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Condensation reactions in silanol–water clusters

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Abstract

Two types of complexes were found in the $2H_3SiOH + nH_2O$ ($n = 1, 2$) systems by B3LYP and MP2 methods. Global energy minima correspond to cyclic structures and less stable open isomers, in which one hydrogen bond is eliminated, are higher in energy by 3–7 kcal/mol. The decrease in the stability of open structures due to the rupture of one hydrogen bond is partly compensated by a weak silicon–oxygen intermolecular interaction. This interaction favors condensation and results in a substantially lower barrier height for the reaction path emerging from the open complex. The catalytic effect of water reveals in the substantial lowering of the barriers heights for both types of transition states in going from $n = 0$ to $n = 2$.

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1. Introduction

Silanol condensation reactions play an important role in the manufacture of inorganic polymers, coatings, glasses, gels, adsorbents and catalysts [1]. Despite the practical importance of these reactions there are few theoretical studies of their reaction mechanism [2–4]. Kudo and Gordon [2] have found the transition state for the condensation of H_3SiOH and showed that the addition of one water molecule drastically reduces the

barrier height. In this work, as well as in two other studies dealing with the theoretical assessment of the condensation reaction mechanism [3,4], the formation of silsequioxanes from multifunctional silanols is studied.

In our previous publication [5] it was shown that the formation of cyclic monofunctional silanol trimers and tetramers, similar to those of water and methanol is an energetically favoured process and its energy gain exceeds those for water and methanol both in absolute and in per monomer values. Since the silanol formation through hydrolysis and subsequent condensation occurs in aqueous media, the structure and transformations of water–silanol complexes are of particular interest. Although there are several experimental and theoretical studies of the water–methanol clusters [6–11], no experimental data on water–silanol

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complexes exist and theoretical investigations are limited to the $H_3SiOH \cdot H_2O$ [12–15] and $2H_3SiOH \cdot H_2O$ systems [2,3]. Recently Cypryk and Apeloig [16] discussed theoretical structures of complexes between disiloxane and disiloxanol with water molecules.

In the present communication we consider the silanol–water clusters consisting of two silanol molecules (the minimal amount for the modelling of condensation reactions) and one or two water molecules. The aim of this study is to examine the potential energy surface of these systems and to predict the effect of silanol–water cluster formation on the classical barrier height for condensation reactions.

2. Theoretical methods

The computational methods employed in this work included some description of electron correlation. These were the hybrid DFT method combining Becke's three parameter exchange functional [17] with the LYP correlation functional [18] (B3LYP) and the second-order Moller–Plesset perturbation theory (MP2) [19] as implemented in the GAUSSIAN 98 program [20]. The basis set was constructed from the double zeta set of Huzinaga, Hay, and Dunning [21], namely Si(11s7p/6s4p), C,O(9s5p/4s2p), H(4s/2s). This basis set was augmented with one set of d polarization functions with [$\alpha_d(Si) = 0.5$ and $\alpha_d(O) = 0.85$] and p polarization functions at H [$\alpha_p(H) = 0.75$], as well as one set of diffuse functions for H and O [$\alpha_s(H) = 0.048273$ and $\alpha_p(O) = 0.059$]. This basis set is designated as DZP + diff. At the MP2/ DZP + diff level the frozen core option was used.

3. Results and discussion

The structure of the silanol dimer was described earlier in our previous communication [5], as well as by Kudo and Gordon [2] and by Sauer and co-workers [22,23]. The only minimum found for this system corresponds to the structure similar to those of water and methanol dimers, in which one

molecule is a proton donor and the other is a proton acceptor (**1** in Fig. 1). Equilibrium value for the hydrogen-bond $O \cdots H$ separation, obtained in this work with the DZP + diff basis set (1.846 Å), lies between those of MP2/6-31G* (1.867 Å) and MP2/6-311G* (1.811 Å) reported by
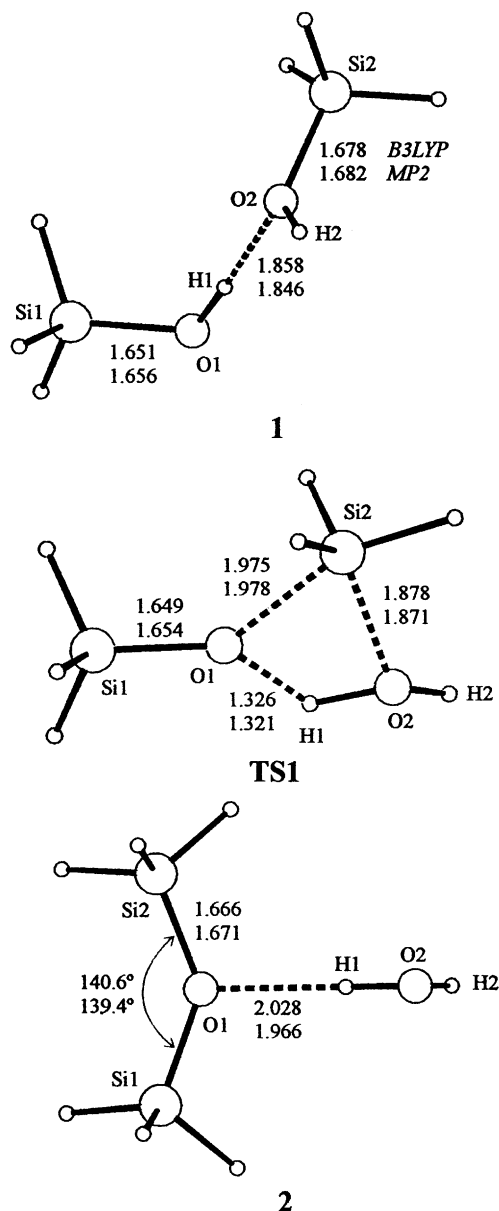

Fig. 1. Equilibrium structures (bond lengths in Å) of stationary points for the 2SiH$_3$OH system.

Kudo and Gordon [2]. In order to access the quality of these three basis sets for the description of the silanol dimer we may compare their behaviour in reproducing the hydrogen bonding in the water dimer, which is the benchmark for theoretical description of hydrogen bonding [24]. Although the r_eO–O value of 2.952 Å , derived from the experimental r_0 values of Odutola and Dyke [25], and corrected for the anharmonicity effects by van-Duijneveldt-van de Rijdt and van-Duijneveldt [26] was generally accepted, in a recent work by Mas et al. [27], a new experimental/theoretically corrected value of 2.910 Å was recommended. The MP2/6-31G* equilibrium O–O separation of 2.915 Å matches well the last experimental value, but the increase of the basis set to 6-311G* results in much poorer agreement (2.849 Å). The MP2 method with the DZP + diff basis set employed in this work yields substantially better agreement (2.922 Å).

The transition state (**TS1**, Fig. 1), similar to that of Kudo and Gordon [2], was found in this work. The MP2/DZP + diff barrier of 21.6 kcal/mol, (ΔE_e value, Table 1) coincides with the single-point MP4/6-31+G* evaluation of Kudo and Gordon [2] based on the optimized MP2/6-31G* geometries (21.6 kcal/mol) and is slightly lower than their single-point CCSD(T)/6-31G* estimate (22.4 kcal/mol).

The structure of the product complex was not reported before. It corresponds to the structure **2** (Fig. 1) in which the water molecule forms a weak hydrogen bond with the bridging oxygen of the disiloxane moiety. Note that the SiOSi angle equilibrium value substantially decreases upon the coordination of a water molecule to oxygen; at the MP2 level from 164° to 139° and at B3LYP from 180° to 141°. This decrease is accompanied by a noticeable lowering of the v_{as} SiOSi theoretical

Table 1
Relative energies (kcal/mol) for stationary points in the $2H_3SiOH + nH_2O$ systems ($n = 0–2$) optimized with the B3LYP and MP2 (frozen core) methods with the DZP + diff basis set ($\Delta E_0 = \Delta E_e + \Delta ZPVE$, $\Delta H_{298} = \Delta E_e + \Delta THERM$)

| n	Structure	B3LYP ΔE_e	MP2			
			ΔE_e	ΔE_0	ΔH_{298}	Imag. freq. (cm^{-1})
0	$2H_3SiOH$	0	0	0	0	0
	1	−6.0	−7.6	−6.2	−5.9	0
	TS1	23.8	21.6	21.6	20.8	692i
	2	−7.7	−11.3	−10.1	−9.4	0
	$H_6Si_2O + H_2O$	−5.4	−7.0	−7.5	−6.6	0
1	$2H_3SiOH + H_2O$	0	0	0	0	0
	3	−18.2	−20.6	−16.3	−17.0	0
	4	−13.8	−16.9	−13.0	−13.5	0
	7	−12.9	−16.6	−12.8	−13.2	0
	8	−14.4	−16.5	−12.5	−13.1	0
	TS2	−13.2	−16.1	−12.5	−13.3	103i
	TS3	14.0	10.9	12.8	11.8	640i
	TS4	9.1	3.2	5.8	3.5	744i
	5	−12.6	−16.7	−13.7	−13.1	0
	6	−14.8	−20.1	−16.2	−16.4	0
	$H_6Si_2O + 2H_2O$	−5.4	−7.0	−7.5	−6.6	0
2	$2H_3SiOH + 2H_2O$	0	0	0	0	0
	9	−31.6	−34.8	−27.7	−29.2	0
	10	−31.9	−34.4	−27.6	−28.9	0
	11	−23.3	−27.2	−20.8	−21.9	0
	TS5	−1.8	−7.1	0.0	−2.8	236i
	TS6	−3.5	−9.0	−3.9	−7.4	588i
	12	−25.2	−32.2	−25.4	−26.7	0
	$H_6Si_2O + 3H_2O$	−5.4	−7.0	−7.5	−6.6	0
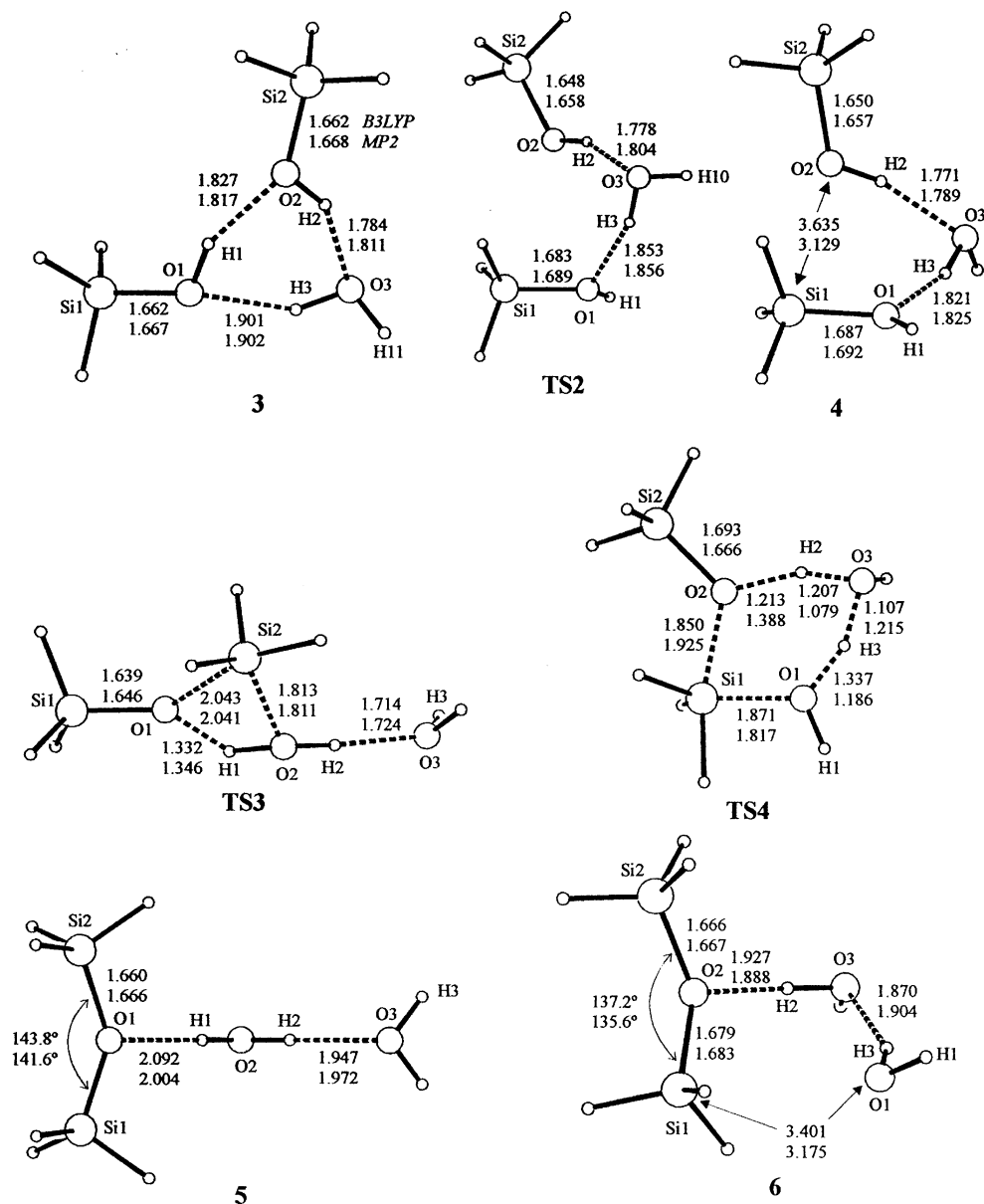
Fig. 2. Equilibrium structures (bond lengths in Å) of stationary points for the $2SiH_3OH + H_2O$ system.

(MP2) harmonic frequency from 1171 cm^{-1} in disiloxane (experimental value -1106 cm^{-1} [28]) to 1082 cm^{-1} in the complex with a water molecule. Thus, small perturbation of oxygen lone pairs results in a significant change of the SiOSi angle and consequently in the decrease of the v_{as} SiOSi frequency. The similar effect was found in hexa-

fluorodisiloxane, where rotations of SiF$_3$ groups with a very low barrier result in a substantial change of the SiOSi angle and the v_{as} SiOSi frequency [29]. This effect was also observed experimentally [30].

The addition of a water molecule to the $2H_3SiOH$ system increases the number of plausible

conformers. The most stable one may correspond to the cyclic arrangement of molecules in the 2 $H_3SiOH + H_2O$ systems, in which these molecules form the maximal number of hydrogen bonds. Indeed, this structure (3, Fig. 2) was found to be a global energy minimum with both B3LYP and MP2 (Table 1). However, the planar structure inherent to the cyclic silanol trimer [5] is not a minimum for the $2H_3SiOH \cdot H_2O$ complex. The energy minimum corresponds to a slightly distorted structure in which one of silanol groups (Si2–O2–H2, Fig. 2) is nearly coplanar to oxygen atoms (τ Si2–O2–O3–O1 = −162°), while the other silanol group (Si1–O1–H1) and the plane of the water molecule form substantially larger dihedral angles with the oxygen atom plane (τ Si1–O1–O2–O3 = −131° and τ H11–O3–O1–O2 = 123°; the atom numbers correspond to those depicted in

Fig. 2 and all the cited equilibrium parameters are from MP2 calculations).

The second most stable complex in the $2H_3SiOH + H_2O$ system has an open structure (4, Fig. 2). It may be produced from 3 by the rotation of the Si1–O1–H1 moiety around the Si1–O1 bond. This rotation moves the H1 atom away from O2 and thus breaks the H1···O2 hydrogen bond between silanol molecules. The transition state for this rearrangement (TS2) is also shown in Fig. 2. The estimated barrier height is only 3.7 kcal/mol at the MP2 level (ΔH_{298}, Table 1). The open complex 4 is less stable than 3 by 3.5 kcal/mol (MP2, Table 1). The rupture of the hydrogen bond in 4 is somewhat compensated by a weak attractive electrostatic interaction between positively charged silicon and oxygen lone pairs of two silanol molecules.
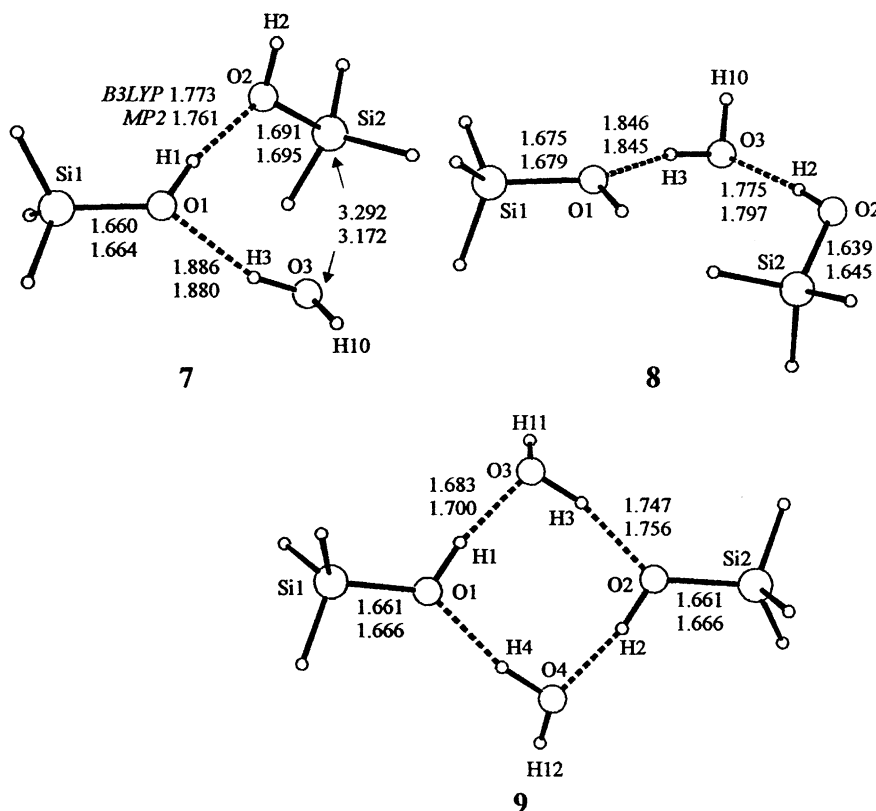

Fig. 3. Equilibrium structures (bond lengths in Å) of two isomers of the $2SiH_3OH + H_2O$ system (7 and 8), and one of the cyclic isomers in the $2SiH_3OH + 2H_2O$ system (9).
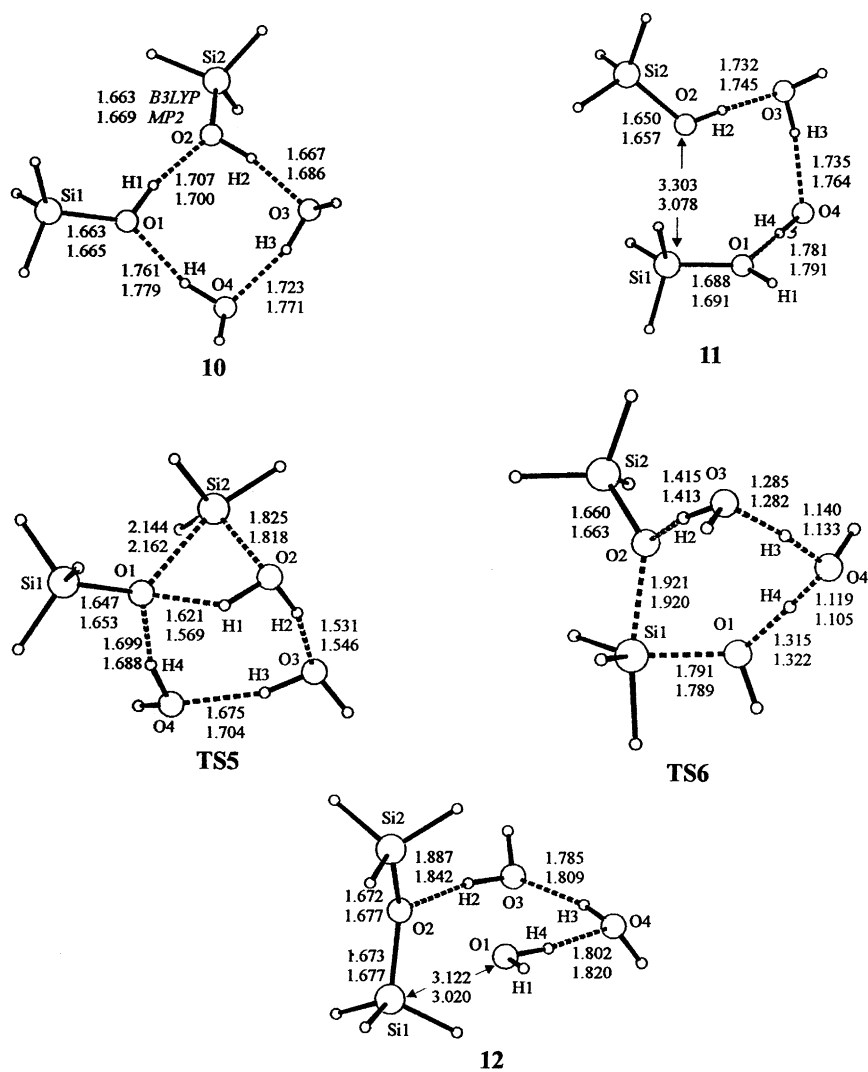
Fig. 4. Equilibrium structures (bond lengths in Å) of stationary points for the $2SiH_3OH + 2H_2O$ system.

The two other energy minima found at the PES of the 2 $H_3SiOH + H_2O$ system (**7** and **8**, Fig. 3) may be regarded as structures derived from **3** and **4**. Isomer **7** is produced from **3** by a rotation around Si2–O2. This motion leads to the rupture of the silanol–water hydrogen bond while leaving the silanol–silanol bonding intact. Isomers **4** and **8** have the similar arrangement of the hydrogen bond network, but the stabilizing Si $\cdots$ O interaction is absent in the latter. The energy difference between them, i.e., 0.4 kcal/mol, may give the estimate of the Si $\cdots$ O interaction energy.

Nevertheless, this weak Si $\cdots$ O attraction provides favorable orientation of silicon and oxygen atoms for the condensation of interacting silanol molecules and, as a result, the barrier height for the transition state (**TS4** in Fig. 2) emerging from **4** is by 8.3 kcal/mol lower than that for **TS3**, which lies on the path connecting **3** with products (ΔH_{298} value, Table 1 and Fig. 5).

The structure of the higher energy transition state (**TS3**) was not reported by Kudo and Gordon [2] (as well as the global minimum **3**). Comparing equilibrium structures of **TS1** (Fig. 1) and **TS3**

(Fig. 2), one may notice that they have the similar arrangement of the Si_2O_2H8 moiety. The additional water molecule in the $2H_3SiOH + H_2O$ system forms a hydrogen bond with a nascent (in the process of condensation) water molecule (**TS3**, Fig. 2). The catalytic effect of the additional water molecule, i.e., the energy difference between **TS3** and **TS1** comprises 9 kcal/mol (ΔH_{298} value, Table 1 and Fig. 5).

There are also two types of product complexes for these two paths. In **5** (downhill motion from **TS3**) both hydrogens of the water molecule attached to the disiloxane oxygen are involved in

hydrogen bonds with disiloxane and another water molecule, while in **6** (obtained from **TS4**) only one hydrogen of each water molecule participates in the bonding. Moreover, **6** exhibit a weak $Si\cdots O$ attractive interaction. These factors result in the energy difference of 3.3 kcal/mol in favor of the product complex **6**.

These two types of reactant complexes, as well as the transition states on their paths to condensation products, were found also for the $2H_3SiOH + 2H_2O$ system. However the addition of one more water results in two plausible structures of cyclic isomers: the one in which silanols are in adjacent positions
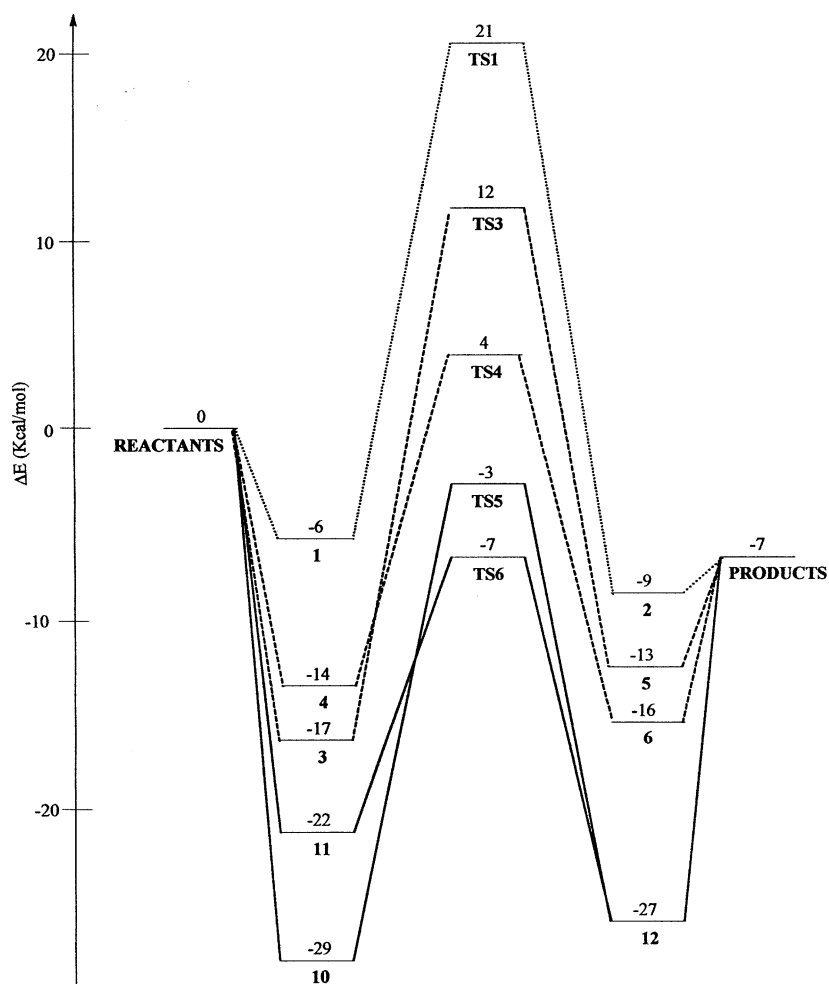

Fig. 5. Potential energy diagram for stationary points for the condensation reaction in the $2SiH_3OH$ system (dotted line) and for two channels of this reaction in the $2SiH_3OH + H_2O$ system (dashed lines) as well as for the $2SiH_3OH + 2H_2O$ system.

(**10**, Fig. 4) and the other in which they are separated by water molecules (**9**, Fig. 3). The first complex appears to be a global minimum at the B3LYP level, but at the MP2 level the global minimum corresponds to **9**, although energy differences between them do not exceed 0.4 kcal/mol.

All attempts to find a transition structure from the structure **9** failed, but it was found for **10**. This structure (**TS5**, Fig. 4) has the arrangement of the heavy atom skeletons (Si1–O1–Si2–O2) similar to those of **TS1** and **TS3**, but the additional water molecule lowers its barrier height by 15 kcal/mol (with respect to **TS3**) Only in the $2H_3SiOH + 2H_2O$ system the energy level of the transition state for condensation becomes lower than that of reactants. Two additional molecules (with O3 and O4) form a ring of hydrogen bonds with a nascent water molecule (with O2) and the siloxane oxygen (O1).

The open structure of the **4** type, i.e., **11** (Fig. 4) was found also for the $2H_3SiOH + 2H_2O$ system. Similar to **4**, it is characterized by a Si $\cdots$ O interaction between silanol molecules. However, the increased flexibility of the three H-bond chain in **11** leads to a shorter Si $\cdots$ O separation than in **4**. This may be the reason of the substantially lower barrier for condensation (**TS6**) emerging from the complex **11** compared with that developing from structure **4** (**TS4**). In contrast to the system with one water molecule, only one product complex (**12**, Fig. 4) was found in the $2H_3SiOH + 2H_2O$ system. The structure of this complex is similar to the product complex **6**, but the more flexible system of three water molecules yields the shorter Si $\cdots$ O contact than in the similar complex with two water molecules.

Thus, the cyclic structures of two silanol molecules with one water molecule (**3**) as well as with two waters (**10**) are global minima in the studied systems and lie lower in energy than the corresponding open structures **4** and **11** by 3 and 7 kcal/mol, respectively. Moreover, the barriers for their condensation (**TS3** and **TS5**) are by 4–8 kcal/mol higher than those for open structures (**TS4** and **TS6**). Although the results obtained in our model cannot be straightforwardly transferred to more complex real systems, in which association and solvent effects play an important role, the tendencies found in this work may evidence that cyclic structures are less prone to condensation and of the existence of these com-

plexes in their most stable forms may provide conditions for greater stability of silanols.

Three kind of hydrogen-bonding involving silanol molecules occur in the studied systems: silanol–silanol (I), silanol donor–water acceptor (II), and silanol acceptor–water donor (III). The analysis of the equilibrium O $\cdots$ H separations obtained in this work shows that, despite variations of these H-bond lengths in particular structures, two tendencies may be revealed: (i) all H-bond distances decrease in the cyclic structures with the growth of the cluster size (1.846–1.700 Å for I, 1.811–1.686 Å for II, 1.902–1.779 Å for III), (ii) the strength of H-bonding (as manifested by H-bond lengths) decrease in the order II > I > III. This conclusion is supported by the analysis of the BSSE corrected interaction energies (E_e) of the corresponding dimers. These values predicted at the MP2 level for silanol–silanol, silanol donor–water acceptor, and silanol acceptor–water donor dimers are 5.4, 5.7, and 4.2 kcal/mol. Note that ΔE_e association energies without the counterpoise corrections give different order of magnitude, i.e., 7.6, 7.4, and 6.0 kcal/mol. Note also that B3LYP systematically overestimates the strength of hydrogen bonding (O $\cdots$ H distances are by 0.01–0.03 Å shorter) but underestimates Si $\cdots$ O contacts with respect to MP2.

4. Conclusions

1. Cyclic hydrogen bound structures are global minima for the $2H_3SiOH + H_2O$ and $2H_3SiOH + 2H_2O$ systems.
2. Open systems with one broken O $\cdots$ H hydrogen bond (with respect to cyclic structures) lie 3–7 kcal/mol higher.
3. The lack of one hydrogen bond in open structures is partly compensated by interacting Si and O atoms of two silanol molecules.
4. These interactions provide better preliminary conditions for condensation and the classical barrier height for these processes was found to be by 4–8 kcal/mol lower than for condensation from cyclic structures.
5. Deeper potential wells and higher barrier heights make cyclic complexes less prone to condensation.

6. The analysis of H-bond distances in the studied complexes and comparison of the BSSE corrected association energies for the corresponding dimers show that the hydrogen bond strength decreases in the order silanol donor–water acceptor > silanol donor–silanol acceptor > silanol acceptor–water donor.

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