Silylated Sulfuric Acid: Preparation of a Tris(trimethylsilyl)oxosulfonium [(Me\(_3\)Si–O)\(_2\)SO\(^+\)] Salt

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Abstract: The chemistry of silylated sulfuric acid, O\({}_2\)S-(OsiMe\(_3\)), (T\(_3\)SO\(_4\)), has been studied in detail with the aim of synthesizing the formal autosilylation products of silylated sulfuric acid, [TSO\(_4\)]\(^-\) and [TTSO\(_4\)]\(^-\), in analogy to the known protonated species, [H\(_2\)SO\(_4\)]\(^+\) and [HSO\(_4\)]\(^-\). The synthesis of the [TTSO\(_4\)]\(^-\) ion only succeeds when a base, such as OPMe\(_3\), that forms a weakly coordinating cation upon silylation, is reacted with T\(_2\)SO\(_4\), resulting in the formation of [Me\(_3\)PO\(_4\)]\(^-\). T\(_3\)SO\(_4\) salts could be isolated starting from T\(_2\)SO\(_4\) in the reaction with [T–H] or [B(C\(_6\)F\(_5\))\(_4\)] or T\(_n\)CH\(_3\)Br\(_n\)H\(_{3n}\) when a weakly coordinating anion is used as counterion. All silylated compounds could be crystallized and structurally characterized.

Almost 50 years of silylum ion chemistry have shown that many applications for silylum ions in the field of catalysis have emerged from the pure basic research of the first decades. The development of silylum ion chemistry is closely related to carbocation chemistry, and it is no coincidence that silicon is also called the “kissing cousin” of carbon. And while we are on the subject of relationships: The [Me\(_3\)Si]+ ion (T\(_n\)+) can also be understood as the “big brother” of the proton (Scheme 1). Replacing H\(^+\) with T\(^+\) has several advantages. Substitution usually results in a thermodynamic and kinetic stabilization (through a larger steric demand) of the species. Furthermore, the neutral dimers H\(_2\) and T\(_2\) show a similar reactivity towards dihalogens (X\(_2\)), that is, they form HX and TX, respectively, in the reaction with X\(_2\), even with X = I\(_2\). Like a free proton that does not exist in the condensed phase, also the T\(^+\) ion is always coordinated either to a neutral solvent, anion or any other Lewis basic site in a molecular system. Therefore, it is not surprising that in analogy to the protonated species, such as [H–X–H]\(^+\) (X = halogen) pseudohalogen) and [H\(_n\)+E]\(^+\) (E = element of group 15 and 16) in aromatic systems, also the silylated species can be isolated in the presence of a weakly coordinating anion (Scheme 1).

Scheme 1. Similarities in the chemistry of an H\(^+\) and a [Me\(_3\)Si]+ ion.

chemistry of a protonated species is often similar to that of a silylated species (Scheme 1). For example, a classical neutralization reaction can also be formulated for the silylated species. Furthermore, the neutral dimers H\(_2\) and hexamethyldisilane T\(_2\), (Me\(_3\)Si\(_2\)), show a similar reaction towards dihalogens (X\(_2\)), that is, they form HX and TX, respectively, in the reaction with X\(_2\), even with X = I\(_2\). Like a free proton that does not exist in the condensed phase, also the T\(^+\) ion is always coordinated either to a neutral solvent, anion or any other Lewis basic site in a molecular system. Therefore, it is not surprising that in analogy to the protonated species, such as [H–X–H]\(^+\) (X = halogen) pseudohalogen) and [H\(_n\)+E]\(^+\) (E = element of group 15 and 16) in aromatic systems, also the silylated species can be isolated in the presence of a weakly coordinating anion (Scheme 1).

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[23] Like the protonated species, all these silylated cations should be regarded as strong Lewis acids that can be utilized as T\(^+\) transfer reagents.

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Interestingly, while the chemistry of \( \text{TiPO}_4 \) and its silylated cationic species \( [\text{TiPO}_4]^+ \) has been explored,\(^{37-39}\) nothing has been reported about a silylated cation of the type \( [\text{TiSO}_4]^+ \) to the best of our knowledge. However, protonated sulfuric acid, \( [\text{H}_2\text{SO}_4]^+ \), was isolated by Minkwitz et al. in a super acidic system (HF/SbF\(_5\)) as \([\text{SbF}_6\]) salt.\(^{40}\) As early as 1945, Patnode and Schmid reported on the synthesis of bis(trimethylsilyl)sulfate, \( \text{Ti}_2\text{SO}_4 \) (1), which they obtained in the reaction of \( \text{TiCl} \) with \( \text{H}_2\text{SO}_4 \) (Scheme 2, Eq. 1).\(^{41}\) Since then, \( \text{Ti}_2\text{SO}_4 \) has often been used as a silylation reagent.\(^{42-50}\)

Following our interest in \([\text{Me}_3\text{Si}]^+\) chemistry, we studied the similarities between sulfuric acid, \( \text{H}_2\text{SO}_4 \), and its silylated congener \( \text{Ti}_2\text{SO}_4 \). Especially, we were intrigued by the idea to synthesize the formal autosilylation products of \( 2\text{Ti}_2\text{SO}_4 \rightarrow [\text{Ti}_3\text{SO}_4]^+ + [\text{TSO}_4]^\text{−} \) in analogy to the autoprotolysis reaction of sulfuric acid: \( 2\text{H}_2\text{SO}_4 \rightarrow [\text{H}_3\text{SO}_4]^+ + [\text{HSO}_4]^\text{−} \).

We started this project with the synthesis of crystalline \( \text{Ti}_2\text{SO}_4 \) (1, \( \text{T} = \text{Me}_3\text{Si} \)) from \( \text{TiCl} \) and 95\% \( \text{H}_2\text{SO}_4 \) (Scheme 2, Eq. 1, Figure 1), which we obtained in 33\% yield after vacuum distillation at 100°C (10\(^{−3}\) mbar, see SI). With \( \text{Ti}_2\text{SO}_4 \) in hand, we reacted it with various bases, such as DMAP (4-(dimethylamino)pyridine), KO\(_t\text{Bu} \) and OPMe\(_3 \) to “neutralize” exactly one \( \text{T}^+ \) ion in order to generate \([\text{TSO}_4]^\text{−} \) (Scheme 2, Eq. 2–5). With KO\(_t\text{Bu} \) as base (independent of the stoichiometry), we always isolated \( \text{K}_2\text{SO}_4 \) and observed in solution the formation of the ether \( \text{Ti}_2\text{O} \_\text{tBu} \) as evidenced by \( ^1\text{H}, ^13\text{C} \) and \( ^29\text{Si} \) NMR studies. Also, the reaction of \( \text{Cs}_2\text{SO}_4 \) with \( \text{Ti}_2\text{SO}_4 \) in toluene in the presence of \( ^{18}\text{Crown}-6 \) (to increase the solubility) did not lead to the formation of a \([\text{TSO}_4]^\text{−} \) salt, but the pyrosulfate \([\text{Cs}_2\text{O} \cdot ^{18}\text{Crown}-6\text{S}_2\text{O}_7]\) (X-ray, see SI) and \( \text{Ti}_2\text{O} \_\text{tBu} \) were produced in a condensation reaction. The reaction with DMAP was carried out in 2:1, 1:1 and 1:2 ratios in CH\(_2\text{Cl}_2 \) and followed by \( ^1\text{H}, ^2\text{O} \) and \( ^17\text{O} \) NMR spectroscopy (Figure S1a–c).

In the \( ^1\text{H} \) NMR spectra, a strong broadening and shift of the two DMAP resonances (\( \delta[^{14}\text{N}] = 132.4 \) and \( 104.7 \) ppm) were observed, increasing with increasing amount of \( \text{Ti}_2\text{SO}_4 \). The two resonances (153 and 174 ppm) in the \( ^17\text{O} \) NMR spectra are shifted to higher field with increasing amount of \( \text{Ti}_2\text{SO}_4 \) and the broad resonance at 153 ppm even vanishes. Interestingly, in the \( ^29\text{Si} \) NMR studies, we always observed only one resonance strongly shifted and not resolved compared to that of pure \( \text{Ti}_2\text{SO}_4 \) (pure \( \text{Ti}_2\text{SO}_4: \delta[^{29}\text{Si}] = 33.6 \) ppm, cf. \( \text{Ti}_2\text{SO}_4/\text{DMAP} \) ratio: 2:1 29.7, 1:1 27.7 and 1:2 24.4 ppm, Figure S1c).

Therefore, we assume a highly dynamic DMAP/\( \text{Ti}_2\text{SO}_4 \) system from which we could only isolate crystalline \([\text{DMAP} \cdot \text{Ti}_2\text{SO}_4]\) (X-ray, see SI). To avoid the problems as discussed before, we tried the slightly weaker base OPMe\(_3 \).

**Scheme 2.** Synthesis of silylated sulfuric acid species \( \text{Ti}_2\text{SO}_4 \) (1), \([\text{TSO}_4]^\text{−} \) (2) and \([\text{Ti}_3\text{SO}_4]^+ \) (3\(^\text{+}\)). Bottom: Lewis representations of 1, 2\(^\text{−}\) and 3\(^\text{+}\) (\( \text{T} = \text{Me}_3\text{Si} \)).
which then, indeed, led to success. When exactly one equivalent of OPMe3 is reacted with one equivalent of pure T2SO4 in toluene, a crystalline trimethylsilylsulfate salt, [Me3P—O—T][T2SO4], is obtained after concentration of the solution in 77% yield (Scheme 2, Eq. 5, Figure 1). Only on one occasion could we isolate from such a reaction mixture one crystal of a side product, which was found to be the doubly desilylated pyrosulfate, [Me3PO—T][TSO2] (X-ray, see SI).

The synthesis of a tri-(trimethylsiloxy)sulfoxonium [T3SO4]+ salt is achieved by reacting [T—H—T][B(C6F5)4] with silylated sulfuric acid in an 1:1 ratio in toluene. Attempts to crystallize the salt [T3SO4][B(C6F5)4] failed both at room temperature and at lower temperatures such as 5°C and -20°C. Attempts to remove the entire solvent in vacuum (1–10-3 mbar) at 60°C resulted in the decomposition of the salt, which can be observed by the formation of a black insoluble residue.[12] The addition of non-polar solvents such as n-hexane to precipitate the salt also failed. Changing the solvent from toluene to 1,2-dichlorobenzene was also unsuccessful. For this reason, we changed the counterion, as we assumed that the decomposition was initiated by a C–F activation at the boron anion. It is known that carboxates are much more chemically robust compared to the [B(C6F5)4]- anion.[4,12,51] Indeed, when [Me3Si][CHB11Br6H6] is reacted with T2SO4 in toluene, colorless crystals of the desired [T3SO4]−-salt are obtained in 68% yield after 30 min ultrasound treatment at 60°C and recrystallization (Scheme 2, Eq. 7). The formation of the [T3SO4]−-ion with [CHB11Br6H6]− as counterion was unequivocally proven by single-crystal X-ray studies (Figure 1, bottom). It should be noted that although we were able to generate the formal autosilylation products of T2SO4 by separate synthesis routes, dissociation into [T3SO4]+ and [TSO4]− was not observed for T2SO4, but [T3SO4]+ and [TSO4]− react to give two T2SO4 molecules immediately.

All three silylated sulfuric acid species [T3SO4]+, T2SO4, and [TSO4]− were studied by different 13C, 17O, 29Si, and 31P NMR techniques in solution (see SI) as well as IR/Raman spectroscopy. As expected, the 31S resonance of [T3SO4]− (δ[31S]=−54.1) was shifted by 22.2 ppm to lower field compared to T2SO4 (δ[31S]=31.9), while a small high-field shift of 3.9 ppm was observed for [TSO4]− (δ[31S]=28.0, cf. 32 [Me-CN-SiMe3])64 35.6 [T2PO4]−[102] and computed 385 ppm for naked [Me3Si]3+[12,54] see SI, Table S3). As the 31S NMR chemical shifts can be used as an indicator for the Si-wire silicon ion character (and the deviation from planarity, see below),[32–54] that is, for the strength of the [Me3Si]+ interaction with the solvent T2SO4, it can be assumed that T2SO4 is a rather strong coordinating solvent utilizing the scale by Cremer et al. (−50 to 90 ppm, cf. 90–190 weakly coordinating, 200–370 weakly interacting, 370–385 noncoordinating solvents and 385 ppm gas phase).[53] Crystals of all three silylated sulfuric acid species are moisture sensitive but thermally considerably stable with defined melting points (Table 1: T2SO4: 48, [Me3PO-T]-T2SO4: 120°C, and [T3SO4][CHB11Br6H6]: 114°C). Interestingly, while [T3SO4][B(C6F5)4] begins to decompose upon concentration in solution at ambient temperatures, [T2SO4][CHB11Br6H6] can be isolated in solution and even melts without decomposition, while decomposition occurs only above 160°C.

Crystallization of all three silylated sulfuric acid species from either n-pentane (T2SO4) or toluene ([Me3PO-T]-T2SO4) and [T3SO4][CHB11Br6H6]) yielded colorless crystals (Figure 1). T2SO4 crystallized in the monoclinic space group C2/c, while [Me3POT][T2SO4] and [T3SO4][CHB11Br6H6] crystallized in the orthorhombic space group Pcbca and P212121, respectively. For all three compounds, there are only relatively weak intermolecular O···H–C interactions (Figures S2–S4, SI), but these are found in each case for the non-silylated O atom of the SO4 core within the silylated species. That is, for [T3SO4]+ with three non-silylated O atoms one finds such interactions with three neighboring [Me3POT]− cations (Figure S3), for T2SO4 correspondingly with two neighboring T2SO4 molecules (Figure S2) and in [T2SO4]− exactly one such interaction (Figure S4), however, with one adjacent cation. In the latter case, interestingly, weak Br−Si−H–Ccation interactions are added. Likewise, weak Br−Si−H–Ccation interactions are found between the H atom attached to the C atom of one carbonate anion and the Br atom in para-position to the C−H bond atom of an adjacent second carbonate anion (Figure S4). This leads to a zig-zag chain of carbonate anions in the solid. The [T3SO4]− cations coordinate with this chain via the above-mentioned weak Br−Si−H–Ccation interactions.

As depicted in Figure 1, the central SO4 core always adopts a highly distorted tetrahedral geometry, with two different S–O bond lengths (Table 1). In accord with electrostatic consideration, with increasing number of Me3Si groups, the Si–O bond lengths are elongated along [T3SO4]< T2SO4 < [T2SO4]−. Similarly, the Si–O–S angles (127.5 to 134.2° (averaged)) and the sum of the angles around the Si atoms (from 332 to 344°) increase, indicating the largest silylum ion character in [T2SO4]+ > T2SO4 > [T3SO4]−.

Table 1: Selected bond lengths [Å] and angles [°] melting points [°C], NMR data [ppm], charge (transfer) [e], and trimethylsilyl affinities (TMSA) [kcal mol−1].

|            | [T3SO4] | T2SO4 | [T2SO4]− |
|------------|---------|-------|---------|
| S−O90      | 1.422   | 1.399 | 1.410   |
| S−O90 [a]  | 1.588   | 1.400 | 1.541   |
| S−O        | 1.683   | 1.731 | 1.761   |
| O−S−O90    | 110.6   | 118.1 |         |
| O−S−O90 [a]| 104.2   | 103.3 | 111.3   |
| qSi         | 28.0    | 31.9  | 54.1    |
| qSi [b]    | 2.572   | 2.639 | 2.702   |
| ΔqSi [c]   | 0.418   | 0.650 | 0.784   |
| TMSA [d]   | 215.9   | 82.9  | 55.5    |

[a] Corresponds to δ(S–O) with O only bound to S. [b] Corresponds to δ(S–O) with O in a S–O–SiMe3 unit. [c] Cf. –2 in [SO4]2−. [d] Trimethylsilyl affinity (TMSA) of Ag+ is defined as the negative of the reaction enthalpy ΔHfAg+ in kcal mol−1 at 298.15 K for the reaction Ag+ + T3SO4− → [AT]−+ [Ag]+ that is the TMSA values given is for the conjugated acid–base pair AgH+/[AT]+.
To get some insight into the charge transfer upon silylation and desilylation, respectively, we computed the partial net charges of the elements and the [Me₃Si] as well as [SO₄] moieties within all three silylated species (Table 1 and S6) at the pbe1pbe/aug-cc-pVDZ level of theory. Two interesting features can be derived from these data: (i) The atomic charges do not change much upon increasing silylation degree. For example, the partial charge at the central S atom only slightly increases along [SO₄]²⁻, [TSO₄]⁻, [T₂SO₄]⁻, [T₃SO₄]⁻, with the overall charge changes by ΔQ = 3e. This moderate change in the atomic charges of sulfur can be ascribed to delocalization over the entire molecular entity. (ii) The formal charge in accord with the computed TMSA value.

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Conflict of interest

The authors declare no conflict of interest.

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