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PYROLYSIS OF 1,2-ETHANEDITHIOL: MICROWAVE SPECTROSCOPIC DETECTION OF VINYL MERCAPTAN, CH_2=CHSH

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Vinyl mercaptan was identified in the thermal decomposition (600-950°C) products of 1,2-ethanedithiol and thiirane. A microwave spectroscopic study of CH_2=CHSH and CH_2=CHSD showed that the molecule is planar with the total dipole moment of 0.896 ± 0.007 D and has the _syn_-form.

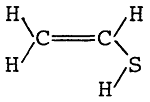
Vinyl mercaptan (ethenethiol) and related enethiols were considered to be very unstable by analogy with vinyl alcohol (ethenol) and not to exist as stable monomers until they were found in photochemical reaction products.[2,3)] We wish to report microwave spectroscopic detection of vinyl mercaptan in the gas phase generated by the pyrolysis of available precursors and some discussion on the reaction mechanism of the decomposition as studied by microwave spectroscopy.

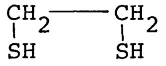
Definite evidence for the formation of vinyl mercaptan was obtained by studying the thermal decomposition products of 1,2-ethanedithiol by microwave spectroscopy. Ethanedithiol was introduced at a pressure of 0.02 - 0.04 Torr through a quartz pyrolysis tube of 6 mm inner diameter into a microwave parallel plate cell of 80 cm length. The pyrolysis temperature ranged from 600°C to 1000°C.

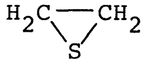
From the observed microwave spectrum it was made clear that the gaseous decomposition products contained among others thiirane, ethanethial, and methanethial.[4)] Thiirane[5)] was first observed at about 650°C and generated most efficiently at 850°C, above which the spectrum of thiirane became weak. Ethanethial[6)] was detected above 700°C and the spectrum was the strongest at a higher temperature (930°C). Methanethial[7)] generated by the cleavage of the C-C bond was observed at higher temperatures (above 800°C). We found that the higher the furnace temperature was raised the stronger was the signal intensity of methanethial. A set of strong lines were observed around 55 GHz in the neighborhood of the absorption lines of ethanethial. The absorption lines were distinguished from those of ethanethial by means of their characteristic temperature dependence, which was very similar to that of thiirane. The spectrum was assigned to the a-type transition of vinyl mercaptan on the basis of the resolved Stark patterns, as well as of the calculated frequencies which were obtained using the molecular parameters estimated from those of molecules with the vinyl skeleton (chloroethene,[8)] and (methylthio)ethene[9)]) and methanethiol.[10)] Other absorption lines of vinyl mercaptan were subsequently observed and assigned. The rotational constants of the normal species are given in Table 1 together with those of the deuterated species. Detailed Stark effect measurements on the several low-J transitions yielded the dipole moment components along the principal axes: $\mu_a = 0.813 \pm 0.003$, $\mu_b = 0.376 \pm 0.010$, and $\mu_{total} = 0.896 \pm 0.007$ D.

The formation of vinyl mercaptan upon pyrolysis of ethanedithiol is in parallel with the generation of vinyl alcohol by flash vacuum pyrolysis of ethylene glycol.[11)] A possible correlation between the electron-impact-induced fragmentation of a molecule and its pyrolytic fragmentation has sometimes been observed.[12)] The mass spectrum of ethanedithiol revealed that the major fragmentation path is the loss of hydrogen sulfide from the parent ion. The present detection of vinyl mercaptan among the pyrolysis products is consistent with the expected correlation stated above.

A microwave spectroscopic study of the pyrolysis products of deuterated ethanedithiol (mixture of d_1 and d_2 species) in parallel with that of the normal species led to the assignment of the CH_2=CHSD species. Their rotational constants, listed in Table 1, provide us with some insight into the structure. Since the inertia defect is small and positive as shown in Table 1, vinyl mercaptan is planar. The substitution coordinates ($|a| = 0.75$ and $|b| = 1.36$) of the hydrogen atom attached to the sulfur atom clearly show that it has a *syn*-form as shown in 1. This *syn*-form was predicted by a recent *ab initio* MO calculation[9)] to be more stable than the *anti*-form. When the same molecular parameters as those in chloroethene[8)] are assumed for the vinyl skeleton the CS bond distance (1.766 Å) is expected to be remarkably shorter than that in alkyl mercaptans and the CCS angle (127°) to be much wider than those in the substituted ethylene molecules (120°). These findings agree with the structural features of vinyl alcohol.[11)] The shortening of a CC single bond adjacent to a double bond is always encountered and is fully discussed in terms of the environmental effect.[13)]


1


$CH_2(SH)—CH_2(SH)$
2


3

Another conceivable precursor 3 of vinyl mercaptan was also examined by using the pyrolysis-microwave technique. Vinyl mercaptan is postulated as an intermediate in the pyrolysis of thiirane yielding H_2S and acetylene.[14)] We observed that above 700°C thiirane isomerized into vinyl mercaptan.

Table 1. Rotational constants (MHz) and inertia defect (amuÅ^2)$^{a)}$

Constant	syn-CH_2=CHSH	syn-CH_2=CHSD
A	49815.42 ± 0.22	42210.99 ± 0.20
B	5835.74 ± 0.07	5797.49 ± 0.06
C	5222.06 ± 0.06	5096.35 ± 0.05
$\Delta^{b)}$	0.0320 ± 0.0015	0.0202 ± 0.0013

a) The uncertainties are 2.5 times the standard deviation derived from the least squares fit on transitions with J less than 4.

b) The inertia defect is calculated by $\Delta = 505379(1/C - 1/A - 1/B)$.

Some information on the decomposition mechanism of ethanedithiol 2 may be obtained from our microwave spectroscopic observation. The spectrum of thiirane 3 observed in the pyrolysis of the deuterated species was as strong as in that of the normal species, whereas the intensity of the spectrum of the normal vinyl mercaptan from the deuterated species was about one half of that in the pyrolysis of the normal species. This indicates that H_2S eliminations from 2 yielding 1 and 3 take different paths. In the formation of 3 the hydrogen atoms of H_2S mainly come from those attached to the sulfur atoms; hence, the deuteration has little influence on the formation of 3. In the formation of 1, however, one of the hydrogen atoms attached to the sulfur atom remains on decomposition. Accordingly, 1 among the decomposition products of 2 cannot result from the rearrangement of 3 in the microwave cell, although it was established in the study of the pyrolysis of ethanedithiol and thiirane that 3 is formed in the pyrolysis of 2 and that 3 isomerizes thermally to give 1.

The present study of vinyl mercaptan has shown that a proper choice of precursors in the pyrolysis leads to generation of unstable molecules formerly synthesized only by a photochemical route.

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