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Fast atom bombardment mass spectra of silatranes and silocanes

I. Mažeika *, S. Grīnberga, A.P. Gaukhman, G.I. Zelchan and E. Lukevics
Institute of Organic Synthesis, Latvian Academy of Sciences, Riga (Latvia)

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Abstract

FAB mass spectra of silatranes evidence in favour of stronger donor-acceptor interaction in condensed phase in comparison with that under electron impact (EI) conditions. In contrast to EI mass spectra not confirming the presence of donor-acceptor interaction in germatranes in gaseous phase, the character of FAB mass spectra displays such N → Ge interaction in these compounds in condensed phase. FAB mass spectra of silocanes are similar to those of silatranes and indicate the existence of N → Si interaction in silocanes, if there is no bulky substituent at the nitrogen atom sterically hindering interaction between N and Si atoms.

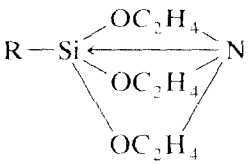
Introduction

EI mass spectra of silatranes and of similar systems containing a N → Si coordinative bond have been investigated extensively [1]. On the other hand, only scarce data exist on FAB mass spectra for a few derivatives of silatranes [2] and homosilatranes [3].

FAB ionization mode, which does not require vaporization prior to ionization, has certain advantages in the analysis of polar substances, to which compounds containing an N → Si bond belong. We therefore investigated in detail FAB spectra of silatranes and their diethanolamine analogues, silocanes, in order to obtain information on donor-acceptor interaction in these molecules. We compared the FAB spectra of silatranes with those of some germatranes. Only a few FAB mass spectra of germatranes have been studied until now [2].

Results and discussion

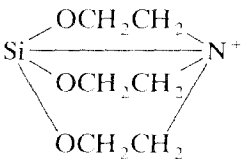
FAB spectra of silatranes Ia–e maintain some characteristics of their EI spectra.



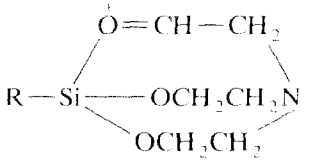
(Ia–e)

(R = C_6H_5 (a), CH_3 (b), C_2H_5 (c), HC≡C (d), CH_3O (e))

Similar to EI spectra, FAB spectra contain the molecular ion $M^{+\cdot}$ of low or medium intensity (Table 1), the ion $(M - R)^+$ being the maximal one. These features are due to N → Si donor–acceptor interaction, facilitating the removal of the Si substituent and the transformation of the coordinative bond into a covalent one (formation of ion **A**).



(A)



(B)

These peculiarities have been considered in detail in many investigations on EI mass spectra of silatranes [1].

In addition to these ions FAB spectra of Ia–e contain the quasi-molecular ion MH^+ and the ion with m/z 150, corresponding to the protonated product of silatrane solvolysis, triethanolamine $HN^+(CH_2CH_2OH)_3$. The formation of the analogous ion, the product of homosilatrane solvolysis with m/z 164, is described in detail in [3], and the intensity of this peak is shown to be dependent both on bombardment duration and on the R substituent at the Si atom.

FAB spectra of silatranes are generally similar to those of homosilatranes [3] but there some differences exist:

(1) In FAB spectra of silatranes Ia–e the fragment ions of the corresponding trialkanolamines, characteristic of the spectra of homosilatranes, are practically absent. To elucidate the influence of the matrix used (thioglycerol in the present work, glycerol in [3]) we have obtained the FAB spectrum of Ic in glycerol and observed that the character of the spectrum is only slightly dependent on the matrix (Table 1); it agrees with the data in [3]. Most likely, the weaker donor–acceptor interaction in homosilatranes is responsible for the easier cleavage of the homosilatrane ring in comparison with that of silatrane. This has been demonstrated previously by calculation of the heat of formation of the N → Si bond from dipole moment data [4].

An $[M - H]^+$ ion peak with 5–37% intensity is present in Ia–e spectra, which is rather rare for FAB spectra. The appearance of $[M - H]^+$ has been studied in [5]: its presence does not depend either on the choice of matrix or on the presence of heteroatoms or polar groups in the molecule, but it is the result of electrophilic attack on the hydrocarbon chain. The probability of $[M - H]^+$ peak formation is increased statistically with the increase in the number of carbon atoms in the

Table 1

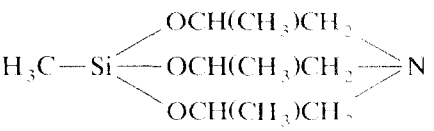
FAB mass spectra of silatranes (I–IV), germatranes (V–VII), 1-phenyl-2-azasilatrane (VIII) and 1-phenyl-3,7-dimethyl-10,11-benzosilatrane (IX), m/z and intensities (% from the maximal peak, in parentheses)

No.	MH^+	$M^{+\cdot}$	$[M-H]^+$	$[M-R]^+$ (A)	$HN^+(CH_2CHR^1OH)_n(CR^2_2CH_2OH)_{3-n}$	$[MH-CHR^1CH_2O]^+$	Others > 10%
Ia	252(14)	251(4)	250(6)	174(100)			
Ib	190(100)	189(17)	188(37)	174(100)	150(40)	146(28)	
Ic [a]	204(78)	203(8)	202(20)	174(100)	150(80)		
Ic [b]	204(85)	203(10)	202(19)	174(100)	150(70)		
Id	200(3)	199(2)	198(3)	174(100)	150(53)		
Ie	206(56)	205(7)	204(15)	174(100)	150(6)	162(11)	
II	232(100)	231(31)	230(50)	216(94)	192(7)	174(17)	172(17) $[A-C_2H_4O]^+$
III	246(47)	245(20)	244(33)	230(100)	206(11)	188(62)	174(47) $[MH-CMe_2CH_2O]^+$; 172(36) $[244-CMe_2CH_2O]^+$; 158(13) $[A-CMe_2CH_2O]^+$
IVa	342(50)	341(15)	340(35)	326(70)	302(60)	222(100)	236(30) $[MH-C_6H_5CHO]^+$; 235(55) $[M-C_6H_5CHO]^+$; 220(70); 194(45); 121(65)
IVb	418(11)	417(8)	416(19)	326(100)	–	298(22)	296(19) $[A-CH_2O]^+$; 311(33) $[M-C_6H_5CHO]^{+\cdot}$ 208(31); 105(56)
V [c]	348(11)	347(5)	–	220(14)	150(100)	–	
VI [c]	312(100)	–	–	296(10)	226(27)	192(39)	146(14)
VII [c]	362(3)	361(1)	–	234(2)	164(100)	–	162(14); 132(20) $[164-CH_3OH]^+$
VIII	251(18)	250(13)	–	173(100)	149(73)	–	222(16) $[MH-NHCH_2]^+$; 208(11) $[MH-NHC_2H_4]^+$; 139(27); 132(32)
IX	328(10)	327(8)	326(5)	250(100)	–		

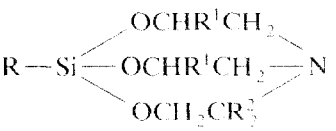
[a] In thioglycerol. [b] In glycerol. [c] The peak intensities and m/z values are given for ^{74}Ge.

molecule. It is evidently not the case with the silatranes under study, because the increase in the number of carbon atoms from 7 in Ib to 11 in III does not increase the $[M-H]^+$ peak intensity. We are inclined to suspect that in the case of silatranes, $[M-H]^+$ ion formation is caused by the withdrawal of the α-hydrogen atom regarding the oxygen, and by the formation of a structure with positively charged oxygen (ion **B**).

FAB spectra of compounds II–IV, containing alkyl and aryl substituents in the silatrane system, maintain the characteristic features of Ia–e spectra, i.e., the existence of MH^+, $[M-H]^+$ and $[M-R]^+$ ions and of the quasi-molecular ion of the corresponding alkanolamine.



(II)



(III, IVa, b)

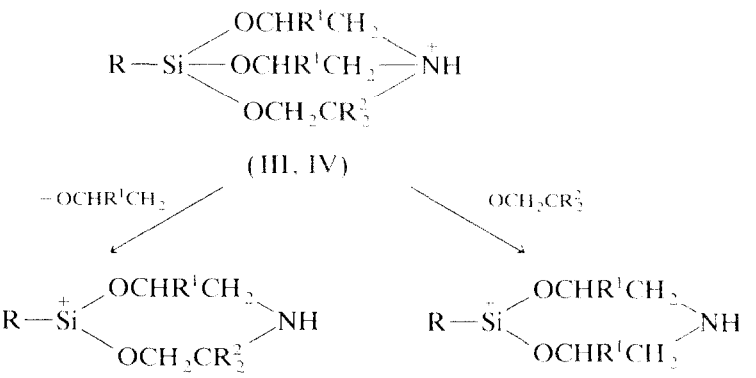
($R = R^1 = R^2 = CH_3$ (III); $R = CH_3$, $R^1 = C_6H_5$, $R^2 = H$ (IVa); $R = C_6H_4CH_3$-*p*, $R^1 = C_6H_5$, $R^2 = H$ (IVb))

As demonstrated earlier [1], during the first fragmentation stage of compounds III and IV under EI, an intensive α-cleavage of the side chain takes place, the latter being characteristic of amines, because of the weakening of the donor-acceptor interaction caused by steric tension (due to substituents) in the cyclic system.

Additional paths of fragmentation also appear in the FAB spectra of compounds III and IV, as distinct from Ia–e: side chains are eliminated from MH^+ to form **C** and **D** ions (Scheme 1, Table 1).

(2) In IVa,b the formation of ions with m/z 235 and m/z 311, respectively, takes place owing to α-cleavage with elimination of the benzaldehyde molecule from the molecular ion (Scheme 2, Table 1).

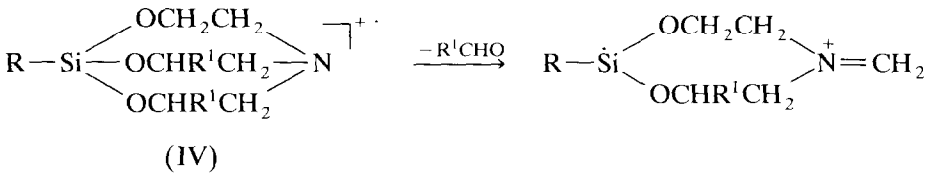
We have compared FAB spectra of silatranes with those of 1-(α-naphthyl) germatrane (V), 1-methyl-3-phenylgermatrane (VI) and 1-(α-naphthyl) homogermatrane (VII). As demonstrated in [6,7], EI spectra of germatranes show



(III, IV)

(**C**) (**D**)

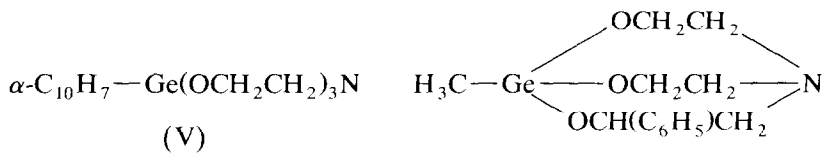
Scheme 1



(IV)

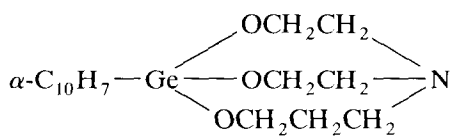
Scheme 2

absence of donor–acceptor interaction in the gaseous phase: (a) by low stability of the molecular ion, (b) by the absence of substituent withdrawal from the Ge atom, (c) by α-cleavage at the nitrogen atom with consecutive elimination of two CHRO molecules (R = H, C_6H_5).



(V)

(VI)



(VII)

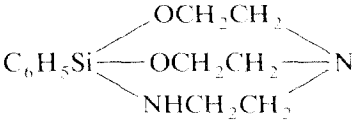
While the EI spectra of germatranes differ considerably from those of silatranes owing to the presence of donor–acceptor interaction in silatranes and to the absence of this kind of interaction in germatranes, FAB spectra of germatranes have common characteristics with those of silatranes. In FAB spectra of V and VII there is no α-cleavage, but substituent withdrawal from Ge takes place. The intensity of the corresponding ion is comparable to that of the quasi-molecular ion MH^+. Apparently, the character of the FAB spectra points out the existence of weak donor–acceptor interaction in germatranes in condensed phase. The same results have been obtained using the NMR method [8].

In contrast to the FAB spectra of V and VII, in the FAB spectra of compound VI, destruction of the cyclic system is observed, giving rise to the ions $[MH - C_2H_4O]^+$ with m/z 266(7) and $[MH - C_6H_5CH_2CHO]^+$ with m/z 192(39). Fragmentation occurs similarly to the processes shown in Scheme 1. Apparently, the donor-acceptor N → Ge interaction is weakened owing to the substitution in the side chain of germatrane.

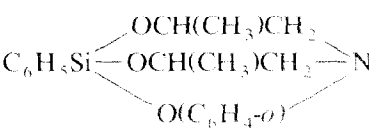
Similar to silatranes I–IV, the FAB spectra of germatranes V–VII contain an intensive peak of the corresponding solvolysis product, protonated trialkanolamine.

FAB spectra of silatrane analogues, 1-phenyl-2-azasilatrane (VIII) and 1-phenyl-3,7-dimethyl-10,11-benzosilatrane (IX), maintain the features characteristic of the FAB spectra of silatranes. In compound VIII, only the nitrogen-containing

half cycle is destructed to form ions $[MH - CH_2NH]^+$ with m/z 222 and $[MH - C_2H_4NH]^+$ with m/z 208 (Table 1).

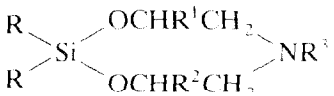


(VIII)



(IX)

EI mass spectra of 1,3-dioxa-6-aza-2-silacyclooctanes or silocanes have been discussed in ref. 1. It was shown that in silocanes, there exists a N → Si donor–acceptor interaction defining the characteristic features of the EI spectra: low stability of $M^{+\cdot}$, an intensive withdrawal of the Si substituent, followed by the elimination of C_2H_4O from the eight-member cycle.



(Xa–f)

(R = C_6H_5, $R^1 = R^2 = H$, $R^3 = CH_3$ (a); R = C_6H_5, $R^1 = R^3 = CH_3$, $R^2 = H$ (b); R = C_6H_5, $R^1 = R^2 = R^3 = CH_3$ (c); R = $C_6H_4CH_3$-*p*, $R^1 = R^2 = H$, $R^3 = CH_3$ (d); R = C_6H_5, $R^1 = R^2 = H$, R^3 = t-C_4H_9 (e); R = CH_3, $R^1 = R^2 = H$, $R^3 = C_6H_5$ (f))

We have also undertaken a study of FAB spectra of silocanes Xa–f (Table 2).

FAB spectra of silocanes Xa–f have the same characteristic features as their EI spectra and differ from the latter by the appearance of the $[M - H]^+$ ion peak and that of the protonated solvolysis product, the corresponding dialkanolamine $HR^3N^+(CH_2CHR^1OH)CH_2CHR^2OH$. FAB spectra of Xa–d are rather similar to those of silatranes Ia–e. Apparently, there exists a N → Si donor–acceptor interaction in the molecules of Xa–d, either in the condensed phase or the gaseous state.

FAB spectra of X change appreciably if the nitrogen atom is substituted by a bulky tert-butyl or phenyl substituent (compounds Xe,f): (1) the intensity of the $[M - R]^+$ ion peak, maximal for Xa–d and Ia–e, decreases noticeably in Xe,f; (2) the ion of the protonated dialkanolamine is more intensive, and the ions of its fragmentation products are formed, (3) some intensive ions appear in the low mass region.

Analogously, in EI spectra of Xe appearance of the $[M - R]^+$ peak of low intensity and formation of the intensive ion peaks with m/z 105(100) ($CH_2NC_6H_5^{+\cdot}$), 104(35) ($HC{\equiv}N^+C_6H_5$) etc. are observed [9].

This indicates weakening of donor–acceptor interaction in compounds Xe,f either in the gaseous or in the condensed phase, due to the presence of the bulky substituent at the nitrogen atom, sterically hindering the approach of Si and N atoms. This conclusion is in accordance with NMR and X-ray data [1, pp. 33, 101].

Experimental

FAB mass spectra were obtained on an AEI mass spectrometer with an Ion Tech. FAB 11NF source (bombarding gas, argon; matrix liquid, 2-thioglycerol).

Table 2

FAB mass spectra of silocanes (X), m/z and intensities (% from the maximal peak, in parentheses)

No.	Xa	Xb	Xc	Xd	Xe	Xf
R	C_6H_5	C_6H_5	C_6H_5	p-$C_6H_4CH_3$	C_6H_5	CH_3
R^1	H	CH_3	CH_3	H	H	H
R^2	H	H	CH_3	H	H	H
R^3	CH_3	CH_3	CH_3	CH_3	t-C_4H_9	C_6H_5
MH^+	300(7)	314(8)	328(6)	328(25)	342(7)	238(91)
$M^{+\cdot}$	299(5)	313(5)	327(4)	327(2)	341(2)	237(100)
$[M-H]^+$	298(11)	312(11)	326(10)	–	340(3)	236(39)
$[M-R]^+$ (E)	222(100)	236(100)	250(100)	236(100)	264(4)	222(18)
$[E-CH_2CHR^1O]^+$	178(22)	178(2)	192(23)	192(10)	–	–
$[MH-CH_2CHR^1O]^+$	254(8)	268(3)	282(2)	284(1)	–	192(34)
$HR^3N^+(-CH_2CHR^1OH)(-CH_2CHR^2OH)$	120(11)	134(3)	148(5)	–	162(100)	182(21)
Others (> 10%)	178(63) $[E-C_2H_4O]^+$		199(15) $C_6H_5SiOH^+$		326(13) $[M-CH_3]^+$; 160(12); 130(44) $[162-CH_3OH]^+$; 106(49) $C_6H_5SiH^+$; 74(41); 57(85) $C_4H_9^+$	207(40); 150(45) $[182-CH_3OH]^+$; 133(48); 106(55) $CH_2N^+HC_6H_5$; 105(72) $CH_2NC_6H_5^{+\cdot}$

The investigated compounds were synthesized according to known methods: I, II [10]; III [11]; IV [12,13]; V [14]; VI, VII [6]; X [15].

The new compound, 1-phenyl-2-azasilatrane (VIII), m.p. 82–85°C, was obtained in small yield by A. Lapsiņa from bis(2-hydroxyethyl)aminoethylamine and phenyltris(dimethylamino)silane.

The previously undescribed 1-phenyl-3,7-dimethyl-10,11-benzosilatrane (IX, m.p. 127–128°C, 50% yield) was synthesized by I. Sleikša by interaction of *N*-bis(2-hydroxypropyl)-*o*-aminophenol with phenyltriethoxysilane in absolute ethanol.

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