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Siloxane Basicity toward Strong Acid in Nonpolar Solution

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Abstract: The relative basicities of ten siloxanes and an ether were studied in benzene by determining from visible spectroscopic measurements the thermodynamic constants for the competition between the substrate and a reference base (4-chloro-2-nitroaniline) for acid (trifluoromethanesulfonic acid): $\mathrm{RB{\cdot}HA + S \rightleftharpoons RB + S{\cdot}HA}$. The K_{eq} values were considered as a measure of basicity with the following order established and explained by inductive effects in the protonated species: permethyl linear siloxanes ($Me_3Si(OSiMe_2)_nOSiMe_3$, $n = 0$–3) > dibutyl ether > $HMe_2SiOSiMe_2H$ > branched siloxanes ($(Me_3SiO)_3SiMe$, $(Me_3SiO)_4Si$) > cyclic siloxanes ($(Me_2SiO)_n$, $n = 3$–5). The ΔH and ΔS values were positive and increased with higher basicity; this behavior was attributed to differential solvation of ion pairs.

The basicity of siloxanes is of academic as well as industrial interest and has been investigated by a variety of methods including acid-catalyzed equilibration,[1] Lewis acid complexation,[2] hydrogen bonding,[3,4] and gas-phase proton-affinity experiments.[5] The development of epoxysilicone systems in which the epoxy groups polymerize under the influence of strong acid (e.g., $HSbF_6$)[6] led to the present investigation of the interaction between siloxanes and a strong protic acid in a nonpolar medium. The earlier studies[1-5] focused on the basicity differences between siloxanes, alkoxysilanes, and ethers and did not distinguish among various types of siloxanes.[7] In this paper I report experiments that clearly differentiate between linear, branched, and cyclic siloxanes as well as a dialkyl ether. The following order of basicity was established by equilibrium measurements: linear siloxanes > dialkyl ether > branched siloxanes > cyclic siloxanes. Trends in enthalpy and entropy parameters were influenced by solvation effects mediated by the basicity of the substrate. These results, combined with previous reports, further demonstrate that basicity is a relative property that is dependent on the strength of the reference acid, the nature of the medium, and the method of measurement.[8]

Method

The position of the equilibrium in the competitive reaction between a reference base and a substrate for acid correlates with the basicity of the substrate (eq 1). A visible spectroscopy

$$\mathrm{RB{\cdot}HA + S \overset{K_{eq}}{\rightleftharpoons} RB + S{\cdot}HA} \tag{1}$$

technique was developed to measure K_{eq} in which a nitroaniline, specifically 4-chloro-2-nitroaniline, was used as the reference base. The visible absorption band of the uncomplexed form of this aniline was free of interference from other species, and the basicity of this particular derivative did not overwhelm that of the substrates but was sufficient to assure that no free HA was present. Trifluoromethanesulfonic acid functioned as the strong acid. The measurements were recorded for samples in benzene, in which all species were soluble at the concentrations used (10^{-4} M). Cyclohexane and CCl_4 were unsuitable solvents due to solid formation. Performing the measurements over a 40 °C temperature range allowed the determination of enthalpy and entropy parameters.

On the basis of polarity and dielectric considerations, free ions will not be present in benzene. The RB·HA species is viewed as an unaggregated ion pair because dielectric data indicated simple ion pairs for a similar protonated aniline in benzene solution that was 100 times more concentrated than that used in this study.[9] The unprotonated reference base is not involved in any association reactions because its absorption band did not shift with concentration, temperature, or the presence of the other compounds.[10-12] The substrates and their ion pairs (S·HA) are presumed to be unaggregated at the concentrations employed.

Results and Discussion

Thermodynamic constants of eq 1 for the siloxane and ether substrates are compiled in Table I. The equilibrium constants have been corrected for symmetry.[13] The absorbance readings from which these constants were derived were reproducible over several cycles of the temperature range studied (20–60 °C). The most striking feature is the substantial difference between linear and cyclic siloxanes. With K_{eq} as a measure of basicity, the linear siloxanes **1–4** are more basic than the cyclic siloxanes **9–11** by more than 1 order of magnitude. The values for the dialkyl ether **5**, the hydride-terminated siloxane **6**, and the branched derivatives **7** and **8** fall between those for the permethyl linear and cyclic siloxanes.

There is no correlation between K_{eq} and the number of oxygen atoms in the substrate. This is demonstrated within the subsets of the trimethylsilyl-stopped linear siloxanes **2–4** (two to four oxygen atoms) and the cyclic siloxanes **9–11** (three to five oxygen atoms) where the K_{eq}'s are identical within experimental uncertainty. Also, the order of siloxane basicity, permethyl linear > branched > cyclic, is followed regardless of the number of oxygen atoms in the substrates compared, and the K_{eq}'s in the series **1**, **3**, **7**, and **8** (successive replacement of Me with $OSiMe_3$) actually decrease with increasing oxygen content. The site of protonation is most certainly at oxygen because those atoms bear substantial

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Table I. Thermodynamic Constants for RB·HA + S $\rightleftarrows$ RB + S·HA[a]

substrate (S)	structure	q[b]	$K_{eq}/q \times 10^2$ (300 K)	ΔG(300 K),[c] kcal/mol	ΔH,[c] kcal/mol	ΔS,[c] cal/(deg·mol)
1	$Me_3SiOSiMe_3$	1	27.8 ± 6.1	0.77 ± 0.14	22.9 ± 4.8	73.6 ± 16.5
2	$Me_3Si(OSiMe_2)_3OSiMe_3$	2	10.5 ± 0.8	0.93 ± 0.05	27.7 ± 1.9	89.2 ± 6.3
3	$Me_3SiOSiMe_2OSiMe_3$	2	10.2 ± 1.1	0.95 ± 0.06	27.7 ± 2.8	89.1 ± 9.5
4	$Me_3Si(OSiMe_2)_2OSiMe_3$	2	10.0 ± 1.1	0.96 ± 0.09	28.1 ± 3.1	90.5 ± 10.7
5	$(CH_3CH_2CH_2CH_2)_2O$	1	9.0 ± 0.5	1.43 ± 0.03	10.2 ± 0.6	29.2 ± 2.2
6	$HMe_2SiOSiMe_2H$	1	5.6 ± 0.2	1.72 ± 0.02	18.0 ± 1.2	54.3 ± 4.0
7	$(Me_3SiO)_3SiMe$	3	4.3 ± 0.2	1.22 ± 0.03	25.2 ± 2.1	79.9 ± 7.2
8	$(Me_3SiO)_4Si$	4	2.2 ± 0.1	1.45 ± 0.02	22.4 ± 0.1	69.9 ± 0.3
9	$(Me_2SiO)_3$	3	0.8 ± 0.1	2.24 ± 0.07	12.0 ± 1.1	32.6 ± 3.4
10	$(Me_2SiO)_4$	4	0.7 ± 0.1	2.13 ± 0.13	9.0 ± 1.5	22.9 ± 4.8
11	$(Me_2SiO)_5$	5	0.5 ± 0.1	2.16 ± 0.09	10.6 ± 1.4	28.0 ± 4.4

[a] Values are the average ± 1 standard deviation of three determinations. The reference base (RB) was 4-chloro-2-nitroaniline, and HA was trifluoromethanesulfonic acid. [b] q is the number of equivalent positions in the substrate that can add a proton.[13] [c] The calculation of this quantity is based on the observed K_{eq}.

negative charge,[14] and the highest occupied molecular orbital in siloxanes is of predominant O 2p character.[15] The above observations indicate that the K_{eq} behavior is not governed simply by the total number of basic sites and that the species under consideration are monoprotonated. In addition, multiple protonations are not likely to occur because the total base concentration ([RB] + [S]) was 3 times that of the acid.

The K_{eq} order is as expected from consideration of inductive effects in the protonated species. The protonated oxygen is stabilized in all of the siloxanes by two neighboring electropositive silicon atoms, but the stabilizing ability of those silicons depends on their substituents. In the cyclic derivatives, *both* silicons adjacent to the protonated center are bonded to oxygen atoms that inductively decrease the degree of electron donation from the silicons to the protonated oxygen. In the linear and branched compounds, only *one* of the neighboring silicons is bonded to oxygen. As a consequence, the protonated cyclic species are the least stable and, therefore, cyclic siloxanes are the least basic. The same reasoning explains why branched siloxanes are less basic than linear siloxanes.

The internal oxygen atoms in the linear siloxanes **2** and **4** are expected in a first approximation to be about as basic as an oxygen in a cyclic siloxane due to the similar environment ($-SiMe_2OSiMe_2-$). Because the K_{eq} values for the linear and cyclic siloxanes are so different, the basicity of the linear derivatives must be dominated by the terminal oxygen atoms, consistent with ^{17}O NMR data.[16] The measurements also demonstrate that the Me_3Si group is inductively more electron supplying than the HMe_2Si group, in agreement with σ-values determined from NMR studies.[17] Differentiation within the linear and cyclic groups is not made because inductive effects fall off as the inverse square of the distance between the group and the charge.[18] The dialkyl ether included in the study is less basic than the comparable linear siloxanes, as predicted by an inductive model. Unfortunately, other ethers and alkoxysilanes (Me_3COEt, Me_3SiOEt, $Me_3SiOCMe_3$) and $Me_3Si(OSiMe_2)_5OSiMe_3$ were too unstable under the experimental conditions to be studied.

The ΔH and ΔS values follow the "law of compensation";[19] that is, they are linearly related ($R^2 = 0.999$). The thermodynamic quantities are not, however, governed solely by the extent of acid–base interaction. If that were the case, then ΔH and ΔS would be more positive for a less basic substrate, the opposite of what is observed. Consideration of the relative degree of solvation of the different ion pairs with respect to the basicity of the substrate can account for the trends in ΔH and ΔS. The values measured for compound **4** with use of the stronger reference base 2-nitroaniline[20] were ΔH = 14.2 kcal/mol and ΔS = 40.6 cal/(mol·deg). These smaller values are the opposite of that expected from base strength alone but can be explained by solvation effects.

The K_{eq}'s for the linear siloxanes **1**, **3**, and **4** and the cyclic siloxanes **9–11** in acetonitrile at room temperature with 2-nitroaniline as the reference base were indistinguishable within experimental error. Furthermore, no temperature dependency was exhibited. These observations are consistent with the importance of ion pair solvation in benzene and demonstrate that basicity measurements depend on the system in which they are determined.

Silicon atoms are Lewis acid sites[21] and as such could be complexed by the triflate anion. The silicons most susceptible to that type of interaction would be those with the greatest number of oxygen neighbors. If anionic complexation were an important feature in this study, a different ordering of the thermodynamic values would be expected. However, a complex interplay in S·HA involving both oxygen–proton and silicon–triflate interactions cannot be unequivocally dismissed. If silyltriflates were formed to an appreciable degree, extensive degradation of the siloxanes would be expected but was not observed (test solutions containing compounds **2–4**, **7**, and **9** exhibited slight decomposition (<10%) during the time (<1 h) of the experiment). The data do not rule out the possibility that silyltriflate–silanol pairs were formed that underwent internal return faster than subsequent condensation reactions.

Silicones, especially cyclic derivatives, are prone to undergo polymerization and redistribution reactions under the influence of triflic acid.[22] This is not of consequence in the present system because most of the strong acid is bound by the amine reference base.

Conclusion

The method, results, and interpretations in this investigation of siloxane basicity complement those from previous works.[1-5] The extent of acid–base interaction between triflic acid and siloxanes in this study is more like that in the gas-phase proton-affinity experiments[5] than that in the hydrogen-bonding experiments.[4] However, only two compounds were involved in both studies (each

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method established that $Me_3SiOSiMe_3$ is more basic than $HMe_2SiOSiMe_2H$) so a detailed comparison is not possible. The technique here gives a measure of (Bronsted) basicity by comparing the relative stabilization of protonated ion-paired species and differentiates between linear, branched, and cyclic siloxanes, whereas the hydrogen-bonding studies provided insight into the (Lewis[23]) basicity differences between siloxanes, alkoxysilanes, and ethers. The order of basicity established in this paper (linear siloxanes > dialkyl ether > branched siloxanes > cyclic siloxanes) can be explained by inductive effects alone and was shown to be medium dependent; the interpretation of hydrogen-bonding results (basicity order: ethers > alkoxysilanes ≫ siloxanes) invoked delocalization of oxygen lone pair electrons;[24] the explanation of proton-affinity data combined lone pair delocalization with polarization of the total electron distribution by the strong acid. All of the techniques and interpretations are valid—there is no one single measure of basicity.

Experimental Section

The siloxanes in this study are commercially available (Petrarch Systems). Benzene and acetonitrile (both Aldrich spectrophotometric grade) and the substrates were distilled (with reduced pressure where appropriate) under nitrogen from CaH_2, then degassed, and stored under N_2. Hexamethylcyclotrisiloxane in benzene was stirred with CaH_2, and then the solvent was removed under vacuum followed by sublimation. The 4-chloro-2-nitroaniline (λ_{max} = 404 nm, ϵ = 4900 M^{-1} cm^{-1}) and 2-nitroaniline (λ_{max} = 391 nm, ϵ = 5300 M^{-1} cm^{-1}) reference bases were recrystallized from dry benzene. Trifluoromethanesulfonic acid (Aldrich) was used as received in ampules that were opened in a drybox (Vacuum Atmospheres) equipped with a HE-493 Dri-Train and maintained under a positive pressure of nitrogen. Glassware was oven-dried (240 °C) and then cooled under vacuum either on a double manifold or in the antechamber of the drybox. All solutions were prepared in the drybox. The integrity of test solutions was monitored by gas chromatography (Hewlett-Packard 5890A equipped with a 30 m × 0.32 mm × 0.25 μm film thickness DB5 column (J & W Scientific) and flame ionization detector).

The reference base and substrates were accurately weighed (at least 1.000 g) into dry Schlenk-type volumetric flasks on an analytical balance outside of the drybox and then frozen in liquid N_2, degassed, thawed, taken into the drybox, and diluted appropriately to give 10^{-3} M stock solutions. Concentrations of triflic acid stock solutions (prepared fresh daily) were determined by titration with standard KOH in MeOH (Aldrich) with use of tetrabromophenolphthalein ethyl ester (Eastman Kodak) as the indicator in toluene/isopropyl alcohol. Aliquots from the substrate, reference base, and acid stock solutions were transferred by pipet (at least 3 mL) to a 25-mL volumetric flask and diluted, resulting in a test solution that was 6×10^{-4} M in substrate and 3×10^{-4} M in reference base and acid. Spectroscopic cells were of a no-air design. A temperature-regulated rectangular cell holder (Perkin-Elmer 570-0705) with a digital controller (Perkin-Elmer 570-0701) was calibrated with a type K thermocouple. The test solutions were maintained at a particular temperature for about 10 min to achieve temperature equilibration and signal stability before data acquisition. Spectra were acquired on a Shimadzu UV-240 spectrophotometer at 20, 30, 40, 50, and 60 °C. The variable-temperature behavior was reproducible with each particular solution. The absorbance of the test solutions increased 77–309% between 20 and 60 °C, depending on the substrate. All absorbance readings were in the range 0.14–1.56.

The equilibrium constant was calculated at each temperature from the absorbance measurement (free RB) and the total amounts of RB, S, and HA. The treatment was simplified by the use of concentrations rather than activities. A linear least-squares fit of $\ln K_{eq}$ vs $1/T$ (all $R^2 \geq 0.95$) allowed determination of ΔH and ΔS and then calculation of ΔG(300 K) and K_{eq}(300 K). Three data sets were analyzed for each substrate and average values ± 1 standard deviation are reported in Table I.

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Interfacial Behavior of Block Polyelectrolytes. 1. Evidence for Novel Surface Micelle Formation†

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Abstract: Monolayers of a polystyrene/poly-4-vinylpyridine AB diblock ionomer, $(PS)_{260}$ $(4\text{-}PVP)_{240}$, fully quaternized with decyl iodide have been studied at the air/water interface with the Langmuir film balance technique. Surface pressure/area isotherms exhibit an abrupt onset and an apparent first-order phase transition at high pressures. Transmission electron micrographs of LB films deposited on carbon-coated copper grids provide direct evidence of self-assembly of the diblock copolymers into circular surface micelles. These surface micelles appear to be quite regular and have an aggregation number of ~120. The distance between micelles (at low surface pressures) is consistent with fully extended dec-4-PVP^+ chains extending radially from a central core of PS coils. These aggregates pack with a surface density ~10^{10} particles per cm^2 at the lowest detectable surface pressures. The apparent first-order phase transition correlates with transmission electron micrograph observations and may originate from a process where the decylated polyelectrolyte block proceeds from a surface-adsorbed state to a submerged, aqueous state as the film is compressed. The entropy of this transition is +7.6 eu and is consistent with the polymeric micelles passing from an ordered 2D state to a less ordered quasi-2D state.

Introduction

Polymer monolayers, spread at the air–water interface, have played an important role in our understanding of the factors controlling polymer–polymer and polymer–interface interactions.[1-3] Details concerning molecular orientations, monomer conformations, and interaction energies are in principle determinable with the surface film balance technique[4] and ancillary spectroscopic

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