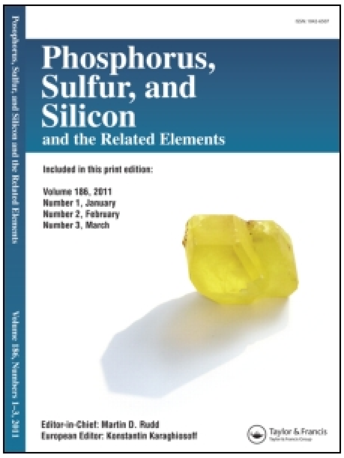

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GAS-PHASE GENERATION OF SILICON OXYSULFIDE BY FLASH VACUUM THERMOLYSIS

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The flash vacuum thermolysis (700–1000°C) of allylthiodi-*tert*-butoxysilane (**2**), propargylthiodi-*tert*-butoxysilane (**3**) and 1,1,3,3-tetra-*tert*-butoxycyclodisilthiane (**4**) has been investigated. In the case of **3** and **4**, the β-elimination of *tert*-butanol and isobutene from the *tert*-butoxy groups was accompanied by a retro-ene reaction or dedimerization, respectively, leading to transient silicon oxysulfide (OSiS, **1**), characterized by low-temperature IR and, in the gas-phase, by mass spectrometry. Silicon monoxide and monosulfide were also identified in these thermolyses by millimeter-wave spectrometry.

Keywords: Flash vacuum thermolysis; gas-phase reactions; silicon-heteroatom double bond; silicon oxysulfide

INTRODUCTION

The transient molecule silicon oxysulfide (OSiS, **1**) has been until now generated by reaction of SiS with atomic oxygen and characterized by IR in an Ar matrix,[1] its electronic structure has also been determined.[2] Compound **1** is a possible interstellar or circumstellar species by analogy

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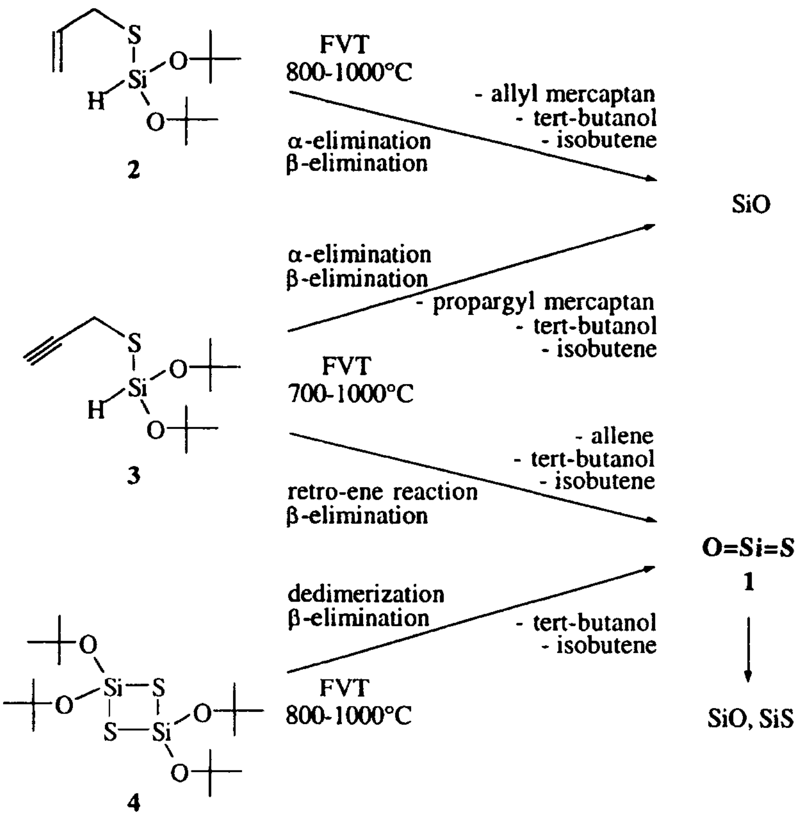
* Corresponding Author.

with its counterpart carbon oxysulfide,[3] and thus its gas-phase spectrometric determination should be of particular interest.

In the context of our work aimed at the generation of reactive silicon-sulfur double-bonded species by flash vacuum thermolysis (FVT),[4,5] we have investigated the FVT of compounds **2**–**4** as possible gas-phase precursors of silicon oxysulfide **1** (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

Allylthio- and propargylthiodi-*tert*-butoxysilanes (**2** and **3**) have been prepared from trichlorosilane by reaction of *tert*-butanol (2 equiv.) in the presence of pyridine to give di-*tert*-butoxychlorosilane, which was treated with allyl or propargyl mercaptan and triethylamine (see experimental). Cyclodisilthiane **4** was previously described.[6] Compounds containing the stuctural fragment O-Si-O have been shown to be generators of silanones upon thermolysis[7] and precursors **2–4** were thus expected to give **1** upon FVT by β-elimination of *tert*-butanol and isobutene, accompanied by retro-ene reaction (from **2** and **3**) or dedimerization (from **4**).

The FVT results are summarized in Scheme 1. Between 800 and 1000°C, allylthiosilane **2** gave only, as stable FVT products characterized by NMR, allyl mercaptan, *tert*-butanol and isobutene. The absence of propene showed obviously that the expected retro-ene reaction was here replaced by an α-elimination of allyl mercaptan, precluding any possibility to obtain the target molecule **1**, and the FVT of **2** was no longer pursued.

The retro-ene reaction should be made easier by replacing the allyl moiety in **2** by a propargyl one[8] and, in fact, the FVT of propargylthiosilane **3**, carried out between 700 and 1000°C, showed, beside *tert*-butanol and isobutene, the formation of propargyl mercaptan (resulting from the above α-elimination) and allene (from the expected retro-ene reaction). The propargyl mercaptan/allene ratio was of *ca* 50:50 at 700°C and increased towards allene with the FVT temperature. The presence of silicon oxysulfide **1** appeared to be effective on the following grounds. A transient band at 1280 cm^{-1}, vanishing rapidly above −130°C, was observed at -196°C in the solid-state IR spectrum of the FVT products of **3**, corresponding likely to the 2ν(Si=S) vibration of **1** (this band has been reported at 1290.2 cm^{-1}in matrix[1]). A second band at *ca* 1260 cm^{-1} may correspond to that described at 1265.4 cm^{-1} in matrix for the ν(Si=O) of **1**[1] but its disappearance, partly masked by the absorption of a stable by-product at 1245 cm^{-1}, was less obvious. Also, a new peak at m/z 76 ($M^{+\cdot}$ OSiS) appeared, increasingly with the temperature, in the FVT/MS coupling experiments.

These results were confirmed by the FVT of cyclodisilthiane **4** between 800 and 1000°C, showing also clearly the IR and MS signals belonging to **1** beside *tert*-butanol and isobutene. A reliable yield evaluation was not possible, due to the high instability and short life-time of **1**. Its concentration in the FVT products remained rather low in the solid-state IR spectra (*e.g.*, FVT of **3** at 750°C: 76 % transmittance at 1280 cm^{-1} for **1**, 53 % at 1955 cm^{-1} for allene) as well as in the gas-phase mass ones (*e.g.*, FVT of **4** at 1000°C: 3.5 % of the total ionization current for the $M^{+\cdot}$ peak of **1** at m/z 76).

It has not been possible to characterize definitely the presence of **1** when coupling the FVT of **3** and **4** with millimeter-wave spectrometry (MWS). In both cases, only SiO (J:9→10 at 434120.2 MHz)[9] and SiS (J:23→24 at 435387.8 MHz)[10] were identified as reactive silicon species. The high concentration, relatively to that of **1**, of *tert*-butanol and isobutene generated in these thermolyses precluded the complete analysis of the low-intensity peaks belonging possibly to **1** in the spectrum.

EXPERIMENTAL

FVT experiments were performed in an empty quartz oven (1 10 cm × i.d. 0.9 cm for IR and MS, 3 × 0.5 cm for MWS) under *ca* 10^{-5} hPa. In view to determine the IR spectra, the oven was coupled with an IR cryostat allowing to trap the FVT products of **3** or **4** (*ca* 25 mg) on a NaCl plate cooled at −196°C and to record immediately the spectra at this temperature and upon warming. For the MS experiments, the oven was directly fitted on the mass spectrometer, the spectra being continuously recorded while increasing the FVT temperature. The used spectrometers were Bruker AC 250 (NMR), Jeol JMS D300 (MS) and Perkin-Elmer PE 1420 (IR). The MWS apparatus and FVT/MWS coupling were the same as already reported.[4]

Allylthiodi-tert-butoxysilane (2) and propargylthiodi-tert-butoxysilane (3).

A solution of trichlorosilane (13.54 g, 100 mmol) in *n*-heptane (200 ml) was cooled at 0°C under nitrogen atmosphere. Pyridine (16.61 g, 210 mmol) and *tert*-butanol (14.82 g, 200 mmol) were added slowly. After heating 3 h at reflux, filtration on Celite and distillation of solvent, *di-tert-butoxychlorosilane* was distilled under vacuum, it polymerized quickly and should be used immediately in the following step [yield 71 %; b.p.(20 hPa): 60–62°C; IR (film): 2227 cm^{-1} (SiH); NMR ($CDCl_3$): $\delta^1H = 5.11$ (s, 1 H) and 1.38 ppm (s, 18 H); $\delta^{13}C$ 76.1 and 31.5 ppm].

Di-*tert*-butoxychlorosilane (1.85 g, 8.79 mmol), triethylamine (0.89 g, 8.79 mmol), and allyl mercaptan (commercial, 8.79 mmol) or propargyl mercaptan (prepared,[11] 8.79 mmol), were diluted in anhydrous ether

(10 ml) and heated at reflux until completion of the reaction (1–4 d). After filtration and removal of solvent, the labile thiosilanes **2** and **3** were purified by bulb-to-bulb distillation under vacuum.

2 (yield 56 %); HRMS: m/z 248.1242 ($M^{+\cdot}$, calcd $C_{11}H_{24}O_2SSi$ 248.12649); IR (film): 3087 and 3060 ($CH=CH_2$), 2200 (SiH), 1643 cm^{-1} (C=C); NMR ($CDCl_3$) : δ^1H = 5.90 (ddt, 1 H, J = 16.9, 9.8 and 6.9 Hz), 5.23 (s, 1 H), 5.18 (≈dq, 1 H, J = 16.9 and 1.3 Hz), 4.53 (≈dq, 1 H, J = 9.8 and 1.3 Hz), 3.24 (≈dt, 2 H, J = 6.9 and 1.3 Hz), 1.37 ppm (s, 18 H); $\delta^{13}C$ = 136.5, 116.0, 75.1, 31.7, 29.2 ppm.

3 (yield 73 %); HRMS: m/z 246.1144 ($M^{+\cdot}$, calcd $C_{11}H_{22}O_2SSi$ 246.11085); IR (film): 3320 (C≡CH), 2187 cm^{-1} (SiH and C≡C); NMR ($CDCl_3$) : δ^1H = 5.29 (s, 1 H), 3.30 (d, 2 H, J = 2.5 Hz), 2.22 (t, 1 H, J = 2.5 Hz), 1.37 (s, 18 H); $\delta^{13}C$ = 81.7, 75.4, 70.7, 31.8, 13.7 ppm.

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