Note

Investigation of Hg(SiMe₃)₂ and Me₃Si radical by photoelectron spectroscopy and theoretical methods

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ARTICLE INFO

ABSTRACT

He I photoelectron spectra of bis-(trimethylsilyl)-mercury and its gas phase thermolysis product, Me₃Si radical, are reported. The first vertical ionization energies were determined to be 7.37 and 7.32 eV, respectively, and compared to calculated values as obtained at different levels of theory. The interpretation of spectra together with the nature of Si-Hg-Si bond is discussed.

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1. Introduction

The use of free radical reactions in the synthetic chemistry has increased intensively since the mid 1980s. In close relation to this area, silicon-centred radicals have also played an important role in organic synthesis, polymer chemistry and material sciences in the last few years [1]. For example, radical polymerization of styrene by trimethylsilyl radicals (Me₃Si) – formed from bis-(trimethylsilyl)-mercury – has been reported [2]. Me₃Si radical can be a key reaction intermediate in such type of processes, consequently its ionization energy is an important thermochemical value.

Various photoionization studies in relation to silicon containing radicals including H₃Si [3], Cl₃Si and HCl₂Si [4] can be found in the literature. Structure and chemical properties of Me₃Si radical is also discussed in detail [5]. Thermochemistry and dissociative photoionization of trimethylsilyl species were investigated by Dávalos and Baer [6]. However, few attempts can be found in the literature aiming to determine the ionization energy (IE) of the trimethylsilyl (Me₃Si) radical [7,8]. The reported values have been determined by mass spectrometry (MS) based on the measurement of appearance energy (AE) of the trimethylsilyl ion from an appropriate precursor. In doing so, difficulties arise in relation to the evaluation of the ionization efficiency curves, and the precision of the thermochemical data used in the thermochemical cycle. As a result, uncertainty of data determined by such an indirect way is larger compared to a direct method. In order to eliminate such sources of error, gas phase generation of radicals followed by IE measurement by photoelectron spectrometry (UPS) is a frequently used and promising technique [9].

bis-(Trimethylsilyl)-mercury is an ideal precursor in order to produce Me₃Si. Considering the high covalent character and low dissociation energy of the mercury–silicon bonds easy and high yield production of Me₃Si radicals via thermolysis can be expected.

In this present work, Hg(SiMe₃)₂ and its gas phase thermolysis product, Me₃Si, have been studied by He I photoelectron spectroscopy. The primary aim was to determine the first ionization energy of radical Me₃Si, but further information concerning the electronic structure of Hg(SiMe₃)₂ has also been deduced.

2. Experimental and computational details

The preparation of Hg(SiMe₃)₂ was performed by Biffar's method [10], modified by Eaborn et al. [11]. Gas phase thermolysis was carried out at different temperatures in the range of 350–750 ℃, in a quartz tube (8 mm i.d.) heated along 25 cm and attached via a cold trap to the gas inlet system of the photoelectron spectrometer (ATOMKI ESA-32, described elsewhere [12]). Prior to thermolysis the sample was evaporated in a moderately heated (~60 ℃) glass sample holder connected to the quartz tube. In the case of Hg(SiMe₃)₂ direct inlet system was used at room temperature. The spectrometer was operated at a resolution of 30 meV measured on the ²P₃/₂ peak of Ar. The spectra were recorded at He I energy, with 20 meV steps by using 3 eV analyzer pass energy. In

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order to support experimental photoelectron spectra *ab initio* and density functional (DFT) quantum chemical calculations were carried out by using the quantum chemical program package GAUSSIAN 03 Revision C.02 [13].

3. Results and discussion

Fig. 1 shows the He I spectrum of $Hg(SiMe_3)_2$, while Fig. 2 presents photoelectron (pe) spectra recorded at different stages of the thermolysis experiment. The low energy part of the precursor spectrum contains two broad bands centred at around 7.4 and 10.4 eV. According to cc-pVTZ (C, H, Si)//cc-pVTZ-PP (Hg) [14] B3LYP calculations the first band can be assigned to a single MO composed by ligand orbitals and atomic Hg orbital of *p*-character. The deconvoluted second band consists of three peaks with maxima at 10.03, 10.43, and 10.75 eV. The first two peaks can be assigned to two degenerate MO pairs localized mainly on the $SiMe_3$-groups, while the third one can be related to ionization from a MO dominated by atomic Hg *s*-character.

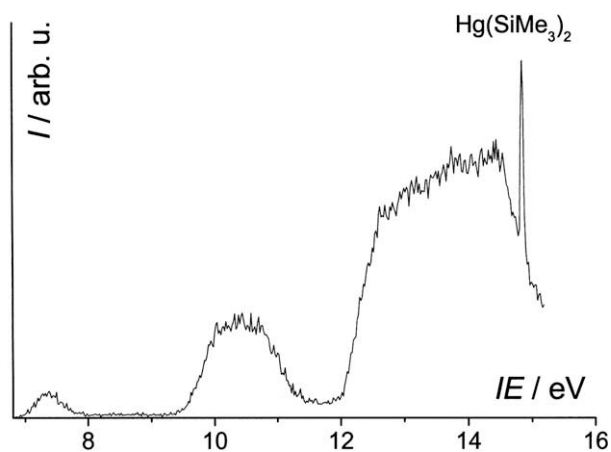Spectrum II on Fig. 2 has been recorded at 350 °C thermolysis temperature, while the cold trap was kept at −10 °C (ice/salt cooling bath). The first band at ~7.3 eV is characteristic both for the precursor and the $SiMe_3$ radical (see later), while the second one at 8.7 eV agrees well with the first *IE* of hexamethyldisilane [15], which is an obvious recombination product of $SiMe_3$ radicals. Spectrum III was produced by introducing the content of the cold trap at room temperature. Both the spectrum and the outlook feature of the sample (yellow crystals) refer to unchanged $Hg(SiMe_3)_2$. We can not explain precisely the origin of the additional feature appearing at ~9.2 eV. Possibly, it can belong to some side-product(s) formed by the reaction between the precursor and the degradation product(s) in the cold trap. Spectrum IV was obtained in such a circumstances that the quartz tube temperature was 750 °C, while the cold trap was kept at −10 °C. The spectrum is similar to spectrum II, however its assignment is different in the light of spectrum V. This last spectrum has been recorded by introducing the content of the cold trap warmed up to room temperature. The only band at 8.7 eV in the low energy part can be ascribed again to the first *IE* of hexamethyldisilane. This experimental fact proves without doubt that spectrum IV belongs exclusively to $SiMe_3$ radical, where the first band can be related to the removal of the unpaired electron providing IE_{1V} = 7.32 eV. An indirect, qualitative support of this conclusion comes from the comparison of area under the first band in spectrum II and IV. In the latter case the relative intensity has increased in comparison to the second one indicating the formation of a species with low ionization energy.

Table 1 summarizes our experimental and calculated IE_{1V}-($SiMe_3$) values. Comparing *IE* values determined by UPS and MS (7.31 eV [8]), excellent agreement is found. As far as calculated *IE*s are concerned, best agreement with the experimental values is given by the EOMIP–CCSD(2) [16] calculations which are superior to B3LYP [17] and CCSD(T) [18] methods, where one can calculate the first ionization energy as a difference in the ground-state energy of the ion at the neutral molecule geometry and that of the neutral molecule [19].

These values are well above the adiabatic ionization energy (6.24 eV) which can be derived from the heats of formation of the radical and its ion based on threshold photoelectron–photoion coincidence spectroscopic investigation of various trimethylsilyl species [6]. This substantial difference can be due to the equilibrium geometry change upon ionization and it is supported by our theoretical calculations performed on B3LYP/6-311G(2d,p) level, resulting 1.02 eV difference between adiabatic and vertical ionization energies. Literature data [5] in agreement with our calculations show that Me_3Si radical is pyramidal (α_{CSiC} = 110°; inversion barrier = 13 kcal/mol), while the trimethylsilylium ion is trigonal planar. Same phenomena have been reported in the case of $SiCl_3$ and $SiHCl_2$ radicals [4]. Finally, the strong similarity between the spectra of the mercury-compound and the Me_3Si radical is the consequence of their very similar MO pattern. The examination of the $Hg(SiMe_3)_2$ MO-s shows that only five of them have notable amplitude on the mercury atom and the trimethylsilyl groups. All the others are very similar (or the same) to those of found in the radical, or in the free mercury atom. So, the Si–Hg–Si bond can be described by only five MO-s, two of which are the HOMO and HOMO-6 having Hg *p*- and *s*-characters respectively,

Fig. 1. He I photoelectron spectrum of $Hg(SiMe_3)_2$.

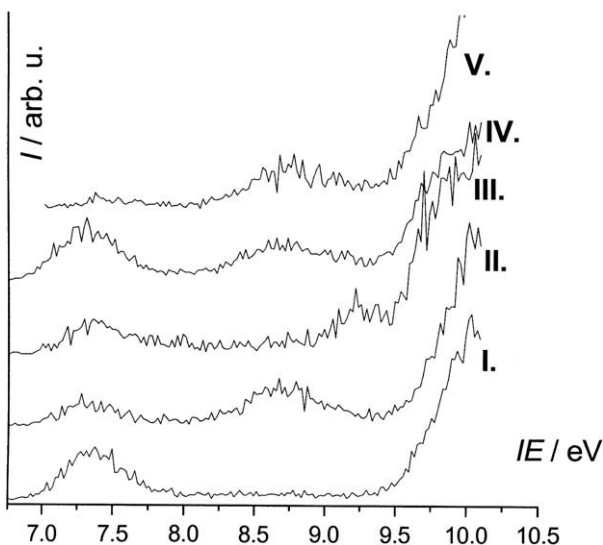**Fig. 2.** Low energy part of He I photoelectron spectra recorded at different stages of the thermolysis experiment. (I) $Hg(SiMe_3)_2$. (II) Volatile thermolysis products at 350 °C. (III) Sample collected in the cold trap (−10 °C) during the thermolysis at 350 °C. (IV) Volatile thermolysis products at 750 °C. (V) Sample collected in the cold trap (−10 °C) during the thermolysis at 750 °C (see text).

Table 1
Experimental and calculated first vertical ionization energies of $SiMe_3$ radical.

Method	Ionization energy (eV)
UPS	(7.32 ± 0.03)
B3LYP/cc-pVTZ/cc-pVTZ-PP	7.26
CCSD(T)/cc-pVDZ	7.24
CCSD(T)/cc-pVTZ	7.39
EOMIP–CCSD(2)/cc-pVTZ	7.36

as mentioned above. This is in line with the simple model for HgMe$_2$ of Fehlner et al. [20], but it has to be supplemented by three additional MO-s, where – according to the population analysis of the DFT calculation – Hg atom participates with d-orbitals. In connection with the calculations it is worth to note that the calculated first ionization energy of HgMe$_2$ and Hg^{t}Bu$_2$ (9.06 eV and 7.28 eV respectively) are lower by 0.3 eV than the measured ones [21] and this is also valid for Hg(SiMe$_3$)$_2$ (IE_{calc} = 7.11 eV versus IE_{meas} = 7.37 eV). If this correction factor (0.3 eV) is applied to IE_{calc}(Hg(SiMe$_3$)$_2$), a very close value to IE_{calc}(Me$_3$Si) is obtained affirming that the first ionization energy of our precursor and that of the corresponding radical are almost identical.

In conclusion, the homolytic fission of the weak Hg–Si bond proved to be a straightforward preparatory step for the generation of Me$_3$Si radical making possible to determine directly its vertical ionization energy.

Acknowledgement

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