Photophysical and Photochemical Processes of 2-Methyl, 2-Ethyl, and 2-*tert*-Butylanthracenes on Silica Gel. A Substituent Effect Study

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The photophysics and photochemistry of 2-methylanthracene (2MA), 2-ethylanthracene (2EA), and 2-tertbutylanthracene (2TBA) adsorbed on silica was studied at a silica/air interface to determine the substituent effect on the above processes. In contrast to anthracene (AN), which forms ground state stable pairs at surface coverages as low as 1% of a monolayer, 2MA, 2EA, and 2TBA show no evidence of any ground state pairing even at high surface coverages. Diffuse reflectance and fluorescence data indicate that 2MA, 2EA, and 2TBA crystallize on the surface at higher surface coverages. Photolysis of 2MA, 2EA, and 2TBA at a silica/air interface proceeds more efficiently than photolysis of AN to produce the corresponding 9,10-endoperoxides formed by the addition of singlet molecular oxygen (type II) to the ground state molecules. Thermally unstable endoperoxides slowly decompose on silica surface to give the corresponding 9,10-quinones and other hydroxylated products of 2MA, 2EA, and 2TBA. Although photolyzed AN/silica samples show a significant amount of dimer formation at low surface coverages, no evidence of any dimer is observed in photolyzed samples of 2MA, 2EA, and 2TBA at low surface coverages. Small amount of dimers (isomeric), however, are observed in the photolyzed samples of 2MA, 2EA, and 2TBA at higher surface coverages suggesting that the crystal forms of these molecules may be involved in the dimerization process. The photolysis rate decreases as the surface coverage is increased. This behavior can be attributed to the involvement of crystals (formed at higher surface coverage) which act as a light sink to absorb the incident light without producing any net chemistry. The photolysis rate decreases by an order of magnitude in the presence of ≤ 1 monolayer of physisorbed water. Time-resolved transient studies of excited triplet states of 2MA, 2EA, and 2TBA have revealed that triplet lifetimes are shortened on wet silica. Furthermore, the efficiency of singlet molecular oxygen formation drops significantly on wet silica. These results suggest that the decrease in photolysis rate is due to lowering of the singlet oxygen quantum yield in the presence of physisorbed water.

Introduction

Polycyclic aromatic hydrocarbons (PAH) comprise a large class of organic pollutants that are formed and released into the environment by incomplete combustion of fossil fuel, coal, wood, gas, oil, garbage, tobacco, and charbroiled meat. Because of their resistance to biodegradation (especially PAHs with four and more condensed rings) they are very persistent in the environment. Since the environmental fate of PAHs (when present in water, adsorbed on soil or air particulates and exposed to sunlight over an extended period of time) could have a significant impact on their remediation processes, our research in the past few years has focused on the photophysical and photochemical behavior of these compounds under environmentally relevant conditions. Light-induced processes have been claimed to enhance transformation of these anthropogenic pollutants in the environment.^{1,2} Although the photophysics and to some degree the photochemistry of a few PAHs adsorbed on silica³⁻⁷ or other inorganic metal oxides⁸ have been reported, detailed studies on the nature and identities of photoproducts formed during phototransformation of these compounds on solid surfaces is scarce.^{9–12} Seventeen PAHs are on the Environmental Protection Agency's priority pollutant list.¹³ To date, we have studied the photochemical behavior of several PAHs14-22 on this list.^{14,15,17,20–22} The main emphasis of these studies has been on photoproduct identification and the mechanism of their formation. However, we have also investigated the role of surface adsorption and other factors that can impact the adsorption and phototransformation of these molecules at a solid/air interface. In a previous paper on the photophysics and photochemistry of anthracene adsorbed on silica, alumina, and cab-o-sil,15 we reported the observation of ground-state stable pairs by anthracene molecules on silica at surface coverages as low as 1% of a monolayer. The stable pairs were shown to be responsible for the observed dimerization of anthracene on silica.¹⁵ A similar phenomenon has been observed for other PAHs that either lead to dimer formation^{14,16} or exhibit the so-called excimer like emission.^{17–19,21,22} To demonstrate the role of substituents on ground-state pairing and phototransformation of anthracene on silica, we examined the photophysics and photochemistry of 2MA, 2EA, and 2TBA. In this paper we report our steady state and transient studies of these molecules at a silica solid/air interface. A detailed account of the photoproducts and the mechanism of their formation upon photolysis of these compounds is also given in this paper.

Materials and Methods

2-Methylanthracene, 2-ethylanthracene, and 2-*tert*-butylanthracene (Aldrich Chemical Co., Inc., Milwaukee, WI) were

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SCHEME 1 . Schematic Diagrams of the Apparatus Used for the Diffuse Reflectance Laser Flash Photolysis and Singlet Molecular Oxygen Lifetime Measurements



chromatographed on silica gel (Baker Analyzed, Phillipsburg, NJ, 60–200 mesh), using cyclohexane as eluent, before use. Purity was determined by gas chromatography (GC) to be >99.8%. Cyclohexane, acetonitrile, methanol, methylene chloride, and toluene were all HPLC grade (Baker Analyzed) and were used as received. Methylene blue (Baker Analyzed) was used as received. 2,5-dimethylfuran (Aldrich, purity 99%) was chromatographed on silica gel before use. Silica-60 (Baker analyzed; 60–200 mesh) was activated at 200 °C in air for at least 24 h before use. It had a surface area of 274 m²/g with an average pore radius of ca. 60 Å¹⁹ as described previously.^{14–22} Percent monolayer surface coverage was calculated by fractal theory reported previously^{15,16} using geometrical areas of 60.7 $\times 10^{-20}$ m²/molecule for 2MA, 64.0 $\times 10^{-20}$ m²/molecule for 2EA, and 67.4 $\times 10^{-20}$ m²/molecule for 2TBA, respectively.

Adsorption of 2MA, 2EA, and 2TBA onto silica surface was achieved by a cyclohexane slurry method described previously.14-22 Aerated silica samples containing adsorbed 2MA, 2EA, and 2TBA (2 g) were photolyzed at 350 nm in uranium glass tubes (330 nm cutoff, outer diameter = 1 in) using a Rayonet RPR-208 photoreactor equipped with a merry-go-round attached in a horizontal configuration as reported before.14-22 Photolysis products and the unreacted starting material were extracted from the surface by multiple washing with methylene chloride, methanol, and acetonitrile to ensure complete removal of all materials from the surface. A final wash of the silica surface with cyclohexane and toluene was performed to remove dimer(s) which are normally insoluble in methylene chloride, methanol, and acetonitrile. Solvents were then removed under vacuum at room temperature and the residue was dissolved in a known volume of acetonitrile or cyclohexane (for dimers only) for quantitative HPLC analysis. Product analysis was carried out by reverse phase HPLC (Hewlett-Packard model 1090) as described previously.¹⁵ Calibration for quantitative HPLC analysis of the photoproducts was performed with authentic samples, which were either commercially available or synthesized. Material balance was better than 80% of total 2MA, 2EA, and 2TBA loss during photolysis.

The 9,10-endoperoxides of 2MA, 2EA, and 2TBA were prepared by photolysis ($\lambda_{ex} = 650$ nm) of an oxygenated solution of each in a 9:1 methylene chloride/methanol mixture using methylene blue as the singlet oxygen sensitizer.¹⁵

Diffuse reflectance spectra were recorded on a Cary 4E UV– vis spectrophotometer (Varian) equipped with an integrating sphere. Steady-state fluorescence spectra were obtained on a Spex-Fluorolog-2 spectrometer equipped with double monochromators on both excitation and emission sides. All spectra were recorded from the front face of the cell containing the solid sample and were corrected for silica background and instrument response using correction factors provided by the manufacturer. Degassed samples for fluorescence measurement were prepared in tubes equipped with a 1 cm quartz sidearm cell and were flame-sealed under vacuum ($P \ge 1 \times 10^{-6}$ Torr).

Diffuse Reflectance Laser Flash Photolysis. Scheme 1 shows the schematic for diffuse reflectance laser flash photolysis (DRLFP) apparatus assembled in our laboratory to carry out time-resolved experiments. The third harmonic (355 nm) of a Minilite II Nd:YAG laser (Continuum) was passed through the P1 prism and S1 shutter and delivered to the sample as the excitation beam. The excitation beam was overlapped with the probe beam delivered to the sample through S2 shutter from either a high pressure 450-W xenon or 250-W mercury-xenon (Oriel Corp.) lamp. The laser and shutters were triggered through an AT-DIO-32F DAQ board (National Instruments). In general, pulse energies of less than 9 mJ/pulse (5 ns pulse width) were employed to irradiate 0.55 cm² exposed area of the sample giving a fluence of 16.4 mJ/cm² per pulse. The laser energy was attenuated using a digital delay generator (DG355, Stanford Research System, Inc.) to delay the Q-switch trigger with respect to flash lamp trigger. The energy of the laser pulse was measured using a beam splitter to direct the beam into a J25LP-1 detector (Molectron) connected to an EPM 1000 laser energy meter



Figure 1. Changes in the absorption profile (obtained by diffuse reflectance) of 2-*tert*-butylanthracene (2TBA) adsorbed on silica as a function of surface coverage for (curve A) 0.012%, (curve B) 0.54%, (curve C) 1.2%, (curve D) 23.7%, and (curve E) 53% of a monolayer. The inset shows normalized diffuse reflectance spectra of anthracene adsorbed on silica for different surface coverages: A (0.5%), B (1.7%), C (3.2%), and D (8.8% of a monolayer).

(Molectron) for read out. Two lenses were used to focus the diffusely reflected light from the sample onto the entrance slit (0.25 mm slit) of a DH10 monochromator (Instrument SA). The exit slit of the monochromator was attached to a PMT (Oriel 77346). The output of PMT was amplified by a two stage amplifier (SR445, Stanford Research Systems, Inc.), and the signal was fed into a LeCroy 9354A transient digitizer which was triggered for data acquisition by a photodiode signal activated by the reflection of the laser beam through P1 prism. For time-resolved absorption experiments, the observed emission signals with probe light on (probe, background signal with laser beam off), laser beam on (pump, probe beam off), and both probe and laser beam on (probe + pump) were stored in three memory slots of the LeCroy transient digitizer. The cuvette containing the solid sample was agitated after each laser shot to avoid possible photodecomposition. The transient reflectance signal ($\Delta R/R$) was calculated using the following equation

$\Delta R/R = [probe - ((probe + pump) - pump)]/probe$

in conjunction with the math functions provided by LeCroy data acquisition software that could be accessed on the transient digitizer. All digitized kinetic signals from the transient digitizer were fed to a 488.2 GPIB board (National Instruments) and stored as ASCII files. The data were then transformed to time-resolved absorption spectra using Origin 4.0 software (Microcal).

Time-resolved diffusely reflected emission (TRDRE) signals from solid samples were collected using an Intensified Charge Coupled detector (ICCD) with a slight modification to Scheme 1 for the DRLFP setup. Diffusely reflected emission from the sample was focused, using a combination of lenses, into the entrance slit of a polychromator (EG&G PARC-1226 with 150 groove/mm holographic grating). The light from the exit port of polychromator was then focused on the front face of a gated ICCD (InstaSpec IV, Andor Technology) operated at -5 °C. Data acquisition was performed using the software (Insta Spec 1.11 version) provided by the manufacturer which was integrated with a DG355 digital delay generator (Stanford Research Systems, Inc.) to control the gate width and the delay timing of the delay generator through a GPIB interface. The mercury lines of a 250-W high-pressure xenon-mercury lamp (Oriel Corp.) were used to align the detection system and calibrate the ICCD. Emission traces collected by ICCD were exported as ASCII files to Origin 4.0 software to be fitted using standard procedures.

Results and Discussion

Photophysical Studies. (a) Steady State. In our previous report on the photochemistry of AN adsorbed on silica, we assigned the observed red-shifted band (centered around 390 nm) in the absorption profile to the ground-state stable pairs, which exhibit a distinct emission spectra.¹⁵ In contrast to AN, diffuse reflectance spectra of 2MA, 2EA, and 2TBA show no evidence of a red-shifted band even at surface loadings as high as 50% of a monolayer indicating that steric factors play an important role in inhibiting the formation of ground-state pairs. Figure 1 shows representative diffuse reflectance spectra for 2TBA adsorbed on silica at various surface loadings. The slight red-shifting observed at high surface coverages (curves D and E, Figure 1 for 23.7 and 53% of a monolayer, respectively) can be attributed to microcrystal formation by 2TBA at these loadings. This notion is further supported by our fluorescence data. Figure 2 shows the changes in emission spectra of 2TBA as a function of surface coverage. As the surface loading is increased from 0.012% to 53% of a monolayer, the emission bands at 385 and 400 nm are displaced with a new band appearing around 410 nm while the intensity of the shoulder at 430 nm increases (curves D and E, Figure 2). The observed red-shifting of emission spectrum as the surface loading is increased can be attributed to the formation of 2TBA microcrystals, which exhibit a different emission spectrum (curve F in Figure 2 shows the emission spectrum of pure 2TBA crystals). Thus, the overall emission at high surface loadings (e.g., 23.7 and 53% of a monolayer, curves D and E, Figure 2) is the sum of contributions from monomeric and microcrystal forms of 2TBA. Similar results have been observed for 2MA and 2EA (not shown). Our steady-state absorption and emission data



Figure 2. Changes in the emission ($\lambda_{ex} = 350 \text{ nm}$) spectra of degassed 2TBA adsorbed on silica as a function of surface coverage for (curve A) 0.012%, (curve B) 0.54%, (curve C) 1.2%, (curve D) 23.7%, and (curve E) 53% of a monolayer. Curve F corresponds to the emission of crystalline form of 2TBA. The inset shows variation in the excitation ($\lambda_{em} = 400 \text{ nm}$ for A and B and $\lambda_{em} = 420 \text{ nm}$ for C) and emission ($\lambda_{ex} = 360 \text{ nm}$) spectra (normalized relative to total area) of anthracene adsorbed on silica (degassed) as a function of surface coverage: A (0.5%), B (3.2%), and C (6.4% of a monolayer).



Figure 3. Time-resolved emission spectra of 2TBA adsorbed on silica $(8.5 \times 10^{-7} \text{ mol/g})$ following laser excitation at 355 nm. A 2 ns gated ICCD camera was used to record the transient emission. Spectra were obtained at 20, 25, 30, and 35 ns time intervals. The inset shows an enlarged portion of the emission spectra taken at 35, 40, and 45 ns after the laser pulse.

clearly show that introduction of bulky alkyl groups into AN moiety inhibits the formation of ground-state pairs at low surface coverages. At high surface loadings these alkyl substituted AN molecules crystallize on silica.

(b) Transient. Excited-state dynamics of 2-alkyl substituted anthracences adsorbed on silica were studied using the timeresolved diffuse reflectance laser flash photolysis technique.²³ All samples were degassed for several days under high vacuum and flame-sealed before conducting transient studies. Timeresolved transient emission of 2TBA adsorbed on silica (2.0 × 10^{-6} mol g⁻¹) using 355 nm excitation is shown in Figure 3. The emission shows spectral features (bands at 388, 406, and 432 nm in Figure 3) similar to those obtained under steadystate irradiation conditions (Figure 2). The emission decay for 2TBA at 406 nm was best fitted to a biexponential decay curve showing a short-lived component with a lifetime of about 5.0 \pm 0.2 ns and a longer lived second component with a lifetime of 33.0 \pm 0.3 ns. A similar treatment of the emission decay profiles for 2MA and 2EA adsorbed on silica (2 × 10⁻⁶ mol



Figure 4. Time-resolved transient difference spectra of 2TBA adsorbed on silica $(4.3 \times 10^{-7} \text{ mol/g})$ showing reflectance changes following laser excitation at 355 nm (laser energy: 5 mJ/pulse) after 19, 88, and 140 us. The inset shows the decay of transient at 420 nm and the biexponential fit of the trace.

 g^{-1}) gave lifetimes in the range 6 and 30 ns, respectively. These lifetimes are in good agreement with the reported values for anthracene on silica²⁴ and suggest that alkyl substituents do not alter the excited singlet state lifetime significantly. Addition of water to silica (3 × 10⁻³ mol g⁻¹) does not affect the short-lived component but shortens the lifetime of the longer lived component to about 20 ns.

Time-resolved transient absorption spectra of degassed 2TBA adsorbed on silica (4.3 \times 10⁻⁷ mol g⁻¹) obtained at 19, 88, and 140 μ s after the laser pulse ($\lambda_{ex} = 355$ nm) are shown in Figure 4. The transient exhibits three peaks at 390, 410, 420 (major), and a shoulder around 435 nm. No evidence of any cation radical formation, which absorbs in the 700-750 nm region, was observed under these conditions. The formation of anthracene cation radical on silica by a biphotonic process has been reported.²⁵ The low energy of excitation light (3-5 mJ/)pulse laser power) used in our experiments accounts for the lack of any cation radical formation under these monophotonic excitation conditions. The fact that this transient was completely quenched in the presence of oxygen further supports the above notion and confirms the absence of any cation radical contribution to the observed transient. Thus, we assign this transient to triplet-triplet absorption, $T_1 \rightarrow T_n$, of the first excited triplet state of 2TBA. The biexponential fit of the decay curve at 420 nm gives a short-lived component with a lifetime of about 5.5 μ s and a long-lived component with a lifetime of 0.24 ms, respectively (inset, Figure 4). Similar transient absorption spectra were also obtained for 2MA and 2EA adsorbed on silica indicating that alkyl substituents did not greatly alter the shape of triplet-triplet absorption relative to that of anthracene. The lifetime of the transients determined for 2MA (9 \times 10⁻⁷ mol g^-1) and for 2EA (6.9 \times 10^{-7} mol g^-1) were 3.8 μs and 0.15 ms and 5.2 μ s and 0.12 ms, respectively. We assign the longerlived component to the triplet state of 2MA, 2EA, and 2TBA. Because the origin of shorter-lived component is not clear to us, we cannot assign it to any particular state.

The triplet lifetime was sensitive to the concentration of the substrate on silica and decreased as the surface loading was increased. We attribute this decrease in lifetime to the quenching of triplet excited state by microcrystals formed at higher surface loadings (i.e., self-quenching by neighboring molecules in close proximity of the excited molecule). The rate constant for quenching of 2TBA triplet state by ground-state molecules was determined to be 4.3×10^5 g s⁻¹ mol⁻¹ from a plot of inverse of the triplet lifetime vs concentration of 2TBA on silica (not shown).



Figure 5. Changes in the decay profile of excited-state triplet (420 nm) of 2TBA (4.3×10^{-7} mol/g) adsorbed on silica as a function of concentration of physisorbed water (355 nm laser excitation). The inset shows plot of triplet decay rate constant *vs* concentration of physisorbed water.

The triplet lifetime was also very sensitive to the presence of physisorbed water on silica and decreased as the water concentration was increased. Figure 5 shows the variation in triplet decay profile for 2TBA adsorbed on silica as the concentration of physisorbed water is increased. From the slope of a plot of $1/\tau_{\rm T}$ vs concentration of water (inset, Figure 5) on silica surface, a bimolecular rate constant of $8.9 \times 10^5 \text{ s}^{-1} \text{ mol}^{-1}$ g was determined for this process. The bimolecular rate constants for 2EA and 2MA were determined to be 4.1×10^5 and $2.4 \times 10^7 \text{ s}^{-1} \text{ mol}^{-1} \text{ g}$, respectively. A plausible explanation for the observed decrease in triplet lifetime in the presence of physisorbed water can be provided as follows. Polar water molecules can easily displace (via hydrogen bonding with silanol groups) loosely held 2-alkylanthracenes from the adsorbed sites allowing the desorbed molecules to be more mobile (diffuse more freely) on the surface. Since solubility of 2-alkylanthracenes in water is very low, the desorbed molecules will tend to aggregate and form microcrystals as evidenced by diffuse reflectance absorption and emission spectroscopy (not shown). The interaction of these molecules with the excited triplet state (a self-quenching process) could result in the observed shortening of the triplet lifetime in the presence of physisorbed water. We believe the difference in bimolecular quenching rate constants calculated for 2MA, 2EA, and 2TBA results from the difference in their water solubility. The bimolecular rate constant for the self-quenching of anthracene in ethanol has been reported to be 5.19 \times 10⁵ M⁻¹ s^{-1.26}

The decrease in the lifetime of excited triplet state will affect the rate of bimolecular processes involving this state (e.g., energy transfer to molecular oxygen to form singlet oxygen). To explain the observed decrease in photodecomposition rate of 2-alkyl substituted anthracenes on silica in the presence of physisorbed water (vida infra), we carried out a time-resolved near-IR study of singlet molecular oxygen emission (1270 nm) using an apparatus similar to that reported by Bilski et al.²⁷ The purpose of this study was to examine the effect of physisorbed water (if any) on the lifetime and/or quantum efficiency of singlet molecular oxygen produced via energy transfer from excited 2MA, 2EA, or 2TBA to molecular oxygen. Figure 6 shows the decay of singlet molecular oxygen emission (1270 nm) on silica, produced by 2TBA via energy transfer (type II), in the presence of physisorbed water. A fit of the decay curves (monoexponential) gives singlet oxygen lifetime values of 3.9 \pm 0.2 μ s for dry silica (curve a), 7.6 \pm 1.9 μ s in the presence of water (curve b), and 10.5 ± 0.6 us in the presence of deuterated water (curve c). A value of 0.9 us was determined



Figure 6. Effect of physisorbed water on the near-IR emission (1270 nm) of singlet molecular oxygen produced by 355 nm laser excitation of an aerated sample of 2TBA adsorbed on silica $(3.4 \times 10^{-6} \text{ mol/g})$ for (curve a) dry, (curve b) 72.6 wt % water/g of silica, and (curve c) 112 wt % water/g of silica. Curve d shows the observed emission from a Suprasil quartz tube. A similar emission curve as d is observed with silica present in the quartz tube.

for the lifetime of the emitting impurity (curve d) present in the Suprasil quartz tube.²⁷ These lifetime data cannot explain the observed decrease in photodecomposition rates for 2MA, 2EA, and 2TBA in the presence of physisorbed water.

The quantum efficiency of singlet oxygen production decreased as the concentration of water on silica was increased. This conclusion was drawn by comparing the intensity of singlet oxygen emission for dry and wet silica extrapolated to t = 0time. The observed emission intensities in the presence of physisorbed water and deuterated water ²⁸ were 0.46 and 0.22, respectively, relative to the intensity from dry silica. Since singlet oxygen is produced upon interaction of molecular oxygen with the excited state of 2MA, 2EA, and 2TBA (type II), a shortening of the excited-state lifetime in the presence of physisorbed water can lead to lower efficiency for its formation. Our transient data indicates that excited singlet states of 2MA, 2EA, and 2TBA are unaffected by the presence of physisorbed water (not shown) while excited triplet states experience a lifetime shortening. Thus, the observed decrease in photolysis rate in the presence of physisorbed water can be attributed to the shortening of 2MA, 2EA, and 2TBA excited-state triplet lifetimes which in turn causes a decrease in the efficiency of singlet molecular oxygen production.

Photochemical Studies. Photolysis of 2MA, 2EA, and 2TBA at a silica/air was carried out in a Rayonet RPR-208 photoreactor equipped with a merry-go-round using 350 nm excitation light source as described previously.15 The photolysis rate was dependent on the surface coverage and decreased as the surface coverage was increased. We attribute this decrease in photolysis rate at higher surface loadings to an inner filter effect induced by crystal formation. These crystals absorb the incident light (competing with 2MA, 2EA, and 2TBA monomeric forms) without producing any net chemistry (light sinks). Figure 7 compares the first-order rate constant for photolysis of AN, 2MA, 2EA, and 2TBA. The rate constant decreases in the following order 2TBA > 2EA > 2MA > AN. The data shows that for the same surface coverage, 2TBA reacts almost twice faster than AN. This difference in reactivity can be explained on the basis of our spectroscopic findings. Steady state absorption and emission results indicate that at this surface coverage a significant portion of AN molecules are present in stable pair form while 2TBA exists mainly in the monomeric form. Absorption of incident light by the AN stable pairs does not lead to a photochemical reaction while the monomeric form of



Figure 7. Plot of first-order rate constant for the loss of anthracene, (\bullet) AN, (\checkmark) 2MA, (\diamond) 2EA, and (\blacksquare) 2TBA at silica/air interface. First-order rate constants calculated from the slopes are: $k_{AN} = 3.1 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$, $k_{2MA} = 4.0 \pm 0.3 \times 10^{-3} \text{ s}^{-1}$, $k_{2EA} = 5.5 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$, and $k_{2TBA} = 5.8 \pm 0.2 \times 10^{-3} \text{ s}^{-1}$.

SCHEME 2. Observed Photoproducts from Photolysis ($\lambda_{Ex} = 350$ Nm) of 2MA, 2EA, and 2TBA at a Silica/Air Interface



2TBA undergoes photochemical conversion to products (*vida infra*). As the surface coverage is increased, the decrease in photolysis rate for 2MA, 2EA, and 2TBA is consistent with the formation of crystals at higher surface loadings. A similar behavior by other PAHs has been reported previously.^{14–22} The photolysis rate was also very sensitive to the presence of physisorbed water on the silica surface. Time-resolved transient studies carried out on AN, 2MA, 2EA, and 2TBA adsorbed on dry and wet silica have revealed that the observed decrease in photolysis rate, in the presence of physisorbed water, results from shortening of the excited-state triplet lifetime (*vida infra*).

Scheme 2 shows the photoproducts formed upon photolysis of 2MA, 2EA, and 2TBA at silica/air interface. Our data indicates that at low surface coverages no photodimer is formed and photooxidation products account for almost 100% of the total products. Although small amounts of photodimers are observed at higher surface coverages, they only account for $\leq 5\%$ of the total products. The observation that photodimers form at higher surface coverages, when the molecules start to crystallize, indicates that crystal forms of 2MA, 2EA, and 2TBA are most likely responsible for the formation of photodimers. The assigned structures of 9,10-photodimers shown in Scheme 2 is based on our solution studies where we observed (by LC–MS) three dimeric products upon photolysis of degassed samples of 2-substituted anthracenes in cyclohexane.

The role of singlet molecular oxygen in the oxidation of 2-substituted anthracenes on silica was examined by conducting the photolysis in the presence of coadsorbed: (a) 2,5-dimethylfuran, a well-known singlet oxygen trap,²⁹ and (b) methylene blue, a good generator of singlet oxygen on the silica surface.³⁰ When a 10:1 mixtures of methylene blue/silica (1 \times 10⁻⁵ mol/ g) and 2-substituted anthracenes/silica (2 \times 10⁻⁵ mol/g) was photolyzed at 650 nm, where the substituted anthracenes do not absorb, only the oxidation products shown in Scheme 2 and no photodimers were observed. Direct photolysis ($\lambda_{ex} = 350 \text{ nm}$) of 2-substituted anthracenes/silica (2 \times 10⁻⁵ mol/g) in the presence of 2,5-dimethylfuran/silica $(2 \times 10^{-4} \text{ mol/g})$ in a 1:1 ratio produced a small amount of dimers but no oxidation products. These results unequivocally implicate the role of singlet molecular oxygen as the intermediate in inducing the oxidation of 2-substituted anthracenes on silica.

Conclusions

Photophysical studies of 2-methyl, 2-ethyl, and 2-*tert*butylanthracenes indicate that in contrast to anthracene, which forms stable pairs at very low surface coverages (1% of a monolayer) when adsorbed on silica, these substituted anthracenes show no evidence of pairing even at surface coverages as high as 53% of a monolayer. At higher surface coverages, these molecules tend to crystallize on silica surfaces. The presence of bulky alkyl groups on the anthracene moiety is most likely responsible for the lack of pairing by these substituted anthracenes. Photodecomposition of 2-substituted anthracenes on silica proceeds more efficiently than anthracene to produce mainly oxidation products and small amounts of isomeric dimers. This enhanced reactivity is attributable to the absence of ground-state pairs, which can act as a light sink without producing any net chemistry. The oxidation products are formed by the addition of singlet molecular oxygen (sensitized by the interaction of excited state of 2-substituted anthracenes with molecular oxygen) to the ground state of 2-substituted anthracenes. The precursor to photodimers appears to be the crystalline forms of these substituted anthracenes.

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References and Notes

(1) Hutzinger, O., Ed. The Handbook of Environmental Chemistry; Springer: Berlin, 1982; Vol. 2, Part B.

(2) Zika, R. G.; Cooper, W. J., Eds. *Photochemistry of Environmental Aquatic Systems*; ACS Symposium Series 327; American Chemical Society: Washington, DC, 1987.

(3) de Mayo, P.; Natarajan, L. V.; Ware, W. R. In Organic Phototransformation in Nonhomogeneous Media; ACS Symposium Series 278 Fox,

M. A., Ed.; American Chemical Society: Washington, DC, 1984; pp 1–19.
(4) Bauer, R. K.; de Mayo, P.; Ware, W. R.; Wu, K. C. J. Phys. Chem.
1982, 86, 3781.

(5) Bauer, R. K.; de Mayo, P.; Okada, K.; Ware, W. R.; Wu, K. C. J. Phys. Chem. **1983**, 87, 460.

(6) de Mayo, P.; Natarjan, L. V.; Ware, W. R. Chem. Phys. Lett. 1984, 107, 187.

(7) Levitz, P.; Van Damme, H.; Keracis, P. J. Phys. Chem. 1984, 88, 2228.

(8) Thomas, J. K. Chem. Rev. 1993, 93, 301.

(9) de Mayo, P.; Okada, K.; Rafalska, M.; Weedon, A. C.; Wong, G. S. J. Chem. Soc., Chem. Commun. **1981**, 820.

(10) Bauer, R. K.; Borenstein, R.; de Mayo, P.; Okada, K.; Rafalska, M.; Ware, W. R.; Wu, K. C. J. Am. Chem. Soc. **1982**, 104, 4635.

(11) Hasegawa, K.; Murase, M.; Kuboshita, M.; Saida, H.; Shinoda, M.; Miyamoto, M.; Shimasaka, C.; Yoshimura, T.; Tsukurimichi, E. *Environ. Sci. Technol.* **1993**, *27*, 1819.

(12) Mao, Y.; Thomas, J. K. Langmuir 1992, 8, 2501.

(13) *Toxicological Profile for Polycyclic Aromatic Hydrocarbons Report*; U. S. Department of Health and Human Services, Public Health Service: Washington, DC, 1993.

(14) Barbas, J. T.; Dabestani, R.; Sigman, M. E. J. Photochem. Photobiol. A: Chem. 1994, 80, 103.

(15) Dabestani, R.; Ellis, K. J.; Sigman, M. E. J. Photochem. Phtotobiol. A: Chem. **1995**, 86, 231.

(16) Dabestani, R.; Nelson, M.; Sigman, M. E. Photochem. Photobiol. 1996, 64, 80.

(17) C. Reyes, C.; Sigman, M. E.; Arce, R.; Barbas, J. T.; Dabestani, R. Photochem. Photobiol. A: Chem. 1998, 112, 277.

(18) Barbas, J. T.; Sigman, M. E.; Arce, R.; Dabestani, R. J. Photochem. Photobiol. A: Chem. 1997, 109, 229.

(19) Sigman, M. E.; Barbas, J. T.; Chevis, E. A.; Dabestani, R. New. J. Chem. 1996, 20, 243.

(20) Barbas, J. T.; Sigman, M. E.; Dabestani, R. *Environ. Sci. Technol.* **1996**, *30*, 1776.

(21) Barbas, J. T.; Sigman, M. E.; Buchanan, A. C.; Chevis, E. A. Photochem. Photobiol. 1993, 58, 155.

(22) Reyes, C. A.; Medina, M.; Crespo-Hernandez, C.; Cedeno, M. Z.; Arce, R.; Rosario, O.; Steffenson, D. M.; Ivanov, I. N.; Sigman, M. E.; Dabestani, R. *Environ. Sci. Technol.* **2000**, *34*, 415.

(23) Wilkinson, F.; Kelly, G. P. *In Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 1; pp 293–314.

(24) Bauer, R. K.; Borenstein, R.; deMayo, P.; Ware, W. R.; Wu, K. C. J. Phys. Chem. **1982**, *86*, 3781.

(25) Wilkinson, F.; Worrall, D. R.; Williams, S. L. J. Phys. Chem. 1995, 99, 6689.

(26) Saltiel, J.; Marchand, G. R.; Dabestani, R.; Pecha, J. M. Chem. Phys. Lett. 1983, 100, 219.

(27) Bilski, P.; Chignell, C. F. J. Biochem. Biophys. Methods 1996, 33, 73.

(28) Deuterated water was employed as a means to see whether singlet oxygen lifetime is increased relative to water indicating preferential diffusion of this species from the surface into the liquid phase. Our data, however, shows no significant change in the lifetime of singlet oxygen for physisorbed water or deuterated water ruling out a substantial contribution from such diffusion.

(29) Gollnick, K.; Griesbeck, A. Photochem. Photobiol. 1985, 41, 2057.

(30) Brkic, D.; Frozatti, P.; Pasquoss, I.; Trifiro, F. J. Mol. Catal. 1977, 3, 173.