Thermochemical Study of the Reactions of Lewis Bases with Bis(ethane-1,2-dithiolato)tin(IV) in Benzene Solution

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Abstract

Thermodynamic data have been obtained by calorimetric titration in benzene solution at 30 °C for reaction of Lewis bases with bis(ethane-1,2-dithiolato)tin(IV) (SnS_4).

Unidentate bases form simultaneously 1:1 and 1:2 adducts with SnS_4, and bidentate bases form 1:1 adducts. The enthalpies of formation of the 1,10-phen adducts are similar to those of 1:2 adducts with py or 4-mepy and the stability of the TMEN adduct is similar to 1:2 adducts of piperidine with similar enthalpies of formation.

Pyridine *N*-oxide is the only non-nitrogen donor observed to form 1:2 adducts with smaller enthalpy changes but a rather big equilibrium constant, due to the smaller steric effect of the pointed N–O ligand.

The Lewis acidity of Sn(IV) compounds is according to the following order: $Ph_2SnS_2 < SnS_4 < SnI_4 < SnCl_4$.

Introduction

The Lewis acidity of tin(IV)tetrahalides is well established [1] and thermodynamic data have been reported in solution at 25 °C for the adducts of cyclic ethers [2]. During the last ten years much work has been done on the thermodynamics of organotin compounds with a wide variety of Lewis bases in different solvents [3–5].

Lewis acidity of the title compound, SnS_4, towards N- and O-atom donors was initially reported by Poller and Spillman [6, 7] who showed that 1:1 adducts are formed with bidentate ligands and that the complexes are *cis* in configuration; unidentate ligands form 1:2 adducts with *trans* configuration except Me_3NO which forms a *cis* adduct. Recent studies on the spirocyclic complexes of tin(IV) show [9, 10] a square pyramidal structure for the 5-coordinate and *trans* octahedral for the 6-coordinate adducts.

This paper reports thermodynamic data for the adduct formation of bis(ethane-1,2-dithiolato)tin(IV) with bidentate and unidentate nitrogen donors and pyridine-*N*-oxide in benzene at 30 °C.

Experimental

Materials

Bis(ethane-1,2-dithiolato)tin(IV) was prepared according to the literature [6] and its purity was checked by elemental analysis and melting point. Pyridine was purified by heating under reflux with potassium permanganate before distillation. Liquid bases were purified by distillation and dried over anhydrous potassium carbonate; 2,2′-bipyridine and 1,10-phenanthroline and pyridine-*N*-oxide were Merck ‘pro analysis’ and used without further purification. Benzene for use as a solvent was analytical reagent grade and dried over calcium hydride.

Calorimetry

Calorimetric titrations in benzene solution were carried out in an LKB 8700 precision calorimeter. Details of the technique used have been described by Graddon and Heng [11]. Briefly, a solution of the base was titrated into 100 ml of a solution of the SnS_4 compound in benzene and the heat change measured after each incremental addition of titrant. The enthalpy of reaction was obtained from the extrapolated, integrated heat of reaction and the adduct formation constant, *K*, calculated at each point; the enthalpy was then refined iteratively to give constant values of *K* throughout the titration.

In the case of all the 1:2 adducts ΔH°_{1+2} and K_{12} could be measured from the titration curve. Resolving these two parameters into four parameters $K_1, K_2, \Delta H_1$, and ΔH_2 was achieved by trial and error using a computer written program, which provides a visual match of experimental points to an enthalpogram computed from the four parameters.

Results and Discussion

Thermodynamic data for all the unidentate bases are summarised in Table I. All these bases form 1:1

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TABLE I. Thermodynamic Data for Formation of 1:2 Adducts of SnS_4 with Unidentate Bases in Benzene Solution at 30 °C

Base	$[SnS_4]$ ($mmol\ l^{-1}$)	K_1 ($l\ mol^{-1}$)	K_2 ($l\ mol^{-1}$)	K_{12} ($l^2\ mol^{-2}$)	$-\Delta H^\circ_1$ ($kJ\ mol^{-1}$)	$-\Delta H^\circ_2$ ($kJ\ mol^{-1}$)	$-\Delta H^\circ_{12}$ ($kJ\ mol^{-1}$)
$BuNH_2$	2.4–9.4	100 ± 10	203 ± 18	2.03×10^4	46 ± 3	49 ± 1	95 ± 4
PyNO	1.3–4.5	15 ± 2	107 ± 9	1.61×10^3	28 ± 1	29 ± 1	57 ± 1
Pip	2.4–9.8	100 ± 10	70 ± 8	7×10^3	58 ± 4	25 ± 1	83 ± 4
4-mepy	1.7–8.3	19 ± 3	36 ± 2	684	15 ± 1	72 ± 2	87 ± 3
Py	3.8–6.7	14 ± 2	12 ± 2	168	15 ± 1	67 ± 2	82 ± 2

TABLE II. Thermodynamic Data for Formation of 1:1 Adducts of SnS_4 with Bidentate Bases in Benzene Solution at 30 °C

Base	SnS_4 ($mmol\ l^{-1}$)	K ($l\ mol^{-1}$)	$-\Delta H^\circ$ ($kJ\ mol^{-1}$)	$-\Delta G^\circ$ ($kJ\ mol^{-1}$)	$-\Delta S^\circ$ ($J\ K^{-1}\ mol^{-1}$)
1,10-phen	1.11–4.00	$>10^4$	77.63 ± 0.96	>23.20	<180
TMEN	1.61–4.13	6.90×10^3	80.10 ± 1.8	22.27	189
2,2′-Bipy	1.74–6.09	1.19×10^3	64.40 ± 0.90	17.80	170

and 1:2 adducts; the titration curves could be fitted well for successive formation of both adducts (eqns. (1) and (2))

$$SnS_4 + B \rightleftharpoons SnS_4B \qquad (1)$$

$$SnS_4B + B \rightleftharpoons SnS_4B \qquad (2)$$

NH_2Bu forms adducts of the highest stability, the enthalpies of formation for the first and second adducts are almost the same, being −46 and −49 kJ mol^{-1} respectively while K_2 is twice as big as K_1; it is interesting to notice that while $NHBu_2$ and NBu_3 do not form addition compounds with SnS_4 in benzene solution, the inclusion of nitrogen in the ring causes piperidine to make adducts of five- and six-coordinate tin(IV) in which the enthalpy formation of the five-coordinate adduct is much more than that of the six-coordinate, even though the stability constants are roughly the same.

Heterocyclic bases form addition compounds of lower stability than the amines but the total enthalpies of formation are not significantly different. The first and second formation constants for adducts of py and 4-mepy are almost the same but $-\Delta H^\circ_2 \gg \Delta H^\circ_1$. Substitution of pyridine by $-CH_3$ in the 4-position increases the adduct stability due to the inductive effect, but substitution at the 2-position produces so great a steric effect that the adduct could not be formed.

Pyridine-*N*-oxide (pyNO) is the only oxygen donor observed to form adducts with SnS_4 in benzene solution. The overall $-\Delta H^\circ$ is distinctly lower than with the nitrogen donors, showing the weaker bond formation but the overall stability constants are higher than for py and 4-mepy; this is due to the smaller steric effect of the pointed N–O ligand.

Reactions with Bidentate Ligands

The complete thermodynamic data for the potentially bidentate ligands are summarized in Table II. 1,10-phenanthroline forms a very stable adduct with heat of adduct formation comparable to the addition of two molecules of py or 4-mepy; the high stability of the adduct is due mainly to the chelation effect. 2,2′-Bipyridine behaves as a bidentate too the reaction being 1:1 with an equilibrium constant of 1190 l mol^{-1}. The difference in ΔH and K between phen and 2,2′-bipy has been observed in many similar systems [3]. The thermodynamic data for tetramethylethylenediamine (TMEN) are comparable with those for the addition of two molecules of piperidine which clearly shows that the extent of solvation for SnS_4 in benzene solution is the same as for the adduct.

Ethane-1,2-dithiolatodiphenyltin (Ph_2SnS_2) does not react with the Lewis bases mentioned here and the result of calorimetric titration of SnI_4 and $SnCl_4$ [12] reveals the following Lewis acidity for Sn(IV) compounds: $Ph_2SnS_2 < SnS_4 < SnI_4 < SnCl_4$.

Attempts to carry out calorimetric titration of SnS_4 with 2-mepy, NBu_3, $NHBu_2$, DMSO and DMFA were unsuccessful, because the heats of reaction are very small; PPh_3, PBu_3, THF and thiophene showed no evidence of reaction with the title compound in benzene solution.

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