ISSN 1070-3632, Russian Journal of General Chemistry, 2016, Vol. 86, No. 1, pp. 9–17. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © N.V. Shugurova, E.I. Davydova, T.N. Sevast'yanova, A.D. Misharev, M. Bodensteiner, M. Scheer, 2016, published in Zhurnal Obshchei Khimii, 2016, Vol. 86, No. 1, pp. 11–19.

Reaction of $TiCl_4$ with Diethyl Ether. Experimental and Quantum-Chemical Study

N. V. Shugurova[a], E. I. Davydova[a], T. N. Sevast'yanova[a], A. D. Misharev[a], M. Bodensteiner[b], and M. Scheer[b]

[a] *St. Petersburg State University, Universitetskaya nab. 7–9, St. Petersburg, 199034 Russia*
e-mail: tns6@yandex.ru

[b] *Institute of Inorganic Chemistry, University of Regensburg, Germany*

Received June 26, 2015

Abstract—The reaction of titanium tetrachloride with diethyl ether at various ratios of components and temperatures was studied by the NMR and mass spectrometry methods. The $TiCl_4·2Et_2O$ complex does not pass in the gas phase. Formation of ethoxytrichlorotitanium among reaction products was established by the X-ray structure analysis. The model of conversion from initial components to titanium dioxide was suggested on the basis of the obtained experimental data and quantum-chemical calculations (B3LYP/def2-SVP level of theory).

Keywords: titanium tetrachloride, diethyl ether, donor-acceptor complexes, ethoxytrichlorotitanium, titanium dioxide

DOI: 10.1134/S1070363216010035

The use of titanium complexes as Ziegler–Natta catalysts [1–3], reagents for a number of organic syntheses [4–6], and precursors for obtaining titanium dioxide [7–10] has attrached much interest to their behavior at elevated temperatures.

Titanium tetrachloride, being a typical Lewis acid, forms 1 : 1 and 1 : 2 complexes with N- and O-containing bases (amines, ethers, ketones, and haloketones) [11–15]. Their vaporization is defined by a competition between ruptures of intra- and intermolecular bonds [11]. Three types of reactions of these compounds proceeding on heating can be distinguished:

(1) vaporization of complexes in the gas phase (possible for saturated molecular structures with strong donor–acceptor bonds);

(2) stepwise or complete dissociation with donor–acceptor bond rupture;

(3) decomposition similar to hydrolysis or ammonolysis with evolution of hydrogen chloride or organochlorine compounds.

Titanium tetrachloride forms donor–acceptor complexes with dimethyl and diethyl ethers [6, 16–25]. It was shown by the NMR method (a solution in SO_2, –84°C) that 1 : 1 and 1 : 2 complexes (*cis*- and *trans*-isomers) are formed in the case of dimethyl ether [18]. In a CH_2Cl_2–CD_2Cl_2 solution at 175 K only the *cis*-form of the 1 : 2 complex with Me_2O was detected by the methods of vibrational spectroscopy (Raman and IR) and NMR spectroscopy [19, 20].

With diethyl ether $TiCl_4$ forms the complex $TiCl_4·2Et_2O$ of *cis*-structure, unstable at room temperature [6, 17, 21–23, 25].

On the basis of the data of UV photoelectronic spectroscopy (UVPES) and electron energy loss spectroscopy (EELS) [21] it was found that the 1 : 2 complex is formed in the gas phase at 70°C. At the ratios of components $TiCl_4$–Et_2O 1 : 1 and 2 : 1 only the signals corresponding to titanium tetrachloride were recorded, which testifies that no forms of gaseous complexes other than $TiCl_4·2Et_2O$ are present. It was shown in [2] that the reaction of $TiCl_4$ with diethyl ether leads to the formation of the 1 : 1 complex.

To refine the composition of complex compounds formed in the $TiCl_4$–Et_2O system and to make clear their thermal behavior, in the present work we have studied the reaction of $TiCl_4$ with diethyl ether.

Table 1. Chemical shifts of signals in ^{1}H and ^{13}C NMR spectra of Et$_2$O and TiCl$_4$·2Et$_2$O

Substance	δ_H, ppm	$\Delta\delta$, ppm	δ_C, ppm	$\Delta\delta$, ppm
Et$_2$O	3.46 q (2H, CH$_2$, J = 7.1 Hz),	–	66.2 (CH$_2$)	–
	1.17 t (3H, CH$_3$, J = 7.1 Hz)		15.6(CH$_3$)	
TiCl$_4$·2Et$_2$O	3.74 q (2H, CH$_2$, J = 7.0 Hz),	0.28	67.5(CH$_2$)	1.3
	1.28 t (3H, CH$_3$, J = 7.0 Hz)	0.11	15.3 (CH$_3$)	–0.3

Reaction products were studied by the mass spectrometry, NMR spectroscopy, and X-ray structure analysis methods. Thermodynamic characteristics of the processes occurring in the titanium tetrachloride-diethyl ether system were calculated by a quantum-chemical method.

To elucidate the composition of complexes forming in the TiCl$_4$–Et$_2$O system, reactions were carried out in a vacuum at various ratios of components: almost twofold excess of the ether (1.00 : 1.98, 1.00 : 1.92), equimolar ratio (1.00 : 1.02), and at tetrachloride excess (1.00 : 0.62). At the 1.00 : 1.98 and 1.00 : 1.92 ratios of the TiCl$_4$–Et$_2$O components right after mixing reagents the crystalline complex TiCl$_4$·2Et$_2$O is formed, which, as it is known [17, 22], is unstable at room temperature. Therefore, to avoid decomposition, the substance was stored at a low temperature (–30°C). At the ratio of TiCl$_4$–Et$_2$O components 1.00 : 1.02 a two-phase liquid system consisting of solid complex TiCl$_4$·2Et$_2$O and its solution in titanium tetrachloride is formed. In the case of the synthesis in the tetrachloride excess with the ratio TiCl$_4$: Et$_2$O = 1.00 : 0.62 a homogeneous yellow solution of the TiCl$_4$·2Et$_2$O complex in TiCl$_4$ was obtained. Thus at any ratio of components the crystalline product of the synthesis was the 1 : 2 adduct.

When studying the TiCl$_4$·2Et$_2$O complex by the NMR spectroscopy and mass spectrometry methods, spectra were measured directly after synthesis in order to avoid its decomposition. The general view of the ^{1}H NMR spectrum of the adduct is the same as for the non-coordinated ether, but signals are shifted downfield, which is characteristic of complex formation [19, 20, 24, 25]. The displacement of the group CH$_2$ chemical shift is 2.5 times greater than that of the CH$_3$ group.

The signal of the CH$_2$ group in the ^{13}C NMR spectrum of the complex is shifted downfield, whereas the position of the CH$_3$ group signal practically does not change with respect to the pure ether, i.e., as in the case of the ^{1}H NMR spectra, the coordination affects the CH$_2$ group much more strongly than the CH$_3$ group. Values of chemical shifts of the ether and complex are presented in Table 1 together with $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$ values. The $\Delta\delta$ values are smaller than the published data [25]. These distinctions are connected with the fact that measurements in [25] were carried out in a titanium tetrachloride excess, which suppresses dissociation of the complex.

Mass spectra of vapor over TiCl$_4$·2Et$_2$O taken in the temperature interval 120–380°C in the range of m/z = 26–430 are presented in Fig. 1.[1] In the mass spectrum of vapor over the TiCl$_4$·2Et$_2$O complex there are no peaks of molecular and fragmental ions of 1 : 1 and 1 : 2 complexes containing a Ti–O bond.

Comparison of the mass spectra of vapor over the TiCl$_4$·2Et$_2$O complex with the mass spectra of the pure components, and also of chlorine derivatives and alcohols as most probable products of the thermal decomposition shows that at 120°C peaks of ions characteristic of diethyl ether (m/z = 31, 47, 74) and peaks of the ions related to titanium tetrachloride are present in the spectra. Furthermore, characteristic peaks of chloroethane EtCl (m/z = 64, 66) are observed in the spectrum. Their intensity decreases as temperature increases: at 220°C the peak of EtCl is absent in the spectrum. The peak with m/z = 28 corresponding to the $C_2H_4^+$ ion,[2] which appears either as a result of proceeding reactions or as a result of dissociative ionization of organic compounds, has the maximum intensity at 120°C. Its intensity decreases with temperature increase. Ethanol signals are absent in the spectrum.

In the mass spectrum taken at 120°C a high intensity of peaks of titanium-containing ions is observed, which sharply decreases on keeping the complex at this temperature within 10 min. As temperature increases, intensity of peaks of these ions increases, and at 330°C starts to decrease again. In the range m/z = 184–192 at 120°C peaks of $TiCl_3OCH_2^+$

---

[1] In Fig. 1 the m/z range is presented up to 240, because there are no peaks in the region of higher values.

[2] The elemental composition of the ion with m/z = 28 was found by measuring the exact weight in a high voltage mode.

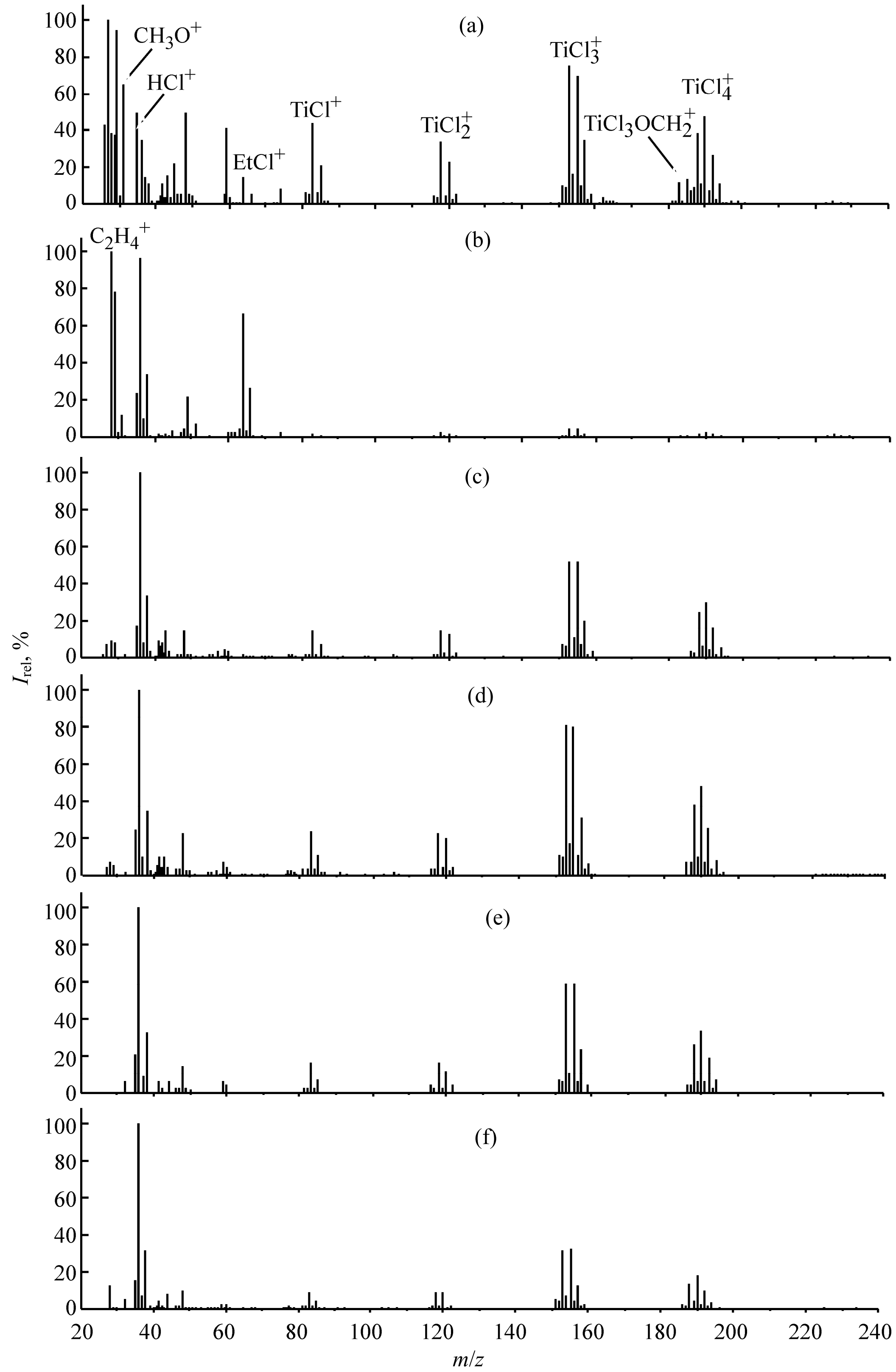

Fig. 1. Mass spectra of vapor over $TiCl_4·2Et_2O$ taken at temperature: 120 (a) at once; (b) 10 min later, (c) 220, (d) 270, (e) 330, and (f) 380°C.

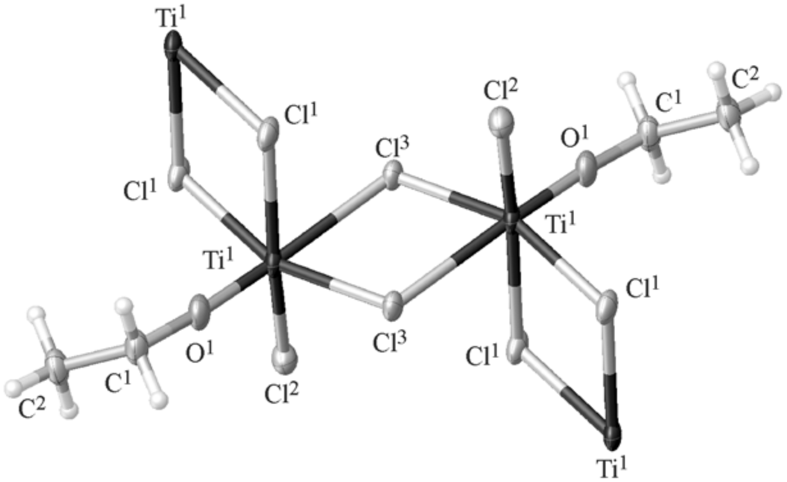

Fig. 2. General view of the $TiCl_3OEt$ molecule.

(titanium is detected by the isotope distribution) are observed in addition to $TiCl_4$.

Relative intensities of peaks of ions corresponding to titanium tetrachloride and chloroethane agree well with experimental data for titanium tetrachloride and with published data for pure EtCl [26].

To study thermal behavior of the complex in more detail, we have fulfilled an experiment with time exposure (100 min), normalizing mass spectra by a standard substance $(C_4F_9)_3N$. In the region of the initial temperature increase (up to 120°C) peaks of ions corresponding to Et_2O, $TiCl_4$, C_2H_4, EtCl, and HCl ionization were detected in the mass spectrum. Their intensity quickly decreases to background level on exposure within 35 min. At further temperature rise up to 170°C the intensities of peaks of the ions corresponding to $TiCl_4$, C_2H_4, and HCl increase. Exposure at this temperature within 10 min also leads to the decrease in the intensity of peaks of ions to the background value. At 220 and 270°C only peaks of ions corresponding to titanium tetrachloride and hydrogen chloride are present in the spectrum, their intensity decreasing to the background level on keeping the sample at 220° within 10 min and at 270°C within 15 min.

Thus, we can conclude that the $TiCl_4{\cdot}2Et_2O$ complex decomposes on heating to liberate diethyl ether, titanium tetrachloride, chloroethane, and ethylene. Moreover, this process begins even at room temperature, as demonstrated by the NMR data.

The singlet with chemical shift of 1.25 ppm corresponding to the CH_2 group is the most intensive in the ^1H NMR spectrum of decomposition products of the complex. Signals at 1.48 and 3.61 ppm point to the formation of chloroethane [27]. The range of chemical shifts from 4.90 to 5.82 ppm is characteristic of alkenes [27]. A weak signal in the region of $\delta \sim 5$ ppm is present in this spectrum, which is attributable to the presence of alkenes in the adduct decomposition products. Hence, even at room temperature, reactions leading to the occurrence of chloroethane, unsaturated hydrocarbons, and also products of their polymerization proceed in the system.

On keeping an evacuated ampule with a solution of the complex in titanium tetrachloride at room temperature within several months colorless crystals of ethoxytrichlorotitanium $TiCl_3OEt$ were grown. Its structure was confirmed by X-ray structure analysis (Fig. 2).

The obtained alkoxide is a polymer, where titanium atoms are in a pseudo-octahedral environment formed by the ethoxy-group oxygen and four bridging and one terminal chlorine atoms. As it is seen from Table 2 bridging Ti^1–Cl^1 and Ti^1–Cl^3 bonds are longer than terminal Ti^1–Cl^2 bonds, but they both are much longer than the Ti–Cl distance in the $TiCl_4$ molecule (2.19 Å [28]). The $Ti^1O^1C^1$ angle is almost right (Table 3). Our data, as seen from Tables 2 and 3, agree well with structural characteristics of $[TiCl_3OEt]_n$ available in the literature [29]. However ethoxytrichlorotitanium in [29] was obtained by the reaction of $Ti(OEt)_4$ with $SiCl_4$, whereas we obtained it by the decomposition of the ether complex of titanium tetrachloride. The association of $TiCl_3OEt$ molecules proceeds with participation of chlorine atoms instead of oxygen atoms of alkoxy group, as in similar $TiCl_2(OR)_2$ and $TiCl(OR)_3$ dimers [30–37].

Table 2. Bond lengths in the $TiCl_3OEt$ molecule

Bond	*d*, Å		Bond	*d*, Å	
	experiment	published data [29]		experiment	published data [29]
$Ti^1–O^1$	1.709(3)	1.704(7)	$Ti^1–Cl^3$	2.3689(14)	2.361(4)
$Ti^1–Cl^1$	2.4062(14)	2.406(4)	$Ti^1–Cl^3$	2.6096(13)	2.602(3)
$Ti^1–Cl^1$	2.5211(13)	2.522(3)	$O^1–C^1$	1.425(6)	1.43(1)
$Ti^1–Cl^2$	2.2346(13)	2.235(3)	$C^1–C^2$	1.497(7)	1.51(2)

Table 3. Bond angles in the $TiCl_3OEt$ molecule

Angle	$\overline{\omega}$, deg		Angle	$\overline{\omega}$, deg	
	experiment	published data [29]		experiment	published data [29]
$Cl^1Ti^1O^1$	98.24(12)	97.7(3)	$Cl^2Ti^1O^1$	98.69(12)	98.6(3)
$Cl^1Ti^1O^1$	90.32(12)	90.0(3)	$Cl^2Ti^1Cl^3$	88.00(4)	88.2(1)
$Cl^1Ti^1Cl^1$	80.85(4)	80.8(1)	$Cl^2Ti^1Cl^3$	97.96(5)	98.2(1)
$Cl^1Ti^1Cl^2$	92.61(5)	92.3(1)	$Cl^3Ti^1O^1$	95.74(12)	95.2(3)
$Cl^1Ti^1Cl^2$	169.57(5)	169.7(1)	$Cl^3Ti^1O^1$	172.80(12)	172.8(3)
$Cl^1Ti^1Cl^3$	160.99(5)	161.9(1)	$Cl^3Ti^1Cl^3$	80.61(4)	81.3(1)
$Cl^1Ti^1Cl^3$	84.03(4)	84.4(1)	$Ti^1O^1C^1$	174.9(3)	176.3(7)
$Cl^1Ti^1Cl^3$	86.27(4)	86.5(1)	$Ti^1Cl^1Ti^1$	99.15(4)	99.2(1)
$Cl^1Ti^1Cl^3$	83.28(4)	83.5(1)	$Ti^1Cl^3Ti^1$	99.39(5)	99.2(1)

A peak of the fragment ion $TiCl_3OCH_2^+$ is observed in the mass spectrum of vapor over ethoxytrichlorotitanium (Fig. 3) at 120–170°C. Its relative intensity is 16% at 120°C, which points to the fact that in the gase phase the alkoxide exists as a monomer. At 170–270°C peaks of chloroethane, hydrogen chloride, and ethylene ions are detected in the spectra. The peaks of ions corresponding to titanium tetrachloride appear in insignificant quantities only at 270°C. It is connected with the fact that alkoxide seems to convert to nonvolatile titanium oxochloride on heating, which disproportionates on the further temperature increase to form titanium tetrachloride and dioxide.

On the basis of published data and experimental results of the present work, we have simulated the processes proceeding in the $TiCl_4–Et_2O$ system on heating. The 1 : 2 complexes, easily formed in the condensed phase, are unstable even at room temperature. The mass spectrometry data allow us to conclude that the dissociation into components and the HCl elimination proceed in parallel on heating. It results in the formation of ethoxytrichlorotitanium, which decomposes to form chloroethane, hydrogen chloride, ethylene, and titanium oxochloride. $TiOCl_2$ disproportionates into highly volatile titanium tetrachloride and poorly volatile titanium dioxide [38, 39].

$$\begin{tikzcd}
TiCl_4{\bullet}2Et_2O(cr.) \arrow[r] \arrow[d, "t^o"] & TiCl_3OEt(cr.) + EtCl(gas) + Et_2O(gas) \arrow[d, "t^o"] & \\
TiCl_4(gas) + 2Et_2O(gas) & 0.5EtCl(gas) + 0.5HCl(gas) + 0.5C_2H_4(gas) + & TiOCl_2(gas) \arrow[d, "t^o"] \\
 & & 0.5TiO_2(s.) + 0.5TiCl_4(gas)
\end{tikzcd}$$

To check the offered model, we have fulfilled quantum-chemical calculations of competing homogeneous gas-phase reactions of the complex decomposition into components or up to ethoxytrichlorotitanium with its subsequent decomposition to titanium oxochloride and dioxide.

The calculations of thermodynamics of the gas-phase processes were carried out by the B3LYP/def2-SVP method. Quantum-chemical calculations are successfully applied to predict the energy of titanium tetrachloride complex formation and to interpret the mechanism of transition from $TiCl_4$ to TiO_2 [40–44].

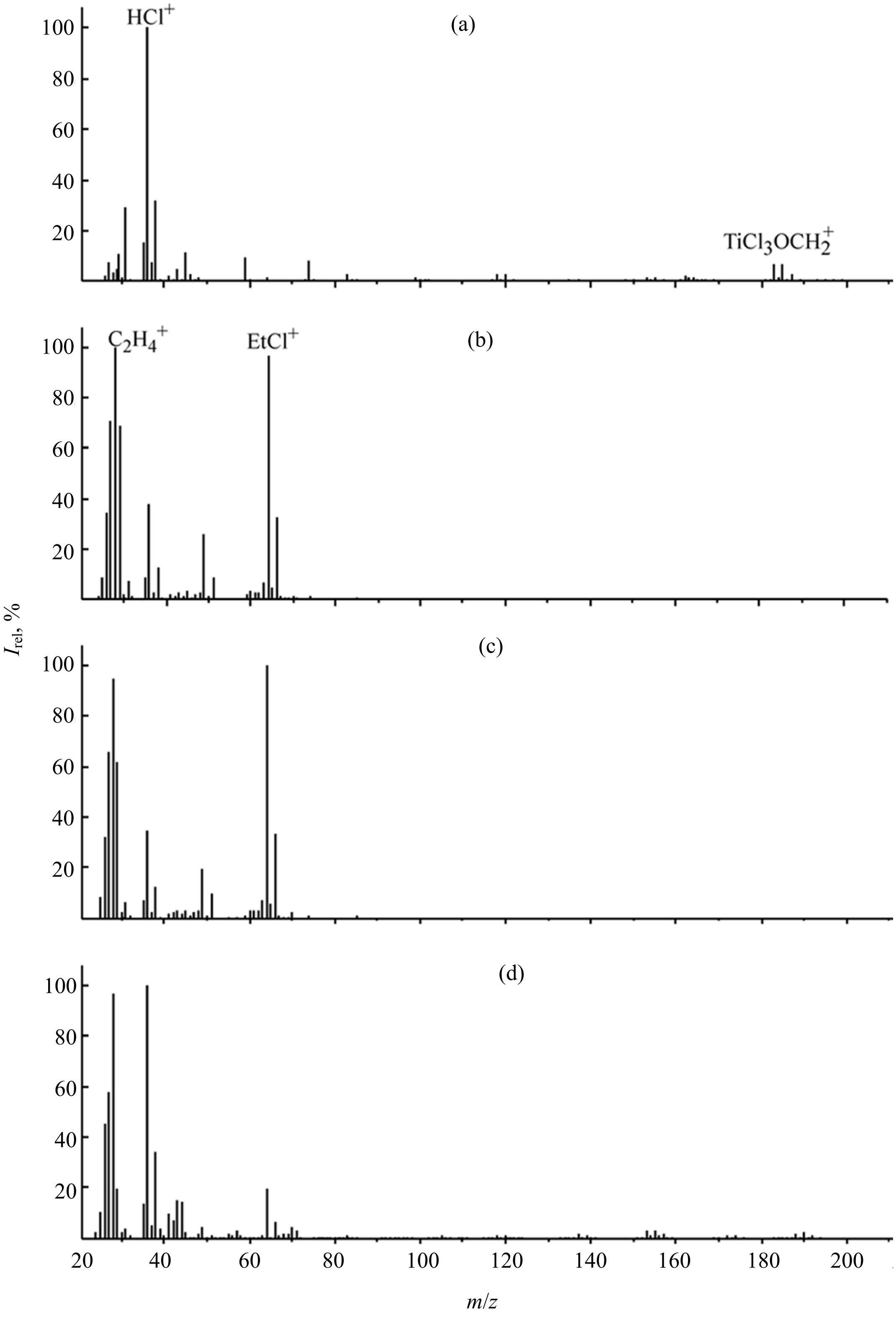

Fig. 3. Mass spectra of vapor over TiCl$_3$OEt taken at temperatures: (a) 120, (b) 170, (c) 220, and (d) 270°C.

Table 4. Energy and thermodynamic characteristics of gas-phase processes (B3LYP/def2-SVP)

Process no.	Process	ΔE^0, kJ/mol	ΔH^0_{298}, kJ/mol	ΔS^0_{298}, J mol^{-1} K^{-1}	ΔG^0_{298}, kJ/mol	ΔG^0_{573}, kJ/mol
1	*cis*-$TiCl_4\cdot 2Et_2O = TiCl_4 + 2Et_2O$	49	34	341	–68	–162
2	*cis*-$TiCl_4\cdot 2Et_2O = TiCl_3OEt + EtCl + Et_2O$	18	1	392	–116	–223
3	$TiCl_3OEt = TiOCl_2 + 0.5EtCl + 0.5HCl + 0.5C_2H_4$	296	280	219	205	135
4	$TiCl_3OEt = 0.5TiO_2 + 0.5TiCl_4 + 0.5EtCl + 0.5HCl + 0.5C_2H_4$	360	344	189	278	217

Results of the fulfilled calculations are presented in Table 4.

Comparison of the thermodynamics of processes 1 and 2 testifies that the decomposition of the complex with alkoxide formation (process 2) is much more favorable than the process of $TiCl_4\cdot 2Et_2O$ dissociation into components (process 1). The decomposition of ethoxytrichlorotitanium with the formation of both gaseous $TiOCl_2$ (process 3) and gaseous TiO_2 (process 4) is thermodynamically unfavorable. Condensation of titanium dioxide decreases the endothermicity of this reaction. Using characteristics of titanium dioxide sublimation calculated on the basis of the reference data [45], ΔH^0 = 619.17 kJ/mol and ΔS^0 = 205.07 J mol^{-1} K^{-1}, we obtain for the heterogeneous reaction

$$TiCl_3OEt(gas) = 0.5TiO_2(s.) + 0.5TiCl_4(gas) + 0.5HCl(gas) + 0.5EtCl(gas) + 0.5C_2H_4(gas),$$

$$\Delta H^0_{298} = 34.4 \text{ kJ/mol}, \Delta S^0_{298} = 86.5 \text{ J mol}^{-1} \text{K}^{-1},$$
$$\Delta G^0_{298} = 8.6 \text{ kJ/mol}, \Delta G^0_{573} = -15.2 \text{ kJ/mol}.$$

The process is favorable thermodynamically, its exothermal effect increases as temperature increases.

Thus, our calculations point to the preferential occurring of process 2 yielding ethoxytrichlorotitanium with its further decomposition yielding titanium dioxide.

In summary it may be said that the similar model of decomposition of titanium tetrachloride ether complexes was considered for analogous systems with ethers [16, 24, 46]. For example, titanium tetrachloride complex with dimethyl ether on heating to 50–60°C converts to chloromethane and titanium methoxide, which further passes into titanium oxochloride and MeCl [24]. The synthesis of the product of diisopropyl ether addition to titanium tetrachloride completely unsuccessful, but $TiCl_3[OCH(CH_3)_2]$ was isolated [16]. If a substituent R in compounds of the type $ROTiCl_3$ is a secondary or tertiary alkyl, disintegration of such compounds proceeds instantly even at low temperatures with the formation of hydrogen chloride, olefins, alkyl chlorides, and polymeric titanium oxochlorides [46].

EXPERIMENTAL

As titanium tetrachloride is easily hydrolyzed in air, all operations of purification, taking sample weights, and synthesis were carried out in vacuum-sealed glass systems completely excluding contact of substances with atmosphere. In the synthesis we used chemically-pure grade titanium tetrachloride and diethyl ether additionally dried and purified according to standard techniques.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DX 300 instrument at room temperature using $CDCl_3$ as a solvent. The mass spectra were taken on an MCh-1321 instrument using a system of direct sample input at ionizing energy of 70 eV in the mode of stepwise heating sample at temperatures 120–380°C.

The single-crystal X-ray structural analysis was carried out on an Oxford Diffraction Gemini Ultra diffractometer with CuK_α radiation (λ = 1.54178 Å) in the range of angles 5.19° < θ < 62.69°. The structure was solved by the direct method with the program SHELXS-97 [47]; refinements on F^2 was carried out by the least squares method using SHELXL-97 [48]. Positions of hydrogen atoms were calculated geometrically and refined in the rigid group approximation. Crystals of $C_2H_5Cl_3OTi$ are of the triclinic system, unit cell parameters at 123 K are as follows: a = 5.9723(5), b = 7.1932(8), c = 8.7000(9) Å, α = 93.988(9)°, β = 98.826(8)°, γ = 110.687(10)°, V = 342.40(7) Å^3, M = 199.28, Z = 2, d = 1.933 g/cm^3, space group P-1. The full data are deposited in the

Cambridge Crystallographic Data Center (CCDC 1407825).

Quantum-chemical calculations were carried out using GAUSSIAN 09 program package [49] by the density-functional method B3LYP with Becke exchange functional B3 [50] and Lee–Yang–Parr correlation functional [51]. A def2-SVP basic set was used for all atoms [52]. Geometrical parameters of all compounds were fully optimized with the following vibrational analysis. All structures correspond to the minima on the respective potential energy surfaces.

ACKNOWLEDGMENTS

The work was fulfilled using the equipment of the research centers of St. Petersburg State University "Research Resources Center for Magnetic Resonance" and "Computing Center of St. Petersburg State University."

REFERENCES

1. Marina, N.G., Monakov, J.B., Rafikov, S.R., and Ponomarenko, V.I., *Russ. Chem. Rev.*, 1983, vol. 52, no. 5, p. 413.
2. Asahara, T. and Kise, H., *Bull. Chem. Soc. Japan*, 1967, vol. 40, p. 2664. DOI: 10.1246/bcsj.40.2664.
3. Lavanant, L., Silvestru, A., Faucheux, Toupet, L., Jordan, R.F., and Carpentier, J.-F., *Organometallics,* 2005, vol. 24, p. 5604. DOI: 10.1021/om050560c.
4. Kostyuk, S.V., Kaputtskii, F.N., Mardukin, V.P., and Gaponik, L.V., *Fiz. Khim. Polimer*., 2002, vol. 8, no. 8, p. 210.
5. Nishigaichi, Y., Fujimoto, M., Nakayama, K., Takuwa, A., Hamada, K., and Fujiwara, T., *Chem. Lett*., 1992, vol. 12, p. 2339. DOI: 10.1246/cl.1992.2339.
6. Shi, M., Jiang, J.-K., and Cui, S.-C., *Tetrahedron,* 2001, vol. 57, p. 7343. DOI: 10.1016/S0040-4020(01)00710-4.
7. Alexandrescu, R., Dumitrashe, V., Mordjan, I., Sandu, I., Savoiu, M, Voicu, I., Fleaca, C., and Piticescu, R., *Nanotechnology,* 2004, vol.15, p. 537. DOI: 10.1088/0957-4484/15/5/023.
8. Wu, Y., Liu, H.-M., Xu, B.-Q., Zhang, Z.-L., and Su, D.-S., *Inorg. Chem*., 2007, vol. 46, p. 5093. DOI: 10.1021/ic070199h.
9. Liu, C., Fu, L., and Economy, J., *J. Mater. Chem*., 2004, vol. 14, p. 1187. DOI: 10.1039/b316426h.
10. Chen, X. and Mao, S.S., *Chem. Rev*., 2007, vol. 107, p. 2891. DOI: 10.1021/cr0500535.
11. Sevast'yanova, T.N. and Suvorov, A.V., *Russ. J. Coord. Chem*., 1997, vol. 23, p. 761.
12. Gur'yanova, E.N., Gol'dshtein, I.P, and Romm, I.P., *Donor–Acceptor Bond*, New York: Halsted, 1975.
13. Davydova, E.I., Sevast'yanova, T.N., and Shugurova, N.V., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 1, p. 160. DOI: 10.1134/S1070363214010241.
14. Davydova, E.I., Sevast'yanova, T.N., Suvorov, A.V., and Timoshkin, A.Yu., *Coord. Chem. Rev*., 2010, vol. 254, p. 2031. DOI: 10.1016/j.ccr.2010.04.001.
15. Sevast'yanova, T.N., Misharev, A.D., Anatsko, O. E, and Suvorov, A.V., *Russ. J. Gen. Chem*., 2002, vol. 72, no. 1, p. 58. DOI: 10.1134/S1070363202010140.
16. Hamilton, P.M., McBeth, R., Bukebrede, W., and Sisler, H.H., *J. Am. Chem. Soc*., 1953, vol. 75, p. 2881. DOI: 10.1021/ja01108a027.
17. Schwartz, D. and Reski, P., *J. Inorg. Nucl. Chem*., 1965, vol. 27, p. 747. DOI: 10.1016/0022-1902(65)80285-8.
18. Tan, L.K. and Bronstein, S., *Inorg. Chem*., 1984, vol. 23, p. 1353. DOI: 10.1021/ic00178a010.
19. Turin, E., Nielson, R.M., and Merbach, A.E., *Inorg. Chim. Acta,* 1987, vol. 134, p. 67. DOI: 10.1016/S0020-1693(00) 84458-8.
20. Turin, E., Nielson, R.M., and Merbach, A.E., *Inorg. Chim. Acta,* 1987, vol. 134, p. 79. DOI: 10.1016/S0020-1693(00)84459-X.
21. Ananthavel, S.P. and Hegde, M.S., *J. Phys. Chem. (A),* 1997, vol. 101, p. 1680. DOI: 10.1021/JP962651G.
22. Troyanov, S.I., Mazo, G. N, Rybakov, V.B., and Budkina, K.V., *Koord. Khim*., 1990, 16, no. 4, p. 466.
23. Gun, G., Pan, Z., and Zhang, Z., *Acta Phys. Chim. Sin*., 1986, vol. 2, p. 278. DOI: 10.3866/PKU.WHXB19860314.
24. Talzi, V. P, Ignashin, S.V., Chudinova, I.P., and Shchupletsov, V. G, *Russ. J. Appl. Chem*., 1998, vol. 71, no. 11, p. 1958.
25. Bose, A.K., Srinivasan, P.R., and Trainor, G., *J. Am. Chem. Soc*., 1974, vol. 96, p. 3670. DOI: 10.1021/ja00818a062.
26. *NIST Chemistry WebBook*, http: webbook.nist.gov/chemistry/.
27. *Spectral Database for Organic Compounds*, http: riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng.
28. Luchinskii, G.P., *Khimiya titana* (Chemistry of Titanium), Moscow: Khimiya, 1971.
29. Niemeyer, M., Goodwin T.J., Risbud, S.H., and Power, P.P., *Chem. Mater*., 1996, vol. 8, p. 2745. DOI: 10.1021/CM960243J.
30. Haase, V.W. and Hoppe, H., *Acta Crystallogr. (B),* 1968, vol. 24, p. 281. DOI: 10.1107/S0567740868002116.
31. Nielson, A.J., Chen, C., Schwerdtfeger, P., and Waters, J.M., *Eur. J. Inorg. Chem*., 2005, p. 1343. DOI: 10.1002/ejic.200400769.

32. Watenpaugh, K. and Caughlan, C.N., *Inorg. Chem*., 1966, vol. 5, p. 1782. DOI: 10.1021/ic50044a031.
33. Weingarten, H. and Van Wazer, J.R., *J. Am. Chem. Soc*., 1965, vol. 87, p. 724. DOI: 10.1021/ja01082a008.
34. Nielson, A.J., Chen, C., and Waters J.M., *Polyhedron,* 2006, vol. 25, p. 2039. DOI: 10.1016/j.poly.2005.12.027.
35. Sevast'yanov, D.V., Sevast'yanov, V.G., Simonenko, E.P., Kemmitt, T., Gainsford, G.J., and Kuznetsov, N.T., *Thermochim. Acta*, 2002, vol. 381, p. 173. DOI: 10.1016/S0040-6031(01)00650-5.
36. Feltz, V.A., *Z. Anorg. Allg. Chem*., 1964, vol. 334, p. 186. DOI: 10.1002/zaac.19643340310.
37. Finnie, K.S., V., Moran, P.D., Bartlett, J.R., and Woolfrey, J.L., *J. Mater. Chem*., 2000, vol. 10, p. 409. DOI: 10.1039/a906662d.
38. Borodin, V.I, Novikov, G.I, Galitskii, N.V., and Suvorov, A.V., *Obshchaya i prikladnaya khimiya* (General and Applied Chemistry), Minsk: Vysheishaya Shkola, 1970, no. 2, p. 119.
39. Dunn, W.E., *Metallurg. Trans. (B),* 1979, vol. 10, p. 293. DOI: 10.1007/BF02652473.
40. Poleshchuk, O.Kh., Kalinina, E.L., Shanina, Yu. A., and Frenking, G., *Russ. J. Coord. Chem*., 2003, vol. 29, p. 53. DOI: 10.1023/A:1021847118400.
41. Cavallo, L., Fedele, R., Morini, G., Ducere, J.-M., Melchior, A., Correa, A., Piemontesi, F., and Tolazzi, M., *Macromol. Symp*., 2007, vol. 260, p. 122. DOI: 10.1002/masy.200751417.
42. Bondaletova, L.I., Bondaletov, V.G, Bondaletov, O.V, and Startseva, K.S., *Fundament. Issled*., 2013, nos. 8–3, p. 551.
43. Wang, T.-H., Navarrete-Lopez, A.M., Li, S., and Dixon, D.A., *J. Phys. Chem. (A),* 2010, vol. 114, p. 7561. DOI: 10.1021/jp102020h.
44. West, R.H., Beran, G.J.O., Green, W.H., and Kraft, M., *J. Phys. Chem. (A),* 2007, vol. 111, p. 3560. DOI: 10.1021/jp0661950.
45. *Termodinamicheskie svoistva individual'nykh veshchestv* (Thermodynamic Properties of Pure Substances), Glushko, V.P., Ed., Moscow: Nauka, 1982, vol. 4, book 2, pp. 105, 107.
46. Razuvaev, G.A., Bobinova, L.M., and Etlis, V.S., *Tetrahedron,* 1959, vol. 6, p. 154. DOI: 10.1016/0040-4020(59) 85009-2.
47. Sheldrick, G.M., *SHELXS97*, Program for Crystal Structure Solution. University of Gottingen, Germany, 1997.
48. Sheldrick, G.M., *SHELXL97*, Program for Crystal Structure Refinement. University of Gottingen, Germany, 1997.
49. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Jr., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, O., Foresman, J.B., Ortiz, J.V., Cioslowski, J., and Fox D.J., *Gaussian 09*, Revision C.01. Gaussian Inc., Wallingford CT, 2009.
50. Becke, A.D., *J. Chem. Phys*., 1993, vol. 98, p. 5648. DOI: 10.1063/1.464913.
51. Lee, C., Yang, W., and Parr, R.G., *Phys. Rev. (B),* 1988, vol. 37, p. 785. DOI: 10.1103/PhysRevB.37.785.
52. Weigend, F. and Ahlrichs, R., *Phys. Chem. Chem. Phys*., 2005, vol. 7, p. 3297. DOI: 10.1039/b508541a.