Thermodynamics of Metal–Ligand Bond Formation
XXXV. Lewis Acidity of Tin(IV) Halides

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Abstract

Thermodynamic data have been obtained for the reactions in benzene solution at 30 °C of tin tetrahalides with the following Lewis bases: triphenylarsine, tetrahydrothiophene, tetrahydrofuran, pyridine-N-oxide, dimethylsulphoxide, dimethylformamide and acetonitrile.

Triphenylarsine forms a 1:1 adduct of low stability with tin tetrachloride and fails to react with the other halides. The other bases when they react form both 1:1 and 1:2 adducts, the reactivity decreasing in the order $SnCl_4 > SnBr_4 > SnI_4$. THT and THF do not react with SnI_4; CH_3CN does not react with $SnBr_4$ or SnI_4. When it is possible to determine data separately for formation of successive adducts it is found that $K_1 > K_2$ for $SnCl_4$ and $SnBr_4$ but $K_1 < K_2$ for SnI_4.

Introduction

The Lewis acidity of tin tetrahalides has been studied extensively and the types of addition compounds formed were reviewed more than twenty years ago [1]. Crystal structure determinations have revealed that 6-coordinate adducts with 'pointed' ligands, such as $SnCl_4(dimethylsulphoxide)_2$ [2], $SnI_4(diphenylsulphoxide)_2$ [3] and $SnCl_4(CH_3CN)_2$ [4] are *cis* octahedral, whereas those with 'blunt' ligands, such as $SnX_4(pyridine)_2$ [5] and $SnCl_4$-$(tetrahydrothiophene)_2$ [6] are *trans* octahedral. In some instances *cis/trans* isomerism has been demonstrated for adducts with dimethylformamide, dimethylacetamide and dimethylsulphoxide [7].

Thermochemical data have been reported for the precipitation of pyridine adducts from hexane solutions [8] and for the formation of tetrahydrofuran adducts of $SnCl_4$ [5], but there has been no wider quantitative study of the Lewis acidity of tin halides, probably because the adducts formed are often insoluble.

This paper reports thermodynamic data, obtained by calorimetric titration in benzene solution at 30 °C, for the reactions of SnX_4 ($X = Cl$, Br, I) with the unidentate bases: triphenylarsine, tetrahydrothiophene (THT), tetrahydrofuran (THF), pyridine-N-oxide, dimethylsulphoxide (DMSO), dimethylformamide (DMF) and acetonitrile.

Experimental

Materials

Tin tetrachloride (BDH) and tin tetrabromide (Aldrich) were purified by distillation. Tin tetraiodide was prepared from tin and iodine [9] and purified by crystallization from chloroform. Acetonitrile was purified by double distillation from phosphorus pentoxide and stored over a molecular sieve; other liquid bases were purified by distillation and stored over anhydrous potassium carbonate. Triphenylarsine and pyridine-N-oxide were purified by crystallization from ethanol. Benzene for use as solvent was purified by freezing and distillation and dried over calcium hydride. All manipulations were carried out in a dry box.

Calorimetry

Calorimetric titrations were carried out in a LKB 8700 calorimeter, using the previously described technique [10]. Briefly, a benzene solution of the base was titrated into 100 ml of a benzene solution of the tin halide and the heat produced was measured after each incremental addition of titrant. The enthalpy change was obtained from the extrapolated integrated heat of reaction and the adduct formation constants, K, calculated at each experimental point. The enthalpy was then refined iteratively by computer to give constant values of K throughout the titration. In cases where both 1:1 and 1:2 adducts were formed the final refinement of the best-fit values of the parameters K_1, K_2, ΔH_1 and ΔH_2 was made using a computer programme which allowed

TABLE I. Thermodynamic Data[a] for Reaction of SnX with Lewis Bases (according to eqns. (1) and (2)) in Benzene Solution at 30 °C.

Base	X	K_1	K_2	$K_1 K_2$	$-\Delta H^{\circ}_1$	$-\Delta H^{\circ}_2$	$-\Delta H^{\circ}_{1+2}$
Ph$_3$As	Cl	15			60 ± 2		
THT	Cl			$>10^8$			86 ± 3
	Br	56	94	5200	46 ± 1	47 ± 3	93 ± 2
THF	Cl	1700	400	7×10^5	62 ± 3	55 ± 3	117 ± 2
	Br	11	5	55	72 ± 2	65 ± 1	137 ± 3
py-NO	I			$>10^8$			108 ± 4
DMSO	Br[b]			$>10^8$			130 ± 3
	I	400	760	3×10^5	44 ± 1	55 ± 1	99 ± 2
DMF	Cl			$>10^8$			160 ± 6
	Br			$>10^8$			130 ± 3
	I	21	78	1640	38 ± 1	47 ± 4	85 ± 3
CH$_3$CN	Cl	7	4	28	50 ± 1	10 ± 1	60 ± 1

[a]K in litre mol^{-1}, ΔH° in kJ mol^{-1}. [b]For SnBr$_4$(benz) + 2DMSO(benz) = SnBr$_4$(DMSO)$_2$(cryst).

visual matching of the experimental points with an enthalpogram calculated using selected values of these parameters.

Data in Table I are the average of at least three determinations for each system; uncertainties quoted for ΔH are mean deviations from the average values. Uncertainties are not quoted for K; previous experience indicates that for single-step reactions K can usually be obtained with an uncertainty of ±10% or less; for two-step reactions the errors are greater and ±25% would be a more realistic estimate. The technique does not allow the measurement of individual values of $K > 10^4$.

Results and Discussion

We have previously reported data for the reactions of organo-tin chlorides [11] and iodides [12] with various Lewis bases in benzene solution. In addition to the expected lower reactivity of the iodides it was also observed that when an intermediate 5-coordinate, 1:1 adduct could be detected it was usual that $K_1 > K_2$ for the chlorides but $K_1 < K_2$ for the iodides.

The results show that all bases except triphenylarsine form 1:2 adducts with detectable 1:1 intermediates.

Triphenylarsine reacts with SnCl$_4$ to form a 1:1 adduct of rather low stability, though the reaction is quite strongly exothermic. With SnBr$_4$ the heat produced was too small to be useful for calorimetric titration, probably because of a very low value of K rather than of $-\Delta H$. No reaction could be observed with SnI$_4$. The implication of these results is clearly that the very bulky ligand does not form stable 6-coordinate adducts and even the 5-coordinate adducts are seriously overcrowded.

Tetrahydrothiophene, which also has a large donor atom, also failed to react with SnI$_4$, but formed both 1:1 and 1:2 adducts with SnCl$_4$ and SnBr$_4$. For the chloride $K_1 \simeq K_2$, but for the bromide $K_1 < K_2$ and this change appears to be due mainly to the entropy term. It corresponds to the lowering of K_1 in the organo-tin iodides, also associated with overcrowding in the 5-coordinate species.

Tetrahydrofuran, which has a small donor atom but is a 'blunt' ligand, also failed to react with SnI$_4$, but formed both 1:1 and 1:2 adducts with SnCl$_4$ and SnBr$_4$. In both cases $K_1 > K_2$, though they are more nearly equal in the bromide; the chloride adducts are more stable though the enthalpy change is greater for the bromide; the lower stability of the bromide adducts is thus entropy determined, again suggesting that overcrowding may be occurring in the 1:1 adduct.

Pyridine-N-oxide, a 'pointed' ligand, forms insoluble adducts with SnCl$_4$ and SnBr$_4$ and a very stable 1:2 adduct with SnI$_4$ without a detectable 1:1 intermediate. Similar behaviour is shown in the reaction of dimethylsulphoxide with SnBr$_4$ (and the adduct precipitates), but SnI$_4$ reacts with this base to form both 1:1 and 1:2 adducts with $K_1 < K_2$. Dimethylformamide behaves in a similar manner, except that in this case all three halides form soluble adducts, but only those of the iodide are of low enough stability to allow detection of the intermediate 1:1 species and again $K_1 < K_2$.

Acetonitrile behaves as a very weak Lewis base towards the tin tetrahalides, despite being a 'pointed' ligand, and only the chloride generated sufficient heat for measurements to be made; these show very low values of K with $K_1 > K_2$.

Though limited on the one hand by the usually very low solubility of stable 1:2 adducts and on the other by the often low stability of soluble adducts,

these results show clearly that the typical behaviour of the tin tetrahalides is the successive formation of 5-coordinate 1:1 and 6-coordinate 1:2 adducts:

$$SnX_4 + B = SnX_4B \tag{1}$$

$$SnX_4B + B = SnX_4B_2 \tag{2}$$

For the chloride and bromide the enthalpy change is greater in the first step and $K_1 > K_2$. The differences between K_1 and K_2, however, are much less than in most systems in aqueous solution where large statistical effects result from the displacement of coordinated solvent molecules. For the iodide the enthalpy change is smaller in the first step and $K_1 < K_2$. This implies an unusually low stability for the 5-coordinate iodide species, as was also observed in the organo-tin iodides. In the present systems too, the most likely explanation for this appears to be a loss of fluxional ability in the 5-coordinate species due to overcrowding.

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