

Structure and bonding in triorganotin halides complexes: a perspective by Energy Decomposition Analysis

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Abstract: In the recent years, organotin compounds have been shown a wide variety of active components for biological systems such as fungicidal and bactericides.^[1-5] They are also very promising antitumor agents against various type of cancer. Also, they are used in organic synthesis as catalysts.^[1-5] This interest is due to their structure and chemical properties, which depends mainly on the number of Sn-C bonds and the electronic properties of X ligands, such as halogens. For instance, the formation of intermediate cation R_nSn^+ in the biological systems, like ATP-Synthase inhibition is one of the steps to determinate the biological activity.^[6-7] Therefore, the study on the Sn-X chemical bond becomes interesting for understanding how the cation is formed and in which alkyl ligands are more favourable, and what the major electronic structural differences among them. In this context, we studied the nature of the Sn-Cl bond in some organotin halides and their dissociation based on energy decomposition analysis (EDA) and Kohn-Sham orbitals. All the geometries were optimized by ORCA package using relativistic Density Functional Theory (DFT) at ZORA-TPSSH/LANL08(d) for Sn and QZVP for C, H and Cl atoms. The interaction energy ΔE_{int} is further analysed in the conceptual framework provided by the Kohn-Sham molecular orbital method, using a quantitative energy decomposition scheme.^[8] These calculations were performed by ADF 2017 package, at ZORA-TPSSH/QZ4P level of theory, applying the C_{3V} symmetry. We are interested how easy the dissociation on Sn-Cl is in the four models. This is important for the applications of the organotin compounds, mainly as fungicides, in which the cation is the most responsible for the action mechanism in the biological systems. The σ orbital term is the dominant contributor to the stabilization of the Sn-Cl bond. From the gross populations of the fragment molecular orbitals (FMOs), we observe σ -donation from one p orbital of chlorine ($P=1,79e$) to the cation fragment anti-bonding orbital (see fig. 1) The energy of σ bond decreases from methyl to butyl and increases for phenyl whereas the π bond energy for Ph_3SnCl is much smaller than others. This term is determinant for the ΔE_{OI} to be lower for Ph_3SnCl . A strong contribution of π orbitals from conjugated system of the Ph_3SnCl is noticed. Despite of ΔE_{Pauli} is larger compared to other complexes, the contribution of π orbitals from conjugated system favours the stability of the Sn-Cl bond. Also, the decreasing of the

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contribution of chlorine p orbitals for the HOMO, from methyl to phenyl ligands (72% to 50%) has to be taken into account. On the other hand, the contribution of the p orbitals from Sn for the LUMO increases from methyl to phenyl ligands (up to around 70%).

Table 1. Analysis of Sn-Cl bond between R_3Sn^+ and Cl^- in triorganotin complexes ^[a]

EDA (kcal/mol ⁻¹)	Me ₃ SnCl	Et ₃ SnCl	Bu ₃ SnCl	Ph ₃ SnCl
ΔV_{elstat}	-204,39	-197,99	-193,03	-201,28
ΔE_{Pauli}	118,77	120,72	123,64	124,64
$\Delta E_{OI}^{[b]}$	-85,94	-86,49	-89,11	-94,05
ΔE_{A1}	-65,79	-66,15	-68,42	-67,74
ΔE_{A2}	-0,05	-0,09	-0,13	-1,80
$\Delta E_{E1:2}$	-17,94	-17,80	-18,13	-23,12
ΔE_{Int}	-171,56	-163,76	-158,5	-170,69
^[a] Computed at ZORA-TPSSH/QZ4P ^[b] Included Metahybrid correction				

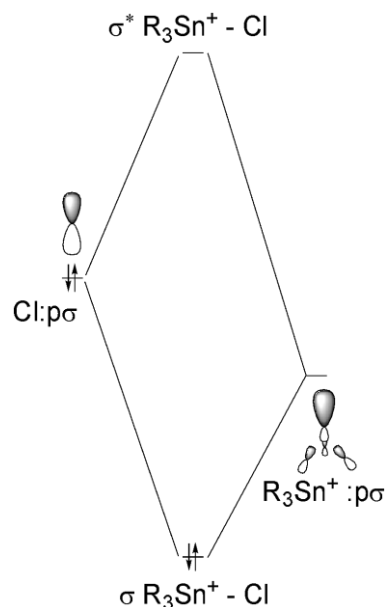


Figure 1. Orbital interaction diagram for Me₃SnCl

Key-words: organotin compounds, energy decomposition analysis, DFT

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