Contributions to the Interpretation of Mass Spectrum of Hexaethoxydisiloxane

Linked scans and M+1, M+2 isotopic effects

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The aim of this article is the study of the fragmentation reactions of hexaethoxydisiloxane initiated by electronic impact in the ionization chamber of a double focusing mass spectrometer. The initiation center of fragmentation reactions is established by quantum calculations. The daughter ions of hexaethoxydisiloxane molecular ion are obtained by linked scan B/E. The primary fragmentation ions with the masses 341, 297, 296 and 269 were obtained experimentally by B/E linked scan by radical induced fragmentation reactions. The eliminations of neutral fragments such as hydrogen, acetaldehyde, ethylene and water from the primary ions and the obtained ions by consecutive elimination reactions were emphasized experimentally by the B/E(1-E)$^{1/2}$ linked scan by charge induced reactions.

Keywords: hexaethoxydisiloxane, mass spectrum, linked scans, M+1, M+2 isotopic effects

Gas chromatography coupled with mass spectrometry (GC-MS) was used to investigate the reactions of hydrolysis, transesterification and condensation in the sol-gel process of tetraethoxysilane (TEOS) and other silicon precursor alkoxides with diferent organic radicals [1-8].

Hexaethoxydisiloxane as TEOS dimer, with structural formula $(C_2H_5O)_6Si_2O$ and molecular weight M=342, is obtained in sol-gel process by hydrolysis–condensation reactions (1)-(3).

Hydrolysis - Condensation Reactions

$$(C_2H_5O)_4Si + H_2O \rightleftharpoons (C_2H_5O)_3Si(OH) + C_2H_5OH \qquad (1)$$

$$2(C_2H_5O)_3Si(OH) \rightleftharpoons \mathbf{(C_2H_5O)_3Si - O - Si(OC_2H_5)_3} + H_2O \qquad (2)$$

$$(C_2H_5O)_3Si(OH) + (C_2H_5O)_4Si \rightleftharpoons$$

$$\rightleftharpoons \mathbf{(C_2H_5O)_3Si - O - Si(OC_2H_5)_3} + C_2H_5OH \qquad (3)$$

The chromatogam of monomers, dimers, trimers and tetramers of TEOS is presented in figure 1.a) for the reaction mixture TEOS : H_2O : EtOH : 1 : 1 : 1.75 (HCl *p*H=3.5); hexaethoxydisiloxane as TEOS dimer and its mono- and dihydrolized species are represented in the partial chromatogram in figure 1.b) at scan (#) numbers 411, 421 and 428. Mass spectra of TEOS dimers are presented in figure 2 with the molecular ions at m/e 342, 314 and 286, respectivelly.

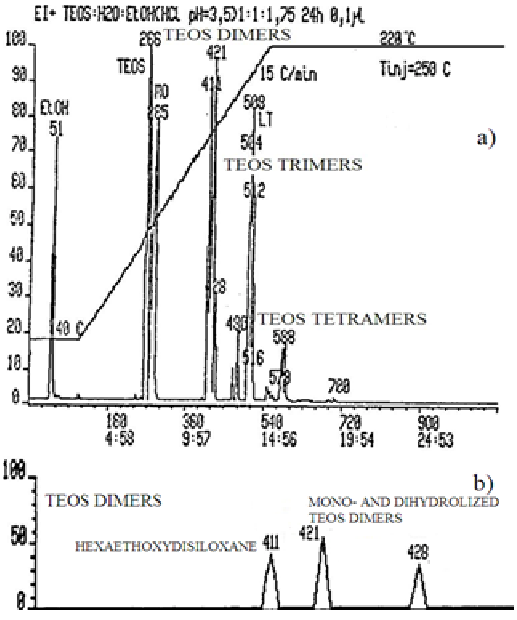

Fig. 1.a) The chromatogram for TEOS monomers, TEOS dimers and TEOS trimers and tetramers; b) The partial chromatogram for TEOS dimers

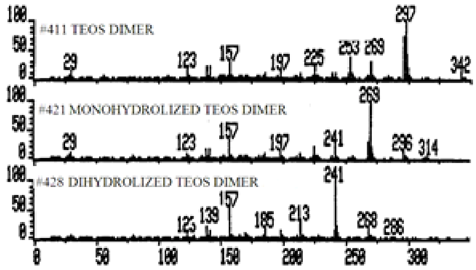

Fig. 2. Mass spectra for TEOS dimers

Scan numbers, structural formulae, structural codes and molecular weights of identified TEOS dimers are presented in table 1.

Table 1

SOME DATA FOR MS IDENTIFIED TEOS DIMERS WITH CHROMATOGRAPHIC SEPARATED SPECIES ACCORDING TO FIGURE 1.a) AND FIGURE 1.b)

Scan No.	Structural formulae	Structural codes	Molecular weight
408	$Si_2O(OC_2H_5)_6$	•–•	342
414	$Si_2O(OH)(OC_2H_5)_5$	•–•–OH	314
425	$Si_2O(OH)_2(OC_2H_5)_4$	•–•<$(OH)_2$	286

Legend: The symbol • encoding Si atom; the symboll •–• encoding siloxane bond Si-O-Si

The author developed a procedure [1,14] for the mass spectra interpretation of some silicon alkoxides and their transesters and oligomers obtained by the sol-gel process. This procedure was applied in previous works [14-15] and in the present work for the interpretation of mass spectrum of hexaethoxydisiloxane.

Mass spectrum of an organic substance, as well as a TEOS dimer such as hexaethoxydisiloxane is the result of a series of unimoleculare consecutive and competitive chemical reactions, which constitutes a pattern of fragmentation [10-13].

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Working conditions for the HP 5890 gas chromatograph	
Injection mode	Splitting injection 1:70
Injection port temperature	250 °C
Injection volume	0.1-0.3 µl
GC-MS interface temperature	280 °C
Column:	A fused silica high performance capillary column
- stationary phase	Silicone oil OV-1;
- size	25 m x 0.25 mm x 0.1 µm film thickness of stationary phase with 70,000 theoretical plates;
- temperature program	40 °C (3 min.), 15 °C/min, to 220 °C (5 min).
- carrier gas	Helium flow rate 1 ml/min
Working conditions for 70-SE, VG Analytical double focusing mass spectrometer	
Acquisition mode	SCN
Ion source temperature	180 °C
Energy electrons	70 eV
Response time	0.03 ms
Accelerating voltage	8 kV
Electronic amplifier	250

Table 2
GC-MS METHOD AND OPTIMISATION PARAMETERS

Experimental part

The development of GC-MS method for TEOS dimers determination in sol-gel processes consisted in establishing of the GC separation conditions of the analyzed components and the establishing of the optimal MS parameters (Table 2).

For the interpretation of mass spectrum TEOS dimer, the linked scans were used to study the metastable ions obtained in the first region without field (FFR1):

1) The B/E linked scan: This method of scanning allows obtaining daughter ions m_2^+ from a preset precursor ion m_1^+. The condition for obtaining the daughter ion is B/E = constant, where B is the magnetic field, and E is the electric field applied in the magnetic and electric sectors of the mass spectrometer. 2) The $(B/E)(1-E)^{1/2}$ linked scan: It is used to obtain the ions which lose small molecules with a preset mass (e.g. water, ethanol, ethylene, acetaldehyde, etc.).

The M+1, M+2 isotopic effects for the obtained ions were calculated by MS Interpreter software from Perkin Elmer.

Results and discussions

The ionization process

The mass spectrum of hexaethoxydisiloxane to the resolution R = 1000 is presented in Table 3. The molecular ion m/e 342 obtained in the electron impact ionization 70 eV has an intensity of 3.9%.

Quantum calculations by MOPAC 7 for neutral and ionized TEOS dimer molecules (fig. 3) show that the

Mass	Intensity	Mass	Intensity	Mass	Intensity	Mass	Intensity	Mass	Intensity
27	5.5	141	15.4	171	3.7	211	3.1	255	2.0
29	44.2	142	1.7	172	0.6	212	0.6	256	0.3
31	1.5	149	3.3	179	2.5	213	3.8	267	2.0
43	2.1	150	0.6	180	0.6	214	0.8	268	2.1
45	1.7	151	2.0	181	3.3	215	0.5	269	15.6
79	1.7	152	0.4	182	0.5	223	1.5	270	3.3
105	1.6	153	3.1	183	3.2	224	1.1	271	1.6
106	0.4	154	0.7	184	0.6	225	10.8	283	2.6
107	2.1	155	2.0	185	3.8	226	1.8	284	0.5
121	0.8	157	18.6	186	0.8	227	1.7	296	42.5
122	1.7	158	2.0	195	2.6	239	4.6	297	100.0
123	12.9	159	1.7	196	0.6	240	1.2	298	22.4
124	1.5	165	3.8	197	6.8	241	4.6	299	8.8
125	4.2	166	0.6	198	1.1	242	0.9	300	1.5
137	1.6	167	4.4	199	1.2	243	0.5	341	0.3
138	0.4	168	0.6	200	0.6	252	5.1	342	3.9 $M^{+\cdot}$
139	16.1	169	3.7	209	3.7	253	18.8	343	1.0
140	1.8	170	0.7	210	0.8	254	4.1	344	0.4

Legend: molecular ion is encoded $M^{+\cdot}$; the primary fragmented ions are thicken in the gray background cells; the ion intensity is expressed as % of basic ion normalized to I = 100.

Table 3
THE MASS SPECTRUM OF HEXAETHOXYDISILOXANE AT THE RESOLUTION R = 1000.

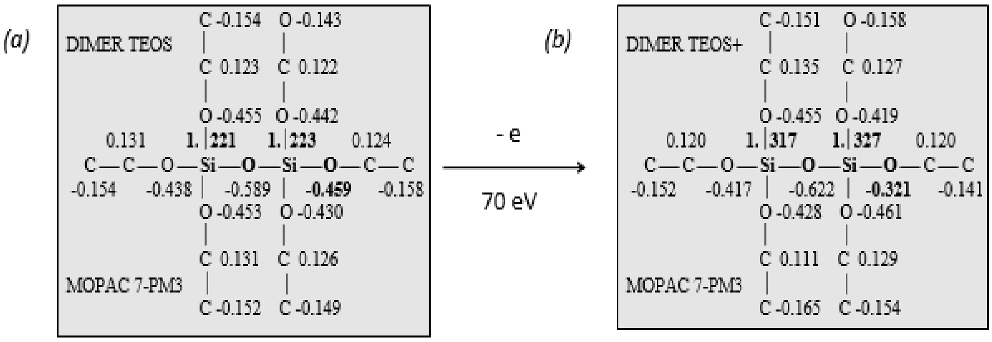


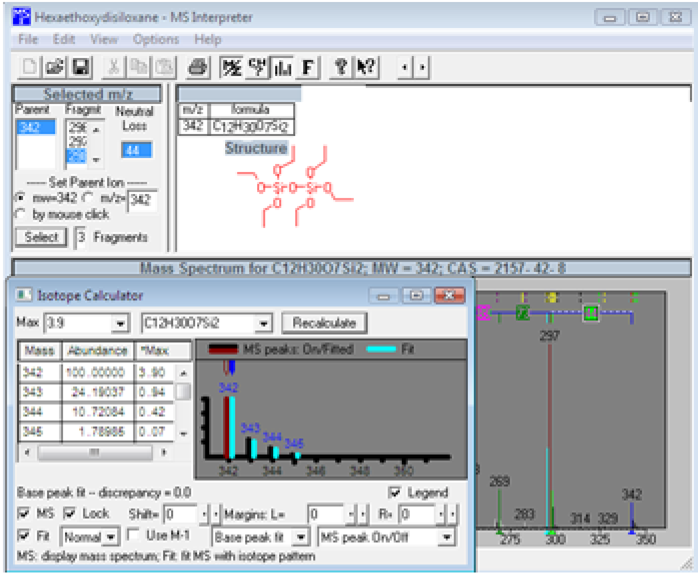
Fig. 3. The net atomic charges by MOPAC 7 quantum calculations: (a) hexaethoxydisiloxane and (b) its molecular ion obtained by eletronic impact ionization at 70 eV. The net negative charge on oxygen atom decreases from -0.459 to -0.321. The charge delocalization is thickened.

Entry	Ionic formula	Ionic mass	Isotopic effects	I_E %	I_C %
1.	$C_{12}H_{30}O_7\,^{28}Si_2$	342	M	3.9→	3.9
	$C_{12}H_{30}O_7\,^{29}Si_2$	343	M+1	1.0	0.9
	$C_{12}H_{30}O_7\,^{30}Si_2$	344	M+2	0.4	0.4
2.	$C_8H_{21}O_6\,^{28}Si_2$	269	M	15.6→	15.6
	$C_8H_{21}O_6\,^{29}Si_2$	270	M+1	3.3	3.1
	$C_8H_{21}O_6\,^{30}Si_2$	271	M+2	1.6	1.5
3.	$C_8H_{21}O_5\,^{28}Si_2$	253	M	18.8→	18.8
	$C_8H_{21}O_5\,^{29}Si_2$	254	M+1	4.1	3.6
	$C_8H_{21}O_5\,^{30}Si_2$	255	M+2	2.0	1.7
4.	$H_5O_6\,^{28}Si_2$	157	M	18.6→	18.6
	$H_5O_6\,^{29}Si_2$	158	M+1	2.0	1.9
	$H_5O_6\,^{30}Si_2$	159	M+2	1.7	1.6

Table 4

THE M+1 AND M+2 ISOTOPIC EFFECTS FOR SAME IONS IN MASS SPECTRUM OF HEXAETHOXYDISILOXANE

Legend: I_E: The intensities obtained experimentally; I_C: The intensities calculated with MS Interpreter software based on experimental value M (ions with ^{28}Si) indicated by symbol ⟶



Mass Spectrum for C12H30O7Si2; MW = 342; CAS = 2157- 42- 8

Set Parent Ion: ● mw=342 ○ m/z= 342 ○ by mouse click

3 Fragments

Max 3.9 C12H30O7Si2

Mass	Abundance	%Max
342	100.00000	3.90
343	24.19037	0.94
344	10.72084	0.42
345	1.78985	0.07

Base peak fit -- discrepancy = 0.0

☑ Legend

☑ MS ☑ Lock Shift= 0 Margins: L= 0 R= 0

☑ Fit Normal ☐ Use M-1 Base peak fit MS peak On/Off

MS: display mass spectrum; Fit: fit MS with isotope pattern

Table 5

THE M+1, M+2 ISOTOPIC EFFECTS FOR MOLECULAR ION WITH m/z 342

FIT THEORETICAL AND EXPERIMENTAL VALUES BY MS INTERPRETER SOFTWARE

initiation center of fragmentation reactions is located on the oxygen atom of an ethoxy group; net negative charge on this atom decreases from -0.459 to -0.321. The siloxane bond is strong in the ionized dimer molecule by charge delocalisation due to +I inductive effect of the silicon atom and -I inductive effect of the oxygen atom.

Another argument concerning the existence of the molecular ion and some fragmentation ions are the M+1 and M+2 isotopic effects measured experimentally compared to the theoretical ones.

According to the isotopic distributions of the atoms that compose an alcoxide as TEOS and its oligomers as hexaethoxydisiloxane, the strongest M+1 and M+2 isotopic effects are due to silicon atom ^{29}Si and ^{30}Si with natural concentration 4.67 % and 3.10 %, respectivelly, followed by the M+1 isotopic effect of carbon atom ^{13}C (1.1 %) [1]. The M+2 isotopic effect of the silicon atom is selectively in the case of silicon alkoxides and their oligomers without halogen atoms.

There is a good agreement between experimental M+1, M+2 isotopic effects for some obtained ions and those calculated theoretically (Table 4); for example is a good agreement between experimental values (1 % and 0.4 %) in Table 4 and those calculated theoretically by MS Interpreter software (Table 5) (0.9 % and 0.4 %) for the molecular ion of hexaethoxydisiloxane with m/e 342 and intensity 3.9 %.

Primary events. The elimination of radicals and an ethanol molecule

Fragmentation ions obtained directly from the molecular ion by cleavages of s bonds can be emphasized by means of the experimental B/E linked scan which gives daughter ions of the radical cation at mass 342. Thus, in figure 4, is visualized that from the molecular ion of hexaethoxydisiloxane, the fragmentation ions are obtained at m/e 341, 297 that correspond at mass differences of 1 amu, 45 amu, which in this case corresponds at the radical eliminations: $H^{\bullet}$, $OC_2H_5^{\bullet}$

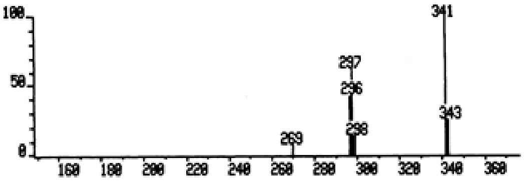
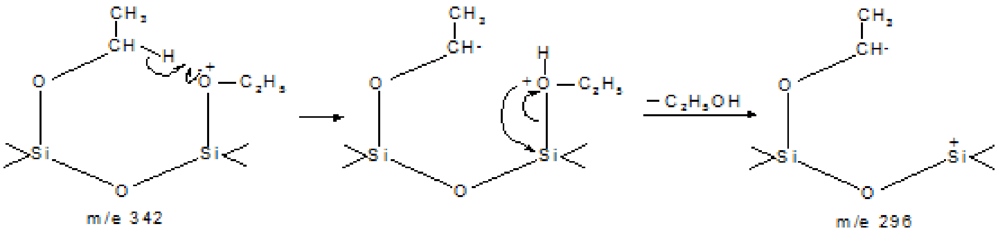


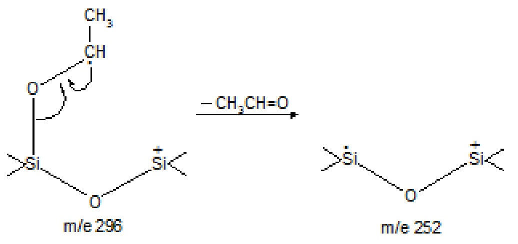
Fig. 4. The daughter ions of hexaethoxydisiloxane molecular ion by linked scan B/E

The daughter ion with ion mass m/e 296 (I=42.5%) shown in figure 4 is obtained by removing ethanol with H atom transposition according to the reaction (4):



(4)

The ion m/e 296 obtained by reaction (4) stabilized by inductive effect is intense although it is a radical cation. Part of ions m/e 296 with a sufficient internal energy decompose further. A very probable reaction is induced by radical, with acetaldehyde elimination, according to equation (5).



(5)

The cation radical with m/e 252 has the intensity I = 5.1 % and even mass as transposition parent ion with m/e 296.

One reaction pathway to obtain the daughter ion m/e 269 of molecular ion m/e 342 is the elimination of a fragment with mass 73 uam; that mean elimination of an ethyl radical and a molecule of acetaldehyde.

Eliminations of neutral molecules from primary ions

The elimination of a molecule of ethanol can be also evidenced experimentally by linked scans (B/E)(1-E)$^{1/2}$. In figure 5.a-e are shown molecular ions and fragmentation ions of hexaethoxy-disiloxane alongside its methoxy transesters TR1D to TR4D that eliminate ethanol. It finds that the elimination of ethanol decrease with increasing transesterification. The elimination of ethanol is an intense reaction for molecular ions of species TEOS dimer and methoxypentaethoxydisiloxane (TR1D) that have six and five ethoxy groups.

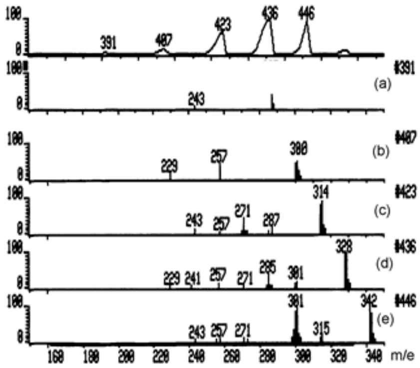


Fig. 5.a-e. The molecular and fragmentation ions of hexaethoxydisiloxane and of some trans-methoxy esters which elimine ethanol obtained by linked scan (B/E)(1-E)$^{1/2}$: (a) TR4D, (b) TR3D, (c) TR2D, (d) TR1D and (e) dimer TEOS

The fragmentation ions of hexaethoxydisiloxane that eliminate acetaldehyde and ethylene by liked scans B/E(1-E)$^{1/2}$ are shown in figure 6 and 7 respectivelly.

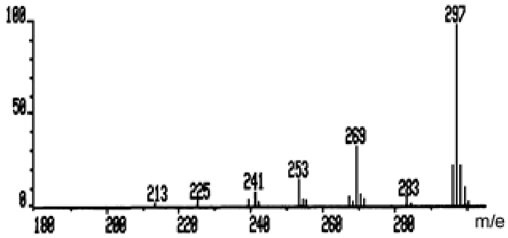


Fig. 6. The fragmentation ions of hexaethoxydisiloxane that eliminates acetaldehyde obtained by linked scan (B/E)(1-E)$^{1/2}$

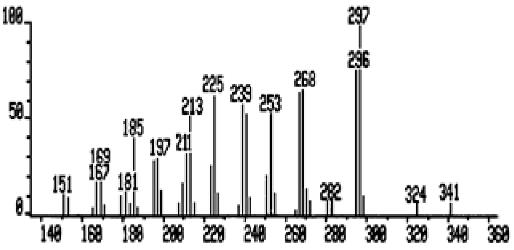


Fig. 7. The fragmentation ions of hexaethoxydisiloxane that eliminates ethylene obtained by linked scan (B/E)(1-E)$^{1/2}$

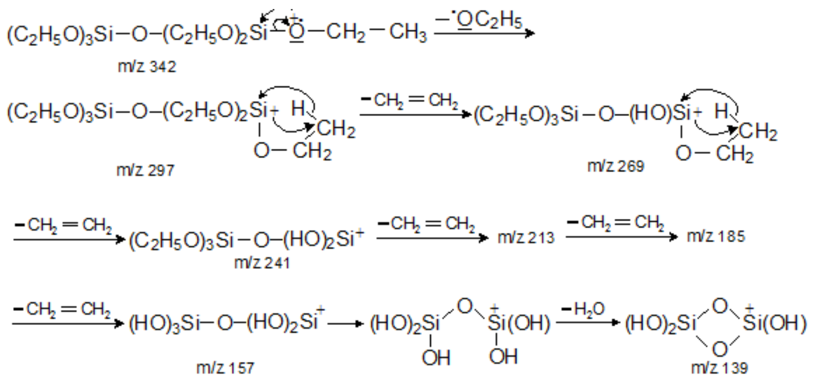
In the mass spectrum of hexaethoxydisiloxane are present two quite intense ions with m/e 139 (I=16.1%) and m/e 123 (I=12.9%).

Thus there can be written, according to the experimental data obtained by linked scan (B/E)(1-E)$^{1/2}$, the reaction pathways to obtaining the ion with mass m/e 139 from the ion with m/e 297 (daughter ion of molecular ion m/e 342) by succesive eliminations of ethylene and water according to the reactions (6).

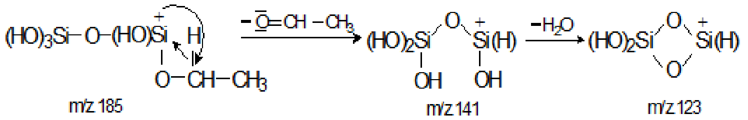
The fragmentation ion with m/e 123 is obtained on the same reaction pathway until they obtained the ion with m/e 185 by elimination of acetaldehyde and water according to the reactions (7).

The ion $H_3O_5Si_2$ with m/e 139 is confirmed by the M+1 isotope effect; experimental value of this effect is 1.8 % (Table 2), and the theoretical calculated value is 1.7 %. The experimental M+1 isotopic effect of ion $H_3O_4Si_2$ with m/e 123 has the value I=1.5 % as against of theoretical value I=1.3 %.

An argument for partial double ionization of molecular ion, at two ethoxy groups from the two silicon atoms, is the presence in the TEOS dimer spectrum of high intensity



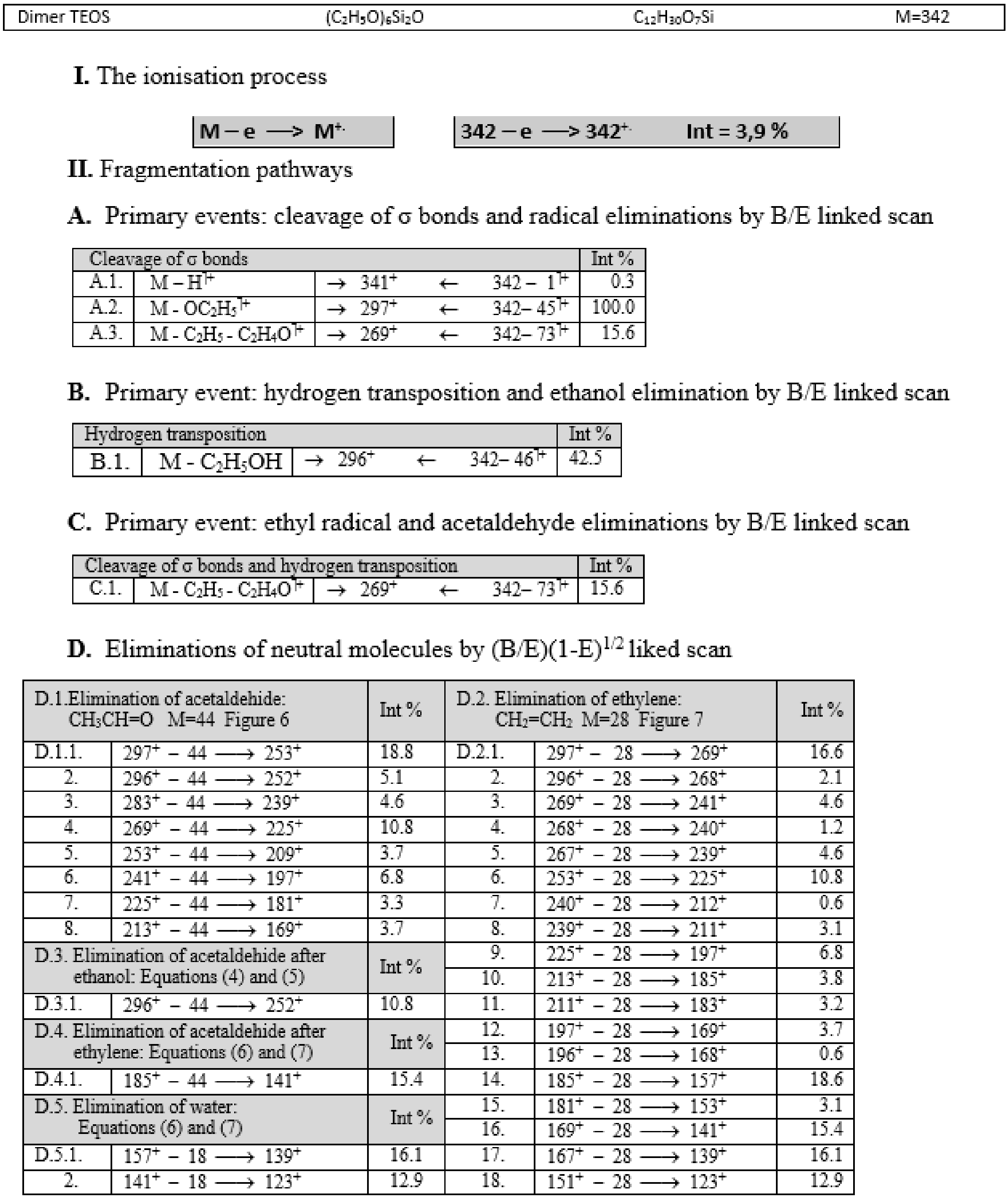
(6)



(7)

Table 6

THE MASS SPECTRUM OF HEXAETHOSYDISILOXANE. FRAGMENTATION PATHWAYS BY LINKED SCANS



Dimer TEOS	$(C_2H_5O)_6Si_2O$	$C_{12}H_{30}O_7Si$	M=342

I. The ionisation process

$M - e \longrightarrow M^{+\cdot}$	$342 - e \longrightarrow 342^{+\cdot}$ Int = 3,9 %

II. Fragmentation pathways

A. Primary events: cleavage of σ bonds and radical eliminations by B/E linked scan

Cleavage of σ bonds				Int %
A.1.	$M - H]^{+}$	$\rightarrow 341^+$	$\leftarrow$ $342 - 1]^{+}$	0.3
A.2.	$M - OC_2H_5]^{+}$	$\rightarrow 297^+$	$\leftarrow$ $342 - 45]^{+}$	100.0
A.3.	$M - C_2H_5 - C_2H_4O]^{+}$	$\rightarrow 269^+$	$\leftarrow$ $342 - 73]^{+}$	15.6

B. Primary event: hydrogen transposition and ethanol elimination by B/E linked scan

Hydrogen transposition				Int %
B.1.	$M - C_2H_5OH$	$\rightarrow 296^+$	$\leftarrow$ $342 - 46]^{+}$	42.5

C. Primary event: ethyl radical and acetaldehyde eliminations by B/E linked scan

Cleavage of σ bonds and hydrogen transposition				Int %
C.1.	$M - C_2H_5 - C_2H_4O]^{+}$	$\rightarrow 269^+$	$\leftarrow$ $342 - 73]^{+}$	15.6

D. Eliminations of neutral molecules by $(B/E)(1\text{-}E)^{1/2}$ liked scan

D.1.Elimination of acetaldehide: $CH_3CH=O$ M=44 Figure 6		Int %	D.2. Elimination of ethylene: $CH_2=CH_2$ M=28 Figure 7		Int %
D.1.1.	$297^+ - 44 \longrightarrow 253^+$	18.8	D.2.1.	$297^+ - 28 \longrightarrow 269^+$	16.6
2.	$296^+ - 44 \longrightarrow 252^+$	5.1	2.	$296^+ - 28 \longrightarrow 268^+$	2.1
3.	$283^+ - 44 \longrightarrow 239^+$	4.6	3.	$269^+ - 28 \longrightarrow 241^+$	4.6
4.	$269^+ - 44 \longrightarrow 225^+$	10.8	4.	$268^+ - 28 \longrightarrow 240^+$	1.2
5.	$253^+ - 44 \longrightarrow 209^+$	3.7	5.	$267^+ - 28 \longrightarrow 239^+$	4.6
6.	$241^+ - 44 \longrightarrow 197^+$	6.8	6.	$253^+ - 28 \longrightarrow 225^+$	10.8
7.	$225^+ - 44 \longrightarrow 181^+$	3.3	7.	$240^+ - 28 \longrightarrow 212^+$	0.6
8.	$213^+ - 44 \longrightarrow 169^+$	3.7	8.	$239^+ - 28 \longrightarrow 211^+$	3.1
D.3. Elimination of acetaldehide after ethanol: Equations (4) and (5)		Int %	9.	$225^+ - 28 \longrightarrow 197^+$	6.8
			10.	$213^+ - 28 \longrightarrow 185^+$	3.8
D.3.1.	$296^+ - 44 \longrightarrow 252^+$	10.8	11.	$211^+ - 28 \longrightarrow 183^+$	3.2
D.4. Elimination of acetaldehide after ethylene: Equations (6) and (7)		Int %	12.	$197^+ - 28 \longrightarrow 169^+$	3.7
			13.	$196^+ - 28 \longrightarrow 168^+$	0.6
D.4.1.	$185^+ - 44 \longrightarrow 141^+$	15.4	14.	$185^+ - 28 \longrightarrow 157^+$	18.6
D.5. Elimination of water: Equations (6) and (7)		Int %	15.	$181^+ - 28 \longrightarrow 153^+$	3.1
			16.	$169^+ - 28 \longrightarrow 141^+$	15.4
D.5.1.	$157^+ - 18 \longrightarrow 139^+$	16.1	17.	$167^+ - 28 \longrightarrow 139^+$	16.1
2.	$141^+ - 18 \longrightarrow 123^+$	12.9	18.	$151^+ - 28 \longrightarrow 123^+$	12.9

ion $C_2H_5^+$ at m/e 29 (I = 44.2%). One reaction pathway to obtain the ion with m/e 142 (I=1.7 %) is elimination of ion $C_2H_5^+$ from double charged ion $171^{++\cdot}$(342/2) with intensity I=3.7 % (Table 3).

Reaction pathways for obtaining mass spectrum of hexaethoxydisiloxane are summarized in Table 6.

Conclusions

The aim of this article was the study of the fragmentation reactions of hexaethoxydisiloxane initiated by electronic impact in the ionization chamber of a double focusing mass spectrometer. Hexaethoxydisiloxane as TEOS dimer with the structural formula $(C_2H_5O)_6Si_2O$ and molecular weight M=342, was obtained in sol-gel process by hydrolysis–condensation reactions.

The author developed in a previous work [14] a procedure for the mass spectra interpretation of some silicon alkoxides and their transesters and oligomers obtained by the sol-gel process. This procedure was applied in present work for the interpretation of mass spectrum of hexaethoxydisiloxane.

Quantum calculations for neutral and ionized TEOS dimer molecules established that the initiation center of fragmentation reactions is located on the oxygen atom of an ethoxy group.

The primary fragmentation ions at m/e 341, 297, 296 and 269 were obtained experimentally by B/E linked scan, by radical induced fragmentation reactions, as the daughter ions of hexaethoxydisiloxane molecular ion.

The eliminations of neutral fragments such as hydrogen, acetaldehyde, ethylene and water from the primary ions and the obtained ions through consecutive elimination reactions were emphasized experimentally by the $B/E(1\text{-}E)^{1/2}$ linked scan by charge induces reactions.

Thus there can be written 35 fragmentation pathways for the primary events and the eliminations of neutral molecules obtained experimentally by the B/E and B/E $(1-E)^{1/2}$ linked scans.

According to the isotopic distributions of the atoms that compose an alcoxide as TEOS and its oligomers as hexaethoxydisiloxane the strongest M+1 and M+2 isotopic effects are due to silicon atoms ^{29}Si and ^{30}Si, followed by the M+1 isotopic effect of carbon atom ^{13}C.

There is a good agreement between experimental M+1, M+2 isotopic effects for some obtained ions and those calculated theoretically; for example is a good agreement between experimental values (1 and 0.4 %) and those calculated theoretically (0.9 % and 0.4 %) for the molecular ion of hexaethoxydisiloxane with m/e 342 and intensity 3.9%.

The interpretation of a mass spectrum is important for the assigning of the structure of a

molecular species with unidentified or wrong registered mass spectrum.

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