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Surface ionization mass spectra of organosilicon compounds

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Abstract

Surface ionization mass spectrometry was performed on 14 organosilicon compounds, by use of a quadrupole mass spectrometer in which the thermionic ion source was a rhenium oxide emitter. The data provide the first measurement of the surface ionization mass spectra of these compounds.

The results are interpreted in terms of the modes of ion formation. Almost all the ion-current is carried by metal-containing ions except for the organosilicons having amino groups. In general the most favored ionization processes, which are shown to be directly related to the ionization energy, are those which give even-electron ions. Some of the mass spectra of the examined silicon compounds are compared with those of the analogous hydrocarbons.

In order to explain the spectra of tetraethylsilane and triethylsilane, the ionization energy of the $(C_2H_5)_3Si$ radical was calculated by the STO-3G method of the Gaussian-80H programs.

Introduction

Interest in organosilicon chemistry has been continually increasing because a variety of uses other than in silicones, have been found for organosilicon compounds during the past decades. The organosilicon compounds have already been mass spectrometrically characterized by electron impact ionization (EI) from their mass spectral patterns [1,2].

The organic aspects of surface ionization (SI) mass spectrometry have been outlined recently, and reveal that the behavior of organic compounds by use of surface ionization is different from the conventional EI method [3,4]. Very recently we extended this technique to the organometallic compounds, since the effect of the contained metal atom in the SI spectrum may be of interest in view of its low

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ionization energy. In a recent communication [5], we reported the salient features of the SI mass spectra of five kinds of metallocenes.

The purpose of this paper is to present the study of a representative selection of organosilicons (σ-bonded organometallic compounds), and to draw attention to surface ionization mass spectrometry, in light of the fact that this technique is becoming increasingly useful in the chemistry of organometallic compounds.

Here we first report and discuss the SI mass spectra of the 14 organosilicon compounds and then show how the mass spectral features can vary with the classified groups. A number of analogous hydrocarbon compounds were included in the study to assess the stability of silicon cations relative to carbon cations, since we felt that the most informative procedure was to compare the spectra of a series of analogous carbon compounds with those of silicon.

Experimental

All measurements were carried out with a Finnigan 3300 GC/MS, which had been modified by the installation of a home-built, combination-type ion source to allow the measurement of SI and EI. The details have been described elsewhere [6,7].

Briefly, the operating procedure for liquid samples involved opening the variable leak valve (Granville-Phillips, series 203) connecting the reservoir to the source and then recording the spectrum. The pressures of the samples ranged from 1×10^{-7} to 1×10^{-6} Torr. A solid sample of triphenylsilane was introduced directly into the ion source through a stainless steel tube (i.d. 3 mm) connected to a glass sampler placed in the gas chromatograph (GC) column oven. The desired pressure of the sample was controlled by varying the GC column oven temperature.

The rhenium oxide emitter was prepared and was used in the presence of O_2 at a controlled pressure of 1×10^{-5} Torr. The emitter temperature was controlled with the use of a dc power supply (0–40 V, 0–8 A, Nippon Stabilizer, Tokyo). The optimum emitter temperature was chosen by changing the heating current of the emitter.

All the samples were purchased from a chemical company (Ieda Chemical, Tsukuba) except for the triethylsilane, diethylsilane and diphenylsilane, which were gifts from Prof. H. Matsumoto of Gunma University. These reagents were used without further purification. The EI mass spectra showed no serious interfering impurities.

For the interpretation of the spectrum, ab initio energy of the highest electronic state was estimated for $(C_2H_5)_3Si$ radical by use of the Gaussian–80H program [8*]. The levels of approximation used were of the single determinant self-consistent field (HF) type. The STO-3G basis set was used. Geometries were optimized at the HF level by analytic gradients.

Results and discussion

Table 1 lists the mass spectrometric results for the SI ions from the 14 organosilicon compounds with the numbering. All the discernible ions are listed. The

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* Reference number with asterisk indicates a note in the list of references.

Table 1. Surface ionization mass spectrum and sensitivity of organosilicon compounds.

Compound (m/z, IE eV)	Intense peak (m/z)	Sensitivity (A torr^{-1})	SI/EI (n)^a	Remarks
Methyl silanes				
1, tetramethylsilane (88, 9.80)	73, $(CH_3)_3Si^+$	3.6×10^{-2}	0.17 (73)	IE(Me_3Si) = 7.1
2, trimethylchlorosilane (108, 10.1)	No peak			
3, trimethylsilylazide (115, 9.7)	73, $(CH_3)_3Si^+$	5.5×10^{-4}	0.94 (100)	
Ethyl silanes				
4, tetraethylsilane (144, 8.9)	87, $(C_2H_5)_2SiH^+$	7.5×10^{-2}	0.31	
	59, $(C_2H_5)SiH_2^+$	3.0×10^{-2}	(87)	
5, triethylsilane (116, 9.5)	87, $(C_2H_5)_2SiH^+$	4.1×10^{-2}	0.12	
	59, $(C_2H_5)SiH_2^+$	3.6×10^{-2}	(87)	
6, diethylsilane (88, 9.8)	No peak			
Phenyl silanes				
7, phenylsilane (108, 9.1)	107, $(M-H)^+$	2.7×10^{-3}	0.038 (108)	
8, diphenylsilane (184, 8.8)	183, $(M-H)^+$	trace		
	181, $(M-3H)^+$	trace		
9, triphenylsilane (262, 8.4)	261, $(M-H)^+$	100^b	0.9	
	259, $(M-3H)^+$	15	(183)	
	183	8		
	181	6		
Amino silanes				
10, diethylaminotrimethylsilane (145, 7.7)	73, $(CH_3)_3Si^+$	1.0×10^{-1}		*Te* 890 K
	72, $(C_2H_5)_2N^+$	3.9×10^{-2}		
	144, $(M-H)^+$	2.7×10^{-2}	0.88	
	130, $(M-CH_3)^+$	7.7×10^{-3}	(145)	
11, dimethylaminotrimethylsilane (117, -)	73, $(CH_3)_3Si^+$	1.9×10^{-2}		*Te* 890 K
	116, $(M-H)^+$	1.6×10^{-2}	2.8	
	44, $(CH_3)_2N^+$	1.1×10^{-2}	(117)	
Disilane and methoxy silane				
12, hexamethyldisilane (146, 8.3)	73, $(CH_3)_3Si^+$	9.5×10^{-2}	0.033 (73)	
13, hexamethyldisiloxane (162, 9.4)	No peak			
14, tetramethoxysilane (152, -)	121, $(M-OCH_3)^+$	1.9×10^{-2}	0.08 (121)	

[a] (n) in the SI/EI column indicates the mass number, n, of the base peak in the EI spectrum. [b] The spectrum of the compound is expressed as the relative intensity in the column labelled sensitivity, because the sensitivity expressed in A torr^{-1} could not be obtained for the solid sample.

spectral data were obtained at an emitter temperature (*Te*) which gave a maximum ion signal for each of them. *Te* was usually 930 K; exceptions to this temperature are noted in the Remarks column of Table 1. The relative abundances of mono-isotopic species are reported. Here, sensitivity is expressed in Amperes of the resulting ion current of the peak in the SI spectrum per unit pressure of the sample (A $Torr^{-1}$). Table 1 also shows the molecular weight, ionization energy (IE) [9], the postulated structure of the observed ions, as assigned by mass and isotope ratios, and SI/EI, the ratio of the highest intensity in the SI mode to that in the EI mode. However, it should be noted that our comparisons were limited to the SI and EI sources we used and provide only a qualitative, but broader understanding of the potential of the SI mass spectrometry in chemical analysis.

The compounds under study may be subdivided into five groups; (i) tetramethylsilane and its derivatives, (ii) ethyl silanes, (iii) phenyl silanes, (iv) amino silanes and (v) disilane and methoxy silane. In the following section, we discuss features in the mass spectra of individual groups of compounds in terms of the ion formation modes [10,11] of the respective species; molecular surface ionization (MSI), dissociative surface ionization (DSI) and associative surface ionization (ASI).

Tetramethylsilane and derivatives

The surface ionization of tetramethylsilane produces DSI ions of $(CH_3)_3Si^+$ with good efficiency. The result is reasonably consistent with the fact that the $(CH_3)_3Si$ radical has a considerably low IE value (7.1 eV [12]). It is assumed that this ion has a structure similar to that of the trimethylcarbonium ion, which is known to be particularily stable [13]. Thus, the stability of the $(CH_3)_3Si^+$ ions is associated with their having an even number of electrons, and being isoelectronic with the neutral stable group III molecules.

The following generalizations have emerged from previous studies [10,11]; for the DSI ions, their intensity is determined not only by the ionization energy, but also by the efficiency of the formation of the dissociative product on the emitter surface, which mainly depends on the bond strength in the molecules. This rule also holds for trimethylchlorosilane (Me_3SiCl). As expected from the high dissociation energy $D(Me_3Si\text{–}Cl) = 116$ kcal/mol [14], $(CH_3)_3Si^+$ ion is not observed for $(CH_3)_3SiCl$. The dissociation reaction which might generate the low IE product of $(CH_3)_3Si$ takes place very slowly.

In contrast, trimethylsilyl azide shows an intense $(CH_3)_3Si^+$ peak, which probably reflects a weaker Si–N bond; whose strength has not been quantified.

Ethyl silanes

As with the tetramethylsilane, we expected a high abundance of $(C_2H_5)_3Si^+$ ions from tetraethylsilane and triethylsilane, but no $(C_2H_5)_3Si^+$ was observed. Instead, ions with *m/z* 59 and 87, in which the hydrogen atom is probably bonded to the silicon atom [rearrangement ions, $(C_2H_5)SiH_2^+$ and $(C_2H_5)_2SiH^+$ respectively], are abundant in the spectra of these compounds.

Metastable transition in surface ionization is sometimes observed in the ionization of organic compounds which have considerably low IE [15]. For example, the mass spectrum [16] of triethylamine shows a great number of fragment ion lines. The variety and the high probability of these decompositions can be associated with the excitational energies of the primary ions, which should lead to an increase in the probability of energy accumulation on individual bonds such that their rupture during the movement of the ions in the quadrupole analyser becomes possible. Since the excitational energy of primary ion is supplied by the energy difference between IE and the work function, the lower IE enhances the probability of metastable decomposition. From this the following speculation can be made for the interpretation of the tetraethylsilane and triethylsilane spectra. The excited $(C_2H_5)_3Si^+$ ion may be formed as a primary metastable ion, which is usually accompanied by metastable transitions [17]. The ions with m/z 87 and 59 could arise from a metastable transition from the $(C_2H_5)_3Si^+$ ion by the loss of C_2H_4 and $2(C_2H_4)$ respectively. This proposal is supported by the MO study. The estimation based on the Koopman theorem shows that the vertical ionization energy of $(C_2H_5)_3Si$ radical is as low as 6.08 eV which is derived from the eigenvalues (-0.22343 a.u.) of the highest electronic state A_1 of an alpha orbital.

Phenyl silanes

The mass spectra of phenylsilane and toluene are compared. The spectral pattern of toluene is quite simple, exhibiting only the $(M-H)^+$ ion, which has been identified as the tropylium ion and is common to almost all alkylbenzenes [18]. An analogous $(M-H)^+$ ion was produced from phenylsilane, but it is not certain whether it is a benzyl- or a tropylium-type ion.

The spectral data of diphenylsilane are similar to those of diphenyl methane [18], except that the ion intensities are different. Large amounts of $(M-H)^+$ and $(M-3H)^+$ are formed from diphenylmethane, but only a trace of these ions is produced from diphenylsilane.

The triphenylsilicon ion $[(C_6H_5)_3Si^+]$ is present in high abundance in the spectrum of triphenylsilane. This suggests that the IE of the $(C_6H_4)_3Si$ radical is probably lower than that of triphenylsilane. The spectra also exhibit small peaks at m/z 181 and 183, which are the major peaks of diphenylsilane.

In summary the mass spectra of all the examined phenylsilanes are similar to those of the analogous carbon compounds but have lower intensities.

Amino silanes

The two amino silane compounds containing an Si–N bond have been studied. The mass spectra show pronounced $(M-H)^+$ peaks. The $(CH_3)_3Si^+$ ion characterizing the side chain of a trimethylsilyl group and its respective amino group ion are also observed. Both $(CH_3)_2N^+$ and $(C_2H_5)_2N^+$ are commonly found in the SI spectrum of aliphatic amine compounds [10].

Two dissociative species produced from these compounds through the cleavage of Si–N bonds are efficiently surface-ionized. This result is very interesting, because these molecules indicate the possibility that more than one ionic species can be generated from one molecule. It is also concluded that rupture of the Si–N bond occurs readily, indicating that the nitrogen is weakly bonded to the Si atom in the molecule.

The mass spectra of **10** and **11** have similar patterns except that there is no $(M-CH_3)^+$ in the spectrum of **11**. This confirms that their main dissociative reaction pathways on the emitter surface are similar.

Disilane and methoxy silane

The ionization of hexamethyl disilane exhibited DSI ions of $(CH_3)_3Si^+$ with good efficiency. This indicates that extensive cleavage of the Si–Si bond occurs in the adsorbed layer.

There is no $(CH_3)_3Si^+$ ion present in the spectrum of hexamethyldisiloxane, although this ion is abundant in the spectra of **1**, **3**, **10**, **11**, and **12**. This result probably reflects the greater Si–O bond strength ($D = 194$ kcal/mol) in the molecule [19].

In the spectrum of the silane compound containing four methoxy radicals, there is the only peak of the $(M - OCH_3)^+$ ion. This spectrum is similar to that of the compound containing four methyl radicals; both compounds provide abundant triradical-metal ions $(M - X)^+$ ($X = OCH_3^{\cdot}$ or $CH_3^{\cdot}$). The efficient dissociation reaction of losing one radical, facilitates the large production of even-electron ions.

Conclusion

The SI mass spectra of organosilicon compounds show a highly non-statistical pattern whereas the EI spectra exhibit many fragment ions owing to statistical cleavage reactions; the SI mass spectral patterns were largely different from those of the EI mass spectra, although some similarity between the SI and EI spectra exists. The spectra were affected by the IE of the molecule, or the dissociative species, and by surface reactions just as other organic materials.

The general conclusions are: (i) molecular ions are not observed for all the tested compounds, but DSI ions are produced by the predominant M–X bond dissociation on the heated surface, (ii) the positive charge remains on the metal-containing species except for amino-radical ions, and (iii) the spectra of the analogous carbon and silicon compounds, show an almost similar tendency for silicon and carbon cations to be formed by surface ionization [18].

Under surface ionization on the rhenium oxide emitter, almost all the silicon compounds provide at least one of the characteristic SI ions, which can be classified into four categories, (i) $(M - H)^+$ ions for molecular weight determination, (ii) informative DSI ions for structural elucidation, (iii) abundant ions for the high-sensitivity analysis and (iv) a small number of peaks in the spectrum which are useful for the mixture analysis.

We have presented what we believe is a new observation; when either diethylaminotrimethylsilane or dimethylaminotrimethylsilane impinges on a heated rhenium oxide emitter, the interaction causes two dissociative species owing to the Si–N cleavage reaction on the emitter to be efficiently and simultaneously surface-ionized.

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