Contributions to the Interpretation of Mass Spectrum of Hexaethoxydisiloxane

VIRGIL BADESCU*
National Research & Development Institute for Chemistry & Petrochemistry -ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania

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) 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 different organic radicals [1-8].

Hexaethoxydisiloxane as TEOS dimer, with structural formula (C₂H₅O)₆Si₂O and molecular weight M=342, is obtained in sol-gel process by hydrolysis-condensation reactions (1)-(3).

Hydrolysis - Condensation Reactions

\[
\begin{align*}
\text{(C}_2\text{H}_5\text{O})_3\text{Si} + \text{H}_2\text{O} &\leftrightarrow \text{(C}_2\text{H}_5\text{O})_2\text{Si(OH)} + \text{C}_2\text{H}_5\text{OH} \quad (1) \\
2\text{(C}_2\text{H}_5\text{O})_2\text{Si(OH)} &\leftrightarrow \text{(C}_2\text{H}_5\text{O})_2\text{Si} - \text{O} - \text{Si(OC}_2\text{H}_5)_2 + \text{H}_2\text{O} \quad (2) \\
\text{(C}_2\text{H}_5\text{O})_2\text{Si(OH)} - \text{H}_2\text{O} &\leftrightarrow \text{(C}_2\text{H}_5\text{O})_2\text{Si} - \text{O} - \text{Si(OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_5\text{OH} \quad (3)
\end{align*}
\]

The chromatogram of monomers, dimers, trimers and tetramers of TEOS is presented in figure 1.a) for the reaction mixture TEOS : H₂O : EtOH : 1 : 1 : 1.75 (HCl pH=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, respectively.

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

* email: virgil_badescu@yahoo.com
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...
The 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 delocalization 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 29Si and 30Si with natural concentration 4.67 % and 3.10 %, respectively, followed by the M+1 isotopic effect of carbon atom 13C (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 by MS Interpreter software (Table 4) (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: \( \text{H}^+ \) and \( \text{OC}_2\text{H}_5^+ \).

**Table 4**

| Entry | Ionic formula | Ionic mass | Isotopic effects | I% | I% |
|-------|---------------|------------|-----------------|----|----|
| 1.    | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 29\text{Si}_2 \) | 342 | M | 3.9 | 3.9 |
|       | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 30\text{Si}_2 \) | 343 | M-1 | 1.0 | 0.9 |
|       | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 29\text{Si}_2 \) | 344 | M-2 | 0.4 | 0.4 |
| 2.    | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 29\text{Si}_2 \) | 269 | M | 15.6 | 15.6 |
|       | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 30\text{Si}_2 \) | 270 | M-1 | 3.3 | 3.1 |
|       | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 29\text{Si}_2 \) | 271 | M-2 | 1.6 | 1.5 |
| 3.    | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 29\text{Si}_2 \) | 253 | M | 18.8 | 18.8 |
|       | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 30\text{Si}_2 \) | 254 | M-1 | 4.1 | 3.0 |
|       | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 29\text{Si}_2 \) | 255 | M-2 | 1.6 | 1.7 |
| 4.    | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 29\text{Si}_2 \) | 157 | M | 18.6 | 18.6 |
|       | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 30\text{Si}_2 \) | 158 | M-1 | 2.0 | 1.9 |
|       | \( \text{C}_2\text{H}_5\text{O}^+ \cdot 29\text{Si}_2 \) | 159 | M-2 | 1.7 | 1.6 |

**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 |
|--------------------------------------------------|
| Entry | Experimental I | Theoretical I |
|-------|----------------|---------------|
| 1.    | 3.9 | 3.9 |
| 2.    | 15.6 | 15.6 |
| 3.    | 18.8 | 18.8 |
| 4.    | 18.6 | 18.6 |

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):
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).

\[
\text{(5)}
\]

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 eliminate ethanol obtained by linked scan (B/E)-(1-E)\(^{1/2}\): (a) TR4D, (b) TR3D, (c) TR2D, (d) TR1D and (e) dimer TEOS

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\(_3\)O\(_5\)Si\(_2\) 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\(_2\)O\(_2\)Si\(_2\) 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
ion C$_2$H$_5$ 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$_2$H$_5$ at double charged ion 171++ 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$_2$H$_5$O)$_6$Si$_2$O 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-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 process.
molecules obtained experimentally by the B/E and B/E (1-E) linked scans.

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

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.

Acknowledgments: The APC was funded by the project PFE 31/2018, Enhancing NIRDCP-ICECHIM research & innovation potential within the inter-disciplinary and cross-sectoral field of key enabling technologies - TRANS-CHEM, founded by Ministry of Research and Innovation, Romania.

References
1. BADESCU, V., Ph. D. Thesis, Roumanian Academy, Bucharest, Inst. Phys. Chem., 1998.
2. BADESCU, V, RADU, M., ZAHARESCU M., VASILESCU, A., J. Sol-Gel Sci. Tech2, 1994, p. 43-49.
3. ZAHARESCU, M., VASILESCU, A., BADESCU V. and RADU, M., J. Sol-Gel Sci. Tech, 8, 1997, p. 59-63.
4. JITIANU, A., BRITCHI, A., DELEANU, C., BADESCU V., ZAHARESCU, M., J. Non-Cryst. Solids, 319, 2003, p. 263-279.
5. ZAHARESCU, M., BADESCU, V., VASILESCU A., JITIANU, A., Emerging Fields in Sol-Gel Science and Technology, Kluwer Academic Publishers, 2003, p. 157-164.
6. BADESCU, V., ZAHARESCU, M., VASILESCU A., RADU, M., Rev. Roum. Chim, 41, 1996,p. 733-740.
7. ZAHARESCU, M., BADESCU, V., VASILESCU A., RADU, M., Rev. Roum. Chim, 42, 1997, p. 633-639.
8. JITIANU, A., BRITCHI, A., BADESCU, V., DELEANU, C., ZAHARESCU, M., Rev. Roum. Chim, 52, 2007, p. 93-99.
9. McLAFFERTY, F. W., Interpretation of Mass Spectra, 4nd edition, Benjamin, Reading, 1993.
10. OPREAN, I., Mass spectrometry of organic compounds, Editura Dacia, Cluj, 1974.
11. WHEELER, G. E., Ph. D. Thesis, New York University, 1987.
12. BETERINGHE, A., ZAHARESCU M. and BADESCU, V., Chapter in Book: Advances in Chemical Modeling Volume 5, Mihai V. Putz Editor, Modeling of some parameters of interest in the sol-gel process, 2015, p. 143-150.
13. BADESCU, V., Rev. Roum. Chim.(Bucharest), 59, no. 10, 2014, p. 875-882.
14. BADESCU, V., Rev. Roum. Chim.(Bucharest), 60, no. 11-12, 2015, p. 1107-1115.

Manuscript received: 29.04.2018