THE PHOTOELECTRON SPECTRUM OF AN UNSTABLE SPECIES IN THE PYROLYSIS PRODUCTS OF DIMETHYLDISULPHIDE

H.W. KROTO and R.J. SUFFOLK

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

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A new photoelectron spectrum has been observed in the pyrolysis products of dimethyldisulphide, CH_3SSCH_3 . As the major product under these conditions is known to be the unstable species thioformaldehyde, H_2CS , the new spectrum has been assigned to this molecule. The first ionisation potential is 9.34 ± 0.01 eV which compares well with the result obtained by other techniques. The evidence for this assignment is discussed.

1. Introduction

Aliphatic thio-carbonyl compounds have in general proved very difficult to study by standard techniques because of their instability. Recently however Johnson and Powell [1, 2] succeeded in observing the microwave spectrum of thioformaldehyde in the pyrolysis products of dimethyldisulphide. In fact the molecule was quite easily produced and at the low pressures at which they worked, ≈ 0.1 mm Hg, the species was found to have a relatively long half-life, of the order of six minutes. Johns and Olsen have also studied the infra-red spectrum [3].

We have followed the same procedure for the production of H_2CS as that used by Johnson and Powell and have studied the pyrolysis products of dimethyldisulphide using a photoelectron spectrometer. We have observed a new spectrum which we have assigned to H_2CS , and we present here a report on the spectrum together with the evidence which supports this assignment.

2. Experimental

Following the procedure in ref. [2], H_2CS was produced by the pyrolysis of CH_3SSCH_3 in a quartz tube. Dimethyldisulphide (Koch Light, pure) was flowed at a pressure of 0.04 mm Hg through a quartz tube 2 mm i.d. and 300 mm long which was heated by a large ribbon type gas burner giving a heated length of about 150 mm. The products of the pyrolysis were passed directly into a Perkin Elmer P.S. 16 photoelectron spectrometer.

With the pressure of CH_3SSCH_3 set at 0.04 mm, the tube was heated and the pressure in the instrument dropped to 0.01 mm. First attempts at the observation of the H₂CS spectra were carried out using a $-126^{\circ}C$ trap before the inlet to the spectrometer to eliminate any possible by-products, i.e., CS_2 , H_2S , CH_3SH etc., but the trap removed all the species and no spectra were observed. The temperature of the trap was increased to $-80^{\circ}C$ with the same result and finally the spectrum was obtained without a trap.

Some experiments were carried out by varying the temperature of the pyrolysis in an attempt to maximise the amount of H_2CS produced. With the quartz tube at a bright orange colour ($\approx 900^{\circ}C$) an increase in the size of the bands due to CS_2 was observed together with a loss in the intensity of the H_2CS . The temperature was progressively reduced, until at the lowest temperature studied $\approx 300^{\circ}C$ an increase in bands belonging to CH_3SH relative to H_2CS and a decrease in the H_2S band was observed. The final temperature used in the study of the H_2CS for this work was $400-500^{\circ}C$ which maximised the H_2CS peaks relative to CH_3SH .



Fig. 1. (a) Spectrum between 8 and 16 eV during pyrolysis, (b) spectrum of the parent CH₃SSCH₃ before pyrolysis.



Fig. 2. (a) Spectrum of the pyrolysis products plus CH_3SH in the region 9.2 to 9.6 eV, (b) spectrum of CH_3SH from 9.2 to 9.6 eV, (c) spectrum of the first band of the new species between 9.2 and 9.6 eV.

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3. Results and discussion

In fig. 1a the complete photoelectron spectrum between 8 and 16 eV obtained from the pyrolysis products is shown. For comparison the spectrum of the parent CH_3SSCH_3 is shown in fig. 1b. This is the spectrum we observe without heating. There are two new features in the spectrum which we have assigned to H_2CS in fig. 1a. These features are shown individually in more detail in figs. 2 and 3.

Unfortunately the first band of the new spectrum is partly overlapped by the first IP of CH₃SH [4]. The feature is composed of a new band with a vertical IP of $9.338 \pm 0.010 \text{ eV}$ (see table 1), a possible second component separated by $\approx 1000 \text{ cm}^{-1}$ and overlapping bands which appear to belong to the first IP of CH₃SH. The situation which occurs is clearly indicated in the series of spectra shown in fig. 2. Fig. 2c shows the first band of the new spectrum. In fig. 2b we show the spectrum in this region obtained from pure CH₃SH, and fig. 2a shows the spectrum obtained when CH₃SH is bled *directly* into the spectrometer together with the pyrolysis products. By a comparison between the spectra shown in fig. 2 we see that the coincidence between the CH₃SH band and that of H₂CS is close, but the overall intensity pattern of this feature is such



Fig. 3. Spectrum of second band of the new species between 11.6 and 12.4 eV.

Vertical ionisation potentials (eV)		
Molecule	IP (eV)	Vibrational interval (cm ⁻¹)
H ₂ CS	9.33(8)	1000
	11.89(9)	880
CH₃SH	9.41(5)	650
	11.90	_
	13.50	-
	14.90	-
	15.5	
CH₃SSCH₃	8.82	_
	9.13	-
	11.15	_
	12.28	-
	13.38	-
	14.67	_
CS ₂	10.06	_
	12.83	550
H ₂ S	10.48	2380
	13.21	940

Table 1

that we can tentatively assign an interval of 1000 cm^{-1} as belonging to H₂CS since under our optimum conditions the contour and relative intensities were always constant. A 1000 cm⁻¹ interval is expected, belonging to the C=S stretching mode (ν_2) of H₂CS⁺. Johns and Olsen [3] predict that in the neutral molecule this frequency is 1150 cm⁻¹. A small reduction is reasonable because the orbital involved in this band is the essentially non-bonding atomic p orbital on sulphur. By comparison the C=O stretching frequency in H₂CO is reduced from 1743 cm⁻¹ in the molecule to 1594 cm⁻¹ in the ion [5].

The second new band shown in detail in fig. 3 fortunately appears to be free from other overlapping features. This band has an adiabatic IP of 11.78 ± 0.01 eV and a vertical IP of 11.90 ± 0.01 eV, and shows a well developed vibrational progression comprising at least six components having an interval of 880 ± 50 cm⁻¹. The intensity of the first component of this band relative to the overall pattern indicates that it is due to the 0–0 transition. This yields a value of 19700 ± 100 cm⁻¹ for the energy of the first excited state of H₂CS⁺ relative to the ground state.

With our system the principal by-products are expected to be H_2S , CS_2 , CS, $(CH_3)_2S$, CH_3SH . We see no band below that observed at 9.34 eV and thus $(CH_3)_2S$ is not present as its first IP is 8.67 eV [4]. We have observed the PES of CS recently [6] and this gives rise to two strong bands at 11.33 eV and 12.56 eV and again these are not observed.

We do, however, observe strong bands due to

 H_2S [7] and CS_2 [8] which fortunately do not overlap the new spectrum and furthermore assist in the calibration. Johns and Olsen [3] reported ethane, methane and acetylene amongst the by-products of the pyrolysis, but we have no evidence of their presence as measured by the photoelectron spectrometer. As we have discussed earlier we observe a small amount of CH₃SH in the first band of the spectrum.

The result for the first IP of H_2CS compares well with the value obtained by Jones and Lossing [9] of 9.44 (± 0.05) eV using electron impact techniques on the pyrolysis products of thiacyclobutane. It is also worth noting that the first IP's of H_2CS and CH_3SH are very close, 9.34 and 9.42 eV [4] respectively. Similarly the first IP of H_2CO and CH_3OH are close at 10.87 and 10.85 eV respectively [5, 10].

The valence orbital configuration of thioformaldehyde is expected to be similar to that of formaldehyde and thus that of the neutral molecule should be

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2(2b_2)^{2-1}A_1$$

The order of the two highest occupied orbitals seems to be well substantiated [11, 12] though for the lower ones there may be some question. The first IP thus should correspond to the ionisation of an electron from the essentially non-bonding p orbital $(2b_2)$ on the sulphur atom. The second electron should come from the bonding $(1b_1) \pi$ orbital. The short progression observed for the first IP and the extended pattern of the second IP are in good agreement with the behaviour expected. The pattern is quite similar to that observed for the corresponding bands in H₂CO. We have not so far been able to assign any other features definitely to H_2CS . The main reason for this is that the region where we expect to see the third IP is overlapped by bands belonging to H_2S and CS_2 .

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