Siloxane Chemistry

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From the Selective Cleavage of the Si-O-Si Bond in Disiloxanes to Zwitterionic, Water-Stable Zinc Silanolates**

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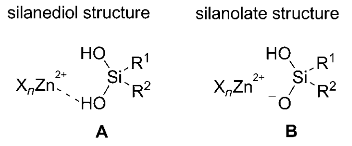
The high stability and relatively low reactivity of the Si-O-Si bond in functionalized siloxanes under ambient conditions is a fundamental property in organosilicon chemistry (such as its high stability towards heat and radiation or its chemical resistance).[1,2] In the course of discussions of sustainability and environmental protection, the demand for a mild and easy cleavage of the Si-O-Si unit in siloxanes has arisen, particularly in the context of recycling widely used silicones. Yet only a few concrete approaches exist to date.[3]

In contrast, molecular metallasilanolates have gained increasing attention in various fields of modern chemistry,[4,5] such as for the preparation of structurally modified silica surfaces (artificial surface design) and as new inorganic materials for homogeneous catalysis reactions.[6] As molecular siloxane compounds containing an $R_3Si\text{-}O\text{-}MX_n$ unit (M = main-group/transition metal, X = variable) are known to be readily hydrolyzed by water to form the corresponding silanols or disiloxanes,[7–9] they have not been considered relevant under aqueous conditions. This mindset has had a critical impact not only on synthetic chemistry but also, for instance, on the interpretation of interactions between transition metals such as zinc and silanol units in enzymes.[10] Juers et al. reported the characterization of the first thermolysin/silanediol complex by X-ray structural analysis.[11,12] In that case, a silanediol inhibitor was bound to the zinc ion of the metalloprotease thermolysin through both hydroxy groups of the silicon. An observed, preferential interaction of the enzyme with one of the oxygen atoms of the silicon unit was referred to as a particularly strong hydrogen bond of one of the hydroxy groups (**A**, Scheme 1). A potential silanolate structure (**B**, Scheme 1) has not been discussed owing to the known sensitivity of such moieties under aqueous conditions.

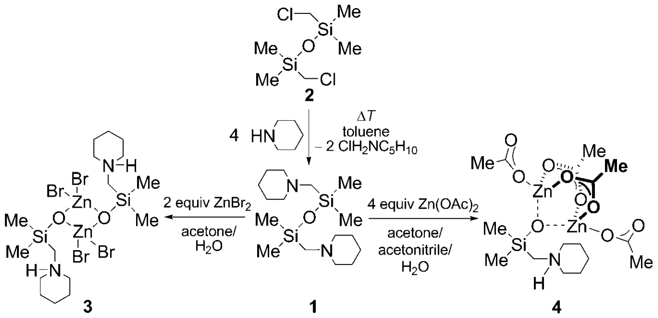


Scheme 1. Central unit of the thermolysin/silanediol complex (simplified): supposed silanediol structure by Juers et al. (left), in which the shortened Zn–O distance was attributed to hydrogen bonding,[11] and a possible silanolate structure with an ionic interaction (right), which was not discussed owing to the known kinetic lability of the Si-O-Zn fragment.

As part of our studies on aminoalkyl-substituted silanes,[13,14] we report herein the unexpected isolation and the characterization of highly stable molecular zinc silanolates containing an Si-O-Zn unit in the presence of water. Their formation by treatment of functionalized disiloxanes with simple zinc(II) salts demonstrates an easy and hitherto unconsidered method for the selective cleavage of the strong and unreactive Si-O-Si bond.

1,3-bis(piperidinomethyl)tetramethyldisiloxane (**1**) was chosen as reactant for our studies concerning the cleavage of the Si-O-Si unit as it is a simple model system for methyl-substituted silicones and to ensure full a condensation of the silanol precursor. Its preparation was accomplished in a two-step synthesis. First, controlled hydrolysis of (chloromethyl)-dimethylchlorosilane gave the corresponding intermediate silanol, which directly condensed under elimination of water to yield 1,3-bis(chloromethyl)tetramethyldisiloxane (**2**). The subsequent treatment of **2** with four equivalents of piperidine resulted in the desired formation of **1** (Scheme 2). For a better understanding of the interactions between the Si–O unit and zinc, we examined the reactivity of the potential metal-directing[15] disiloxane **1** towards zinc salts. Zinc(II) bromide and zinc(II) acetate were chosen as two of the simplest representatives.

Astonishingly, the treatment of **1** with two equivalents of zinc(II) bromide or four equivalents of zinc(II) acetate in the presence of water and under ambient atmosphere resulted in the selective cleavage of the strong and unreactive Si-O-Si



Scheme 2. Synthesis of **1** and selective Si-O-Si bond cleavage with $ZnBr_2$ and $Zn(OAc)_2$ to form the water-stable silanolates **3** and **4**.[16]

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bond to form quantitatively the two uncommon crystalline solids **3** and **4** (Scheme 2 and Figure 1).

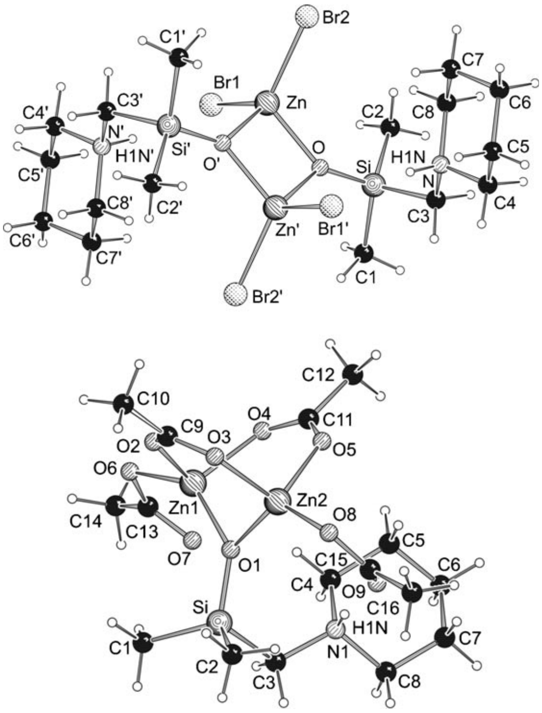

Figure 1. Molecular structures of **3** (top) and **4** (bottom, one of two molecules in the asymmetric unit). Selected bond lengths [Å]: **3**: Br1–Zn 2.3950(11), Br2–Zn 2.3359(10), O–Si 1.621(4), O–Zn 1.981(4), O–Zn′ 1.983(4), Zn–O′ 1.983(4), symmetry transformation ′: $-x$, $-y+1$, $-z+2$; **4**: O1–Si1 1.626(3), O1–Zn2 1.955(3), O1–Zn1 1.975(2), O3–Zn2 1.971(3), O5–Zn2 1.959(3), O6–Zn1 2.001(3), O7–Zn2 1.976(3), O8–Zn2 1.921(3).

Compound **3** crystallized from acetone/water in the monoclinic space group $P2_1/n$ as colorless needles, and **4** crystallized from acetone/acetonitrile/water in the monoclinic space group $P2_1/c$ as colorless plates.[16] Compound **3** forms a dimeric structure with an inversion center located in the middle of its Zn-O-Zn′-O′ ring. The asymmetric unit of **4** contains two molecules. In comparison to **3**, only one $R_2R'SiO$ unit is present in **4** with two zinc atoms coordinated to the oxygen atom at silicon. To complete its coordination sphere, each zinc atom is coordinated by three additional oxygen atoms of the acetate groups; two acetate units bridge both zinc atoms. Consequently, the successful isolation of these structures demonstrates the following two facts: 1) Contrary to previous opinion, molecular metallasilanolates are obviously stable under aqueous conditions. 2) Zinc compounds are able to cleave Si–O bonds. Below, the uncommon structures of **3** and **4** will be discussed in detail, with special focus on their high stability in the presence of water. Afterwards, we will take a closer look at the bond cleavage process.

In the in the X-ray diffraction analyses of **3** and **4**, hydrogen atoms were found and freely refined at the nitrogen atoms in both molecules and not at the oxygen atoms of the Si–O units, thus leading to a positive charge located at the amino function counterbalanced by a negative charge located at the oxygen atom. Thus, there is no hint of the expected silanol-like structure (Si-OH-Zn; **A** in Scheme 1) as proposed for molecular metal silanediols under aqueous conditions (e.g. the thermolysin/silanediol complex).[11] Instead, heretofore unknown silanolate complexes with central Si-O-Zn fragments are formed that are highly stable in the presence of water (**B** in Scheme 1). Quantum chemical calculations [B3LYP/6-31+G(d)][17] on the silanolate **3** (Si-O-Zn) and its hypothetical silanol (Si-OH-Zn; hydrogen atom not bound to nitrogen) further provided an energetic preference for **3** of 157 kJ mol^{-1}, thus confirming the experimental observation.

How can this uncommon stability be explained? The central $R_2R'Si\text{-}O\text{-}ZnX_2X'$ units of **3** and **4** possess fourfold-coordinated zinc atoms comparable to the pseudo-tetrahedral coordination geometry of zinc in many of its coordination compounds.[10,18] All O–Zn bond lengths are comparable, with 1.981(4) Å (O–Zn) for **3** and 1.975(2) (O1–Zn1) and 1.955(3) Å (O1–Zn2) for **4**. These distances are significantly longer than the sum of the covalent radii of oxygen and zinc (1.89 Å), but they are in the same range as the zinc–oxygen distances in various, mostly ionic, zinc silicates such as willemite (mean value 1.98 Å).[19] Consequently, the high stability of **3** and **4** under aqueous conditions can be understood by charge separation between the positively charged nitrogen atom and the negatively charged oxygen atom. It is well known that zwitterionic species strongly stabilize molecular structures, for example, in many biological systems (such as amino acids).[20] Analogously, the intramolecular zwitterionic effect present in **3** and **4** enables their synthesis and causes their extraordinary high stability in the presence of water.

Nevertheless, the following central question emerged: Are the shown structures of **3** and **4** maintained in solution? To answer this decisive question, we performed detailed NMR spectroscopic studies in solution and the solid state (all spectra are shown in the Supporting Information). In both cases, only one defined compound could be identified in solution, thus underlining the homogeneity of the bulk material, not only in the crystal (the homogeneity of the crystalline material was further confirmed by powder X-ray diffraction analysis). The ^{29}Si NMR spectra of **3** and **4** in solution showed one resonance signal each at $\delta = 4.7$ (**3**) and 6.3 ppm (**4**); these chemical shifts are in the same range as those in the solid-state spectra. NMR spectroscopic quantum chemical calculations [GAIO/B3LYP/IGLO-II//B3LYP/6-31+G(d)][17] on **3** and **4** confirmed the chemical shifts of the ^{29}Si signals in this range. Only one resonance was identified for **3** ($\delta = 3.7$ ppm) in the solid state, whereas two signals were located for **4** ($\delta = 6.6$ and 6.9 ppm). This observation is in agreement with the X-ray structural analysis of **4**, which possesses two molecules in the asymmetric unit, which results in two signals (the same is true for the ^{13}C and ^{15}N signals). The ^{13}C signals of both molecules have comparable values in the solid state and in solution. It is noteworthy that the ^{13}C signals of the piperidinomethyl groups are shifted downfield compared to the reactant **1**, which is a clear indication of protonated nitrogen atoms. A further interesting detail in the ^{1}H NMR spectra is that the $NCH_2\mathit{CH_2}CH_2$ (in **3**) and $N\mathit{CH_2}CH_2CH_2$ and $NCH_2CH_2\mathit{CH_2}$ (in **4**) groups each give different resonance signals, thus indicating the complexation of the zinc salt to the silicon fragment. Further NMR spectroscopic measurements of **3** and **4** in the presence of the free disiloxane **1** showed only the appearance of the resonance signals of the disiloxane, whereas the addition of the particular zinc salt had no effect on the spectra. Thus, the split proton resonance signals of **3** and **4** can only be attributed to the coordination of the zinc salt and not to the existence of additional compounds in solution (e.g. a hydrobromide or hydroacetate). Consequently, the NMR spectroscopy studies indicate that **3** and **4** have the same structures in solution as in the solid state.

For a better understanding of the ongoing processes of the presented reaction, one decisive question remains: How can the mechanism for the cleavage of the Si-O-Si bond in **1** and the formation of **3** and **4** be understood? To get a deeper insight, we performed DFT calculations[17] for a zinc-assisted hydrolysis of the model system $(H_2NCH_2)SiH_2OSiH_3$ (**C**, smaller model for **3**) via a pentacoordinated transition state (Figure 2). $ZnBr_2(H_2O)_2$ (**D**) was chosen as a possible starting compound for the zinc salt under aqueous conditions.

In the first step of the bond cleavage, the zinc compound **D** is coordinated by the aminomethyl sidearm of the disiloxane **C** under abstraction of one molecule of water. Additionally, the coordination of the oxygen atom of the Si-O-Si unit to the zinc center results in the approach of the reactive groups forming the starting system **E** of the subsequent cleavage reaction. The formation of **E** is favored by 40 kJ mol^{-1} compared to the uncoordinated starting molecules and thus should readily proceed at room temperature.

Further approach of the remaining water molecule to the silicon center of the model system **E** results in the formation of the pentacoordinated transition state **TS** with the leaving $O(ZnBr_2){-}SiR_3$ group arranged in axial position.[21] The elongation of the Si–O bond and its subsequent cleavage results in the formation of the experimentally observed Si-O-Zn unit of the zinc silanolate. This transition state showed a barrier of 103 kJ mol^{-1}, which can be overcome at room temperature. Unconsidered proton-transfer processes, which easily proceed under aqueous conditions, should further stabilize the produced formal silyl cation, thus resulting in a significant decrease of the energy barrier of these gas-phase calculations.

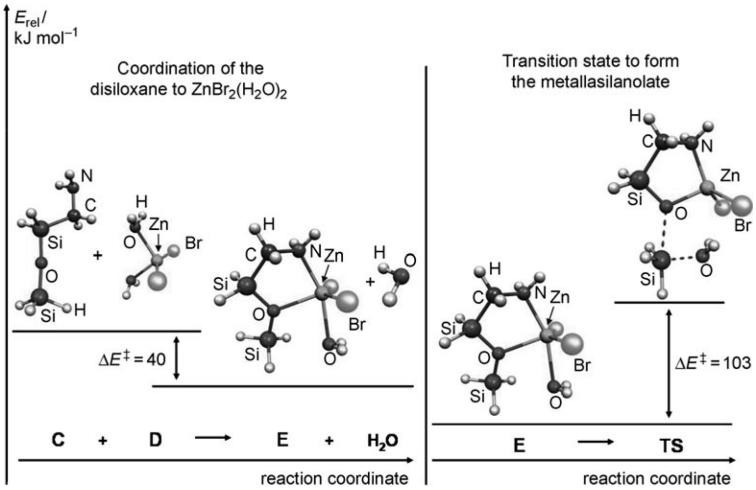

Figure 2. Coordination of the disiloxane $(H_2NCH_2)H_2SiOSiH_3$ (**C**) to $ZnBr_2(H_2O)_2$ (**D**) forming the starting compound **E** of the subsequent metallasilanolate building (left); transition state **TS** for the metallasilanolate formation (right).

The presented formation of water-stable molecular zinc silanolates by selective Si-O-Si bond cleavage in aminomethyl-functionalized disiloxanes with zinc(II) salts is a remarkable reaction for the understanding of siloxane chemistry. Not only are these hydrolysis-resistant metallasilanolates of transition metals the first molecular systems of their kind, but the reaction also demonstrates a simple way to cleave the strong Si-O-Si bond under mild conditions. The understanding of this basic process is further of special interest in materials science for artificial surface design as well as in many chemical processes, including silanes in the presence of water and amines. Moreover, the presented reaction suggests a starting point for a better chemical understanding of, for example, biological processes in nature, including siloxanes and metal-containing compounds.[22] At the moment we are varying amino ligands, substituents at silicon, and the metal salt to gain a deeper understanding of this reaction.

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[1] Examples can be found in all commonly used chemistry textbooks. Because of this high stability and low reactivity, silicones have a variety of applications, for example, as insulating compounds, as silicone polymers, as greases, or even as flexible catheters in medicine.

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