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Behavior of organic compounds confined in monoliths of sol–gel silica glass. Effects of guest–host hydrogen bonding on uptake, release, and isomerization of the guest compounds†

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Various proteins, catalysts, and other compounds can be encapsulated or diffused into porous sol–gel glasses, but little is known about their interactions with the glass matrix. We report unexpectedly large effects that hydrogen bonding between organic compounds and sol–gel silica has on equilibria and reactions involving these guest compounds. Silica monolith immersed in a solution takes up the organic solute. Styrene, which is incapable of hydrogen bonding, becomes evenly distributed between external solution and the glass. Aniline and *N*,*N*-diethyl-*p*-methoxybenzamide, which are capable of hydrogen bonding, become extracted into the glass when the solvent (neat CCl_4) does not interfere with their hydrogen bonding with silica. They become evenly distributed between the solution and the glass when a component of the solvent (DMF added to CCl_4) or chemical modification (trimethylsilylation) of the silica surface suppresses hydrogen bonding of the guests with the surface. Ultraviolet spectra show that silica–guest interactions are present when the guest uptake is excessive and absent when this uptake is balanced. Ultraviolet spectra of aniline show that the hydrogen atoms are donated by silica to the guest. Not only the extent, but also the rate, of uptake is enhanced when the guest makes hydrogen bonds to the silica matrix; suppression of these bonds lowers the uptake rate. Silica monolith extracts *trans*-3,3′-diacetylazobenzene from a CCl_4 solution 1250-fold. Upon addition of DMF, hydrogen bonds are broken, and the monolith completely releases the solute into the external solution. Five derivatives of azobenzene (3,3′-dimethyl-, 3-acetyl-, 3,3′-diacetyl-, 3,5-diacetyl-, and 3,3′,5,5′-tetraacetylazobenzene), which differ in the propensity for accepting hydrogen atoms, served as photochromic probes and showed the effect of hydrogen bonding on reactivity. Both the photoinduced (*trans*-to-*cis*) and the subsequent thermal (*cis*-to-*trans*) isomerizations of the five derivatives obey the first-order law in glass as well as in free solution. When the solvent (neat CCl_4) allows hydrogen bonding, the proportion of the isomers in the photostationary state differs between the glass and solution, and the rate constant for the thermal reaction is two to four times (in different derivatives) smaller in the glass than in solution. Evidently, hydrogen bonding retards the rearrangement of the probe molecules in the silica matrix. When hydrogen bonding is abolished (by addition of DMF to CCl_4), the compositions of the photostationary state in the glass and in solution become equal, and so do the rate constants. Effects of hydrogen bonding on enzymes encapsulated in sol–gel glass and on the distribution of analytes between the glass monolith and the sample solution should be taken into consideration when designing accurate biosensors.

Introduction

Controlled hydrolysis of alkoxides and polymerization of the resulting oxyacids, the sol–gel method, is useful in several branches of chemistry and engineering. Moderate processing conditions enable encapsulation of various organic, inorganic, and biological molecules in glasses having adjustable properties.[1–8] The method is used for the fabrication of sensors, catalyst supports, coatings, special polymers, and other new materials.[9–19]

The guest compounds can be added at the onset of the polymerization and encapsulated in the glass, or they can be diffused into the porous glass after it has solidified. In either case interactions at the molecular level between glass matrix and guest molecules, which govern mobility and chemical reactivity of those guests, are poorly understood. To examine these interactions, we have determined the affinity of sol–gel silica glass toward various organic compounds as guests, and we have studied dynamical properties of some of these guests inside the matrix. Other research of this kind has recently been undertaken.[20–24]

Work in our laboratory has shown that small molecules may behave quite differently in free solution and in the same solvent but confined in the pores of a hydrogel.[25–27] Soaking of silica glass in electrolyte solutions, no matter how prolonged, may not ensure equal partitioning of certain ions between the glass and the solution. At a pH value at which the pore walls are negatively charged, anions, such as $[Fe(CN)_6]^{3-}$, are only partially taken up, whereas cations, such as $[Ru(NH_3)_6]^{3+}$, are excessively taken up by the glass from the surrounding solution. In either case, internal and external concentrations of the ion remain unequal after the equilibrium is reached. If the electrostatic interactions are left unchecked, the unequal distribution of an ionic analyte would invalidate a biosensor.

Hydrogen bonding is subtler and more specific than electrostatic interactions.[28,29] Evidence for the existence of this bonding in sol–gel silica glass has been reported.[21,30–33]

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†One table (absorptivities of azobenzene derivatives) and nine figures (UV absorption spectra of styrene and *N*,*N*-diethyl-*p*-methoxybenzamide in solution and in silica glass; UV absorption spectra of aniline and *N*,*N*-diethyl-*p*-methoxybenzamide in solution and in trimethylsilylated silica glass; uptake of all three guests in silica glass pretreated with HCl or NaOH or not pretreated; and ^1H NMR, ^{13}C NMR, and mass spectra of 3,5-diacetylazobenzene and 3,3′,5,5′-tetraacetylazobenzene) are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/jm/b0/b005823h/

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However, to our knowledge, there is no published evidence for the effects of hydrogen bonding on equilibria and reactions involving the guest compounds within sol–gel silica.

Because hydrogen bonds are relatively strong and directional, they may greatly affect physical and chemical processes in doped glasses. Not much is known about these important interactions, which are likely to affect properties and performance of biosensors, immobilized catalysts, and various composite materials prepared by the sol–gel method. These phenomena deserve thorough investigation, and this study is a piece of it. We detected hydrogen bonding, found examples of its enormous effect on uptake of guests by silica, learned how to enhance and abolish this bonding, and showed that it can affect mobility of guest molecules and their rate of reaction. By studying hydrogen bonding and its influence on thermodynamic and kinetic properties of absorbed and encapsulated molecules in sol–gel silica monoliths, one can learn to control chemical processes inside the matrix and to prepare silica glasses with specific and desired properties.

Experimental procedures

Instrumentation

Proton and ^{13}C NMR spectra were recorded with a Varian 400 MHz instrument; infrared spectra, with a Bio Rad FTS-7 instrument; and UV absorption spectra, with a Perkin-Elmer Lambda 18 spectrophotometer whose cuvette holder was connected to the thermostated circulator bath Model 9500 from Fisher Scientific Co. Photochemical reactions were done with a Rayonet 100 reactor, which has six fluorescent tubes designated 3500 Å.

Chemicals

Distilled water was further demineralized to a resistivity greater than 17 MΩ cm. Tetramethyl orthosilicate and acetonitrile were purchased from Fisher Chemical Co; aniline, styrene, thionyl chloride, *p*-anisic acid, nitrosobenzene, 3-aminoacetophenone, 1,1,1,3,3,3-hexamethyldisilazane (HMDSZ), carbon tetrachloride, benzene, and anhydrous *N,N*-dimethylformamide (DMF), from Aldrich Chemical Co; and 3,3′-dimethylazobenzene, from Trade TCI Mark.

Hazards

Tetramethyl orthosilicate, benzene and CCl_4 are highly toxic; the last two chemicals may cause cancer. Protective gloves and effective fume hood must be used in experiments with these compounds.

Preparation of silica monoliths

The silica sol was prepared by a standard procedure.[34] A mixture of 15.76 g of tetramethyl orthosilicate, 3.38 g of water, and 0.30 g of 0.040 M HCl was kept in an ice-cooled ultrasonic bath for 30 min. Upon addition of 36.26 mL of a 10 mM sodium phosphate buffer at pH 7.00, gelation began. The sol was quickly poured into polystyrene cuvettes sized $10 \times 10 \times 40$ mm, and left at 4 °C. During the aging for 14 days, the samples were kept soaked and were washed with water twice a day. The aged samples were exposed to air, still at 4 °C, for another 14 days of partial drying and shrinking. The resulting transparent monoliths, prisms sized $8 \times 8 \times 27$ mm, were soaked in acetonitrile and stored at 4 °C for further use. All monoliths used in this study had this size. Defective or nonstandard monoliths were rejected, for the sake of reproducibility and accuracy of the experiments.

Dehydration of silica monoliths

Two silica monoliths sized $8 \times 8 \times 27$ mm were soaked in 300 mL of stirred acetonitrile in a capped 500 mL Erlenmeyer flask. The solvent was twice replaced with fresh 300 mL portions, after 2 h and again after 21 h. This last soaking lasted for an additional 24 h. The monoliths were then soaked in 150 mL of stirred CCl_4 in a capped 250 mL Erlenmeyer flask. The solvent was replaced with a fresh 150 mL portion after 24 h, and the soaking continued for an additional 24 h. In some experiments, the second solvent was a 9 : 1 v/v mixture of CCl_4 and DMF. The Erlenmeyer flasks were always capped, to protect the dry solvents from the moisture in the air. Dehydrated silica monoliths were stored for further experiments in a fresh portion of the same solvent in which they had been soaked last, pure CCl_4 or a 9 : 1 v/v mixture of CCl_4 and DMF.

Trimethylsilylation of silica monoliths

A silica monolith sized $8 \times 8 \times 27$ mm was exhaustively soaked, with stirring, in a succession of relatively large volumes of many solvents and solutions. These liquids, the volume of their portions, the time of the soaking in each fresh portion, the number of fresh portions, and the function of each liquid were as follows: Acetonitrile, 350 mL, 24 h, one, for rinsing; a mixture of 90 mL acetonitrile and 10 mL acetyl chloride, 2 h, one, for removal of water; acetonitrile, 400 mL, 12 h, six, for removal of acetyl chloride and reaction products; a mixture of 90 mL acetonitrile and 10 mL 1,1,1,3,3,3-hexamethyldisilazane (HMDSZ) under a nitrogen atmosphere, 24 h, five, for trimethylsilylation;[35] acetonitrile, 400 mL, four, for removal of HMDSZ and reaction products; and finally CCl_4, 150 mL, 24 h, two, for removal of previous solvents. Upon first contact with HMDSZ the transparent monolith turned cloudy white, but it became transparent again later.

This procedure was repeated with several monoliths. The trimethylsilylated monoliths were stored in CCl_4 for further experiments.

Infrared spectra of dehydrated and trimethylsilylated silica glasses

Silica monoliths of both kinds were ground in a mortar, the powder was dried in a vacuum desiccator for 1 h, and the spectroscopic sample was placed between NaCl plates.

Pretreatment of silica monoliths with acid and base

Two silica monoliths sized $8 \times 8 \times 27$ mm were soaked in 200 mL of a 0.10 M HCl solution, and the other two were soaked in 200 mL of a 3.2×10^{-4} M NaOH solution, all in capped 500 mL Erlenmeyer flasks, with stirring overnight. All four monoliths were then dehydrated by the procedure described above.

General procedure for uptake experiments

Stock solutions of guest compounds in CCl_4 were prepared as 2.05 mM in styrene, 0.48 mM in aniline, and 0.43 mM in *N,N*-diethyl-*p*-methoxybenzamide, so that their UV absorbances were not too high. Dehydrated silica monoliths sized $8 \times 8 \times 27$ mm were the hosts. Each monolith was soaked in 50.0 mL of a stock solution in a capped vial. The monolith stood upright, with one of its 8×8 mm sides resting on the flat bottom of the vial and the other five sides exposed to the solution. From time to time the monolith without the surrounding solution was transferred to the 10 mm quartz cuvette kept in the sample holder of the spectrophotometer. An identical but undoped silica monolith made in the same batch as the doped monolith was put in another 10 mm quartz cuvette, and kept in the reference holder. Both monoliths were held in the same place and the same position in all experiments, so that their absorbances could be accurately compared. The UV spectra were scanned at the rate of 120 nm min^{-1}, and the doped monolith was returned to the solution of the guest compound (the dopant) and soaked further. The UV measurements were made more frequently early in the experiment, while the uptake was relatively fast, and less frequently later, when the uptake slowed down. At the end of the uptake experiment, the UV spectrum of the soaking solution partially depleted of the guest compound was compared with the UV spectrum of the stock solution of this guest. The width in mm (w) of the soaked monolith was measured with the caliper, and the absorbance of this monolith multiplied by $10/w$, so that it could be compared with the absorbance of the stock solution.

Uptake and release of *trans*-3,3′-diacetylazobenzene

This compound was chosen for the determination of the maximum uptake of a guest compound by the sol–gel silica glass. A dehydrated monolith sized 8 × 8 × 27 mm was soaked in 200 mL of a stirred 9.30×10^{-4} M solution of the title compound in CCl_4. The capped Erlenmeyer flask was wrapped in aluminium foil, to prevent photoisomerization of the *trans*-isomer. Decrease of its concentration in the external solution was monitored occasionally by UV spectroscopy. Aliquots of *ca.* 0.30 mL of the external solution were diluted by *ca.* 2.5 mL of CCl_4, to lower their absorbance below 1.0; both the aliquot and the solvent were weighed with an analytical balance, so that the accurate dilution factor be known. Then the UV spectrum was recorded, and from it the concentration of the title compound in the external solution was determined. Slight decreases in the volume of the soaking solution after each successive removal of aliquots were taken into account in the successive determinations of its concentration. When this concentration almost ceased decreasing with time, the uptake experiment was ended.

The release of the title compound by the monolith was triggered by adding 20.0 mL of DMF to the external solution. Increase in the concentration of the title compound in the external solution was followed by UV spectroscopy, as described above. When this concentration nearly reached the initial value of 9.30×10^{-4} M, the experiment was ended.

Calculation of the volume required for *trans*-to-*cis* isomerization

We accepted a published mechanism for isomerization of azobenzene.[36–39] Conformation of the *trans*-isomer was optimized with the program Hyperchem 4.5. All five stages of the isomerization were examined separately for each azobenzene derivative.[40] The structures at each of the five stages were superimposed and treated as one structure, the van der Waals volume of which was then calculated by the program GRASP 1.2. This volume can accommodate the entire isomerization process of the given derivative. This procedure was repeated for each of the five derivatives of azobenzene.

Determination of absorptivities of azobenzene derivatives

The following procedure was used for the *trans*-isomers of all five azobenzene derivatives. A sample of *ca.* 17 mg, weighed to 0.01 mg, was dissolved in 500.0 ± 0.2 mL CCl_4, in a volumetric flask. The UV spectrum of this solution allowed direct calculation of absorptivities of the *trans*-isomer at various wavelengths.

Absorptivities of the *cis*-isomer were determined indirectly. A sample of *ca.* 1.0 mg of the *trans*-isomer was dissolved in 10.0 mL of a 95 : 5 v/v mixture of CCl_4 and $CDCl_3$, in a volumetric flask. The UV spectrum was recorded, and the solution was irradiated (by the procedure to be described next) until its UV spectrum ceased to change, *i.e.*, until the photostationary state (designated pss) for the isomerization was reached. The relative concentrations of the *trans* and *cis*-isomers were determined from the intensities of the ^{1}H NMR resonances for the methyl groups in these isomers. Although thermal isomerization is slow and the composition of the pss is practically constant over a relatively short time (see below), for the sake of accuracy the NMR spectrum was taken promptly. From the known initial concentration and absorptivity of the *trans*-isomer, the UV spectrum of the mixture of isomers, and the composition of this mixture, the absorptivity of the *cis*-isomer was determined. The results are given in Table S1 in the supplementary information.

trans-to-*cis* photoisomerization of azobenzene derivatives

To a quartz cuvette sized 10 × 10 × 40 mm with all walls transparent (so-called fluorescence cuvette) was fused a ground-glass joint. The joint could be closed, to prevent evaporation of the solvent held (together with the doped monolith) in the cuvette. The following procedure was used for all five derivatives of azobenzene. A dehydrated silica monolith sized 8 × 8 × 27 mm was soaked in 50.0 mL of a solution of the *trans*-isomer in a 9 : 1 v/v mixture of CCl_4 and DMF; DMF ensured that the guest compound uniformly penetrated into silica (see the general description of uptake experiments). The uptake was followed by UV spectrophotometry. When the absorbance of the *trans*-isomer in silica reached that in the external solution, the monolith and 1.50 mL of the soaking solution were transferred to the special cuvette and always kept in the same position inside it. The capped cuvette was irradiated, always in the same position with respect to the lamps. The walls transmitted UV light from all sides. The ultraviolet spectrum of the monolith was taken occasionally. When it ceased changing, the photostationary state (pss) was reached. Absorbances were converted to concentrations according to eqns (1) and (2), in which A is absorbance, ε is absorptivity, subscript o denotes initial concentration, and lack of a subscript denotes the concentration at the time of measurement.[41] The experimental results were fitted by the linear least-squares method, eqn. (3), in which t is time and k_1 is the apparent first-order rate constant for the intramolecular photoisomerization.[41]

$$[cis] = \frac{1 - \frac{A}{A_o}}{1 - \frac{\varepsilon_{cis}}{\varepsilon_{trans}}}\,[trans]_o \qquad (1)$$

$$[trans] = [trans]_0 - [cis] \qquad (2)$$

$$\ln\frac{[trans]_0 - [trans]_{pss}}{[trans] - [trans]_{pss}} = \frac{[trans]_0}{[trans]_0 - [trans]_{pss}}k_1 \cdot t \qquad (3)$$

cis-to-*trans* thermal isomerization of azobenzene derivatives

The following procedure was used for all five derivatives of azobenzene. A dehydrated silica monolith sized 8 × 8 × 27 mm was soaked in 50.0 mL of a 5×10^{-5} M solution of the pure *trans*-isomer. Two solvent systems were used. In one series of experiments neat CCl_4 was used and in the other series, a 9 : 1 v/v mixture of CCl_4 and DMF was used. As before, when absorbance of the monolith reached that of the surrounding solution, the monolith was transferred to the special cuvette for UV irradiation. This time, the photoisomerization was just a method for preparing the *cis*-isomer, whose thermal isomerization was the reaction of interest. When the solvent was neat CCl_4, the monolith was transferred without the external solution, to avoid continued uptake of azobenzene during irradiation. When mixed solvent system was used, the monolith was transferred with 1.50 mL of the soaking solution, because in this case there was no danger of continued uptake.

The capped cuvette was irradiated in the photochemical reactor (as described above) until the UV spectrum ceased changing, a sign that the photostationary state was reached. To the solvent-free monolith was then added 1.5 mL of neat CCl_4, and the monolith that had been immersed in the mixture of CCl_4 and DMF was left so. The liquid around the monolith is needed to conduct the heat to the monolith. In both cases, the sealed cuvette was immersed above the level of the monolith and the surrounding liquid in the water bath at 50.0 ± 0.5 °C; thermal isomerization at a lower temperature would be impractically slow. The cuvette would occasionally be transferred to the spectrophotometer, and thermal isomerization would be followed by recording UV spectra. When the isomerization was completed, in experiments employing neat CCl_4 its spectrum was also taken, to detect possible leakage of the azobenzene from the monolith.

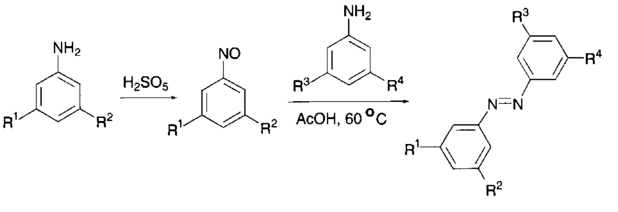
Ultraviolet bands of the five azobenzene derivatives reach their maxima at different wavelengths. The maximum absorbance was converted to the concentration of the *trans*-isomer according to eqns. (1) and (2). The change of concentration in time was fitted by the linear least-squares method to eqn. (4), in which k_2 is the first-order rate constant for thermal isomerization. Other quantities were defined in connection with eqn. (3).[41]

$$\ln\frac{[\mathit{trans}]_0-[\mathit{trans}]_{\mathrm{pss}}}{[\mathit{trans}]_0-[\mathit{trans}]}=k_2\cdot t \tag{4}$$

Preparation of *N,N*-diethyl-*p*-methoxybenzamide

To a solution of 17.4 g (0.11 mol) of *p*-anisic acid in 50.0 mL of benzene were added 17.6 mL of thionyl chloride and several drops of DMF. The mixture was refluxed in a strong fume hood until gas evolution ceased, for *ca.* 2 hours. Benzene was cautiously evaporated under reduced pressure, and *p*-anisoyl chloride was obtained in almost theoretical yield. It was used without further purification.

A solution of 21.8 g of *p*-anisoyl chloride (0.13 mol) in 50.0 mL of diethyl ether was added slowly in a dropping funnel to a solution of 40 mL of diethylamine (0.39 mol) in 150 mL of diethyl ether, kept at 0 °C. Upon complete addition of *p*-anisoyl chloride, the reaction mixture was stirred for 2 h at room temperature and extracted with 200 mL of diethyl ether. The organic layer was washed with three 150 mL portions of water, 0.10 M HCl, 0.10 M NaOH and one portion of brine and dried with magnesium sulfate. The organic solvent was evaporated, and the crude title compound was recrystallized from methanol. The yield was 18.9 g or 70%; mp 42–43 °C, as reported;[42] ^{1}H NMR in $CDCl_3$: δ 1.17 (br, 6 H), 3.40 (br, 4 H), 3.82 (s, 3 H), 6.89 (m, 2H) and 7.34 (m, 2H).



Symbol	R¹	R²	R³	R⁴
B	H	H	CH₃CO	H
C	CH₃CO	H	CH₃CO	H
D[44]	H	H	CH₃CO	CH₃CO
E	CH₃CO	CH₃CO	CH₃CO	CH₃CO

Scheme 1

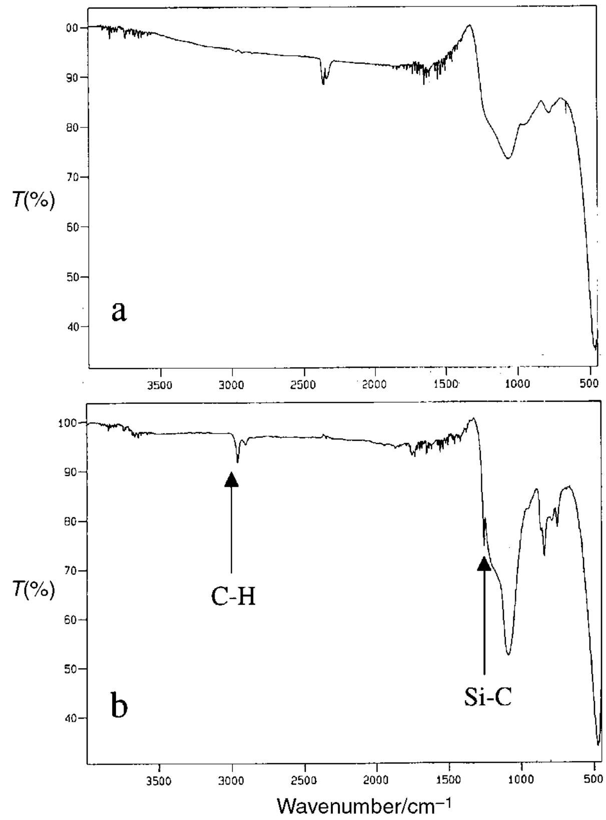


Fig. 1 Infrared spectra of pulverized sol–gel silica monoliths (a) before and (b) after treatment with hexamethyldisilazane. The highlighted bands in (b) are characteristic of the $Si(CH_3)_3$ groups.

Preparation of azobenzenes

See Scheme 1.[43,44] All derivatives of nitrosobenzene were synthesized by oxidation of the corresponding derivatives of aniline with Caro's acid.[45] A solution containing 3.0 mmol of nitrosobenzene or its derivative and 3.0 mmol of a derivative of aniline in 15 mL of glacial acetic acid was heated at 60 °C for 12 h, poured into an ice-cold, saturated aqueous solution of $NaHCO_3$, and extracted with benzene. Evaporation of benzene gave a crude solid. Its purification on a silica-gel column yielded a pure azobenzene derivative. Chromatographic conditions are given below.

3-Acetylazobenzene. Eluent was a 9 : 1 v/v mixture of benzene and ethyl acetate. Orange needles, mp 88–89 °C (*cf.* 88–90 °C);[43] ^{1}H NMR in $CDCl_3$: δ 2.68 (s, 3 H), 7.51 (m, 3 H), 7.61 (t, 1 H), 7.93 (m, 2 H), 8.08 (m, 2 H) and 8.46 (s, 1 H); ^{13}C NMR in $CDCl_3$: δ 26.9, 122.9, 123.1, 127.0, 129.2, 129.5, 130.3, 131.5, 138.1, 152.5, 152.7 and 197.6.

3,5-Diacetylazobenzene. Eluent was a 6 : 4 v/v mixture of benzene and ethyl acetate. Orange needles, mp 87–89 °C. ^{1}H NMR in $CDCl_3$: δ 2.72 (s, 6 H), 7.54 (m, 3 H), 7.96 (m, 2 H), 8.62 (t, 1 H) and 8.64 (d, 2 H); ^{13}C NMR in $CDCl_3$: δ 27.0, 123.3, 126.5, 129.3, 129.5, 132.0, 138.5, 152.3, 153.0 and 196.9; LRMS-CI: calcd for M^+ of $C_{16}H_{14}N_2O_2$ 266, found 266.

3,3′-Diacetylazobenzene. Eluent was a 8 : 2 v/v mixture of benzene and ethyl acetate; mp 133–134 °C (*cf.* 131–134 °C);[46] ^{1}H NMR in $CDCl_3$: δ 2.67 (s, 6 H), 7.61 (m, 2 H), 8.07 (m, 4 H) and 8.46 (s, 2 H). ^{13}C NMR in $CDCl_3$: δ 26.9, 123.1, 127.2, 129.6, 130.8, 138.2, 152.5, and 197.5.

3,3′,5,5′-Tetraacetylazobenzene. Eluent was a 5 : 2 : 3 v/v/v mixture of benzene, ethyl acetate, and chloroform; mp 221–224 °C; ^{1}H NMR in CDCl$_3$: δ 2.75 (s, 12 H), 8.67 (t, 2 H) and 8.70 (d, 4 H); ^{13}C NMR in CDCl$_3$: δ 27.0 , 126.7 , 130.3 , 138.6, 152.5 and 196.7; LRMS-CI: calcd for M$^+$ of $C_{20}H_{18}N_2O_4$ 350, found 350.

Results and discussion

Hydrogen bonding between silica glass and guest compounds

Hydrogen bonds between sol–gel silica and guest compounds embedded in it (during formation of the glass) or absorbed in it (by diffusion into the preformed glass) are widely assumed to exist, but were directly detected only recently.[21,30–33] Not much is known about these important interactions, which are likely to affect properties and performance of biosensors, immobilized catalysts, and various composite materials prepared by the sol–gel method. Beyond detecting hydrogen bonding, we wish to understand their effects on equilibria and reactions of guest compounds within a sol–gel silica monolith.

Treatment of the silica monolith

After aging and partial drying, the pores in the silica monoliths contain water that must be removed lest it interfere with the hydrogen bonds under study. We extracted water with a succession of solvents chosen so that each dilutes and removes the previous one. These exhaustive procedures took considerable time. The dehydration procedure achieved the overall dilution factor of *ca.* 10^{11}. The trimethylsilylation procedure was applied to the dehydrated glass and included chemical as well as extractive dehydration. The additional dilution factor in the trimethylsilylation procedure reached *ca.* 10^{43}. Much smaller factors probably would have been sufficient, but we strove for very accurate experiments.

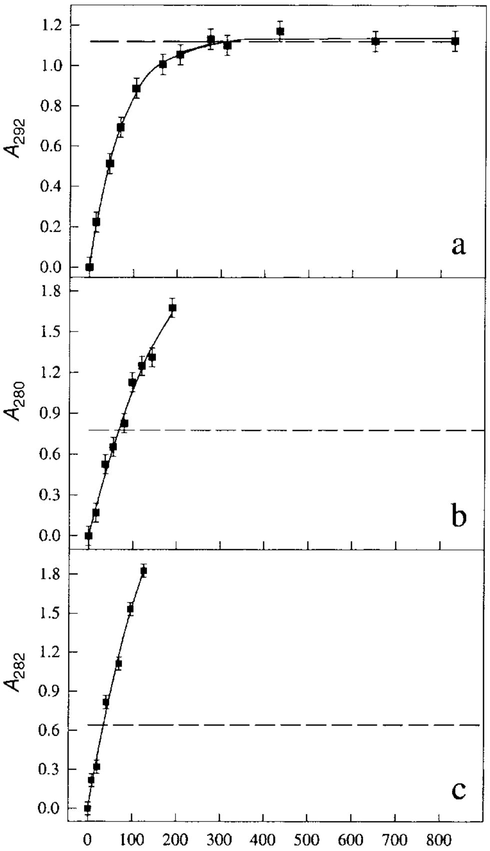


Fig. 2 Uptake of (a) styrene, (b) aniline, and (c) *N*,*N*-diethyl-*p*-methoxybenzamide by sol–gel silica glass when it is capable of hydrogen bonding to the guest compounds. Glass monolith sized 8 x 8 x 27 mm is soaked in a 50.0 mL solution of each solute in CCl$_4$. As the guest enters, its absorbance in the glass increases. The dashed line marks the absorbance of the external solution. Uptake is balanced in (a) and excessive in (b) and (c).

Trimethylsilylated silica does not show any bands in the 1650–1790 cm^{-1} region in the infrared spectrum (Fig. 1). The absence of carbonyl groups proves that acetyl chloride does not react with silanol hydroxy groups during the dehydration preceding treatment with hexamethyldisilazane.

Balanced and excessive uptake of the guest compounds by silica glass

Because sol–gel silica is porous, it is widely assumed that molecules smaller than the pores can diffuse in and out of the matrix and that their concentrations in the matrix and in the surrounding solution will become equal, *i.e.*, that the uptake will be balanced. Research in this laboratory has already refuted this assumption in cases when both the silica matrix and the guest are charged.[25–27] If these charges are alike, the host matrix partially rejects the guest; if the charges are opposite, the matrix takes up the guest excessively. We term this phenomenon *imbalanced uptake*.

Electrostatic interactions, which we studied before,[25–27] are strong and isotropic. In this study we examine the consequences of subtler interactions. Hydrogen bonding is relatively strong but also anisotropic and selective. These characteristics make hydrogen bonding extremely important for equilibria and chemical reactivity.[28,47–49]

The three compounds serving as guests are shown below. Styrene is incapable of hydrogen bonding; aniline can both accept and donate hydrogen atoms; and *N*,*N*-diethyl-*p*-methoxybenzamide can only accept them. These three compounds as probes allowed us to examine the capacity of sol–gel silica monoliths as both acceptor and donors of hydrogen. We also managed to enhance and abolish hydrogen

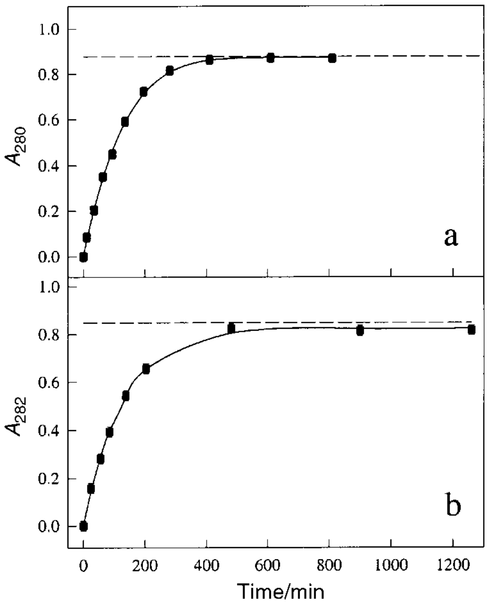
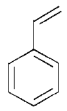
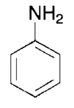


Fig. 3 Uptake of (a) aniline, and (b) *N*,*N*-diethyl-*p*-methoxybenzamide by sol–gel silica glass when it is incapable of hydrogen bonding to the guest compounds. Glass monolith sized 8 x 8 x 27 mm is soaked in 50.0 mL of a 9 : 1 v/v mixture of CCl$_4$ and DMF; the latter component in the mixture prevents hydrogen bonding between silica and the guest. As the guest enters, its absorbance in the glass increases. The dashed line marks the absorbance of the external solution. Uptake is balanced in both cases.

bonding simply by adjusting the solvent properties, as will be explained below.





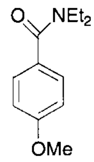


Fig. 2 shows that when the solvent was neat CCl_4, uptake of styrene was balanced, whereas the uptake of the other two guests was excessive. Fig. 3 shows that when CCl_4 contained 10% by volume of DMF, the uptake of these two guests became balanced as well.

Excessive uptake of relatively nonpolar organic molecules into the highly polar matrix such as silica is unexpected on the basis of the well-known principles of extraction and partition chromatography. When excessive uptake occurs, there must exist special attractive interactions between the host and the guest. Interaction of CCl_4 with silica has just been reported.[50] These interactions are to be expected because chlorine atoms in organic molecules are known to form weak hydrogen bonds.[51] Styrene, which lacks heteroatoms and is incapable of hydrogen bonding, lacks special attraction to the silica surface and cannot displace CCl_4 from the silica surface. Consequently, its uptake by the silica monolith is balanced. The other two guests have nitrogen and oxygen atoms, which can form relatively strong hydrogen bonds to silica, and therefore displace CCl_4 from the silica surface. Consequently, their uptake by silica is excessive. When the hydrogen-bonding solvent DMF is present in large excess over the guests, it abolishes excessive uptake of these two guests.

Ultraviolet-spectroscopic evidence for hydrogen bonding

Fig. S1 in the supplementary information shows that the absorption spectrum of styrene does not change when this compound enters the silica matrix. The absence of interaction with the matrix is consistent with the balanced uptake observed for styrene. Fig. S2 in the supplementary information shows that the spectrum of *N*,*N*-diethyl-*p*-methoxybenzamide does change when its uptake is excessive (from neat CCl_4), but does not change when its uptake is balanced (in the presence of DMF). Perturbation of the chromophore is diagnostic of its interaction with silica. That perturbation and excessive uptake occur together probably is more than a coincidence; the two phenomena likely exist in a causal relationship.

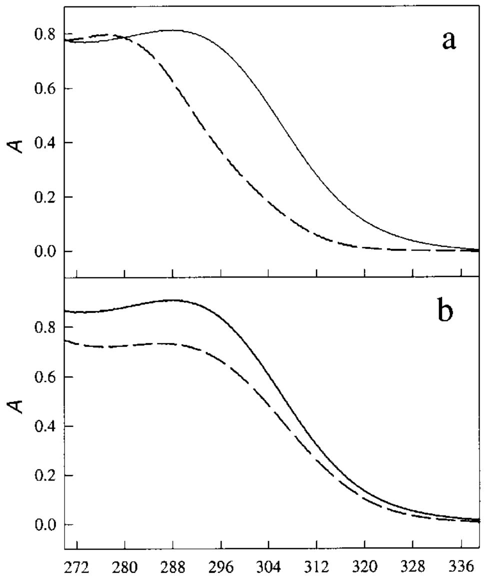


Fig. 4 Absorption spectra of aniline in solution (solid line) and inside sol–gel silica glass (dashed line). The solvent is (a) CCl_4 and (b) a 9 : 1 v/v mixture of CCl_4 and DMF. Note the large blue shift in (a) as aniline enters the glass from the solution. Hydrogen bonding between aniline and silica is present in (a) and absent in (b).

Because the UV spectrum of aniline is well understood, this compound is used as a reliable probe for hydrogen bonding. Blue shift signifies hydrogen acceptance; red shift, hydrogen donation.[52–55] Fig. 4 shows a large blue shift when aniline is taken up from the solution in neat CCl_4 and no spectral change when aniline is taken up from the solution containing also DMF. Evidently, aniline accepts hydrogen from the silica matrix when the silanol groups on its surfaces are available. When, however, silanol groups are saturated with DMF, a good acceptor, hydrogen bonding between silica and aniline is abolished.

Large uptake and complete release of *trans*-3,3′-diacetylazobenzene by silica glass

As Fig. 2 shows, the concentration of hydrogen-bonding guests becomes approximately three times greater in the glass than in the external solution after approximately three hours of soaking, when these experiments were ended. To find out the maximum capacity of silica for a guest, we chose the title compound, which contains two hydrogen-accepting acetyl groups, because we had a good supply of it. The experiment lasted for 11 days, until the uptake practically ceased. The results are shown in Fig. 5.

We define the uptake coefficient as the ratio of the guest concentrations in the glass and in the solution surrounding the glass. Concentration of the guest in 200 mL of solution decreased from 9.3×10^{-4} M to 1.2×10^{-4} M in a sealed container. The "departed" quantity of it must have accumulated in the silica monolith, whose overall volume is 1.7 mL. Because only *ca.* 65% of this volume is pores[25] and therefore accessible to the guest, the aforementioned ratio of concentration "inside" and "outside" is 1.5×10^{-1} M to 1.2×10^{-4} M, or 1250. We did not thoroughly study the other derivatives of azobenzene, but they too are likely to show greatly excessive uptake.

This surprisingly large number shows how important hydrogen bonding between silica matrix and guests compounds can be. Clearly, this bonding must be taken into consideration in studies of diffusion and partition of solutes between sol–gel materials and the surrounding media and in careful studies of equilibria and rates of reactions inside sol–gel materials.

Upon addition of DMF to the depleted external solution, the absorbed guest was fully released by the silica monolith in *ca.*

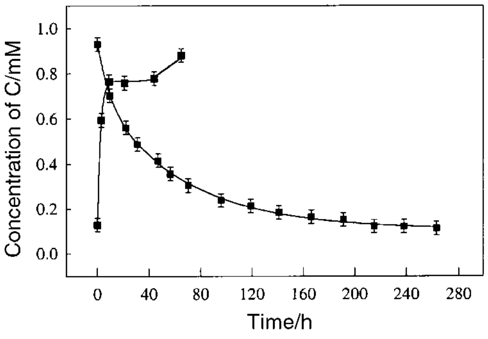


Fig. 5 Uptake (the downward plot) and release (the upward plot) of *trans*-3,3′-diacetylazobenzene (designated C) by sol–gel silica glass, followed by the UV spectrophotometry of C in the external solution. The glass monolith sized 8 × 8 × 27 mm was soaked in 200.0 mL of a stirred 9.30×10^{-4} M solution of C in CCl_4. For release, 20 mL of DMF was added to the external solution.

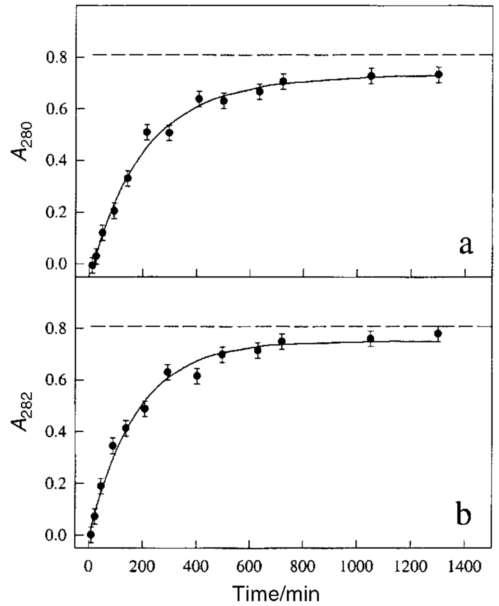


Fig. 6 Uptake of (a) aniline and (b) *N*,*N*-diethyl-*p*-methoxybenzamide by sol–gel silica glass chemically modified with $Si(CH_3)_3$ groups, which preclude hydrogen bonding between the guest compounds and silica. For conditions, see caption to Fig. 2.

75 h, much faster than it had been taken up. Clearly, hydrogen bonds between silica and the guest can be broken by a competing hydrogen-acceptor.

Our finding holds promise for practical applications of sol–gel silica. This material can efficiently extract from solution a solute with complementary hydrogen-bonding ability and then release this solute upon addition of a small amount of a suitable solvent. This cycle is reminiscent of molecular sieves, analytical and preparative separations, and controlled delivery of drugs.

Nearly-balanced uptake of the guest compounds by chemically-modified silica glass

Upon exhaustive treatment of silica monolith with hexamethyldisilazane, hydroxy groups on the surface were “capped” with the $Si(CH_3)_3$ groups. As Fig. 1 shows, these organic groups are evident by the infrared bands at *ca.* 3000 and 1260 cm^{-1}, corresponding to C–H and Si–C vibrations, respectively.

Both compounds that show excessive uptake by pristine silica (Figs. 2b and 2c) show nearly-balanced uptake by the modified silica (Figs. 6a and 6b) even though the solvent, CCl_4, allows hydrogen bonding. We attribute the absence of this bonding to trimethylsilylation. Hydroxylic hydrogen atoms to be donated to the guests are absent, and the oxygen atoms that might accept hydrogen atoms from aniline are protected by the bulky $Si(CH_3)_3$ groups. Fig. 6 shows that concentration of each guest in the silica host levels off slightly below the concentration in the external solution. If real, this small “under-achievement” may be the result of the steric bulk of the capping groups.

The chromophores that were markedly perturbed by the pristine silica (Fig. 4) are only slightly affected by the modified silica (Fig. S3 in the supplementary information). Because hydrogen bonding is suppressed, the slight change presumably is a result of a nonspecific effect of the altered medium. Again, excessive uptake coincides with marked spectral change, whereas nearly or completely balanced uptake coincides with little or no spectral change.

Evidently, excessive uptake of hydrogen-bonding guests can be abolished not only by adding a competing solvent but also by modifying the silica surface. This finding corroborates our view, stated above, that the competing solvent DMF lines the surfaces of porous silica and prevents the guest molecules from forming hydrogen bonds with these surfaces.

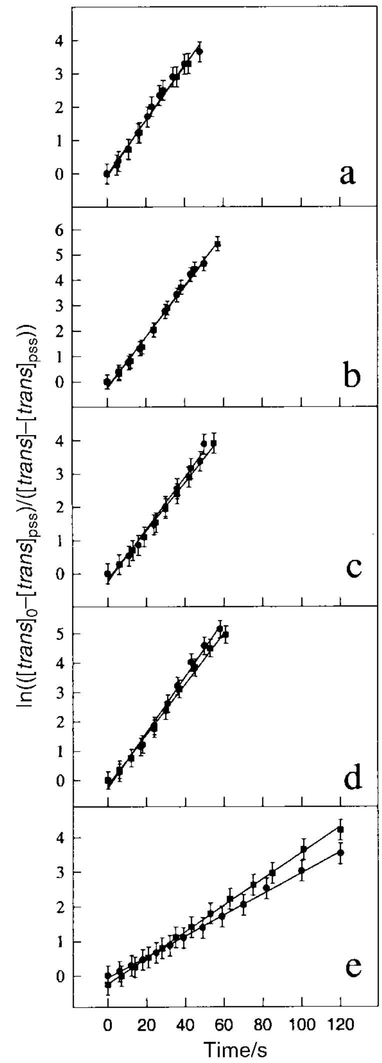


Fig. 7 Kinetics of photoinduced (*trans*-to-*cis*) isomerization of (a) 3,3′-dimethylazobenzene, designated A, (b) 3-acetylazobenzene, designated B, (c) 3,3′-diacetylazobenzene, designated C, (d) 3,5-diacetylazobenzene, designated D, and (e) 3,3′,5,5′-tetraacetylazobenzene, designated E, in solution (■) and inside sol–gel silica glass (●) when hydrogen bonding between the azobenzene derivatives and silica is suppressed. The solvent in all experiments was a 9 : 1 v/v mixture of CCl_4 and DMF; the latter component in the mixture makes hydrogen bonds to silica. Solid lines are fittings to first-order rate law.

Rate of uptake of the guest compounds by silica monoliths

The time at which the concentration of the guest compound inside the silica monolith becomes equal to the concentration in the external solution may be taken as an approximate measure of the rate of uptake if, as in our study, the external concentrations are similar in all experiments. In the case of balanced uptake, internal concentration levels off with time. In the case of excessive uptake, internal concentration continues to increase.

As Fig. 3 shows, the equalization time was *ca.* 400 min for both guests that are capable of hydrogen bonding. When this bonding was suppressed, they were taken up at the same rate. As Fig. 2b and 2c show, the two rates became greater and quite different when hydrogen bonding was allowed; then the equalization times were 75 and 35 min.

In attempts to alter the uptake rates, we treated silica monolith with acid or with base before dehydration. Fig. S4 in the supplementary information shows, however, that the

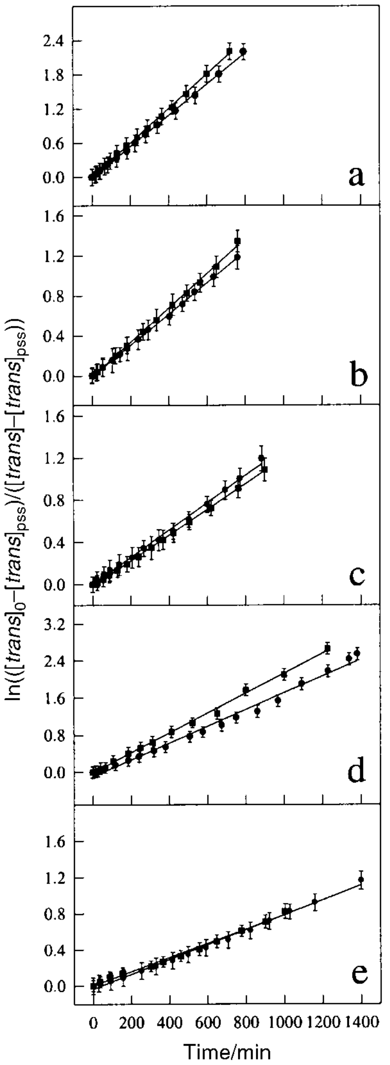


Fig. 8 Thermal (*cis*-to-*trans*) isomerization of (a) 3,3′-dimethylazobenzene, designated A, (b) 3-acetylazobenzene, designated B, (c) 3,3′-diacetylazobenzene, designated C, (d) 3,5-diacetylazobenzene, designated D, and (e) 3,3′,5,5′-tetraacetylazobenzene, designated E, in solution (■) and inside sol–gel silica glass (●) when hydrogen bonding between the azobenzene derivatives and silica is suppressed. The solvent in all experiments was a 9 : 1 v/v mixture of CCl_4 and DMF; the latter component in the mixture makes hydrogen bonds to silica. Solid lines are fittings to first-order rate law.

differently-treated monoliths resembled each other and untreated monoliths in the rates of uptake of the same hydrogen-bonding guest in CCl_4, the solvent that allows this bonding.

Table 1 Estimated volume needed for thermal (*cis*-to-*trans*) isomerization of five azobenzene derivatives and first-order rate constants k_2 in the absence of hydrogen bonding in solution and inside sol–gel silica glass. The solvent in both cases is a 9 : 1 v/v mixture of CCl_4 and DMF

Compound	Symbol	Volume/Å^3	10^3 k_2/min^{-1}	
			In solution	In silica
3,3′-Dimethylazobenzene	A	334	3.02±0.02	2 .73±0.02
3-Acetylazobenzene	B	392	1.72±0.02	1.56±0.01
3,3′-Diacetylazobenzene	C	425	1.21±0.01	1.29±0.01
3,5-Diacetylazobenzene	D	462	2.10±0.08	1.80±0.03
3,3′,5,5′-Tetraacetylazobenzene	E	505	0.78±0.02	0.78±0.02

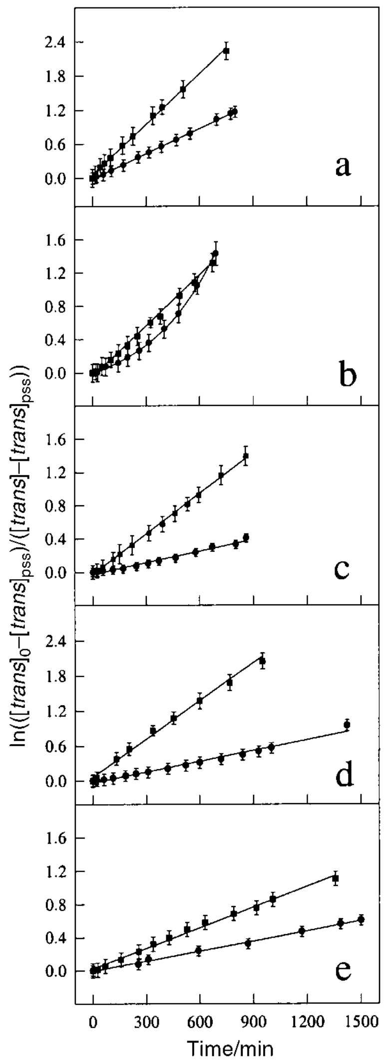


Fig. 9 Thermal (*cis*-to-*trans*) isomerization of (a) 3,3′-dimethylazobenzene, designated A, (b) 3-acetylazobenzene, designated B, (c) 3,3′-diacetylazobenzene, designated C, (d) 3,5-diacetylazobenzene, designated D, and (e) 3,3′,5,5′-tetraacetylazobenzene, designated E, in solution (■) and inside sol–gel silica glass (●) when hydrogen bonding between the azobenzene derivatives and silica is present. The solvent in all experiments was CCl_4. Solid lines are fittings to first-order rate law.

When the silica surface was modified with the bulky $Si(CH_3)_3$ groups, the uptake slowed down; the equalization time for both guest compounds exceeded 1000 min. Again, suppression of hydrogen bonding seems to lower the rate of uptake.

Clearly, rate of uptake varies greatly when hydrogen bonding is allowed or abolished and when the silica surface is chemically modified. Even before quantitative studies of the rate are done, our semiquantitative finding should be taken into account in studies of equilibria and chemical reactions involving sol–gel glasses doped with enzymes and other chemicals.

Kinetics of azobenzene isomerization

Isomerization of azobenzene has been used to explore the microstructure and rigidity of solid polymers.[56–58] In principle, this process can be used in optical storage systems, nanodevices, and molecular switches. Other researchers have applied this elegant method to assess the steric constraint of sol–gel glass on molecules contained in it.[41,59,60] The function of this glass in various applications depends on the mobility and

Table 2 Percentage of the *cis* isomer in the photostationary state reached in *trans*-to-*cis* isomerization of five azobenzene derivatives in solution and inside sol–gel silica glass when hydrogen bonding between these derivatives and silica is absent and present

Compound	Symbol	In solution[a]	In silica	
			Without H-bonding[b]	With H-bonding[a]
3,3′-Dimethyl-azobenzene	A	92±4	92±4	80±4
3-Acetylazo-benzene	B	89±4	89±4	82±4
3,3′-Diacetylazo-benzene	C	78±4	82±4	75±4
3,5-Diacetylazo-benzene	D	70±4	70±4	68±4
3,3′,5,5′-Tetraacetyl-azobenzene	E	49±3	48±3	19±2

[a]Solvent is CCl_4. [b]Solvent is a 9 : 1 v/v mixture of CCl_4 and DMF.

Table 3 Fist-order rate constants k_2 and their ratio for thermal (*cis*-to-*trans*) isomerization of four azobenzene derivatives in solution and inside sol–gel silica glass when hydrogen bonding between azobenzene and silica is present. The solvent in both cases is CCl_4

Compound	Symbol	$10^3\ k_2/\text{min}^{-1}$		
		In solution	In silica	$\frac{k_2^{\text{solution}}}{k_2^{\text{silica}}}$
3,3′-Diacetyl-azobenzene	C	1.63±0.02	0.46±0.02	3.5
3,5-Diacetyl-azobenzene	D	2.09±0.08	0.60±0.02	3.5
3,3′,5,5′-Tetraacetyl-azobenzene	E	0.83±0.02	0.41±0.02	2.0

chemical reactivity of the dopant.[23] Because hydrogen bonding greatly affects the extent and the rate of uptake and release of guest compounds by the host glass, we study quantitatively the influence of hydrogen bonding on a reaction of a series of guest molecules absorbed in the host matrix. Interconversion of geometric (*cis* and *trans*) isomers of azobenzene is shown in eqn. (5). It is a simple reaction, amounting to motion of molecular parts. We chose it because its kinetics are well known.[61–63]

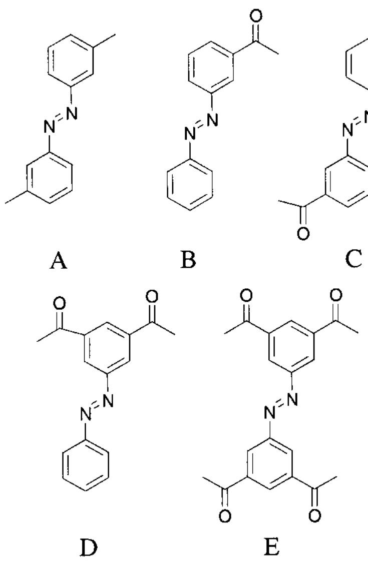
$$trans\text{–azobenzene} \overset{h\nu,k_1}{\rightleftarrows} cis\text{–azobenzene} \xrightarrow{\Delta,k_2} trans\text{–azobenzene} \qquad (5)$$

The so-called forward reaction is effected by UV light, and it is relatively fast. The so-called back reaction is spontaneous at room temperature but slow. We studied it at 50.0 °C, in the dark.

Study of the forward reaction presents pitfalls. The first-order rate constant for photoisomerization changes when the amount of light absorbed by the irradiated sample changes. The absorbed amount, in turn, depends on the concentration of the sample and on the irradiation wavelength. To avoid errors in kinetic analysis, we determined the order of the reactions of the various azobenzene derivatives, but did not calculate or compare the rate constants k_1. Fortunately, study of the back reaction is straightforward. This was shown with various photochromic molecules, which proved useful for exploration of polymers.[40,41,56,59,60,64–69] Above the glass-transition temperature the back reaction inside the polymer is monophasic, as in solution. Below this temperature, however, the reaction inside the polymer is biphasic or multiphasic. This change in kinetics has been attributed to heterogeneity of the matrix and variability of the free volume felt by the photochromic molecules.

The azobenzene derivatives

We purchased the compound designated A and synthesized and purified those designated B to E. Their propensity for accepting hydrogen atoms increases with the number of acetyl substituents. We studied the effect of these substituents, and therefore of hydrogen bonds, on the thermal isomerization shown in eqn. (5).



(0)

Uptake and isomerization of azobenzene derivatives in silica glass when hydrogen bonds are absent

In these experiments the solvent was a 9 : 1 v/v mixture of CCl_4 and DMF. The latter component, a hydrogen acceptor, binds to silica and forestalls its hydrogen bonding to azobenzene derivatives. All five guests showed balanced uptake into the silica monoliths. Both photoinduced and thermal reactions in eqn. (5) for all five compounds taken up in silica were monophasic, as linear plots in Fig. 7 and 8 show. Table 1 shows that the rate constants k_2 for thermal isomerization (the second reaction in eqn. (5)) are virtually the same in solution and in the glass. Table 2 shows that the photoisomerization (the first reaction in eqn (5)) occurs to the same extent in solution and in the glass. Evidently, in the absence of hydrogen bonding these two media are equal as environments for the isomerization. When azobenzene cannot make hydrogen bonds to the matrix, this photoprobe does not differentiate between bulk solvent and solvent confined in the glass pores. A similar conclusion was reached in a study of isomerization in which hydrogen bonding was not possible because the protic solvent was present.[41,59,60] Clearly, the glass matrix itself does not restrict the motion required for the isomerization.

The largest photoprobe, the one designated E, requires the volume of *ca.* 505 Å^3 for isomerization. A sphere of this volume has a diameter of *ca.* 10 Å. Evidently, the pores in sol–gel silica are larger than this size.

Uptake and isomerization of azobenzene derivatives in silica glass when hydrogen bonds are present

In these experiments the solvent was neat CCl_4. All five azobenzene derivatives showed excessive uptake by silica monoliths because of hydrogen bonding to silica. In the case of the compound C, which we studied in detail (see above), this excess is 1250-fold.

The thermal back reaction (the second step in eqn. (5)) of all five photoprobes was studied separately in solution and inside the silica. Because these probes are different compounds, which differ in the substituents and in electron delocalization, "vertical" comparisons in Table 3 are unwarranted.[62,70–73] We make only "horizontal" comparisons, those of the same compound in two environments. As Fig. 9 shows, isomerization of all five photoprobes in solution, and of all except B in silica, were monophasic. The reaction of the compound B in silica appeared biphasic.

At the end of the long kinetic experiments, the neat CCl_4 surrounding the monoliths was checked by UV spectrophotometry. The compounds A and B leaked from the silica, and the compounds C, D, and E did not. The biphasic reaction of B probably is caused by the simultaneous isomerization, at different rates, of this compound in silica and in the surrounding solution. The reaction of A may appear monophasic if the rates in silica and in solution are comparable. For the sake of accuracy, we omitted compounds A and B from Table 3.

Kinetic results for the compounds C, D, and E are not complicated by leakage. They are given in Table 3. Thermal isomerization is slower in silica than in solution. Mobility of azobenzene within silica seems to be hindered by hydrogen bonding to the pore surfaces. Both photoprobes having two acetyl groups (C and D) show similar rate of isomerization and the same degree of hindrance, 3.5-fold. The photoprobe having four acetyl groups (E) shows a lesser hindrance, but this fact may be an indirect, not a direct consequence of hydrogen bonding. The more extensive bonding of E with silica hindered already the photoinduced reaction, the *trans*-to-*cis* isomerization, so that only *ca.* one-half of the *trans* isomer initially present in silica was converted to the *cis* isomer. Only that half of the total compound E within the glass underwent the thermal conversion back to the *trans* configuration.

Conclusion

Specific interaction between the host matrix and the guest molecules may restrict or broaden the applicability of doped sol–gel glasses in chemistry, biochemistry, and materials science. Hydrogen bonding is an important interaction, whose implications have yet to be explored.

This study shows that sol–gel silica can donate hydrogen atoms to acceptor molecules occluded in the silica monolith. Hydrogen bonding can cause enormous excess in uptake of hydrogen-bonding solutes from solution and can modulate reactivity of the compounds trapped in glass monoliths. When hydrogen bonding is suppressed, the uptake becomes balanced, and the reactivity becomes normal. These results should caution those who design biosensors and other devices that depend on uptake and other equilibria involving sol–gel glasses. The same results, however, encourage those who seek new applications of sol–gel glasses as molecular sieves and means for gradual or controlled delivery of substances such as drugs.

Acknowledgements

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