradiation at 254 nm. Photolysis at 350 nm did produce trace amounts of unidentified materials, which probably result from secondary product photochemistry and/or thermal instability of the major products. The half-life for photolysis at 350 nm was not determined; however, photolysis of PH occurred much slower than photolysis of anthracene with the same 350-nm light source (*4a*). Similarly, photolysis (450-W medium pressure mercury vapor lamp) of PH on silica has previously been reported to occur 50 times more slowly than anthracene (*2*). The invariance of the product set with changing excitation wavelength indicates that changes in mechanism do not occur upon excitation to singlet states S_N (N > 1) with 254-nm light.

When **3** was sorbed on silica, it was observed to undergo a slow thermal oxidation, proceeding through a transient green intermediate, to form primarily quinone **2**. When **3** was adsorbed on silica and photolyzed (254 nm) under the experimental conditions used for direct PH photolysis, **2** was observed as the major product along with lesser amounts of **1**, **4**, and **5**. The photolysis of **2** (254 nm), adsorbed on silica, under similar conditions gave **4** and **5**. The presence of cosorbed tetrahydrofuran, a good hydrogen atom source, was observed to increase the rate of photolysis of sorbed **2**.

SCHEME 2



These results can be best explained by invoking a mechanism (Scheme 2) wherein PH absorbs light and is promoted to an electronic state S_N (N ≥ 1), from which it relaxes to the S_1 state. Intersystem crossing (isc) leads to formation of the lowest triplet state (T_1) of PH from which singlet molecular oxygen forms by energy transfer (*vide infra*). The ground-state (S_0) of PH reacts with the resulting singlet molecular oxygen to give the thermally unstable 9,10-dioxetane of PH or possibly the corresponding peroxirane, which may rearrange to the dioxetane (*vide infra*). The 9,10-dioxetane of PH in turn undergoes thermal ring opening and further oxidation to give the various products (indicated by Δ r.t. in Scheme 2). Photooxidation of **2** leads to the formation of **4** and **5** as shown by the control experiments described above and depicted in Scheme 2. Photooxidation of **3** has also been shown to produce **1**, **2**, **4**, and **5** on the silica surface. Bimolecular reactions are not important since there is no appreciable change in product distribution upon increasing the coverage of PH on the surface. There is, however, a decrease in the yield of higher oxidation products with increasing coverage (Table 1). This may be due to the formation of these products at the more reactive sites on the silica surface.

Singlet molecular oxygen addition to olefins has been addressed theoretically at the semi-empirical level (*16*). The most reactive site for the addition of singlet molecular oxygen to PH is across the 9,10-positions, as observed for other Diels–Alder reactions with PH and explained in terms of the π-localization energy (*17*). Our observation of products arising primarily from oxidation of the 9,10-positions of PH under direct and sensitized photolysis are in agreement with a singlet molecular oxygen-mediated reaction, as are the previously reported results for sensitized photolysis of PH in solution (*7*). The stereochemistry observed for photochemically derived diol **3** suggests that it arises from homolytic scission of the peroxide bond in a dioxetane intermediate with subsequent hydrogen atom abstraction (see Scheme 2). Further, dialdehydes such as **1** can easily be derived from the same dioxetane intermediate. An alternative mode of singlet molecular oxygen addition across a double bond involves the initial formation of a peroxirane (*16*). The peroxirane can possibly rearrange to the dioxetane, although this rearrangement has a high calculated barrier in peroxiranes derived from an olefin that was part of a six-member ring (*16a*). Alternatively, a peroxirane could be reduced by a double bond in PH to produce 2 mol of oxirane, e.g., the potential carcinogen 9,10-epoxy-9,10-dihydrophenanthrene (*7*, *16b*). This may account for the reported formation of this compound in solution (*7*); however, we do not observe any evidence for its formation on silica.

The interaction of oxygen with electronically excited states can produce a theoretical optimum quantum yield for singlet oxygen production (φ_Δ) of 2, a value that is rarely observed (*18*). Achieving the optimum φ_Δ requires an S_1-T_1 energy gap $\gg 7882\ \mathrm{cm}^{-1}$ (*19*). The reported value of φ_Δ for PH is only 0.5 in methanol (*18*), and the source of singlet oxygen, in this case, is limited to oxygen quenching of the T_1 state of PH. This is due to the small S_1-T_1 splitting in PH (7300 cm^{-1}) (*19*), which is less than the 0,0 excitation energy of $O_2(^1\Delta_g)$ (7882 cm^{-1}). Singlet oxygen production is not depicted as accompanying intersystem crossing (isc) in Scheme 2. It has previously been shown that the rate of oxygen quenching of pyrene triplets on silica ($1.7 \times 10^6\ \mathrm{m}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$) is approximately twice as fast as on alumina ($9.4 \times 10^5\ \mathrm{m}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$) (*20*). The relative rate of PH(T_1) quenching on silica versus alumina is likely to resemble the behavior reported for pyrene quenching. This assertion is supported by the fact that the two molecules are very similar in size, thereby allowing them to occupy similar surface sites and experience similar effects of shielding from oxygen bombardment at the surface. The lifetime of the triplet state of PH, relative to that of pyrene, is irrelevant to this argument since our concern is with the rate of oxygen quenching of the T_1 state of PH on silica versus alumina. On the basis of these arguments, the previously reported enhancement in photolysis rate on alumina ($t_{1/2} = 45$ h) (*2*) relative to the rate on silica ($t_{1/2} = 150$ h) (*2*) cannot be explained by the differential quenching of the triplet state of PH by oxygen on these two substrates. The enhanced rate of photolysis on alumina is more likely due to additional mechanistic pathways involving Lewis acid sites on the alumina (*20*). The previously observed PH photodegradation half-lives on fly ash (49 h) (*2*) and on carbon black (>1000 h) (*2*) are more difficult to address. The large variation in fly ash color and composition offer the possibility of multiple mechanistic pathways involving oxidation by singlet oxygen and/or electron transfer. Both processes can be initiated by energy transfer or direct photolysis and possibly inhibited by competitive absorption of the incident light. The long life time observed on carbon black is likely due to several processes including competitive absorption of the incident light, energy transfer from PH to the large constituent PAH in carbon black, and more facile reactions of singlet oxygen with the substrate.

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