Condensation mehanisms of monomeric tin hydroxide molecules and formation of polymorphic stannic acids: a quantum chemical study

O. Filonenko, A. Grebenyuk, V. Lobanov

Chuiko Institute of Surface Chemistry, National Academy of Science of Ukraine, Ukraine, Kyiv, 17 General Naumov Str., *E-mail:* filonenko_ov@ukr.net

The Hartree-Fock method (valence-only basis set SBKJC, expanded by with polarization d and p functions (sbkjc(d,p))) was used to analyze possible formation mechanisms of hydrated tin dioxide nanoparticles, which are polymeric forms of stannic acids. It has been shown that the interaction of two $Sn(OH)_4$ molecules leads to the formation of distannate bridges (Sn–O(H)–Sn), characteristic of bulk samples of tin dioxide.

Keywords: stannic acid, formation mechanism, quantum chemical study

Introduction

Hydrated forms of tin dioxide are widely used in organic synthesis as catalysts, as well as sorbents for the platinum group metals, gold, copper, and mercury from aqueous solutions. In addition, hydroxides and oxide-hydroxides of tin (so-called stannic acids) are precursors in the synthesis of nanosized forms of tin dioxide. The latter cause increased interest due to the combination of a number of their unique optical and electrophysical properties. In addition, such materials are non-toxic and economically available. Thus, SnO_2 nanoparticles are widely used as an anode material in lithium-ion batteries, transparent electrodes of solar batteries, LEDs, various electronic and optical coatings, materials for gas sensors [1].

As a rule, two individual forms are distinguished: α- and β-stannic acids, which differ in composition, acidity and solubility. First, α-stannic acid $SnO_2 \cdot nH_2O$ ($1 < n \leq 2$) is precipitated under the action of alkalis on solutions of tin (IV) salts. Over time, its sediment gradually turns into β-stannic acid $SnO_2 \cdot nH_2O$ ($n < 1$), losing water. Upon further drying of the sediment, SnO_2 nanoparticles are obtained [2].

To date, there are no unambiguous ideas about the relationship between the structure and properties of these acids. The growth mechanisms of nanostructured forms of dioxide are not fully elucidated. In order to find the pattern of formation of these acids, a systematic quantum chemical study on the equilibrium spatial structure and energy characteristics of the cluster models of nanoparticles of hydrated forms of tin dioxide was performed, as well as on the mechanisms of formation of the simplest nanostructures from the initial forms of $Sn(OH)_4$.

Computational method

Calculations were carried out using the Hartree-Fock method within the PC GAMESS package (FireFly 8.2.0). The choice of the basis set is due to an attempt to satisfy the condition of reproduction of the characteristics of possible hydrogen bonds and an adequate description of systems with heavy atoms (Sn). These requirements are met by the SBKJC valence-only basis set with respective effective core potential expanded by polarization d and p functions (SBKJC(d,p)). The results of calculations with this basis set, as can be seen from Table 1, reproduce well the literature data on the structural parameters of the $Sn(OH)_4 \equiv SnO_2 \cdot 2H_2O$ molecule obtained with much wider basis sets [3]. There are no experimental data for the isolated $Sn(OH)_4$ molecule due to its instability in the gas phase. Electronic correlation was taken into account within the framework of the second-order Möller-Plesset perturbation theory.

Table 1. Structural parameters of an isolated $Sn(OH)_4$ molecule

Structural parameters **Method**	**R (Sn–O), nm**	**R (O–H), nm**	**∠ O–Sn–O, degrees**	**∠ Sn–O–H, degrees**
B3LYP/SBKJC	0.193	0.099	106.0; 116.6	124.8
B3LYP/3-21G(d)	0.196	0.099	106.3; 116.0	113.6
PBE0/SBKJC	0.193	0.098	106.0; 116.7	124.7
PBE0/3-21G(d)	0.195	0.099	106.2; 116.2	114.3
RHF/MP2/SBKJC	0.194	0.099	105.8; 117.0	125.0
RHF/MP2/3-21G(d)	0.198	0.099	106.4; 115.8	115.4
RHF/MP2/SBKJC(d,p)	**0.194**	**0.098**	**105.5; 117.7**	**111.3**
MP2/Aug-cc-pVTZ (Sn); 6-311+G(d,p) (O, H) [3]	**0.195**	**0.096**	**105.6; 117.5**	**111.2**

The energy effect (ΔE_{react}) and Gibbs free energy (ΔG_{react}) of reactions at 298 K were determined according to the formulas:

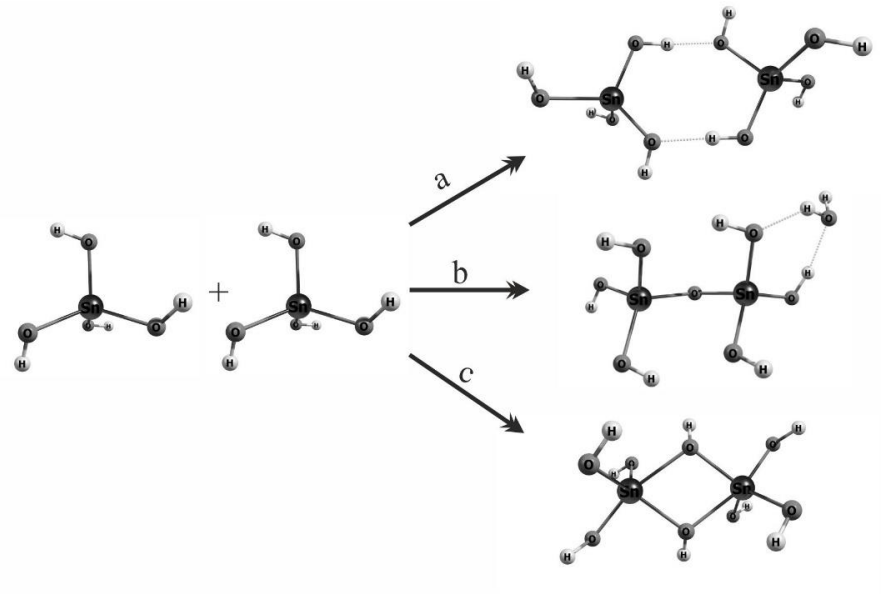
$$\Delta E_{react} = E_{tot}(\text{reaction products}) - E_{tot}(\text{reagents}),$$
$$\Delta G_{react} = G^0_{298}(\text{reaction products}) - G^0_{298}(\text{reagents}),$$

where $G^0_{298} = E_{tot} + ZPE + G_{0\rightarrow 298K}$, E_{tot} – the total energy of the corresponding optimized structure is 298 K, and the energy of zero vibrations (ZPE) and temperature correction $G_{0\rightarrow 298K}$ was obtained from the diagonalization of the Hessian matrices of normal vibrational frequencies for the reaction products and reactants.

Results and discussion

The transformation of the $Sn(OH)_4$ molecule starts from with the formation of dimers. Dependent on the method of interaction, various intermediate structures can be formed. Three primary processes were considered. First of all, the formation of a hydrogen-bonded complex (a) is possible (see Figure). Condensation of two $Sn(OH)_4$ molecules leads to the formation of a dimer where the link –Sn–O–Sn– is present, and elimination of a water molecule, which is connected to the hydroxyl groups of the formed dimer by hydrogen bonds (b). Two $Sn(OH)_4$ molecules can form a coordination dimer (c), where two Sn atoms become five-coordinated, and the oxygen atoms of two hydroxyl groups become three-coordinated. The structure of the formed dimer contains a four-membered cycle –Sn–O–Sn–O–, which is present in bulk solid-phase samples of tin dioxide.

The calculated energy effect and Gibbs free energy of the considered reactions are given in Table 2, from which it can be seen that the formation of a coordination dimer is the most advantageous both energetically and thermodynamically, since the mentioned quantities are correlated with each other. It was believed that further transformations of the particles lead to an increase in their size and dehydration, that is, to the gradual formation of alpha- and beta-stannic acids.



Possible routes and products of the interaction between $Sn(OH)_4$ molecules.

Table 2. Energy (ΔE_{react}) and Gibbs free energy (ΔG_{react}) (kJ/mol) of interactions between two $Sn(OH)_4$ molecules

	a	**b**	**c**
ΔE_{react}	-63.23	-88.16	-134.86
ΔG_{react}	1.31	-20.70	-66.38

Conclusions

From the above data, it follows that $Sn(OH)_4$ molecules tend to form two types of associates: hydrogen-bonded and stronger coordination, the transitions between them lead to the formation of Sn–O–Sn and Sn–OH–Sn bridges, which is accompanied by an increased coordination numbers of atoms. Structures that include water molecules coordinated to Sn atoms can lose them quite easily, as evidenced by the small values of activation energy and coordination energy (several kJ/mol); as a result, intermediates with pentacoordinated Sn atoms are formed, the further transformations of which lead to the formation of denser structures that have signs of crystallinity characteristic of solid SnO_2.

References

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