

# Monitoring Chemical Reactions by Variable Temperature Photoelectron Spectroscopy. A New Thermal Reaction \*

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Variable temperature photoelectron (vtpe) spectroscopy is applied to ethane-1,2-dithiol. Thereby it is shown that this molecule thermally reacts to thiirane and hydrogen sulphide at the very low pressure applied in the pe experiment.

In this communication we point at the potentiality of variable temperature photoelectron (vtpe) spectroscopy<sup>1</sup> in exploiting gas-phase chemical reactions and even in detecting hitherto unknown reaction paths as the following example demonstrates.

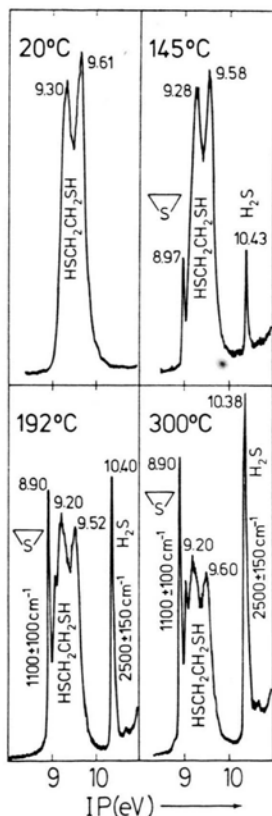


Fig. 1. Sulphur lone pair ionization region of the photoelectron spectra of ethane-1,2-dithiol at four selected temperatures (20 °C, 145 °C, 192 °C, and 300 °C). The spectra at elevated temperatures exhibit additional bands arising from thiirane and hydrogen sulphide. The numbers associated with each band are vertical ionization potentials in eV. The numbers arranged vertically denote measured vibrational spacings.

Figure 1 shows the photoelectron (pe) spectra of ethane-1,2-dithiol at four selected temperatures (20 °C, 145 °C, 192 °C, and 300 °C)\*\*. The spectrum at room temperature contains two bands in the sulphur lone pair region. This two-band structure indicates that the lone pair ionizations in the anti and gauche rotamers of this molecule occur at nearly the same energy<sup>+,\*\*</sup>. Very interestingly, the spectra at higher temperatures exhibit two new sharp bands. Their intensity grows with increasing temperature. The comparison of these bands with respect to their location and vibrational structure (i.e. the spacing and Franck-Condon-envelopes) with the lone pair ionization bands in thiirane<sup>2</sup> and hydrogen sulphide<sup>3</sup> displayed in Fig. 2 unambiguously reveals

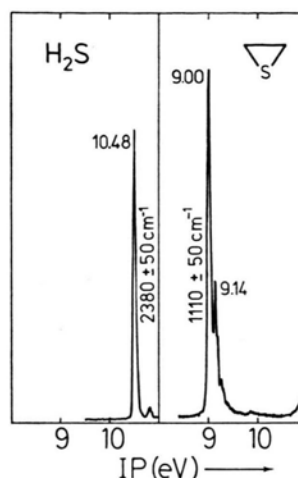
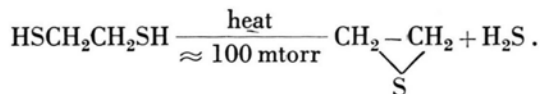


Fig. 2. Sulphur lone pair ionization regions of the photoelectron spectra of thiirane and hydrogen sulphide at room temperature. The horizontal and vertical numbers associated with the bands are vertical ionization potentials and vibrational spacings, respectively.

that one band is due to the presence of thiirane and the other to hydrogen sulphide in the gas stream. Moreover both components grow with rising temperature at the expense of the starting material. From these results we must conclude that at the very low pressure (about 120 mtorr) applied in the pe experiment ethane-1,2-dithiol thermally reacts to thiirane and hydrogen sulphide according to



This gas-phase reaction has not been previously described.

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- \* Part 62 of: Theory and Application of Photoelectron Spectroscopy. Part 61: W. Schäfer and A. Schweig, submitted for publication.
- \*\* The spectra were recorded on a Perkin-Elmer PS-16 spectrometer equipped with a heated target chamber. Heating is accomplished by a bifilar stainless steel electric heater and the sample temperature is measured by a thermocouple inserted in the gas stream. Calibration was made using an acetylene/nitrogen mixture.
- + The relative abundances of anti and gauche rotamers were determined to be 62% and 38% at 70 °C by electron diffraction (I. Hargittai and G. Schulz, Chem. Commun., 323 [1972]) and 58% and 42% at room temperature (25 °C) from vibrational analysis (M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, Bull. Chem. Soc. Japan **38**, 1734 [1965]).
- ++ The conclusion is supported by CNDO/S (K. W. Schulte and A. Schweig, Theoret. Chim. Acta **33**, 19 [1974]) calculations on the lone pair splittings in anti (0.12 eV) and gauche (0.41 eV) conformers. Thus the mean splitting value (0.27 eV) is in close agreement with the measured (0.31 eV) one. The rather broad band shapes point at unresolved closely spaced anti and gauche ionizations.
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- <sup>2</sup> A. Schweig and W. Thiel, Chem. Phys. Letters **21**, 541 [1973].
- <sup>3</sup> D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, Molecular Photoelectron Spectroscopy, Wiley, London 1970.