

Fragmentation of methylphenylsilane and trimethylphenylsilane: A combined theoretical and experimental study



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ABSTRACT

The electron impact ionization (EII) of methylphenylsilane (MPS), dimethylphenylsilane (DMPS) and trimethylphenylsilane (TMPS) was investigated using the mass spectrometry technique. The composition of fragmentation products from MPS and TMPS measured in this work is interpreted with respect to the ionization energy, appearance energies of fragments and bond dissociation energies of selected bonds. The results are compared to the previously published experimental data for DMPS. Comparison with the theoretical bond dissociation energies calculated using the density functional theory (DFT) calculations is presented. Using the combined experimental and theoretical approaches, we have focused our recent studies on the common features as well as basic differences of the fragmentation schemes of all three molecules. The elimination of the H₂ molecule, specific for MPS but rarely observed in the other two compounds, was also of high interest in our studies. It can run in two mechanisms: (i) loss of two hydrogens one-by-one and (ii) elimination of H₂ in one step. We can predict which mechanism is more probable according to the DFT calculated energy profile of reaction. The calculated predictions were in correlation with the composition of fragmentation products determined experimentally from mass spectra.

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1. Introduction

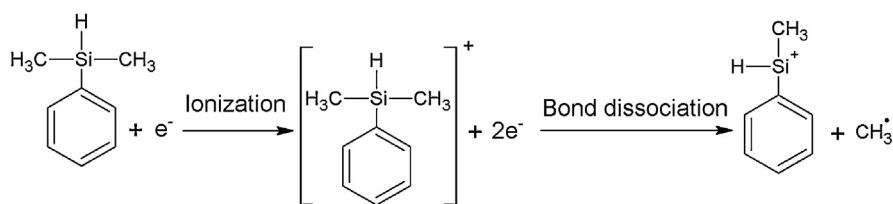
The chemical vapor deposition technique has been used for thin film production for more than 50 years. The main applications of organosilicon precursors are in microelectronics [1], and the automotive and food industries [2]. During the 1980s, this deposition technique was improved by adding plasma to the process. Plasma enhanced chemical vapor deposition (PECVD) or plasma assisted chemical vapor deposition (PACVD) allow the use of many new types of precursors, especially organosilicones which offer several advantages. Organic groups have nearly infinite options for proper control of deposited layers. Additionally, they are compatible with other organic compounds and provide elasticity, preventing the layer from cracking. Silicon atoms support binding to inorganic substrates including glass [3]. Hexamethyldisiloxane (HMDSO) and tetraethyl orthosilicate (TEOS) are used as PECVD precursors very

often [4]. Fragmentation of organosilicones by electron impact is the critical point with respect to plasma based CVD techniques. The presented study deals with the investigation of organic content roles in organosilicones that differ by number of CH₃ functional groups in their structure.

The organosilicon molecules play a key role in plasma physical chemistry [5,6]. However, they can also be applied in the understanding of the fragmentation process. The understanding of structure–properties relations can be highlighted by the cases, which are structurally similar and have different responses. Particularly, we would like to find the relation between primary chemical structure and the fragmentation properties of the MPS, DMPS and TMPS compounds. These three molecules have similar structures, however, their electron fragmentation products proved to be significantly different according to the mass spectra. The reason is probably that the detailed individual mechanisms may be specific for three such molecules. We found that some reactions show common features. For example, dissociation of two hydrogens from the molecules sometimes runs step-by-step and in other cases runs irregularly. The mechanism in two variants is present for all molecules. We believe that some reactions can be observed in

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Scheme 1. Scheme of dimethylphenylsilane fragmentation process: Phase 1: electron induced ionization; Phase 2: bond dissociation; in the scheme it is only an example; in reality, the fragmentations can run in several ways according to the bond being cleaved [22].

general in the mechanism independent of the molecule. We combine the quantum chemical simulations and experimental technique (mass spectra of fragments obtained by monochromatic electron impact) in order to find the most important reactions causing a specific behavior for the fragmented molecule.

We describe the mechanism, where the bond dissociation is preceded by electron impact ionization while a radical ion appears. The radical ion can be subject to three types of fragmentation reactions: cleavage of σ bond, cleavage of two σ bonds, and cleavage with complex rearrangements [7]. The cleavage of single bonds can run serially. Moreover the fragments can be subject to the bond cleavage. In the literature, the fragmentation of simple systems was mostly focused on the study of the electron impact phase [8,9]. The process was studied experimentally and theoretically in order to analyze detailed aspects of the process such as ionization cross section of molecules that is the probability of an ionization process during an electron impact. The experimental description of the process was focused on the electron impact cross section of a molecule [10,11]. The electron impact cross-section is an efficient part of the atom's cross-section, where the electron can induce ionization and thus determine the ability of ionization of a given molecule or atom. Most of the authors describe the cross-section to the charge +1, however, the cross-sections for ionization to the charge +2 can be measured, too [12]. The first calculations of ionization cross-sections appeared in works by Khare et al. [13,14] and Deutsch and Märk [15]. Later, the cross-sections were calculated theoretically using different theoretical models such as the binary encounter dipole (BED) model [16] and the binary-encounter-Bethe which is a simpler version of the BED theory [17]. The BED model combines mathematical description of a Mott cross-section and a Bethe-dipole cross-section. The cross section is a term of the plane-wave Born approximation [18]. In general, the molecular ions are not too stable under electron impact and they rapidly form various fragments. The process after ionization depends on the energy profile of bond dissociation. The phenylsilane dissociation by electron impact ionization was described in the literature as a typical example of similar compounds [19,20]. The organosilicon molecules are also interesting from a theoretical point of view. The silicon as a central atom has more complex orbitals than a carbon atom in analogous molecules, and the C–Si bond is covalent. The Si–H and Si–C bonds can be broken more easily than the C–H and C–C bonds, and thus the chemical reactivity of organosilicon molecules is higher than that of corresponding hydrocarbons [21]. Some aspects of their fragmentation process are presented in literature. The fragmentation mechanism of the DMPS molecule shown by Scheme 1 was proposed [22].

The mechanism presented in Scheme 1 is an example of one dissociation reaction to the DMPS molecule. However, the second phase, bond dissociation, can vary for different molecules. There can be a large combination of the bonds being dissociated. The complete description of the process needs many parameters such as ionization energies, appearance energy, and the heat of formation. All the parameters for the many radicals and ions must be known. Some of the parameters (i.e. appearance energy, ionization energy) and mass spectra were presented in literature [22–25].

The fragmentation was also described theoretically by quantum chemical calculations. In the first approximation, Boese and Scuseria [26] performed second-order Møller–Plesset perturbation theory (MP2) and density functional theory (DFT) calculations with a polarized basis set (6-31G*) for computing the fragmentation energy from the energies of fragmentation products and of the original molecule. The energy and optimized geometry were calculated using the MP2 and DFT methods, respectively. Next, the ionization process (the first step in Scheme 1) was also included in the theoretical calculations [27]. Veszprémi et al. [28] calculated the ionization energy of the TMPS molecule using complete neglect of the differential overlap method with spectroscopic parameterization (CNDO/S) and measured it based on the mass spectrum produced by ultraviolet photoelectron spectroscopy. Choe [27] calculated the dissociation energies required to lose benzene from the phenylsilane derivatives (except for the TMPS molecule) by use of the DFT calculations at the B3LYP/6-311++G(d,p) level. The DFT calculations showed that the increase of methyl substituents in the silicon atom made the dissociation process easier.

The fragmentation is considered as a series of consecutive steps. The fragmentation mechanisms differ for three similar compounds: MPS, DMPS, and TMPS. This difference leads to different fragmentation products. Some partial reactions are observed in the fragmentation of all molecules. The calculations enable us to identify the similar steps, and describe their energy profiles. The data from simulation needed to be calculated in order to have a detailed picture of the fragmentation pattern.

2. Methodology

2.1. Experiment

In this work, we have measured the electron ionization of methylphenylsilane (molecular weight 122.24 g/mol) and trimethylphenylsilane (molecular weight 150.29 g/mol) molecules. Both samples are liquids and were obtained from Sigma–Aldrich with high purity ($\geq 98\%$ for MPS and $\geq 99\%$ for TMPS).

The experiments were done using the crossed electron-molecule beam apparatus. The apparatus was described in detail in the work of Stano et al. [29]. A schematic view of the main parts is shown in Fig. 1. The electron beam is formed by a trochoidal electron monochromator (TEM), where the electron energy resolution of the electron beam in the present experimental study was 300 meV. The electron beam energy resolution was obtained experimentally according to the procedure described in [29]. We have measured the finite width of the electron energy distribution function with the retarding field method. The 300 meV represents the full width of half the maximum measured electron energy distribution function peak. The molecular beam is formed in the molecular beam source (MBS) by effusion of gas phase MPS/TMPS samples through a capillary (0.5 mm diameter and 4 mm long) into the reaction chamber.

The temperature of the molecular beam source was ~ 300 K, and the pressure can be varied in the range 1–10 Pa. The molecular beam crosses the electron beam perpendicularly. Due to a weak

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