The effect of the halide on the Lewis acidity of organotin halides

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Abstract

Thermodynamic parameters for adduct formation by R_nSnX_{4-n}, where R is methyl, ethyl, or butyl, and X is Cl, Br, or I, with tributylphosphine (TBP) in benzene and chlorobenzene solvents are reported. These data are combined with previously reported data for the same systems with triphenylphosphine oxide (TPPO). The enthalpies of adduct formation generally increase in the order Cl < Br < I thus producing a reversal of the acid-strengthening effects due to substitution of more electronegative elements. Equilibrium constants, however, increase in the order I < Br < Cl, indicating a dominance of the entropy term for formation of these organotin halide adducts with TBP and TPPO.

Introduction

In 1966 Bolles and Drago [1,2] reported the results of two studies on Me_3SnCl and Me_3SnI adduct formation with several bases in CCl_4 solvent. The enthalpy change for the organotin chloride adduct with dimethylacetamide in CCl_4 solvent was found to be -7.9 ± 0.3 kcal mol^{-1} while that for the organotin iodide was -9.4 ± 0.3 kcal mol^{-1}. The $J(^{119}Sn-CH_3)$ coupling constant was approximately the same for both adducts and the rehybridization energy was assumed to be similar in both cases. The larger enthalpy of formation for the iodine adduct was attributed to differences in the magnitude of the tin–halogen bond energy and a reduced sensitivity of the tin–halogen bond energy to changes in hybridization of the tin as the size of the halogen increases. Adding to this unexpected behavior of the enthalpies was that the equilibrium constant for the iodide complex was much less than that for the chloride complex.

Subsequent investigations by Yoder et al., [3] found that the enthalpies of adduct formation and the equilibrium constants for the interaction of trimethyltin halides with triphenylphosphine oxide (TPPO) also followed the trend reported by Bolles

and Drago. Yoder et al., suggested that the more exothermic enthalpy of adduct formation for the tin halides containing the least electronegative halogen was due to the formation of a stronger bond between tin and the base. Stronger tin-base bonds would cause a greater loss in entropy of the adduct which in turn would lead to smaller equilibrium constants.

These organotin adducts produce an apparent reversal of the usual acid-strengthening effects produced by substitution of more electronegative elements. In addition, these adducts display the unusual effect of decreasing equilibrium constant with increasing exothermicity of bond formation. Thus, a further study of the effects produced by different halogens on the thermodynamic parameters of organotin halide-base adducts was undertaken.

Experimental

Reagents. Tributylphosphine was obtained from Aldrich Chemical Co. in 98% purity and checked for the presence of tributylphosphine oxide by ^{31}P NMR spectroscopy. In most cases it was vacuum distilled and then stored over molecular sieves. In several causes the purity was considered sufficiently high to use directly as obtained from Aldrich. The organotin acids were purified by vacuum sublimation or distillation. Purity was checked by proton, ^{13}C, and ^{119}Sn NMR spectra and melting points, and in all cases was believed to be greater than 98%. Benzene was dried over sodium and stored over molecular sieves. Chlorobenzene was distilled over P_2O_5 under nitrogen atmosphere.

Calorimetry. The Parr solution calorimeter Model 1451 thermistor bridge was utilized for the detection of temperature changes. The calorimeter was housed in an HE-43-2 DriLab constructed by Vacuum Atmospheres. The DriLab contained the calorimeter, a balance, and all necessary reagents so that the entire analysis from solution preparation to data collection could be carried out in a dry atmosphere. The analysis was carried out by a batch wise technique. A base was injected into a 100 ml solution of the acid in benzene which was contained in the reaction vessel. Usually a series of 10 successive injections of the base was made into the acid solution. After each injection an electrical calibration was carried out so that the heat resulting from each injection could be calculated. Then a new concentration of acid was utilized and the injection process repeated. The concentration of the acid solutions ranged from 0.01 to 0.1 M and the concentration of base ranged from 0.002 to 0.15 M. The enthalpy of solution at infinite dilution of TBP in benzene was 1.14 $\pm$ 0.05 and in chlorobenzene was 0.01 $\pm$ 0.01 kcal/mol. The schematic mapping techniques used for data analysis have been previously described [4,5].

NMR Analyses. Preparation of solutions and determination of equilibrium constants have been previously described [4,5].

Discussion

Drake et al. [6,7], carried out a series of investigations on the effects of halogens on chemical shifts and core binding energies for the compounds Me_3MX, Me_2MX_2, and $MeMX_3$, where X = Cl, Br, I and M = C, Si, Ge, Sn. From their studies, they concluded that for Me_nGeX_{4-n} compounds, the core binding energies of Ge $3d$ orbitals are "fairly similar for each value of n regardless of the nature of the

halogen ... thus, the halogens appear to have fairly similar electronegativities. This is consistent with the steadily increasing s-orbital participation by the halogen along the series $Cl > Br > I...$". They further note that "although the amount of this s-orbital participation is uncertain in absolute terms, the relative changes have the effect of reducing differences in the electronegativities of the halogens. Thus changes in core-level binding energies are more sensitive to the number of halogens present than to the nature of the halogen". Because similar trends are found for other organometallic compounds containing C, Si, and Sn, it seems that the same conclusions apply to Me_nSnX_{4-n} compounds. Bolles and Drago [1] rationalized the increase in $J(^{119}Sn-CH_3)$ with increasing donor strength of various bases on the adducts of Me_3SnI by assuming that the formal charge that tin manifests toward the methyl groups is due to increasing s-character in the tin–carbon bond. Thus the total charge on tin decreases with increasing s-character of the hybrid orbitals.

It seems certain that the number of halogens attached to R_nSnX_{4-n} significantly influences the acidity of the compound. Both equilibrium constants and enthalpies of adduct formation increase considerably through the series R_3SnX, R_2SnX_2, $RSnX_3$ [4,8,9,10,11]. However, electronegativity differences apparently do not strongly affect the formal positive charge on the tin of R_nSnX_{4-n} compounds. Thus effects due to the decreasing electronegativities of the halogens ($Cl > Br > I$) may not be significant.

The data of Table 1 show that the equilibrium constants for R_nSnX_{n-4} adducts with TBP and TPPO undergo a regular decrease from Cl to Br to I. Because the enthalpy becomes more negative or at best stays about the same in the same order $Cl < Br < I$, the entropy must be the dominant factor. The bonding between R_nSnX_{4-n} and the base produces new vibrations associated with the Sn–base bond. The higher the frequencies of the new vibrations, the greater the loss in entropy. Thus the thermodynamic data indicate stronger bonds and hence correspondingly higher vibrational frequencies in the adduct in the order $I > Br > Cl$.

The enthalpies change for the formation of an adduct with R_nSnX_{4-n} may be expressed as the sum of the solvation enthalpy and the intrinsic enthalpy of the Sn–base bond ΔH^{int}; then, for a reaction of the type

A + B = AB
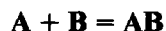
$$\Delta H = H^{solv}_{AB} - \left(H^{solv}_A + H^{solv}_B \right) + \Delta H^{int}_{AB}$$

$$= \Delta H^{solv} + \Delta H^{int}$$

where ΔH^{solv} is the solvation enthalpy of **AB**, **A**, and **B**, and ΔH^{int} is the enthalpy of bond formation for the adduct. The solvation of the adducts will be about the same for adducts which contain similar acids with the same base. In fact, it is known that the solvation of the adduct contributes relatively little to ΔH [12,13]. Therefore for the reaction of a series of acids with the same base in the same solvent, differences in ΔH will be due mainly to differences in the solvation of the free acid and the intrinsic enthalpy of the Sn–base bond. ΔH^{solv} will be positive thus making an unfavorable contribution to ΔH. ΔH^{int} will be negative and will favor adduct formation.

A similar analysis may be made of the entropy

$$\Delta S = \Delta S^{solv} + \Delta S^{int}$$

$$= S^{solv}_{AB} - \left(S^{solv}_A + S^{solv}_B \right) + \Delta S^{int}$$

Table 1

Thermodynamic parameters for adduct formation of $R_nS_nX_{4-n}$ with TBP and TPPO in benzene solvent, 298K

TPPO	K	$-\Delta H$ (kcal mol^{-1})	$-\Delta S$ (cal mol^{-1}K^{-1})
Me$_3$SnCl [a]	21.4±0.5 14 [b]	8.1±0.1	21
Me$_3$SnBr [a]	19±1 18 [b]	8.3±0.1	22
Me$_3$SnI [a]	11±1 12 [b]	9.4±0.3	27
Me$_3$SnCl [c]	4.0–3.1	7.9	23.8–24.2
Me$_3$SnI [c]	1.6	9.4±0.3	30.6
Me$_2$SnCl$_2$ [d]	126±19 460 [b]	9.3±0.1 8.8±0.4 [e]	21.6 17.3
Me$_2$SnBr$_2$ [d]	40±2 108 [b]	11.0±0.1 9.9±0.5 [e]	29.6 24.9
Bu$_2$SnCl$_2$ [d]	118±13 122 [b]	9.2±0.1	21.4
Bu$_2$SnBr$_2$	40±9 33 [b]	8.8±0.6	22.2
Et$_3$SnCl [a]	9.1±0.4 14 [b]	8.3±0.2	23.7
Et$_3$SnBr [a]	7.6±0.5 16 [b]	8.7±0.2	25.7
TBP			
Bu$_2$SnCl$_2$	293±28 313 [b] 322±17 [f]	13.6±0.1 – 13.1±0.2 [f]	34.3 – 31.8 [a]
Bu$_2$SnBr$_2$	220±30	14.2±0.5	36.9
Bu$_2$SnI$_2$	14±1	13.1±0.5	38.7
Me$_2$SnCl$_2$	926±217 909 [b] 1002±60 [f]	14.5±0.1 – 12.9±0.4 [f]	35.1 – 28.9
Me$_2$SnBr$_2$	277±20	14.7±0.1	38.1
Me$_2$SnI$_2$	53±2	14.5±0.1	40.8
TBP [g]			
Me$_2$SnCl$_2$	K_1: 1600±200 K_2: 7±2	13.7±0.1 7±2	31.3 19.6
Me$_2$SnBr$_2$	803±60	13.9±0.1	33.3
Me$_2$SnI$_2$	86±10	13.7±0.2	37.1

[a] Ref. 3. [b] Determined by NMR analysis. [c] Ref. 1,2. [d] Ref. 4. [e] Calculated from a combination of NMR and calorimetric data. See ref. 4. [f] Y. Farhangi, O.P. Graddon, J. Organomet. Chem., (1975) 87, 67. [g] Chlorobenzene solvent.

The solvation of the free acid reduces the entropy of the free acid and thus favors the formation of adduct. Loss of translational and rotational degrees of freedom during adduct formation will produce a decrease in intrinsic entropy. The heavier the tin halide the greater (more negative) the entropy loss will be for translation and rotation. The gain in intrinsic entropy that results from six new vibrational degrees of freedom in the adduct will depend on the strength of the Sn–base bond in the adduct. If the new vibrational degrees of freedom have high frequencies the entropy

Table 2

Solvation of Me$_3$SnX in benzene, 298 K (kcal mol^{-1})

	ΔH_s [a]	ΔH [b]	ΔH^{solv}
Me$_3$SnCl	4.42 ± 0.20	13.6 [c]	−9.2
Me$_3$SnBr	1.02 ± 0.13	11.3 ± 1.0 [d]	−10.3
Me$_3$SnI	0.49 ± 0.13	11.5 ± 1.0 [d]	−11.0

[a] Ref. 3. [b] Enthalpy of vaporization of the iodide and bromide, enthalpy of sublimation for the chloride. [c] The enthalpy of formation of the liquid is reported as −50.9 ± 2.5 kcal mol^{-1} [15], and that of the gas as −41.8 kcal mol^{-1} [17]. The enthalpy of fusion of Me$_3$SnBr may be calculated to be 4.5 kcal mol^{-1} [15,16]. If the enthalpies of fusion of Me$_3$SnBr and Me$_3$SnCl are assumed to be the same, the enthalpy of formation of solid (Me$_3$)SnCl is calculated to be −55.4 kcal mol^{-1}. [d] Ref. 15.

gain will be less than if the new vibrations are of low frequency. That is, if the intrinsic bond enthalpy is large, the entropy loss due to high frequency vibrations in the adduct will be correspondingly large. Overall, the translational and rotational losses exceed the vibrational gains and ΔS^{int} is negative. ΔS^{solv}, however, will be positive.

A strong intrinsic bond enthalpically favors formation of the adduct but at the same time produces an unfavorable entropy. Strong solvation produces an overall unfavorable ΔH but a favorable ΔS contribution to the free energy.

It is possible to evaluate the solvation of each acid in the series Me$_3$SnCl, Me$_3$SnBr, and Me$_3$SnI by benzene solvent. The enthalpies of solution of all three acids in benzene are known [14] and data are available which will allow the calculation of the enthalpy required to transfer each acid from the gas phase to benzene. The enthalpies of vaporization of the bromide and iodide are available from the literature [15]. Me$_3$SnCl is a solid and hence the enthalpy of sublimation must be known. There are two literature sources [16,17] from which the enthalpy of sublimation may be calculated but there is considerable disagreement in the two. If the enthalpy of fusion for Me$_3$SnCl is assumed to be the same as that of Me$_3$SnBr, the data given in Table 2 can be calculated. These data for the chloride seem to be quite consistent with other data reported for the bromide and iodide and with the trends expected for the replacement of one halogen by another. Based on trends for enthalpies of vaporization, for example, it would be expected that ΔH_{vap} should be about 11.5 for the iodide, 10.5 for the bromide, and 9.5 for the chloride. The data used give 11.5 ± 1, 11.3 ± 1, and 9.1 for the Cl, Br, and I, respectively. The enthalpy of transfer from the gas phase to benzene is then −9.2, −10.3, and −11.0 kcal mol^{-1}, respectively, for the chloride, bromide, and iodide. Thus the iodide is more solvated than the bromide which is in turn more solvated than the chloride. Formation of the adduct by the chloride is more favored enthalpically by this solvation but entropically the solvation favors adduct formation by the iodide.

The data of Table 1 show that the overall enthalpy for adduct formation generally increases (becomes more negative) in the order Cl < Br < I. Because solvation effects would produce the opposite, the intrinsic bond strength must also follow the order Cl < Br < I. The trend in equilibrium constants (Cl > Br > I) is due to an increasingly negative ΔS for formation of the chloride, bromide, and iodide adducts, respectively. The trend in ΔS must be attributed to a greater intrinsic entropy loss because solvation effects on the entropy act to produce an opposite trend.

It is assumed that the same rationale applies to the dihalides; i.e., solvation increases in the order Cl < Br < I and intrinsic bond strength to the base increases in the order Cl < Br < I.

The intrinsic changes dominate in these cases. In other solvents solvation effects may be more important.

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