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Fragmentation of 2-thienylsilanes under electron impact

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Abstract

The electron impact (EI) mass spectra of 2-thienylsilanes have been studied. It has been found that species containing the Si=S bond take part in fragmentation, indicating intramolecular interaction of the silicon and sulphur atoms under EI conditions. The mass spectra are characterized by silicon-containing ions and also by intense peaks of silicon-free ions. Based on the mass spectrometric data, the following sequence of Si–R relative strengths in thienylsilanes is found: $Si–CH_3 <$ Si–H < Si–(2-thienyl) < Si–Cl.

Introduction

In contrast to the carbon derivatives of thiophene [1], until recently mass spectrometric studies of thienylsilanes have been scarce [2–5]. Nevertheless, the mass spectra of these compounds present interest because of the possibility of positive charge localization on the two heteroatoms: sulphur and silicon, which can lead to new fragmentation patterns.

Results and discussion

EI mass spectra were recorded for the thienylsilanes I–III.

Quantitative characterization of the most intense and characteristic peaks in the mass spectra of I–III are presented in Table 1.

The high intensity of the molecular ion of tetra(2-thienyl)silane (Id) (100%) is determined by the molecule's symmetry and by the possibility of charge localization both on the π-system of the cycle and on the silicon atom. Differences in stability of molecular ions (W_M, % of total ion current) for tetra(2-furyl)silane (37.0 [6]), Id (20.5%) and tetraphenylsilane (17.8% [7]) are in agreement with changes in interaction of the silicon atom and the aromatic system in the order: 2-furyl > 2-thienyl > phenyl [8].

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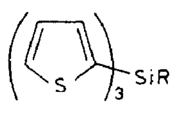
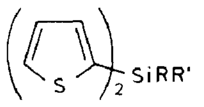
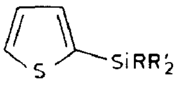


(Ia : R = H ;
Ib : R = CH_3 ;
Ic : R = Cl ;
Id : R = 2-thienyl)

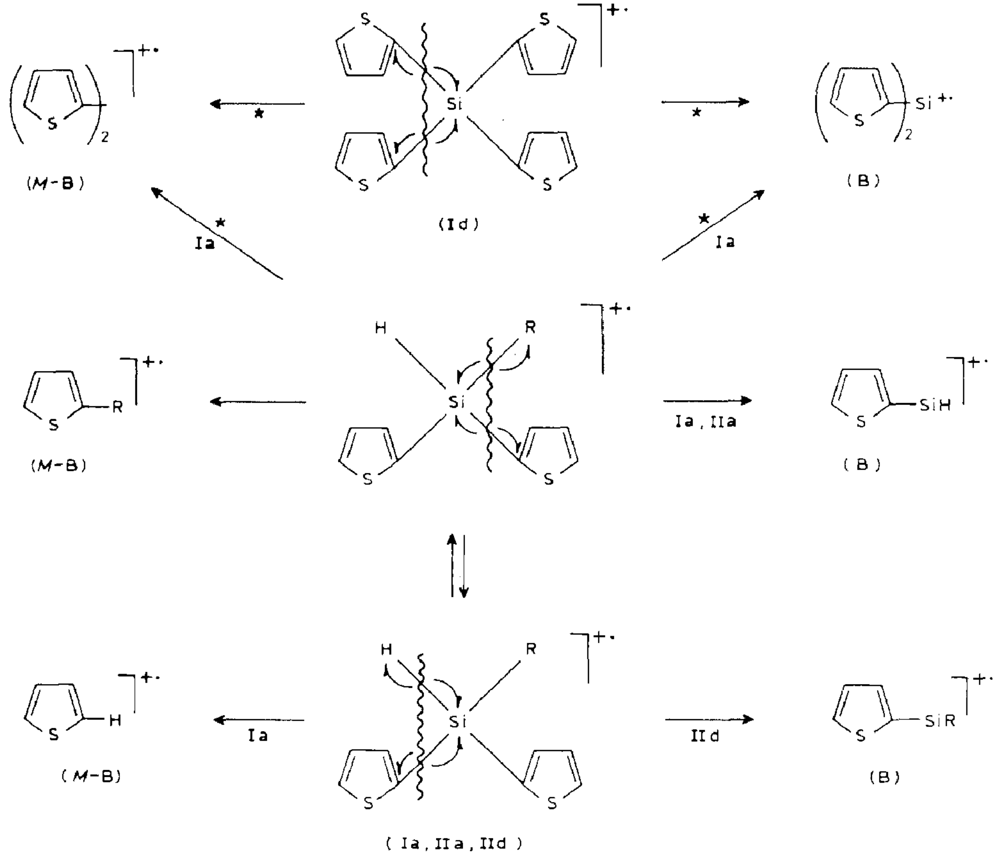


(IIa : R = R' = H ;
IIb : R = R' = CH_3 ;
IIc : R = R' = Cl ;
IId : R = H , R' = CH_3)



(IIIa : R = R' = H ;
IIIb : R = R' = CH_3 ;
IIIc : R = R' = Cl ;
IIId : R = H , R' = CH_3 ;
IIIe : R = H , R' = Cl ;
IIIf : R = CH_3 , R' = Cl)

Distortion of molecular symmetry induced by the introduction of other substituents at the silicon atom (Ia–Ic) leads to decreased molecular ion contribution to the total ion current (Table 1). Variation in W_M for II and III is insignificant in comparison with Ia–Ic. This is apparently connected with a decrease in the possibility of charge delocalization over several heterocycles, on the one hand, and with an increase in the number of decomposition pathways owing to variation in the Si–R bond strength, on the other hand.



Scheme 1

Table 1

Characteristic peaks in mass spectra of 2-thienylsilanes I–III

Ions	*m/z* (relative abundances, %)													
	Ia	Ib	Ic [a]	Id	IIa	IIb	IIc [a]	IId	IIIa	IIIb	IIIc [a]	IIId	IIIe [a]	IIIf [a]
$M^{+\cdot}$	278 (88)	292 (46)	312 (47)	360 (100)	196 (100)	224 (35)	264 (39)	210 (53)	114 (100)	156 (23)	216 (96)	142 (25)	182 (23)	196 (58)
A$^+$: $[M-C_4H_3S]^+$	195 (25)	209 (7)	229 (12)	277 (28)	113 (13)	141 (7)	181 (12)	127 (9)	–	73 (6)	181 (91)	–	99 (4)	113 (17)
$[M-R]^+$	277 (19)	277 (100)	277 (6)		195 (56)	209 (100)	229 (10)	209 (14) 195 (100)	113 (72)	141 (100)	133 (23)	181 (11) 127 (100)	181 (18) 147 (7)	181 (100) 161 (23)
$B^{+\cdot}$	194 (100) 112 (5)	–	–	194 (20)	112 (55)	–	–	126 (27)	112 (18)	–	98 (6)	58 (11)	–	–
$[M-B]^{+\cdot}$	84 (11) 166 (5)	–	166 (100)	166 (10)	84 (17)	–	166 (100)	–	84 (7)	–	118 (9)	–	84 (100)	98 (7)
C^+	111 (38)	111 (18)	63 (22)	111 (25)	111 (44)	111 (7)	63 (12)	111 (46)	111 (5)	–	63 (25)	111 (5)	63 (27)	63 (43)
216	(7)			(18)										
179	(25)			(59)										
143	(18)	(10)		(30)	(7)									
134	(65)	(5)	(12)	(35)	(14)		(8)	(6)						
97						(5)								(10)
85	(27)	(6)		(17)	(25)			(10)					(9)	
51	(45)	(9)	(9)	(28)	(42)	(8)	(5)	(17)		(5)		(7)	(7)	(11)
W_M (%)	13.6	16.2	13.2	20.4	13.3	14.2	14.1	13.2	15.4	11.9	14.6	9.7	8.0	9.5

[a] ^{35}Cl peaks.

Table 2

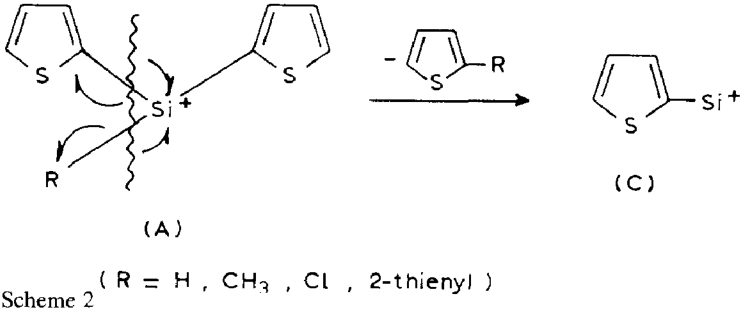
Estimation of the relative Si–R bond strength in 2-thienylsilanes

Compound	$I_{A_{Ri}}/\Sigma I_{A_{Ri}}$ (%)				Relative bond strength
	R = (2-thienyl)	R = H	R = CH_3	R = Cl	
Ia	57	43			Si–CH_3 < Si–H < Si–Cl
Ib	7		93		
Ic	66			34	
Id	100				
IIa	19	81			Si–H < Si–(2-thienyl)
IIb	7		93		Si–CH_3 < Si–(2-thienyl)
IIc	55			45	Si–(2-thienyl) < Si–Cl
IId	7	12	81		Si–CH_3 < Si–H

The abundance of silacenium ions A^+ (Table 1) originating from bond rupture between the substituent and the silicon atom is proportional to bond strength. The contribution of each A^+_{Ri} ion type (Table 2) versus the sum of intensities of all A^+_{Ri} ions permits one to estimate the relative strength of the Si–R bond in the molecular ions of thienylsilanes: Si–CH_3 < Si–H < Si–(2-thienyl) < Si–Cl.

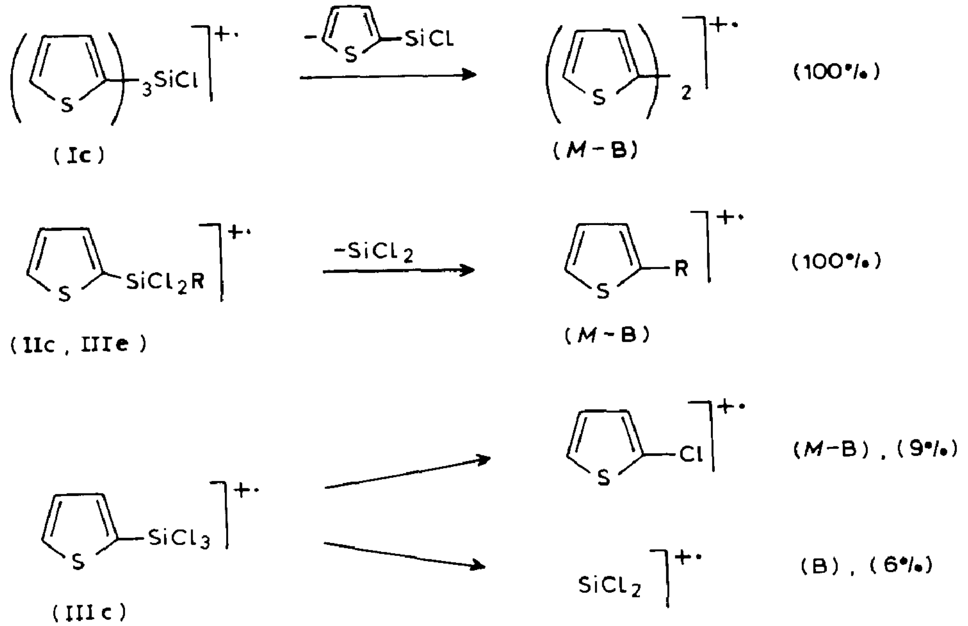
The sequence obtained is in accordance with the variation in bond dissociation energies in trimethylsilanes [9]. The fragmentation of 2-thienylsilanes occurs with elimination of dithienyl (Ia, Id) or thiophene (Ia, IIa, IId) from the rearranged molecular ion, resulting from migration of one of the thienyl groups or of a hydrogen atom to the other thienyl ring. Pseudomolecular silicon(II)-containing ions $B^{+\cdot}$ are formed as a result of this elimination (Table 1, Scheme 1). A similar loss of diphenyl is observed upon fragmentation of tetraphenylsilane [10]. In addition, I–III undergo decomposition, the charge being retained by the silicon-free moiety of the molecule leading to the $[M - B]^{+\cdot}$ ions. The increased intensity of $[M - B]^{+\cdot}$ ion peaks in comparison with the phenylsilanes (10 and 5% for dithienyl and diphenyl ions in Id and in tetraphenylsilane [11], correspondingly) can be explained by the participation of the sulphur atom in charge localization.

The ion C^+, analogue of the ion A^+ for silicon(II) (Table 1, Scheme 2) is produced by the loss of dithienyl, thiophene, methylthiophene or chlorothiophene from ion A^+. Possibly, the formation of the ion C^+ also involves rearrangement.



Scheme 2

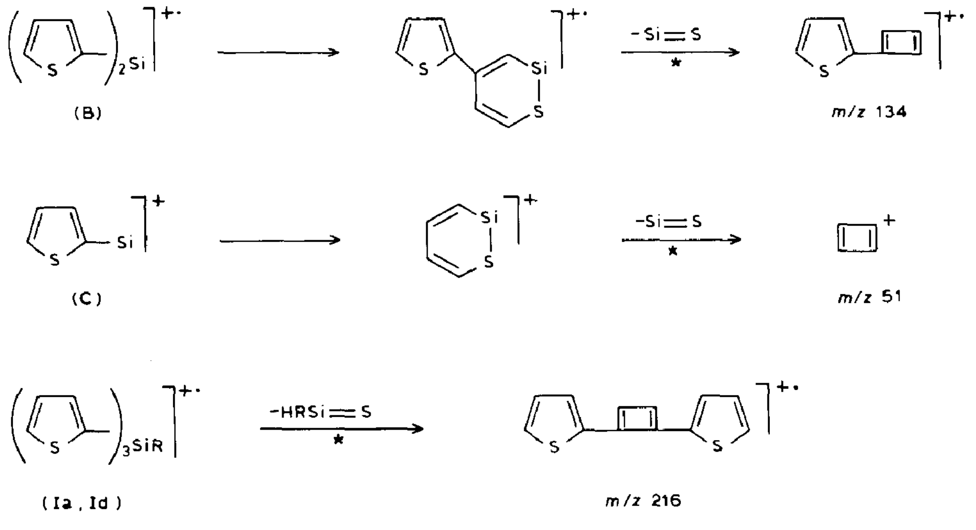
The peaks of $[M - B]^{+\cdot}$ ions are more intense than those of $B^{+\cdot}$ only for chlorothienylsilanes Ic, IIc and IIIe (Table 1, Scheme 3) and are the base peaks in their mass spectra. A preferable charge localization on the silicon-free fragment $[M - B]^{+\cdot}$ is determined both by the high ionization potential of dichlorosilylene



Scheme 3

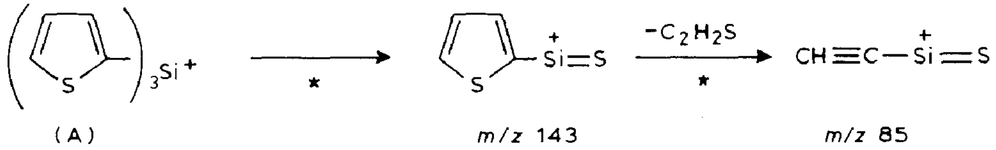
(11.9 eV versus 8.9 eV for thiophene [12]) and by the Si–R bond strength (Table 2), because the migration of the substituent R to the thienyl ring leads to $[M - B]^{+\cdot}$. Thus, IIIc forms both the $(M - B)^{+\cdot}$ and $B^{+\cdot}$ ions of low abundance, whereas IIIf forms only $(M - B)^{+\cdot}$ of similar intensity (Table 1).

It should be noted that intramolecular interaction of both heteroatoms in thienylsilanes (sulphur and silicon) is manifested under EI conditions. The fragmentation is characterized by elimination of the neutral species Si=S (Scheme 4) and by appearance of the silanethione ions $[RSi{=}S]^+$ (Scheme 5). To date, there is no clear-cut evidence as to the existence of stable compounds having the Si=S double



Scheme 4

bond [13]. Mass spectrometric data indicating the participation of neutral and charged species of silanethiones ($H_2Si{=}S$ [14], $[Me_2Si{=}S]^{+\cdot}$, $[MeSi{=}S]^+$, $[Et_2Si{=}S]^{+\cdot}$, $[EtSi{=}S]^+$ [15]) in fragmentation have been discussed in terms of a possible n_S–$3d_{Si}$ transannular interaction in compounds initially lacking the Si–S bond. A similar interaction is impossible in the molecules of thienylsilanes. The migration of thienyl groups in molecular or fragment ions with subsequent expansion of the thiophene cycle by a silicon atom may possibly cause this specific fragmentation. Apparently, migration of the thienyl group in molecular and fragment ions (except for the silicon-free ions shown in Scheme 4) is responsible also for the formation of ions *m/z* 179 and 97, whose elemental compositions are $C_9H_7S_2$ and C_5H_5S, respectively.



Scheme 5

Experimental

Mass spectra of I–III were obtained with a MS-25 gas chromatograph/mass spectrometer operated at 70 eV. The source temperature was 200 °C. A glass column packed with OV-101 was used, carrier gas-helium. The precise ion masses with *m/z* 216, 179, 166, 143 and 134 (resolution 40000) and metastable transitions were determined on a MS-50 apparatus. Compounds I–III were synthesized according to [8,16].

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