increase in bond order of the CO molecule.

These results in combination with our earlier photoelectron studies provide a rather detailed picture of the electronic structure of the ZnO–CO surface complex shown in Figure 1. The decrease in 4σ–5σ splitting upon coordination (as observed in the He(II) photoelectron spectrum) indicates that the CO is acting as a 5σ donor, removing electron density from an orbital which is weakly antibonding with respect to the CO molecule. There is simultaneously a net donation of negative charge from the CO molecule toward the surface (as determined from He(I) photoelectron work function studies) thus indicating that little π backbonding into the $2\pi^*$ orbital of the CO molecule occurs. The net effect is to increase the CO bond order as is reflected by the increase in CO stretching frequency.

This geometric and electronic structure picture of CO on ZnO has implications concerning its reactivity, in particular with respect to the synthesis of methanol. The polarized molecule has a strengthened CO bond, initially making C–O bond rupture less probable but making the molecule susceptible to heterolytic attack by dissociated H_2, which is known to adsorb as $Zn–H^-$ and $O–H^+$.[14]

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Registry No. Carbon monoxide, 630-08-0; zinc oxide, 1314-13-2; methanol, 67-56-1.

Photophysics of Polycyclic Aromatic Molecules on Semiconductor Powders[1]

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Abstract: Several aromatic molecules (pyrene, perylene, anthracene, methylanthracene, pyrenecarboxaldehyde, and bromopyrene) have been adsorbed on TiO_2 particles suspended in water. The unsubstituted arenes show significant changes in their absorption and emission spectra which comment on the nature of the adsorbed state. Substituted molecules exhibit spectra characteristic of polar environments. Coadsorption of other molecules, e.g., OH^-, I^-, or dimethylaniline, onto TiO_2 containing pyrene changes the emission spectrum to that characteristic of pyrene in a polar medium. Pulsed laser studies show that little if any movement of adsorbed molecules occurs on the TiO_2 surface. The fluorescence of adsorbed pyrene shows two well-defined time regions, one with a $t_{1/2}$ of 5 ns and the other with $t_{1/2}$ of 200 ns. The data show that at least two sites of adsorption exist for pyrene on TiO_2. The data are discussed in terms of spectroscopy established for these molecules in homogeneous solution and simple colloids such as micelles.

Introduction

The last decade has seen an increasing amount of interest in the photochemistry at interfaces,[2-5] in such systems as micelles, microemulsions, and, more recently, colloidal semiconductors.[6-12] The concept of all this work is to utilize the unique properties of the interfaces, or surfaces of these materials, in order to help to drive selected features of photochemical reactions. In particular, photoinduced electron-transfer reactions have been of prime importance because of their possible use in the storage of solar energy either as electrical energy[13] or as ionic products.[14]

Work with semiconductors has held particular appeal because of the strong photochemical properties of these materials. For example, TiO_2 colloids with very large surface areas may be prepared in aqueous solution. These colloids readily adsorb receptor molecules such as methyl viologen. On photoexcitation an electron is transferred from the semiconductor to the receptor, e.g., methyl viologen, and subsequent chemistry leads to useful products such as hydrogen, etc.[15,16]

These systems possess other features, which are slightly removed from the above type of photochemistry. For decades there has been a tremendous amount of interest in the use of catalysts to drive selected thermal reactions. Here it is recognized that the adsorption of molecules onto the active surfaces gives rise to molecules with enhanced properties, which give rise to the selected reactions that are considered to be useful.[17,18] Several different photophysical methods have been developed recently in micellar systems which enable comment to be made on the environments of molecules adsorbed on catalytic surfaces, or at active interfaces.[19-22] For example, ease of excimer formation, and quenching of excited states, comment on the movement of molecules on surfaces, the technique of fluorescence polarization comments on the local degree of rigidity of bound molecules, while fluorescence spectra of adsorbed probe molecules can comment on the environment of the polarity of molecules at sites of adsorption.[23,24] These techniques have been successfully used to study the adsorption of molecules on solid surfaces such as aluminum oxide and on silica gel.[19,25,26] This paper describes the use of selected

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probe molecules to comment on the nature of adsorbed molecules on the surface of TiO_2 particles suspended in water. Polyaromatic molecules such as pyrene and derivatives of pyrene are adsorbed on the TiO_2, when the excited state properties of these molecules comment on the unique environment in which these molecules lie.

Experimental Section

A. Preparation of TiO_2 Powder. TiO_2 was prepared by acid hydrolysis of titanium tetraisopropoxide as reported in an earlier communication.[27] The size of the prepared particles when suspended in water was determined to be 2000 ± 200 Å, as determined by the technique of dynamic light scattering with a Nicomp instrument. In the absence of any stabilizing agent the particles tend to coagulate over 10 h and slowly settle out of solution. Absorption spectra of suspensions of TiO_2 powder in water show a sharp increase in spectral absorbance below 4000 Å. Absorbance above 4000 Å is weak and is attributed to scattering of light by the large particles. No emission of light from excited TiO_2 was detected under any circumstance.

B. Preparation of Samples. The organic probe molecules used in this study (pyrene, perylene, anthracene, methylanthracene, and pyrenecarboxaldehyde) were either purified by recrystallization from suitable solvents such as methanol or hexane, or were purified by rapid mixing of hot ethanolic solutions of the probes with water, when the probes are precipitated out in the pure form, and may be filtered clear of the aqueous ethanol solution. Probes prepared in such a manner were dried under vacuum at 42 °C. The probe molecules were subsequently dissolved in a small quantity of hexane, and this solution was stirred with TiO_2 powder, followed by sonication for 30 min. The mixture was subsequently heated to remove the solvent. Under these conditions small crystals of solid pyrene were observed deposited on the dry TiO_2 powder. The unabsorbed crystalline pyrene was removed by several extractions of the TiO_2 with hexane followed by drying at room temperature. The samples were stored in the dark to avoid photochemical decomposition. If the samples are allowed to stand for several days in room light or sunlight, the whole sample tends to turn brown from the photolytic formation of various products. The second adsorption technique used was much similar to that used in micellar preparations. The pyrene to be deposited on the TiO_2 was first deposited on the container walls by evaporation of a hexane solution of the probe, and the TiO_2 water suspension was stirred with this sample for 0.5 h followed by sonication for 10 min. Small quantities of the pyrene are solubilized in water and subsequently transferred to TiO_2, until eventually all the pyrene is adsorbed from the walls of the vessel onto the TiO_2 powder. In order to ensure that all the pyrene on the TiO_2 sample was indeed adsorbed, samples (5 mg) were suspended in a small quantity of hexane (10 mL) and sonicated for 30 min, followed by centrifugation at 4000 rpm for 20 min. The particles of TiO_2 with adsorbed pyrene were pelleted to the bottom of the container, and excess pyrene was left in the supernatant hexane solution. The amount of pyrene adsorbed on TiO_2 particles was determined by extraction of the sample several times with hexane, followed by measurement of the absorption spectrum in the hexane by conventional methods on a spectrophotometer. The effectiveness of hexane in extracting pyrene from the TiO_2 surface is confirmed by the observation that no absorption spectrum of pyrene, or other products, could be detected on the suspended TiO_2 following extraction by hexane. The spectrum of pyrene in hexane is well established, and using the known extinction coefficient the total amount of pyrene absorbed on the sample was calculated. Similar techniques were used for other probes. Experimental techniques used in this study were: fluorescence measurements on a standard Perkin-Elmer MPF 44B spectrofluorimeter, and absorption spectra on a Perkin-Elmer 552 spectrophotometer. Fluorescence polarization, and fluorescence excitation spectra were also recorded on the MPF 44B fluorescence spectrofluorimeter. Lifetimes of the excited species were measured by laser flash photolysis, which has been described previously. Lasers used were a nitromite nitrogen laser with pulses of 120 ps and a wavelength 3371 Å, and Lambda Physik excimer and N_2 laser with 3-ns pulses of 308-nm or 3371-Å light. The absorption spectra of transitory species or the emission of excited states following excitation of the sample were recorded by conventional rapid spectrophotometry, where the signals were captured in a Tektronix 7912 A transient capture device. The data stored in this instrument was subsequently displayed on a Tektronix 4052 A microprocessor, and the various physical parameters necessary for discussion of properties of the molecules were calculated.

Particle-Size Measurement. The TiO_2 particle sizes were measured on a Nicomp particle analyzer. In this instrument the light (single mode 6328-Å He–Ne laser Light) scattering from the sample is used to measure the diffusion constant D of the particle in the fluid of known viscosity η. The Stokes–Einstein relationship,

$$D = kT/6\pi\nu\eta R$$

is then used to calculate the particle radius R.

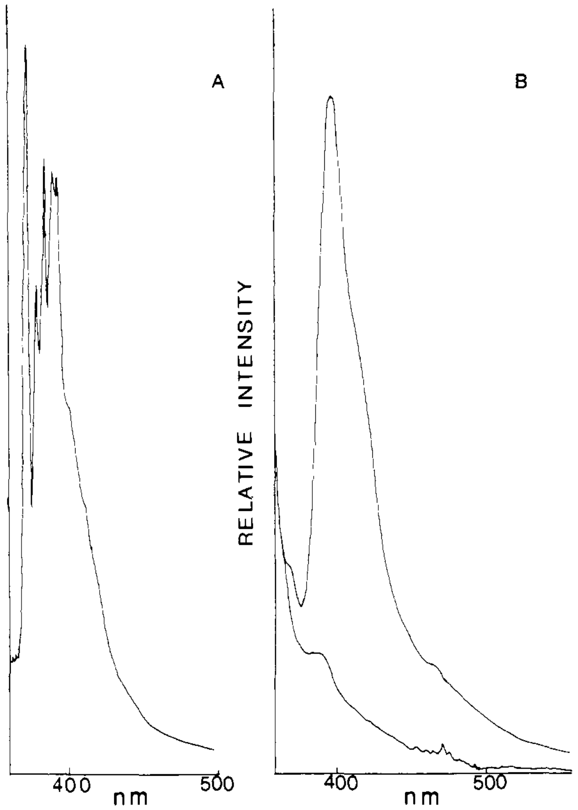

Figure 1. Emission spectra of pyrene excited at 345 nm: (A) adsorbed on TiO_2 extracted with hexane; (B) adsorbed on TiO_2 suspended in water.

Effective Concentrations of Adsorbed Species. The effective concentrations of adsorbed species at the particle surfaces were calculated from the total quantity of adsorbed species, with the assumption that this material was confined to within 10 Å of the particle surface. The typical concentration of adsorbed species is 0.32 mol of pyrene (0.25 mg of pyrene/g of TiO_2). The 10-Å value for the adsorption layer of pyrene was selected from the long-axis dimension of pyrene. Any pyrene located beyond this distance is essentially in the water phase. A small value would perhaps be more realistic, and this would increase the local pyrene concentration. This in turn would tend to predict even more excimer formation, which is not what is observed.

Results

Emission Spectra of Probes Adsorbed on TiO_2 Particles. The Experimental Section defined the technique for adsorption of various aromatic probe molecules onto the surface of TiO_2 particles. As will be seen subsequently, the emission and absorption spectra of most of these molecules adsorbed on TiO_2 were markedly different from those observed in simple homogeneous solution. Extraction of the probe molecules back from the TiO_2 particles with hexane shows that they were chemically unchanged by the adsorption process. Hence, the spectral changes observed on TiO_2 were not due to a chemical decomposition of the molecules on the particle, but were due to the nature of the physical absorption process. Figure 1A shows the emission spectra recorded for pyrene in hexane in solution. The spectrum is well defined with several emission maxima, 373, 392 nm, etc. Figure 1B shows the emission spectrum of pyrene adsorbed on TiO_2 particles in aqueous suspension. It is immediately apparent that the spectra are quite different. The highly structured pyrene emission spectrum in hexane is quite unlike that for pyrene absorbed on TiO_2 which exhibits one peak around 400 nm. It is also pertinent to note that the intensity of this latter spectrum of pyrene absorbed on TiO_2 is considerably weaker by about a factor of 3 compared with that of pyrene in hexane solution. Figure 2B shows the

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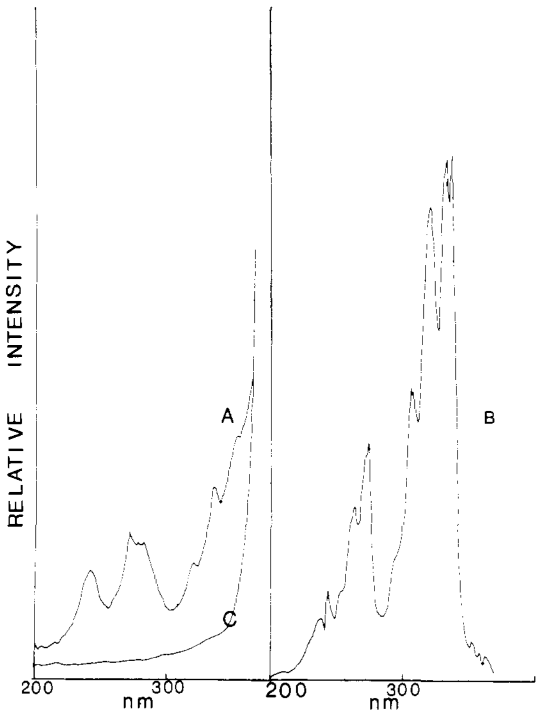

Figure 2. Excitation spectra of pyrene emission monitored at 395 nm: (A) adsorbed on TiO_2 suspended in water; (B) dilute methanolic solution; (C) scattering due to particle.

excitation spectrum of pyrene either in methanol solution or, in Figure 2A, that of pyrene on the TiO_2 particle. Once again, the conventional excitation spectrum, which in many instances mirrors the absorption spectrum of pyrene, is dramatically changed when the pyrene is absorbed on TiO_2 particles. Although three peaks are observed below 350 nm for pyrene on TiO_2 particles, nevertheless the absorption band in TiO_2 samples to the first excited state in the region of 330 nm is much weaker compared with the other bands below 300 nm. The reverse is true in homogeneous solution. Nevertheless, pyrene on TiO_2 still absorbs a significant quantity of light over the laser wavelengths used, which are 3080 and 3371 Å. Figure 2A also shows curve C which is the scatter of the TiO_2 particle without any pyrene. Although significant light scatter occurs in TiO_2 samples, nevertheless it is quite clear that the pyrene excitation spectra is significantly different from anything observed in homogeneous solution. The shape of the excitation spectrum for pyrene on TiO_2 particles also indicates that there is no energy transfer from excited TiO_2 to the pyrene, as the excitation spectrum does not show any indication of the TiO_2 absorption which increases continuously from below 4000 Å. It is pertinent to note the following experiments in conjunction with the TiO_2 particle studies. In earlier work it was shown that pyrene adsorbed on aluminum oxide, Al_2O_3, showed a structured emission spectrum quite characteristic of pyrene in a polar environment.[26] However, in the presence of 1 atm of oxygen the pyrene emission is severely quenched, leaving behind a weak emission spectrum which is very similar to that observed for pyrene adsorbed on TiO_2 (Figure 1B). Thus it seems that the two different oxides, Al_2O_3 and TiO_2, both provide a unique environment for pyrene on the oxide surfaces, an effect which is much more pronounced on TiO_2 particle compared to aluminum oxide. It is interesting to note that no excimer emission is observed for pyrene adsorbed on TiO_2 particles. No pyrene excimer was observed under conditions where the local concentration of pyrene on the TiO_2 particles is 0.3 M. Pyrene excimer is observed under these conditions of high concentration in homogeneous solution[26] and on Al_2O_3 and on SiO_2.[19] These results tend to indicate that pyrene is immobilized when absorbed on TiO_2. Measurements of the fluorescence polarization of pyrene emission on the TiO_2 particle give a degree of polarization of 0.26 which is indicative of a very strongly bound pyrene that is immobile over the period of observation which is some 200 ns. Ethylpyrene exhibits a typical substituted pyrene emission spectrum in acetonitrile with peaks at 3760, 3830, 3870, 3970, and 4170 Å. When adsorbed on TiO_2 an emission spectrum with broad peaks at 3760 and 3970 Å is observed. This behavior is unlike pyrene where adsorption on TiO_2 essentially eliminates the 370-nm emission.

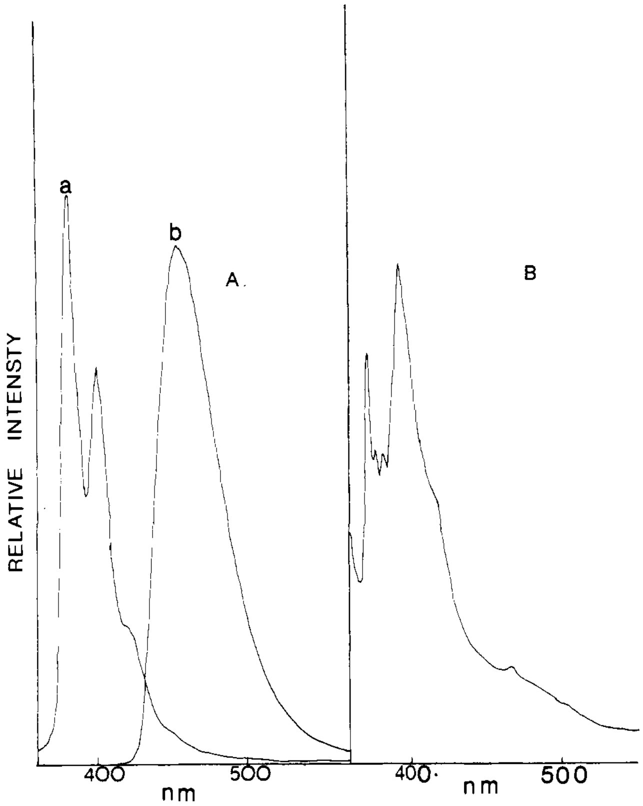

Figure 3. Emission spectra of substituted pyrene: (A, a) pyrene carboxaldehyde adsorbed on TiO_2 suspended in water; (A, b) pyrene carboxaldehyde dissolved in methanol; (B) bromopyrene adsorbed on TiO_2 suspended in water. Deaerated solution excited at 345 nm.

Pyrenecarboxaldehyde and Bromopyrene. The probe pyrene-1-carboxaldehyde is also readily adsorbed onto TiO_2 particles. Figure 3A, curve b, shows the characteristic emission spectra of pyrenecarboxaldehyde in methanol solution. It was established in earlier studies that the emission spectrum of pyrenecarboxaldehyde is quite dependent on the polarity of the environment, the spectrum moving to the red with increasing polarity and also exhibiting an increased quantum for emission.[24] In nonpolar environment pyrenecarboxaldehyde has a weak emission spectrum centered around the 4000-Å region. As can also be seen in Figure 3A, curve a, pyrenecarboxaldehyde adsorbed on TiO_2 particle has quite a strong emission spectrum with two peaks, the spectrum being quite reminiscent of that of a substituted pyrene in homogeneous solution.

Figure 3B shows the emission spectrum of bromopyrene absorbed on TiO_2 suspended in water. Bromopyrene has no significant emission when excited in hexane solution. This is attributed to the bromine heavy-atom effect which induces intersystem crossing, thus increasing the triplet yield of the molecule and while significantly reducing both the lifetime and yield of the fluorescence. No emission was observed from bromopyrene in hexane solution under conditions where a relatively strong emission spectrum of bromopyrene was observed on TiO_2 particles, Figure 3B.

Perylene. Perylene, although quite insoluble in most solvents, is readily absorbed from methanol solution onto TiO_2 particles. Figure 4, curve B, shows the emission spectrum of perylene when absorbed on TiO_2 particles. The excitation wavelength used was 3450 Å, and the emission peak maximum is around 5800 Å. However, it is well established that perylene in homogeneous solution shows a structured emission with peaks at 4400 and 4660 Å. In this system it is quite clear that transfer of excitation energy

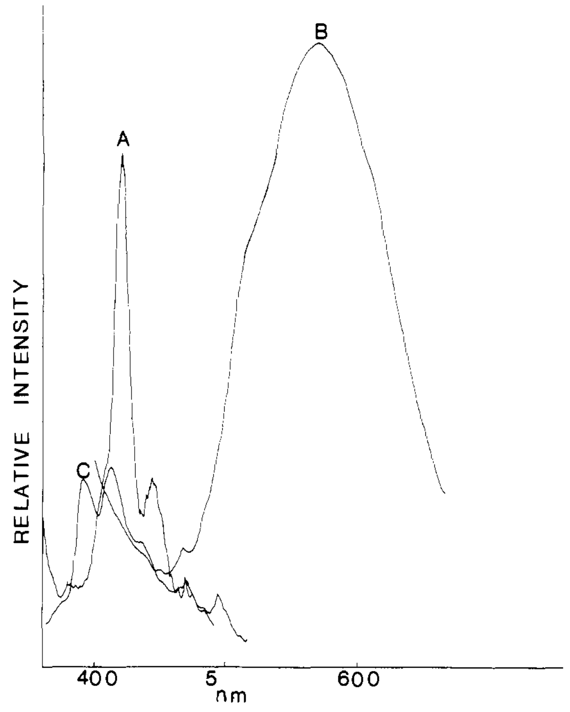

Figure 4. (A) Emission spectrum of anthracene adsorbed on TiO_2; (B) emission spectrum of perylene adsorbed on TiO_2; (C) emission spectrum of 9-methylanthracene adsorbed on TiO_2 excited at 254 nm. Deaerated aqueous solution excited at 345 nm.

from TiO_2 to perylene does not occur, as identical spectra are obtained on exciting perylene above and below 4000 Å, while TiO_2 absorbs only below 4000 Å.

Anthracene and Methylanthracene. Both anthracene and methylanthracene may be adsorbed onto TiO_2 particles, and the resulting emission spectra of the excited probes are shown in Figure 4 as curves A and C. Methylanthracene and anthracene in homogeneous solution show several fluorescence maxima in the 4000-Å range. Methylanthracene when absorbed on TiO_2 exhibits an emission spectrum that is similar to spectra C in Figure 4. However, anthracene on TiO_2 exhibits a quite different spectrum, with one very strong peak around 4200 Å and a hint of a weaker peak at about 4500 Å. The excitation spectrum of anthracene, with the emission channel monitored at 4200 Å, gives maxima at 2520, 3500, 3620, 3830, and 4030 Å. This spectrum is different from the absorption spectrum of anthracene in cyclohexane, or other homogeneous solvents, where absorption peaks are observed at 3200, 3400, 3560, and 3750 Å. In the case of methylanthracene on TiO_2, the fluorescence peaks observed at 3900 and 4120 Å are quite similar to those observed in methanol solutions. It appears that a rough generalization can be made at this time, namely, that unsubstituted molecules such as pyrene, anthracene, and perylene show quite different emission and absorption spectra, when these molecules are adsorbed on TiO_2 particles in aqueous suspension. However, the substituted molecules such as bromopyrene, ethylpyrene, and methylanthracene show fluorescence spectra which are quite similar to those observed in homogeneous solution.

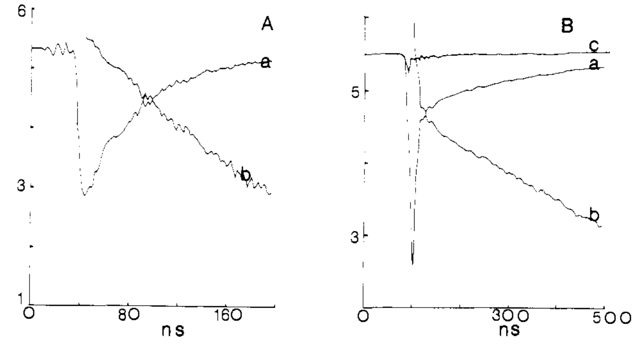

Figure 5. Emission intensity decay of the colloidal solution. Deaerated solution excited at 337 nm with nitrogen laser and monitored at 395 nm: (A) emission decay for pyrenecarboxaldehyde/TiO_2. (B) emission decay for pyrene/TiO_2. Trace c shows scattering due to particles.

Table I. Excited-State Properties of Polyaromatic Molecules Adsorbed on Titanium Dioxide Particles[a]

	medium			
	cyclohexane		TiO_2 suspended in water	
substrate	emission max, nm	lifetime, ns	emission max, nm	lifetime, ns
pyrene	373, 384	200	400	290
pyrenecarboxaldehyde	455[b]		380, 400	58
bromopyrene			373, 394	
perylene	440, 466	6.4	570	36.2
methylanthracene	390, 412	4.6	390, 410	10.1
anthracene	380, 400		420, 445	7.1
naphthalene	320, 335	96	400, 470	90

[a] Concentration: less than 10^{-4} M in cyclohexane where the excimer formation is negligible; about 1 mg of substrate/g of TiO_2; 2–5 mg of the power suspended in 10 mL of water. Excitation at 345 nm. [b] In methanol.

Lifetime Studies. Figure 5A shows the time profiles for decay of the fluorescence of pyrenecarboxyaldehyde, and Figure 5B that for pyrene when these molecules are adsorbed on TiO_2 particles. In homogeneous solution excited pyrene shows an exponential decay with a long lifetime, 200 ns. However, excited pyrene on TiO_2 particles, curve a in section B, exhibits a nonexponential decay with an initial fast portion with a lifetime of about 5 ns, followed by a slower portion with a decay time of about 290 ns. Approximately 70% of the excited states decay by the fast portion and 30% by the slower rate of 200 ns half-life. The initial fast decay is not due to light scattering from the TiO_2 particles as shown by trace c which exhibits a typical signal from an excited TiO_2 suspension without any absorbed pyrene. Trace b in Figure 5B shows a log plot of the pyrene emission vs. time and it can be seen that the slow emission exhibits a reasonable exponential decay giving a lifetime of 290 ns. Adsorption of lower quantities (0.02 mg of pyrene/g of TiO_2) of pyrene onto TiO_2 leads to a simple fast exponential decay; the longer lived emission occurs only under conditions of high pyrene adsorption. These data indicate two sites for the adsorption of pyrene on TiO_2: initial adsorption at low concentrations occurs at sites where the emission lifetime is severely curtailed; at higher pyrene surface content these initial sites are filled and further adsorption occurs at sites where little emission quenching is observed. Figure 5A, curve A, shows the decay of pyrenecarboxyaldehyde when adsorbed in TiO_2. One exponential decay is observed in this case as illustrated by the semilog plot of the data curve b, with a half-life of 40 ns. This is considerably longer than the lifetimes about 2 ns reported for pyrenecarboxyaldehyde in homogeneous solution. Table I summarizes the data for various aromatic probe molecules adsorbed on TiO_2, both the spectral emission maxima, and the lifetimes as compared with similar behavior in homogeneous solution, such as cyclohexane.

Emission Quenching Studies. The fluorescence of excited molecules adsorbed on TiO_2 may be quenched or altered by the addition of suitable quenching molecules such as methyl viologen or nitrobenzene to the system. Figure 6 shows the quenching of the pyrene fluorescence on TiO_2 by methyl viologen, nitrobenzene, and iodide ion, plotted both as Stern–Volmer plots (emission intensity without quencher divided by the emission intensity with quencher), and also as the reciprocal of the half-life of the emission vs. quencher concentration. The additives only quench the long-lived emission and have no effect on the short-lived 5-ns emission. Hence, the quenching process is inaccurately described by Stern–Volmer kinetics. The rate constants quoted are calculated from the observed rate of change of the "long-lived" emission and the quencher bulk concentration, and are dynamic rate constants. In the case of nitrobenzene the rate constant of the

Table II. Emission Quenching Rate Constants for Pyrene Adsorbed on TiO_2 by Electron Donors and Acceptors[a]

medium	quencher	$k_{qt} \times 10^{-9}$ M^{-1} s^{-1}	$k_{qI} \times 10^{-9}$ M^{-1} s^{-1}
acetonitrile	DMA	15.8	12.5
	$PhNO_2$	21.2	21.2
water	DMA	new peak at 373 nm	
	$PhNO_2$	5.0	0.98
	MV^{2+}	7.04	0.88
	I^-	1.73	
	Cu^{2+}	<0.1	<0.1

[a] TiO_2 = 5 mg/10 mL; pyrene = 0.25 mg/g of TiO_2; solutions deaerated by bubbling with nitrogen; excited at 345 nm.

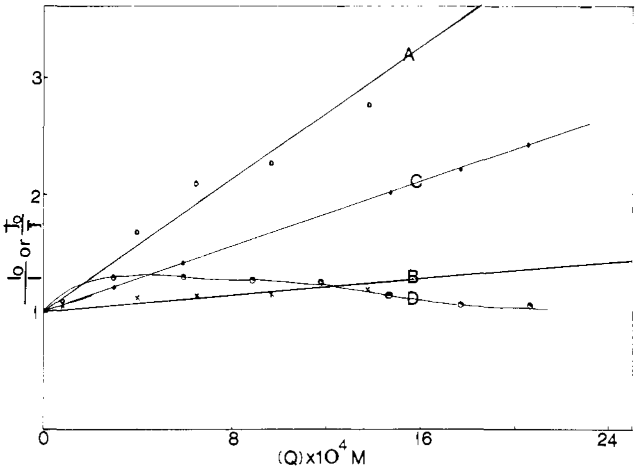

Figure 6. Stern-Volmer plot for various quenchers: (A) MV^{2+} quencher (lifetime quenching); (B) MV^{2+} quencher (emission intensity quenching); (C) $PhNO_2$ quencher (lifetime quenching); (D) iodide quencher (emission intensity quenching).

dynamic quenching is measured as 5.0×10^9 M^{-1} s^{-1}. This rate constant is calculated from the rate of decay in the presence of the nitrobenzene and also the amount of nitrobenzene in the bulk solution. Some uncertainty is associated with this latter number as the volume in which the nitrobenzene is situated at the particle surface is difficult to estimate. In the case of pyrene and nitrobenzene the mechanism of the quenching reaction of e^- transfer from pyrene to nitrobenzene, as observed in homogeneous solution. Figure 7 shows the transitory absorption spectra of pyrene on the particle surface measured 1 μs following the excitation pulse, curve A, and curve B in the presence of nitrobenzene. The spectrum in the absence of nitrobenzene, curve A, shows no identifiable absorption maxima that can be attributed to a triplet or ionic state of pyrene, which normally absorbs over the wavelength range of 4000–6000 Å. However, in the presence of nitrobenzene two peaks appear, one at about 4400 Å and another at about 5300 Å, which are approximately located in the correct region for the pyrene cation. Further evidence to substantiate formation of pyrene cation is not forthcoming. However, in homogeneous solution the quenching reaction of pyrene excited states by nitrobenzene is an electron-transfer reaction, giving the pyrene cation, and by association with these earlier data,[28] a similar quenching mechanism is proposed for this system when adsorbed on TiO_2 particles.

The quenching data with iodide are more complicated than those associated with methyl viologen and nitrobenzene. Initial addition of iodide increases the luminescence intensity, followed by a gradual decrease at higher iodide concentrations. Increasing the pH of the system to 13 also increases the luminescence intensity and leads to an increase in the intensity of the 370-nm peak, to an extent where it is stronger than the 395-nm peak. Similar effects are observed with dimethylaniline. Figure 8 shows that the addition of dimethylaniline to the pyrene–TiO_2 system tends to decrease the extent of the initial fast decay while increasing the extent of the emission due to the long-lived decay (insert in Figure 8). The emission spectra are changed by addition of dimethylaniline; the single peak (λ 3950 Å) associated with pyrene on TiO_2 decreases in intensity and a second peak at about 3700 Å grows in. Thus, the spectrum appears to look more like that of a substituted pyrene. The new fluorescence spectrum induced by the addition of DMA is not due to a replacement of the pyrene by dimethylaniline at the TiO_2 surface, as the new emission spectrum is unlike that of pyrene in water. Other experiments indicate that addition of other organic materials, acetonitrile and benzyl alcohol, up to 0.1% volume by volume had no effect on the pyrene emission spectrum on TiO_2. Thus, the effect in Figure 8 is unique to the addition of dimethylaniline to the pyrene–TiO_2 system. Another feature of DMA which is similar to iodide is that addition of small concentrations of dimethylaniline to pyrene on TiO_2 causes an increase in the emission intensity. The excitation spectrum of the pyrene–dimethylaniline–TiO_2 system and the absorption spectrum also show significant differences from the excitation spectra and absorption spectra of pyrene and DMA in homogeneous solution, and when either of these molecules is adsorbed separately on TiO_2, for example, the absorption spectrum of DMA and pyrene on TiO_2 shows an absorbance around 300 nm.

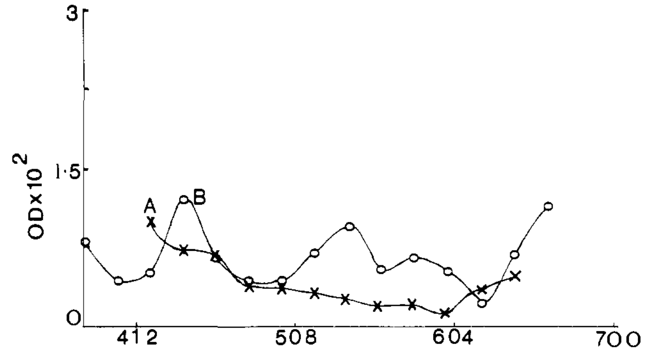

Figure 7. (A) Transient spectra of the deaerated aqueous colloid pyrene/TiO_2 1 μs after the pulse. (B) Transient spectra of pyrene/TiO_2 in the presence of 2 mM nitrobenzene.

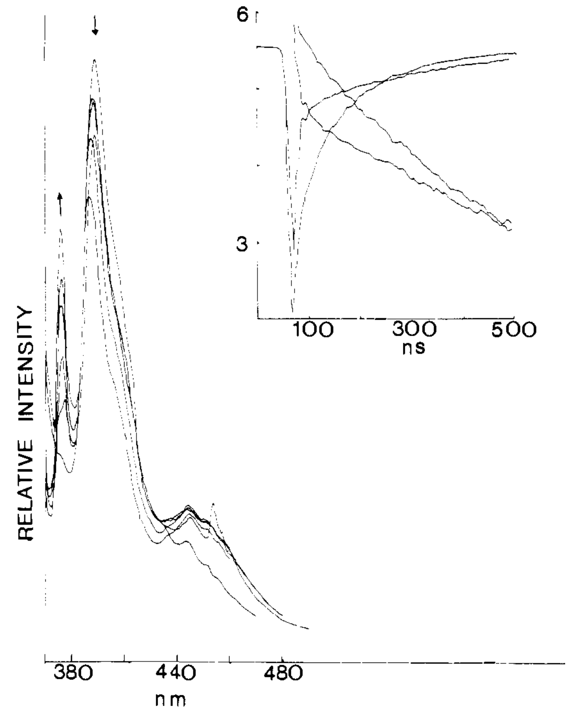

Figure 8. Changes in emission spectra with the addition of DMA. Decay of pyrene emission with and without DMA.

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(28) S. Atik; Thomas, J. L. *J. Am. Chem. Soc.*, **1983**, *105*, 4515.

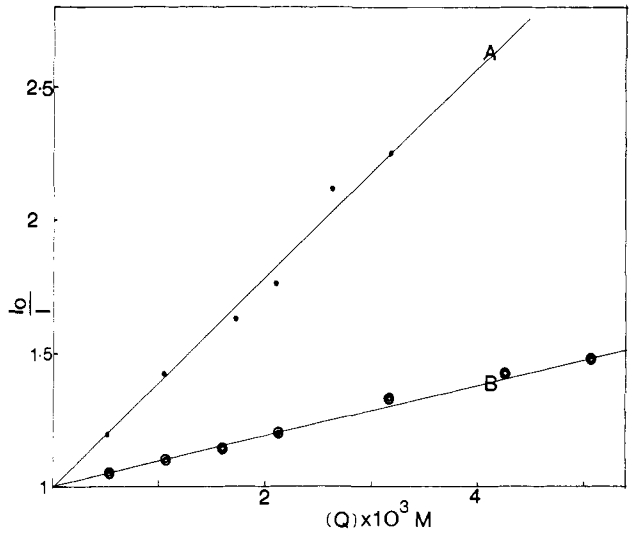

Figure 9. Stern–Volmer plots for the emission intensity quenching of pyrene aldehyde by (A) MV^{2+} and (B) nitrobenzene.

Figure 9 shows the quenching Stern–Volmer plot of I_0/I vs. quencher concentration for the quenching of the emission of pyrenecarboxaldehyde absorbed on TiO_2, by methyl viologen, curve A, and by nitrobenzene, curve B. In this system it is not possible to accurately measure the shortened decay lifetimes in the presence of quencher. However, by using the Stern–Volmer plots and the lifetime of the excited pyrenecarboxaldehyde, it is possible to calculate a quenching rate constant of 2.3×10^9 M^{-1} s^{-1} for the quenching of the pyrenecarboxyaldehyde emission by methyl viologen. A similar treatment of the nitrobenzene data gives a quenching rate constant of 6.8×10^9 M^{-1} s^{-1}. In both quenching rate constants the bulk quencher concentration was used to calculate the second-order rate constant. These rate constants are similar to those observed in homogeneous solution. The quenching could occur by quencer adsorbed on the surface, and by quencher bombarding the surface from bulk solution.

Discussion

The foregoing data clearly show that species adsorbed on TiO_2 surfaces in aqueous suspension exhibit absorption and emission spectra, which are quite different from those exhibited by these molecules in homogeneous solution or in other simple colloids such as micelles. It can be stated qualitatively that molecules without any substitution on the aromatic rings such as pyrene, perylene, anthracene, and naphthalene exhibit emission and absorption spectra which are quite unlike those exhibited by these molecules in homogeneous solution. However, derivatives of these molecules such as methylanthracene, ethylpyrene, pyrenecarboxaldehyde, or bromopyrene show spectra which are reminiscent of substituted pyrenes or substituted anthracenes in homogeneous solution. It is instructive to consider pyrene as an example of the molecules which shows significantly different spectra on adsorption in TiO_2. Adsorption of pyrene onto TiO_2 particles leads to a significant decrease in the pyrene fluorescence emission and to a change in the spectrum such that the 0–0 transition near 3700 Å is eliminated and a single transition observed around 3950 Å remains, the position of the strongest emission peak in hydrophobic solvents, which in the least solvent-dependent emission peak.[29] Another feature is that adsorbed pyrene exhibits two lifetimes in these samples, one which is extremely short-lived with ~5 ns lifetime, and one which is much longer lived with a 290-ns lifetime.[30] The two lifetimes suggest that pyrene may be adsorbed at two different sites, one where it is significantly quenched and one where its lifetime is relatively unaffected. It is difficult to identify the exact nature of the adsorption which gives rise to the unusual events observed in this work. However, it might be suggested that pyrene and other unsubstituted molecules are adsorbed strongly and uniformly at the oxide surface. This rigidity principle is upheld by the fact that excimers of pyrene are not observed even at high adsorbed concentrations of pyrene, indicating little mobility of the pyrene on the TiO_2 surface. Such an adsorption might tend to promote only significant emission at about 3950 Å, i.e., in the peak which is least solvent dependent. The quenching, as exhibited by the fast 5-ns decay is presumably due to electron transfer from the pyrene to the TiO_2 conduction band. It is suggested that the changes in emission spectra and excitation spectra of other molecules are also connected with the same principle of strong uniform adsorption of the molecules on the oxide surface. However, substitution along the ring, as with methylanthracene or bromopyrene, produces adsorption which is not uniform, and little effect on adsorption is observed on the emission or the excitation spectrum of the molecule. Perhaps it is pertinent to comment on the fact that the emission spectra of bromopyrene and pyrenecarboxaldehyde are very similar to those of a substituted pyrene, whereas these molecules in homogeneous solution either show no fluorescence as with bromopyrene, or show a significantly different and altered fluorescence with pyrenecarboxaldehyde owing to the n–π^*–CHO transition being in close conjunction with the π–π^* pyrene transition. It is suggested that, with both these molecules, adsorption leads to a significant interaction with the substituted group, either carboxaldehyde or bromine, both of which are strong electron-accepting groups. Hence, it is suggested that electron donation from the TiO_2 to the pyrene substituent group occurs at the adsorption site. The e^- donation essentially leads to a strong resonance within these groups which tends to isolate them from the arene ring such that excitation of such a complex will have strong π–π^* character and transitions characteristic of pyrenes are observed. It is also significant to note that the fluorescent lifetimes of these molecules are much longer on TiO_2 than observed in homogeneous solution. This also agrees with an adsorption process that promotes the π–π^* character of the adsorbed molecule. It may be suggested that the short-lived emission of adsorbed pyrene is due to adsorption at a site where an electron is donated from pyrene into the TiO_2, whereas the longer lived emission is due to adsorption at a site where this process is minimized. The stronger electron affinities of pyrenecarboxaldehyde and bromopyrene show reduced adsorption at sites where electron donation to the TiO_2 occurs and, hence, only a longer lived adsorption at the alternate site takes place.

The quenching rate constants of excited probes on the TiO_2 surfaces by MV^{2+} and nitrobenzene are similar to those observed in homogeneous solution. As pyrene excimer emission is not observed even at a concentration 10^4 times that of homogeneous solution, it is thus suggested that pyrene is unsolubilized in the TiO_2 surface, in agreement with the polarization studies. As pyrene shows little movement on the TiO_2 surface, it is then suggested that the mobilities of MV^{2+} and nitrobenzene are also low. Hence the observed quenching is attributed to bombardment of the surface sites by quenchers from the bulk phase.

Finally, the data in Figure 8 suggest that the strongly polar nature of the TiO_2 surface promotes the formation of complexes of DMA and pyrene as witnessed by changes in the emission and excitation spectrum and by an increased lifetime of the emission.

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[29] The 395-nm emission peak also corresponds to the symmetrical vibronic motion of pyrene as studied by IR techniques. In polar hydroxylic solvents, solvent hydrogen bonding with the pyrene relaxes the symmetry of the molecule and increases the intensity of the 370-nm (O–O bond) emission. Adsorption of pyrene to TiO_2 may also be via H atom bonding to the O atoms of the surface. If the pyrene is bonded uniformly to the surface so that the symmetry of the molecule is not relaxed, then only the 395-nm emission is strong as in hydrophobic solvents. Coadsorption of other molecules, e.g., OH^-, dimethylaniline, etc., interfaces at the pyrene adsorption site relaxing the pyrene symmetry and leading to an increase in the 370-nm emission as in polar hydroxylic solvents.

[30] An alternative explanation could be that pyrene is adsorbed both as individual molecules and as clusters of pyrene. The latter would tend to give excimer emission as in pyrene crystals. However, it is possible that the TiO_2 surface modifies the behavior of clusters of pyrene in a fashion that is in accord with the experimental data. Nothing is known of such effects, and we tend to favor the two-site adsorption mechanism for pyrene.

It is interesting to note that DMA increases the pH of the solution and shows similar spectral effects to that of increased pH. However, the time dependence is quite different in the two cases; OH^- leads to one short decay, while DMA leads to one long decay. Hence, the mechanisms of the two effects are quite different. It is intriguing to note that in the case of pyrene, the complex shows an emission which is very similar to a substituted pyrene. In other words, the single emission peak of pyrene at 3950 Å is replaced by spectrum with two peaks, one at 3900 Å and a second in the region of 3700 Å. Adsorption of dimethylaniline itself on the particle does not give rise to spectra of this type. Hence, the new emission and excitation spectra are due to the complex of DMA and pyrene on the TiO_2 surface. It is known that excitation of mixtures of DMA and pyrene leads to an exciplex formation in many solvents,[31] and that exciplex emissions are observed in hydrophobic solvents. The spectra of the exciplexes are at much longer wavelengths (λ >4600 Å) than those observed in the TiO_2 samples.

The similarity of the DMA-pyrene-TiO_2 complex emission to that of a substituted pyrene suggests that the complex alters the nature of the adsorption of pyrene on TiO_2 and the interaction of DMA with pyrene on TiO_2 is not of the exciplex type. These preliminary data indicate the unique nature of the interaction of aromatic molecules with a TiO_2 surface. Further studies are required in order to pin down specific details of the adsorption process. Studies, such as those outlined above, may be useful in probing the active sites of catalysts.

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(31) Birks, J. B. "Photophysics on Aromatic Molecules"; Wiley-Interscience: New York, 1970.

Comprehensive Theoretical Study of Isomers and Rearrangement Barriers of Even-Electron Polyatomic Molecules H_mABH_n (A, B = C, N, O, and F)

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Abstract: Potential energy surfaces for the polyatomic neutral species H_mABH_n (A, B = C, N, O, F) are studied by ab initio molecular orbital theory. Only systems with an even number of electrons are considered. All are found to be most stable as electronic singlet states with normal structures corresponding to maximum valence. Less stable singlet isomers, with abnormal valency, are found for HNC, H_2NCH, HOCH, H_2NN, H_3NCH_2, H_3NNH, and H_3NO. Barriers for rearrangement by 1,2-hydrogen shift to the normal-valent form are estimated. Other possible 1,2-hydrogen-shifted singlet isomers, H_2CC, H_3CCH, H_3CN, H_2COH_2, H_2CFH, NOH, $HNOH_2$, HNFH, H_2OO, and HFO, either have shallow potential minima or do not correspond to minima at all. Triplet equilibrium structures, in the abnormal-valence coordination, also exist and are more stable than corresponding singlet structures for H_3CCH, H_3CN, and HON. They are separated from other triplet isomers, in the normal valence coordination, by high barriers. The theory predicts that singlet CH_2, NH, and O will insert into NH_3, OH_2, and FH without activation in all cases.

1. Introduction

The set of polyatomic compounds H_mABH_n with two nonhydrogen atoms A and B contains the parent molecules for the various kinds of AB bonds. If A and B are restricted to carbon, nitrogen, oxygen, and fluorine, the molecules are $H_3C{-}CH_3$, $H_2C{=}CH_2$, $HC{\equiv}CH$, $H_3C{-}NH_2$, $H_2C{=}NH$, $HC{\equiv}N$, $H_3C{-}OH$, $H_2C{=}O$, $H_3C{-}F$, $H_2N{-}NH_2$, $HN{=}NH$, $H_2N{-}OH$, $HN{=}O$, $H_2N{-}F$, $HO{-}OH$, and $HO{-}F$. All have been studied extensively by molecular orbital techniques and all are known experimentally. In every case, the structure consistent with the normal rules of valency is found to be the most stable.

Other structures are possible for these molecules. The unsaturated species may have triplet states corresponding to $H_2\dot{C}{-}\dot{C}H_2$, $H\dot{C}{=}\dot{C}H$, $H_2\dot{C}{-}\dot{N}H$, $H\dot{C}{=}\dot{N}$, $H_2\dot{C}{-}\dot{O}$, $H\dot{N}{-}\dot{N}H$, and $H\dot{N}{-}\dot{O}$. Other isomers with abnormal valences can be derived, in principle, by 1,2-hydrogen shifts:

$$H_mABH_n \rightarrow H_{m-1}ABH_{n+1}$$

Some of these structures are known experimentally (e.g., HNC). Others are postulated as reactive intermediates and may also exist as singlets or triplets. Many of these isomeric forms and associated rearrangement barriers have been studied by a variety of theoretical techniques.[2]

All of the structures derived by 1,2-hydrogen shift from singly bonded normal valence forms can be represented formally as complexes of normal molecules with carbenes, nitrenes, or singlet oxygen, Scheme I. These may alternatively be represented as

Scheme I

$$\begin{gathered}
H_3C{-}CH_3 \rightarrow \ddot{C}H_2{\cdots}CH_4 \\
H_3C{-}NH_2 \rightarrow \ddot{C}H_2{\cdots}NH_3 \text{ or } \ddot{N}H{\cdots}CH_4 \\
H_3C{-}OH \rightarrow \ddot{C}H_2{\cdots}OH_2 \text{ or } \ddot{O}{\cdots}CH_4 \\
H_3C{-}F \rightarrow \ddot{C}H_2{\cdots}FH \\
H_2N{-}NH_2 \rightarrow \ddot{N}H{\cdots}NH_3 \\
H_2N{-}OH \rightarrow \ddot{N}H{\cdots}OH_2 \text{ or } \ddot{O}{\cdots}NH_3 \\
H_2N{-}F \rightarrow \ddot{N}H{\cdots}FH \\
HO{-}OH \rightarrow \ddot{O}{\cdots}OH_2 \\
HO{-}F \rightarrow \ddot{O}{\cdots}FH
\end{gathered}$$

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(2) For a review see: Schaefer, H. F., III *Acc. Chem. Res.* 1979, *12*, 288.

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