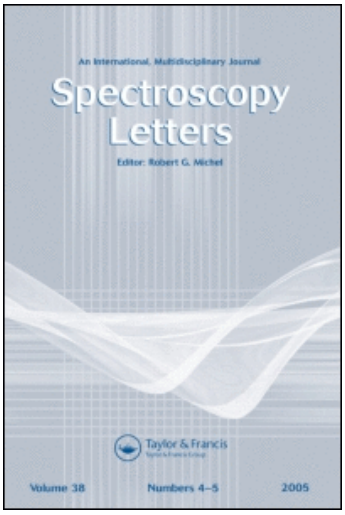

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Generation, Detection and Electronic Structure of Dimethyl Germanone by Photoelectron Spectroscopy and Quantum Calculations

C. Guimon[a]; G. Pfister-Guillouzo[a]; G. Rima[b]; M. El Amine[b]; J. Barrau[b]
[a] Laboratoire de Physico-Chimie Moléculaire, PAU, France [b] Laboratoire de Chimie des Organominéraux, TOULOUSE Cedex, France

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GENERATION, DETECTION AND ELECTRONIC STRUCTURE OF DIMETHYL GERMANONE BY PHOTOELECTRON SPECTROSCOPY AND QUANTUM CALCULATIONS[1]

Germanone, UV photoelectron spectroscopy, pyrolysis, ab initio calculations

C. Guimon and G. Pfister-Guillouzo

Laboratoire de Physico-Chimie Moléculaire, UA 474
I.U.R.S., Avenue de l'Université, 64000 PAU, France

G. Rima, M. El Amine and J. Barrau

Laboratoire de Chimie des Organominéraux, ERA 829
Université Paul Sabatier
118, Route de Narbonne, 31062 TOULOUSE Cedex, France

Chemists have long been interested in species containing multiple P_π-P_π bonds between a group IVB element, e.g. silicon and germanium, and a heteroatom (N, O, P, S, etc...). It is nevertheless only during the past several years[2] that these entities could be characterized by chemical trapping. The very high reactivity of these compounds and thus their short lifetime have long been a major obstacle to their characterization. Certain of them ($Me_2M=S$, M=Si, Ge) have recently been demonstrated using mass spectrometry[3,4] and photoelectron spectroscopy[4,5]. The monomer $Me_2M=S$ has thus been characterized by subjecting the trimer $(Me_2MS)_3$ to flash thermolysis under reduced pressure (~ 300°C and 5.10^{-2} mbar) directly in the ionization chamber of a photoelectron spectrometer.

We wished to extend this study to $R_2Ge=O$. It was found that the corresponding trimers were much more stable than their sulfur containing homologues and so we were unable to decompose them thermally. For this reason, we chose two other precursors with apparently higher potentiality :

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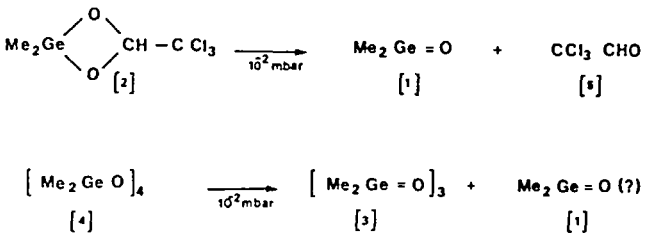


$$[Me_2GeO]_4 \xrightarrow{10^{-2}\,mbar} [Me_2Ge=O]_3 + Me_2Ge=O\ (?)$$
[4] [3] [1]

We have in fact observed that the cyclic compound [2] could not be distilled since it decomposes immediately in a primary vacuum to yield the chloral [5] and the trimer [3], the latter arising from the recombination of the monomer [1][6].

Thermolysis of the tetramer [4] similarly furnishes the trimer [3] and the monomer, which could be characterized by chemical trapping[6].

The present report is the attempt to carry out these thermolysis in order to characterize the monomer [1] by photoelectron spectrometry. In parallel to this experimental study, we performed a theoretical study of dimethylgermanone [1] and in particular calculated the first ionization potentials.

EXPERIMENTAL AND CALCULATION CONDITIONS

Photoelectron spectra were recorded on an Perkin Elmer PS 18 instrument equiped with a Helectros HeI-HeII source. Compounds [2] and [4] were decomposed under reduced pressure (< 10^{-1} mbar) in a variable temperature probe[5,7] where the evaporation chamber is separated from the ionization chamber by a metallic tube about 30 cm long which is independently heated. The vapors can thus reach about 400°C before being ionized. All spectra were calibrated with the $^2P_{1/2}$ and $^2P_{3/2}$ lines of xenon (12.13 and 13.43 eV) and of argon (15.76 and 15.93 eV).

Calculations were performed with the PSHONDO[8] variant of the HONDO[9] program, in which pseudo potentials are also included. The basis set is of the 4-31G type with polarization orbitals (d) on germanium. Corrections of polarization and of correlation of ionization potential calculations were estimated with the method of perturbations[10].

RESULTS AND DISCUSSION

The photoelectron spectra (HeI) of the trimer [3] and the tetramer [4] at minimal temperature (90°C for [3] and ambient temperature for [4])are shown in Figs 1 and 2a. The primary difference between these spectra is the respective intensities of their first two bands, with ionization potentials being comparable (table 1). The first band of [4] is in fact more intense than the second (Fig. 2a), in contrast to the spectrum of [3] (Fig. 1), whose intensity characteristics are the same as its sulfur homologue $[Me_2GeS]_3$[5]. In the case of both compounds, these initial bands are related to the combinations of the non-bonding orbitals of oxygen atoms.

The spectrum of [4] remains practically unchanged up to 280°C. It subsequently changes rapidly above this temperature, yielding the spectrum shown in Fig. 2b, which is an evident correspondence to the trimer [3]. Thus the tetramer thermally decomposes (~ 300°C) to furnish trimer and the monomer [1] by difference, although the latter could not be demonstrated in the resulting spectrum.

The spectra of compound [2] were recorded at different temperatures (Figs 3a and 3b). Here again, the decomposition of this compound is obvious, since some of the spectra include the characteristics of the chloral [5][11], whose spectrum is shown in Fig. 4 and the ionization potentials in table 1.

When vapor temperature is increased, the shape of the spectrum changes relatively rapidly (starting at 150°C). Thus, the 320°C spectrum (Fig. 3b) retains the characteristic bands of chloral (with slightly different intensities due to the superimposition of other bands) and also furnishes the first bands (9.3, 9.8 and 10.5 eV) of the trimer [3] spectrum. This is not the case for the spectrum recorded at 95°C (Fig. 3a), which exhibits only the first two bands at 9.7 and 10.2 eV. In the latter case, it would thus appear that compound [2] indeed decomposes according to the reaction described above. In the light of the intensities of these spectral bands (Fig. 3a) compared to the chloral (Fig. 4) spectrum, the following potentials can be attributed to the monomer [1]: 9.7, 10.2, 11.0 and 12.1 eV. At temperatures higher than 150°C, the monomer apparently recombines as a result of thermal agitation, yiel-

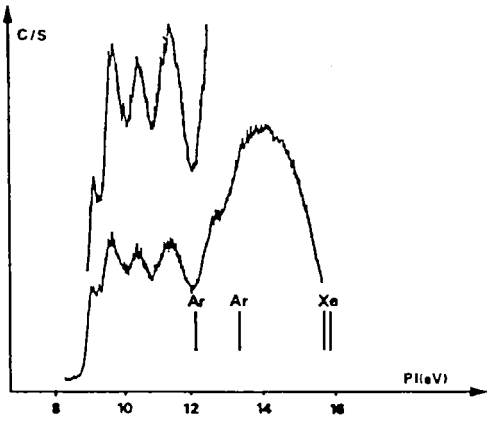


Figure 1

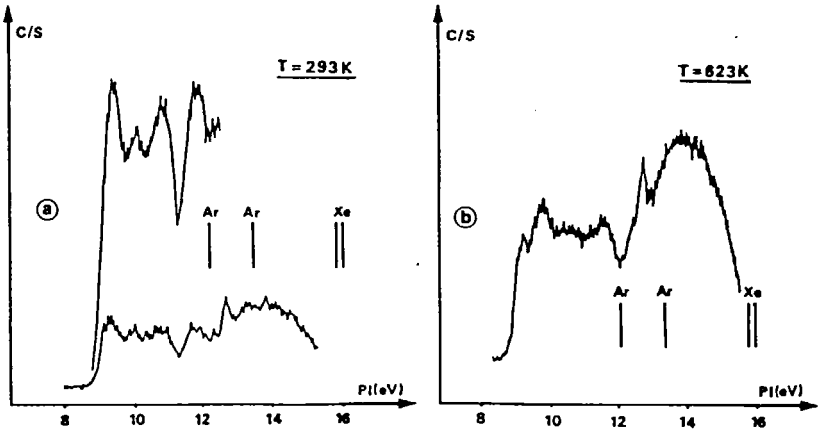


Figure 2

Table 1 - Ionization potentials (eV) of trimer [3], tetramer [4] and chloral [5]

[3] $[Me_2GeO]_3$	9.3	9.8	10.5	11.5						
[4] $[Me_2GeO]_4$	9.3	10.	10.7	11.75						
[5] CCl_3CHO	10.9	11.	11.65	12.1	12.7	13.05	14.5	15.6	16.6	17.3

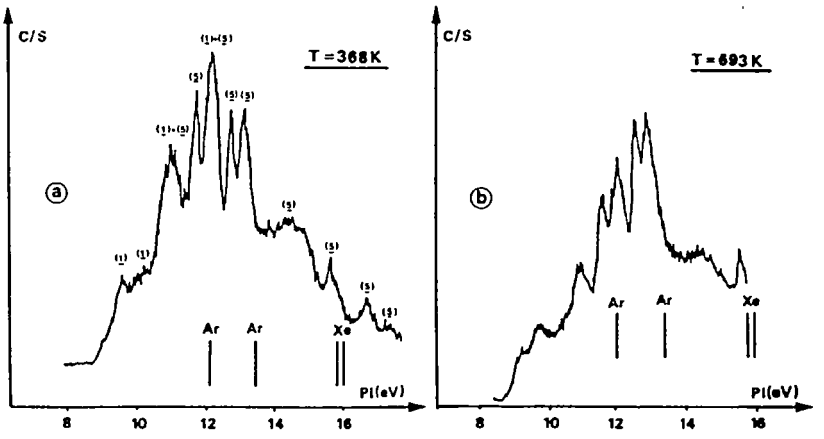


Figure 3

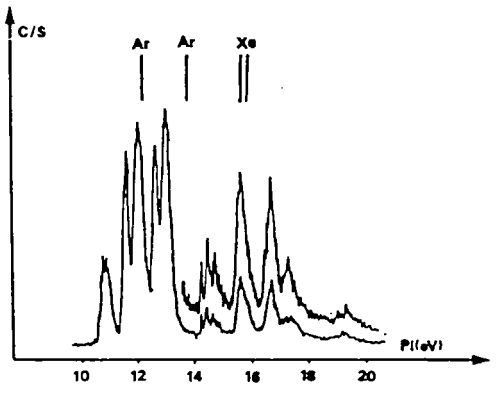


Figure 4

ding the stable trimer. This explains why only the trimer is visible when the tetramer is decomposed at 350°C.

We wished to confirm these experimental results by estimating the ionization potentials of dimethylgermanone with the PSHONDO[10] method. The calculated values are listed in table 2, where we remark the excellent correlation between experimental and theoretical values when we consider the effects of polarization (pol.) and the loss of interpair correlation (corr.) of the ion. In general, the former

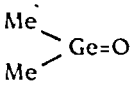
Table 2 - Calculated (IP_{calc}) and experimental (IP_{exp}) ionization potentials of dimethylgermanone

ε_i - eigen values of SCF calculation (= -IP within the Koopmans' approximation)

Pol - ion polarization correction

Corr - correction for the loss of interpair correlation of the ion

IP_{calc} : - ε_i + Pol.+ Corr.



ε_i	Pol.	Corr.	P.I. Calc.	P.I. Exp.
-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_{GeO})	-1.54	+0.27	10.86	11.
-13.12 (σ_{GeC})	-0.43	+0.13	12.83	12.1

are higher for non-bonding orbitals than for π type bonding orbitals, in contrast to the latter. This is indeed what was observed for dimethylgermathione (pol. = -0.73 eV for n_S and -0.55 eV for $\pi_{Ge=S}$). In the case of dimethylgermanone, on the other hand, the polarization correction is higher for the $\pi_{Ge=O}$ orbital (-1.66 eV) than for n_o (-1.32 eV).

This result is explained by the intense polarization of the $\pi_{Ge=O}$ orbital which thus exhibits a high non-bonding character (the localization of this orbital on oxygen is even slightly greater than that of the n_o HOMO). This lone pair character for the π orbital had been suggested by Trinquier[12] in the theoretical study of $H_2Ge=O$ and is in agreement with the very similar values of ionization potentials associated with n_o and $\pi_{Ge=O}$ (in contrast to acetone which shows a difference of 2.9 eV and even dimethylgermathione where the difference is 0.95 eV). The same is true for the following orbital of the other lone pair of oxygen which interacts with the σ_{Ge-O} orbital, also highly localized on oxygen.

This polarization of the last three occupied orbitals is shown at the level of net charges (table 3) of dimethylgermanone,

Table 3 - Net atomic charges and dipolemoment μ (Debye) of dimethylgermanone [1] and dimethylgermathione
H : hydrogen in the molecular plane (C_{2v} symmetry)
H' : hydrogen out of molecular plane

$Me_2Ge = X$

X	Ge	X	C	H	H'	μ(D.)
O	0.438	-0.552	-0.422	0.185	0.147	6.01
S	0.159	-0.290	-0.414	0.184	0.148	5.26

which are differentiated to a much greater extent than in the sulfur homologue and in acetone.

CONCLUSION

The present work has enabled us to characterize dimethylgermanone [1] in reduced pressure (< 10^{-1} mbar) vapor phase spectroscopy. Until the present, the existence of this compound has been shown only indirectly by chemical trapping. It was nevertheless necessary to record its photoelectron spectrum at a relatively low temperature (less than 100°C) since at higher temperatures, intermolecular collisions resulting from thermal agitation cause the monomer to recombine into the highly stable trimer. This explains why only the trimer can be detected when the tetramer is decomposed at around 300°C.

In addition to confirming our attribution of the ionization potentials of this molecule, the ab initio calculations performed show that the Ge=O bond is highly polarized, reflected by the proximity of the first two ionization potentials associate with the σ type n_o lone pair of oxygen and the $\pi_{Ge=O}$ orbital, which has a strong character of a π type n_o lone pair. This polarization and the relatively low values of the first ionization potentials also explain the very high reactivity of dimethylgermanone and thus its short lifetime.

Acknowledgments

The calculations have been performed on the CRAY-ONE of Centre de Calcul Vectoriel pour la Recherche, Ecole Polytechnique, Palaiseau, France (ATP CRAY 1983).

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