Thermal Decomposition of Thiirane and 2-Methylthiirane: An Experimental and Theoretical Study

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The thermal decomposition of thiirane and 2-methylthiirane was investigated in a flow system by following the changes in their photoelectron spectra at various temperatures. Similar decomposition patterns were observed in both cases. Thus at 600 °C, formation of sulfur and an alkene was detected. At higher temperatures, conversion of thiirane into ethenethiol and thioacetaldehyde, and of 2-methylthiirane into *cis*- and *trans*-prop-1-ene-1-thiol was observed. Hydrogen sulfide, alkynes, carbon disulfide and thiophene were detected as products of secondary reactions. The experimental data pertaining to the rearrangement processes are compared with potential energy profiles, calculated by using the MNDO/CHAIN procedure. A mechanism involving initial C–S bond breaking, followed by 1,2-hydrogen shift, is suggested by the results.

The reactivity of the three-membered heterocyclic compound, thiirane, varying from thermal fragmentation to electrocyclic ring opening, has been the subject of many experimental and theoretical studies.[1–6] Two important modes of reaction have been observed by Lown *et al.*[1] At temperatures below 250 °C, sulfur and ethene were formed in stoichiometric yields, while at higher tempertures rearrangement to ethenethiol occurred. The low temperature mode of reaction follows first order kinetics and a pseudounimolecular mechanism involving thiirane in a low-lying triplet excited state was proposed.[1–3]

The formation of ethenethiol in the second mode of reaction was postulated by Sherwood *et al.* as proceeding through a concerted pathway involving a bicyclic transition state.[4] However, these authors did not consider a stepwise pathway involving homolysis of a C–S bond as the first step, which is a possible alternative because of the strained cyclic structure of thiirane. Furthermore, another expected product of isomerization, thioacetaldehyde, was not detected in these studies, although its absence was explained in terms of the relatively small difference in bond energy between the C–S single and double bond.[1] It is also known that thioacetaldehyde is a short-lived species with a tendency to polymerize,[7,8] and therefore may have escaped detection.

For these reasons, we have reexamined the thermal decomposition of thiirane, focussing on the isomerization process using the technique of photoelectron spectroscopy. One of the advantages of using photoelectron spectroscopy as a tool to investigate reactions is that semi-stable species, under suitable conditions, can be readily detected and their electron properties characterized.[9,10] For comparison, the decomposition of 2-methylthiirane was also examined. The presence of the methyl group in the latter compound is expected to lead to more channels for isomerization, and interesting species such as *cis*- and *trans*-prop-1-ene-1-thiol, prop-1-ene-2-thiol, thioacetone and thiopropionaldehyde may be generated as products.

To aid in the elucidation of the various pathways, semi-empirical MNDO calculations of the reaction energy profiles have been carried out. In this regard we were encouraged by progress reported in the literature on the use of the UHF and the HE-CI versions of the MNDO or AM1 procedures in calculating the heats of formation and activation enthalpies for processes involving radicals and biradicals.[11–16] An MNDO theoretical study of the reactions of sulfur with hydrocarbon molecules has been reported by McKee.[5]

Experimental

Photoelectron (PE) spectra were measured on a Leybold–Heraeus UPG 200 spectrometer with resolution of 18–25 meV, using argon and iodomethane as calibrant gases. ^{1}H NMR spectra were recorded on a Bruker ACF 300 MHz spectrometer.

The compounds thiirane and 2-methylthiirane were obtained commercially and purified by distillation under reduced pressure. Pyrolysis was carried out in a flow system at low pressure as described previously.[17] Progress of the reaction was monitored by on-line recording of photoelectron spectra. In most cases a long-path pyrolyser was used. This consisted of a 45 cm long quartz tubing of 1.2 cm inner diameter and lightly packed with quartz wool. Heating was achieved through a tube oven 30 cm in length. Pyrolysis was also carried out in a short-path pyrolyser which consisted of a 6.5 cm long molybdenum tubing of 0.45 cm inner diameter. The end of the tubing was only 1 cm from the ionizing photon beam. Heating of the short-path pyrolyser was achieved both resistively and by electron bombardment.

AM1[18] and MNDO[19] calculations were carried out with the AMPAC program[20] running on a VAX 6430 computer. Transition states were located using the CHAIN, POWELL and FORCE algorithms provided in the AMPAC program, and characterized by having one and only one imaginary vibrational frequency. Calculations were carried out with the normal RHF version, and where it was necessary to accommodate for possible radical character, calculations were performed by using the spin-unrestricted Hartree-Fock version of MNDO (UMNDO), and the 'half-electron' approximation[21] with 3 × 3 configuration interaction (MNDO-HE-CI).

Results and Discussion

Changes Observed During Pyrolysis.—Pyrolysis of the thiiranes was usually performed at a pressure of about 1 mbar.† During pyrolysis, as the temperature was gradually increased, the spectral bands of the parent compound diminished, while new bands due to products emerged. At the end of an experiment, a yellow solid identified as sulfur by mass spectral analysis was usually found at the cold end of the quartz tubing. Some carbonaceous materials were also found to deposit on the quartz wool.

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† 1 bar = 10^5 Pa.

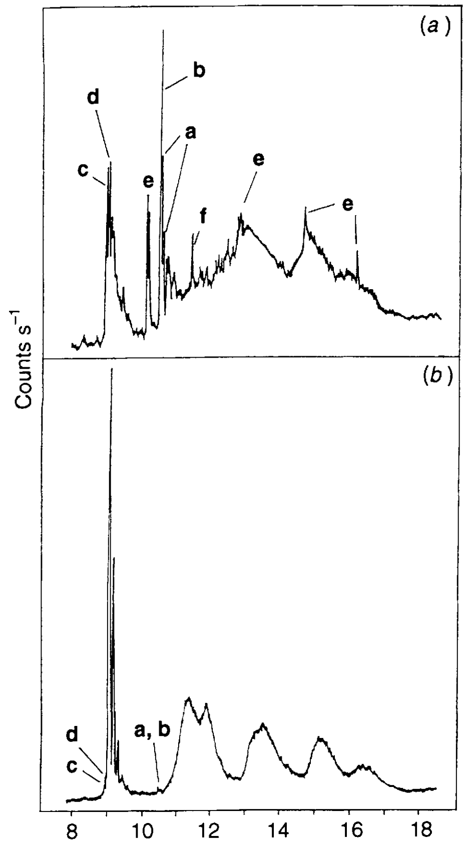

Fig. 1 Spectral changes during pyrolysis of thiirane at (*a*) 700 °C and (*b*) 900 °C. Products: **a**, C_2H_4; **b**, H_2S; **c**, $CH_2{=}CHSH$; **d**, CH_3CHS; **e**, CS_2 and **f**, HC≡CH. Apart from the small signals marked as **a**–**d**, the figure in (*a*) shows the spectrum of thiirane.

Heating of thiirane in the long-path pyrolyser up to 600 °C produced no observable changes in the photoelectron spectrum. At 600 °C, ethene was observed in the PE spectrum.* At 700 °C, there were some changes in the spectrum with the emergence of two bands at 8.92 and 8.98 eV which could be attributed to the first ionization bands of ethenethiol and thioacetaldehyde, respectively (*vide infra*), and another group of bands around 10.5 eV identifiable as the first ionization bands of ethene and hydrogen sulfide.[22] At higher temperatures, carbon disulfide and acetylene were also formed. The changes are shown in Fig. 1.

The ethenethiol produced could be isolated by the use of two cold traps placed downstream from the heated zone. The first trap was used to collect the condensables at liquid nitrogen temperature. During fractional evaporation of the trapped mixture, the second trap was used to collect the fraction containing ethenethiol which evaporated at −90 °C. The identity of ethenethiol[23] was confirmed by comparing its NMR spectrum with that published in the literature.[24]

If thioacetaldehyde were a product of the thiirane reaction, it would have polymerized in the first cold trap.[8] This was verified by the following observation. When the trapped mixture was vaporized at temperatures up to −20 °C, what remained was a liquid residue. Heating the vapour of the liquid to 600 °C in the flow tube yielded a PE spectrum shown in Fig. 2, which compared well with that published for thioacetaldehyde,[7] showing a sharp band at 8.98 eV and two broad bands around 11.0 and 12.8 eV. Furthermore, direct warming of the trap containing the liquid residue gave rise to decomposition of a trace amount of a white solid at the cold part of the container. The mass spectrum of the white deposit showed lines at *m*/*z* 59 (64%), 60 (100), 92 (14), 115 (33), 124 (6) and 180 (34) which fitted well with the reported fragmentation pattern of the trimer of thioacetaldehyde.[25]

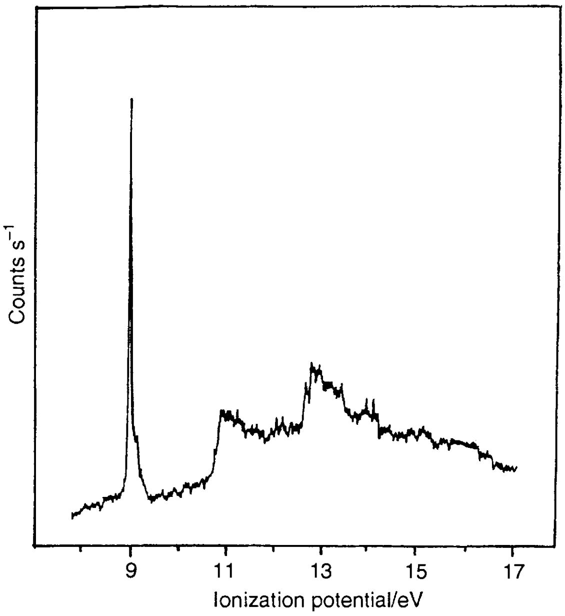

Fig. 2 Spectrum of thioacetaldehyde detected by heating the vapour of a trapped polymeric mixture from pyrolysis of thiirane

The spectral changes upon pyrolysis of 2-methylthiirane are shown in Fig. 3. Decomposition started around 600 °C, when bands due to hydrogen sulfide and propene appeared. At 700 °C, an additional band at 8.69 eV due to prop-1-ene-1-thiol was detected.[23] By comparing the NMR spectra of the species collected in a cold trap with the published spectra,[26,27] it was established that both *cis*- and *trans*-isomers of prop-1-ene-1-thiol were formed in comparable amounts. When the temperature was raised to 800 °C, ionization bands due to carbon disulfide were observed. Further increase in temperature caused a decrease in intensity of bands due to prop-1-ene-1-thiol, and at the same time an increase in intensity of bands due to hydrogen sulfide and carbon disulfide. At temperatures higher than 850 °C, secondary products such as acetylene and methyl acetylene were detected. A polymeric mixture was also found by cold trapping. Upon heating of the more volatile fraction of the polymeric mixture, bands at 8.6 and 8.8 eV emerged but no conclusion could be drawn as to their identity.

When the short-path molybdenum pyrolyser was used, somewhat different results in the pyrolysis of thiirane and 2-methylthiirane were obtained. Only the low temperature mode, formation of an alkene and sulfur, was observed. The PE spectra shown in Fig. 4, obtained upon complete decomposition of the two cyclic compounds, clearly indicate the formation of diatomic sulfur,[28] its detection being facilitated by the use of the short-path pyrolyser. The failure to detect ethenethiol and prop-1-ene-1-thiol as products was consistent with the observation that such species readily polymerize on metal surfaces.[4]

Table 1 summarizes the characteristic ionization bands observed for the products in the composite spectra (Figs. 1, 3 and 4) during pyrolysis. The identity of each species was further confirmed by its own spectrum recorded upon differential vaporization. In Table 2 the products are classified as main or

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* The difference in reaction temperatures between this work and that reported by Lown *et al.*[1] was due to different reaction conditions. While a static system was used in the work of Lown *et al.*, a flow system was employed in the present work. The contact time in the latter was only a fraction of a second.

Table 1 Characteristic bands (in eV) of product species in the composite spectra

Diatomic sulfur	S_2	9.41	11.82	13.20	14.62	
Hydrogen sulfide	H_2S	10.48				
Carbon disulfide	CS_2	10.06	12.83	14.47	16.19	
Ethene	C_2H_4	10.51	12.85	14.66		
Propene	C_3H_6	9.72	12.31	13.23	14.48	15.90
Acetylene	$HC{\equiv}CH$	11.40				
Ethenethiol	$CH_2{=}CHSH$	8.92				
Thioacetaldehyde	CH_3CHS	8.98				
Prop-1-ene-1-thiol	$CH_3CH{=}CHSH$	8.69				

Table 2 Pyrolysis products from the thermal decomposition of thiirane and 2-methylthiirane

Compound	Major	Minor
Thiirane	sulfur,[a] C_2H_4 $CH_2{=}C(H)SH$ $CH_3(H)C{=}S$ H_2S, CS_2	$HC{\equiv}CH$ Thiophene[b]
2-Methylthiirane	sulfur,[a] C_3H_6 *cis*- and *trans*-$CH_3C(H){=}C(H)SH$ H_2S, CS_2	$HC{\equiv}CH$ $CH_3C{\equiv}CH$ C_2H_4[b]

[a] S_2 was detected during pyrolysis in the short-path pyrolyser. [b] Observed only during vaporization from cold trap.

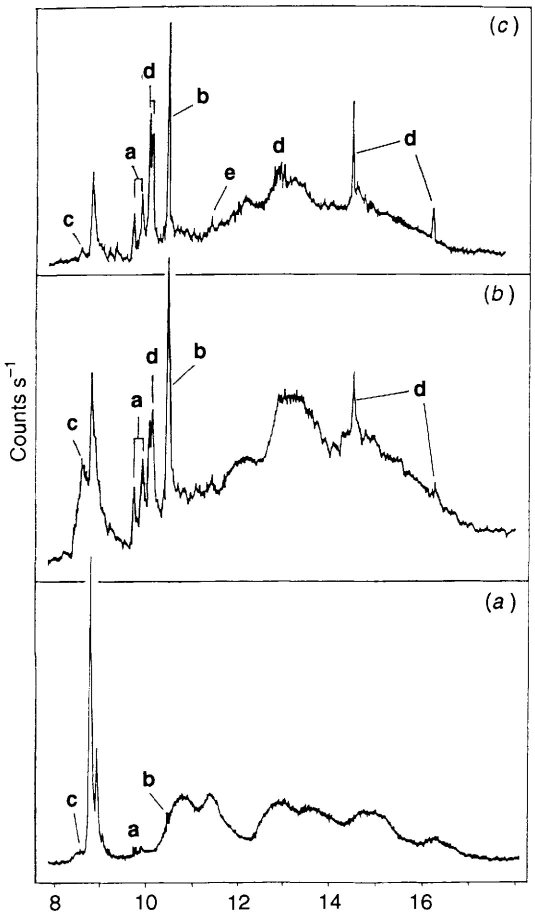


Fig. 3 Spectral changes during pyrolysis of 2-methylthiirane at (*a*) 600 °C, (*b*) 800 °C and (*c*) 850 °C. Products: **a**, C_3H_6; **b**, H_2S; **c**, $CH_3CH{=}CHSH$; **d**, CS_2 and **e**, $HC{\equiv}CH$. Apart from the small signals marked as **a**–**c**, the figure in (*a*) shows the spectrum of 2-methylthiirane.

minor on the basis of the vapour pressures of individual components released during differential vaporization.

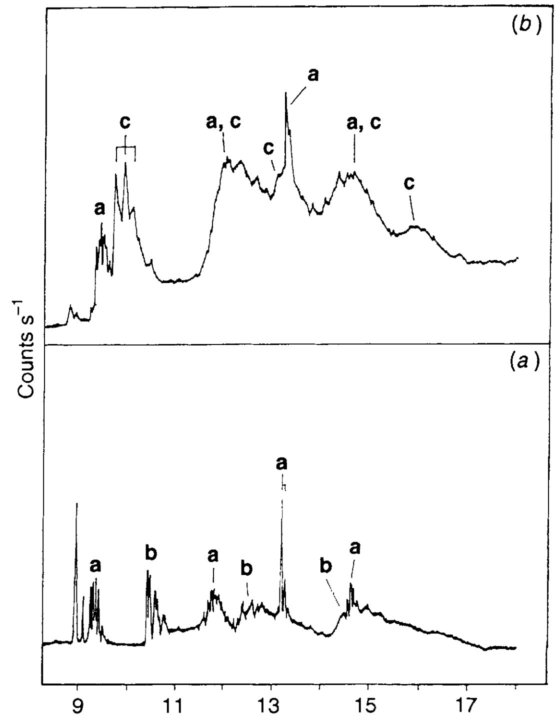


Fig. 4 Spectral changes upon pyrolysis of (*a*) thiirane and (*b*) 2-methylthiirane at 700 °C using the short-path pyrolyser. Products: **a**, S_2; **b**, C_2H_4 and **c**, C_3H_6.

Modes of Rearrangement and Decomposition.—Our results confirm the low temperature mode of reaction of thiirane reported earlier.[1] The results obtained by using the short-path pyrolyser provide further clear evidence of diatomic sulfur as an initial product, and the fact that only S_2 and ethene were detected is in agreement with the stoichiometric nature found earlier[1] for this mode of reaction. This observation also applies to 2-methylthiirane.

As mentioned earlier, our main interest was the thermal rearrangement of thiirane at temperatures above 600 °C. At such temperatures, our results show that thioacetaldehyde was produced along with ethenethiol although the aldehyde was not observed in the earlier studies.[1,4] The relative intensities of the ionization bands of the two isomers shown in Fig. 1 suggest that these two compounds were produced in comparable amounts. Thioacetaldehyde can either be formed by isomerization of ethenethiol (tautomerism), or by the direct rearrangement of thiirane itself. A question which conventional kinetic data could not readily resolve is whether the conversion of thiirane into ethenethiol or thioacetaldehyde proceeds through concerted pathways involving simultaneous bond making and bond breaking, or through stepwise pathways characterized by the intermediacy of radical species. To investigate these possibilities, we have carried out calculations related to the energetics of these processes, using semiempirical MO methods.

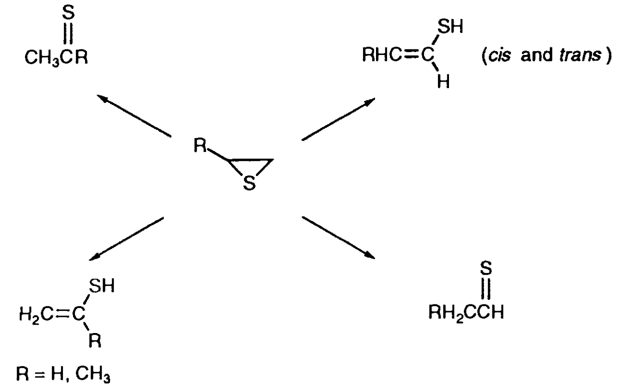
We started by calculating the heats of formation of thiirane and 2-methylthiirane and their various rearrangement pro-

Table 3 Comparison of MNDO and AM1 heats of formation of various isomers of C_2H_4S and C_3H_6S

Compound	AM1/ kJ mol^{-1}	MNDO/ kJ mol^{-1}
Thiirane	129	79
Ethenethiol	66	63
Thioacetaldehyde	82	70
2-Methylthiirane	99	47
trans-Prop-1-ene-1-thiol	24	20
cis-Prop-1-ene-1-thiol	26	22
Prop-1-ene-2-thiol	39	31
Thioacetone	49	38
Thiopropionaldehyde	54	48

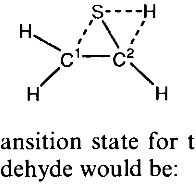
ducts. The results obtained by using both AM1 and MNDO parametrizations are given in Table 3. It can be seen that for the acyclic species the values given by the two methods are comparable, although the AM1 values are consistently slightly higher. For the two cyclic compounds the AM1 values are higher than the MNDO values by 50 kJ mol^{-1}. Comparison with the experimental heats of formation, 82 kJ mol^{-1} for thiirane and 46 kJ mol^{-1} for 2-methylthiirane,[29] clearly demonstrates that the MNDO method gives better results, the AM1 method overestimating the strain energy of the three-membered ring. The former method was therefore employed for the study of the possible reaction pathways.

Scheme 1 summarizes the various possible rearrangement pathways for the two compounds. For thiirane only two processes need to be considered.

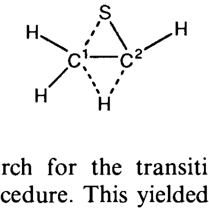


Scheme 1

Thiirane. If the rearrangement of thiirane into ethenethiol were to proceed through concerted pathways involving a 1,2-hydrogen shift, the transition state could have the following bicyclic structure as proposed by Sherwood *et al.*[4]



A similar bicyclic transition state for the rearrangement of thiirane into thioacetaldehyde would be:



We began the search for the transition states using the MNDO-CHAIN procedure. This yielded two structures **TSa** and **TSb** (see Fig. 5) in which the C^1–S distances were respectively 2.76 and 2.75 Å, indicating that bond breaking was virtually complete. Subsequent UMNDO optimization confirmed a biradical stationary point **b** (see Fig. 5) at a C^1–S distance of 2.675 Å and a CCS angle of 114°. That the biradical species **b** was an intermediate was further indicated by the potential energy surfaces and the corresponding contour diagrams shown in Figs. 6 and 7, for the conversion processes thiirane to ethenethiol (**a**→**c**) and thiirane to thioacetaldehyde (**a**→**d**) respectively. These surfaces were calculated by assigning fixed values to the chosen coordinates and optimizing all the others. Note that the surfaces at the region around **b** are relatively flat with respect to variation in the CCS angle beyond 90°, as can be expected from the large C^1–S distance. The barrier height for recombination of radical **b** is very low, indicating that **b** is a very unstable intermediate. Within a period of a few cycles of vibration after its formation, **b** would either revert to **a** or proceed to product formation. As such the conversion of **a**→**c** or **a**→**d** is not a clear-cut stepwise process marked by distinct kinetic steps, nor is it a synchronous concerted process in which both the C^1–S bond breaking and 1,2-hydrogen shift proceed concurrently to similar extents along the reaction coordinate. It is perhaps best described as a non-synchronous two-stage concerted process, by analogy with the classification of some Diels–Alder reactions.[15,30]

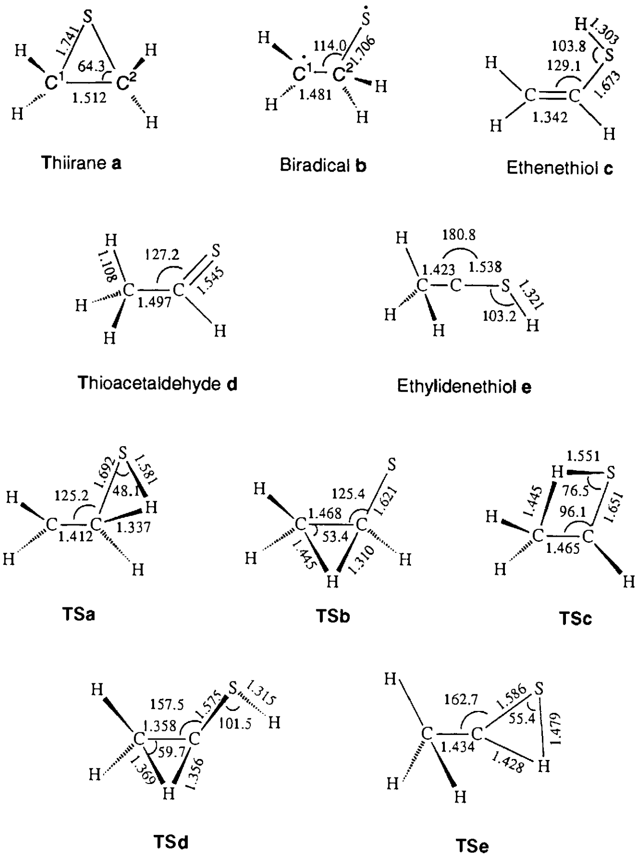


Fig. 5 UMNDO optimized geometries of various C_2H_4S species

The UMNDO heats of formation for biradical-like species are known to be too negative by 50–100 kJ mol^{-1} due to overestimation of the correlation energy.[14,31] This overestimation can be corrected to some extent by including configuration interaction (CI) and application of the MNDO/CI method usually leads to some improvement.[5,14] Since both UMNDO and MNDO/CI normally lead to similar geometries,[15] we have carried out single point 3 × 3 CI calculations using the UMNDO optimized geometries. The results obtained from both methods are presented in Table 4 and the UMNDO

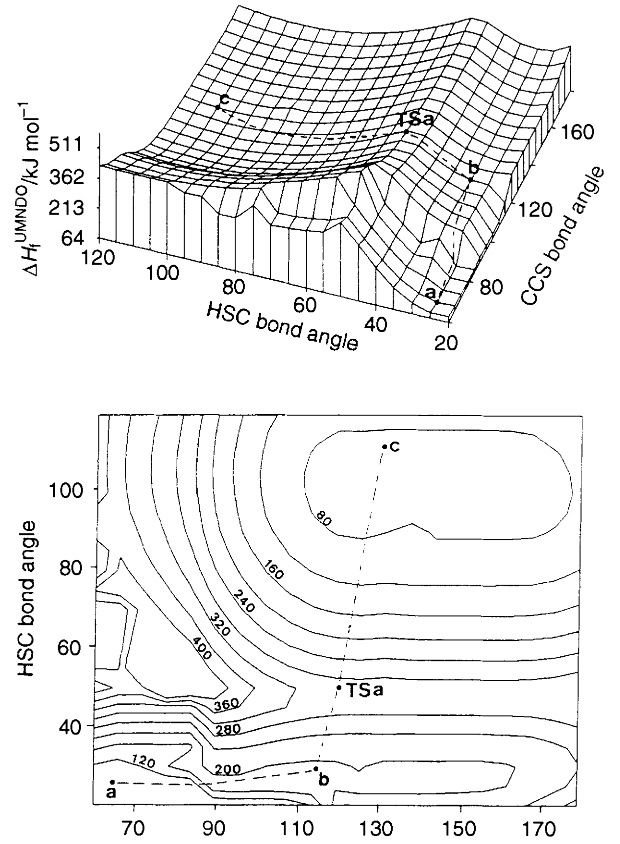


Fig. 6 UMNDO potential energy surface and contour diagram for the reaction **a**→**c**

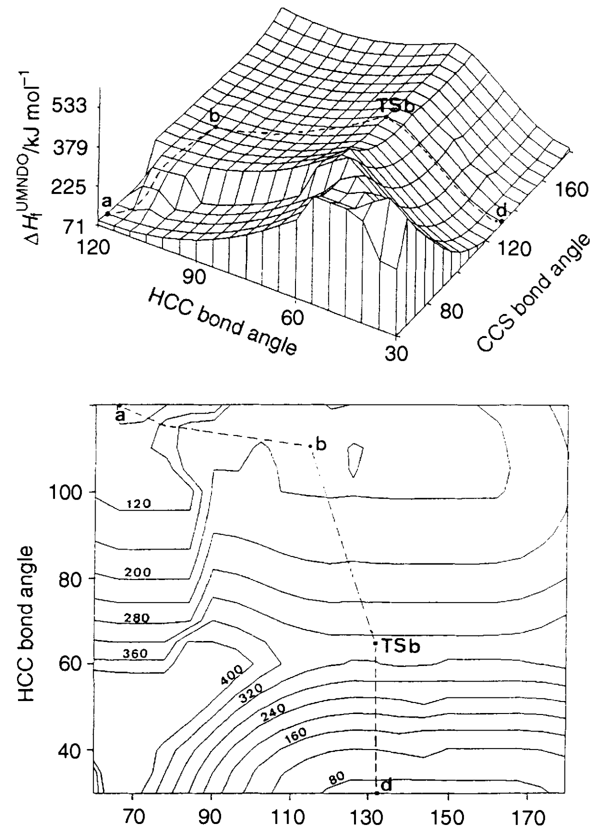


Fig. 7 UMNDO potential energy surface and contour diagram for the reaction **a**→**d**

Table 4 UMNDO and MNDO–HE–CI calculated heats of formation for various C_2H_4S species[a]

	UMNDO		MNDO–HE–CI[b]
Species	ΔH_f/kJ mol^{-1}	$\langle S^2 \rangle$	ΔH_f/kJ mol^{-1}
Thiirane (**a**)	79	0.00	74
Biradical (**b**)	191	1.01	212
Ethenethiol (**c**)	63	0.03	25
Thioacetaldehyde (**d**)	70	0.00	39
Ethylidenethiol (**e**)	223	0.77	234
TS:**b**→**c** (**TSa**)	316	0.77	309
TS:**b**→**d** (**TSb**)	338	0.73	329
TS:**c**→**d** (**TSc**)	335	1.06	376
TS:**c**→**e** (**TSd**)	391	0.00	385
TS:**d**→**e** (**TSe**)	401	1.02	388

[a] Singlet states for biradical species. [b] Single point calculations at UMNDO optimized geometries. TS = Transition State.

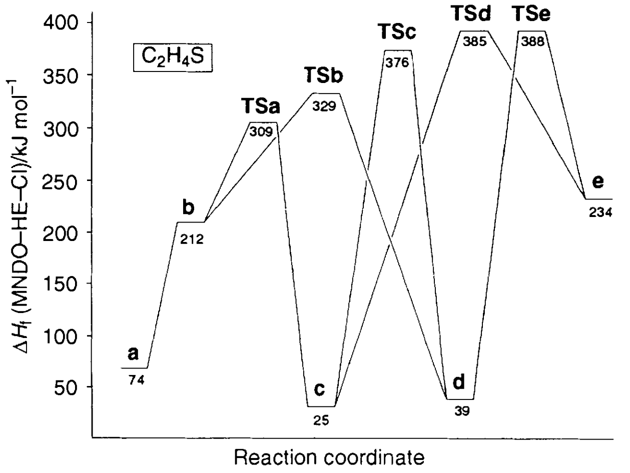


Fig. 8 Schematic reaction profiles obtained by MNDO–HE–CI calculations for the rearrangement of C_2H_4S species. The number below each horizontal line is the calculated heat of formation.

optimized geometries of individual species are given in Fig. 5. Note that of the two sets of data in Table 4, the MNDO/CI values for species **b** and **e** are higher than those calculated from UMNDO, as expected for the radical character of the species. With the exception of **TSc**, the MNDO/CI values for the other species are somewhat lower than the UMNDO values. Generally, similar trends in heats of formation for the different species are predicted by the two methods. Since the MNDO/CI method appears to give more accurate results, we have used MNDO–HE–CI values to set up reaction profiles.

The calculated reaction profiles using the MNDO–HE–CI method are illustrated in Fig. 8. Thus, in the first step of rearrangement, homolytic C–S bond fission occurs to produce the biradical intermediate **b**. With high enough energy, **b** can pass over a second barrier to give either ethenethiol (**c**) or thioacetaldehyde (**d**). In both cases, a 1,2-hydrogen shift occurs through a cyclic transition state. The barrier heights from thiirane to these transition states (**TSa** and **TSb**) were calculated to be 235 and 255 kJ mol^{-1}, respectively. The first value is in good agreement with an earlier estimate of 230–272 kJ mol^{-1} for the conversion of **a** to **c**.[4] As there is a difference of 20 kJ mol^{-1} in barrier heights, the calculation thus predicts that product **d** is relatively minor compared to **c**.

The isomerization of **c** to **d** provides an alternative path for the formation of **d**. The reaction can proceed through a 1,3-hydrogen shift which was predicted to occur *via* transition state **TSc** with a barrier of 351 kJ mol^{-1}. Since this value is 96 kJ mol^{-1} higher than that calculated for rearrangement of thiirane

Table 5 UMNDO and MNDO–HE–CI calculated heats of formation for various C_3H_6S species[a]

Species	UMNDO		MNDO–HE–CI[b]
	ΔH_f/kJ mol^{-1}	$\langle S^2 \rangle$	ΔH_f/kJ mol^{-1}
2-Methylthiirane (**1**)	47	0.00	43
Biradical (**2**)	141	0.99	165
trans-Prop-1-ene-1-thiol (**3**)	20	0.09	−13
cis-Prop-1-ene-1-thiol (**4**)	22	0.10	−9
Thiopropionaldehyde (**5**)	48	0.00	18
Biradical (**6**)	174	0.95	190
Prop-1-ene-2-thiol (**7**)	31	0.00	−1
Thioacetone (**8**)	38	0.00	8
TS:**2**→**3** (**TS1**)	269	0.77	264
TS:**2**→**4** (**TS2**)	271	0.77	265
TS:**2**→**5** (**TS3**)	297	0.71	291
TS:**3**→**5** (**TS4**)	298	1.05	324
TS:**4**→**5** (**TS5**)	298	1.05	324
TS:**6**→**7** (**TS6**)	290	0.80	283
TS:**6**→**8** (**TS7**)	314	0.77	306

[a,b] See Table 4 footnotes.

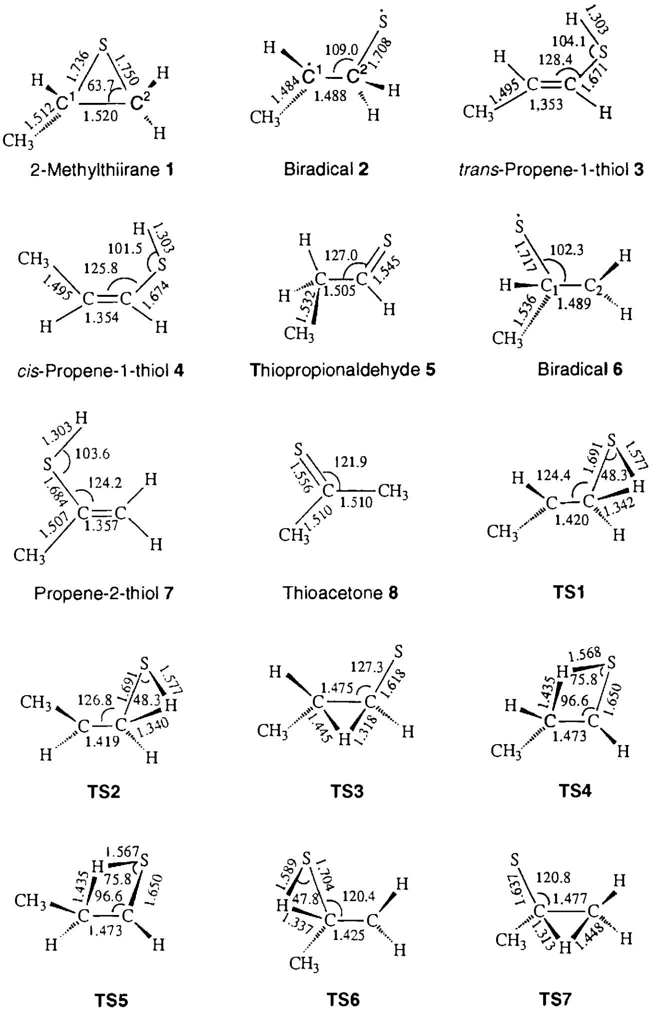


Fig. 9 UMNDO optimized geometries of various C_3H_6S species

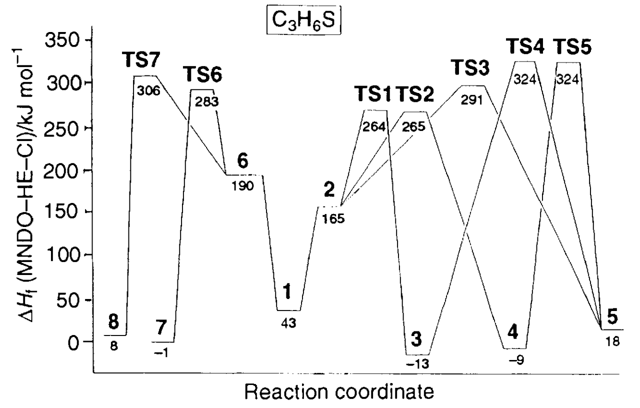


Fig. 10 Schematic reaction profiles obtained by MNDO–HE–CI calculations for the rearrangement of C_3H_6S species. The number below each horizontal line is the calculated heat of formation.

$$CH_2{=}CH\text{-}SH \rightarrow CH_3\text{-}C\text{-}SH \rightarrow CH_3\text{-}C(H){=}S$$

Scheme 2

(**a**→**d**), the MNDO/CI calculations thus suggest that **d** is only formed through the latter process. It is noted that the UMNDO method, however, gave a difference in barriers of only 13 kJ mol^{-1} for the processes **c**→**d** and **a**→**d**.

Another possible isomerization pathway from c to d is one which involves two consecutive 1,2-hydrogen shifts through the intermediacy of ethylidenethiol (**e**), CH_3–C–SH (Scheme 2). The calculated reaction profile, shown in Fig. 8, indicates that **e** is separated from **c** and **d** by energy barriers of 151 and 154 kJ mol^{-1} respectively, and is therefore a stable intermediate. However, the high energy barrier of 360 kJ for formation of **e** from **c** would render this an energetically unfavourable isomerization pathway. The reaction profile connecting species **c**, **d** and **e** *via* transition states **TSd** and **TSe** is qualitatively similar to that calculated by Smith *et al.* for the analogous system ethenol–hydroxyethylidene–acetaldehyde, using a high level *ab initio* MO method.[32]

2-Methylthiirane. The reaction profiles for the rearrangement of 2-methylthiirane into the various isomers were calculated in a similar way as for thiirane. A comparison of the heats of formation obtained for the relevant species using UMNDO and MNDO–HE–CI methods is presented in Table 5. The calculated geometries of these species, shown in Fig. 9, are very similar to those predicted for the thiirane system. In Fig. 10, the MNDO–HE–CI calculated reaction profiles are shown. It can be seen that the conversion of 2-methylthiirane (**1**) into *trans*- (**3**) and *cis*-prop-1-ene-1-thiol (**4**) proceeds in a similar manner as for thiirane, through the formation of a biradical intermediate (**2**), with barrier heights of 221 and 222 kJ mol^{-1} respectively. The similarity of the two values is in line with the mere 3.5 kJ mol^{-1} for the rotational barrier about the central C–C bond of **2**, obtained in a separate UMNDO optimization. It would also imply that the two isomers should be produced in comparable yields, as was indeed observed experimentally.

Another process, the formation of thiopropionaldehyde (**5**), involves a 1,2-hydrogen shift from the α to the β carbon in the intermediate **2**. The overall activation energy is 248 kJ mol^{-1}, which is appreciably higher than that for the formation of the prop-1-ene-1-thiols (**3** and **4**). In our experiment we have found no concrete evidence for the formation of this species, except for the observation of a sharp band at 8.60 eV in the PE spectrum obtained upon heating the vapour of a volatile fraction of a trapped mixture. The alternative route, a 1,3-hydrogen shift in *trans*- and *cis*-prop-1-ene-1-thiol (**3** and **4**) leading to the formation of **5**, is predicted to be even less favourable with barriers of 337 and 333 kJ mol^{-1} respectively.

So far we have focussed on the breaking of the $(CH_3)C–S$ bond as the initial step for the rearrangement of 2-methylthiirane. The breaking of the other C–S bond would lead to the formation of the biradical intermediate **6**, which lies 25 kJ mol^{-1} above species **2** according to the CI calculations. In this case the calculated activation energies for formation of prop-1-ene-2-thiol (**7**) and thioacetone (**8**) are 240 and 259 kJ mol^{-1}, respectively, which are about 20 to 40 kJ mol^{-1} higher than that for the formation of prop-1-ene-1-thiol. Experimentally, there was no clear evidence for the formation of **7** and **8**.

Side reactions. Although our main concern in this work was the isomerization of the thiirane compounds, the experimental results showed that secondary reactions led to the formation of hydrogen sulfide, alkynes, carbon disulfide and thiophene, as could be expected for a high temperature pyrolysis system. The facts that an olefin and diatomic sulfur were the only products obtained when thiirane or 2-methylthiirane was heated in the short-path pyrolyser, and that the olefin thiol as well as the products of secondary reactions were obtained when the long-path pyrolyser was used, strongly suggest that the secondary reactions mainly originated from the olefin thiols. Although there has been no detailed experimental investigation of the thermal reactions of olefin thiols, it seems probable that hydrogen sulfide and some alkynes were produced from the elimination reactions of the thiols. Furthermore, thiophene has been observed as a side product in the photochemical formation of ethenethiol from hydrogen sulfide and acetylene, and in the high temperature preparation of ethenethiol from vinyl chloride, possibly due to an association reaction of two ethenethiol molecules *via* a radical mechanism.[33,34] Finally, the formation of carbon disulfide apparently proceeds through some bimolecular processes. Carbon disulfide has been observed as a product in the IR laser photolysis of thiirane in the presence of SF_6 as sensitizer.[35] The proposed pathway involves extrusion of a singlet sulfur atom from a highly vibrationally excited thiirane molecule, and the insertion of the sulfur atom into a C–H bond of a second thiirane molecule as important intermediate steps.[35]

Conclusions

The relative barrier heights for the isomerization of thiirane and 2-methylthiirane calculated by the UMNDO and MNDO-HE-CI methods are in qualitative agreement with the experimental observations for the high temperature mode of reaction of these compounds. The theoretical results also suggest that the conversion of thiirane and 2-methylthiirane into olefin thiols and of thiirane into thioacetaldehyde proceeds through a non-synchronous concerted pathway with the formation of a biradical species **b** preceding a 1,2-hydrogen shift. Such a mechanism is in harmony with the concurrent formation of *trans*- and *cis*-prop-1-ene-1-thiol in the isomerization of 2-methylthiirane.

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