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Surface Diffusion of Organosiloxane Ligands Covalently Bound to Silica

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Abstract: Evidence for the lateral diffusion of covalently bound molecules on silica surfaces is reported. A slow growth of pyrene excimer fluorescence was observed from silica samples, sparingly derivatized with (3-(1-pyrenyl)propyl)-dimethylchlorosilane, after exposure of these samples to water. This excimer formation was attributed to the migration of ligands over the surface, despite their continued covalent attachment to the surface. Time evolution of the excimer population was successfully modeled using a simple theory for diffusion-controlled reactions in two dimensions. Diffusion coefficients at room temperature were small ($\approx 10^{-20}$ cm^2/s), and the encounter distance for excimer formation was reasonable (6 Å). The surface migration appears to proceed through a hydrolyzed intermediate that rebinds to adjacent silanol sites on the silica surface, since the process could be stopped by blocking adjacent sites. The activation energy for migration (16.3 ± 0.6 kcal/mol) and small preexponential factor are consistent with the barrier to surface diffusion being hydrolysis of the surface siloxane bond.

Introduction

Covalent binding of organosilane reagents to silica, glass, and other oxide surfaces has been a successful approach to developing a variety of materials, including surface-modified chromatographic supports,[1] glass- and mineral-reinforced composites,[2] and self-assembled monolayers.[3,4] The chemical nature of these surfaces is influenced by the organization of attached ligands,[3–6] changes in which can modify adsorption properties, stability, or performance of a material.

In this work, the stability of molecules attached to silica by siloxane bonds is investigated. Evidence is presented for the surface migration of covalently bound ligands in the presence of water through a small equilibrium population of hydrolyzed molecules. Plueddemann[2,7] first proposed that reversible hydrolysis and surface migration of silane coupling agents allowed these agents to relieve mechanical stresses in composite materials. While exposure to water did not lead to loss of adhesion between a resin and solid filler, axial stress, Plueddemann proposed, would be a driving force for surface siloxane bonds to hydrolyze and reform at adjacent surface sites. The two-dimensional mobility of covalently bound ligands along the surface of the oxide could provide a chemical relaxation mechanism for relieving mechanical stresses without loss of adhesion. While this model could account for stress relaxation and stability of silane-coupled composites in the presence of water, to date no direct evidence for the migration of siloxane-bound surface ligands has been reported, nor have the rates of surface diffusion of such ligands been estimated.

Diffusion of physisorbed molecules at gas/solid and liquid/solid interfaces has been previously investigated. Bauer, de Mayo, et al.[8,9] studied the quenching of fluorescence from adsorbed pyrene by adsorbed 2-halonaphthalene on silica surfaces. They found evidence of diffusion of molecules between silica particles and observed the effects of surface pretreatment on quenching rates. More recently, Krasnansky et al.[10] reported anomalously large rates of fluorescence quenching by oxygen of pyrene physisorbed to pyrogenic silica at low temperatures. They could account for the results by including surface diffusion in the transport of quencher. Oelkrug et al. found evidence for the mobility of acridine adsorbed onto silica surfaces by observing triplet–triplet annihilation in the decay kinetics of excited triplet states.[11]

Diffusion of physisorbed molecules at liquid/solid interfaces has also been investigated. Bogar et al.[12] and Ståhlberg et al.[13] observed pyrene excimer formation rates on alkylated (C18-modified) silica surfaces in contact with liquids. These studies reported dynamic excimer formation, indicating that pyrene diffuses on the alkylated surface. Diffusion coefficients and microviscosities of the surface layer were estimated using a three-dimensional theory for diffusion-controlled reactions. More recently, rates of surface diffusion of iodine at a methylated (C1) silica/solution interface were determined from rates of quenching of the fluorescent probe (3-(1-pyrenyl)propyl)dimethylchlorosilane (3PPS), covalently immobilized at low coverages on porous silica.[14] Diffusion coefficients of iodine at the liquid/solid interface were 2–3 orders of magnitude smaller than the coefficients for diffusion in bulk solution and varied with the composition of the overlying solvent.

While surface diffusion of physisorbed species is well established, the migration of chemisorbed or covalently bound ligands has not been reported. In this study, a slow growth of excimer fluorescence emission from 3PPS on silica is attributed to migration of covalently bound ligands over the surface. The pyrene ligands are not significantly liberated from their covalent attachment to the surface, as revealed by solubility experiments. The time evolution of the excimer formation is measured and successfully modeled using a two-dimensional diffusion theory, and the values of surface diffusion coefficients for chemisorbed species are obtained along with reasonable estimates of the encounter radius for excimer formation. The migration could be

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arrested by blocking adjacent silanol bonding sites with trimethylsilyl groups. The temperature dependence of the migration rate was also investigated, and the activation barrier to surface diffusion was determined.

Experimental Section

Materials. Porous microparticulate silica used in this study was Whatman Partisil 10, having a particle diameter of 10 μm, a mean pore diameter of 90 Å, and a nitrogen BET surface area of 320 m^2/g. The synthesis of (3-(1-pyrenyl)propyl)dimethylchlorosilane (3PPS) and its subsequent reaction with silica have been described in detail elsewhere.[15,16] Surface coverages of 3PPS probe molecules were controlled stoichiometrically by limiting the amount of 3PPS added to the reaction. Covalent attachment of 3PPS on the silica surface was assured by washing away any physisorbed reagent from the derivatized silica with a series of spectral grade solvents (chloroform, tetrahydrofuran, acetonitrile, methanol, and acetone), any of which is capable of desorbing 3PPS that is not covalently bound. Following this procedure, one observes persistent fluorescence having the spectral and temporal characteristics of 3PPS probes. Further modification of the 3PPS-labeled silica with trimethylsilyl (C1) groups was accomplished by reaction with trimethylmonochlorosilane (TMCS) as previously described.[17] After TMCS derivatization, silica samples were also subjected to the washing procedure described above to eliminate any physisorbed TMCS reagent on the surface.

Spectral grade chloroform was dried and stored over molecular sieves prior to its use in derivatizing silica. Phosphoric acid, 85% from EM Science, was used as received. Water was purified in-house using a Barnstead Nanopure system fed from a Corning glass still.

Analytical Methods. Elemental carbon analysis performed by M-H-W Laboratories (P.O. Box 15149, Phoenix, AZ 85018) was used to determine the surface concentration of immobilized ligands on the silica. The specific fractions of carbon of two silica samples with surface-bound 3PPS were 0.8% and 0.5% (w/w). The surface coverages estimated from the elemental analysis and the nitrogen BET surface area are 0.10 ± 0.01 μmol/m^2 and 0.06 ± 0.01 mol/m^2, respectively. The carbon content of the higher coverage sample further modified by C1 ligands was also analyzed by M-H-W Laboratories and was found to be 6.3% (w/w), including the 3PPS coverage mentioned above. Subtracting the contribution from 3PPS yields 5.5% (w/w) for the C1 ligands alone. This value infers a surface density of trimethylsilyl groups of 4.7 μmol/m^2, which is saturation coverage.

The fraction of hydrolyzed 3PPS on the surface was determined by rinsing 0.05 g of the silica (immersed in water for 60 days) with 600 mL of methanol. The filtrate was concentrated by evaporation of solvent to reduce the volume to 10 mL, and the 3PPS concentration was determined from the intensity of its fluorescence emission calibrated using a 1-methylpyrene standard. For quantifying the hydrolyzed 3PPS fraction in the case of acid catalysis, a 0.02-g sample exposed to 5% phosphoric acid at 42 °C for 24 h was rinsed with 300 mL of methanol. Due to the presence of acid in the filtrate which could affect the quantum yield, the fluorescence intensity was calibrated by using standard additions of 1-methylpyrene to the unknown solutions.

Fluorescence Emission Spectra. Fluorescence emission spectra were acquired from 0.02-g pyrene-labeled silica gel samples suspended in 3 mL of water or water/methanol solution. Samples were prepared utilizing a spectroscopy cell equipped with a stopcock and a 50-mL pear-shaped Pyrex flask opposite a quartz capillary having an inner diameter of 3 mm. After dispersion of silica gel in water or water/methanol mixture in the pear-shaped flask, the cell was inverted, and the silica slurry was allowed to settle for 15 min into the capillary before the first fluorescence spectrum could be collected. Temperature was controlled by circulating silicone fluid from a Haake constant-temperature bath through the cell holder. For the water vapor experiments, pyrene-labeled silica gel was allowed to equilibrate with water vapor in a closed container at room temperature. For each fluorescence observation, the silica was vacuum degassed and transferred under vacuum to the quartz capillary in the spectroscopy cell described above to acquire fluorescence spectra.

All fluorescence emission spectra were collected with a Farrand scanning spectrofluorometer (Model 801) and chart recorder. The excitation wavelength was 300 nm, and the emission monochromator was scanned from 300 to 600 nm. A long-pass filter (WG 335 from Scott Optical Glass Filters) was used to block Rayleigh scattering light. For emission spectra, the bandwidths of the excitation and emission monochromators were set at 10 and 2.5 nm, respectively; for excitation spectra, the bandwidths were 2.5 and 10 nm for excitation and emission, respectively. The wavelength-dependent response of monochromator and photomultiplier was corrected utilizing a standard lamp from Optronic Laboratories, Inc. (Model 245M). In order to determine corrected areas of the fluorescence emission peaks, the spectra recorded on the chart recorder were digitized using a Hewlett-Packard 7470A plotter and Graphpad software running on an IBM-PC clone. The digitized intensities were corrected for the monochromator/detector response and then integrated numerically. Time-resolved fluorescence decay data were acquired using a synchronously pumped dye laser nanosecond fluorometer with time-correlated single photon counting detection, as described in detail elsewhere.[17]

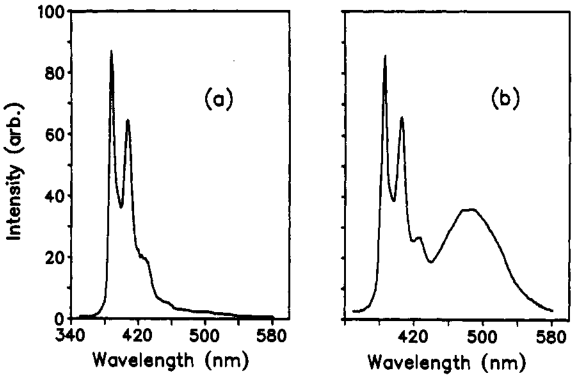

Figure 1. Fluorescence emission spectra from 3PPS bound to silica. (a) Sample stored in a desiccator following derivatization. (b) The same sample kept in contact with water for 24 days.

Results and Discussion

Evolution of Fluorescence Emission from 3PPS Bound to Silica. Fluorescence emission spectra from pyrene, covalently bound to a silica surface at low coverage (0.10 ± 0.01 μmol/m^2), are shown in Figure 1 for samples stored under two different conditions. Figure 1a shows the fluorescence spectrum from a sample kept dry following derivatization, and Figure 1b is from a silica sample immersed in water for 24 days. The structured fluorescence in the region of 370–410 nm corresponds to isolated pyrene molecules or monomer emission;[18] the broad structureless band centered at 480 nm is assigned to excimer emission from excited pyrene dimers either preassociated in their ground state or formed dynamically in the excited state.[18,19] For the sample kept dry, there is no detectable excimer emission, while significant excimer emission is observed from the same silica after it is immersed in water or stored in the humid atmosphere.

One possible reason for the excimer formation after exposure of the sample to water is that solvation of the silica surface by water gives neighboring pyrene rings sufficient mobility to form an excimer within the excited-state lifetime. There is considerable evidence, however, that solvation is not responsible for the appearance of excimer emission. Brief exposures to water (24 h) do not produce detectable excimer; solvation of the silica surface would be rapid compared to this time period. Furthermore, exposing the sample to methanol, an even better solvent for pyrene, does not produce excimer emission. This result is not surprising, since the average distance between surface-bound molecules in this sample is quite large. Assuming a homogeneous distribution of ligands on the surface, the average distance between ligands is 40 Å, which is an order of magnitude greater than the interaction distance to form either dynamic excimers or preassociated

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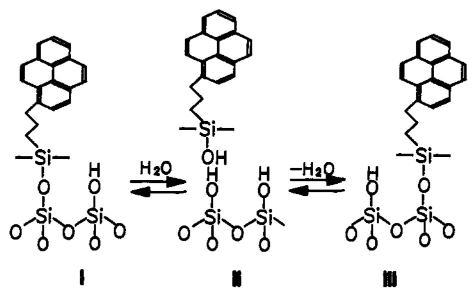

Figure 2. Proposed mechanism of surface migration of 3PPS ligands.

dimers.[19,20] Finally, there is consistent spectroscopic and kinetic evidence (see below) that the excimer emission is from preassociated pyrene rings, which would further rule out the influence of mobility of the ligands (on the time scale of the excited-state lifetime) as a critical factor in producing excimer emission.

Since the observation of excimer emission bands from this sample requires exposure of the sample to water for a long period of time, it is reasonable to propose that water hydrolyzes surface siloxane bonds, allowing pyrene molecules to diffuse across the silica surface (see Figure 2) and encounter other pyrene molecules on the surface. While siloxane bonds are relatively stable in water, slow hydrolysis of these bonds occurs, especially at elevated temperatures and in the presence of acidic, basic, or nucleophilic catalysts.[21-23] Plueddemann has proposed a dynamic equilibrium between the condensation and hydrolysis of siloxane bonds with glass or mineral oxide surfaces, where the activity of water controlled the stability of the surface structure.[2,7] This proposal raises a question of whether (a) hydrolysis leads to complete loss of covalent binding of 3PPS ligands to the surface followed by diffusion of a physisorbed form of the reagent, I → II in Figure 2, or (b) hydrolysis produces a small equilibrium concentration of hydrolyzed reagent which can rebind to the surface at adjacent silanol sites leading to diffusion across the surface, I → II → III in Figure 2.

To determine the extent of hydrolysis associated with surface diffusion, the amount of hydrolyzed 3PPS was determined following a 60-day exposure of the derivatized silica to water. A 50-mg sample was rinsed with 600 mL of methanol, the filtrate was concentrated by evaporation of solvent, and the fluorescence intensity of the solution-phase 3PPS was measured and calibrated against standard solutions. The capability of methanol to displace physisorbed pyrene from a silica surface was checked by liquid chromatography, where the equilibrium ratio of adsorbate to dissolved pyrene was found to be 0.082 in a packed column. Given the small ratio of silica to methanol in the rinsing experiment, the fraction of physisorbed 3PPS remaining on the surface at equilibrium should be less than 2×10^{-5}. From the fluorescence appearing in the filtrate, the fraction of physisorbed 3PPS was found to be only 0.1% of the total 3PPS ligands on the silica surface. As a further indication that the fraction of hydrolyzed 3PPS is small, the rinsing procedure did not change the excimer/monomer fluorescence intensity ratio. This result agrees with a recent quantitative study of hydrolysis of monofunctional C18 ligands from silica under comparable conditions; following a 2-month exposure of a packed column to an acetonitrile/water solution (60/40 v/v), the accumulated fractional loss of stationary phase from the surface determined by GC–MS measurements was found to be 0.04%.[24] Therefore, while surface diffusion of 3PPS likely depends on hydrolysis of surface siloxane bonds, the equilibrium of the condensation reaction with the silica surface appears to strongly favor the covalently bound form of the 3PPS ligand even in the presence of water.

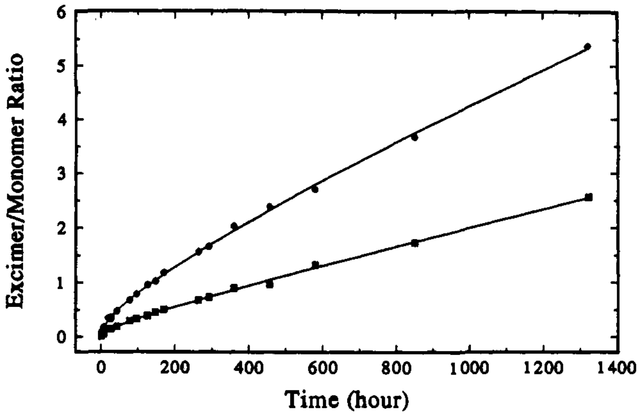

Figure 3. Excimer/monomer fluorescence intensity ratios versus time from samples kept in contact with water. The least-squares best fits to eq 4 are also plotted (solid lines). (a, ●) 0.1 μmol/m² 3PPS on silica. (b, ■) 0.06 μmol/m² 3PPS on silica.

Kinetic Investigation of Surface Excimer Formation. To establish whether surface migration of a chemisorbed ligand is responsible for the appearance of an excimer population, the time evolution of the formation of excimer was measured to determine if it follows the kinetics expected for a diffusion process. Excimer/monomer fluorescence intensity ratios (from peak areas following correction for monochromator and detector efficiencies) were measured to determine the relative population of excimer and to follow the encounter between 3PPS molecules on the surface. The time course of the surface reaction was measured for two silica samples having different 3PPS coverages, and the results are plotted in Figure 3.

If the encounters between surface-bound molecules that result in excimer emission arise principally from bimolecular encounters,

$$\mathrm{M} + \mathrm{M} \rightarrow \mathrm{E} \qquad (1)$$

then the expected time evolution of the excimer/monomer population ratios, derived from simple second-order kinetics, is given by

$$[\mathrm{E}]/[\mathrm{M}] = k[\mathrm{M}]_0 t \qquad (2)$$

where $[\mathrm{M}]_0$ is the initial monomer surface concentration (mol/cm²) of 3PPS molecules and k is the rate coefficient for second-order surface reaction (cm² mol⁻¹ s⁻¹).

The longer-term reaction kinetics in Figure 3 indeed follow the behavior predicted by eq 2, where the excimer/monomer ratio increases linearly with time. The slopes of the linear regions are proportional to initial concentration of 3PPS on the surface, $[\mathrm{M}]_0$, indicating that the steady-state reactivities of both samples can be explained by the same rate constant. The curvature of the plot of the excimer/monomer ratio versus time indicates an initially larger rate coefficient, which is an expected transient phenomenon in diffusion-controlled reactions. The initial rate coefficient is largely due to a higher initial concentration of reactant molecules around any reaction center and gradually decays to a steady-state concentration gradient.[25,26]

While diffusion-controlled reactions in three-dimensional systems have been well studied,[25,26] a simple extension of Smoluchowski theory to two-dimensional systems is not possible since boundary conditions at an infinite distance from the reaction

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site cannot be satisfied in two dimensions.[27-30] Several modifications of three-dimensional diffusion theory for two-dimensional problems have been suggested.[28,29] Owen studied the fluorescence quenching in lipid bilayer membranes, where diffusing molecules are a size comparable to the membrane thickness, Z, and the transport is effectively two-dimensional.[28] A two-dimensional diffusion theory was developed by treating this system as an infinitely long cylinder, which is mathematically tractable. Due to the boundary conditions, the net motion of quencher molecules in this cylindrical system is radial and two-dimensional.[28] Using this theory for the case of a membrane of negligible thickness, $Z \rightarrow 0$, and evaluating the integral according to Almgren,[29] an approximate form for the rate coefficient (cm^2 mol^{-1} s^{-1}) for a two-dimensional diffusion controlled reaction is given by

$$k = (14.180 D^{1/2} R t^{-1/2} + 3.17 D) N_{\mathrm{av}} \tag{3}$$

where D (in cm^2/s) is the mutual diffusion coefficient, R (in cm) is the encounter radius at which reaction occurs, and N_{av} is Avogadro's number (in mol^{-1}); the approximation is valid (<10% expected error) for a limited time into the reaction,[28] $t \leq 50R^2/D$.

Using the rate coefficient from eq 3 in eq 2 leads to a function,

$$[\mathrm{E}]/[\mathrm{M}] = [\mathrm{M}]_0 N_{\mathrm{av}} (14.180 D^{1/2} R t^{1/2} + 3.17 D t) \tag{4}$$

the form of which successfully fits the experimental results in Figure 3. In order to estimate the diffusion coefficient and encounter radius from the results, however, the excimer/monomer population ratios must be known, which requires knowledge of the relative fluorescence quantum yields of these species. The fluorescence quantum yields of alkyl-substituted pyrene monomer and excimer have not been reported in the literature; the relative intensity of excimer/monomer for 1-methylpyrene has, however, been compared to pyrene and found to be identical (within 5%).[31] The fluorescence quantum yields of pyrene monomer and excimer in several solvents have been reported.[18] For the polar solvents investigated, the quantum yield ratio (E/M) averages 1.15, with a standard deviation of 0.2. We therefore approximate the fluorescence quantum yield ratio of monomer to excimer for 3PPS as unity and equate the corrected intensity ratios of excimer/monomer to the population ratios of these species; the uncertainty of this assumption in the population ratios (20%) dominates the uncertainty in the reported rates below.

Under this assumption, the data in Figure 3 are fit to eq 4 to extract the mutual diffusion coefficient from the steady-state behavior; from the value of D and the fitting results from the early, $t^{1/2}$-dependent behavior, the encounter distance, R, is obtained. For the higher coverage sample, the mutual diffusion coefficient and encounter distance were found to be $D = (3.6 \pm 0.7) \times 10^{-20}$ cm^2/s and $R = 5.9 \pm 0.6$ Å, respectively. The value found for the encounter radius is quite reasonable in view of the interaction distance for pyrene to form excimers or preassociated dimers, estimated to be 3–4 Å,[20] and the additional radius from a binding site provided by the surface binding linkage. The encounter radius is also consistent with the root-mean-square distance between small monomeric silanes in a saturated monolayer on a silica surface. Saturation coverage by trimethylchlorosilane on the same silica, 4.7 μmol/m^2, corresponds to a root-mean-square distance between bound ligands of 5.9 Å, identical to the observed encounter distance for excimer formation by migration. Lochmüller et al. have estimated, using space-filling models, the maximum distance between sites at which two 3PPS molecules bound to silica could form excimer to be between 11 and 18 Å, depending on the conformation of the ligands on the surface.[6] Our results show encounter distances that are smaller than these estimates and probably indicate a more restricted geometry for formation of excimer by migration across the silica surface. The smaller encounter distance is consistent with the spectroscopic evidence that migration leads to pyrene rings that are preassociated on the surface (see below).

The diffusion coefficient of a surface-bound 3PPS molecule, which is half of the mutual diffusion coefficient, is estimated to be $D = 1.8 \times 10^{-20}$ cm^2/s. This is an extremely small value and results in the evolution of excimer population over a period of more than 1 month. The value is perhaps not surprising, since the barrier to the surface diffusion of a chemisorbed species is related to breaking covalent bonds, the strengths of which are much greater than thermal energy at room temperature. The coefficients of surface diffusion of chemisorbed metal atoms on metal surfaces have been determined from STM measurements; the reported diffusion coefficients at room temperature[32,33] are the same order of magnitude as these results.

The data from the lower coverage sample plotted in Figure 3 were also fit to eq 4, resulting in a value for the diffusion coefficient that was indistinguishable from that of the higher coverage sample. Because the kinetics were carried out under identical conditions, the same diffusion coefficient is expected. The fitted result for the encounter radius for the lower surface coverage sample was 30% smaller than for the higher surface coverage sample, which is just beyond the expected error range. We have some suspicion that this sample was exposed to water vapor in air prior to the start of the experiment. Since equation 3 is valid under the assumption that the reactant molecules initially have a homogeneous distribution, any evolution in the distribution prior to the start of an experiment reduces the magnitude of the coefficient on the $t^{1/2}$-dependent term.

It is worth noting that in the Owen theory, eq 3, the steady-state part of the rate coefficient is independent of encounter distance, which is in contrast with the usual proportional dependence in Smoluchowski theory. This discrepancy arises from the change of boundary conditions from three to two dimensions. One solution to this discrepancy has been suggested by Adam and Delbrüück,[27] where the molecules on a two-dimensional surface is assumed to be a circular disk with an encounter radius R, and where a second circular boundary is established at $b = (1/\pi\rho_{\mathrm{a}})^{1/2}$ (ρ_{a} is the density of reactants on the surface). This corresponds to associating each molecule on the surface with an area πb^2 equal to its average fraction of the available surface area. The result yields the following expression for the steady-state surface diffusion rate coefficient:[27]

$$k = 2\pi D/[\ln(b/R) - c] \tag{5}$$

where D is the mutual diffusion coefficient (cm^2/s) and $c = 0.5$. Berg and Purcell[34] proposed that the constant c is equal to 0.75, while Keizer[35] used statistical thermodynamic theory to show that the value for c is $[\gamma - \ln(\sqrt{2})] = 0.2306$ (γ is Euler's constant). In this treatment, the dependence of the steady-state rate coefficient on the encounter radius is introduced by its ratio to the boundary condition, which is a function of surface coverage. To check the results reported above, eq 5 was also used to estimate the surface diffusion constant from the steady-state part of the rate coefficient. The value of b for eq 5 was determined from

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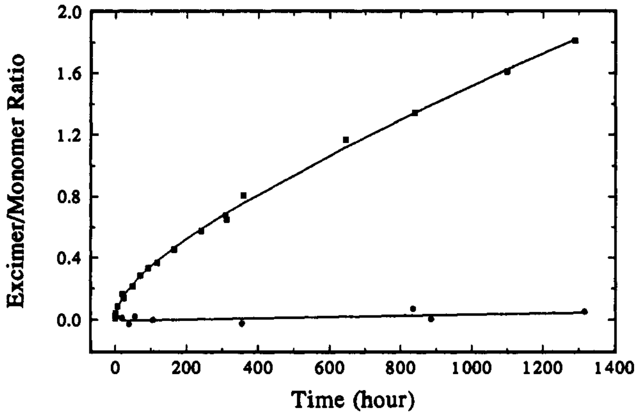

Figure 4. Excimer/monomer fluorescence intensity ratios versus time from samples kept in contact with 75%:25% water:methanol solution. (a, ■) 0.1 μmol/m^2 3PPS on silica and the fit to eq 4 (solid line). (b, ●) The same sample further modified by Cl ligands and the best fit to a straight line.

the surface coverage of 3PPS and the surface area of the silica, and the value of $R = 5.9$ Å obtained above was used for the encounter distance. From these parameters, eq 5 predicts a steady-state rate constant given by $k = 3.77$ and $3.25\ DN_{av}$ for the high and low surface coverage samples, respectively. For the samples used in this study, therefore, the two-dimensional diffusion theory that includes boundary conditions related to surface coverage, the steady-state rate coefficient agrees within 20% with the simpler theory of Owen, where $k = 3.17$ D.

Effects of Chemical Conditions on Surface Diffusion. The rate of forming excimers by 3PPS ligands on a silica surface appears to follow the kinetics of a diffusion-controlled process in a two-dimensional space, with the expected dependence on initial surface coverage by the ligand, $[M]_0$, and a reasonable value for an encounter distance. This kinetic evidence does, however, prove the mechanism proposed in Figure 2, that bound ligands can hop from one silanol site to another through a hydrolyzed intermediate. As a further test of this mechanism, a silica sample with 0.1 μmol/m^2 3PPS was subsequently derivatized with a large excess of trimethylchlorosilane (TMCS), resulting in a saturated coverage by TMCS groups of 4.7 μmol/m^2. While a significant population of silanols (about 50%) remains unreacted on the silica surface at this coverage, further derivatization is sterically inhibited since the size of the ligands is greater than the average distance between silanols on the surface. If 3PPS can migrate on this surface, then access to adjacent silanols is not required, and the hydrolyzed, physisorbed 3PPS could diffuse. The results of this experiment in Figure 4 show that migration on the methylated (C1) silica surface is indeed negligible. Excimer emission intensity is within the uncertainty range of the monomer emission in the 480-nm spectral region, and no increase can detected with time (the uncertainty in slope includes zero). Thus, accessible silanol groups adjacent to 3PPS appear to be required for migration, which is consistent with the mechanism I → II → III in Figure 2.

The migration experiment for the methylated (C1) silica was carried out in a 75%:25% (v/v) water:methanol mixture instead of pure water since the hydrophobic TMCS silica could not be wetted without reducing the surface tension of the solvent. To check on the effects of adding 25% methanol to the solvent, a control 3PPS silica without TMCS was also tested on this solvent, and the data are plotted in Figure 4. The growth of excimer emission was readily detected, although the rate is slower than that in pure water. These data also could be fit by eq 4, where the mutual diffusion coefficient $D = (9.1 \pm 1.8) \times 10^{-21}$ cm^2/s was found to be smaller by a factor of 0.25 than that for the same sample in contact with pure water, and the encounter distance $R = 5.8 \pm 0.6$ Å remains indistinguishable from the pure water result. While the change in the overlaying solvent has been shown to change the conformation of surface-bound pyrene ligands,[6,36] the effect on the encounter radius appears to be small in this case. The smaller surface diffusion coefficient in the mixed solvent is expected since the activity of water in this mixture[37] is smaller than that in pure water by a factor of 0.56. It is interesting that a ≈2-fold reduction in water activity produces a ≈4-fold reduction in the migration rate. The hydrolysis of siloxanes has recently been shown to proceed by nucleophilic activation, leading first to a pentacoordinate silicon intermediate followed by a slow, rate-determining step of coordination by water (giving a hexa-coordinate transition state).[23] In the absence of other nucleophiles, two water molecules could be acting as the activating and attacking nucleophiles, respectively, in the rate-determining step, which would result in a quadratic dependence of the rate on the activity of water; this is in close agreement with the observed results. The higher order dependence of the diffusion rate on water activity is consistent with a hydrolyzed intermediate (II in Figure 2) and probably rules out a concerted reaction mechanism where the silane hops from one silanol to another in a single step.

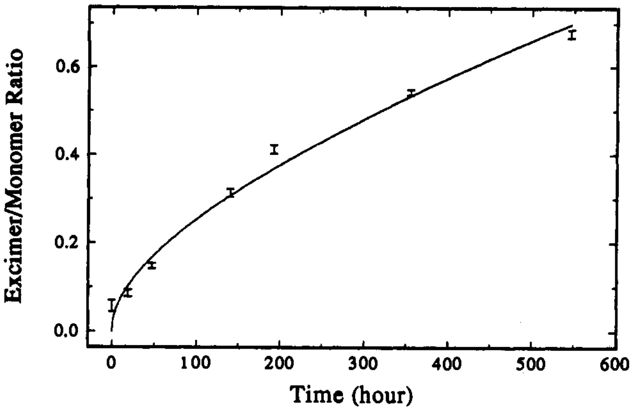

Figure 5. Excimer/monomer fluorescence intensity ratios versus time from 0.1 μmol/m^2 3PPS on silica, exposed to water vapor. The fit to eq 4 is also shown (solid line).

The slight solubility of pyrene in water raises a question of whether surface migration of 3PPS proceeds via diffusion of the hydrolyzed intermediate through overlaying solvent. The lack of migration of 3PPS on the methylated (C1-derivatized) silica surface indicates that the migration process proceeds by binding to neighboring silanols. Furthermore, the migration of 3PPS in contact with methanol:water solution, in which pyrene is more soluble, was found to be slower than migration in pure water. These results, along with the high fraction of 3PPS that remains covalently bound to the surface, show that the rate of rebinding to the silica (II → I or II → III in Figure 2) is much faster than the desorption rate of the hydrolyzed reagent (II) into the solution. To further address the question about the role of bulk solvent in the migration process, an experiment was carried out in which pyrene-labeled silica was exposed only to water vapor and no bulk water or other solvent was added during the collection of fluorescence spectra. Under these conditions, the excimer emission peak centered at 480 nm was still observed to be growing with time, indicating that bulk water is not required for the ligands to migrate. The kinetic data for surface migration of a 0.1 μmol/m^2 3PPS sample exposed to 100% relative humidity conditions are plotted in Figure 5, along with a fit to eq 4. From the fit of the data, a mutual diffusion coefficient $D = (5.1 \pm 1.1) \times 10^{-21}$ cm^2/s and an encounter radius of 6.0 ± 0.9 Å are found. The encounter radius is indistinguishable from that observed for the same sample in contact with bulk water, while the diffusion constant is a factor of 7 smaller. The reduction in diffusion rate

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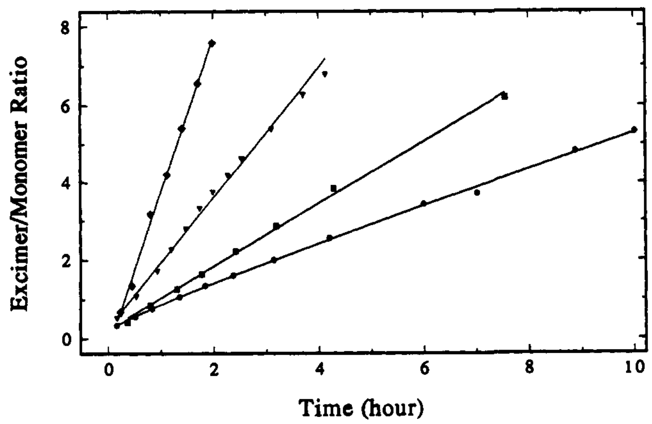

Figure 6. Excimer/monomer fluorescence intensity ratios versus time from 0.06 μmol/m^2 3PPS on silica, kept in contact with aqueous phosphoric acid (5%) at four temperatures, 42.2 °C (◆), 34.3 °C (▼), 23.1 °C (■), and 14.5 °C (●). The fits to eq 4 (14.5 °C) and straight lines (others) are also plotted (solid lines).

is probably due to the lower activity of water on the silica surface under these conditions, leading to a slower rate of hydrolysis, as discussed above. Contact between the surface and bulk water, however, is clearly not required for the migration process to occur.

A final study of the effects of chemical conditions on the migration process is to test whether the rate can be increased by addition of a catalyst. Acids are well known to catalyze both hydrolysis and condensation of siloxane bonds,[21,22] where the former process is proposed to represent the barrier to migration as in Figure 2. A recent study of acid treatment of *n*-alkyl chromatographic stationary phases revealed that solute retention characteristics of the column could be altered without significant loss of surface-bound ligands.[38] This differs significantly from treatment with strong aqueous base, where significant dissolution of surface ligands was observed,[39] perhaps due to attack of the silica framework. Using acid treatment conditions (5% aqueous phosphoric acid) which had been shown to be compatible with retention of siloxane-bound alkyl ligands on silica,[38] the migration rate of 3PPS was tested for the effect of catalysis. As shown in Figure 6, the excimer/monomer ratio for 3PPS rises much faster under these conditions, with detectable excimer being produced in only a few hours rather than several days. These results follow the kinetics described by eq 4, although the greater speed of reaction makes detection of the $t^{1/2}$ behavior more difficult to observe under all but the lowest temperature conditions. The mutual diffusion coefficient at room temperature, $D = (1.9 \pm 0.4) \times 10^{-17}$ cm^2/s, was 500 times larger than the diffusion rate for a sample in contact with pure water. The diffusion rate showed a strong dependence on temperature, which would be expected for the large activation barrier of breaking a covalent bond (see below).

The extent of hydrolysis of surface-bound 3PPS molecules under conditions of acid catalysis was quantitatively determined. After the sample was kept in 5% phosphoric at 42 °C for 24 h, the amount of 3PPS that was found to be hydrolyzed from the surface was determined by a fluorescence measurement to be 1.5% of the total surface-bound 3PPS. This result also agrees with a recent quantitative study of hydrolysis of monofunctional C18 ligands from silica under acidic conditions. Following a 2-month exposure of a packed column to an acetonitrile/water solution (60/40 v/v) containing 0.1% trifluoroacetic acid, the accumulated loss of stationary phase from the surface determined by GC–MS measurements was found under these conditions to be 0.8%.[24]

Activation Energy for Siloxane Migration on Silica. The surface migration of 3PPS on silica is proposed to involve covalently bound ligands; therefore, the activation barrier to migration should require breaking of a siloxane bond. To further test this proposed mechanism, the temperature dependence of the migration rate was measured to determine the activation energy. Excimer/monomer ratios were measured as function of time at two higher temperatures in the case of pure water; the results follow the kinetics described by eq 4 as shown in Figure 7. The corresponding Arrhenius plot, shown in Figure 8, is linear and yields an activation energy of 16.3 ± 0.6 kcal/mol. The magnitude of this result indicates that the barrier to migration exceeds the energy range of physisorption and is consistent with covalently bound ligands migrating on the surface. While no measurements of activation energies for hydrolysis of alkylsiloxanes on silica could be found reported in the literature, a temperature-dependent study of hydrolysis of a trialkoxysilane reported an activation energy of 9.8 kcal/mol[40,41] in a pH 4.0 buffer. A temperature-dependent study of the reaction of gas-phase methoxytrimethylsilane with silica at elevated temperatures reported an activation energy for binding to a surface silanol of 22 kcal/mol.[42] While the latter result is not directly comparable, the results place the observed energy barrier to surface migration of 3PPS within a reasonable range for breaking siloxane bonds.

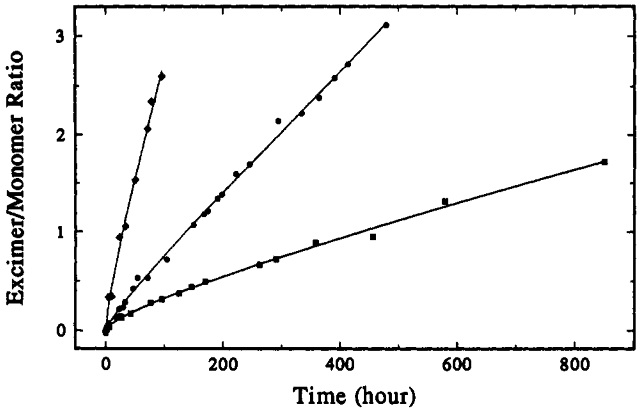

Figure 7. Excimer/monomer fluorescence intensity ratios versus time from 0.06 μmol/m^2 3PPS on silica, kept in contact with pure water at three temperatures, 52.2 °C (◆), 41.7 °C (●), and 24.3 °C (■). The fits to eq 4 are also plotted (solid lines).

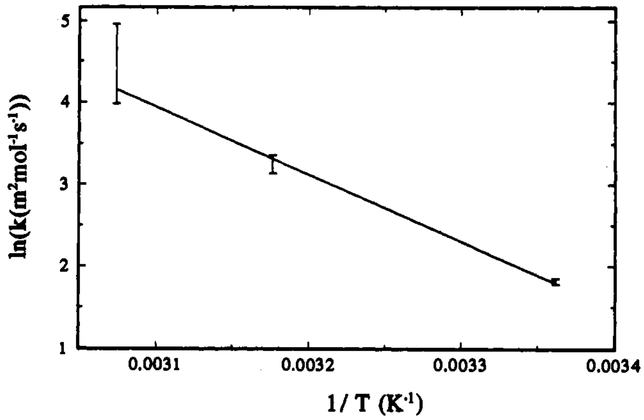

Figure 8. Arrhenius plot of logarithm of the steady-state encounter rate constant versus reciprocal temperature for 0.06 μmol/m^2 3PPS on silica in contact with water.

The effect of acid catalysis on the energy barrier to migration was also examined in an Arrhenius plot (Figure 9) of the results from Figure 6. The plot is again linear within the uncertainty

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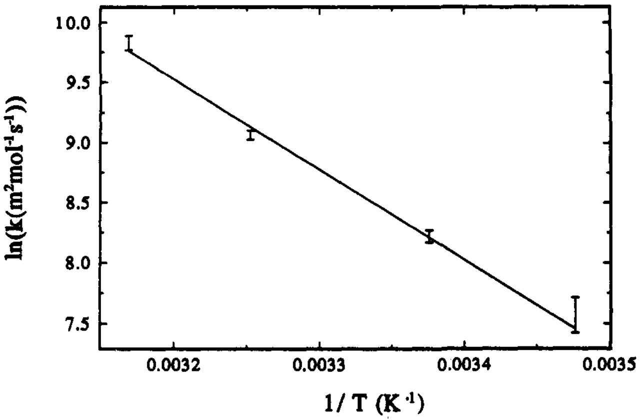

Figure 9. Arrhenius plot of logarithm of the steady-state encounter rate constant versus reciprocal temperature for 0.06 μmol/m² 3PPS on silica in contact with 5% phosphoric acid.

of the measured rates, and the activation energy was determined from the slope to be 14.9 ± 0.3 kcal/mol. Acid catalysis thus lowers the activation energy for migration compared to that for reaction in pure water by 1.4 ± 0.7 kcal/mol, which is consistent with a ≥10-fold increase in the surface diffusion rate under these conditions.

A final question that can be asked about the migration kinetics from the Arrhenius plots relates to the magnitude of the preexponential factor. In the case of the acid-catalyzed migration data in Figure 9, the uncertainty of the estimated intercept is small enough that the magnitude of the preexponential factor can be examined. From the intercept value, the preexponential factor for surface encounter is $A_r = (3.5 \pm 1.5) \times 10^{14}$ m² mol^{-1} s^{-1}, corresponding to a barrier-free mutual diffusion coefficient of $D_{max} = (2 \pm 1) \times 10^{-10}$ cm²/s. If migration proceeds by hopping to adjacent silanols on the silica surface, then the diffusion coefficient can be converted to a unimolecular hopping rate using the mean-square distance between silanols, $\langle x^2 \rangle$. Converting the silanol density of silica gel, 8 μmol/m²,[1] to $\langle x^2 \rangle$ and dividing this result into $4D_{max}/2$ (recalling that the mutual diffusion coefficient for the reactants is twice that of the individual species and the random walk is in a two-dimensional space) yields a preexponential factor expressed as a hopping rate, $A_h = (2 \pm 1) \times 10^5$ s^{-1}. This rate is much smaller than typical unimolecular preexponential factors near room temperature of 10^{12}–10^{13} s^{-1}; it could derive either from a small transmission coefficient at the transition state (low probability of leaving the original silanol after hydrolysis) or from large entropy of activation for the hydrolysis step.

When McNeil et al. measured the temperature dependence of hydrolysis of alkoxysilanes, they fit their results to absolute rate theory and found a large activation entropy, $\Delta S^{\ddagger} = -39$ cal K^{-1} mol^{-1}; this large entropy barrier was attributed to a highly ordered transition state, with perhaps more than one water molecule associated with it.[40] This interpretation is consistent with the higher order dependence on water activity that was observed in the surface migration rate, discussed above. To compare the slow hopping rate for surface migration with the high entropy barrier for alkoxysilane hydrolysis reported by McNeil et al., we convert the activation entropy to the equivalent Arrhenius preexponential factor using the relation[41] $A = (ekT/h) \exp(\Delta H^{\ddagger}/R)$, where e is the natural log base. From this relationship, the preexponential factor describing the hydrolysis of a trialkoxysilane in pH 4.0 buffer at room temperature is $A_{hyd} = 5 \times 10^4$ s^{-1}. This result is remarkably close (within a factor 4) to the estimated preexponential factor for the hopping rate discussed above. The agreement between these results strengthens the conclusion that hydrolysis of the surface–siloxane bond is indeed the barrier to migration of 3PPS on silica.

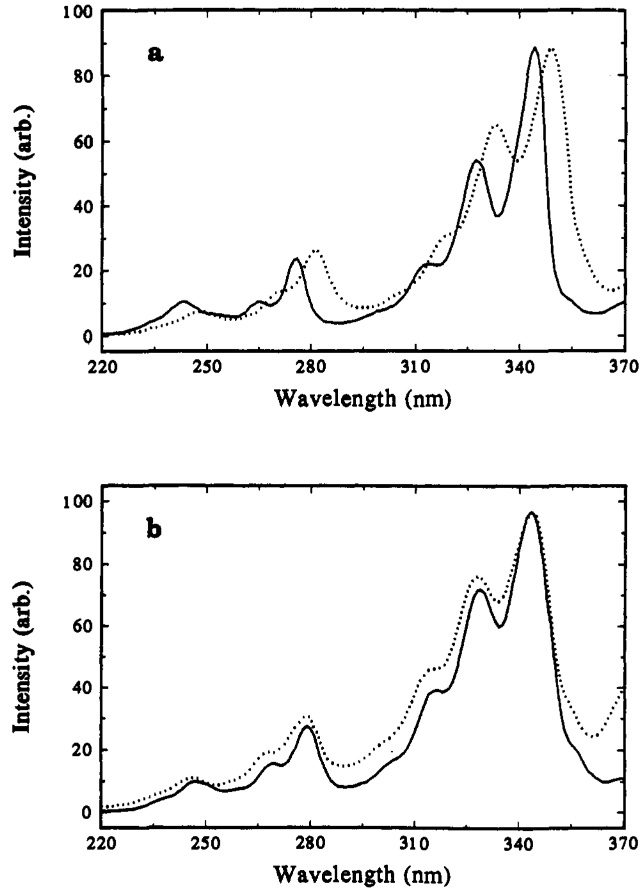

Figure 10. Fluorescence excitation spectra from 3PPS bound to silica. Solid line is for emission monitored at 400 nm (monomer), and dots are for emission monitored at 480 nm (excimer). (a) 0.10 μmol/m² 3PPS after 10 days of exposure to water vapor. (b) 0.16 μmol/m² 3PPS immediately after derivatization. Both samples were transferred to methanol and degassed (freeze–pump–thaw method).

Mechanism of 3PPS Association on Silica Surfaces. The excellent fit of the 3PPS encounter kinetics to the simple bimolecular reaction model of eq 4 indicates that pyrene molecules which encounter each other on the surface remain associated. The dissociation of excimer species could not be detected in the kinetic data. In order for 3PPS molecules, originally dispersed widely and randomly over the surface, to be strongly associated upon encounter, some mechanism for their association is required to explain the results. Evidence of strong interactions between 3PPS pyrene moieties that encounter each other by migration on the silica surface can be found in the fluorescence excitation spectrum of the excimer. Figure 10a compares the excitation spectra of excimer and monomer emission from a 0.1 μmol/m² 3PPS sample following 10 days of exposure to water vapor. The excimer excitation spectrum exhibits a large red shift, Δλ = 4.8 ± 0.8 nm, relative to that of monomer. This shift persists even after a 100-fold dilution of the sample with pure underivatized silica, ruling out a self-absorption artifact as its origin.[15,43] The large difference between excitation spectra of excimer and monomer species is evidence of ground-state preassociation between pyrene rings rather than a dynamic excimer formation process.[19] This is consistent with the model that was used to fit the migration data, which requires a strong association between 3PPS molecules that collide on the silica surface.

Winnik[19,44] has used peak-to-valley intensity ratios to describe differences between excitation spectra of preassociated excimer and monomer species. Using this method, further evidence is obtained to support a ground-state preassociation mechanism:

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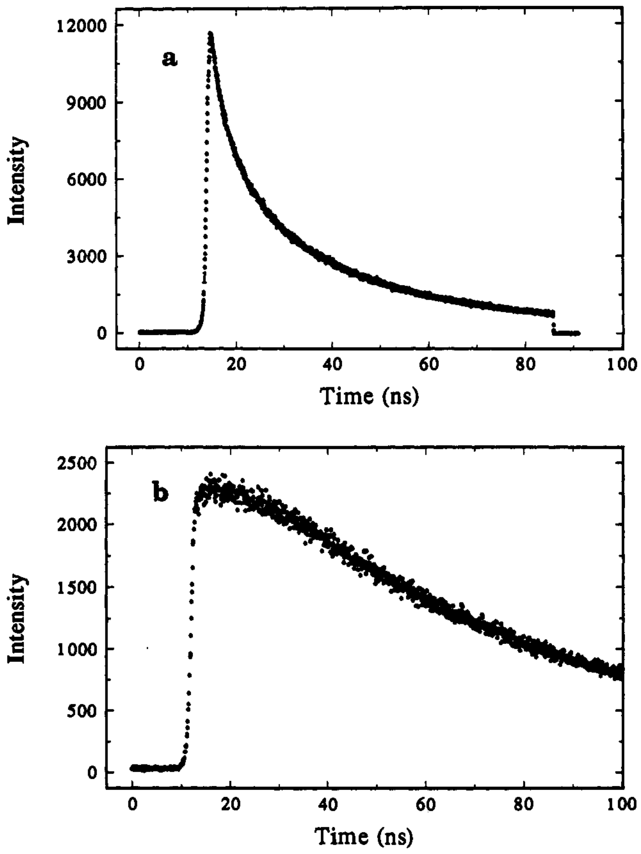

Figure 11. Time-resolved excimer fluorescence from 3PPS silica. Emission monitored at 500 nm. (a) 0.10 μmol/m^2 3PPS after 10 days of exposure to water vapor. (b) 0.16 μmol/m^2 3PPS immediately after derivatization. Both samples were transferred to methanol and degassed (freeze–pump–thaw method).

peak-to-valley ratios between 335 and 355 nm in the excitation spectra of monomer and excimer are 2.4 and 1.6, respectively. Together with the 4.8-nm red shift, these results are very similar to those reported for pyrene-labeled celluloses, where preassociation of pyrene labels is observed.[44] Additional evidence for ground-state association of 3PPS ligands is found in the time-resolved fluorescence emission from the excimer, shown in Figure 11a. Fluorescence from the migrated excimer rises instantly upon the excitation by the laser. The absence of a rise time further indicates that the pyrene rings are preassociated in their ground state.

The ground-state association of 3PPS pyrene rings on the silica surface observed for excimer derived from surface migration stands in contrast with previous findings of Lochmüller et al.,[6,15] where higher coverage 3PPS silicas produced dynamic excimer emission with little evidence of ground-state preassociation. To test this finding, a 3PPS silica sample was prepared having sufficient coverage (0.16 μmol/m^2) to produce excimer immediately following the surface derivatization without exposure to water. The excitation spectra for monomer and excimer for this sample are compared in Figure 10b, and the time-resolved excimer emission is plotted in Figure 11b. The excitation spectra for the monomer and excimer show no detectable wavelength shift, and peak-to-valley ratios between 335 and 355 nm for monomer and excimer spectra are 1.6 and 1.4, respectively, indicating that nearly indistinguishable ground-state monomer species are initially excited. The time-resolved excimer emission clearly shows a slow (8 ns) rise time. These results both verify the previous observation[6,15] of a dynamic excimer formation process for 3PPS molecules that are initially bound at sufficiently high coverage that they can associate with neighboring ligands during the excited-state lifetime of the monomer.

These results differ from those for the migrated excimer population, where strong ground-state association is inferred from both the excitation spectra and the time-resolved emission behavior. While this association is necessary to explain the observed 3PPS migration kinetics, the specific chemical origins of the association between 3PPS molecules (that does not appear in a freshly prepared sample) are presently not known. It is possible that at low surface coverages, 3PPS migrates to a specific binding site where ground-state association with another ligand is more likely. This idea is consistent with a more restricted geometry for ground-state preassociation corresponding to smaller encounter distance (6 Å) found in this work, compared to the >15 Å average distances for dynamic excimer formation between randomly bound 3PPS ligands.[6] Evidence of migration to specific binding sites for association is manifested in the excited-state decay kinetics of the residual 3PPS monomer population which evolves over the same slow time scale as excimer formation upon exposure to water.[45] The monomer decay kinetics become inhomogeneous, producing a short-lived population that appears to interact strongly with neighboring silanols. To better understand how the reactivity of different silanol sites might affect the association of 3PPS molecules with the surface and each other, we are presently investigating the role of silanol reactivity in evolution of surface structures using ^{29}Si NMR.[45]

Conclusions

In this study, the slow growth of excimer emission from 3PPS on silica could be attributed to migration of covalently bound ligands over the surface. The time evolution of the excimer population was successfully modeled using a two-dimensional diffusion theory. Surface diffusion coefficients could be estimated, along with reasonable values for the encounter radius for excimer formation. The migration appears to proceed through a hydrolyzed intermediate that can rebind to adjacent silanol sites on the silica surface. The activation energy for the process is consistent with hydrolysis of the surface siloxane bond. The higher order dependence of the migration rate on water activity and a small Arrhenius preexponential factor are consistent with a large entropy barrier for hydrolysis.

Water-activated surface migration of siloxane-bound ligands could allow relaxation to mechanical stress in silane-coupled polymer/glass composites, as previously suggested.[2,7] The changing retention characteristics of reversed-phase liquid chromatographic columns exposed to aqueous solution, particularly at low pH,[38] could derive from slow annealing of the surface structure through the migration of ligands to different binding sites. While the observed diffusion coefficients for this process are extremely small due to the large activation energy and entropy barrier to migration, diffusion over distances of only 10 Å would greatly alter the ligand conformation and surface energetics of a high-coverage material.

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