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Metastable Ion Studies: Ethyl(methoxy)(chloro)silanes

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Metastable ion scanning was used to investigate the fragmentation patterns of ethyl(trimethoxy)silane, ethyl(dimethoxy)chlorosilane and ethyl(methoxy)dichlorosilane, their deuterated counterparts and ethyltrichlorosilane. For these compounds the molecule ion has a low abundance using 70 eV electron impact ionization. In all cases the base peak corresponds to the loss of neutral C_2H_5. When chemical ionization is employed with isobutane, usable peaks representative of the molecule ions are observed.

INTRODUCTION

Metastable ion scanning and deuterium labeling have been used to determine the fragmentation routes for ethyl(trimethoxy)silane (**1**), ethyl(dimethoxy)chlorosilane (**3**) and ethyl(methoxy)dichlorosilane (**5**), their deuterated methoxy counterparts (**2**, **4** and **6**, respectively) and ethyltrichlorosilane (**7**). Fragmentation mechanisms for other alkyl(alkoxy)silanes have been reported, in which fragment ions were hypothesized to form with relatively uncomplicated rearrangement patterns.[1–6] However, when metastable ion scanning or mapping techniques were employed, more complicated fragmentation patterns were supported.[7–9]

Mass-analyzed ion kinetic energy (MIKE) spectra have been described for several silanes,[10] silazanes[11] and siloxanes[12,13] and for organic molecules.[10] The metastable ion mapping technique has been described.[14–18] For example, hexamethyldisiloxane has exhibited several rearrangement reactions involving hydrogen atom and methyl group migrations accompanying the losses of H_2, CH_4, H_2O, C_2H_2, C_2H_4 and CH_3SiH.[12] These assignments were supported by a study on similar compounds containing several substituents other than methyl groups.[13] These trisilanes and trisiloxanes were shown to undergo analogous fragmentation mechanisms using EI (electron impact) ionization, CI (chemical ionization) and metastable ion scanning or mapping. Migration of the substituents was observed in all of the compounds in the same way that methyl groups were shown to migrate in the previous study. However, this was only observed where EI and not CI was used. Therefore, it may be that the higher energy used in EI is needed for the migration process.

EXPERIMENTAL

The 70 eV EI mass spectra and the metastable ion scanning spectra (at constant *B*/*E*) were obtained using a Kratos MS-25RF gas chromatograph/double-focusing mass spectrometer of forward geometry with a DS-90 data system. The technique of metastable ion scanning is described in detail elsewhere.[19–22] The source temperature was 150 °C, the scan speed was 3 s per decade, the mass range was 17–500 u, and the mass resolution was 1000.

$C_2H_5Si(OCH_3)_3$ (**1**), $C_2H_5Si(OCD_3)_3$ (**2**), $C_2H_5Si(OCH_3)_2Cl$ (**3**), $C_2H_5Si(OCD_3)_2Cl$ (**4**), $C_2H_5Si(OCH_3)Cl_2$ (**5**) and $C_2H_5Si(OCD_3)Cl_2$ (**6**) were synthesized by slowly adding CH_3OH or CD_3OD to ethyltrichlorosilane (Aldrich) in a dry nitrogen atmosphere at 0 °C and removing gaseous HCl with vacuum into a liquid nitrogen trap. The reaction mixture was separated using a 30 m J and W Scientific DB-5 (5% phenyl-, 95% methyl-silicone) capillary column with an injector temperature of 250 °C and an oven temperature of initially 50 °C for 5 min, then increased at 10 °C min^{-1} up to 280 °C. Metastable ion scanning was carried out on each of the ions illustrated in Schemes 1–4. For CI spectra, isobutane was used as the chemical ionization source gas. The pressure of isobutane was adjusted until a CI spectrum could be obtained. The molar ratio of source gas to silane was ~1000 : 1.

RESULTS AND DISCUSSION

The silanes exhibited similar fragmentation patterns with a low-abundance molecule ion using 70 eV EI ionization. At 70 eV the base peak corresponds to the loss of neutral C_2H_5. Fragments lost in the fragmentation process include dihydrogen, hydrogen chloride, atomic chlorine, dichlorine, ethylene and formaldehyde. The 70 eV EI mass spectra are summarized in Table 1. When CI was used with isobutane, strong ions representative of the molecule ions $(M + H)^+$ were observed.

The fragmentation assignments for $C_2H_5Si(OCH_3)_3$ were deduced from a comparison of the metastable ion spectra of the normal and deuterium-labeled substances (**1** and **2**). The loss of an ethyl group is followed by the consecutive loss of the neutral formaldehyde fragment (Scheme 1). Although there is a peak of *m*/*z* 119 in the spectrum of the non-deuterated compound, there is no significant corresponding peak in the mass spectrum of

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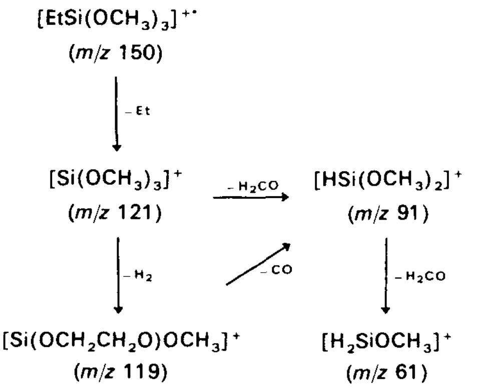
Table 1. Relative abundances (%) of ions for compounds 1–7

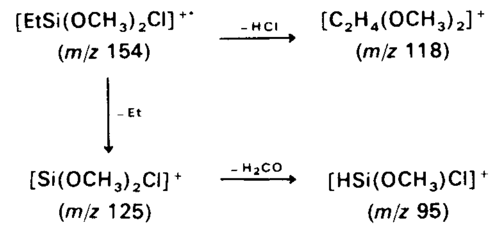
m/z	1	2	3	4	5	6	7
166							3.0
164							9.0
163						4.7	
162				1.1	1.0		9.1
161						7.0	
160				2.9	4.9		
159		0.6					
158					6.6		
156			1.6				
154			4.4				
150	1.0						
139							4.4
138							1.7
137							33.9
136						12.7	5.2
135				1.3		5.2	99.6
134				2.7	1.3	67.7	5.4
133		1.0		35.7	12.2	8.3	100.0
132		4.4		7.9	5.2	100.0	
131		10.2		100.0	68.5		
130		100.0			8.0		8.9
129		1.9	1.5		100.0		5.8
128		0.9	3.0		1.2	1.7	47.2
127		6.4	43.9		2.1	3.3	9.8
126		0.4	9.3	1.5		4.5	70.3
125		2.9	100.0	4.3	2.1	6.2	2.6
124		0.4			2.5		
123	7.9	0.4	2.9		3.9		
122	6.4				6.4		
121	100.0						
120	2.2						
119	9.4		4.6				
118			1.0				
117					1.5		
115		0.2			1.8	1.3	
113		0.5					
112		0.3					
104						1.7	
103					2.0		
102						8.4	2.8
101				9.4	10.8	2.7	5.3
100		1.2		3.0	2.6	14.6	13.4
99		3.1		27.6	14.8	4.7	8.0
98		29.2		4.0	3.2	5.7	19.7
97		3.6	12.5	4.4	1.4	4.8	
96		3.0	3.4	1.9	2.1		
95		1.3	35.4		3.3		
94		0.3	3.5		5.0		
93	2.6	0.9	1.1		1.0		
92	5.0						
91	62.9	0.7	2.3				
90	5.8		1.9				
89	3.5		1.1				
88		0.2			2.6		
86		1.6			13.7		
84		2.3			22.6		
83					1.4		
82		0.4		1.2			
81		1.2	1.7				
80		0.7					
79		0.6					
78		0.7					
77	2.0						
74		0.1					
69		0.2					
68	1.4						
67		0.4	1.0	1.8			
66		4.4		1.2		1.1	
65		2.8	3.1	2.1	3.7	2.9	7.9
64		1.9		1.3	1.2		2.1
63		0.6	2.5	2.4	6.8	6.9	21.5
62		6.4		8.7		7.3	
61	11.3		1.4				
60	2.7	0.4			1.1		
59	11.8		7.1		5.5		
55		0.9					
53		2.1					2.2
52					1.7		
51		1.2			9.6		
50		0.2			4.9		

the deuterated compound (at *m/z* 125, the loss of a methoxy group from the molecule ion); however, a peak at *m/z* 126 (loss of D_2 from the *m/z* 130 ion) is observed. Also, the metastable ion spectrum for the non-deuterated compound shows that the *m/z* moiety is produced only from the *m/z* 121 ion, and it decomposes to *m/z* 91. Therefore, the metastable ion spectra do not support the loss of a methoxy group.[8] From bond energy considerations it would be reasonable to postulate the structure of the *m/z* 119 fragment as $(CH_3O)\overline{SiOCH_2CH_2O}^+$, rather than $Si(OCH_2)_2(OCH_3)^+$.[23]

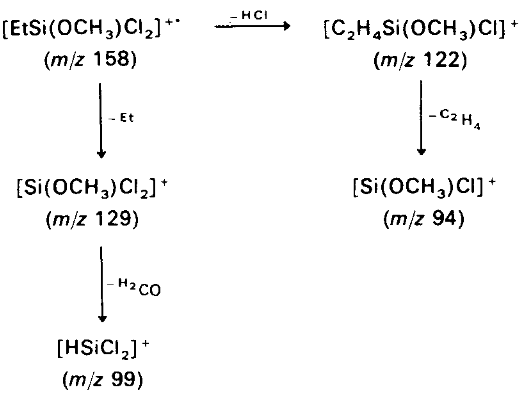
In the deuterated and non-deuterated versions of the chlorinated species (3–6, the loss of the ethyl group is followed by the loss of formaldehyde (Schemes 2 and 3). The dichlorinated compounds (5 and 6) exhibit the loss of HCl in competition with the loss of the ethyl group (Scheme 3). The loss of HCl is also detectable in the metastable ion spectra of the monochlorinated compounds, but the peaks are not as strong. The loss of formaldehyde follows the loss of an ethyl group and, in the case of 5, the loss of C_2H_4, following the HCl loss, is observed. However, the peak corresponding to the loss of C_2H_4 (*m/z* 97) is not detected in the deuterated compound 6.



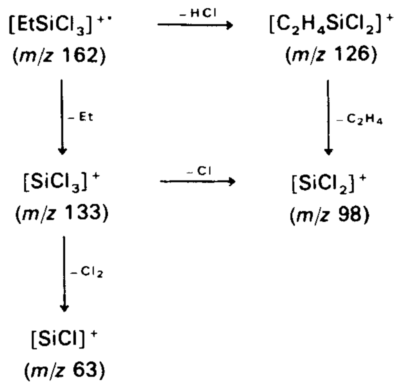
Scheme 1



Scheme 2



Scheme 3



Scheme 4

Ethyl(trichloro)silane (7) fragments by two initial paths: the loss of an ethyl group and via HCl loss. The resulting fragments then lose a chlorine atom or ethylene, respectively, to form $[SiCl_2]^+$. The $[SiCl]^+$ forms from $[SiCl_3]^+$ by loss of Cl_2 (Scheme 4).

The fragmentation mechanisms are similar for all seven compounds. The mass spectra infer, from relative peak intensities,[24] that the Si—O bond is not as readily broken as the Si—C or the Si—Cl bonds. This corresponds with bond energy data. The relative molecule ion abundances, when compared with that of the $[M - C_2H_5]^+$ fragment, increase in the order $[C_2H_5Si(OMe)_3]^+ < [C_2H_5SiCl(OMe)_2]^+ < [C_2H_5SiCl_2(OMe)]^+ < [C_2H_5SiCl_3]^+$. It is reasonable for this ordering to be related to the relative amount of $(p \rightarrow p)_\pi$ bonding and, therefore, to the observed stability of the planar ions: $^+Si(OMe)_3 > {}^+SiCl(OMe)_2 > {}^+SiCl_2(OMe) > {}^+SiCl_3$. This observation suggests that the methoxy groups are the stabilizing factor in forming the intense base peaks in the spectra.

It is more complicated to compare further decomposition of the base peak, via loss of formaldehyde, for the compounds in the group studied. Statistically, there are more chances for this reaction to take place with the trimethoxysilane than with the dimethoxysilane and even less for the monomethoxy species. Also, the remaining methoxy groups may stabilize the resulting fragment ions. The trend observed, when the abundances of the fragment ions are compared with those of their corresponding base peaks, is in the order of $[HSi(OCH_3)_2]^+ > [HSi(OCH_3)Cl]^+ > [HSiCl_2]^+$, with $[HSi(OCH_3)_2]^+$ having the highest observed stability.

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