

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Quantum Chemical Modeling of Regents and Products in the Process of Siloxane Airgel Formation.

Bolatbek Kh Khusain*, Irina A Shlygina, Aleksandr R Brodsky and Murat Zh Zhurinov

JSC "D.V.Sokolosky Institute of Fuel, Catalysis and Electrochemistry" 050010, Kunayev Street 142, Almaty, Republic of Kazakhstan.

ABSTRACT

Quantum chemical calculations of reagents and products participating in different stages of tetraethoxysilane (TEOS) hydrolysis were performed using the Hartree-Fock method (HF) and the Density Functional Theory (DFT/B3LYP) with basis 6-31g(d',p'). The geometry and full energy of the molecules was optimized and enthalpy of the stages was calculated. In the framework of the methods endothermic nature of all stages of TEOS hydrolysis was revealed. Similar calculations were made for tetramethoxysilane. It was found that all stages of methoxyhydroxysilane hydrolysis are exothermic. The enthalpy is about 1 kcal/mole. Calculations with the DFT/B3LYP method also gave exothermic effect for the stages of hydrolysis. So, the calorific effect of alkoxy silane hydrolysis depends on alkyl substituent. Specific interactions of proton with all reagents and products of tetraethoxyorthosilicate hydrolysis were calculated using the same methods. Full energies of the molecules and protonated complexes were used for calculation of enthalpies of all stages of hydrolysis. It was found that all stages of hydrolysis are endothermic even more than in the case of non-protonated molecules. With use of semi-empirical PM6 software it was shown that proton takes part in diethoxydihydroxysilan conversation. Silicon atom is connected with a water molecule when the proton is attached to the oxygen of ether bond. This explains the catalytic properties of the proton in hydrolysis of TEOS.

Keywords: quantum chemical calculations, molecular modeling, silicate airgel

**Corresponding author*

INTRODUCTION

Silica is the most common substance on the Earth. The structure is based on their "oxygen tetrahedron" 4 oxygen atoms linked to a silicon atom. The silicon in these compounds is tetravalent. However, there are a lot of different substances: silica, silicate glass, adhesives etc., different "packaging" tetrahedra [1, 2]. Recently, a large widely dispersed artificially produced amorphous silicates with nanoparticles - aerosil, silica gels and aerogels [3].

They have a different structure in the bulk and on the surface of particles, a different method of connecting circuit tetrahedra and dangling bonds with hydroxyl groups of the surface. The differences are determined by the technology of manufacturing of dispersed silicates. This phenomenon is called "technological polymorphism". It was found that the base structure of silicate aerogels comprise chains or belts, built from the remnants of orthosilicic acid [4-6]. Structure chains resembles carbon polymers, with the difference that the carbon chains of carbon atoms joined together, and siloxane - silicon atoms are linked via oxygen atoms, each of which adds further two hydroxy groups ("oxygen tetrahedron" is present here). Chains may be crosslinked by condensation with elimination of water, belt structure (tapes) are formed in these cases. Their experimental detection due to the fact that the tape, unlike chains, no diol hydroxyl groups [7].

Meanwhile silicate aerogels differ significantly in their properties, especially for pore volume and surface area. The formation of the structure of the aerogel, apparently, can be important every stage of its genesis - the formation of orthosilicic acid in successive stages of the hydrolysis reaction of tetraethoxysilane (TEOS), colloidal solution structure (sol) with polymeric silicates (String polysilicon acids of different lengths); fusion sol particles and the formation of nanosized silica gel frame. The first phase of construction of the gel structure of the model it is important to have an understanding of the structure and energy characteristics of the participants in the hydrolysis reaction. Hydrolysis of the TEOS molecules proceeds in four stages in accordance with the replacement of 4 ethoxy groups per hydroxyl. Settlements in these reactions the reactants and products allow us to determine the nature of the enthalpy changes at different stages, to estimate the shift of equilibrium in these reversible processes.

To investigate the mechanisms of reactions in solution must take into account the solvent, since the intermolecular interaction of reactants and products can not only shift the balance, but also to change the mechanism of the reaction [8-10]. Complexes formed by the reagent and solvent molecules may be intermediates in the transformation of reactant to product. When drying aerogels solvent characteristics are also important. For example, the specific surface area of aerogels based on silicon oxide, obtained by the supercritical drying ethers approximately twice the surface area of aerogels obtained by drying in ethanol. Their porosity is also higher. It may also vary and phase composition of the aerogels obtained in different solvents [11-15]. Such calculations must precede the construction of models ultramicro and micron scale.

The purpose of this study is carrying out quantum chemical calculations of molecules of reactants and products at different stages of the hydrolysis reaction enthalpy for the evaluation of individual steps in the evaluation of the effect of the protonation of the molecules of reactants and products in the value of the enthalpy of the reaction mechanism and flow.

METHODS

Quantum chemical calculations were carried out with the help of licensed software Gaussian-09 package [16] Hartree - Fock (HF) method and the density matrix functional (DFT) c exchange-correlation functional B3LYP [17-18] with the basis set 6-31G (D', P'). Full geometry optimization was carried out for all molecules. Close by the level of calculations are given in [19-20].

Influence of solvent in quantum chemical calculations take into account in two ways [21]:

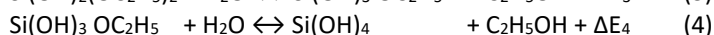
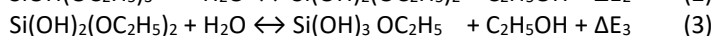
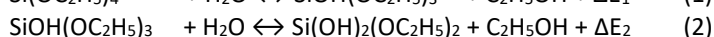
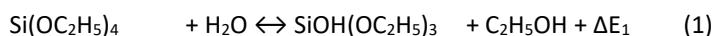
- as the direct interaction of the solvent and solute molecules (known as a specific interaction); it is necessary to consider, for example, the possibility of hydrogen bond formation in solution or protonation (supermolecule approximation);

- as the interaction of solute molecules, located in the cavity of a certain medium (solvent) with certain properties, with the electric fields of the environment (the approach "self-consistent reaction field" - self consistent reaction field (SCRFF)), including PCM model - Polarizable Continuum Model (for constructing cavity model of overlapping spheres) and IPCM - (isodensity PCM). This are so-called continuous models.

Hydrophilic silicas form colloidal solutions, which is first necessary to consider the interaction with water molecules and protons explicitly supermolecule in approximation.

RESULTS

Successive stages of the hydrolysis of tetraethoxysilane described reaction equations:



The difference between the total energies ΔE starting materials and products in equilibrium characterizes a reversible chemical reaction. equilibrium shift towards the formation of products corresponds to the sign "-" in the sense of ΔE . For reaction (1) ΔE determined by the expression (5):

$$\Delta E = E_{\text{TOT}}\text{SiOH}(\text{OC}_2\text{H}_5)_3 + E_{\text{TOT}}(\text{C}_2\text{H}_5\text{OH}) - E_{\text{TOT}}(\text{Si}(\text{OC}_2\text{H}_5)_4) - E_{\text{TOT}}(\text{H}_2\text{O}) \quad (5)$$

The expressions for ΔE are similar in reactions 2-4. The values of the total energies of the reactants and the reaction products obtained by the ab initio Hartree-Fock method are presented in Table 1. Below ΔE_n values calculated from the respective values of the total energies:

$$\begin{aligned} \Delta E_1 &= 0,001456 \text{ a.u.} \rightarrow 0,0396 \text{ eV} \rightarrow 0,91 \text{ kcal/mol} \\ \Delta E_2 &= 0,0007093 \text{ a.u.} \rightarrow 0,0193 \text{ eV} \rightarrow 0,44 \text{ kcal/mol} \\ \Delta E_3 &= 0,0012947 \text{ a.u.} \rightarrow 0,0352 \text{ eV} \rightarrow 0,81 \text{ kcal/mol} \\ \Delta E_4 &= 0,0013396 \text{ a.u.} \rightarrow 0,0364 \text{ eV} \rightarrow 0,84 \text{ kcal/mol} \end{aligned} \quad (6)$$

Table 1 also contains charges on the atoms of silicon and oxygen, the total charges on the atoms of the ethyl group Q_n in fractions of the electron charge (e), the energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) orbitals (in atomic units and electron volts) and the values of the dipole moments Dip (in units of $e \cdot \text{\AA}$). Some geometrical parameters hydroxy tetraethoxysilane shown in Figure 1.

Table 1: Quantum chemical calculations of HF / 6-31G (D', P') tetraethoxysilane hydrolysis products

Characteristic	Molecules				
	$\text{Si}(\text{OC}_2\text{H}_5)_4$	$\text{SiOH}(\text{OC}_2\text{H}_5)_3$	$\text{Si}(\text{OH})_2(\text{OC}_2\text{H}_5)_2$	$\text{Si}(\text{OH})_3\text{OC}_2\text{H}_5$	$\text{Si}(\text{OH})_4$
E_{TOT} , a.u.	-903,160883	-825,098350	-747,036563	-668,974191	-590,911774
$Q(\text{Si})$, e	1,537	1,500	1,454	1,419	1,390
$Q(\text{O1})$, e	-0,688	-0,658	-0,655	-0,650	-0,649
$Q(\text{O2})$, e	-0,688	-0,684	-0,653	-0,647	-0,649
$Q(\text{O3})$, e	-0,688	-0,687	-0,683	-0,654	-0,649
$Q(\text{O4})$, e	-0,688	-0,690	-0,686	-0,686	-0,649
$Q(\text{H1})$, e	-	0,295	0,296	0,299	0,302
$Q(\text{H2})$, e	-	-	0,297	0,300	0,302
$Q(\text{H3})$, e	-	-	-	0,299	0,302
$Q(\text{H4})$, e	-	-	-	-	0,302
$Q_1(\text{C}_2\text{H}_5)$, e	0,304	-	-	-	-
$Q_2(\text{C}_2\text{H}_5)$, e	0,304	0,321	-	-	-
$Q_3(\text{C}_2\text{H}_5)$, e	0,304	0,308	0,314	-	-
$Q_4(\text{C}_2\text{H}_5)$, e	0,304	0,309	0,316	0,319	-

E(HOMO), a.u.	-0,43341	-0,43582	-0,44134	-0,44670	-0,49571
eV	-11,79	-11,86	-12,01	-12,15	-13,49
E(LUMO), a.u.	0,21206	0,20203	0,19267	0,18475	0,17681
eV	5,77	5,50	5,24	5,03	4,81
Dip, e \cdot \AA	0,0000	0,4431	0,4218	0,5263	0,0029
Note: E _{TOT} (H ₂ O) = -76,0244596 a.u.; E _{TOT} (C ₂ H ₅ OH) = -154,0855371 a.u.					

As it is shown in Table 1, on the silicon atom, the charge is positive, and varies from 1.537 (tetraetoksi-) to 1.390 (tetragidroksisilan) by replacing ethoxy radical at the hydroxyl group. Charges on oxygen atoms in ether groups etoksigidroksisilanov have values from -0.69 to -0.68 (e), a hydroxy group - -0,66-0,65 (e). The total charge of the ethyl group in etoksigidroksisilanah varies slightly from 0.30 to 0.32, the charge on the hydrogen atoms in the hydroxyl group - from 0.29 to 0.30 (e).

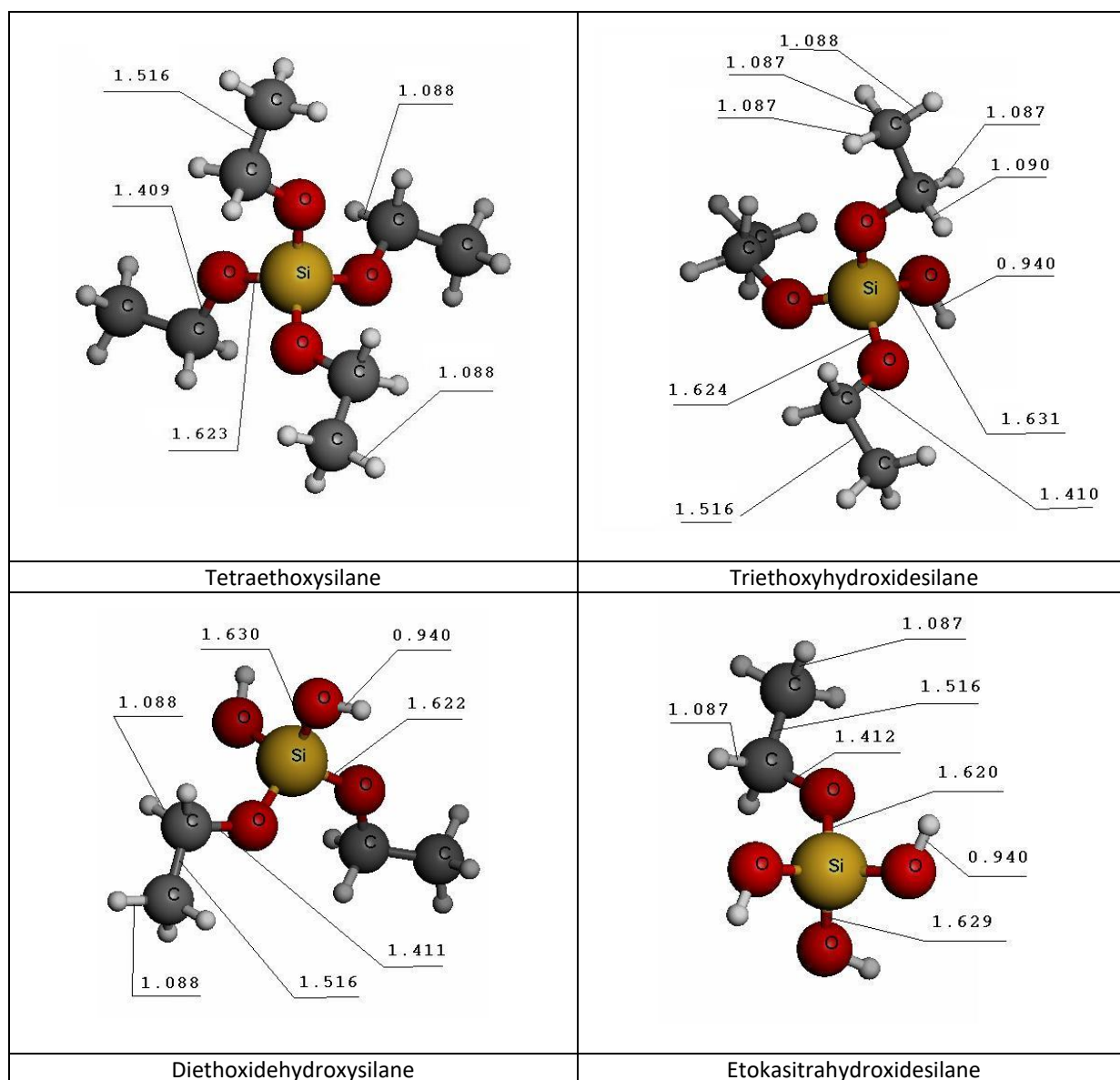


Figure 1: Some geometrical parameters to optimize the structure of hydroxy tetraethoxysilane, HF / 6-31G calculation (d', p')

The hydroxy tetraethoxysilane HOMO energy, which Kupmensa theorem can be compared to the ionization potential (IP), taken with the opposite sign, changes depending on the degree of hydrolysis of from -11.8 to -13.5 eV (ie, according to the calculation of PI tetragidroksisilana 1.7 eV higher than the PI

tetraethoxysilane). Electron affinity (LUMO energy with opposite sign) to the hydroxy tetraethoxysilane in the same row is increased (from -5.8 to -4.8 eV). The dipole moment for tetraetoksi- tetragidroksisilana and virtually zero for hydroxy containing 1, 2, and 3 of the OH group varies as 0.44; 0.42 and 0.53 e • Å. Consequently, tetraethoxysilane molecule somewhat more polar, has a slightly smaller PI and slightly larger electron affinity than tetragidroksisilana molecule.

The expressions (6) reveals that each stage of the reaction is endothermic hydrolysis. The values of ΔE does not vary systematically with increasing degree of hydrolysis.

In order to monitor the effect of the method of calculation on the energy of the molecules of reactants and products in various stages of hydrolysis of TEOS molecules were calculated by the DFT method with the exchange-correlation functional B3LYP (Table. 2).

Table 2: Calculation of the starting materials and products of the hydrolysis reaction of tetraethoxysilane with the DFT exchange-correlation potential B3LYP, with the basis 6-31G (D', P').

Characteristic	Molecules				
	Si(OC ₂ H ₅) ₄	SiOH(OC ₂ H ₅) ₃	Si(OH) ₂ (OC ₂ H ₅) ₂	Si(OH) ₃ OC ₂ H ₅	Si(OH) ₄
E _{TOT} , a.u.	-907,4787077	-828,8568717	-750,2347411	-671,6127787	-592,9906333
Q(Si), e	1,059660	1,027715	1,001318	0,980390	0,963358
Dip, e•Å	0,0000	0,4897	0,6945	0,4582	0,0023

Note: E_{TOT} (H₂O) = -76,4204729 a.u.; E_{TOT} (C₂H₅OH) = -155,0419928 a.u.

Calculation ΔE_n values (n = 1 - 4) is carried out in accordance with (5). Used this beautiful values are given in Table 2.

$$\begin{aligned}
 \Delta E_1 &= 0,0003161 \text{ a.u.} \rightarrow 0,0086 \text{ eV} \rightarrow 0,20 \text{ kcal/mol} \\
 \Delta E_2 &= 0,0006107 \text{ a.u.} \rightarrow 0,0166 \text{ eV} \rightarrow 0,38 \text{ kcal/mol} \\
 \Delta E_3 &= 0,0004425 \text{ a.u.} \rightarrow 0,0120 \text{ eV} \rightarrow 0,28 \text{ kcal/mol} \\
 \Delta E_4 &= 0,0006255 \text{ a.u.} \rightarrow 0,0170 \text{ eV} \rightarrow 0,39 \text{ kcal/mol}
 \end{aligned}
 \tag{7}$$

To take into account the role of the alkyl substituent calculations tetramethoxysilane molecules were carried out.

The difference between the total energies ΔE of the starting materials and products determined by the expression (8), similar to (5): It characterizes the chemical equilibrium reactions. equilibrium shift towards the formation of products corresponds to the sign "-" in the sense of ΔE .

$$\Delta E = E_{TOT}(\text{SiOH}(\text{OCH}_3)_3) + E_{TOT}(\text{CH}_3\text{OH}) - E_{TOT}(\text{Si}(\text{OCH}_3)_4) - E_{TOT}(\text{H}_2\text{O}) \tag{8}$$

Below are the values of enthalpy of reaction for different metoksisilanov hydrolysis steps similar to (6) for ethoxysilanes.

$$\begin{aligned}
 \Delta E_1 &= -0.0017541 \text{ a.u.} \rightarrow -0.0477 \text{ eV} \rightarrow -1.10 \text{ kcal/mol} \\
 \Delta E_2 &= -0.0016981 \text{ a.u.} \rightarrow -0.0462 \text{ eV} \rightarrow -1.06 \text{ kcal/mol} \tag{9} \\
 \Delta E_3 &= -0.0015392 \text{ a.u.} \rightarrow -0.0419 \text{ eV} \rightarrow -0.96 \text{ kcal/mol} \\
 \Delta E_4 &= -0.0014970 \text{ a.u.} \rightarrow -0.0407 \text{ eV} \rightarrow -0.94 \text{ kcal/mol}
 \end{aligned}$$

From (9) it follows that all the stages of the hydrolysis reaction metoksigidroksisilanov exothermic, the equilibrium is shifted towards the formation of products, the energy gain of the order of 1 kcal / mol. The calculations by the density functional with the exchange-correlation functional B3LYP gave even more exothermic effect at all stages of the hydrolysis reaction.

Thus ethoxy and methoxysilane have similar parameters of the electronic structure. The degree of oxidation of the silicon atom in methoxy and ethoxysilanes practically identical. Charges on the oxygen atoms

in the ester groups constitute metoksisilanov -0.67 electron charge fraction (e), a hydroxy group -0.65 (e), i.e. have a somewhat smaller negative charge than the corresponding tetraetilsilana atoms. The total charge of the methyl group in metoksisilana from +0.29 to +0.30, the charge on the hydrogen atoms in the hydroxyl groups of hydroxy tetramethylsilane is of the order of +0.30 e. The ionization potentials, electron affinity, the dipole moments of the methoxy and hydroxy ethoxysilanes differ slightly, ethoxysilane more polar.

TEOS hydrolysis reaction is carried out in isopropyl alcohol in the presence of water and an organic acid which provides an excess of protons (pH ~ 2 - 3). In connection with these terms and conditions of the quantum-chemical calculations were carried out for the protonated molecules with varying degrees of substitution of ethoxy groups to the hydroxyl. Calculated complexes in which proton (Figure 2) is reacted with ethereal oxygen atom or a hydroxyl group alkoksigidroksilana.

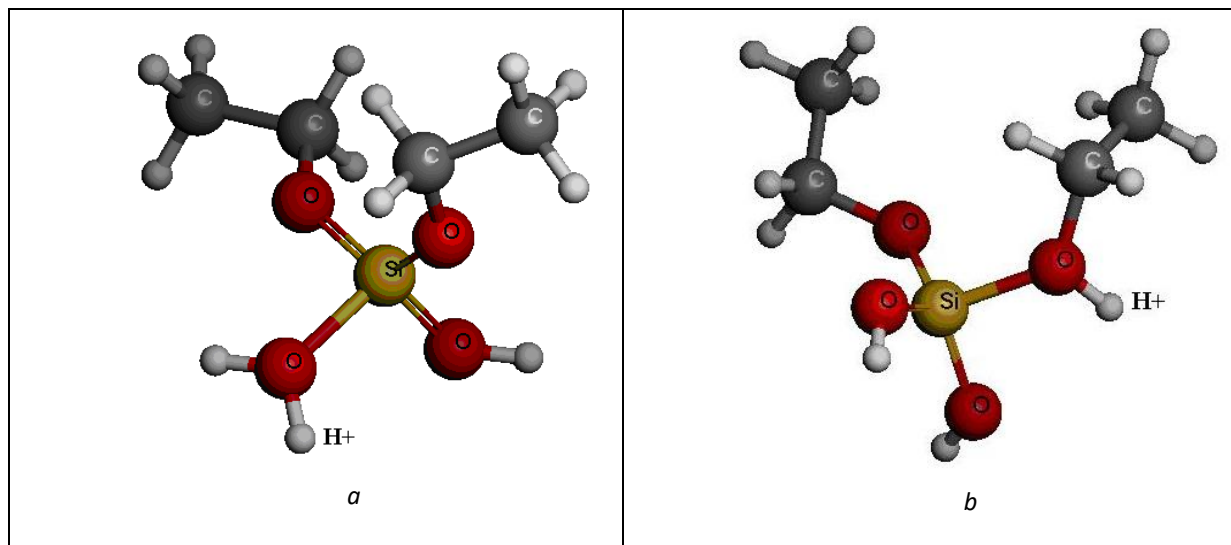
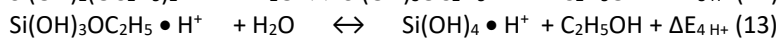
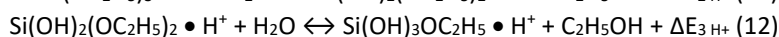
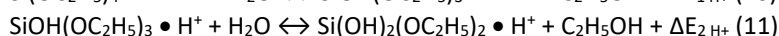
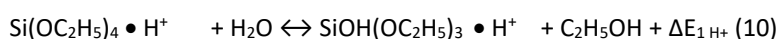


Figure 2: Diethoxidehydroxysilane protonated form *a* - protonation of the oxygen atom of the hydroxy; *b* - protonation of the oxygen atom ethoxy.

The equations of the successive stages of the hydrolysis reaction of the protonated molecules tetraethoxysilane:



where the enthalpy of the reaction (1) is defined as

$$\begin{aligned} \Delta E_{1\text{H}^+} = & E_{\text{TOT}}(\text{SiOH}(\text{OC}_2\text{H}_5)_3 \cdot \text{H}^+) + E_{\text{TOT}}(\text{C}_2\text{H}_5\text{OH}) \\ & - E_{\text{TOT}}(\text{Si}(\text{OC}_2\text{H}_5)_4 \cdot \text{H}^+) - E_{\text{TOT}}(\text{H}_2\text{O}) \end{aligned} \quad (14)$$

Calculate values of the remaining values $\Delta E_{n\text{H}^+}$ + performed analogous to the expression (5), and the results are given in (15-16). The values of the total energies of molecules and their protonated forms used in the (15-16) for calculating the enthalpy of the reaction are shown in Table 2.

Protonation of the group -O-C₂H₅:

$$\begin{aligned} \Delta E_{1\text{H}^+} &= 0,0050746 \text{ a.u.} \rightarrow 0,1381 \text{ eV} \rightarrow 3,18 \text{ kcal/mol} \\ \Delta E_{2\text{H}^+} &= 0,0055679 \text{ a.u.} \rightarrow 0,1515 \text{ eV} \rightarrow 3,50 \text{ kcal/mol} \\ \Delta E_{3\text{H}^+} &= 0,0057846 \text{ a.u.} \rightarrow 0,1574 \text{ eV} \rightarrow 3,63 \text{ kcal/mol} \end{aligned} \quad (15)$$

Protonation of the group -O-H:

$$\begin{aligned}
 \Delta E_{2H^+} &= 0,0054869 \text{ a.u.} \rightarrow 0,1493 \text{ eV} \rightarrow 3,44 \text{ kcal/mol} \\
 \Delta E_{3H^+} &= 0,0067069 \text{ a.u.} \rightarrow 0,1825 \text{ eV} \rightarrow 4,21 \text{ kcal/mol} \\
 \Delta E_{4H^+} &= 0,0077568 \text{ a.u.} \rightarrow 0,2111 \text{ eV} \rightarrow 4,87 \text{ kcal/mol}
 \end{aligned}
 \tag{16}$$

Table 3: The total energy of the molecules of reactants and products and their protonated forms at different stages of the hydrolysis reaction of TEOS

Characteristic	Molecules				
	Si(OC ₂ H ₅) ₄	SiOH(OC ₂ H ₅) ₃	Si(OH) ₂ (OC ₂ H ₅) ₂	Si(OH) ₃ OC ₂ H ₅	Si(OH) ₄
E _{TOT} , a.u.	-903,160883	-825,098350	-747,036563	-668,974191	-590,911774
Mol*H ⁺ -O-C ₂ H ₅	-903,509122	-825,4429697	-747,3763243	-669,3094622	-
ΔE _{H+1} , a.u.	-0,348239	-0,3446197	-0,3397613	-0,3352712	-
eV	-9,4756	-9,3771	-9,2449	-9,1227	-
Kcal/mol	-218,59	-216,32	-213,27	-210,4	-
Mol*H ⁺ -O-H	-	-825,4302493	-747,3636849	-669,2959031	-591,227069
ΔE _{H+2} , a.u.	-	-0,3318993	-0,3271219	-0,3217121	-0,315295
eV	-	-9,0310	-8,9010	-8,7538	-8,5792
Kcal/mol	-	-208,34	-205,34	-201,94	-197,91
E _{TOT} (H ₂ O) = -76,0244596 a.u.; E _{TOT} (C ₂ H ₅ OH) = -154,0855371 a.u.					
ΔE _{H+1} - protonation energy of the oxygen group -O-C ₂ H ₅					
ΔE _{H+2} - protonation energy of the oxygen group -O-H					

From the data (15-16) that protonation by group -O-H, -O-C₂H₅, and leads to a significant increase in the endothermic effect at all stages of the hydrolysis reaction. Energy protonation decreases with decreasing number of ethoxy substituent in the molecule of tetraethoxysilane.

Thus, according to the selected approximation calculation is not protonation leads to a shift in the equilibrium towards the formation of the hydrolyzed products. In this organic acid are used as catalysts in the process. In [22] suggested that protonation methoxysilane water molecule forms a coordinate bond to a silicon atom, and this structure is relevant to intermediate stages of hydrolysis. To study the probability of such a reaction mechanism of calculations performed by PM6 supermolecule consisting of the original molecule of tetraethoxysilane, protonated on oxygen atom ethoxy, and forming a coordination bond with a water molecule.

Figure 3 shows the results of calculation of THEOS complex with a water molecule. Ia, IIa, IIIa - the original geometry of the intermediate complexes tetraethylsilana in the hydrolysis reaction, Ib, IIb, IIIb - the result of the full optimization of the geometry of these complexes.

The complex Ia oxygen atom of the water molecule is located at a distance from 1,80Å TEOS silicon atom. When fully optimize the geometry of the original structure was obtained complex Ib, in which the corresponding distance between the molecules of water and TEOS is 3,69Å.

Complete optimization of the geometry of the ester group on the protonated TEOS molecules in a complex with a water molecule (IIa; +1 charge of the complex, multiplicity 1) leads to the result (IIb), according to which the stored water coordination bond between the oxygen atom and the silicon atom in TEOS length which amounted to 1,98 Å.

Initial geometry IIIa complex derived from optimized IIb complex geometry by tearing a proton from a water molecule, while the net charge of the complex becomes 0, multiplicity 1. As a result of optimization of the geometry of this complex breaks Si-O bond protonated ester group, and a molecule of ethanol is removed from the hydroxylated TEOS molecules.

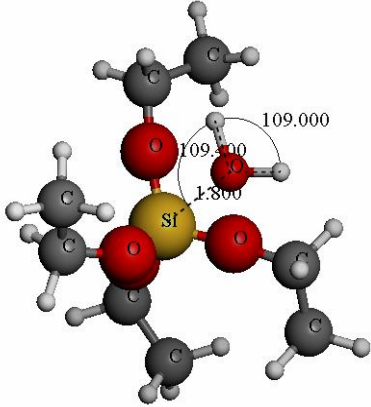
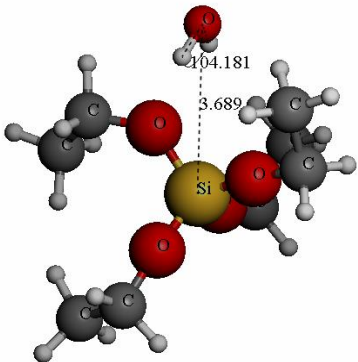
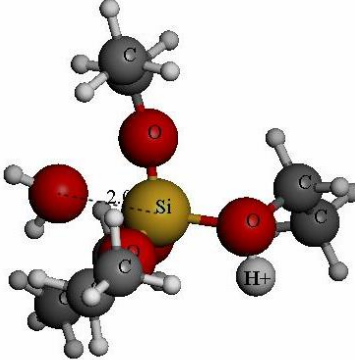
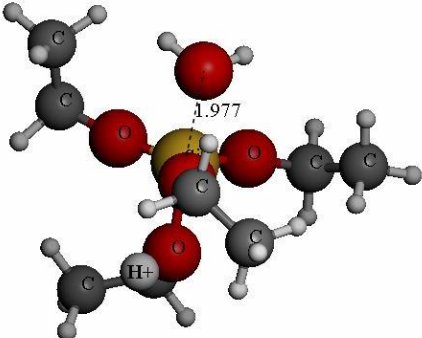
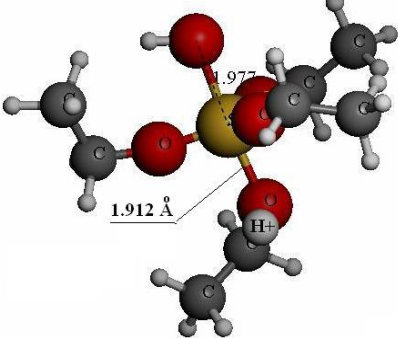
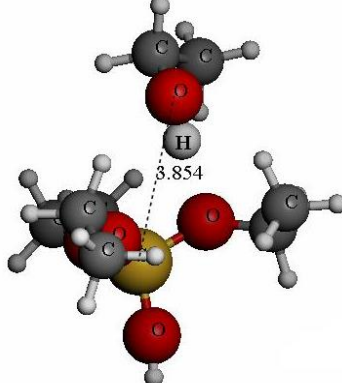
Complex	The original geometry	The optimized geometry
TЭOC+H ₂ O char=0 mult=1	 <p style="text-align: center;">Ia</p>	 <p style="text-align: center;">Ib</p>
TЭOC(H ⁺)+ + H ₂ O char=+1 mult=1	 <p style="text-align: center;">IIa</p>	 <p style="text-align: center;">IIb</p>
TЭOC(H ⁺)+ + OH ⁽⁻⁾ char=0 mult=1	 <p style="text-align: center;">IIIa</p>	 <p style="text-align: center;">IIIb</p>

Figure 3: Initial and optimized geometry of a number of intermediate complexes in the reaction of TEOS hydrolysis; calculation of p / e by PM6

DISCUSSION

The calculation method of B3LYP / 6-31G (d', p') changes in charges on the silicon atom and the dipole moments in qualitative agreement with the corresponding values in the calculation of HF method. The values of ΔE also positive, with increasing degree of hydrolysis, and also does not vary systematically ΔE_n value is less than 0.4 kcal / mole, i.e. half the corresponding values in (6). Nonmonotonic change ΔE may be associated with changes in the dihedral angles of the C-C-O-Si, C-O-Si-O with an internal rotation about the bonds of C-O and O-Si in molecules with varying degrees of substitution of hydroxyl group of an organic radical.

In contrast to the results obtained for ethoxysilanes, all stages of the hydrolysis reaction metoksigidroksisilanov exothermic, the equilibrium is shifted towards the formation of products, the energy gain of the order of 1 kcal / mol. The calculations by the density functional with the exchange-correlation functional B3LYP gave even more exothermic effect at all stages of the hydrolysis reaction.

The results obtained, in accordance with which the calculated thermal effects ethoxysilanes hydrolysis reactions are endothermic in nature, are unexpected and require further investigation. The experimentally observed shift in the equilibrium towards the formation of the reaction products may be associated with the influence of the solvent and that the process in the condensation products are removed from the reaction medium. The calculations used the high-level methods at the same time was obtained the optimum geometry of the molecules, which will further increase the accuracy of calculations.

Ab initio HF method and the density matrix functional in basis 6-31G (D', P') shows that the approach adopted by the hydrolysis reaction enthalpy TEOS reactant protonated molecules are endothermic, ie protonation itself does not lead to a shift in the balance side product formation in any of the reaction steps. However, the geometry of the molecule change protonation agent so that it becomes low coordination bond with the silicon atom of the water molecule. Such complex can be an intermediate stage in the accession to the silicon atom of the hydroxyl group. Removal of one of the protons of water does lead to the attachment of the hydroxyl group to the silicon atom. Thus there is a barrier-free cleavage of a molecule of ethanol, together with the original attached proton.

Therefore, the assumption about the necessity of protonation of the ester group of TEOS to form a complex with water and further attachment of the hydroxyl group to the silicon atom, expressed in [7], confirmed in the framework of spent quantum chemical calculations.

CONCLUSION

The calculations of the molecules of reactants and products of various stages of the hydrolysis reaction of TEOS with full geometry optimization for all structures ab initio Hartree-Fock (HF) and density functional DFT with the exchange-correlation functional B3LYP, using a set of basic functions 6-31g (D', P'). It is found that the effects of thermal reactions are endothermic. The thermal effect is in the range 0.5-1.0 kcal / mol, and has no strict dependence on the number of substituted alkoxy groups.

In this case all the stages of the hydrolysis reaction methoxygidroksisilans, exothermic, the equilibrium is shifted towards the formation of products, the energy gain of the order of 1 kcal / mol. The calculations by the density functional with the exchange-correlation functional B3LYP gave even more exothermic effect at all stages of the hydrolysis reaction. Therefore, within the calculations, the thermal effect in the alkoxy silane hydrolysis reaction depend on the alkyl substituent.

Ab initio HF method and the density matrix functional in basis 6-31G (D', P') shows that the approach adopted by the enthalpy of TEOS hydrolysis reactions for protonated reagent molecules are endothermic in nature, that is in line with the approach of not protonation shifts equilibrium towards products formation. In this series of calculations based on the semiempirical PM6 showed that protonation of TEOS on the oxygen atom of the ester group promotes the formation of a coordination bond between a silicon atom and a water molecule. This complex is an intermediate in the addition reaction of hydroxyl ethyl alcohol and cleavage from silicon atoms. This explains the catalytic properties of the protons in the reaction of TEOS hydrolysis.

ACKNOWLEDGEMENT

The study was supported by the Head Office of the "Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan" under the grant 1931 / GF4 under contract number 315 of 12/05/2016

REFERENCES

- [1] Ailer R. Chemistry of Silica. Mir, Moscow, 1982.

- [2] Libau F. Structural Chemistry of Silica. Mir, Moscow, 1988.
- [3] Shabanova NA, Sarkisov PD. Sol-Gel Technologies. Bases of Sol-Gel technology. IKTs "Akademkniga", Moscow, 2004.
- [4] Sheka EF, Markichev IV, Natkanets I, Khavryuchenko VD. Physics of elementary particles and atomic nuclei 1996; 27(2): 493-560.
- [5] Khavryuchenko VD, Sheka EF. Journal of Structural Chemistry 1994; 35(2): 215-223.
- [6] Khavryuchenko VD, Sheka EF. Journal of Structural Chemistry 1994; 35(3): 305-308.
- [7] Khavryuchenko VD, Sheka EF. Journal of Structural Chemistry 1994; 35(2): 74-77.
- [8] Entelis SG, Tiger HP. Reaction Kinetics in the Liquid Phase. Chemistry, Moscow, 1973.
- [9] Fialkov UJ. The Solvent as a Control Chemical Tool. Chemistry, Leningrad, 1990.
- [10] Aslanov LA, Zakharov MA, Abramychева NL. Ionic Liquids in a Series of Solvents. Publ. house MGU, Moscow, 2005.
- [11] Lermontov SA, Malkova AN, Sipjagina NA, Baranchikov AE, Petuhov DI, Ivanov VK. Journal of Inorganic Chemistry 2015; 60: 1283-1286.
- [12] Lermontov SA, Sipjagina NA, Malkova AN, Baranchikov AE, Erova KE, Petuhov DI, Ivanov VK. Journal of Inorganic Chemistry 2015; 60: 549-553.
- [13] Chukin GD. Surface Chemistry and Dispersed Silica Structure. Paladin Press, "Printa", Moscow, 2008.
- [14] Khavryuchenko VD, Sheka EF. Journal of Structural Chemistry 1994; 35(2): 215-223.
- [15] Khavryuchenko VD, Sheka EF. Journal of Structural Chemistry 1994; 35(3): 305-308.
- [16] Gaussian 09, Revision C.01, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov F, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ, Gaussian, Inc., Wallingford CT, 2010.
- [17] Dunning TH Jr. J Chem Phys 1989; 90: 1007-1023.
- [18] Becke DJ. Chem Phys 1997; 107: 8554-8560.
- [19] Fernandez L. Journal of Molecular Modeling 2012; 18(7): 3301-3310.
- [20] Cheng X, Zhao Y. Journal of Molecular Modeling 2016; 22(9): 211-220.
- [21] Burshtein KJ, Shorygin PP. Quantum Chemical Calculations in Organic Chemistry and Molecular Spectroscopy. Science, Moscow, 1989.
- [22] Aelion R, Loebel A, Eirich F. J Am Chem Soc 1950; 72: 5705-5712.