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Organotin bond dissociation energies: An interesting challenge for contemporary computational methods

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ABSTRACT

Organotin compounds are very important in material design as well as in biomedical and biochemical applications. However, little is known about their BDEs experimentally or computationally. Thus, a variety of common quantum chemical methods in combination with several approaches to treating relativistic effects of the tin core electrons were used to calculate the BDEs of organotin compounds. Our results show that the BDEs are very sensitive to the choice of the computational method and to the treatment of relativistic effects.

1. Introduction

Organotin compounds [1–4] are important for many reasons including their use as stabilizers for polyvinyl chloride plastics [5–8], as anti-tumor drugs [9–12], as anti-fungal agents [13], and as neuroprotective agents [14]. In organic synthesis, they are used in many types of reactions, notably in Stille coupling [15], as reagents that promote regioselective substitution [16,17], and as catalysts [18–22].

The making and breaking of chemical bonds is central to all chemical processes. Understanding the energetic changes associated with these processes provides insight into the design of new molecules. In particular, with a clear understanding of such energetic changes, the reactivity of various compounds can be better understood. Experiment has been key to obtaining bond energies involving various elements, however, bonds that involve tin have not been studied extensively. Given the important uses and applications of tin compounds, knowledge of the strengths of bonds involving tin is critical. Thus, our interests lie in the determination of the homolytic bond dissociation enthalpies (BDEs) [23] of bonds between tin and light main group elements.

While extensive compilations of experimental BDEs exist for many types of chemical bonds, values for bonds involving heavier elements such as tin are not so readily available [24–26]. The reason for the lack of such data is because the experimental techniques used are time consuming and difficult [23,27]. Experiments have been done to obtain BDEs involving tin, but as noted by Blanksby and Ellison [23], such values likely suffer from significant errors. Computational methods provide a viable and complementary alternative. Furthermore, Basch [28] and Whittleton et al. [29] have shown the applicability of using such methods to determine the BDEs of organotin complexes.

Basch [28] concluded that the order of bond strength is Sn–O > Sn–S > Sn–N in agreement with chemical intuition. However, he used only a limited set of molecules (i.e., H_3SnOH, H_3SnNH_2, H_3SnSH and H_3SnSMe). Furthermore, consistency in absolute BDEs was not found for the levels of theory used, i.e., MP2, CCSD(T) and B3LYP with a large-core ECP basis set [28]. In the work of Whittleton et al. [29]. a larger set of molecules was studied with BDEs calculated at the MP2/SDB-aug-cc-pVTZ level of theory, but the paucity of experimental values made it difficult to validate the accuracy of the results. For those bonds for which BDEs were available from experiment, the RMS deviation of the computed values [29] from the experimental values was 23.5 kJ mol^{-1}. It should be noted that in the work by Basch [28] and Whittleton et al. [29], a large-core ECP basis set was used. Such basis sets model 46 of the 50 electrons with pseudo-potentials. Thus, only four valence electrons are treated explicitly. Whittleton et al. [29–31] obtained accurate geometries for organotin systems with both the SDB-aug-cc-pVTZ and the LANL2DZdp large-core ECP basis sets in combination with the B3LYP functional.

Herein, we have chosen to include relativistic effects by means of the Douglas–Kroll–Hess (DKH) method [32,33] (with the TZP-DKH basis set), where all 50 electrons of tin are included explicitly. In addition we have used small-core and large-core-ECP containing

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basis sets that model 28 and 46 electrons with pseudo-potentials, respectively. We have also investigated several DFT methods and post-HF methods.

2. Computational methods

The B3LYP functional [34–36], as implemented in the Gaussian 09 software suite [37], with the SVPD [37,38] basis set was used to optimize the geometries of the molecules (and their respective fragments) shown in Scheme 1. Frequencies were calculated at the same level of theory to confirm that all optimized structures correspond to minima (zero imaginary frequencies). It should be noted that geometry optimizations with both the SDB-cc-pVTZ and the ATZP basis sets led to insignificant differences. The latter results are not included for the sake of brevity.

Single-point calculations at the B3LYP/SVPD geometries were then used to calculate the BDEs with a large variety of methods. Given that diffuse and polarization functions have been shown [29] to improve the accuracy of results for tin-containing compounds (with the exception of the basis sets specifically designed for the DKH calculations), we have used such basis sets.

The well known B3LYP, M06-2X and ωB97XD DFT functionals as well as the MP2 and CCSD(T) methods were chosen to calculate the BDEs. To better understand how relativistic effects affect the BDEs, several methods were investigated. In particular, the Douglas–Kroll–Hess (DKH) method [32,39] using the TZP-DKH basis set, basis sets containing effective core potentials (ECP) to model 28 (small-core ECP) or 46 (large-core ECP) core electrons of tin and the ZORA method were used. For the latter method, the ADF program [40–46] was employed, whereas for the former methods, the Gaussian 09 program was used.

With the B3LYP functional, BDEs were calculated at the B3LYP-DKH/TZP-DKH, B3LYP/def2-SVPD+6-311G(2d,p), B3LYP/SDB-aug-cc-pVTZ and the B3LYP/ATZP (with and without the ZORA approximation) levels of theory. It should be noted that the composite of basis sets, such as def2-SVPD+6-311G(2d,p), signifies that the former basis set describes the tin atoms whereas the latter basis set describes all remaining atoms.

With the M06-2X [47] functional, BDEs were obtained at the M06-2X/def2-TZVPD+6-311G(2d,p) and M06-2X/SDB-aug-cc-pVTZ levels of theory.

With the ωB97XD [48] functional, BDEs were obtained at the ωB97XD/SDB-aug-cc-pVTZ+6-311G(2d,p) and the ωB97XD/SDB-aug-cc-pVTZ levels of theory.

With the MP2 method, BDEs were obtained at the MP2/SDB-aug-cc-pVTZ and the MP2-DKH/TZP-DKH levels of theory.

There is a serious lack of accurate experimental BDEs of organotin compounds and, therefore, to assess the accuracy of the DFT and MP2 values we have carried out CCSD(T) calculations, which are generally accepted as the “gold standard” of quantum chemistry [49]. Due to the N^7 scaling of the CCSD(T) calculations, some calculations could not be completed with our computational resources and are denoted by DNF herein. The BDEs were calculated at the CCSD(T)-DKH/TZP-DKH, CCSD(T)/TZP and CCSD(T)/SDB-aug-cc-pVTZ levels of theory.

$H_3Sn{-}H$ $H_3Sn{-}CH_3$ $H_3Sn{-}NH_2$ $H_3Sn{-}NMe_2$ $H_3Sn{-}OH$

$H_3Sn{-}OMe$ $H_3Sn{-}F$ $H_3Sn{-}SH$ $H_3Sn{-}SMe$

$Me_3Sn{-}H$ $Me_3Sn{-}CH_3$ $Me_3Sn{-}NH_2$ $Me_3Sn{-}NMe_2$ $Me_3Sn{-}OH$

$Me_3Sn{-}OMe$ $Me_3Sn{-}F$ $Me_3Sn{-}SH$ $Me_3Sn{-}SMe$

Scheme 1. The tin compounds used in the calculation of the BDEs.

A summary of all the levels of theory discussed above is contained in Table 1. For convenience we will hereafter refer to these as methods 1–14.

Homolytic bond dissociation energies (BDEs) were calculated according to the general chemical reaction [50]:

$$YSn - X \rightarrow YSn^{\cdot} + X^{\cdot}$$

where Y = Me_3 or H_3 and X = H, CH_3, NH_2, NMe_2, OH, OMe, F, SH, or SMe. The electronic energy changes for each reaction were then corrected to enthalpies. The BDEs were not corrected for basis set superposition errors following the recommendation of Alvarez-Idaboy and Galano [51]. As stated above all BDEs reported herein have been corrected by the addition of enthalpic corrections calculated at the B3LYP/def2-SVPD level of theory.

3. Results and Discussion

3.1. Tin-Hydrogen Bond

As discussed in the introduction, it is difficult to determine BDEs experimentally for even relatively small tin compounds. The rate of hydrogen abstraction by a *t*-butyl radical was used to estimate a Sn–H BDE of 318.5 kJ mol^{-1} for Me_3Sn–H [52]. This can be compared to a value for the Sn–H bond in Bu_3Sn–H measured by photoacoustic calorimetry of 310 kJ mol^{-1} [53], later corrected to 326 kJ mol^{-1} [27]. In comparison, the Ge–H BDE of Me_3Ge–H was measured to be 4 kJ mol^{-1} less than that for Bu_3Ge–H [54]. In the present work, we have chosen to use the value of 318.5 kJ mol^{-1} for Me_3Sn–H [52] as our reference value to compare with calculated Sn–H BDEs for the 14 methods (see Table 1). Individual differences from this experimental value are shown in Fig. 1. Several methods show agreement to within 10 kJ mol^{-1} of the experimental value. Of the methods used, the best agreement is obtained with the CCSD(T)/SDB-aug-cc-pVTZ (method 14) level of theory, which calculates a BDE of 318.5 kJ mol^{-1}. Calculations with the CCSD(T) method using the DKH procedure to account for relativistic effects (method 10) did not finish for CH_3Sn derivatives. CCSD(T) calculations without relativistic corrections (method 11), calculated a BDE ~40 kJ mol^{-1} too low.

For methods 1 and 2, an interesting result is observed; both methods calculate BDEs to within 6.5 kJ mol^{-1} of the experimental value, but method 2 ignores relativistic effects. However, if we compare the values obtained with methods 4, 5 and 6 then it is apparent that the inclusion of relativistic effects via the use of ECPs

Table 1
Methods, relativistic corrections and corresponding basis functions for calculating BDEs.

	Method	Relativistic corrections	Basis set
1[a]	B3LYP	ZORA	Slater type-TZVP
2[a]	B3LYP	None	Slater type-TZVP
3[b]	B3LYP	DKH	TZP-DKH
4[b]	B3LYP	Def2-ECP for tin	def2-TZVPD+6-311G(2d,p)
5[b]	B3LYP	SDB-ECP for tin	SDB-aug-cc-pVTZ
6[b]	B3LYP	None	ATZP
7[b]	M06-2X	Def2-ECP for tin	def2-TZVPD+6-311G(2d,p)
8[b]	MP2	DKH	TZP-DKH
9[b]	ωB97XD	SDB-ECP for tin	SDB-aug-cc-pVTZ
10[b]	CCSD(T)	DKH	TZP-DKH
11[b]	CCSD(T)	None	TZP
12[b]	M06-2X	SDB-ECP for tin	SDB-aug-cc-pVTZ
13[b]	MP2	SDB-ECP for tin	SDB-aug-cc-pVTZ
14[b]	CCSD(T)	SDB-ECP for tin	SDB-aug-cc-pVTZ

[a] Calculations done using the ADF code.

[b] Calculations done using the Gaussian 09 code. All single point calculations to obtain the BDEs were calculated at the B3LYP/SVPD optimized geometries.