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THERMODYNAMICS OF METAL—LIGAND BOND FORMATION

XXVIII *. LEWIS ACIDITY OF ORGANOTIN CARBOXYLATES AND ISOCYANATES

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Summary

Thermodynamic data are reported for the formation in benzene solution of 1/1 adducts of $Ph_2Sn(OCOMe)_2$, $Bu_2Sn(OCOMe)_2$ and $Bu_2Sn(OCOEt)_2$ with pyridine, 4-methylpyridine, NBu_3, PBu_3, *N,N,N′,N′*-tetramethyl-1,2-diaminoethane and 1,10-phenanthroline; also for adducts of $Bu_2Sn(NCO)_2$ with pyridine, 4-methylpyridine and PBu_3. Several bases apparently caused disproportionation of the isocyanate. These tin compounds are weaker Lewis acids than R_2SnCl_2 or $R_2Sn(NCS)_2$ and there is no evidence that they add more than one equivalent of base.

Thermodynamic data are also reported for the formation of 1/1 and 1/2 adducts of organotin chlorides and $Bu_2Sn(NCS)_2$ with pyridine-*N*-oxide, which is generally a slightly stronger Lewis base than pyridine towards organotin compounds.

Introduction

The ability of organotin halides to behave as Lewis acids is well known: many adducts are known with bases, such as pyridine (py) or dimethylsulphoxide (DMSO), in which the coordination number of the tin atom is increased to five or six. Similar behaviour is shown by corresponding isothiocyanates, but there appear to have been few reports of Lewis acid behaviour in tin compounds in which the tin is bound to oxygen or nitrogen. Compounds such as the organotin carboxylates, however, often exist in polymeric forms, implying increased coordination number of the tin atom; this is confirmed in the crystal structure of tribenzyltin acetate [2], in which the coordination number of each tin atom is

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* Part XXVII, see ref. 1

raised to five by bridging acetate groups. Five-coordination in compounds of the type $R_3Sn(OCOMe)$ has also been demonstrated by Mossbauer studies [3] and recently the formation of complex acetate ions $[Sn(OCOMe)_5]^-$ and also $[Sn(OCOMe)_6]^{2-}$ has been shown by conductimetric studies in acetic anhydride solution and by the isolation of various salts [4], in one of which the coordination number of the tin atom is raised to seven [5].

We have previously reported thermodynamic data for the formation of base adducts of organotin chlorides and isothiocyanates in solution in non-donor solvents [6—8]. We have now extended these studies to the selected organotin carboxylates: $Ph_2Sn(OCOMe)_2$, $Bu_2Sn(OCOMe)_2$ and $Bu_2Sn(OCOEt)_2$. We have also studied the reaction of the diisocyanate, $Bu_2Sn(NCO)_2$ with a variety of Lewis bases. This paper reports thermodynamic data for these reactions in benzene solution, obtained by calorimetric titration; it also reports some additional data for the reaction of organotin chlorides with pyridine-*N*-oxide (py-NO). The alkoxide $Bu_2Sn(OMe)_2$ was also studied, but gave no evidence of Lewis acidity.

Reactions of organotin carboxylates with bases

The titration of unidentate nitrogenous bases, phosphines or pyridine-*N*-oxide into benzene solutions of $R_2Sn(OCOR')_2$ was accompanied by the liberation of heat, showing that reaction was taking place. When dimethylsulphoxide or 2,2'-bipyridine (bipy) was used as titrant there was no evidence of reaction and when 1,10-phenanthroline (phen) was used as titrant there was only a very small amount of heat liberated. With the more reactive bases the calorimetric titration data were consistent with the formation in solution of 1/1 adducts of moderate stability and rather small enthalpies of formation. Thermodynamic data for these reactions are given in Table 1.

Tributylphosphine had been found previously to form fairly stable adducts ($K > 300$ mol^{-1}) with R_2SnCl_2 and $Bu_2Sn(NCS)_2$ with enthalpies of formation in the range $50 < -\Delta H° < 80$ kJ mol^{-1} [6]. Other tertiary phosphines formed similar adducts but of rather lower stability [8]. The 1/1 adducts now observed with $R_2Sn(OCOR')_2$ are much less stable and with considerably smaller enthalpies of formation. These tin compounds are thus much weaker Lewis acids than the chlorides towards phosphines. This weaker acidity appears to be essentially an inductive effect and may be related to the lower electron-withdrawing power of the OCOR' group compared to Cl.

Tertiary amines were found to induce disproportionation in the organotin chlorides [6] but this does not occur with the acetates or the propionate. These form 1/1 adducts with tributylamine or *N,N,N',N'*-tetramethyl-1,2-diaminoethane (tmed). Enthalpies of adduct formation with tmed are near double those with NBu_3, suggesting that tmed behaves as a bidentate ligand, giving a coordination number of six; there are also small increases in the adduct stabilities, which support the proposition that the tmed is chelate. If this is so, however, the effect of chelation on adduct stability is much less than is commonly observed in aqueous solution; this is probably because in aqueous solution a favorable entropy change accompanies chelation, due to displacement of coordinated solvent, but in benzene solution there are not likely to be great differences in the degree of solvation of $R_2Sn(OCOR')_2$ and its adducts.

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF LEWIS BASES WITH ORGANOTIN CARBOXYLATES IN BENZENE SOLUTION AT 30°C

Base	Tin compound	K (l mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	$-\Delta G°$ (kJ mol^{-1})	$-\Delta S°$ (J K^{-1} mol^{-1})
PBu_3	$Bu_2Sn(OCOMe)_2$	11.3 ± 0.2	26.2 [a]	6.1 ± 0.1	66
PBu_3	$Bu_2Sn(OCOEt)_2$	7.3 ± 1.0	26.2 [a]	5.0 ± 0.4	70
NBu_3	$Bu_2Sn(OCOMe)_2$	15.8 ± 1.2	14.8 ± 0.8	7.0 ± 0.3	26 ± 3
NBu_3	$Bu_2Sn(OCOEt)_2$	10.3 ± 0.6	15.8 ± 0.8	5.9 ± 0.2	33 ± 3
NBu_3	$Ph_2Sn(OCOMe)_2$	80.3 ± 4.2	14.2 ± 1.0	11.0 ± 0.2	11 ± 4
tmed	$Bu_2Sn(OCOMe)_2$	46.4 ± 2.1	28.7 ± 1.4	9.7 ± 0.2	63 ± 5
tmed	$Bu_2Sn(OCOEt)_2$	46.0 ± 0.6	26.6 ± 0.5	9.7 ± 0.1	56 ± 2
tmed	$Ph_2Sn(OCOMe)_2$	81.9 ± 7.7	22.9 ± 1.1	11.1 ± 0.3	39 ± 4
py	$Bu_2Sn(OCOMe)_2$	3.1 ± 0.2	21.6 ± 0.5	2.9 ± 0.2	62 ± 2
py	$Bu_2Sn(OCOEt)_2$	2.6 ± 0.2	21.2 ± 0.5	2.4 ± 0.2	62 ± 2
py	$Ph_2Sn(OCOMe)_2$	19.3 ± 0.6	27.6 ± 0.5	7.4 ± 0.2	67 ± 2
4-mepy	$Bu_2Sn(OCOMe)_2$	4.7 ± 0.2	25.7 ± 1.5	3.9 ± 0.2	74 ± 2
4-mepy	$Bu_2Sn(OCOEt)_2$	3.5 ± 0.3	25.5 ± 0.3	3.2 ± 0.3	74 ± 2
4-mepy	$Ph_2Sn(OCOMe)_2$	49.4 ± 4.6	30.8 ± 0.5	9.8 ± 0.3	69 ± 3
phen	$Bu_2Sn(OCOMe)_2$	23.5 ± 0.1	37.0 [a]	8.0 ± 0.1	96
phen	$Bu_2Sn(OCOEt)_2$	13.9 ± 0.7	37.0 [a]	6.6 ± 0.2	100
py-NO	$Bu_2Sn(OCOMe)_2$	31.0 ± 1.5	16.8 ± 0.8	8.7 ± 0.2	27 ± 3
py-NO	$Bu_2Sn(OCOEt)_2$	23.4 ± 1.6	15.3 ± 0.9	8.0 ± 0.2	24 ± 4
py-NO	$Ph_2Sn(OCOMe)_2$	70.0 ± 4.6	30.8 ± 1.2	10.7 ± 0.1	66 ± 5

[a] Titrations could not be taken beyond 50% adduct formation; value of $\Delta H°$ selected on basis of ampoule experiments.

The enthalpies of formation of adducts with NBu_3 are rather smaller than with PBu_3. Though enthalpies as small as these are probably the result of numerous minor factors among which Sn—N and Sn—P bond strengths may not even be dominant, these results do suggest that in these compounds the tin atom is neither particularly "hard" nor "soft", but falls in the intermediate category [9].

Heterocyclic bases had previously been found [6] to form both 1/1 and 2/1 adducts with R_2SnCl_2, whereas bidentate bases, such as phen or bipy formed very stable 1/1 adducts. It was thus apparent that the tin atom in these compounds readily became six-coordinate. In contrast to this the carboxylates $R_2Sn(OCOR')_2$ form only 1/1 adducts of quite low stability with pyridine or 4-methylpyridine (mepy) and these have much smaller enthalpies of formation. Enthalpies of formation of the 1/1 adducts of carboxylates with phen or bipy are only slightly larger, as are their stabilities. If phen is chelate in these adducts, it seems likely that the two Sn—N bonds are weaker than in the pyridine adducts. A similar effect has been found in the phen adducts of many mercury compounds [10]. The failure of chelation to stabilise the adducts with these carboxylates is further shown by the lack of any evidence of reaction with bipy, which apparently behaves only as a 2-substituted pyridine.

Pyridine-*N*-oxide also forms 1/1 adducts with $R_2Sn(OCOR')_2$. The rather small enthalpies of reaction, comparable to those with NBu_3, again suggest that the tin atom is not a very "hard" Lewis acid centre. The relatively high stabilities of these adducts probably arise from the smaller steric interference of the exposed oxygen donor atom. Since the behaviour of pyridine-*N*-oxide as a Lewis

TABLE 2

BEST-FIT PARAMETERS FOR ADDITION OF SUCCESSIVE MOLECULES OF PYRIDINE-N-OXIDE TO ORGANOTIN HALIDES IN BENZENE SOLUTION AT 30°C

Tin compound	K_1 (l mol^{-1})	K_2 (l mol^{-1})	$-\Delta H_1^\circ$ (kJ mol^{-1})	$-\Delta H_2^\circ$ (kJ mol^{-1})	$-\Delta H_{1+2}^\circ$ (kJ mol^{-1})
Ph_2SnCl_2	∞	85	39	42	81
Me_2SnCl_2	1000	40	37	21	58
Bu_2SnCl_2	500	50	32	9	41
$Bu_2Sn(NCS)_2$	2×10^4	200	42	30	72
$PhSnCl_3$	∞	∞	65	65	130

base towards tin atoms has not been previously reported, we also studied the reaction of this base with several organotin chlorides.

Organotin chlorides and pyridine-N-oxide

Calorimetric titration of pyridine-N-oxide into benzene solutions of organotin chlorides or $Bu_2Sn(NCS)_2$ liberated heat. As in the reaction of these tin compounds with heterocyclic bases, the titration data could only be interpreted by assuming the formation of both 1/1 and 1/2 adducts (see eqns. 1 and 2). The

$$R_2SnCl_2 + \text{py-NO} \rightleftharpoons R_2SnCl_2 \cdot \text{py-NO} \tag{1}$$

$$R_2SnCl_2 \cdot \text{py-NO} + \text{py-NO} \rightleftharpoons R_2SnCl_2(\text{py-NO})_2 \tag{2}$$

best-fit thermodynamic data obtained by analysis of the calorimetric titration data [6] are summarised in Table 2.

With R_2SnCl_2 pyridine-N-oxide forms much more stable adducts than pyridine, though their enthalpies of formation are slightly smaller. It appears that pyridine-N-oxide is a stronger base than pyridine towards these compounds, but the increased adduct stability is due to the smaller steric effect of the exposed oxygen donor atom. With $Bu_2Sn(NCS)_2$, in which the linear NCS groups could be expected also to reduce steric effects the stabilities and enthalpies of formation of pyridine and pyridine-N-oxide adducts are much more nearly the same. As with the other bases studied, the organotin carboxylates are much weaker acids than the corresponding chlorides.

Lewis acidity of $Bu_2Sn(NCO)_2$

As a Lewis acid $Bu_2Sn(NCS)_2$ is similar to R_2SnCl_2, for example forming both 1/1 and 1/2 adducts with pyridine, though those of the isothiocyanate are rather more stable, probably because of the reduced steric effect of the linear NCS group [6]. The isocyanate, $Bu_2Sn(NCO)_2$, however, is much more like the carboxylates. With pyridine, 4-methylpyridine or tributylphosphine in benzene solution it forms only 1/1 adducts of fairly low stability and with small enthalpies of formation; details are given in Table 3.

With the bases NBu_3, py-NO, bipy and tmed the calorimetric data can only be interpreted as representing formation of adducts with the ratio of tin/base of

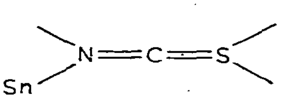
TABLE 3

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF LEWIS BASES WITH $Bu_2Sn(NCO)_2$ IN BENZENE SOLUTION AT 39°C

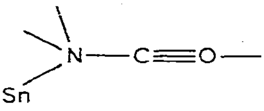
Base	K (l mol^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})	$-\Delta G^\circ$ (kJ mol^{-1})	$-\Delta S^\circ$ (J K^{-1} mol^{-1})
pyridine	34.6 ± 1.9	25.4 ± 0.5	8.9 ± 0.2	54 ± 2
4-mepy	46.8 ± 2.9	27.5 ± 0.6	9.7 ± 0.2	59 ± 3
PBu_3	18.2 ± 1.0	38.3 ± 2.1	7.3 ± 0.2	102 ± 7

2/1. It is possible with bipy and tmed that this could represent the formation of adducts in which each N atom of the base is coordinated to a different tin atom, but it seems more probable that all these reactions involve disproportionation with the formation of base adducts of $Sn(NCO)_4$. Unfortunately attempts to prepare this compound were unsuccessful, as were attempts to identify $SnBu_4$ or other disproportionation products in dilute solution by NMR methods.

The difference in Lewis acidity between $Bu_2Sn(NCO)_2$ and $Bu_2Sn(NCS)_2$ is quite remarkable. It is apparently established that the NCO and NCS groups are both N-bonded to the tin [11]. The much greater acidity of the tin atom in $Bu_2Sn(NCS)_2$ may perhaps be explained by a dominance of the resonance form I in this compound, compared with the alternative form II in $Bu_2Sn(NCO)_2$: this



(I)



(II)

would lead to a greater electron density of the N atom in the isocyanate and so to less electron-withdrawing effect on the tin atom. There is a comparable difference in the Lewis acidity of isocyanates and isothiocyanates in the compounds $py_2Co(NCO)_2$ and $py_2Co(NCS)_2$ [12], though in this case there is probably only a small difference in the enthalpies of addition of further pyridine, despite a very great difference in the stabilities of the adducts $py_4Co(NCO)_2$ and $py_4Co(NCS)_2$.

Experimental

Materials. Organotin chlorides and $Bu_2Sn(NCS)_2$ were obtained from sources and by methods previously described [6]. $Bu_2Sn(OMe)_2$ was prepared from Bu_2SnCl_2 and sodium methoxide by the published procedure [13]. $Bu_2Sn(OCOMe)_2$ and $Bu_2Sn(OCOEt)_2$ were prepared by addition of Bu_2SnCl_2 to a slight excess of potassium acetate or propionate, suspended in dry ethanol [14]; after stirring for twenty minutes at 75°C, solid matter was filtered and ethanol distilled off; the liquid residue was taken up in benzene, filtered, benzene evaporated from the filtrate and the residue distilled in vacuo; $Bu_2Sn(OCOMe)_2$ distilled at 142°C under 1 Torr and $Bu_2Sn(OCOEt)_2$ at 100°C.

$Ph_2Sn(OCOMe)_2$ was prepared from Ph_2SnCl_2, which was added to 30% excess of silver acetate suspended in dry diethyl ether; the mixture was stirred at room temperature for about an hour, silver salts removed by filtration and ether evaporated; $Ph_2Sn(OCOMe)_2$ remained as an analytically pure solid, which could not be improved by crystallisation.

$Bu_2Sn(NCO)_2$ was prepared by an adaptation of a method described for organosilicon isocyanates [15]: Bu_2SnCl_2 was added to about 30% excess of silver cyanate suspended in dry benzene; after heating under reflux for three hours silver salts were removed by filtration; benzene was then evaporated from the filtrate at 100°C and the solid residue purified by sublimation in vacuo at 200°C. The purity of all tin compounds prepared was checked by C, H and N (when appropriate) analyses.

Liquid bases were purified by distillation and stored over anhydrous potassium carbonate; 1,10-phenanthroline was crystallised from ethanol and pyridine-*N*-oxide sublimed in vacuo. Benzene was frozen, then distilled and stored over calcium hydride. Benzene solutions of phen were dried azeotropically before use.

Calorimetry. All calorimetric measurements were made on a LKB 8700 calorimeter, using previously described techniques [16]. A benzene solution of the base, or when adduct stability was very low the pure liquid base, was titrated into 100 ml of a solution of the tin 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. Values of the enthalpy in the tables are the mean of three titrations over a range of concentrations of the tin compound; uncertainties are mean deviations. Values of K are similarly averaged and uncertainties in K are the sum of mean deviations from three titrations and the average standard deviation in single titrations. Uncertainties in ΔG° and ΔS° are derived. Where ampoule breaking experiments have been used the data have been treated as if representing additional points on the titration curve at concentrations of base which were inaccessible by the titration procedure.

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