J. Am. Chem. Soc. **1995,** *117,* 11989−11992

Bimolecular Interactions in (Et)$_3$SiOH:Base:CCl$_4$ Hydrogen-Bonded Solutions Studied by Deactivation of the "Free" OH-Stretch Vibration

W. Tandy Grubbs,[†] Thomas P. Dougherty,[‡] and Edwin J. Heilweil*

Contribution from the Molecular Physics Division, Room B268, Building 221,
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received July 10, 1995[⊗]

Abstract: Picosecond infrared (IR) pump-probe measurements of the OH-stretch ($\nu = 1$) population lifetime were performed for uncomplexed (Et)$_3$SiOH in room temperature, tertiary (Et)$_3$SiOH:base:CCl$_4$ hydrogen-bonded solutions (base = acetonitrile, tetrahydrofuran, and pyridine). When base is present in solution, the intrinsic OH-stretch T_1 vibrational population lifetime (183 ± 6 (1σ) ps for (Et)$_3$SiOH in CCl$_4$) is reduced by bimolecular (Et)$_3$SiOH:base hydrogen-bonding encounters. The base concentration dependence of the "free" OH-stretch vibrational deactivation rate is analyzed by a Stern−Volmer kinetic model and a least-squares fit to all the data yielded a single rate constant $k_{BM} = 1.2 \pm 0.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1} for (Et)$_3$SiOH:base bimolecular encounters. This value is in agreement with estimates for the bimolecular diffusion limit. k_{BM} was found to be the same for all (Et)$_3$SiOH:base interactions studied, suggesting that the bimolecular OH-stretch deactivation mechanism is relatively insensitive to the proton-accepting strength of the base.

Introduction

There is a growing need to address the role hydrogen bonding plays in the vibrational energy dynamics of liquid-phase biomolecular systems. To meet this end, recent picosecond time-resolved infrared (IR) pump-probe experiments on hydrogen-bonded solutions have focused on topics such as enhanced vibrational relaxation in acid−base complexes,[1] IR pump-induced dissociation of hydrogen-bonded complexes,[2,3] inhomogeneous broadening of IR bandshapes,[2−4] and the rates of hydrogen-bond formation and dissociation.[5] Tertiary solutions consisting of dilute hydrogen-bonded acid−base species dissolved in noninteracting solvents (such as carbon tetrachloride) have proven to be particularly appropriate for such studies because one can focus on dilute 1:1 acid−base hydrogen-bonded complexes.[1,6−9] This characteristic is in sharp contrast to previous IR pump-probe studies on concentrated water[4] and alcohol[2,3] solutions where time-dependent observables can be attributed to overlapping spectral contributions from hydrogen-bonded dimers, trimers, and multimers.

IR absorption spectra of tertiary solutions reveal an equilibrium between "free" and hydrogen-bonded acid−base species

$$[\text{acid}] + [\text{base}] \underset{k_{\text{diss}}}{\overset{k_{\text{form}}}{\rightleftharpoons}} [\text{acid}\cdots\text{base}]$$

For example, the IR spectrum of a (Et)$_3$SiOH:CH$_3$CN:CCl$_4$ solution reveals two bands in the OH-stretching region: a narrow band at 3692 cm^{-1} corresponding to "free" (Et)$_3$SiOH and a broader band at 3547 cm^{-1} corresponding to the OH-stretch in 1:1 (Et)$_3$SiOH:CH$_3$CN hydrogen-bonded complexes (see Figure 1). While earlier transient IR experiments focused on vibrational energy dynamics within hydrogen-bonded acid−base complexes,[1−3] there have been relatively few studies of how the above equilibrium affects vibrational energy relaxation of the "free" acid. Specifically, the vibrational population lifetime of the proton-donating functional group in the "free" acid can be reduced if the vibrational decay rate and bimolecular encounter rate between "free" acid and base molecules are similar. This effect was recently demonstrated for a mixture of dilute pyrrole and CH$_3$CN in room temperature CCl$_4$.[1] In this case, the encounter rate between "free" pyrrole and CH$_3$CN molecules was measured to be comparable to the relaxation rate of the noncomplexed NH-stretching vibration (T_1 = 49 ± 3 ps) of pyrrole in CCl$_4$. This work reported here represents the first comprehensive IR pump-probe investigation of this phenomenon in room temperature hydrogen-bonded solutions, (Et)$_3$SiOH:base:CCl$_4$, using three different bases: acetonitrile (CH$_3$CN), tetrahydrofuran (C$_4$H$_8$O), and pyridine (C$_5$H$_5$N).

(Et)$_3$SiOH:base:CCl$_4$ solutions are particularly amenable to hydrogen-bonding studies because: (1) (Et)$_3$SiOH has a low propensity for self-association, compared to alcohols (e.g., methanol and ethanol),[2,3] and it therefore only hydrogen bonds with the selected base; (2) the relatively large OH-stretch IR absorption (peak cross section at 3692 cm^{-1}, $\sigma \approx 0.006$ Å^2 or $\epsilon \approx 150$ dm^3 mol^{-1} cm^{-1}) allows one to study dilute solutions, further minimizing self-association of (Et)$_3$SiOH; (3) since the OH-stretch population lifetime of "free" (Et)$_3$SiOH in CCl$_4$ (T_1 = 183 ± 6 ps) is long compared to the OH ($\nu = 1$) lifetimes of

---

[†] Present address: Department of Chemistry, Stetson University, DeLand, FL 32720.

[‡] Present address: Department of Chemistry and Physics, Beaver College, Glenside, PA 19038.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) Grubbs, W. T.; Dougherty, T. P.; Heilweil, E. J. *J. Phys. Chem.* **1995,** *99,* 10716.

(2) Graener, H.; Ye, T. Q.; Laubereau, A. *J. Chem. Phys.* **1989,** *91,* 1043.

(3) Graener, H.; Ye, T. Q.; Laubereau, A. *J. Chem. Phys.* **1989,** *90,* 3413.

(4) Graener, H.; Seifert, G.; Laubereau, A. *Phys. Rev. Lett.* **1991,** *66,* 2092.

(5) Seifert, G.; Graener, H. *J. Phys. Chem.* **1994,** *98,* 11827.

(6) Spencer, J. N.; Campanella, C. L.; Harris, E. M.; Wolbach, W. S. *J. Phys. Chem.* **1985,** *89,* 1888.

(7) Werner, R. L.; Quinn, J. M.; Haken, J. K. *Spectrochim. Acta,* **1982,** *38A,* 887.

(8) Karjalainen, J.; Ruostesuo, P. *Acta Chem. Scand. A* **1980,** *34,* 573.

(9) Spencer, J. N.; Gleim, J. E.; Hackman, M. L.; Blevins, C. H.; Garrett, R. C. *J. Phys. Chem.* **1978,** *82,* 563.

0002-7863/95/1517-11989$09.00/0

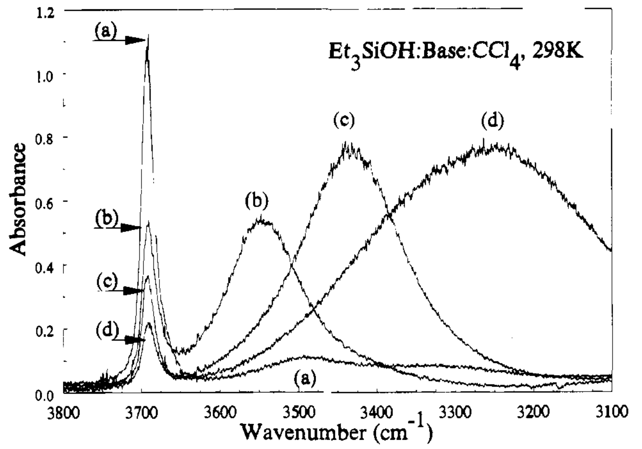

Figure 1. FTIR spectra (OH-stretching region) of 0.073 mol dm^{-3} (Et)$_3$SiOH in room temperature CCl$_4$ with (a) no base present and 0.891 mol dm^{-3} of bases (b) CH$_3$CN, (c) C$_4$H$_8$O, and (d) C$_5$H$_5$N. The narrow band at 3692 cm^{-1} corresponds to "free" (Et)$_3$SiOH and the broad bands at 3547, 3435, and 3254 cm^{-1} in spectra b–d, respectively, arise from 1:1 hydrogen-bonded complexes. The weak bands at 3490 and 3300 cm^{-1} in trace a correspond to self-associated (Et)$_3$SiOH dimers and multimers. The decrease in absorption around 3300 cm^{-1} in trace b, relative to trace a, occurs because the addition of base to solution interferes with (Et)$_3$SiOH self-association.

alcohols in CCl$_4$ (e.g., T_1(MeOH) ≈ 15 ps),[10] the reduced vibrational relaxation times in the presence of base are easily measurable with picosecond time resolution; and (4) CCl$_4$ is an IR-transparent medium that exhibits minimal interaction with solute molecules, allowing one to study only (Et)$_3$SiOH–base interactions.

Results and Discussion

Static FTIR absorption spectra of a binary solution containing 0.073 mol dm^{-3} (Et)$_3$SiOH in room temperature CCl$_4$, along with tertiary (Et)$_3$SiOH:base:CCl$_4$ solutions containing equimolar amounts of CH$_3$CN, C$_4$H$_8$O, or C$_5$H$_5$N (0.89 mol dm^{-3} base), are shown in Figure 1. These spectra have been corrected for cell and excess base absorptions by spectral subtraction. The IR absorption frequencies (and bandwidths) of the OH-stretching vibration in 1:1 (Et)$_3$SiOH–base complexes occur at 3547 cm^{-1} (105 cm^{-1} fwhm [full width at half maximum]), 3435 cm^{-1} (148 cm^{-1} fwhm), and 3254 cm^{-1} (344 cm^{-1} fwhm) for CH$_3$CN, C$_4$H$_8$O, and C$_5$H$_5$N bases, respectively. The decreasing vibrational frequency and increasing bandwidth of the perturbed OH-stretching vibration in (Et)$_3$SiOH–base complexes correlates well with the proton-accepting strength (basicity) of the corresponding bases.[11,12] The change in peak absorption at 3692 cm^{-1} that occurs after adding base to solution (see Figure 1) can be used to calculate the equilibrium constant (K_{eq}) for hydrogen-bond formation.[8] In this manner, K_{eq} was found to be 0.96, 2.69, and 5.67 dm^3 mol^{-1} for solutions containing CH$_3$CN, C$_4$H$_8$O, and C$_5$H$_5$N, respectively.

Transient IR measurements of the OH-stretch vibrational relaxation lifetime (T_{obs}) for "free" (Et)$_3$SiOH (0.1 mol dm^{-3}) were performed at a number of CH$_3$CN, C$_4$H$_8$O, and C$_5$H$_5$N concentrations. For these experiments, the "free" OH-stretching vibration ($\nu = 0 \rightarrow 1$ transition) at 3692 cm^{-1} was excited with an IR pump pulse and vibrational population (energy) decay was measured with a variably time-delayed IR probe pulse tuned to 3525 cm^{-1} (monitoring the 167 cm^{-1} anharmonically shifted $\nu = 1 \rightarrow 2$ OH-stretch transient absorption). The transmission of the probe pulse through the sample was obtained by alternately averaging 400 lasers shots with the pump on (T) and with the pump off (T_0) over an appropriate range of pump-probe delay times, τ_d (see Experimental Section for more details). Using this approach, one obtains the time-dependent difference in optical density (ΔOD) at the $\nu = 1 \rightarrow 2$ vibrational transition which is unaffected by the presence of static 1:1 complex absorptions at 3525 cm^{-1} depicted in Figure 1.

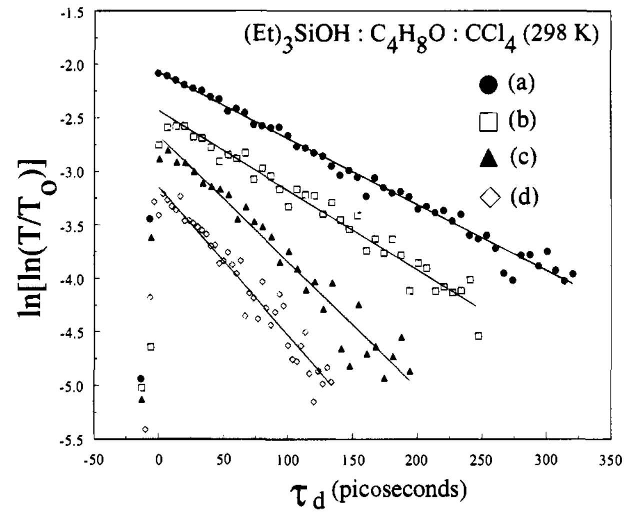

Figure 2. Transient absorption (pump "free" OH-stretch $\nu = 0 \rightarrow 1$, probe $\nu = 1 \rightarrow 2$) decays for (Et)$_3$SiOH:C$_4$H$_8$O:CCl$_4$ solutions with (a) 0.0, (b) 0.239, (c) 0.469, and (d) 0.690 mol dm^{-3} C$_4$H$_8$O. Linear fits to several decay data at each concentration yielded T_{obs} lifetimes of (a) 183 ± 6, (b) 130 ± 6, (c) 85 ± 3, and (d) 74 ± 2 ps.

Representative transient absorption difference signals, plotted as ln[ln(T/T_0)] versus τ_d, are shown in Figure 2 for (Et)$_3$SiOH:C$_4$H$_8$O:CCl$_4$ solutions at a number of C$_4$H$_8$O concentrations. The vibrational relaxation times (T_{obs}) obtained from linear least-squares fits to these decays decrease monotonically with increasing C$_4$H$_8$O concentration. Transient absorption decays obtained for solutions containing CH$_3$CN and C$_5$H$_5$N showed a similar variation in T_{obs} versus base concentration. For the base concentrations used (<0.8 mol dm^{-3}), no obvious deviation from linearity in these decays was found which might arise from removal or appearance of unexcited ($\nu = 0$) complexes after silanol excitation (see below).

A concentration dependence of the vibrational relaxation rate can be described by a Stern–Volmer kinetic process,[13]

$$\frac{1}{T_{obs}} = \frac{1}{T_1} + k_{BM}[\text{base}]$$

where T_1 is the OH-stretch ($\nu = 1$) vibrational relaxation time in the absence of base and k_{BM} is a bimolecular rate constant whereby vibrational deactivation of the uncomplexed OH-stretching vibration occurs through acid–base encounters. This equation is valid in the limit [(Et)$_3$SiOH] ≪ [base]. A master plot of T_{obs}^{-1} versus [base] (Figure 3) for the three solutions studied here reveals that k_{BM} (the slope) is independent of the identity of the base. A linear fit to all the data yields a value for k_{BM} of 1.2 ± 0.2 × 10^{10} dm^3 mol^{-1} s^{-1}. The insensitivity of k_{BM} to the identity of the base is unexpected considering the large variation in hydrogen-bonding strength and K_{eq} that is exhibited for CH$_3$CN, C$_4$H$_8$O, and C$_5$H$_5$N solutions. The

---

(10) Heilweil, E. J.; Casassa, M. P.; Cavanagh, R. R.; Stephenson, J. C. *J. Chem. Phys.* **1986**, *85*, 5004.

(11) Catalán, J.; Gómez, J.; Couto, A.; Laynez, J. *J. Am. Chem. Soc.* **1990**, *112*, 1678.

(12) Kolling, O. W. *Anal. Chem.* **1982**, *54*, 260.

(13) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; John Wiley and Sons: New York, 1981.

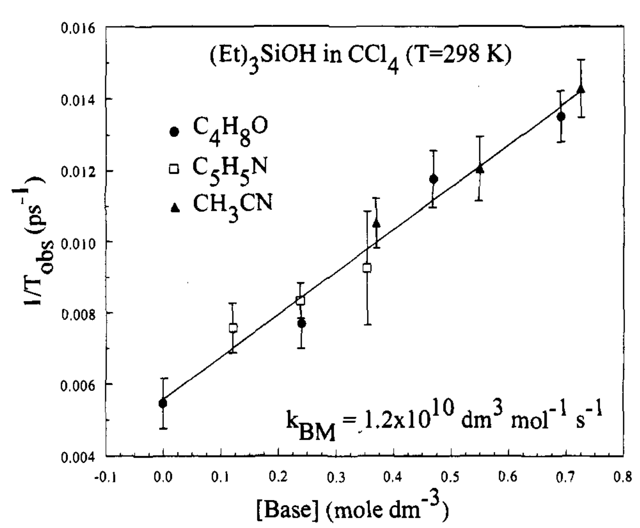

Figure 3. "Free" OH relaxation rate (T_{obs}^{-1}) of $(Et)_3SiOH$ versus concentration of base (Stern–Volmer plot) for $(Et)_3SiOH$:base:CCl_4 solutions. A linear least-squares fit yields a single bimolecular relaxation rate of $k_{BM} = 1.2 \pm 0.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}.

proton-accepting strength (the basicity) of the base is 3.3×10^{-4} cm^{-1} for CH_3CN, 5.5×10^{-4} cm^{-1} for C_4H_8O, and 6.4×10^{-4} cm^{-1} for C_5H_5N (these basicities are Kamlet–Taft parameters).[11,12] The variation in basicity, and also the variation in K_{eq} reported above, might lead one to believe that certain acid–base encounters would be more effective in deactivating OH-stretch vibrational energy. Our results suggest that this is not the case.

An estimate of the bimolecular encounter rate using the Stokes–Einstein diffusion model[14] yields 0.73×10^{10} dm^3 mol^{-1} s^{-1} for CCl_4 solutions at 298 K, a value similar to our measurement of k_{BM}. This agreement, along with the arguments presented above, suggests that the bimolecular OH deactivation rate is mostly dictated by diffusion-limited acid–base encounters, and is relatively insensitive to the magnitude of the acid–base hydrogen-bonding interaction. For base concentrations larger than those studied here (>0.8 mol dm^{-3}), one would also expect T_{obs}^{-1} shown in Figure 3 to reach a base-dependent limiting value since near 2 mol dm^{-3} there would be (on average) one base molecule per "free" acid solvent shell. Such experiments are feasible (with sufficient "free" $(Et)_3SiOH$ absorption) and could potentially yield more information about solvation shell interactions, steric effects, and vibrational energy transfer rates to accepting base species.

It is interesting to note, however, that the value of k_{BM} measured for $(Et)_3SiOH$:base encounters in CCl_4 ($1.2 \pm 0.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) is approximately half the value measured for pyrrole:CH_3CN encounters in CCl_4 ($2.5 \pm 0.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) reported earlier.[1] This difference is likely to be due to the more effective steric shielding of the OH functional group in $(Et)_3SiOH$ compared to the minimal shielding of the NH functional group that occurs in the planar ring structure of pyrrole.

It is important to consider whether deactivation of the "free" OH-stretch in $(Et)_3SiOH$ through bimolecular encounters with base molecules occurs through formation of acid–base hydrogen-bonded complexes or is simply a collisional effect. The effect of the hydrogen-bonding interaction in OH-stretch deactivation was then explored by measuring the OH-stretch population lifetime of "free" $(Et)_3SiOH$ in solutions that exhibit no hydrogen-bonding interactions, $(Et)_3SiOH$:hexane:CCl_4, and in solutions that exhibit only weak interactions, $(Et)_3SiOH$:benzene:CCl_4. If the OH-stretch lifetime exhibits a concentration dependence with added hexane or benzene, then one could argue that bimolecular OH-stretch deactivation results from intermolecular vibrational energy transfer into accepting modes of the collider (e.g., CH-stretch or CH-bend modes). For these experiments, T_{obs} was found to be relatively insensitive to the presence of hexane or benzene in solution; the value of T_1 only decreased a maximum of 20% for hexane or benzene concentrations as high as 1.3 mol dm^{-3}. This result suggests that hydrogen-bonding interactions play the dominant role in the bimolecular OH-stretch vibrational deactivation mechanism.

One can further speculate whether the measured bimolecular rate (k_{BM}) corresponds to the formation rate (k_{form}) for $(Et)_3SiOH$–base hydrogen-bonded complexes in CCl_4;

$$\frac{d[(Et)_3SiOH\cdots base]}{dt} = k_{form}[(Et)_3SiOH][base]$$

If OH-stretch deactivation occurs purely through complex formation, then the value $(k_{BM}[base])^{-1}$ represents the average formation time for $(Et)_3SiOH$–base hydrogen-bonded complexes. Using this argument for a 1.6 mol dm^{-1} base solution yields on average a 52 ps complex formation time. However, other mechanisms could contribute to the observed OH-stretch deactivation rates, such as bimolecular dipole–dipole interactions between $(Et)_3SiOH$ and base molecules, or one could also argue for the existence of pseudocomplexes that form and dissociate on a relatively short time scale (<10 ps). Therefore, we cannot yet guarantee that k_{BM} is an accurate measure of k_{form}.

However, if we assume $k_{BM} = k_{form}$, then one must also consider that (1) complexes are constantly dissociating (due to the steady-state equilibrium) and (2) perhaps the OH-stretch ($\nu = 1$) vibrational excitation persists after acid–base complexation. Since the "free" acid and 1:1 complexes are in dynamic equilibrium ($K_{eq} = k_{form}/k_{diss}$), the extraction of 1:1 complex species vibrational relaxation, dissociation, and formation rates must include all these processes in a complete analysis of the kinetics. In the latter case, additional kinetic pathways such as vibrationally excited $(Et)_3SiOH$ directly forming excited or ground state 1:1 complex may also be convolved in our measurements, and these contributions (presumed to be negligible) require further examination.

One could argue that the transient absorption decays measured at 3525 cm^{-1} do not truly represent population deactivation of the "free" OH-stretch, and instead, the OH-stretch absorption merely shifts to lower frequencies (see Figure 1). The prospect of experimentally detecting ground state or vibrationally excited $(Et)_3SiOH$:base complexes by probing at 3525 cm^{-1} and at the red-shifted $\nu = 1 \rightarrow 2$ OH-stretch was therefore considered. The following kinetic scheme was assumed for this dynamic system:

$$\begin{tikzcd}
{[(Et)_3SiOH^*] + [base]} \arrow[r, shift left, "k_{BM}"] \arrow[d, "k_1"] & {[(Et)_3SiOH^*\cdots base]} \arrow[l, shift left, "k_{diss}"] \arrow[d, "k_2"] \\
{[(Et)_3SiOH] + [base]} \arrow[r, shift left, "k_{BM}"] & {[(Et)_3SiOH\cdots base]} \arrow[l, shift left, "k_{diss}"]
\end{tikzcd}$$

where $[(Et)_3SiOH^*]$ and $[(Et)_3SiOH^*\cdots base]$ indicate the concentration of OH-stretch $\nu = 1$ excited species, $k_1 = 5.46 \times 10^{-3}$ ps^{-1} is the experimentally measured "free" OH-stretch

---

(14) Levine, I. N. *Physical Chemistry*; McGraw-Hill, Inc.: New York, 1983; pp 538–39.

(15) Heilweil, E. J.; Cavanagh, R. R.; Stephenson, J. C. *J. Chem. Phys.* **1988**, *89*, 230.

relaxation rate when no base is present in solution, and $k_{diss} = k_{BM}/K_{eq}$ is the microscopic acid–base dissociation rate.

To obtain a value for k_2, transient IR absorption experiments were conducted which directly pumped the OH-stretching vibration of $(Et)_3SiOH$:base complexes (thereby directly creating $[(Et)_3SiOH^{*}\cdots base]$) and then probed $\nu = 1$ vibrational energy decay (via $\nu = 1 \rightarrow 2$ transient absorption) of this complex to the ground state ($[(Et)_3SiOH\cdots base]$). These experiments yielded $k_2 = 0.029 \pm 0.006$ and 0.13 ± 0.02 ps^{-1} for $[(Et)_3SiOH^{*}\cdots CH_3CN]$ and $[(Et)_3SiOH^{*}\cdots C_4H_8O]$ complexes, respectively. The measurement of long-lived complex OH-stretch vibrational population lifetimes may be slightly affected by the competing equilibrium dissociation process (worst case for the $(Et)_3SiOH$:acetonitrile complex with $K_{eq} = 0.96$ decreases the observed k_2 rate of 1/35 ps^{-1} by 14%) or by direct photodissociation. k_2 was not measured for $[(Et)_3SiOH^{*}\cdots C_5H_5N]$, but its value is assumed to be larger than the values measured for CH_3CN and C_4H_8O complexes using arguments presented in ref 1.

Modeling of the transient populations for the $(Et)_3SiOH$:acetonitrile system designated in the above kinetic scheme was undertaken using first-order rate equations. By incorporating directly measured values for the initially excited $(Et)_3SiOH^{*}$ concentration (10% of the ground state concentration of 0.05 mol dm^{-3}), k_1, k_2, and the assumed complex formation rate (k_{BM}), one obtains the variation in $[(Et)_3SiOH^{*}\cdots$acetonitrile$]$ and the other coupled species concentrations as a function of time. These calculations indicate that the concentration of $[(Et)_3SiOH^{*}\cdots$acetonitrile$]$ could build up to a maximum of 15–20% of the initially excited "free" silanol concentration in ca. 30 ps and decay with a 100 ps time constant. For example, experiments that pump the "free" OH-stretch of $(Et)_3SiOH$ and probe the OH-stretch ($\nu = 1 \rightarrow 2$) transient absorption of the vibrationally excited, newly-formed complexes could yield a 30 ps delayed, 1–2% peak absorption signal which is slightly above our experimental detectability. This and related experiments designed to follow the transient populations of these species are underway to refine the above kinetic model.[16]

While many aspects of the "free" $(Et)_3SiOH$ OH-stretch deactivation mechanism remain unclear, these measurements have demonstrated that hydrogen-bonding interactions play a dominant role. Future experiments will focus on whether deactivation through bimolecular encounters in hydrogen-bonded systems occurs through formation of vibrationally excited or unexcited hydrogen-bonded complexes or involves acid–base encounters that do not form stable hydrogen-bonded complexes and if vibrationally excited complexes photodissociate with measurable quantum yield.[16]

Conclusions

We reported picosecond two-color IR pump-probe absorption experiments that measured the role $(Et)_3SiOH$:base hydrogen-bonding interactions play in governing the vibrational relaxation lifetimes of the "free" OH-stretching vibration in room temperature $(Et)_3SiOH$:base:CCl_4 solutions. Transient $\nu = 1$ population decay data were collected for solutions containing three different bases, CH_3CN, C_4H_8O, and C_5H_5N, at a number of concentrations. The OH-stretch vibrational relaxation rate (T_{obs}^{-1}) was described by the sum of two processes: a base-independent intramolecular vibrational energy decay pathway ($T_1 = 183 \pm 6$ ps), and a base-dependent pathway involving bimolecular hydrogen-bonding encounters. The concentration dependence of the OH-stretch relaxation rate is described by a Stern–Volmer kinetic equation and a least-squares fit to the data yielded a bimolecular rate constant $k_{BM} = 1.2 \pm 0.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. This value of k_{BM} is independent of the identity of the base and is very close to an estimate of the bimolecular diffusion rate calculated for solutes in CCl_4 at 298 K. The insensitivity of the "free" OH-stretch relaxation rate in $(Et)_3SiOH$:CCl_4 solutions to the addition of up to 1.3 mol dm^{-3} hexane or benzene confirms that the bimolecular OH deactivation mechanism involves $(Et)_3SiOH$:base hydrogen-bonding interactions, and is not governed by a collisional intermolecular energy transfer mechanism.

Experimental Procedures

Materials. The $(Et)_3SiOH$, bases, and carbon tetrachloride where obtained from commercial sources and used without further purification, except CH_3CN, which was dried over molecular sieves prior to use. FTIR spectra of the $(Et)_3SiOH$:base:CCl_4 mixtures showed no evidence for impurities that might interfere with the experimental results. For all transient IR pump-probe experiments, a flowing sample cell with CaF_2 windows was utilized (1 mm path length) to minimize IR pump-induced heating in the focal region.

IR Pulse Generation and Transient IR Apparatus. The equipment for generating picosecond tunable IR pump and probe pulses in the 3 μm region is described in detail elsewhere[1,10,15] and is briefly summarized here. A 12 μJ IR pump pulse (3692 cm^{-1}) was generated at 20 Hz by mixing an amplified R6G dye laser pulse (7 ps fwhm, 571 nm) with 80% of an amplified pyridine dye laser pulse (1 ps fwhm, 724 nm) in a 2 cm long $LiIO_3$ crystal. A 50 nJ IR probe pulse (3525 cm^{-1}) was similarly generated by mixing the remaining 20% of the amplified pyridine dye laser pulse with an amplified pulse from a second R6G dye laser (7 ps fwhm, 577 nm) in a 0.5 cm long $LiIO_3$ crystal. The IR pump-probe cross correlation was measured by sum frequency generation in a 2 mm long $LiIO_3$ crystal and yielded a 4 ps fwhm instrument response.

The pump and probe pulses were focused into the sample with a 100 mm CaF_2 lens and the beam waists were measured to be approximately 100 μm fwhm at the focus. After passage through the sample, the probe pulse intensity was monitored with a liquid N_2 cooled InSb detector. Fluctuations in the probe pulse intensity were normalized by monitoring a fraction of the probe pulse before the sample with a matched InSb detector. Molecular reorientation was demonstrated in earlier work to make a sizable contribution to our transient signals near $\tau_d = 0$, and therefore the pump and probe were polarized at the magic angle (54.7°) to remove this contribution.

Acknowledgment. We are grateful to Dr. Steven M. Arrivo for obtaining measurements of the OH ($\nu = 1$) relaxation lifetime of the $(Et)_3SiOH$:CH_3CN complex and performing kinetic modeling of acid–base interactions. Drs. Grubbs and Dougherty were NIST/NRC Postdoctoral Associates while performing these investigations. This work was supported by internal NIST-STRS (Scientific and Technical Research and Services) funding.

JA952272L

---

[16] Arrivo, S. M.; Grubbs, W. T.; Heilweil, E. J. In preparation.