Density Functional Study of the Complexation Reaction of $Sn(CH_3)_3X$ (X = F, Cl, Br and I) with Halide Anions

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Keywords: Tin / Halides / HSAB / Density functional calculations / NMR spectroscopy

The Lewis acid-base reaction between $Sn(CH_3)_3X$ and Y^- (with X, Y = F, Cl, Br and I) has been studied using quantum chemical calculations. Complexation energies were calculated at the Density Functional Theory (DFT) level and rationalized on the basis of a local application of the hard and soft acids and bases principle. It was observed that smaller differences in the local softness of the interacting sites in the Lewis acid and base correspond to stronger interactions. Moreover, the calculated sequences in complexation energies can be reproduced using equations containing chemical concepts introduced within the framework of conceptual density functional theory and rooted in the hard and soft acids and bases principle and referring only to the reactants. A method of treating the electronegativity and softness of the halide anions is presented based on a Taylor expansion of the electronegativity of the neutral halogens and the softness-polarizability proportionality. Experimental evidence for the calculated sequences was gathered from measured ^{117}Sn chemical shifts and ^1J (^{13}C-$^{119/117}$Sn) coupling constant changes upon complexation.

Introduction

It is well-known that four-coordinate Sn^{IV} compounds bearing electronegative groups react with nucleophiles to form pentacoordinate stannate complexes through expansion of the coordination sphere.[1] An example is the following Lewis acid-base reaction

$$Sn(CH_3)_3X + Y^- \rightarrow Sn(CH_3)_3XY^- \qquad (a)$$

where both X and Y are halogens. A detailed and systematic theoretical and experimental analysis of this reaction has not yet been provided. Tudela and co-workers[2] performed experimental and theoretical studies on tri- and tetrahalodiorganostannate salts and studied, inter alia, their complexation reactions. In their studies, they considered the following reactions:

$$SnR_2X_2 + X^- \rightarrow SnR_2X_3^- \qquad (b)$$

$$SnR_2X_3^- + X^- \rightarrow SnR_2X_4^{2-} \qquad (c)$$

with R being an alkyl group (more specifically Me or Et) and X being F, Cl, Br or I. They concluded,[2] from computations at the Hartree−Fock level, that the formation of the pentacoordinate anions is an exothermic process, while the formation of the octahedral compounds is endothermic, these compounds thus being unstable in the gas phase. They also confirmed that the exothermicity of reaction (b) increased with the electronegativity of the halogen X.

In the present combined theoretical and experimental study, DFT calculations have been performed for the energetics of reaction (a), in order to gain insight into the nature of the tin atom in these interactions. As such, the resultant sequences were assessed on the basis of predictions resulting from the application of the hard and soft acids and bases principle,[3] using reactivity descriptors defined within the framework of conceptual density functional theory.[4] These descriptors, such as the chemical potential,[5] the electronegativity,[5,6] chemical hardness and softness,[7,8] Fukui functions,[9] local softness[8,10] and hardness[11] have been used quite exhaustively among others and by our group for the study of general Lewis acid-base reactions and have proven to be valuable in the interpretation of observed differences in reactivity.[4f,12]

High level ab-initio computational studies on tin compounds are still relatively scarce[13] as are the interpretations of observations in tin chemistry using the above mentioned reactivity indices.[14−16] Recently, our group has contributed significantly to this area, computing ^{119}Sn chemical shifts using Gauge-Including Atomic Orbitals and interpreting them via group electronegativities and hardness,[14] studying

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DOI: 10.1002/ejic.200300044

the interaction of the tin nanocluster $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ with negatively charged and neutral nucleophiles[15] and investigating the simultaneous complexation of a Sn containing crown ether compound with positive and negative ions.[16]

Experimentally, it is well-known that ^{117}Sn NMR spectroscopic data are useful for assessing the complexation of R_3SnX compounds with nucleophiles and halide anions, since this gives rise to low frequency changes in the $^{119(117)}$Sn chemical shifts as well as increasing the magnitude of the $^1J(^{13}C\text{-}^{119/117}Sn)$ coupling constants reflecting increases in the percentage of s character of the hybridized atomic orbitals of the tin upon change from four- to five-coordination.[17,18] For the sake of comparison of the calculations and in the context of our long standing interest in NMR studies on Sn compounds,[19] experimental ^{117}Sn chemical shifts δ as well as $^1J(^{13}C\text{-}^{117}Sn)$ coupling constants are provided for equilibrium mixtures of reaction (1) for X = Cl, Br and Y = F, Cl, Br and I. To the best of our knowledge, such a systematic and internally consistent NMR study of these systems has not yet been published.

The combined theoretical and experimental data provide insight into the Lewis acidity of tin compounds, place the tin element in the context matter of hard or soft character and provide, via a number of reactivity descriptors, the rationalization of its behavior in reaction (a).

Theory, Computational and Experimental Details

All molecular systems were optimized at the B3LYP level[20] using the cc-pVTZ basis set for C and H,[21] the aug-cc-pVTZ basis set for F, Cl and Br,[22] the SDB-cc-pVTZ for Sn and the aug-SDB-cc-pVTZ for I[23] using Gaussian 98.[24]

On the carbon and hydrogen atoms, the standard Dunning cc-pVTZ (correlation consistent polarized valence triple zeta[21]) basis set was used, while on the F, Cl, and Br halides, the diffuse-function augmented version of the same basis sets (aug-cc-pVTZ[22]) was employed. For the heavier tin and iodine atoms, we employed regular and diffuse-function augmented versions, respectively, of the SDB-cc-pVTZ basis set,[23] which is a valence basis set of cc-pVTZ quality optimized for use with a large-core (46-electron) Stuttgart−Dresden relativistic effective core potential.[25]

Since the 4d orbitals of free tin are energetically quite close to the valence s orbitals of the halides (particularly the 2s of fluorine), it could not be taken for granted that the large −core RECPs would be sufficient. In order to ascertain that this was indeed the case, we repeated our calculations for $Sn(CH_3)_3F$ and $Sn(CH_3)\ F^-$ with a small-core (28-electron) ECP on tin.[26] The accompanying basis set was developed for the purpose of this work as follows: (a) a 28s23p17d well-tempered basis set[27] was placed on Sn, the inner 28 electrons replaced by the RECP, and an SCF calculation carried out; (b) all primitives contributing less than 0.0001 to any atomic orbital were deleted, leaving an 18s15p11d basis set; (c) this "pruned' basis set was contracted based on the SCF orbitals; (d) the 2nd through 5th outermost s and p primitives were expanded, as were the four othermost d primitives; (e) additional d and f functions were optimized at the CISD level, correlating valence electrons only; (f) in order to accommodate angular correlation from the (4d) orbital, additional (2f1 g) functions were optimized for the difference between the valence+(4d) and valence CISD correlation energies. The use of this small core basis set yielded, for these two systems, only minor differences in geometry and complexation energy. When the small core ECP on Sn was used, the Sn−F distance in the $Sn(CH_3)_3F_2^-$ complex was 2.103 Å. Upon using the large core ECP this distance changes by less than 1 mÅ. The complexation energies using the large and small core Sn ECP amount to −52.1 and −50.7 kcal/mol respectively. As a result, the large core ECP on Sn was used throughout this study.

Anions of the type $Sn(CH_3)_3X_2^-$ show a trigonal-bipyramidal geometry with the methyl groups (average distance Sn−C = 2.17 Å) in the equatorial position. The average Sn−X bond lengths decrease in the order Sn−I (2.98 Å) > Sn−Br (2.77 Å) > Sn−Cl (2.61 Å) > Sn−F (2.09 Å). The Cartesian coordinates of all geometries are available in the supplementary material. All structures were confirmed to be minima by vibrational frequency calculations. DFT complexation energies, enthalpies and free energies were computed on this basis. In view of the extent of the basis set used and the conceptual difficulties arising from the use of effective core potentials, no correction for the basis set superposition error has been included.

In order to judge the effect of the solvent, the free energies of solvation of the Lewis acid-base complexes were estimated using the PCM model.[28]

As stated in the introduction, in addition to the generally accepted computational advantages of density functional theory, it has also been a source for the introduction of chemical concepts readily known by chemists but in most cases defined only on an empirical basis. Also several principles, such as Sanderson's principle of electronegativity equalization and Pearson's hard and soft acids and bases and maximum hardness principles have received theoretical justification. The complexation energy sequences of reaction (a) were rationalized using a local version of the hard and soft acids and bases principle. This principle, introduced by Pearson in the 1960s, states that hard acids prefer to bond to hard bases and soft acids to soft bases.[3] This principle and related chemical concepts have received theoretical justification within the framework of conceptual density functional theory. It can be adopted locally as follows: consider the interaction between a site k in a Lewis acid and a site l in the Lewis base. Application of the local HSAB principle would imply that the interaction between these sites will be favorable when the difference in their local softness is small, as was shown by Gazquez et al.[29] and elaborated among others by our group.[12,30] The local softness[10] can be obtained as described in Equation (1)

$$s(\mathbf{r}) = Sf(\mathbf{r}) \tag{1}$$

where S is the global softness of the system[8] and $f(\boldsymbol{r})$ the so-called Fukui function,[9] a frontier MO reactivity index defined as the derivative of the electron density of the system with respect to the number of electrons at a constant external (i.e. due to the nuclei) potential:

$$f(\boldsymbol{r}) = \left(\frac{\partial \rho(\boldsymbol{r})}{\partial N}\right)_v \tag{2}$$

Due to the discontinuity of $\rho(\boldsymbol{r})$ with respect to N, left and right derivatives have to be associated with Equation (2):

$$f^-(\boldsymbol{r}) = \left(\frac{\partial \rho(\boldsymbol{r})}{\partial N}\right)_v^- \tag{3}$$

$$f^+(\boldsymbol{r}) = \left(\frac{\partial \rho(\boldsymbol{r})}{\partial N}\right)_v^+ \tag{4}$$

corresponding to the cases of electrophilic and nucleophilic attacks, respectively. In the present contribution, the so-called condensed Fukui functions[31] were calculated as described in Equation (5) and (6), where $N_k(N + 1)$, $N_k(N)$ and $N_k(N - 1)$ are the number of electrons on atom k in the $N + 1$, N and N - 1 electron system.

$$f_k^-(\boldsymbol{r}) \approx N_k(N) - N_k(N-1) \tag{5}$$

$$f_k^+(\boldsymbol{r}) \approx N_k(N+1) - N_k(N) \tag{6}$$

The condensed local softnesses are then obtained by multiplying the appropriate Fukui function with the global softnesses, approximated as described in Equation (7), where IE and EA are the vertical ionization energies and electron affinities respectively.

$$S \approx \frac{1}{IE - EA} \tag{7}$$

In a final stage, the complexation energy was calculated using Equation (8) derived within the framework of the hard and soft acids and bases principle,[29] which was already applied successfully in the past.[32] This equation results from a decomposition of the interaction energy of two systems A and B into two terms: the first term, ΔE_v, representing the energy change at constant external potential and corresponding to the charge transfer process between A and B at constant external potential, and the second term, an energy change, equivalent to a reshuffling of the charge distribution at constant chemical potential ΔE_μ, :

$$(\Delta E_{\text{int}})_{AB} = -\frac{1}{2}\left(\frac{(\mu_A - \mu_B)^2}{S_A + S_B}\right)(S_A S_B) - \frac{1}{2}\left(\frac{\lambda}{S_A + S_B}\right) \tag{8}$$

In this expression μ is the chemical potential of A and B. The chemical potential μ has been calculated using Equation (9).

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v \approx \frac{IE + EA}{2} \tag{9}$$

The parameter λ has been shown to be proportional to an effective number of valence electrons involved in the interaction between A and B. Pal and co-workers have recently defined the parameter λ as the change in the electronic densities of the system before and after the interaction process.[32c,32d,32e] In this work however, the choice was made to set this parameter equal to 0.5, in accordance with previous studies by Gazquez and Mendez[29a] and our group.[32b] This methodology avoids the evaluation of λ using information about the electronic structure of the product and thus enhances the predictive ability of the method.

If the interaction on A is localized on an atomic site k, Equation (8) changes to Equation (10), where $f_{A,k}$ is the Fukui function value of the site k of system A.

$$(\Delta E_{\text{int}})_{Ak,B} = -\frac{1}{2}\left(\frac{(\mu_A - \mu_B)^2}{S_A f_{A,k} + S_B}\right)(S_A f_{A,k} S_B) - \frac{1}{2}\left(\frac{\lambda}{S_A f_{A,k} + S_B}\right) \tag{10}$$

In the evaluation of the condensed Fukui functions and local softnesses, NPA charges[33] were used showing less basis set dependence than the Mulliken[34] type charges[35] and avoiding certain difficulties associated with electrostatic potential based charges[36] for atoms buried withing the molecule.[37]

The trend in DFT complexation energies was compared with experimental data. It is well-known that the ^{119}Sn or ^{117}Sn resonance shifts to lower frequency when the tin nucleus extends its coordination.[17] Typically a difference of 150−200 ppm is noticed when going from coordination 4 to 5.[17] At the same time the $^1J(^{13}\text{C-}^{119/117}\text{Sn})$ coupling constant increases by 100−150 Hz.[17,18] Both parameters are useful for detecting complexation in the reaction of Sn(CH$_3$)$_3$X with halide anions. Thus standard 1D ^{1}H-decoupled ^{117}Sn spectra were recorded with a Bruker Avance 250 spectrometer. Solutions of Sn(CH$_3$)$_3$Cl and Sn(CH$_3$)$_3$Br in CDCl$_3$ were mixed with equimolar amounts of (CH$_3$CH$_2$CH$_2$CH$_2$)$_4$NY (Y = F, Cl, Br, I). For two of the salts (Y = Br and I) more aliquots were added in order to perform a titration experiment from which the association constant K_{ass} for the complex formation could be determined by fitting the experimental chemical shift to Equation (18) (vide infra) using a two parameter ($K_{\text{ass}}^{-1} = K_{\text{diss}}$, δ_{bound}) non-linear regression as implemented with SigmaPlot 2000 software (Jandel Scientific).

Results and Discussion

The DFT reaction energies, enthalpies and free energies of reaction (1) for X or Y = F, Cl, Br and I can be found

Table 1. Hybrid HF-DFT complexation energies ΔE, enthalpies ΔH (298.18 K) and free energies ΔG (298.15 K) for the reaction $Sn(CH_3)_3X + Y^- \rightarrow Sn(CH_3)_3XY^-$ with X, Y = F, Cl, Br and I. Also listed are the PCM free energies of solvation ΔG_s of the Lewis acid-base complexes $Sn(CH_3)_3XY^-$. All values are in kcal/mol

(X, Y)	ΔE	ΔH	ΔG	ΔG_s
(F,F)	−52.1	−52.3	−45.8	−35.0
(F,Cl)	−25.6	−25.6	−17.3	−31.8
(F,Br)	−20.6	−20.5	−12.9	−31.2
(F,I)	−15.6	−15.4	−7.6	−30.5
(Cl,F)	−57.5	−57.3	−49.0	−31.8
(Cl,Cl)	−28.9	−30.4	−19.3	−28.4
(Cl,Br)	−23.2	−23.0	−16.7	−27.9
(Cl,I)	−17.4	−17.7	−9.5	−26.3
(Br,F)	−59.8	−59.4	−51.7	−31.2
(Br,Cl)	−30.5	−30.2	−23.8	−27.9
(Br,Br)	−24.5	−25.3	−17.0	−27.4
(Br,I)	−18.3	−19.1	−10.2	−26.0
(I,F)	−62.6	−62.1	−53.9	−30.5
(I,Cl)	−32.5	−32.7	−24.2	−26.3
(I,Br)	−26.2	−27.0	−17.8	−26.0
(I,I)	−19.5	−19.7	−12.3	−24.9

in Table 1. Also given in this table are the free energies of solvation of the acid-base complexes estimated using the PCM model. As can be seen, the values of ΔE, ΔH and ΔG are all negative, implying that the formation of the products from the starting compounds is an energetically favourable process which is also exergonic in all cases. Moreover, one can make the following general conclusions: for a given halogen X in the Lewis acid, the complexation energies become less negative when going from F^- to I^-. For a given Lewis base Y^-, the complexation energies become more negative going from $Sn(CH_3)_3F$ to $Sn(CH_3)_3I$. As such, the complexation energy of $Sn(CH_3)_3I$ with F^- is the most negative. This indicates that the Sn atom in these Lewis acids preferably interacts with the hardest anion (F^-) in the series of nucleophiles and that a complexation with the softest anion (I^-) is always the least favourable. From the application of the HSAB principle, it can be concluded that the Sn atom is essentially hard in these compounds, in line with our previous work on the $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ nanocluster and the Sn containing crown ether compounds.[15,16] The free energies of solvation become more negative with decreasing size of the Lewis acid-base complex, in line with a simple Born-type[38] model. The ΔG_s values follow the same trends as the ΔG values so that, although there is a very large contribution of ΔG_s to the energy of association in solution, the trends are almost identical as in the gas phase (vide infra).

In order to gain more insight into the trends of the gas-phase complexation energies, they were interpreted within the framework of the HSAB principle, using the method of "softness matching", introduced and applied in many of our previous papers.[30] As the interaction occurs between the electrophilic Sn atom in the trimethyltinhalides and the nucleophilic halide ion, the most favorable interaction should take place when the difference of the local softnesses on both of these atoms is the smallest.

The difficulty lies however in the determination of the softness, both global and local, of the halide anions. It has been suggested repeatedly[39] that in order to estimate the relative ordering of the hardness of anions, the hardness of the corresponding uncharged radicals can be used, that is, the hardnesses of F^-, Cl^-, Br^- and I^- should have the same ordering as those of F, Cl, Br and I. However, now absolute hardness values are needed, since these can now be compared with those of the Lewis acids for which the usual approach can be adopted. Furthermore, the values of the electronegativities of the halide anions are also unknown. However, they can in principle be estimated from a Taylor series expansion of the electronegativity with respect to the charge q on the atom.[4a] Indeed :

$$\chi(q) \approx \chi^0 + 2\eta^0 q \tag{11}$$

where χ^0 and η^0 are the electronegativity and hardness of the corresponding uncharged system. Since for an anion $q = -1$, this equation can be rewritten as shown in Equation (12), indicating that the electronegativity of the anion $[\chi(-1)]$ is the difference of the electronegativity χ^0 and twice the hardness η^0 of the corresponding neutral atom..

$$\chi(-1) \approx \chi^0 - 2\eta^0 \tag{12}$$

Table 2. Polarizabilities of Y [α (Y)] and Y^- [α (Y^-)] (au), together with their hardnesses η (Y) and η (Y^-) (eV). Also given are the condensed local softnesses $s^-_{Y^-}$ of the bases Y^- (The condensed Fukui functions are all equal to 1) and the electronegativities of Y χ(Y) (eV)

Atom (Y)	α (Y)	α (Y^-)	η (Y)	η (Y^-)	$s^-_{Y^-}$	χ(Y)
F	3.57	8.85	7.11	2.86	4.75	10.64
Cl	14.82	28.78	4.70	2.42	5.62	8.38
Br	21.43	41.97	4.20	2.14	6.35	7.75
I	32.81	56.68	3.65	2.11	6.44	6.94

These values can also be found in Table 2. As can be seen, this leads in most cases to very small and even negative estimates of the electronegativity of the anion. As a result, the electronegativities of these anions were set equal to zero in this work.

The next problem consists of estimating the absolute hardness of the anions. In order to deal with this problem, the following approach was adopted. It has been proposed several times[40] that the global softness is proportional to the polarizability of the system. We then assumed that the ratio of the global softness values of the neutral halogen atom and the halide anion is equal to the ratio of their polarizabilities as described in Equation (13) so that an estimate of the global softness of Y^- can be obtained as demonstrated in Equation (14).

$$\frac{S_{Y^-}}{S_Y} \approx \frac{\alpha_{Y^-}}{\alpha_Y} \tag{13}$$

$$s_{Y^-} \approx \frac{\alpha_{Y^-}}{\alpha_Y} s_Y \tag{14}$$

The hardness of the halide ions Y^- (= $1/(2S_{Y^-})$) obtained in this way which are, to the best of our knowledge, the first absolute, theoretically evaluated, numerical gas phase values, are given in Table 2, together with the polarizability and the hardness of the corresponding neutral halogens and the polarizabilities of the halide anions. As can be seen by comparison with the global hardness values of the Lewis acids $Sn(CH_3)_3X$ given in Table 3, these anions are all softer than the Lewis acids. Moreover, as stated many times in the literature,[39] the hardness sequence is $\eta(F^-) > \eta(Cl^-) > \eta(Br^-) > \eta(I^-)$.

Table 3. Chemical potential μ (eV), hardness η (eV) and polarizabilities α (au) of the Lewis acids considered in this work. Also given are the condensed Fukui functions, local softness and charges on the Sn atom, all in au

Lewis acid	μ	η	α	f^+_{Sn}	s^+_{Sn}	q_{Sn}
$Sn(CH_3)_3F$	−4.30	5.71	74.3	0.24	0.57	2.19
$Sn(CH_3)_3Cl$	−4.23	5.47	90.5	0.25	0.61	1.91
$Sn(CH_3)_3Br$	−4.22	5.24	99.7	0.29	0.75	1.82
$Sn(CH_3)_3I$	−4.13	4.93	114.9	0.36	1.00	1.71

The condensed local softnesses for the Lewis acids and bases are given in Table 2 and 3. As can be seen with the use of Figure 1, the principle of softness matching (i.e. looking for the smallest softness difference between the acceptor atom in the Lewis acid and the donor atom in the Lewis base) perfectly explains the two above mentioned sequences for the complexation energies. From Figure 1, it can be seen that all the Lewis acids are harder than the Lewis bases and since F^- is the hardest Lewis base, the smallest local softness difference always occurs with F^-. Furthermore, since the softness of the Sn atom in $Sn(CH_3)_3I$ is the highest, the complexation energies of this compound with the halide ions are more negative than for the other $Sn(CH_3)_3X$ compounds. In the next step, the complexation energies were correlated with the absolute value of the softness difference between the Sn atom and the Lewis base as shown in Equation (15).

$$\Delta s = \left| s^+_{Sn} - s^-_{Y^-} \right| \tag{15}$$

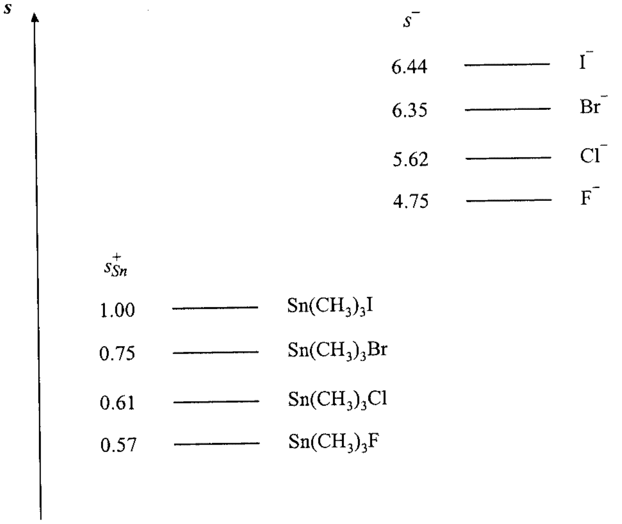

Figure 1. Relative ordering of the local softness of the Sn atom in the $Sn(CH_3)_3X$ compounds and the halide anions. All values are in au

From the HSAB principle, it can be inferred that the smaller the value of this difference, the more negative the complexation energy should be. This can indeed be deduced from Figure 2, where the correlation is shown (r^2 = 0.91).

In a final step, the complexation energies, as determined from Equation (10) were correlated with the DFT values from Table 1. This correlation (r^2 = 0.94) is depicted in Figure 3. As stated in Section 2, the parameter λ, which is proportional to the effective number of valence electrons part-

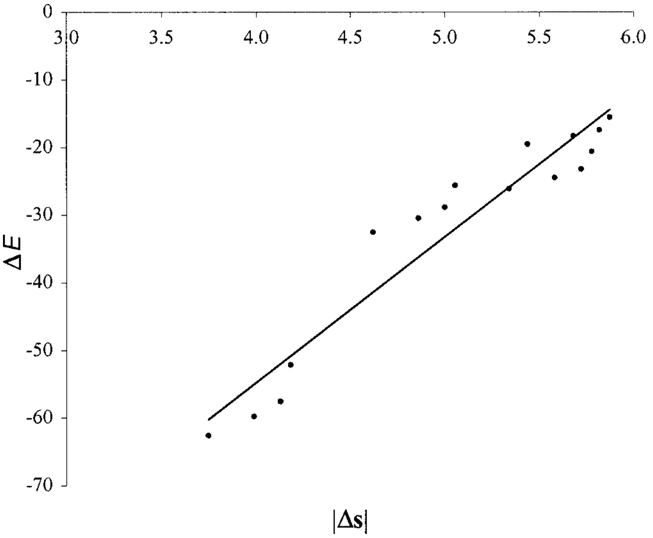

Figure 2. Correlation of the softness difference (au), defined in Equation (15) with the ab-initio complexation energies (kcal/mol)

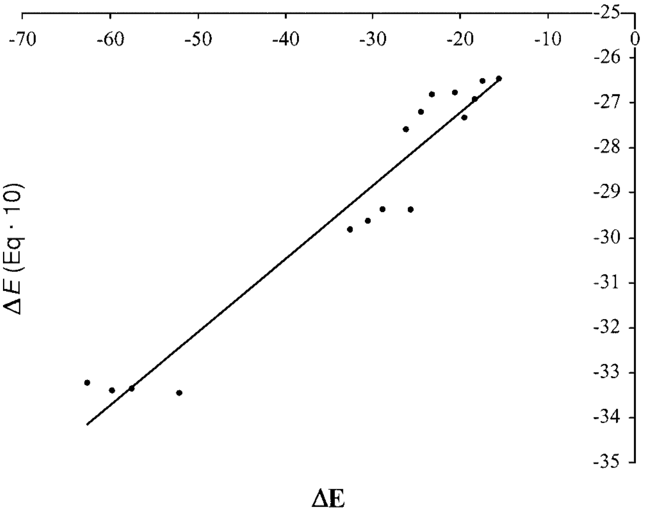

Figure 3. Correlation of the complexation energies (kcal/mol), as calculated from Equation (10) with the ab-initio complexation energies (kcal/mol).

icipating in the interaction, was arbitrarily set to 0.5. With this value, the second term in Equation (10) is dominant and accounts for 77 (X,Y = I) to 88% (X,Y = F) of the total interaction energy. Moreover, the correlation coefficient r^2 does not drop below 0.9 when λ is varied between 0.3 and 1.0. This is again a fine example of the usefulness of the concepts introduced within the framework of conceptual DFT. The correct trends in complexation energies can be recovered from equations involving properties only associated with the reagents.

The Lewis acidities of the tin compounds have also been analyzed by considering the charge of the tin atoms in the different compounds, given in Table 3. Assuming that a more positive tin reflects a higher Lewis acidity, the charge sequence shown in Table 3 should also reflect the acidity sequence.

$Sn(CH_3)_3F > Sn(CH_3)_3Cl \approx Sn(CH_3)_3Br \approx Sn(CH_3)_3I$

This trend is however the reverse of that seen in the computed complexation energies. Moreover, it can be deduced from Table 3 that electronegativity differences apparently do not strongly affect the charge on the tin atom. This leads to the conclusion that the interaction of the tin halides with halide ions is essentially orbitally controlled and not charge controlled. Indeed, when using the concept of softness matching, one considers the reaction to be orbitally controlled, whereas in the case of hard-hard interactions, charge control is implied. It has been argued recently by Chattaraj[41] that the maximum Fukui function (or local softness) site is the best for the frontier-controlled soft-soft reactions whereas for the charge-controlled hard-hard interactions the preferred site is associated with the maximum net charge and not necessarily the minimum Fukui function.

Our results for the relative Lewis acidities of $Sn(CH_3)_3F$, $Sn(CH_3)_3Cl$, $Sn(CH_3)_3Br$ and $Sn(CH_3)_3I$ are in line with the findings of Frenking et al.[42] They have shown that for the Lewis acids BX_3 (with X = F, Cl, Br and I), the hydride affinity increases from BF_3 to BI_3, although the p(π) population is higher in BI_3 than in BF_3. Moreover, they demonstrated that the electronic structure of the Lewis acid alone is not sufficient to determine the affinity toward a nucleophile.

^{117}Sn chemical shifts and $^1J(^{13}C\text{-}^{117}Sn)$ coupling constants for $Sn(CH_3)_3Cl$ and $Sn(CH_3)_3Br$ mixed with an equimolar amount of $(CH_3CH_2CH_2CH_2)_4N^+X^-$ are summarized in Table 4. As the anion exchange is fast on the ^{117}Sn NMR timescale the experimental chemical shifts and $^1J(^{13}C\text{-}^{117}Sn)$ coupling constants are weighted averages of free and complexed species and as such reflect the amount of complexation or, indirectly, the association constant of the formed complex. The NMR measurements show, for a given halogen X, a difference in chemical shift and $^1J(^{13}C\text{-}^{117}Sn)$ coupling constant between the uncomplexed and complexed species that decreases along the series F > Cl > Br > I in accordance with the calculated complexation energies. Since however the difference in chemical shift is not only dependent on the strength of the formed complex but also influenced by the nature of the complexing halide, a more elaborate ^{117}Sn NMR titration experiment was performed for two of the salts, in order to determine the association constants in an independent way.[43] The dependence of the ^{117}Sn chemical shift on the concentration of complexed species is given by the Equation (16), where $\delta_{obsd.}$ is the ^{117}Sn chemical shift of the fast exchanging triorganotin compound observed for a given analytical concentration $[Y^-]_0$, whereas δ_{bound} and δ_{free} are the ^{117}Sn chemical shifts of the complexed and free R_3SnX respectively.

Table 4. ^{117}Sn chemical shifts and $^1J(^{13}C\text{-}^{117}Sn)$ coupling constants for compounds $(CH_3)_3SnCl$ and $(CH_3)_3SnBr$ in $CDCl_3$ before and after addition of an equimolar amount of $(CH_3CH_2CH_2CH_2)_4NX$; $\Delta\delta$ refers to the difference in chemical shift between the complexed and uncomplexed species

X	$Sn(CH_3)_3Cl$ δ (ppm)	Δδ	$^1J(^{13}C\text{-}^{117}Sn)$ (Hz)	$Sn(CH_3)_3Br$ δ (ppm)	Δδ	$^1J(^{13}C\text{-}^{117}Sn)$ (Hz)
–	170.7	–	360	137.1	–	345
F	−41.4	212.1	530	−34.1	171.2	515
Cl	−24.0	194.7	496	−8.2	145.3	474
Br	−12.1	182.8	480	7.7	129.4	454
I	47.5	123.2	430	22.1	115.0	437

$$(\delta_{obs} - \delta_{free}) = \frac{\left[R_3SnXY^-\right]_e}{\left[R_3SnX\right]_0}(\delta_{bound} - \delta_{free}) \tag{16}$$

The actual equilibrium concentration of the adduct $[R_3SnXY^-]_e$ in solution obeys Equation (17) with $C = [R_3SnX]_0 + [Y^-]_0$, where, in both equations, $[R_3SnX]_0$ represents the analytical concentration of the trimethyltin halide under consideration.

$$\left[R_3SnXY^-\right]_e = \frac{1}{2}\left\{\left(C + K_{ass}^{-1}\right) - \sqrt{\left(C + K_{ass}^{-1}\right)^2 - 4\left[R_3SnX\right]_0\left[Y^-\right]_0}\right\} \tag{17}$$

Substituting Equation (17) into Equation (16) and solving $\delta_{obsd.}$ gives Equation (18)

$$\delta_{obs} = \delta_{free} + \frac{(\delta_{bound} - \delta_{free})\left\{\left(C + K_{ass}^{-1}\right) - \sqrt{\left(C + K_{ass}^{-1}\right)^2 - 4\left[R_3SnX\right]_0\left[Y^-\right]_0}\right\}}{2\left[R_3SnX\right]_0} \tag{18}$$

By fitting $\delta_{obsd.}$ to Equation (18) using a non-linear regression the parameters $K_{ass}^{-1} = K_{diss}$ and δ_{bound} were obtained. These data are summarized in Table 5. From this

Table 5. Dissociation constants of the complexes $(CH_3)_3SnClY^-$ and $(CH_3)_3SnBrY^-$ in $CDCl_3$ solution, obtained by fitting ^{117}Sn chemical shifts to Equation (18)

X	$Sn(CH_3)_3Cl$	$Sn(CH_3)_3Br$
I^-	$(8 \pm 2) \times 10^{-2}$	$(9 \pm 2) \times 10^{-2}$
Br^-	$(1.3 \pm 0.4) \times 10^{-2}$	$(3.1 \pm 0.1) \times 10^{-2}$

table it is again clear that Br^- forms more stable complexes than I^- for a given $(CH_3)_3SnX$ in accordance with our earlier statement and the calculated complexation energies. Comparison of the dissociation constants of $(CH_3)_3SnCl$ for both complexing anions with those of $(CH_3)_3SnBr$ indicate that the first one has slightly higher association constants than the latter one, whereas the calculations predict the reverse order. However for both the calculated complexation energies and the experimentally obtained assocation constants the differences between the two are rather small. From the experimentally determined association constants, it can indeed be deduced that the difference in complexation free energy between $(CH_3)_3SnCl$ and $(CH_3)_3SnBr$ amounts to 0.51 and 0.07 kcal/mol upon complexation with Br^- or I^- respectively, which is well below what is considered to be chemically accurate in quantum chemical computations. Moreover, the computed free energy differences for these compounds are also below 1 kcal/mol. The addition of the free energies of solvation of the Lewis acid-base complexes, computed using the PCM model, to the gas phase free energies of complexation in the case of the reaction of $Sn(CH_3)_3Cl$ and $Sn(CH_3)_3Br$ with Br^- reverses the gas phase trend in agreement with the solution phase dissociation constants. In the case of the complexation of $Sn(CH_3)_3Cl$ and $Sn(CH_3)_3Br$ with I^- however, the reversal is not achieved. The difference between the gas phase and solution phase free energies however being reduced to around 0.4 kcal/mol.

The ${}^1J({}^{13}C\text{-}{}^{117}Sn)$ coupling constants in Table 4, being weighted averages of those in the free and complexed species, reflect the geometry of the formed complexes. These data indeed depend on the percentage of s character in the Sn−C bond and thus the trigonal bipyramidal character of the resultant compound. Inspection of the data indicate that the highest values are found after complexation with F^-, followed by Cl^-, Br^- and finally I^-, again in accordance with the calculated complexation energies.

Conclusions

A combined theoretical and experimental NMR study of the complexation reaction between $Sn(CH_3)_3X$ and a halide ion Y^- ($X, Y = F^-, Cl^-, Br^-$, and I^-) has been carried out.

For a given Lewis acid, the ab-initio complexation energy becomes more negative upon going from F^- to I^-. For a given Lewis base, $Sn(CH_3)_3I$ is always found to give the most negative interaction energies. It was shown that complexation energies become more negative when the softness difference between the acceptor atom in the Lewis acid and the donor atom in the Lewis base becomes smaller, in agreement with the hard and soft acids and bases principle. Moreover, a quantitative agreement of the DFT complexation energies and an expression, derived within the framework of conceptual density functional theory, has been put forward. In this way, high level ab-initio computed complexation energies of medium sized tin compounds, combined with the first ab-initio evaluation of halide anion hardness, have provided insight into the ordering of the Lewis acidities of these compounds and in the interpretation of the strength of the Lewis acid-Lewis base interaction in terms of the HSAB principle in a parameter free context. Both experimentally measured ${}^{117}Sn$ chemical shifts and ${}^1J({}^{13}C\text{-}{}^{119}Sn)$ coupling constants for the $Sn(CH_3)_3Cl$ and $Sn(CH_3)_3Br$ compounds confirm the computed complexation energy ordering $F^- > Cl^- > Br^- > I^-$. In addition, association constants of these two Lewis acids with Br^- and I^- have been calculated and lead to the same conclusion.

Acknowledgments

P. G. wishes to acknowledge the Free University of Brussels (VUB) and the Fund for Scientific Research Flanders (Belgium) (FWO) for continuous support to his group. R. W. and M. B. are indebted to the Fund for Scientific Research Flanders (Belgium) (FWO) for a research grant (G.0016.02). This work was partially supported by the Helen and Martin A. Kimmel Center for Molecular Design (JM). R. V. R wishes to thank the Colombian Institute for Science and Development, Colciencias, and the Universidad de Cartagena (Cartagena, Colombia) for a PhD fellowship.

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Received January 17, 2003