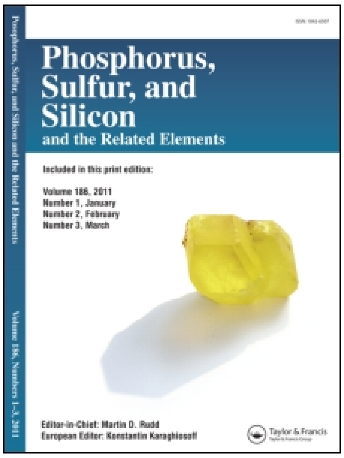

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Studies by P.E.S. of Highly Reactive Sulphur Species

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STUDIES BY P.E.S. OF HIGHLY REACTIVE SULPHUR SPECIES

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Abstract We report the first spectroscopic detection (photoelectron spectroscopy) of germathione, silathione and germanone, which previously had been characterized only by chemical trapping.

INTRODUCTION

The last few years have shown an increasing interest in species with a P_π-P_π bond between a group IVB element and a heteroatom. The difficulty to isolate these compounds is related to their high reactivity, generally they can only be characterized by chemical trapping (1).

In this work we present the evidence and characterization, by photoelectron spectroscopy, of germathione and germanone. We have generated these two compounds directly in the ionization chamber by flash-thermolysis under reduced pressure ($5.1o^{-2}$ mbars) of appropriate precursors.

Experimental results as well as those from a theoretical approach will be used to discuss the electronic characteristics of these species.

EXPERIMENTAL AND CALCULATION CONDITIONS

Photoelectron spectra were recorded with a Perkin-Elmer PS18 equiped with a HeI HeII source. Thermolysis was performed with a variable temperature probe. The evaporation chamber is separated from the ionization chamber by about 3o cm of independently heated me-

tallic tube. The spectra were calibrated by the $^2P_{1/2}$ and $^2P_{3/2}$ bands of Xenon (12.12 and 13.43 eV) and of Argon (15.76 and 15.93 eV).
Calculations were performed with the PS HONDO program (2) variant of the HONDO programm in which pseudo potentials are included (3). The basis set is of the 4-31G type with d-polarization orbitals on the germanium. Polarization and correlation orbitals effects were approximated using a procedure based on a partial perturbative treatment (4).

GERMATHIONE DETECTION

We have chosen as a precursor for the flash pyrolysis reaction the corresponding trimers.
Spectra of the trimers of dimethyl germathione and of diethyl germathione were analyzed between 8o° and 3oo°C. We have also examined the silathione trimer to verify the coherence of our conclusions. We could observe either a total displacement of the equilibrium trimer $\rightleftharpoons$ monomer or a partial conversion, or the formation of the dimer from the initially formed monomer.
In order to be able to unambigously conclude on this last possibility, we have determined the ionization potentials of the di-n-butyl germathione and di-neopentyl germathione dimers which are known to be stable.
For these two compounds two weak bands at 8 eV and 8.45 eV are observed: they are associated with the ionization of the bonding and antibonding combinations of π lone pairs of the sulphur atoms. At 9.35 eV for both compounds the strong band probably contains several ionizations: those from the σ pairs of sulphur and Ge-S bond. From 11 eV on an intense band is present associated with the ionizations of the alkyl groups (fig. 1).

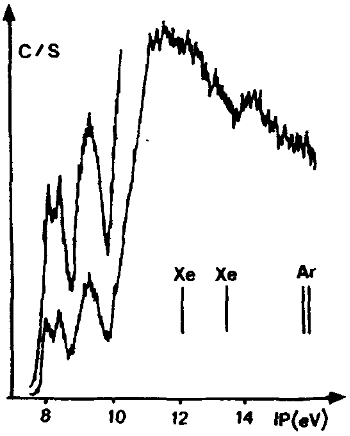


Figure 1: Photoelectron Spectrum of (n $Bu_2GeS)_2$

Trimer spectra recorded between 6o and 8o°C are comparable for the three compounds with, as expected, a slight overall stabilization of ionization potentials for the silicon derivative (fig. 2a and 3a).

The characteristics of these spectra are: a band around

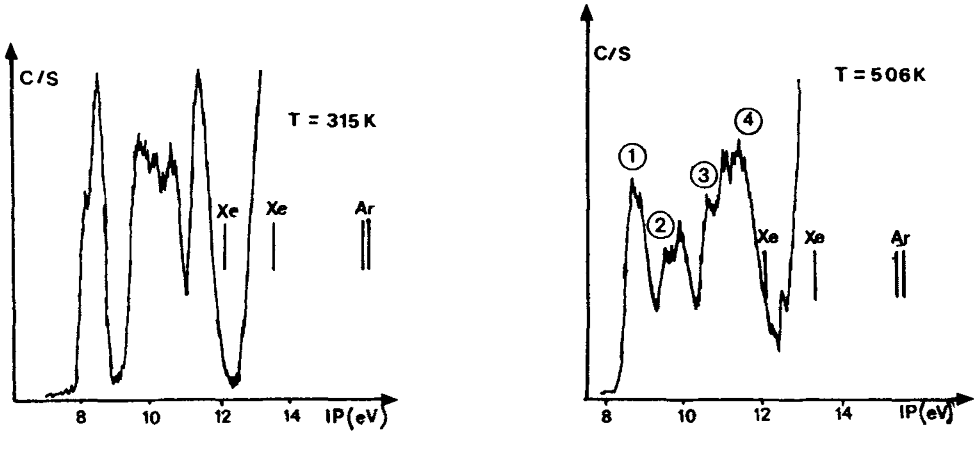


Figure 2: Photoelectron spectra of $(Me_2GeS)_3$

a) at 315 K b) at 5o6 K

9 eV with a shoulder at the low energy side, between 1o and 11 eV a large and intense band containing three distinct ionization potentials and at 11.5 eV a well separated band.

The first band corresponds to ionization of the π lone pairs on sulphur (symetry combinations a_1 and e).

For these three compounds a significant change in the spectra as a function of temperature was observed, the spectra recorded between 25o and 28o°C are totally different from those corresponding to the trimers.

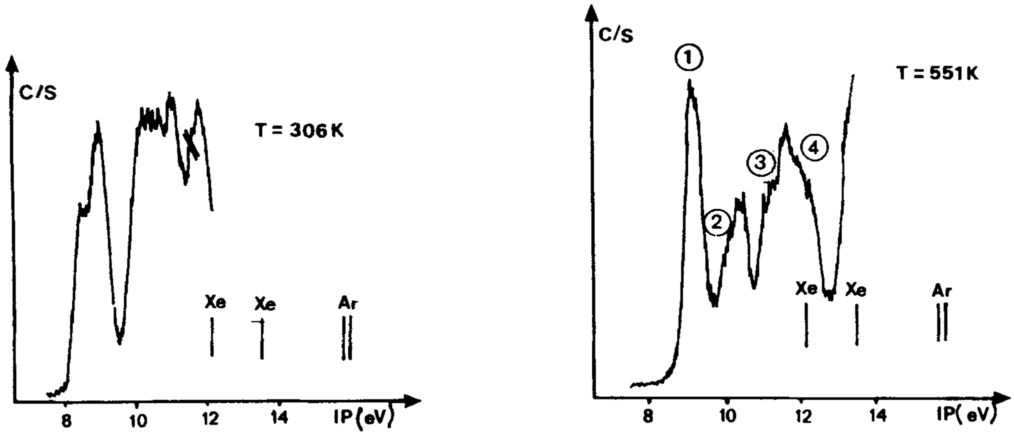


Figure 3: Photoelectron spectra of $(Me_2SiS)_3$

a) at 3o6 K b) at 551 K

The spectra of methylated germanium and silicon derivatives are similar: first band very intense compared to the second one which represents two signals and a large and strong third band (fig. 2b and 3b).

On the other hand the spectrum of the ethyl derivative shows two medium intensity peaks at 8.33 eV and 8.7 eV, a large band between 9.4-9.9 eV and an intense band at 1o.95 eV with a shoulder at 1o.6 eV. This very different allure suggests a thermal degradation mechanism leading either completely or partially to different entities (fig. 4).

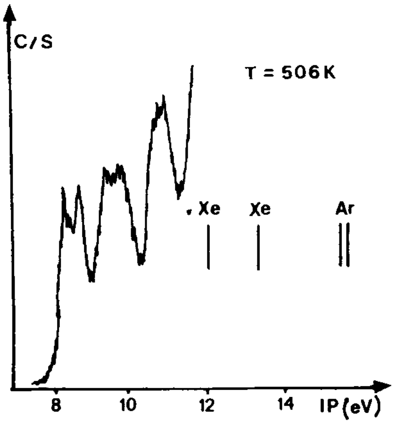


Figure 4: Photoelectron spectrum of $(Et_2GeS)_3$

The spectra of methyl derivatives can only be interpreted in terms of a coexistence of dimer and monomer. From the spectrum of the n-butyl germathione dimer we expect for the dimer dimethylated from two weak bands around 8.5 eV (changing from a n-butyl) to a methyl group causes a stabilization of ionization potentials) and an intense band above 9.5 eV. Relative intensities of the first bands and the presence of two distinct bands in the 9.5 eV region can only be explained by a high concentration of monomer; the two expected weak ionizations for the dimer in the low energy region are covered by the intense first band of the monomer associated with ionization of the non bonding pair of sulphur (band 1). There are two bands in the spectra which simultaneously increase in intensity over a temperature range of 3o° compared to the decreasing intensity of the first band:

they are at 9.9o and 11.15 eV for the germanium derivative and 1o.4 and 11.55 eV for the silicon derivative. It seems reasonable to attribute these to the presence of dimer.

The bands at 9.5o eV (germanium derivative) and 1o.1o eV (silicon derivative) significantly decrease in intensity: we attribute them to the ionization of the π electrons of the GeS and SiS bonds of the monomer. The weak intensity of this π ionization compared to that of the ionization of the non bonding is also observed in thioformaldehyde (5).

The bands at 9.9o eV and 1o.15 eV which are less sensitive to irradiation changes can only come from the dimer.

Taking into account previous experimental observations we can attribute to this form the ionization potentials observed at 11.15 and 11.55 eV which are the two ionizations of the third band whose intensity decreases using He II. The two other ionization potentials in this region 1o.75-11.47 eV and 11.o5-12.1o eV are associated with the monomeric form (bands 3 and 4).

On the other hand, if we examine the spectrum recorded at 28o^{O} for diethyl germathione trimer (fig. 4) it appears less modified compared to the original spectrum. The most notable point is the presence of two sharp bands of weak intensity at 8.33 eV and 8.7o eV which it seems logical to attribute to the dimer which under the experimental conditions would be the major component. The formation of monomer is not excluded but then ionization potentials which should be associated with it have not been detected.

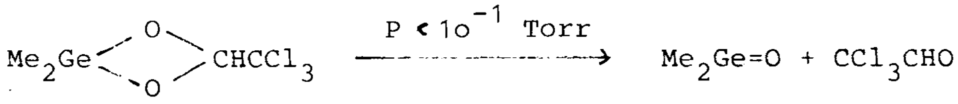
The behaviour of the ethylated derivative can be explained either by a rapid rate of dimerization of the monomer or by the presence of trimer and dimer in the pyrolysis mixture.

We note that the presence of a single intense band at 1o.95 eV in this case is coherent with the assignment of the band at 11.15 eV to the dimer in the methyl derivative.

This analysis of the variable temperature photoelectronic spectra of the trimeric derivatives of germathione and silathione allows us to conclude without ambiguity. in favour of the existence of the monomer forms of dimethyl germathione and dimethyl silathione. The characteristic ionization potentials of these species are shown in Table 1.

GERMANONE DETECTION

We wanted to extend this study to $R_2Ge=O$. The corresponding trimers are considerably more stable than their sulphur analogues; because of this we were not able to decompose them thermally. We therefore chose another precursor which should decompose more easily.



Experimentally this species cannot be distilled because under a primary vacuum it immediately decomposes to yield chloral and the trimer, the latter arising from the recombination of the monomer (6).

The photoelectron spectrum of the trimer at 9o°C is shown in fig. 5. We observe the same intensity characteristics as for the sulphur analogue.

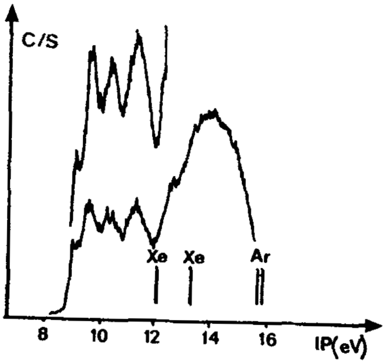


Figure 5: Photoelectron spectrum of $(Me_2GeO)_3$

The spectrum of the cyclic species has been recorded at different temperatures (fig. 6a and 6b). The decomposition of this compound is obvious as we find in the spectrum the characteristic bands of chloral (7). When vapour temperature is increased, the shape of the

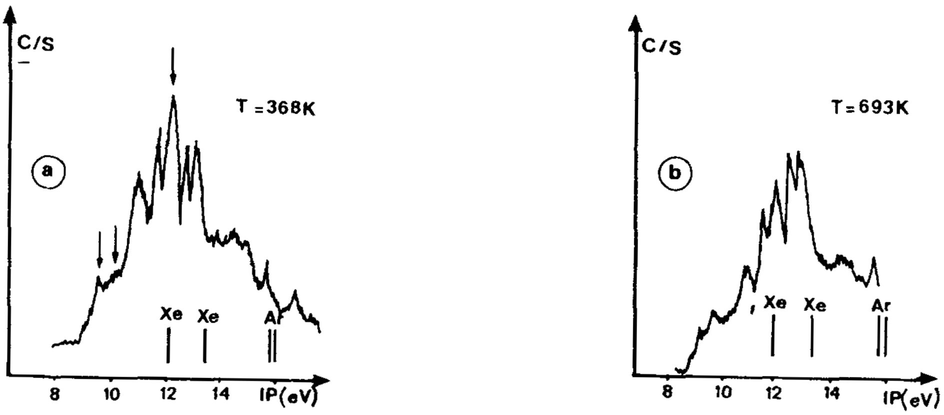
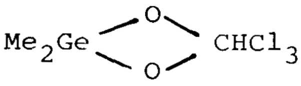


Figure 6: Photoelectron spectra of  $Me_2Ge(O)_2CHCl_3$

a) at 368 K b) at 693 K

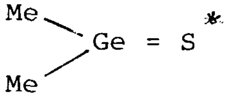
spectrum changes relatively quickly (starting at 15o°C). Thus the spectrum registered at 32o°C (fig. 6b) shows the first bands (9.3; 9.8 and 1o.5 eV) of the trimer spectrum with the characteristic bands of chloral (with slightly different intensities due to the superimposition of other bands).

This is not the case for the spectrum recorded at 95°C (fig. 6a) which only exhibits the first two bands at 9.7 and 1o.2 eV. It seems thus that in this last case the cyclic product decomposes according to the reaction described above. On comparing the intensities of the bands of this spectrum (6a) with those of chloral (fig. 5) we can attribute the following ionization potentials to the monomer: 9.7, 1o.2, 11, 12.1 eV. Above 15o°C the monomer apparently recombines as a result of thermal agitation yielding the stable trimer.

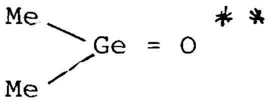
ELECTRONIC STRUCTURE OF GERMATHIONE AND GERMANONE

We wished to confirm the assignments by estimating the ionization potentials of germathione and germanone with the PS HONDO method. The calculated values are reported in table 1. We can note the excellent agreement of the experimental and theoretical values when we consider polarization effects (pol.) and loss of inter pair correlation (correl.) of the ion. In general, the first contribution is higher for non bonding orbitals than for π bonding orbitals, in contrast to the second one. There are the observed phenomena for dimethyl germathione (pol. = o.72 eV for n_S and o.57 eV for π Ge = S). In the dimethyl germanone case the polarization correlation is higher for the π Ge=O orbital (-1.66 eV) than for n_O (-1.32 eV).

TABLE 1: Calculated and experimental ionization potentials of dimethyl germathione and dimethyl germanone.



i		Pol. effect.	Corr.	Cal. IP	Exp. IP
- 8.95	n_S	+ 0.72	- 0.31	8.54	8.60
- 9.42	$\pi_{Ge=S}$	+ 0.57	- 0.40	9.25	9.55
- 11.40	σ_{Ge-S}	+ 0.53	- 0.27	11.14	10.75
- 12.62	σ_{Ge-C}	+ 0.57	- 0.19	12.25	11.47



i		Pol. effect.	Corr.	Cal. IP	Exp. IP
-10.72	n_O	+ 1.32	- 0.20	9.59	9.7
-10.97	$\pi_{Ge=O}$	+ 1.66	- 0.50	9.81	10.2
-12.13	σ_{Ge-O}	+ 1.54	- 0.27	10.86	11.
-13.12	σ_{Ge-O}	+ 0.43	- 0.13	12.83	12.1

* Structural parameters Ge=S = 2.02 A, Ge-C = 1.98 A, $\widehat{CGeS} = 120^{o}$

* * Structural parameters Ge=O = 1.63 A, Ge-C = 1.98 A, $\widehat{CGeO} = 120^{o}$

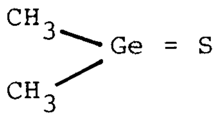
This result shows an obvious difference in the electronic reorganisation of the first ionic states of germathione and germanone. This points out the limits of a direct correlation between experimental ionization potentials and the electronic characteristics of these species in their ground state.

Such a stabilization of the ionic state of germanone can only be interpreted in terms of a strong polarization in this system, especially for the $\pi_{Ge=O}$ orbital. This would mean that this orbital is non bonding as suggested by G. Trinquier (8) and is in agreement with the very close values for the ionization potentials associated with the lone pair n_O and the orbital $\pi_{Ge=O}$ and the SCF energies. This small difference can be compared with the values of 2.9 eV (9.73 - 12.65 eV) for acetone (9) and 3.2 eV (1o.9-14.1 eV) for formaldehyde (1o).

In the same way, although the effect is smaller, the difference of approximately 1 eV observed between the ionization potentials in the n_S lone pair and the orbital $\pi_{Ge=S}$ compared to 2.4 eV (9.38 eV n_S - 11.76 π C=S) for thioformaldehyde shows a polarization of the π system in this molecule larger than for the thiocarbonyl derivatives.

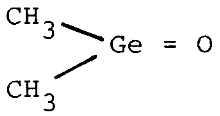
The polarity of the π bonds shown by their π charges (table 2) causes their high reactivity: dimerisation or trimerisation reactions, addition of amine or alcohol. The fact that at 3oo°C the germanone monomer recombines almost completely to the trimer and that the germathione dimer and monomer are simultaneously present under the same conditions is in agreement with the predicted reactivity.

TABLE 2: π charges and net atomic charges.



π charges			Net charges				
Ge		S	Ge	S	C	H	H'
pπ	dπ	pπ					
0.48	0.06	1.51	0.169	-0.290	-0.414	0.184	0.148

μ = 5.25 D



π charges			Net charges				
Ge		O	Ge	O	C	H	H'
pπ	dπ	pπ					
0.43	0.08	1.54	0.44	-0.552	-0.442	0.185	0.147

μ = 6.01 D

H in molecular plane ($C_{2\nu}$ symmetry); H' out molecular plane.

On the other hand the first ionization potentials associated with the ionization of the non bonding n_S and n_O pairs are very close to those observed for the corresponding carbon species 9.73 eV for acetone and 8.1 eV for thiofenchone for which it is necessary to take the destabilizing effects of the cycle into account (11).

The inductive effect of the metal atom is in this case compensated by the $n_\sigma.d_{Ge}$ transfer which appears quite important, being calculated of o.167 for germathione and o.2 for germanone.

One of the characteristics for these systems is the nature of the Ge-X bond. The ionization of the electrons of this bond is associated with the third ionization potential. We observe similar values at low energy 1o.75 eV for dimethylgermathione, 11 eV for dimethylgermanone. This suggests a higher localization of electrons on oxygen than on sulphur and a higher polarity of the Ge=O σ bond. This appears elsewhere for the σ charges: in the case of germathione the $\sigma^S \longrightarrow d_\sigma^{Ge}$ transfer is not compensated by the σ Ge-S bond polarity unlike for germanone.

CONCLUSION

In this work we have been able to identify by photoelectron spectroscopy in the gas phase dimethyl germathione and dimethyl germanone whose existence has only be infered by chemical trapping experiments.

The observed ionization potentials are interpreted in terms of the highly polar character of the π Ge=O and π Ge=S bonds. This polarization and the relatively low ionization potentials explain the very high reactivity of these species and their low lifetime.

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