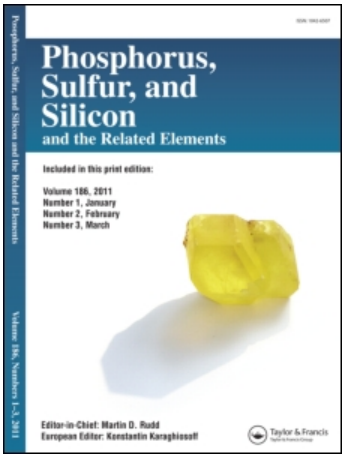

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Mohmand, Smamsher and Bock, Hans(1983) 'GAS-PHASE REACTIONS 38[1]. Temperature-Controlled Di-and Trimerisation of Thioacetaldehyde', Phosphorus, Sulfur, and Silicon and the Related Elements, 14: 2, 185 — 188
To link to this Article: DOI: 10.1080/03086648308075941
URL: http://dx.doi.org/10.1080/03086648308075941

Phosphorus and Sulfur, 1983, Vol. 14, pp. 185–188
0308-664X/83/1402-0185/$18.50/0

GAS-PHASE REACTIONS 38[1].

Temperature-Controlled Di- and Trimerisation of Thioacetaldehyde

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(*Received April 20, 1982*)

The best method so far to prepare thioacetaldehyde proves to be the gas-phase pyrolysis of ethylallylsulfide. Trapping of the monomer at 140 K yields the dimer, 2,4-dimethyl-1,3-dithietane, and at 190 K the trimer, 2,4,6-trimethyl-1,3,5-trithiane.

Die bislang beste Methode zur Darstellung von Thioacetaldehyd ist die Gasphasen-Pyrolyse von Ethylallylsulfid. Ausfrieren des Monomeren bei 140 K führt zum Dimeren, 2,4-Dimethyl-1,3-dithietan, und bei 190 K zum Trimeren, 2,4,6-Trimethyl-1,3,5-trithian.

Among the numerous methods reported to generate short-lived thiocarbonyl derivatives $R_2C{=}S$ in the gas-phase,[2-6] the thermal decomposition of allylsulfides (Figure 1) has many advantages:[1-5] usually, the starting material is easy to synthesize, the energetically favored 'leaving molecule' propene—or, if CH bonds in α position to sulfur are missing, allyl radical[1,7]—provides a clean low-temperature decomposition channel, and from the condensed pyrolysis mixture, propene[2-4] or hexadiene-1,5[1,7] can be removed by fractionate evaporation. As a typical example, the PE spectroscopically guided generation and isolation of pink thioacetaldehyde is presented (Figure 1).

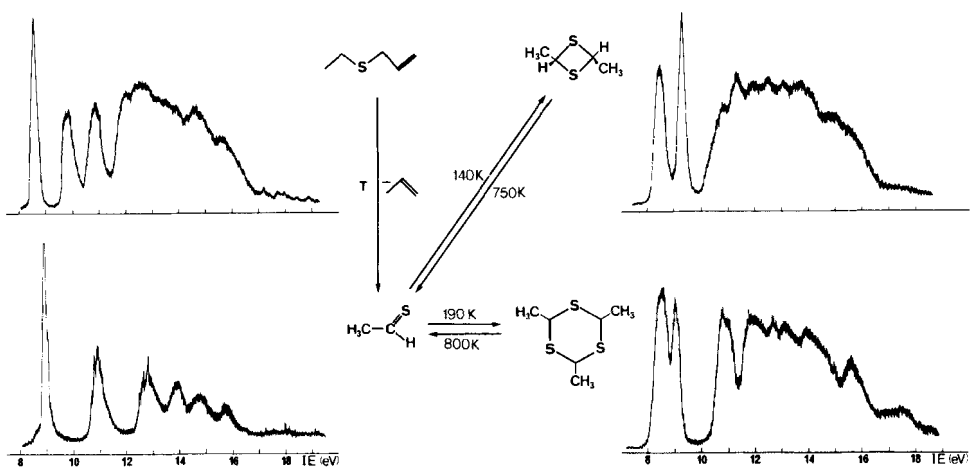

FIGURE 1 Helium (I) photoelectron spectra of ethyl allyl sulfide, of thioacetaldehyde and of its dimer, 2,4-dimethyl-1,3-dithietane,[4] as well as of its trimer, 2,4,6-trimethyl-1,3,5-trithiane[5].

The reaction diagram (Figure 1) can be substantiated straightforwardly by qualitatively rationalizing the PE spectroscopic molecular fingerprints especially in the respective low energy regions:[9,10] Among the 12 p-type ionizations of ethyl allyl sulfide, $C_5H_{10}S$, to be found within the He(I) measurement region,[9,10] the 3 separated bands at 8.6, 9.8 and 10.8 eV are assigned to the radical cation states with predominant contributions of the π-type sulfur lone pair n_S^{π}, the allyl π_{CC} system and the in-plane sulfur lone pair n_S^{σ}.[4,11] Splitting off the allylic π system as propene to form thioacetaldehyde changes the low-energy PE band pattern into the needle-like in-plane lone pair n_S of the thiocarbonyl group,[4,11] and its π_{CS} system. Dimerisation leads to 2 sulfur lone pair n_S bands at 8.5 and 9.3 eV in the intensity ratio 1:1, and trimerisation to 3 n_S^{π}-type ionizations collapsing into 2 bands in the intensity ratio 2:1 at 8.6 and 9.0 eV.[8]

Pure thiacetaldehyde is obtained on heating the dimer to 750 K.[4,12]

The trimer needs some 50 K more to depolymerize,[13] indicating already its higher thermal stability. The highest oven temperature, 820 K, has to be applied to split off propene from the ethyl allyl sulfide and, consequently, small amounts of ethylene are observed PE spectroscopically which are formed presumably via population of the energetically close next decomposition channel:

$$H_3C-C(=S)-H \xrightarrow{820\ K} H_2C{=}CH_2 + \tfrac{1}{8}\,S_8 \qquad (1)$$

Attempts to isolate the thiocarbonyl compounds in cooling traps[1] revealed: using an isopentene bath at 140 K (by occasionally stirring with liquid nitrogen, cf. experimental part) yields a yellow oil, which can be purified by high vacuum-line distillation and characterized by PE spectroscopy (Figure 1). With an ethanol bath cooled to 190 K a viscous material is obtained, which on short-way distillation becomes cristalline. The product can be further purified by sublimation and identified by its PE spectrum (Figure 1). Its ^{1}H-NMR spectral analysis compared to literature[14] suggests a conformer ratio equatorial:axial = 44:56.

The thioacetaldehyde dimerisation is in contrast to the behaviour of both analogous derivatives observed during trapping experiments: thioformaldehyde $H_2C{=}S$ yielding only the insoluble polymer, (H_2CS), and thioacetone $(H_3C)_2C{=}S$ being obtained so far only as the trimer, $(CH_3C)_2CS)_3$. Obviously, the formation of the thioacetalhyde dimer, 2,4-dimethyl-1,3-dithietane, must be determined kinetically, while the thermodynamically more stable trimer—as judged by its higher gas-phase decomposition temperature—can be isolated only on cooling to less low temperature.

Applying matrix isolation techniques i.e. pyrolysis in an argon flow system and deposition at about 10 K in argon onto a BaF_2 disc allows to register the vibronic spectrum[15] of pink[15] monomeric thioacetaldehyde, displaying the thiocarbonyl stretching frequency $\nu_{C=S} = 1147\ cm^{-1}$.

EXPERIMENTAL

Material and Apparatus

Ethylallylsulfide is prepared according to Ref. 16 from ethylmercaptane, sodium methylate and allylbromide; $Kp^{720} = 115$–$116°C$. Pyrolyses are carried out in a quartz tube (length 35 cm, diameter 1.4 cm) connected to an U-shape condensation

trap[2] and via teflon valves to the PE spectrometer at one end and to the storage trap at the other end. The compounds are evaporated from the storage trap at 320 K; the quartz tube is heated in a temperature-controlled oven of 30 cm length. The individual experiments were carried out as follows: After recording the PE spectrum of the starting material, the temperature of the oven was raised in 50 K steps until the ionization pattern began to change. Subsequently, the decomposition temperature was optimized within a ±20 K interval.[2] The photoelectron spectra were recorded on a modified Perkin-Elmer PE 16 spectrometer and calibrated with the Xenon ($^2P_{3/2}$) and Argon ($^2P_{3/2}$) ionization lines. Resolution was of the order of 30 meV throughout the experiments. All mass spectra have been registered connecting the above apparatus to the heated inlet system of a Varian MAT CH 7 instrument.

Thioacetaldehyde Dimerization and Trimerization

The pyrolysis of ethylallylsulfide has been carried out under 0.15 mbar pressure at 820 K oven temperature. The gas flow, pumped by the diffusion pump of the PE spectrometer passes the U-shape condensation trap cooled to ~140 K using an isobutane bath which is occasionally stirred with liquid nitrogen. After ~10 hours collecting material, the cooling bath was allowed to warm up to room temperature thereby evaporating small amounts of unpyrolyzed starting material together with the propene evolved. The remaining viscous yellow oil is purified by distillation under 10^{-3} mbar reduced pressure. 2,4-Dimethyl-1,3-dithietane ($C_4H_8S_2$, m.w. 120.19), m/e = 120 (fragmentation peaks: 60, 59).

2,4,6-Trimethyl-1,3,5-trithiane ($C_6H_{12}S_3$, m.w. 180.29), cool-trapped at 190 K (ethanol, occasionally stirred with liquid nitrogen). Purification by short-way distillation and repeated sublimation of the obtained crystals. m/e = 180 (main fragmentation peaks: 120, 60, 59).

ACKNOWLEDGMENT

The research project has been supported by Land Hessen, Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

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