

The Selective Thermal Fragmentation of 2,2'-Dipropynyl Sulfide to Propynethial and Allene†

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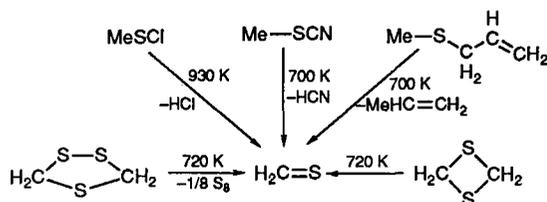
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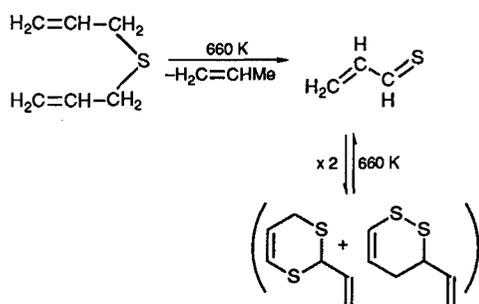
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The thermolysis of 2,2'-dipropynyl sulfide in a flow system under almost unimolecular conditions, which above 830 K selectively yields propynethial and allene, is optimized by photoelectron spectroscopic real-time gas analysis and, according to semiempirical energy hypersurface calculations, possibly proceeds *via* an intramolecular hydrogen transfer.

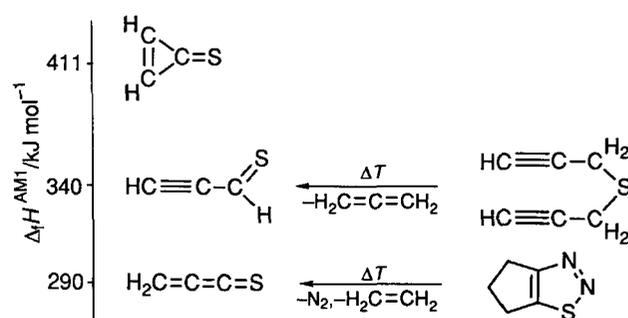
Thioaldehydes abound in diverse areas of nature: thus the parent molecule thioformaldehyde, which now can be prepared on earth in many ways^{1a} (Scheme 1), was first detected in interstellar space,^{1b} whereas its vinyl derivative thioacrolein, best generated in the gas phase by propene split-off from diallyl sulfide and storable as a dimer^{2a} (Scheme 2), is found in the biosphere *e.g.* as one of the odorous components of garlic.^{2b}



Scheme 1 Selected pathways^{1a} for the thermal generation of thioformaldehyde



Scheme 2 Preparation and storage of thioacrolein



Scheme 3 AM 1 enthalpies of formation for the three normal valence isomers C₃H₂S

Quantum chemical evaluation predicts thioacrolein to be the most stable structure of thirteen feasible normal-valence C₃H₂S isomers.^{2a} In contrast, an analogous enthalpy of formation estimate for the more unsaturated ensemble C₃H₂S suggests a different sequence (Scheme 3).

The two valence isomers with the lower calculated enthalpies, propadienethione³ and propynethial,⁴ have been generated from different precursors^{3a,4a} (Scheme 3), structurally characterized by microwave spectroscopy^{3b,4c} and isolated in a matrix.^{3c,4b} In order to gather additional information on the temperature dependence, the thermal fragmentation of 2,2'-dipropynyl sulfide^{4,5} has been reinvestigated in a flow system at 10⁻³ mbar pressure within the temperature interval 300 to 1200 K by real time photoelectron spectroscopic (PES) gas analysis⁵ (Fig. 1).

After recording the photoelectron spectrum of 2,2'-dipropynyl sulfide at room temperature, the low-pressure flow-system was heated while continuously registering the respective PES band patterns.⁵ At about 830 K, novel needle-like peaks at 9.22 and 11.03 eV became visible and at 1070 K, the initial ionization bands at 9.01, 12.24 or 13.6 eV had vanished [Fig. 1(a)

† For part 87 of the series Gas-phase Reactions, see L. Zanathy, H. Bock, D. Lentz, D. Preugschat and P. Botschwina, *J. Chem. Soc., Chem. Commun.*, 1992, 403.

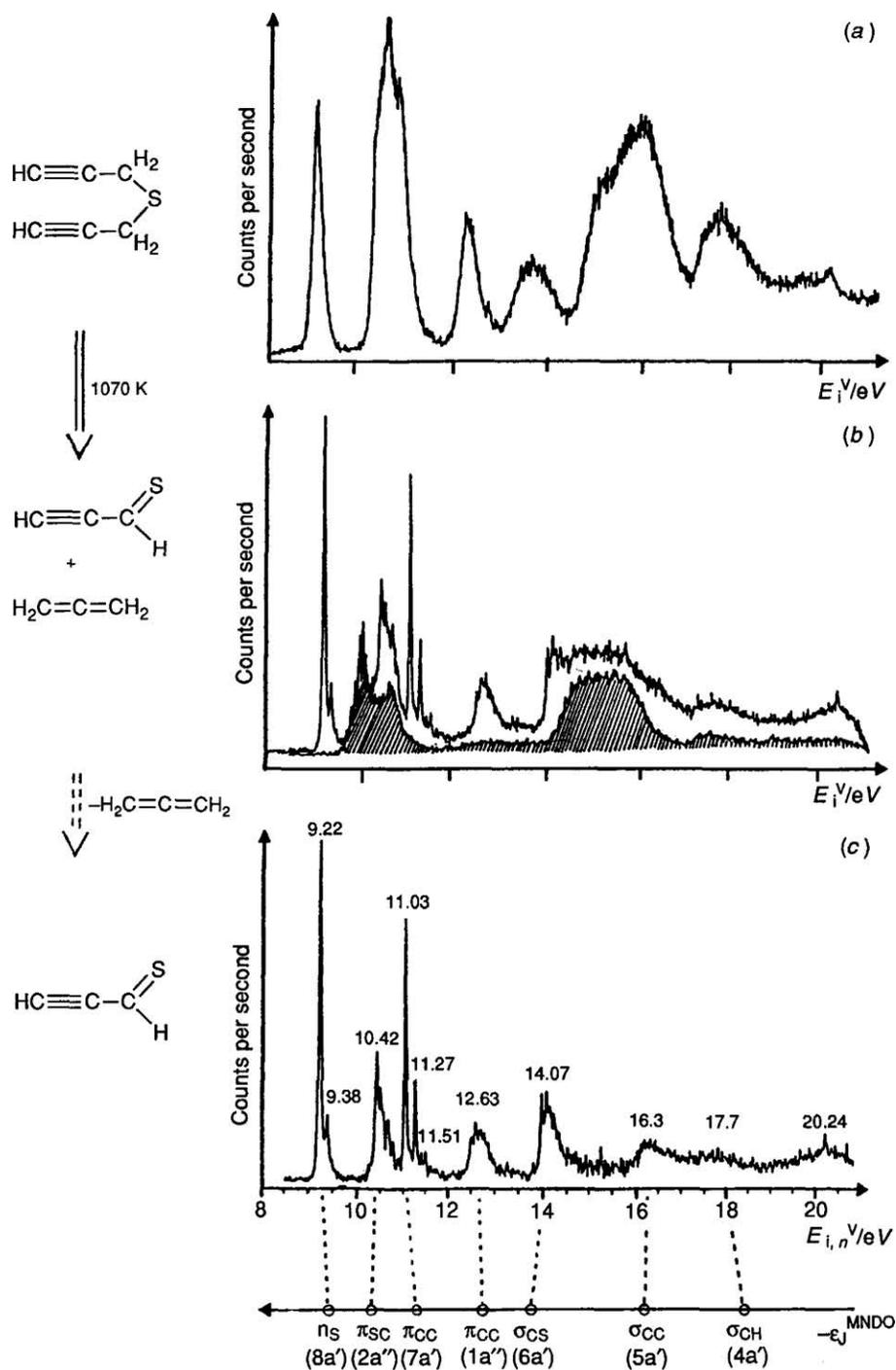


Fig. 1 He(I) photoelectron spectra [calibrated with ${}^2\text{P}_{3/2}(\text{Ar})$ at 15.76 eV] (a) of 2,2'-dipropynyl sulfide at 300 K, (b) of its thermal fragmentation mixture at 1070 K and (c) after digital subtraction of the prerecorded ionization pattern of allene⁶ [shaded in (b)], of propynethial together with its Koopmans' assignment, $E_{i,n}^v = -\epsilon_j^{\text{MNDO}}$, based on the eigenvalues from a fully geometry-optimized MNDO calculation.⁸

and (b)]. Digital subtraction of a prerecorded PE spectrum of allene⁶ [shaded in Fig. 1(b)] yields an ionization pattern, which by Koopmans' correlation, $E_{i,n}^v = -\epsilon_j^{\text{MNDO}}$,[†] with the MNDO eigenvalues can be straightforwardly assigned to propynethial [Fig. 1(c)].

Both the structure of propynethial and the charge distribution, as predicted by the well-parametrized MNDO/CI procedure⁷ (Fig. 2) are largely in accord with expectations. The C≡C triple bonds are in general of about 120 pm length and the C=S double bond lengths, which are more strongly sub-

stituent-dependent, are frequently found between 155 pm (S=C=S) and 161 pm (H₂C=C=S).⁸ The C—C single bond is rather short compared with the presumably more polarized one of 145 pm length⁹ in the iso(valence)electronic oxygen analogue propynal. With regard to the charge distribution, the acetylene hydrogen is calculated to be positive with compensation by the alternating carbon, while the thioaldehyde group results as an unpolarized subunit.

No traces of either the isomer H₂C=C=C=S, predicted to be thermodynamically more stable (Scheme 3), or its anticipated degradation products HC≡CH and C=S were observed under the measurement conditions chosen. Therefore, despite the twelve degrees of freedom for the six-atom molecule HC≡CC(H)=S, the calculation of an approximate energy

[†] RSC Journals follow IUPAC recommendations with regard to abbreviations. Elsewhere in the literature ionisation energy is often denoted as IE.

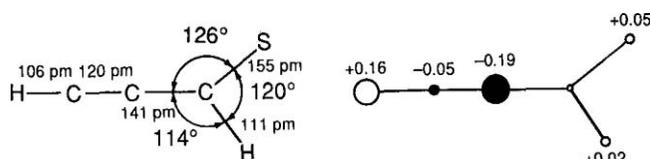


Fig. 2 Structure and charge distribution of propynethial from a fully geometry-optimized MNDO/CI calculation

hypersurface for its gas-phase generation under (almost) unimolecular conditions has been attempted [Fig. 3(a)]. The starting point is the optimum conformation of the precursor 2,2'-dipropynyl sulfide, for which an MNDO/CI geometry optimization predicts an approximate *cis*-configuration with a dihedral angle of about 60° between the two linear C—C≡CH subunits [Fig. 3(b)]. The barrier to the saddle point, at which

one (H₂)CC=C(H) linkage is calculated to be bent to enable the formation of a planar six-membered ring intermediate with a rather short contact distance (H)C—H···C(H) of only 130 pm, is calculated to amount to about 220 kJ mol⁻¹ [Fig. 3(b)]. This value agrees well with the experimental temperature of about 830 K, § at which the propynethial ionization peaks at 9.22 and 11.03 eV (Fig. 1) are first recognized in the PE spectrum of the heated flow system.

The enthalpy difference for the endothermic reaction is estimated as about 100 kJ mol⁻¹ [Fig. 3(b)]. The enthalpy hypersurface [Fig. 3(a)] is approximated on the basis of the assumptions specified and, therefore, should be viewed with considerable caution. Nevertheless, it provides a rationale to explain why neither the precalculated more stable isomer H₂C=C=C=S (Scheme 3) nor its degradation products could be detected by photoelectron spectroscopy. For the formation of this molecule, two hydrogen atoms of the same H₂C group need to be moved simultaneously and an intramolecular pathway to accomplish this is not easy to imagine.

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References

- (a) H. Bock, T. Hirabayashi and S. Mohmand, *Chem. Ber.*, 1982, **115**, 492 and references cited therein; (b) M. W. Sinclair, J. C. Ribes, N. Fourikis, R. D. Brown and P. Godfrey, *Int. Astron. Union Circ.*, No. 2362 (Nov. 1971).
- (a) H. Bock, S. Mohmand, T. Hirabayashi and A. Semkow, *Chem. Ber.*, 1982, **115**, 1339; (b) E. Block, *Sci. Am.*, 1985, **252**, 119; cf. also E. Block, S. Ahmad, J. L. Catalfamo, M. K. Jain and R. Apitz-Castro, *J. Am. Chem. Soc.*, 1986, **108**, 7048.
- (a) R. D. Brown, P. D. Godfrey, P. S. Elmes and D. McNaughton, *J. Chem. Soc., Chem. Commun.* 1987, 573; (b) R. D. Brown, K. G. Dyall, P. S. Elmes, P. D. Godfrey and D. McNaughton, *J. Am. Chem. Soc.*, 1988, **110**, 789; (c) E. Suzuki and F. Watari, *Chem. Phys. Lett.*, 1990, **168**, 1.
- (a) V. A. Korolev, J. Tamas, K. Ujszasky, A. K. Malt'sev and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, **36**, 2228; *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, **36**, 2152; (c) R. D. Brown, P. D. Godfrey, R. Champion and M. Woodruff, *Aust. J. Chem.*, 1982, **35**, 1747.
- For a review, see H. Bock, B. Solouki, S. Aygen, M. Bankmann, O. Breuer, R. Dammel, J. Dörr, M. Haun, T. Hirabayashi, D. Jaculi, J. Mintzer, S. Mohmand, H. Müller, P. Rosmus, B. Roth, J. Wittmann and H. P. Wolf, *J. Mol. Struct.*, 1988, **173**, 32 and references cited therein, especially H. Bock and B. Solouki, *Angew. Chem.*, 1981, **93**, 425; *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 427.
- Cf. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules*, Halsted Press, New York, 1981, p. 64.
- M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
- Cf. I. Hargittai, *The Structure of Volatile Sulfur Compounds*, Reidel, Dordrecht, 1985.
- M. Sugie, T. Fukuyama and K. Kuchitsu, *J. Mol. Struct.*, 1972, **14**, 333.

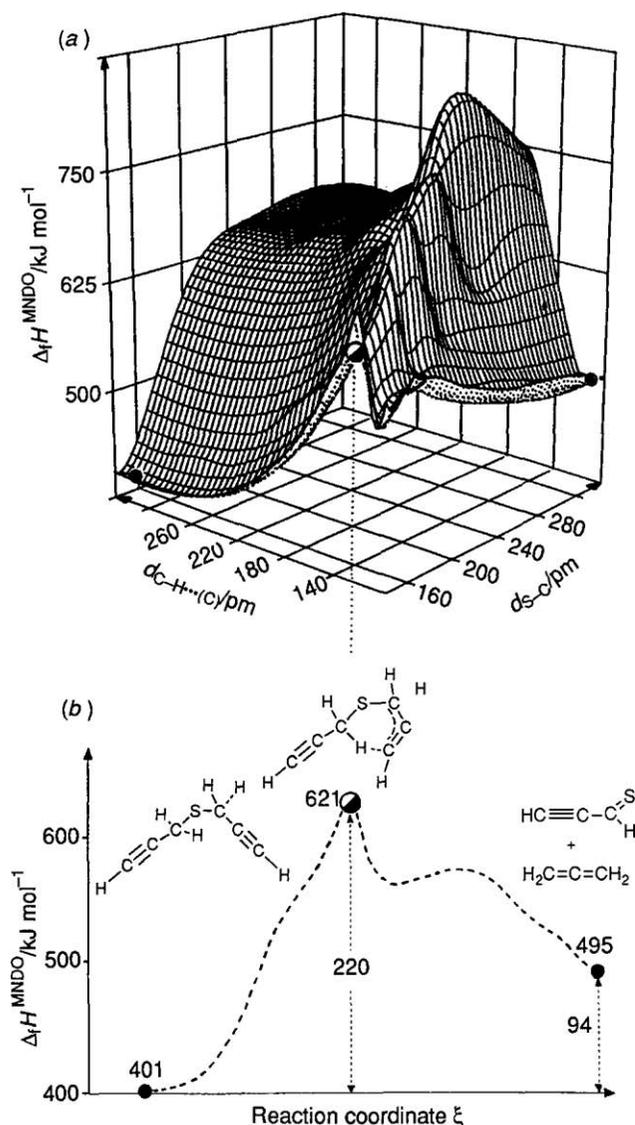


Fig. 3 (a) MNDO/CI enthalpy of formation hypersurface for an intramolecular thermal fragmentation of 2,2'-dipropynyl sulfide to propynethial and allene, based on the assumption that the chosen coordinates $\Delta d_{C-H \cdots C}$ and Δd_{S-C} represent the essential molecular dynamics (●: minima, ○: saddle point, ---: presumable reaction pathway). (b) Reaction profile [cf. (a): ●—○—●] with calculated energy differences and optimized MNDO/CI structures

§ For seven thermal fragmentations under identical measurement conditions, a linear regression, $E_a = -387 + 0.797 T_{begin}$ ($\sigma = 0.0948$), has been found between calculated activation barriers E_a and the respective temperatures T_{begin} , at which changes in the ionization pattern have been detected by PES (K. Oswald, PhD Thesis, University of Frankfurt, 1992). For the activation barrier of 220 kJ mol⁻¹ approximated for the thermolysis of dipropynyl sulfide, a temperature of about 770 K is expected accordingly.