

## Electronic Spectra of Thioformaldehyde and the Methyl Thiyl Radical

IN the flash photolysis of some simple sulphur containing molecules in the gas phase, we have recently observed several new electronic spectra in absorption. Largely on the basis of chemical evidence from widely different molecular systems, carriers have been assigned to  $\text{CH}_2\text{S}$  (thioformaldehyde) and  $\text{CH}_3\text{S}$  (methyl thiyl radical). We also comment briefly on some aspects of the kinetics and photochemistry.

Using flash energies up to 2,500 J and a single optical pass through a 75 cm long reaction vessel, spectra were recorded with a Hilger medium quartz spectrograph on Ilford *HP3* plates sensitized with sodium salicylate. All experiments were conducted at about 293° K.

Fig. 1 shows spectra in the 210–220 nm region which were recorded in the flash photolysis of  $\text{CH}_3\text{SSCH}_3$  (dimethyldisulphide). The strong, short lived, feature at 216 nm is the Herzberg  $\text{CH}_3$  band<sup>1</sup>, and in addition three new spectra are indicated. The red-shaded band, with a short wavelength head at about 211.75 nm, exhibits a "coarse fine-structure" which seems to be the result of the presence of the  $\text{CH}_2\text{S}$  molecule. This species persists for several seconds after flashing. The single, diffuse, band centred at about 218.5 nm is assigned to the  $\text{CH}_3\text{S}$  radical which has a decay time comparable with that of the  $\text{CH}_3$  radical. Fig. 1 also shows two narrow bands, disposed one on each wavelength extreme of the  $\text{CH}_3$  transition, but assignment of this spectrum is still preliminary. The 211.7 nm feature has been observed in the flash photolysis of  $\text{CH}_3\text{SSCH}_3$ ,  $\text{CH}_3\text{SCH}_3$ ,  $\text{CH}_3\text{SH}$ ,  $\text{COS} + \text{CH}_4$ ,  $\text{CH}_2\text{N}_2$  (diazomethane) +  $\text{COS}$ ,  $\text{CH}_2\text{N}_2 + \text{H}_2\text{S}$ , and  $\text{CH}_2\text{N}_2 + \text{CS}_2$ . The  $\text{CH}_3$  transition was detected in each of the first four molecular systems. In the experiments with  $\text{CH}_2\text{N}_2$  with either  $\text{COS}$  or  $\text{H}_2\text{S}$ , the intensity of the 211.7 nm band was independent of the flash energy—provided the diazomethane was entirely photolysed.

From purely chemical evidence unequivocal assignment of the 211.7 nm band to  $\text{CH}_2\text{S}$  is difficult because direct production of  $\text{CH}_2\text{S}$  in a primary photochemical process

cannot be clearly demonstrated. It is considered that the carrier of the band must contain each of the elements C, H and S. The spectrum has been detected only in systems which contain all three elements, and there are no plausible structures to which the band can be attributed which contain only a pair of the elements.

Production of  $\text{CH}_2\text{S}$  by disproportionation of  $\text{CH}_3\text{S}$  radicals in the photosensitized decomposition of  $\text{CH}_3\text{SSCH}_3$  has been demonstrated by free-radical mass-spectrometry<sup>2</sup>. The production of  $\text{CH}_2\text{S}$  has also been proposed on the basis of end product analysis in static direct-photolysis experiments with  $\text{CH}_3\text{SSCH}_3$  (ref. 3) and in the  $\text{COS} + \text{CH}_4$  photochemical system<sup>4</sup> (subsequent to  $\text{S}(\text{D})$  insertion into  $\text{CH}_4$ ). It must be formed as a major intermediate via the  $\text{CH}_3\text{S}$  radical in the flash photolysis of the compounds containing the  $\text{CH}_3\text{S}$  group. The 211.7 nm band would seem to correspond to a major product for it can be observed with flash energies down to a few hundred joules. From a study of the kinetics of the diazomethane reactions, we conclude that the carrier of the 211.7 nm band results from a fast reaction of the  $\text{CH}_2$  radical either with  $\text{COS}$  or  $\text{H}_2\text{S}$ . The transition complexes can be written respectively  $\text{C}_2\text{H}_2\text{SO}$  and  $\text{CH}_2\text{S}$ , and the only common fragment with appropriate properties is  $\text{CH}_2\text{S}$ . The "coarse fine-structure" of the band appears to correspond to "K" sub-bands due to quantization of rotation about the axis of low moment of inertia. Analysis of the sub-band structure could not be attempted because of inadequate dispersion. A broad band at 208 nm detected in absorption following irradiation of dimethyl disulphide in a hydrocarbon glass at 77° K has been previously attributed to the  $\text{CH}_2\text{S}$  monomer<sup>5</sup>.

The band at 218.5 nm was observed quite strongly in the flash photolysis of  $\text{CH}_3\text{SSCH}_3$ ,  $\text{CH}_3\text{SCH}_3$  and  $\text{CH}_3\text{SH}$ . The maximum intensity of the band approximately coincided with the maximum intensity of the photolytic flash over a wide range of flash energies and initial pressures. We therefore conclude that the carrier is a primary product of the photodecomposition in these experiments and attribute the spectrum to the methyl thiyl radical. Perhaps the assignment is obvious because of the extreme improbability that any other transient species could be produced in roughly equal yield from the three parent compounds.

Incidental to these experiments we have shown that neither the  $\text{CH}_3$  spectrum nor that of  $\text{CH}_2\text{S}$  is observed in the flash photolysis of  $\text{CS}_2$  (210 nm system) in the presence of  $\text{CH}_4$ . Thus the atomic sulphur must be produced almost entirely in its electronic ground state, which confirms earlier findings<sup>6</sup>.

A. B. CALLEAR  
J. CONNOR  
D. R. DICKSON

Physical Chemistry Laboratory,  
Lensfield Road,  
Cambridge.

Received December 23, 1968.

<sup>1</sup> Herzberg, G., and Shoosmith, J., *Canad. J. Phys.*, **34**, 523 (1956).

<sup>2</sup> Jones, A., Yamashita, S., and Lossing, F. P., *Canad. J. Chem.*, **46**, 833 (1968).

<sup>3</sup> Steer, R. P., and Knight, A. R., *J. Phys. Chem.*, **72**, 2145 (1968).

<sup>4</sup> Gunning, H. E., and Strausz, O. P., *Reactions of Sulphur Atoms, Adv. in Photochem.*, **4**, 143 (Interscience, 1966).

<sup>5</sup> Rosengren, K. J., *Acta Chem. Scand.*, **16**, 2284 (1962).

<sup>6</sup> Callear, A. B., *Proc. Roy. Soc., A*, **276**, 401 (1963).

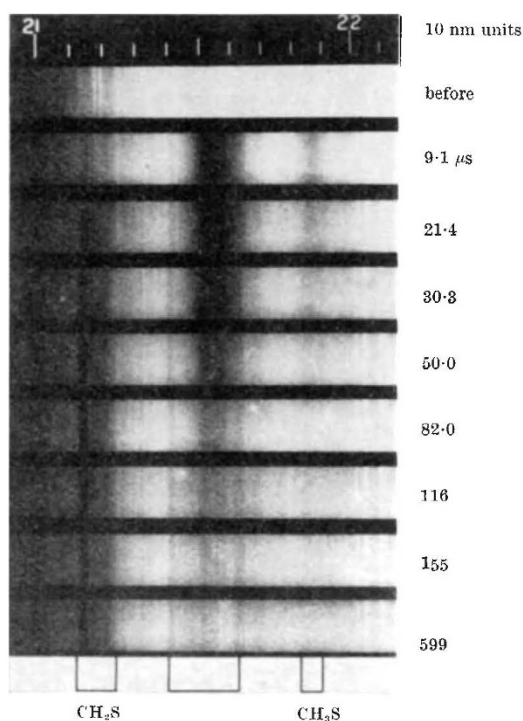


Fig. 1. Transient spectra in flashed dimethyldisulphide.

## Ternary Compounds of Uranium-Carbon and the Group VIII A Elements

TERNARY compounds of uranium and carbon with the first row elements of group VIII A in the periodic table have been known for some time. This is because of the relevance of the appropriate ternary phase relationships