Unstable Intermediates in the Gas-phase.[1] Formation of Thioformaldehyde from Trithiolan

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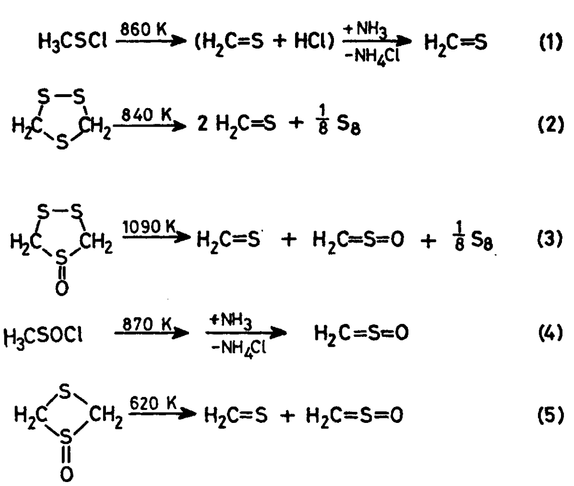
Summary Pure thioformaldehyde $H_2C{=}S$ in the gas phase is most conveniently prepared by heating 1,2,4-trithiolan to 840 K; the corresponding trithiolan 4-oxide yields a mixture of $H_2C{=}S$ and $H_2C{=}S{=}O$.

THE molecule $H_2C{=}S$ which has been detected in interstellar space[2] has also been generated on earth in reaction mixtures[3,4] and recently it has been prepared pure[5] by heating methanesulphenyl chloride to 860 K and removing the HCl eliminated by injection of ammonia [reaction (1)]. In general, gas-phase reactions like reaction (1) are most conveniently optimized by using a photoelectron spectrometer for analysis; with a 0·1 g sample and a pressure of *ca.* 13 Pa the temperature range 300—1500 K can be investigated in 50 K steps in a single day.[6]‡



We have studied a range of potential precursors for preparing thioformaldehyde and have found that pyrolysis of 1,2,4-trithiolan provides the best route; at 840 K it decomposes quantitatively (Figure: A) to yield pure thioformaldehyde [reaction (2)] and sulphur which is deposited outside the oven zone.

Analogously, 1,2,4-trithiolan 4-oxide[8] produces at 1090 K a gaseous mixture of thioformaldehyde and thioformaldehyde oxide§ [Figure: B; reaction (3)], as shown by superposition of the p.e. spectra of both thioformaldehyde (Figure: A) and pure thioformaldehyde oxide (Figure: C) prepared by pyrolysis of methanesulphinyl chloride with subsequent NH_3 injection [reaction (4)]. Further confirmation was supplied by the thermolysis of dithietan *S*-oxide [reaction (5)],[4] p.e. spectroscopic analysis of which proves that the gaseous products are identical to those of reaction (3).

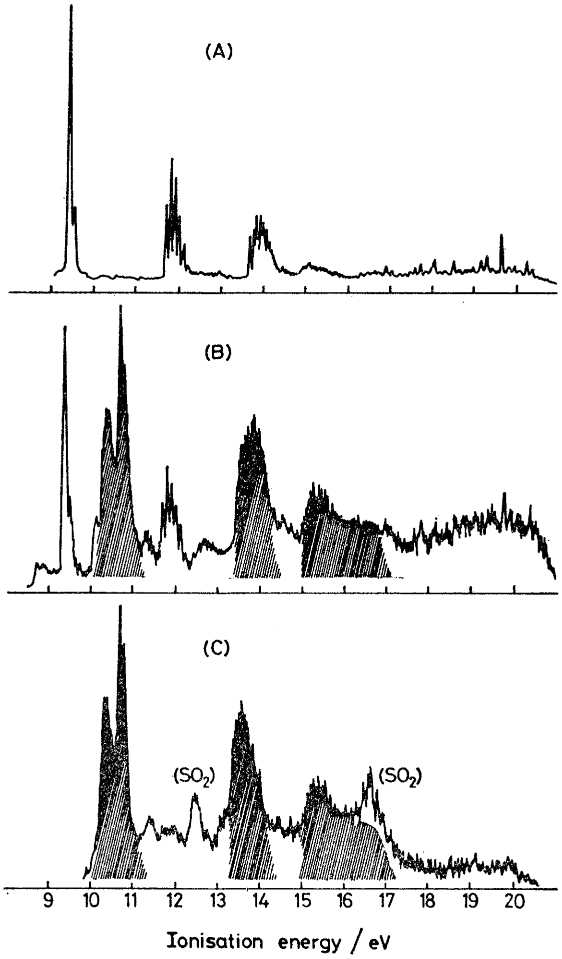


FIGURE. P.e. spectra of the gaseous pyrolysis products from (A) trithiolan (giving $H_2C{=}S$), (B) trithiolan *S*-oxide [giving $H_2C{=}S$ + $H_2C{=}S{=}O$ (shaded peaks)], and (C) methanesulphinyl chloride after removal of HCl with NH_3 (giving $H_2C{=}S{=}O$, contaminated with SO_2 as pyrolysis by-product).

(*Received*, 22*nd December* 1976; *Com.* 1396.)

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‡ An alternative useful optimization procedure (ref. 7) involves the use of a pyrolysis system coupled directly to a mass spectrometer operating at low eV.

§ The formation of CH_2S and CH_2SO was independently established *via* microwave spectroscopy (ref. 7). We thank Professor R. E. Penn for these experiments.

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[4] E. Block, H. Bock, S. Mohmand, P. Rosmus, and B. Solouki, *Angew Chem.*, 1976, **88**, 380; *Angew. Chem. Internat. Edn.*, 1976, **15**, 383.

[5] B. Solouki, P. Rosmus, and H. Bock, *J. Amer. Chem. Soc.*, 1976, **98**, 6054.

[6] *Cf. e.g.* H. Bock and S. Mohmand, *Angew. Chem.*, 1977, **89**, 105; *Angew. Chem. Internat. Edn.*, 1977, **16**, 104.

[7] E. Block, R. E. Penn, R. J. Olsen, and P. F. Sherwin, *J. Amer. Chem. Soc.*, 1976, **98**, 1264.

[8] We have found that this antibacterial component of the red alga *Chondria californica* (S. J. Wratten and D. J. Faulkner, *J. Org. Chem.*, 1976, **41**, 2465) can be conveniently prepared in pure form in 60% yield by oxidation at -30 °C of a tetrahydrofuran–Bu^{t}OH solution of 1,2,4-trithiolan with 6% H_2O_2 in Bu^{t}OH in the presence of a catalytic quantity of V_2O_5 [F. E. Hardy, P. R. H. Speakman, and P. Rubson, *J. Chem. Soc.* (*C*), 1969, 2334].

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