



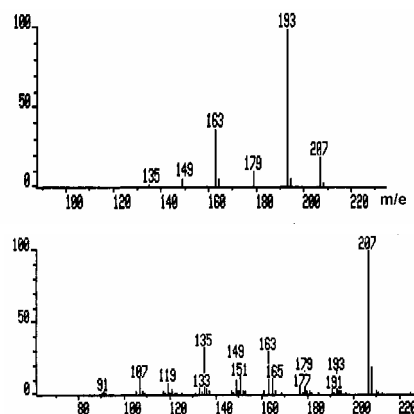
CONTRIBUTIONS TO THE INTERPRETATION OF MASS SPECTRUM OF TETRAETHOXYSILANE (TEOS). PART II: CHARGE INDUCED REACTIONS. ELIMINATIONS OF NEUTRAL FRAGMENTS¹

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The aim of this article in continuation of Part I is the study of the fragmentation reactions of tetraethoxysilane (TEOS) as a precursor in the sol-gel process initiated by electronic impact in the ionization chamber of a double focusing mass spectrometer. In Part I the primary fragmentation ions at masses 207, 193, 179 and 163 were obtained experimentally by B/E linked scan by radical induced fragmentation reactions. In Part II eliminations of neutral fragments from the primary ions and the obtained ions by consecutive elimination reactions were evidenced experimentally by the B/E and B/E(1-E)^{1/2} linked scans. On this basis charge induced reactions with eliminations of acetaldehyde, ethylene and hydrogen are presented. The existence of fragmentation ions thus obtained is supplementary argued by measuring the ion masses at high resolution and the M+1, M+2 isotopic effects and by the calculation of the double bond equivalent (DBE).



INTRODUCTION

In Part I¹ the primary fragmentation ions at masses 207, 193, 179 and 163, then the daughter ions of the TEOS molecular ion at m/e 208, were obtained experimentally by B/E linked scan in radical induced fragmentation reactions.

In this paper the author applies a procedure, presented in Part I¹, to the TEOS mass spectrum interpretation for the fragmentation ions obtained by charge induced reactions with eliminations of neutral fragments by the B/E and B/E(1-E)¹⁻² linked scans.

The first objective of the author^{2,12} was the separation and identification of molecular species obtained in sol-gel process by gas chromatography coupled with mass spectrometry (GC-MS).

The basic factors that influence sol-gel process have been studied systematically by GC-MS: the type of precursor alkoxide, the nature of the solvent, the quantity of water used in hydrolysis, the reactant mixing order and the catalyst type. The results were published between 1994 and 2007.³⁻⁹

The second objective of the author^{1-2,13,18} was the development of a procedure for the mass spectra interpretation of some silicon alkoxides and their transesters and oligomers obtained by the sol-gel process.

The relationship between the chemical structure of the molecules and their mass spectra has been highlighted by McLafferty¹⁰ by applying qualitative physical-organic method; according to this theory the relative intensity of fragmentation ions is determined

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by (1) the stability of the reaction products and of the bond strength. A complementary theory has been developed by Djerassi¹¹ within a physical-organic method: (2) the charge and radical localization after ionization contributes to establish the initiation centers of the fragmentation reactions.

EXPERIMENTAL

The experimental data for this paper were obtained on a GC-MS tandem produced by VG-Analytical, England. Speed scans for GC-MS applications have been performed on a 70-SE double-focusing mass spectrometer.

Hewlett Packard 5890 Gas Chromatograph with a fused silica capillary column was effective for the separations of complex mixtures such as those obtained in the sol-gel process. The GC-MS interface was direct one and it was done inert by glass plating. The complete control of all scan functions of the instrument was provided by a VG Digital Scan Controller interface.

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

The B/E linked scan: This experimental MS method of scanning allows obtaining daughter ions m_2^+ from a preset precursor ion m_1^+ . The condition for obtaining the daughter ion is $B/E = \text{constant}$, where B is the magnetic field, and E is the electric field applied in the magnetic and electric sectors of the mass spectrometer.^{2,13}

The $(B/E)(1-E)^{1/2}$ linked scan:^{2,13} It is used to obtain by experimental MS method the ions which lose small molecules at a preset mass (e.g. ethylene, acetaldehyde, etc.).

According to the isotopic distributions of the atoms that compose an alcoxide as TEOS the strongest M+1 and M+2 isotopic effects are due to silicon atom (4.67 and 3.10 %), followed by the M+1 isotopic effect of carbon atom (1.1%).^{1,14-19}

The M+2 isotopic effect of the silicon atom is selectively in the case of silicon alcoxides and substituted alcoxides without halogen atoms. To calculate more precisely the M+1, M+2 isotopic effects the ion intensity was measured on a statistical basis to high resolution (5000).

Working conditions

For the HP 5890 gas chromatograph: A fused silica high performance capillary column of 25 m x 0,25 mm, with 70,000 theoretical plates; stationary phase: silicone oil OV-1, with a thickness of 0.1 μ m; the temperature inside the oven: 40 °C, for 3 minutes; temperature programming up to 220 °C with a temperature gradient of 15 °C/min; injector temperature: 250 °C; carrier gas (helium) flow-rate: 1 ml/min; splitting injection 1: 70; the volume of injected sample: 0.1-0.3 μ L.

For 70-SE, VG Analytical double focusing mass spectrometer: Excitation source with electronic impact at 70 eV; response time: 0.03 ms; accelerating voltage: 8 kV; temperature in the ion source: 180 °C; electronic amplifier: 250.

RESULTS AND DISCUSSION

Contributions to the interpretation of mass spectrum of tetraethoxysilane (TEOS)

Mass spectrum of TEOS in NBS spectra library as described in¹⁻² contain the molecular ion at m/e 208 together with the M+1 and M+2 isotopic effects at m/e 209 and 210 and 46 fragmentation ions.

For this work has been achieved a library of the mass spectra obtained for TEOS in the different sol-gel reaction mixtures², analyzed by GC-MS at a resolution of R=1000 and presented in Fig. 1.

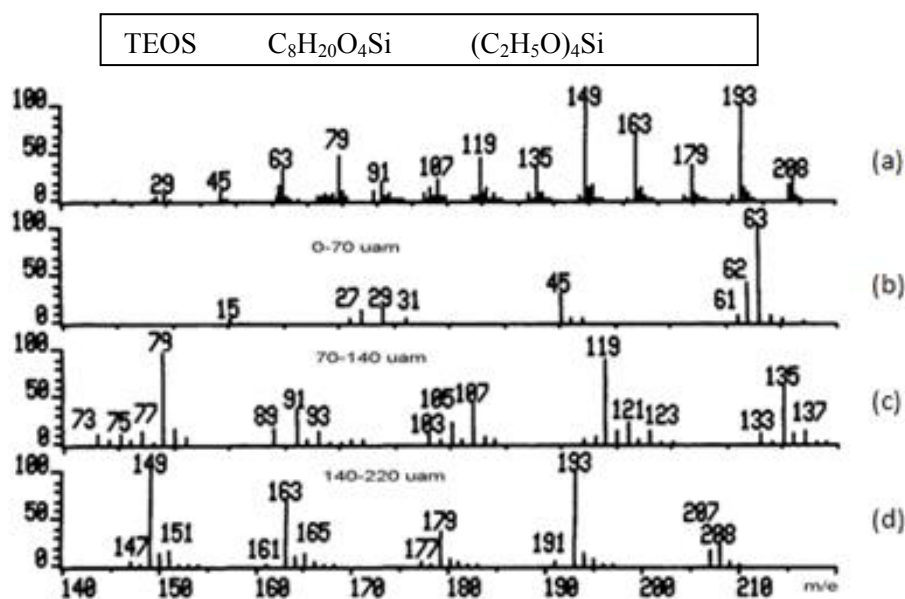


Fig. 1 – Mass spectrum of tetraethoxysilane (TEOS) as an average of 12 mass spectra at resolution 1000; (a) full, (b) 0-70 amu (c) 70-140 amu and (d) 140-220 amu.

It shows the TEOS mass spectrum obtained by averaging the 12 TEOS mass spectra and contains the molecular ion at m/e 208 with adjacent isotopic ions at m/e 209 and m/e 210 together with 84 fragmentation ions. Increased numbers of TEOS fragmentation ions at high resolution ($R=5000$ and $R=6600$) will be presented in the upcoming works.

As a general rule for the following presentations, informative input data about an ion in the mass spectrum are presented in a text box on a white background and the results, which are the arguments for the existence of an ion obtained in fragmentation reactions, are presented in a text box on a grey background.¹

Charge induced reactions. Eliminations of neutral fragments from the primary fragmentation ions and from the obtained ions by consecutive elimination reactions

The molecular masses of small molecules which are eliminated from the primary fragmentation ions with m/e 207, 193, 179 and 163

were put in evidence experimentally by the B/E linked scan. Thus the daughter ions of the primary fragmentation ion with m/e 193 at m/e 165, m/e 149 and m/e 191 were evidenced experimentally by the B/E linked (Fig. 2) at the next preset masses 28 amu (ethylene), 44 amu (acetaldehyde) and 2 amu (hydrogen molecule) respectively.

The highlighting of the fragmentation ions losing small molecules (-28, -44 amu) was performed experimentally by the B/E(1-E)^{1/2} linked scan. Thus they were obtained the fragmentation ions which eliminate acetaldehyde (Fig. 3) and those which eliminate ethylene (Fig. 4).

Based on experiments with the B/E and B/E(1-E)^{1/2} linked scans they can write successive and competitive reactions of small molecule eliminations such as acetaldehyde and ethylene.

Because of limited in scope of this paper, all reactions with elimination of acetaldehyde and ethylene cannot be written with getting experimentally of ions by linked scans and accurate mass measurements.



Fig. 2 – The daughter ions of the primary fragmentation ion with m/e 193 obtained by the B/E linked scan.

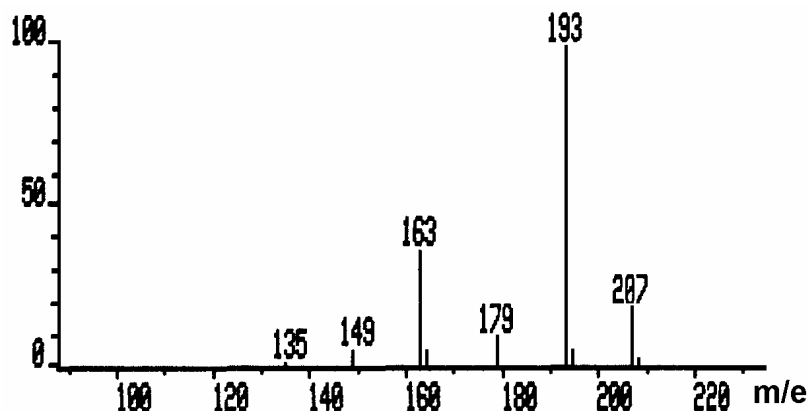


Fig. 3 – The TEOS fragmentation ions which eliminate acetaldehyde obtained by the B/E(1-E)^{1/2} linked scan.



Fig. 4 – The TEOS fragmentation ions which eliminate ethylene obtained by the $B/E(1-E)^{1/2}$ linked scan.

Thus, in paper are presented only the B.1.(1) and B.2.(2) reaction pathways with elimination of acetaldehyde and B.3.(3) and the B.4.(4) reaction pathways with elimination of ethylene. Among the elimination of molecular hydrogen reactions are shown the B.5.(5) and B.6.(6) reaction pathways.

Reactions with the acetaldehyde elimination

The elimination of an acetaldehyde molecule is produced as follows:

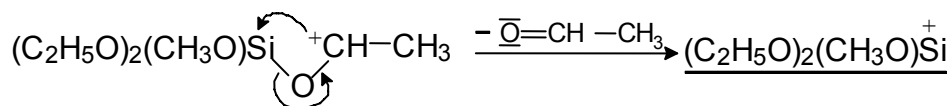
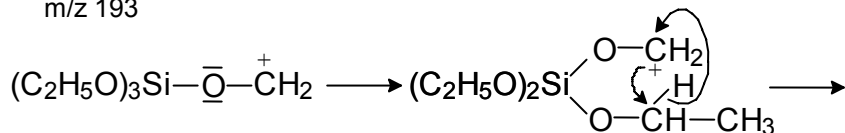
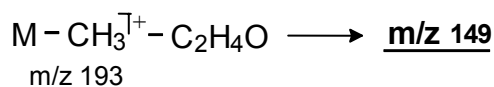
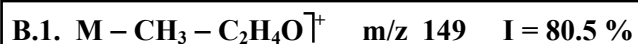
(1) Transposition of a methylene hydrogen atom of a ethoxy group to the center of positive

charge of cyclic transition states with 4, 5 or 6 atoms, and

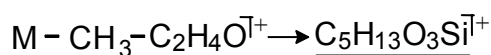
(2) Heterolytic cleavage of Si-O bond with positive charge displacement on silicon atom and thus obtaining a stable silicon ion.

Thus, the fragmentation ions with m/e 163, 149, 135, 119, 105 and 91 are obtained (Fig. 3); most of these ions are of high intensity in mass spectrum of TEOS (Fig. 1.a,c).

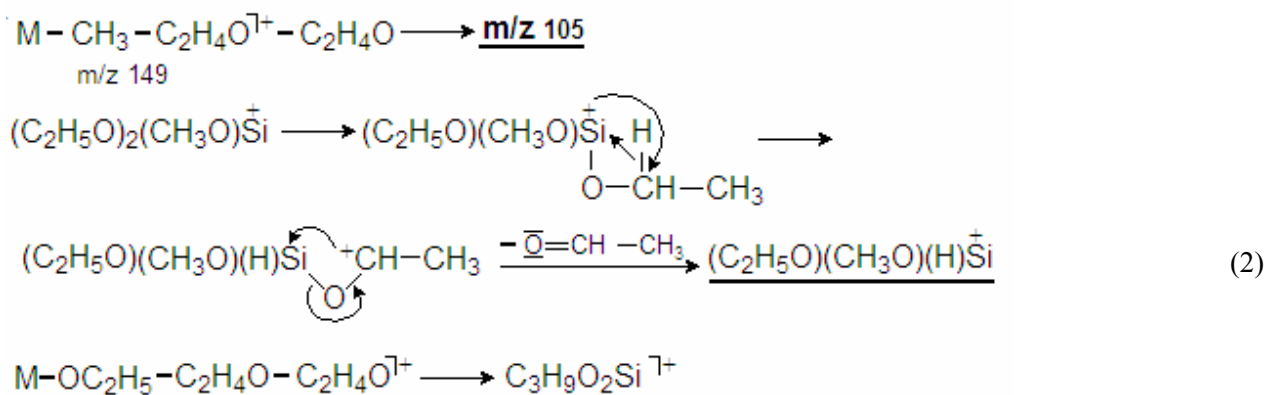
The reaction pathways according to Equations B.1.(1) and B.2.(2) for obtaining the ions with m/e 149 and 105 from the ions with m/e 193 and m/e 149 with elimination of acetaldehyde are outlined below:



(1)



$M_{ELE} = 149.0634 \quad M_{OBS} = 149.0628 \quad \Delta M = 0.6 \text{ mmu} \quad DBE = 0.5$

B.2. $M - CH_3 - C_2H_4O - C_2H_4O^{\bar{1}+}$ m/z 105 $I = 5.3\%$


$$M_{ELE} = 105.0372 \quad M_{OBS} = 105.0363 \quad \Delta M = 0.8 \text{ mmu} \quad DBE = 0.5$$

Reactions with the ethylene elimination

The elimination of an ethylene molecule is produced as follows:

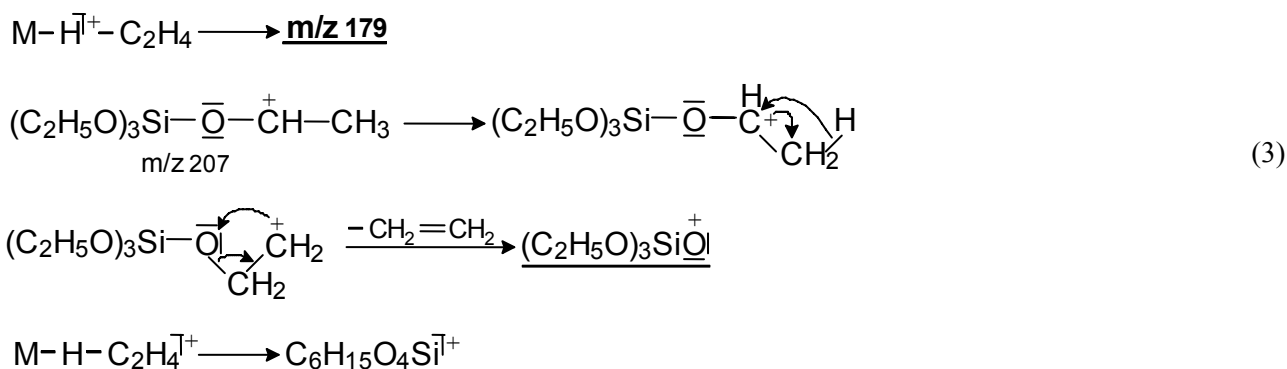
(1) Transposition of a methylene hydrogen atom of an ethoxy group at the center of positive charge of cyclic transition states with 3, 4, 5 or 6 atoms, and

(2) Heterolytic cleavage of O-C bond with positive charge displacement on oxygen atom and thus obtaining an oxycation; this is stabilized by

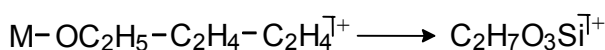
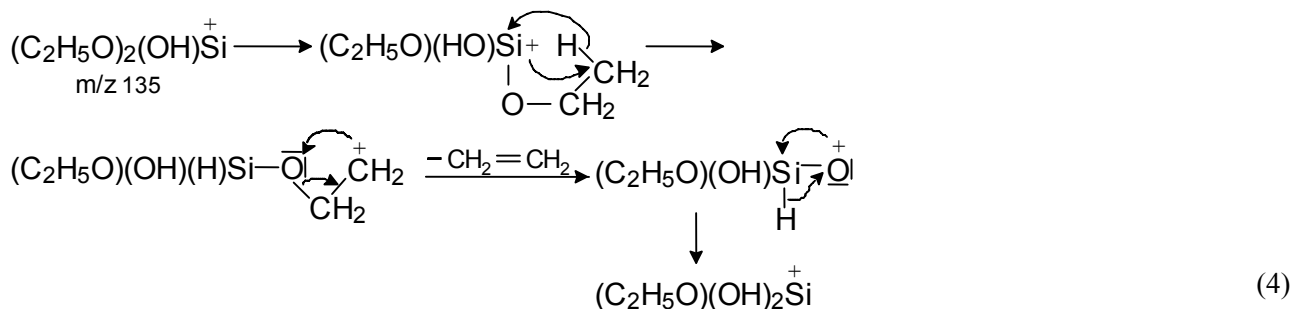
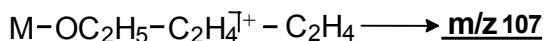
the transposition of hydrogen atom to the charge center obtaining carbocations or siliconium ions.

Thus, the fragmentation ions with m/e 179, 165, 151, 137, 135, 123, 109, 107, 91, 79 and 63 are obtained (Fig. 4); most of these ions are of low intensity in mass spectrum of TEOS (Fig. 1.a-d).

The reaction pathways according to Equations B.3.(3) and B.4.(4) for obtaining the ions with m/e 179 and 107 from the ions with m/e 207 and m/e 135 with elimination of ethylene are outlined below:

B.3. $M - H - C_2H_4^{\bar{1}+}$ m/z 179 $I = I_1 + I_2 = 22.9\%$


$$M_{ELE} = 179.0740 \quad M_{OBS} = 179.0746 \quad \Delta M = -0.7 \text{ mmu} \quad DBE = 0.5$$

B.4. $M-OC_2H_5-C_2H_4-C_2H_4^{\bar{+}}$ m/z 107 $I=11.4\%$


$M_{ELE} = 107.0164$	$M_{OBS} = 107.0170$	$\Delta M = -0.6$ mmu	$DBE = 0.5$
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**Reactions with the elimination
of a hydrogen molecule**

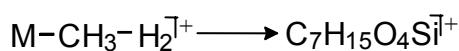
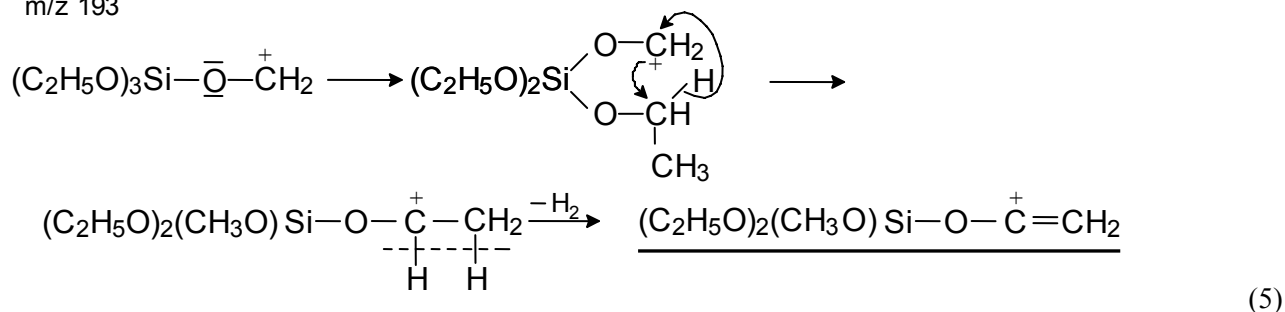
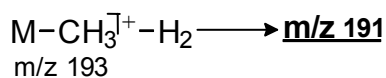
The elimination of a hydrogen molecule is produced as follows:

(1) Transposition of a methylene hydrogen atom of a ethoxy group to the center of positive charge of cyclic transition states with 4, 5 or 6 atoms, obtaining a carbocation, and

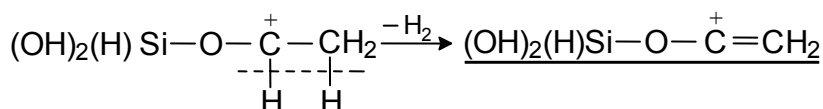
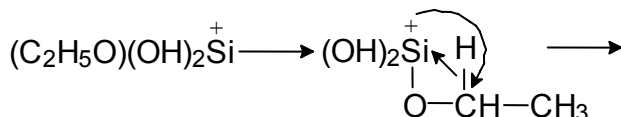
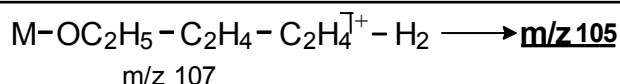
(2) The elimination of a hydrogen molecule by a cyclic transition state of four atoms: two of carbon and two of hydrogen.

Thus, the fragmentation ion with m/e 191 by B/E linked scan (Fig. 2) and the fragmentation ion with m/e 105 by accurate mass measurement (Table 1) are obtained; both of these ions are of low and very low intensity in mass spectrum of TEOS (Fig. 1.c,d).

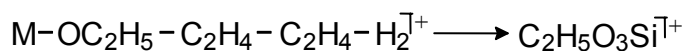
The reaction pathways according to Equations B.5.(5) and B.6.(6) for obtaining the ions with m/e 191 and 105 from the ions with m/e 193 and m/e 107 with elimination of a hydrogen molecule are outlined below:

B.5. $M-CH_3-H_2^{\bar{+}}$ m/z 191 $I=0.8\%$


$M_{ELE} = 191.0740$	$M_{OBS} = 191.0753$	$\Delta M = -1.3$ mmu	$DBE = 1.5$
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B.6. $M-OC_2H_5-C_2H_4-C_2H_4-H_2^{\dagger+}$ m/z 105 $I = 4.0\%$


(6)



$$M_{ELE} = 105.0008 \quad M_{OBS} = 104.9960 \quad \Delta M = 4.8 \text{ mmu} \quad DBE = 1.5$$

The ions resulting from the elimination reactions according to Equations (1)-(6) are presented in Table 1 with their structural formulas. In the table are presented arguments in favor of the obtained ions as the double bond equivalent (or

nesaturation) (DBE)¹⁹ and the ion masses measured accurately at high resolution (5000) compared with those measured at standard resolution (1000).

Table 1

The structural formulas for the ions in the TEOS mass spectrum obtained according to Equations (1)-(6). The accurate mass measurement of ions at high resolution and the double bond equivalent (DBE). Legend: * the average of six determinations; > 10 mmu and < -10mmu outside of the accepted error; — absent ion from the spectrum

Entry	Structural formulas	Intensity % Resolution		DBE	Accurate mass	Observed mass. Accepted error: ± 10 mmu /Resolution	
		1000	5000*			1000	5000
1.	$(C_2H_5O)_4^{28}Si^+$	16.8	16.6	0	208.1130	-4.9	-1.0
2.	$(C_2H_5O)_3^{28}Si-O-C^+H-CH_3$	6.9	6.6	0.5	207.1052	-5.7	-2.2
3.	$(C_2H_5O)_3^{28}Si-O-C^+H_2$	100.0	100.0	0.5	193.0896	< -10	0.8
4.	$(C_2H_5O)_2(OCH_3)^{28}Si-O-C^+=CH_2$	2.3	0.8	1.5	191.0739	< -10	—
5.	$(C_2H_5O)_3^{28}Si-O^+$	27.3	23.9	0.5	179.0739	-1,2	-2.3
6.	$(C_2H_5O)(OCH_3)^{28}Si^+$	92.9	81.1	0.5	149.0633	4.8	0.6
7.	$(C_2H_5O)_2(OH)^{28}Si^+$	22.9	18.1	0.5	135.0477	6.0	-1.3
8.	$(C_2H_5O)(HO)_2^{28}Si^+$	16.9	12.3	0.5	107.0164	2.6	-0.6
9.	$(C_2H_5O)(CH_3O)(H)^{28}Si^+$	9.9	5.3	0.5	105.0371	>10	0.9
10.	$(HO)_2(H)^{28}Si-O-C^+=CH_2$	↑+	4,1	1.5	105.0008	>10	4.6

Table 2

The M+1 and M+2 isotopic effects (gray background cells) for the ions from the TEOS mass spectrum at high resolution obtained according to Equations (1)-(6). Legend: I_A : The average of six intensities obtained experimentally; I_C : The M+1 and M+2 intensities calculated based on experimental value M (ions with ^{28}Si) indicated by symbol \rightarrow

Entry	Ionic formula	Accurate mass	The ion intensity from the TEOS mass spectrum at high resolution (5000) Etalon Merck at different time intervals						I_A %	I_C %
			1	2	3	4	5	6		
1.	$\text{C}_8\text{H}_{20}\text{O}_4$ ^{30}Si	210.1099	0.85	0.68	0.86	0.93	0.80	0.73	0.81	0.83
2.	$\text{C}_8\text{H}_{20}\text{O}_4$ ^{29}Si	209.1126	2.65	3.19	2.92	3.45	2.75	2.92	2.98	2.42
3.	$\text{C}_8\text{H}_{20}\text{O}_4$ ^{28}Si	208.1130	15.19	16.48	17.25	17.18	17.67	15.95	16.62 \rightarrow 16.62	16.62
4.	$\text{C}_7\text{H}_{17}\text{O}_4$ ^{30}Si	195.0864	4.07	3.97	5.51	4.96	4.96	4.22	4.62	4.87
5.	$\text{C}_7\text{H}_{17}\text{O}_4$ ^{29}Si	194.0891	11.56	12.28	12.31	12.91	12.38	12.57	12.34	13.24
6.	$\text{C}_7\text{H}_{17}\text{O}_4$ ^{28}Si	193.0896	100.0	100.0	100.0	100.0	100.0	100.0	100.0 \rightarrow 100.0	
7.	$\text{C}_6\text{H}_{15}\text{O}_4$ ^{30}Si	181.0708	1.34	1.33	2.02	1.44	1.65	1.42	1.53	1.14
8.	$\text{C}_6\text{H}_{15}\text{O}_4$ ^{29}Si	180.0735	3.33	3.39	4.00	3.61	4.19	3.59	3.69	2.89
9.	$\text{C}_6\text{H}_{15}\text{O}_4$ ^{28}Si	179.0739	23.22	24.77	24.16	23.42	24.48	23.10	23.86 \rightarrow 23.86	
10.	$\text{C}_5\text{H}_{13}\text{O}_3$ ^{29}Si	150.0626	8.33	7.94	9.17	9.00	8.72	7.62	8.46	8.86
11.	$\text{C}_5\text{H}_{13}\text{O}_3$ ^{28}Si	149.0633	79.75	78.82	83.05	82.82	83.91	78.32	81.11 \rightarrow 81.11	
12.	$\text{C}_4\text{H}_{11}\text{O}_3$ ^{30}Si	137.0445	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	0.78
13.	$\text{C}_4\text{H}_{11}\text{O}_3$ ^{29}Si	136.0473	1.70	1.81	1.84	1.61	2.06	1.60	1.77	1.78
14.	$\text{C}_4\text{H}_{11}\text{O}_3$ ^{28}Si	135.0477	18.14	18.69	18.59	18.96	17.90	16.04	18.05 \rightarrow 18.05	
15.	$\text{C}_2\text{H}_7\text{O}_3$ ^{30}Si	109.0132	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	0.51
16.	$\text{C}_2\text{H}_7\text{O}_3$ ^{29}Si	108.0160	0.83	0.87	1.11	1.06	1.23	0.87	0.99	0.93
17.	$\text{C}_2\text{H}_7\text{O}_3$ ^{28}Si	107.0164	12.34	12.78	12.16	12.90	12.24	11.56	12.33 \rightarrow 12.33	
18.	$\text{C}_3\text{H}_9\text{O}_2$ ^{30}Si	107.0340	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	+ \uparrow	0.22
19.	$\text{C}_3\text{H}_9\text{O}_2$ ^{29}Si	106.0367	0.46	0.46	0.64	0.37	0.62	0.51	0.51	0.50
20.	$\text{C}_3\text{H}_9\text{O}_2$ ^{28}Si	105.0371	5.25	4.44	5.70	5.60	5.55	5.38	5.32 \rightarrow 5.32	

The observed masses of all ions obtained in equations (1) - (6) at high resolution ($R = 5000$) and the majority of the observed masses at standard resolution ($R = 1000$) are placed in the preset mass error of ± 10 mmu (Table 1).

The experimental accurate mass measurements of ions at high resolution are strong arguments for

confirming the reaction pathways B.1.(1)-B.6.(6) from the TEOS mass spectrum.

Another argument concerning the existence of some fragmentation ions obtained according to Equations (1)-(6) are the M+1 and M+2 isotopic effects compared to the theoretical ones measured experimentally at resolution 5000 (Table 2). The

average values I_A of the ion intensities were obtained experimentally from 6 replicates by GC-MS analyses of a TEOS standard from Merck. Theoretical values I_C of the M+1 and M+2 ion intensities were calculated based on experimental value M (ions with ^{28}Si).

There is a good agreement between experimental M+1, M+2 isotopic effects and those calculated theoretically for the most of ions obtained in the equations (1)-(6) (Table 2).

The accurate mass measurements at high resolution and the experimental M+1, M+2 isotopic effects of over 90 ions from TEOS mass spectrum will be presented in the upcoming work.

CONCLUSIONS

The procedure for the interpretation of mass spectra for alcoxysilanes previously presented in Part I was applied for tetraethoxysilane (TEOS) in charge induced reactions.

Based on experiments with the B/E and B/E(1-E)^{1/2} linked scans, performed on a double-focusing mass spectrometer, they can write successive and competitive reactions with small molecule eliminations at preset masses.

The daughter ions of the primary fragmentation ion with m/e 193 at m/e 165 and m/e 149 were put in evidence experimentally by the B/E linked at the 28 amu (ethylene) and 44 amu (acetaldehyde) preset masses. The daughter ion with m/e 191 of small intensity is also evidenced experimentally at a 2 uam preset mass (hydrogen molecule).

The (B/E)(1-E)^{1/2} linked scan was used to obtain the ions which eliminate acetaldehyde and ethylene.

Based on these linked scans six reaction pathways are presented: The reaction pathways for obtaining the ions with m/e 149 and m/e 105 from the ions with m/e 193 and m/e 149 with elimination of acetaldehyde; the reaction pathways for obtaining the ions with m/e 179 and m/e 107 from the ions with m/e 207 and m/e 135 with elimination of ethylene; the reaction pathways for obtaining the ions with m/e 191 and m/e 105 from the ions with m/e 193 and m/e 107 with elimination of a hydrogen molecule.

The existences of the molecular ion at m/e 208 and of the ions at m/e 149, m/e 105, m/e 179, m/e 107 m/e 191 and m/e 105 are supplementary argued by the accurate mass measurements of the ions at high resolution (5000) and the double bond equivalents (DBE) determinations.

The existences of the molecular ion at m/e 208 and of the ions at m/e 149, m/e 105, m/e 179, m/e 107 and m/e 105 are also argued by M+1 and M+2 isotopic effects for the TEOS ions containing silicon atoms at high resolution (R = 5000) calculated based on experimental M values (ions with ^{28}Si).

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REFERENCES

1. V. Bădescu, *Rev. Roum. Chim.*, **2014**, *59*, 875-882.
2. V. Bădescu, "The alkoxide reactivity studied by ionic processes in the gas phase", *Ph. D. Thesis*, Roumanian Academy, Bucharest, Inst. Phys. Chem., 1998.
3. V. Bădescu, M. Radu, M. Zaharescu and A. Vasilescu, *J. Sol-Gel Sci. Tech.*, **1994**, *2*, 43-49.
4. M. Zaharescu, A. Vasilescu, V. Bădescu and M. Radu, *J. Sol-Gel Sci. Tech.*, **1997**, *8*, 59-63.
5. A. Jitianu, A. Britchi, C. Deleanu, V. Bădescu and M. Zaharescu, *J. Non-Cryst. Solids*, **2003**, *319*, 263-279.
6. M. Zaharescu, V. Bădescu, A. Vasilescu and A. Jitianu, "Emerging Fields in Sol-Gel Science and Technology", Kluwer Academic Publishers, 2003, p. 157-164.
7. V. Bădescu, M. Zaharescu, A. Vasilescu and M. Radu, *Rev. Roum. Chim.*, **1996**, *41*, 733-740.
8. M. Zaharescu, V. Bădescu, A. Vasilescu and M. Radu, *Rev. Roum. Chim.*, **1997**, *42*, 633-639.
9. A. Jitianu, A. Britchi, V. Bădescu, C. Deleanu and M. Zaharescu, *Rev. Roum. Chim.*, **2007**, *52*, 93-99.
10. F. W. McLafferty, "Interpretation of Mass Spectra", 4th edition, Benjamin, Reading, 1993.
11. H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden Day, San Francisco, 1967, p. 86.
12. G. E. Wheeler, *Ph. D. Thesis*, New York University, 1987.
13. I. Oprean, "Mass spectrometry of organic compounds", Editura Dacia, Cluj, 1974.
14. F. G. Kitson, B. S. Larsen and C.N. McEwen, "Gas Chromatography and Mass Spectrometry", Academic Press, 2002, Appendix 9, p. 359.
15. E. Pretsch, P. Bühlmann and C. Affolter, "Structure Determination of Organic Compounds. Tables of Spectral Data", 3rd edition, Springer, 2000, p. 24.
16. R.K. Boyd, C. Basic and R. A. Bethem, "Trace Quantitative Analysis by Mass Spectrometry", John Wiley & Sons, 2008, p. 7.
17. Mass Spectral Libraries, V2.1, Isotope Calculator Soft Program, NIST 2005, Perkin Elmer, Inc. 2006.
18. Mass Spectral Libraries, V2.1, Mass Spectrum Interpreter Soft Program, NIST 2005, Perkin Elmer, Inc. 2006.
19. E. de Hoffmann and V. Stroobant, "Mass Spectrometry. Principles and Applications", 3rd edition, Wiley, 2007, p. 258, 456.

