Microwave Spectrum of Thioketen, $H_2C{=}C{=}S$

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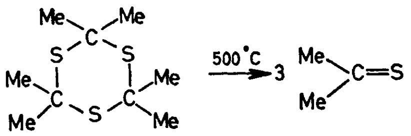
Summary The microwave spectrum of thioketen, $H_2C{=}C{=}S$, has been detected when hexamethyltrithian is pyrolysed at 900 °C.

USING microwave spectroscopy to analyse the products of pyrolysing hexamethyltrithian (the trimer of thioacetone) at 900 °C we have detected the unstable species thioketen. The microwave technique is particularly suitable for characterising this type of molecule because under the low pressure conditions (*ca.* 10—30 μm Hg) which are an optimum for microwave detection the collision rate is low enough for the species to survive for several seconds.

Some evidence of thioketen has been previously published[1] in which the compound t-butyl ethynyl sulphide is pyrolysed at 460 °C

$$(CH_3)_3CSC{\equiv}CH \xrightarrow{460\,^{\circ}C} H_2C{=}C{=}S$$

Hexamethyltrithian, the cyclic trimer of thioacetone, was prepared by reacting H_2S (or P_2S_5) with acetone in hydrochloric acid solution.[2] It has previously been shown that when hexamethyltrithian is passed through a quartz tube at a temperature of about 500 °C and a pressure of 30μm Hg, thioacetone is produced (Scheme) and can be detected by microwave and photoelectron spectroscopy[3] in the pyrolysis products. The products of pyrolysis are flowed directly into the cell of a microwave spectrometer or the target chamber of a photoelectron spectrometer.



SCHEME

In an attempt to observe thioketen the temperature of the furnace was raised to about 900 °C and the spectrum shown in the Figure is obtained. This spectrum has been assigned as the $J = 3 \leftarrow 2$ transition of a prolate asymmetric rotor. The measured frequencies and derived ground state rotational constants are given in the Table.

TABLE

Frequencies of observed lines and rotational constants/MHz.

Assignment	Frequency	Obs. — Calc.
$3_{13} \leftarrow 2_{12}$	33 438·37	$-0·002$
$3_{22} \leftarrow 2_{21}$	33 607·84	0·074
$3_{21} \leftarrow 2_{20}$		$-0·073$
$3z_{3} \leftarrow 2_{02}$	33 611·70	0·003
$3_{12} \leftarrow 2_{11}$	33 783·23	$-0·002$

A_0 = 282 081 (assumed from keten[4])
B_0 = 5 659·45 ±0·03
C_0 = 5 544·50 ±0·03
D_{JK} = 0·170 ±0·004

As can be seen in the Figure, the lines with K_A even have approximately one third the intensity of those for which K_A is odd. This intensity pattern is consistent with that of a molecule which possesses two identical H nuclei and C_2 symmetry about the A axis, as is expected in thioketen. The $C_2(A)$ operation permutes the two spin ½ H nuclei and spin statistics predict the 3:1 intensity ratio. Note that the $K_A = 2$ lines are not quite resolved (Table). Thus the observed line is a broad unresolved doublet and the same height as the $K_A = 0$ line, which is a singlet. No other strong lines appear (or are expected to appear) in the region 26·5—40 GHz, the range of the microwave spectrometer.

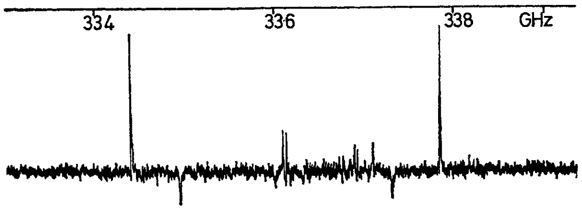


FIGURE. The spectrum of the $J = 3 \leftarrow 2$ R-branch transition of thioketen, H_2CCS. The $K_A = 0$ and $K_A = 2$ lines lie close together at approximately the centre of the spectrum and are flanked symmetrically by the $K_A = 1$ lines. Frequencies and assignments are given in the Table. Note that the $K_A = 2$ transitions yield a single broad line which is not quite resolved.

A preliminary estimate of 1·56 Å for the C=S bond length can be made if the structure of the H_2 C=C group is assumed to be the same as in keten.[5] A comparison of the CO bond lengths in CO (1·128 Å),[6] H_2CCO (1·161 Å)[6] and H_2CO (1·204 Å)[5] with the CS bond lengths in CS (1·535 Å)[5] and H_2CS (1·611 Å),[7] predicts a C=S bond length of 1·56 Å for the thioketen molecule.

The way in which the new species is produced, as well as the assignment of the four observed lines (Table) to a $J = 3 \leftarrow 2$ transition are thus entirely consistent with the thioketen molecule. In particular, the number of lines, their relative intensities and the derived values of the rotational constants B_0 and C_0 are in perfect agreement. The Obs.—Calc. column of the Table provides final proof of this assignment of the lines. An accurate determination of the structure and properties of thioketen is in progress.

It thus seems that the further process,

$$(CH_3)_2C{=}S \xrightarrow{900°C} H_2C{=}C{=}S + CH_4$$

occurs at the higher temperature producing thioketen as expected.

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[1] E. G. Howard Jr., *Chem. Abs.*, 1962, **57**, P13617f.

[2] D. S. Breslow and H. Skolnik, 'Multi-sulphur and sulphur and oxygen 5- and 6- membered heterocycles,' Part II Interscience, New. York, 1966.

[3] H. W. Kroto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, in the press.

[4] J. W. C. Johns, J. M. R. Stone, and G. Winnewisser, *J. Mol. Spectroscopy*, 1972, **42**, 523.

[5] A. P. Cox, L. F. Thomas, and J. Sheridan, *Spectrochim. Acta*, 1959, **15**, 542.

[6] W. Gordy and R. L. Cook, 'Microwave Molecular Spectra,' Wiley, New York, 1970.

[7] D. R. Johnson, F. X. Powell, and W. H. Kirchhoff, *J. Mol. Spectroscopy*, 1971, **39**, 136.