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THERMODYNAMICS OF METAL—LIGAND BOND FORMATION

XVII*. BASE ADDUCTS OF TIN COMPOUNDS R_3SnCl AND R_3SnNCS

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Summary

Thermodynamic data are reported for reaction of tin compounds R_3SnCl and R_3SnNCS (R = Me, Et, Pr, Bu, Ph) with various bases in benzene solution. R_3SnCl form 1/1, 5-coordinate adducts of low stability with pyridine or 4-methylpyridine; the slightly higher stability of corresponding adducts of R_3SnNCS is due to entropy effects. Adducts of R_3SnNCS with 1,10-phenanthroline are only a little more stable, showing the reluctance of the tin atom to achieve a coordination number greater than five. *N,N,N′,N′*-tetramethyl-1,2-diaminoethane gave either 1/1 adducts or 5-coordinate 1/2 adducts, depending upon the group R and the concentration of R_3SnNCS. Other bases, such as tertiary amines or phosphines also react with R_3SnNCS, but in most cases the reactions are complex and probably involve disproportionation and formation of R_4Sn.

Introduction

The molecular compounds of tin(IV) are among the classic examples of Lewis acids, the tin atom acting as an acceptor for one or two electron pairs and increasing its coordination number from four to five or six by addition of bases, such as amines, phosphines or sulphoxides. Among the organotin halides reactivity increases from compounds of the type R_4Sn (R = alkyl or aryl), which show no readiness to increase their coordination number, to the halides, SnX_4, which are strong Lewis acids.

In a previous paper [1] thermodynamic data were reported for the addition of a variety of bases to organotin compounds of the types R_2SnX_2 and $RSnX_3$ in benzene solution; data were also reported for the addition of pyridine and

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* For Part XVI see ref. 1.

4-methylpyridine to Ph_3SnCl, but attempts to study the addition of bases to trialkyltin chlorides were not then successful, though these halides are known to form 5-coordinate adducts with nitrogenous bases and the crystal structure of $Me_3SnCl \cdot py$ has been determined [2]. The trialkyltin isothiocyanates form more stable adducts than the halides [3] and seemed likely to provide an opportunity to obtain data for the formation of 5-coordinate adducts, without the complication of the simultaneous formation of 6-coordinate adducts, which was observed with R_2SnX_2 and $RSnX_3$.

This paper reports thermodynamic data, obtained by calorimetric titration in benzene solution, for the reaction of R_3SnNCS (R = Me, Et, Pr, Bu, Ph) with pyridine, 4-methylpyridine, 1,10-phenanthroline, tributylamine, *N,N,N',N'*-tetramethyl-1,2-diaminoethane (tmen) and tributylphosphine. Satisfactory data have now also been obtained for the reaction of R_3SnCl with pyridine and 4-methylpyridine and confirm the low stabilities and relatively low enthalpies of formation of these adducts.

Experimental

Materials

Trialkyltin chlorides, Me_3SnCl, Pr_3SnCl, Bu_3SnCl and Ph_3SnCl (ROC/RIC) were purified by distillation or crystallisation where necessary; Et_3SnCl was prepared from tetraethyltin and tin(IV) chloride and purified by fractional distillation in vacuo. The purity of all the chlorides was checked by C, H and Cl analysis.

The isothiocyanates, R_3SnNCS, were prepared from the chlorides by reaction with anhydrous potassium thiocyanate in dry acetone [3,4]; after evaporation of the acetone the tin compounds were extracted from potassium chloride and thiocyanate with dry ether or light petroleum and recovered by evaporation of the solvent; purity was checked by C, H and N analyses.

Pyridine was heated under reflux with potassium permanganate before distillation and stored over anhydrous potassium carbonate; 4-methylpyridine was purified by fractional distillation and stored over anhydrous potassium carbonate. 1,10-Phenanthroline (Merck, pro analys) was used without further purification, except for removal of water by azeotropic distillation when benzene solutions were prepared. *N,N,N',N'*-tetramethyl-1,2-diaminoethane and tributylphosphine (ROC/RIC) were distilled and stored over anhydrous potassium carbonate. Benzene for use as solvent in calorimetry was purified by crystallisation, dried over anhydrous sodium sulphate and stored over calcium hydride.

Calorimetry

Calorimetric titrations in benzene solution were carried out in an LKB 8700-2 titration calorimeter; details of the technique used have been described [5]. Briefly, a benzene solution of the base was titrated into 100 ml of a benzene solution of the tin compound and the heat produced measured after the addition of each increment; the enthalpy of reaction was obtained from the extrapolated, integrated heat of reaction, after correction for dilution effects. The equilibrium constant, *K*, was calculated at each experimental point and the enthalpy adjusted by iterative refinement until constant values of *K* were found throughout the reaction.

Values of ΔH^0 in Tables 1 and 2 are the means of refined values from at least three titrations over the stated range of concentrations of the tin compound; uncertainties in ΔH^0 are mean deviations. Since K is small in nearly all of these systems, values of K were recalculated for each titration using the mean value of ΔH^0 and the values of K in the tables are the mean of values so obtained; uncertainties in K are the sum of the mean deviations from different titrations and the average standard deviations; uncertainties in ΔG^0 and ΔS^0 are derived.

Results and discussion

Trialkyltin chlorides

As expected these gave 1/1 adducts with pyridine and 4-methylpyridine in benzene solution. The thermodynamic data obtained are given in Table 1, which also includes previously reported [1] data for Ph_3SnCl.

The values of K and ΔH obtained for the system Me_3SnCl/pyridine agree very well with those reported [6] for this system in carbon tetrachloride solution (K 1.85 l mol^{-1}, ΔH^0 −27 kJ mol^{-1} at 27°C). In the case of Pr_3SnCl the adduct formation constants were so small that it was not possible to obtain values for the enthalpy of reaction by extrapolation; arbitrary values, slightly lower than those obtained for Et_3SnCl, were therefore selected for the calculation of the equilibrium constant. In view of the very low values of K so obtained it seems likely that these arbitrarily selected values of the enthalpy are too large and K consequently too small; there is however no way in which a more accurate enthalpy can be obtained and it is clear in any case that the adducts of Pr_3SnCl are even less stable than those of the other trialkyltin chlorides.

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF R_3SnCl WITH PYRIDINE AND 4-METHYLPYRIDINE IN BENZENE SOLUTION AT 30°C

(K in l mol^{-1}, ΔH^0, ΔG^0 in kJ mol^{-1}, ΔS^0 in J K^{-1} mol^{-1})

R	$[R_3SnCl]$ (mmol l^{-1})	Base	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
CH_3	10.0-30.0	py	1.9 ± 0.2	30.9 ± 3.2	1.6 ± 0.3	97 ± 11
CH_3	5.0-30.0	4-mepy	2.8 ± 0.2	33.6 ± 1.4	2.6 ± 0.2	102 ± 6
C_2H_5	10.0-30.0	py	2.0 ± 0.3	26.3 ± 2.0	1.8 ± 0.4	81 ± 8
C_2H_5	10.0-30.0	4-mepy	3.5 ± 0.5	27.0 ± 1.1	3.2 ± 0.4	79 ± 5
C_3H_7	5.0-20.0	py	0.3 ± 0.1	25 [a]	−3.0 ± 0.3	73 ± 1
C_3H_7	5.0-30.0	4-mepy	0.7 ± 0.1	26 [a]	−1.1 ± 0.5	82 ± 2
C_4H_9	10.0-30.0	py	2.2 ± 0.2	19.3 ± 0.3	2.0 ± 0.3	57 ± 2
C_4H_9	10.0-30.0	4-mepy	6.3 ± 0.6	19.3 ± 0.3	4.6 ± 0.3	48 ± 2
C_6H_5	14.8-71.0	py	1.1 ± 0.1	41.0 ± 0.0	0.3 ± 0.2	134 ± 2
C_6H_5	7.0-71.7	4-mepy	2.3 ± 0.1	44.8 ± 0.7	2.1 ± 0.1	141 ± 3

[a] Arbitrary value.

Enthalpies of adduct formation for Me_3SnCl, Et_3SnCl and Bu_3SnCl decrease slightly as the chain length increases, probably because of the inductive effect of the additional CH_2 groups; all are considerably smaller than for Ph_3SnCl and about half the enthalpies of formation of 1/1 adducts with compounds of the type R_2SnCl_2.

Tin isothiocyanates R_3SnNCS

Replacement of Cl by NCS leads to increased stability of the adducts with pyridine and 4-methylpyridine and the formation of adducts with a number of other bases. Thermodynamic data for the formation of 1/1 adducts are summarised in Table 2.

Pyridine and 4-methylpyridine. While there are only small differences between either enthalpies of formation or stabilities of the adducts of these bases with R_3SnCl and R_3SnNCS when R is one of the larger alkyl groups, the difference is much more noticable when R = Me or Ph. The greater stability of the adducts of the isothiocyanates is clearly due to entropy effects; this is particularly well shown by the isoequilibrium temperatures ($\Delta H/\Delta S$), which lie in the range 300-350°C for all the chloride or isothiocyanate systems except those involving Me_3SnNCS and Ph_3SnNCS, for which they are about 400°C. The lower entropy resistance to adduct formation by these two compounds may probably be sought in more extensive solvation of them, made possible by the combination of the linear NCS group and relatively compact Me or Ph groups. Apparently the longer chains in the higher alkyl isothiocyanates are as effective as the bulky chlorine atoms in Ph_3SnCl in restricting the number of solvent

TABLE 2

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF R_3SnNCS WITH BASES IN BENZENE SOLUTION AT 30°C

K in $l\ mol^{-1}$, ΔH^0, ΔG^0 in $kJ\ mol^{-1}$, ΔS^0 in $J\ K^{-1}\ mol^{-1}$

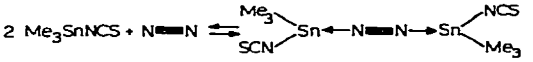
R	$[R_3SnNCS]$ (mmol l^{-1})	Base	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
CH_3	2.0-5.0	py	30.3 ± 1.6	23.2 ± 1.8	8.6 ± 0.2	48 ± 7
CH_3	1.0-5.0	4-mepy	38.9 ± 1.2	33.3 ± 1.0	9.2 ± 0.1	80 ± 4
C_2H_5	10.0-20.0	py	8.5 ± 0.7	38.0 ± 1.0	5.4 ± 0.2	110 ± 4
C_2H_5	5.0-20.0	4-mepy	14.0 ± 1.5	41.0 ± 0.6	6.7 ± 0.3	113 ± 3
C_3H_7	5.0-30.0	py	5.0 ± 0.3	24.7 ± 0.9	4.1 ± 0.2	68 ± 4
C_3H_7	10.0-30.0	4-mepy	8.2 ± 0.4	29.5 ± 0.5	5.3 ± 0.2	80 ± 3
C_4H_9	10.0-30.0	py	5.4 ± 1.0	24.3 ± 0.1	4.2 ± 0.5	66 ± 2
C_4H_9	10.0-30.0	4-mepy	7.5 ± 0.7	28.6 ± 0.8	5.1 ± 0.3	78 ± 4
C_4H_9	10.0-20.0	phen	11.4 ± 0.2	26.7 ± 4.4	6.1 ± 0.1	68 ± 15
C_4H_9	3.0-20.0	tmen	16.7 ± 1.8	11.2 ± 0.5	7.1 ± 0.3	14 ± 3
C_6H_5	10.0-30.0	py	49.1 ± 1.8	42.0 ± 0.6	9.8 ± 0.1	106 ± 3
C_6H_5	3.0-10.0	4-mepy	75.0 ± 14.0	44.0 ± 2.3	10.9 ± 0.5	109 ± 9
C_6H_5	2.0-5.0	phen	75.5 ± 4.2	70.2 ± 9.1	10.9 ± 0.2	196 ± 30
C_6H_5	0.2-1.0	tmen	362 ± 40	27.6 ± 1.6	14.8 ± 0.3	42 ± 6
C_6H_5	0.4-0.7	Bu_3N	289 ± 19	26.0 ± 1.1	14.3 ± 0.2	39 ± 4

molecules which can be accommodated close to the tin atom and consequently suffer displacement on adduct formation.

Bipyridine and phenanthroline. Despite the moderately high stability of some of the pyridine adducts, 2,2′-bipyridine gave little sign of reaction with any of the tin compounds. This shows clearly that it does not behave as a bidentate donor, leading to 6-coordination, though it may possibly behave as an α-substituted pyridine and give 5-coordinate adducts of very low stability.

In contrast to bipyridine 1,10-phenanthroline formed 1/1 adducts in solution and data for the formation of those with Bu_3SnNCS and Ph_3SnNCS are included in Table 2. The results reveal interesting differences between these two compounds. The enthalpy of formation of $Bu_3SnNCS \cdot$ phen is not significantly different from that of the pyridine adduct, though its stability is a little higher; this suggests that, like pyridine, phenanthroline occupies a single coordination site, forming two rather weak Sn—N bonds of greater than usual length, perhaps even of unequal lengths. The enthalpy of formation of $Ph_3SnNCS \cdot$ phen is much greater than that of the pyridine adduct, suggesting the formation of the two Sn—N bonds, each comparable to that in $Ph_3SnNCS \cdot$ py. The phenanthroline adduct is accordingly more stable, but the increase in stability is less than would be expected from the greater enthalpy of formation; this again is well shown by the different isoequilibrium temperatures: about 360°C for the phenanthroline adduct, compared with 400°C for the adducts with pyridine or 4-methylpyridine. Some additional entropy resistance to adduct formation could be expected if the rotational freedom of the phenanthroline molecule were restricted because two Sn—N bonds are formed, as suggested by the high enthalpy of formation. When the concentration of Ph_3SnNCS was increased above about 5×10^{-3} *M* addition of phenanthroline led to the precipitation of the adduct, which was isolated and shown by analysis to have the stoicheiometry 1/1.

Tributylamine and tetramethyldiaminoethane. The compounds R_3SnNCS reacted with the tertiary amine *N,N,N′,N′*-tetramethyl-1,2-diaminoethane (tmen), which is potentially bidentate. However the calorimetric titration curves obtained with Me_3SnNCS required the assumption of a reaction in which each nitrogen atom was coordinated to a separate tin atom:

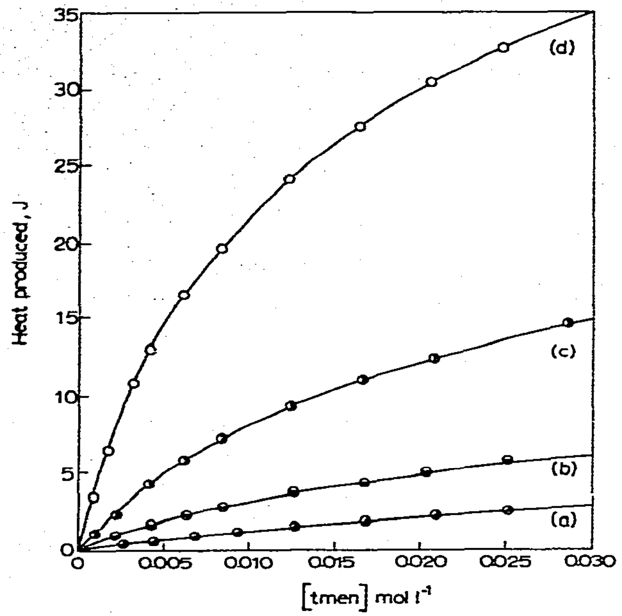


giving an equilibrium constant of the form:

$$K = \frac{[Sn_2B]}{[Sn]^2[B]}$$

The experimental data fit very well to curves calculated for this form of equilibrium constant, taking *K* 3500 l^2 mol^{-2} and ΔH —60 kJ mol^{-1} (Fig. 1); if the enthalpy and free energy of reaction are assumed to be the same for both tin atoms, this gives ΔH —30 kJ g-at Sn^{-1}, *K* 59 l mol^{-1} for the formation of each Sn—N bond, comparable to the data for coördination of one molecule of pyridine.

With Bu_3NCS tmen apparently gave only a 1/1 adduct in solution; data are included in Table 2. The very low value for the enthalpy of reaction, accom-



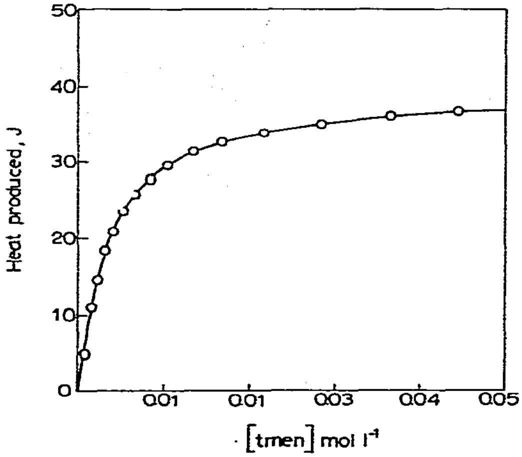


Fig. 1. Calorimetric titration of Me_3SnNCS with tmen. Experimental points for $[Me_3SnNCS]$ 0.003 *M* (a), 0.005 *M* (b), 0.010 *M* (c) and 0.020 *M* (d). Curves computed for $K = [Sn_2B]/([Sn]^2[B]) = 3500\ l^2\ mol^{-2}$, ΔH^0 —30 kJ g-at Sn^{-1}.

Fig. 2. Experimental points for calorimetric titration of 0.01 *M* Ph_3SnNCS with tmen. Curve computed for $K = [prod]^2/([Sn]^2[B]) = 500\ l^2\ mol^{-2}$, ΔH^0 —45 kJ g-at Sn^{-1}.

panied by a formation constant a little larger than that for $Bu_3SnNCS \cdot py$, is similar to the behaviour of phenanthroline and suggests the formation of a chelate adduct with two weak, possibly unequal, Sn—N bonds, in which the bidentate base might be considered as occupying a single coordination site.

With Ph_3SnNCS a change of stoichiometry was observed with changing tin concentration. At low concentrations of Ph_3SnNCS ($<10^{-3}$ *M*) the calorimetric titration results were consistent with formation of a 1/1 adduct with a low enthalpy of formation but of comparatively high stability; data are included in Table 2. At higher concentrations the results are no longer compatible with formation of a 1/1 adduct, but can be accounted for by the formation of two molecules of product (Fig. 2). Unfortunately it was not possible to increase the concentration of Ph_3SnNCS to the point where constant values of K and ΔH could be obtained for this reaction, as precipitation occurred. However, it seems clear that these tin(IV) compounds form 1/1 adducts with tmen at low tin concentrations, but other products are formed as the concentration of the tin compound increases. An adduct precipitated from the more concentrated solutions was shown by analysis to be $(Ph_3SnNCS)_2$tmen.

The unidentate amine tributylamine might be expected to behave similarly to tmen, but without the possibility of forming compounds of the type $(R_3SnNCS)_2B$. The calorimetric titration results obtained with tributylamine were not, however, consistent with the formation of 1/1 adducts, but required equilibrium

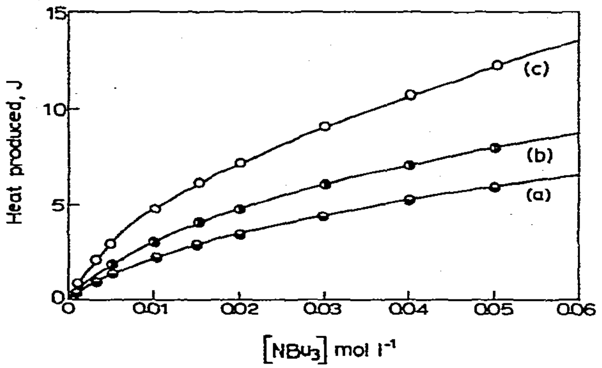


Fig. 3. Calorimetric titration of Bu_3SnNCS with NBu_3. Experimental points for $[Bu_3SnNCS]$ 0.015 *M* (a), 0.020 *M* (b) and 0.030 *M* (c). Curves computed for $K = [\text{product}]/([Bu_3SnNCS][NBu_3]^{2/3}) = 1.42$, ΔH^0 —25 kJ g-at Sn^{-1}.

constants of various other forms. With Bu_3SnNCS the form of equilibrium constant required was:

$$K = \frac{[\text{Product}]}{[Bu_3SnNCS][BuN]^{2/3}}$$

which can be accounted for by the reaction:

$$3\ Bu_3SnNCS + 2\ Bu_3N \rightleftharpoons Bu_4Sn + BuSn(NCS)_3(Bu_3N)_2 \qquad (3)$$

Fig. 3 shows the fit of experimental points to computed curves for this reaction, assuming this equilibrium with ΔH^0 —25 kJ g-at Sn^{-1} and K 1.42; Fig. 4 shows PMR spectra which support the proposition that Bu_4Sn is a product of the reaction.

Results of titrations of tributylamine into very dilute ($<10^{-3}$ *M*) solutions of Ph_3SnNCS were consistent with formation of a 1/1 adduct; data are included in Table 2. With higher concentrations of Ph_3SnNCS a different form of equilibrium constant was required:

$$K = \frac{[\text{Product}]}{[Ph_3SnNCS][Bu_3N]^{1/2}}$$

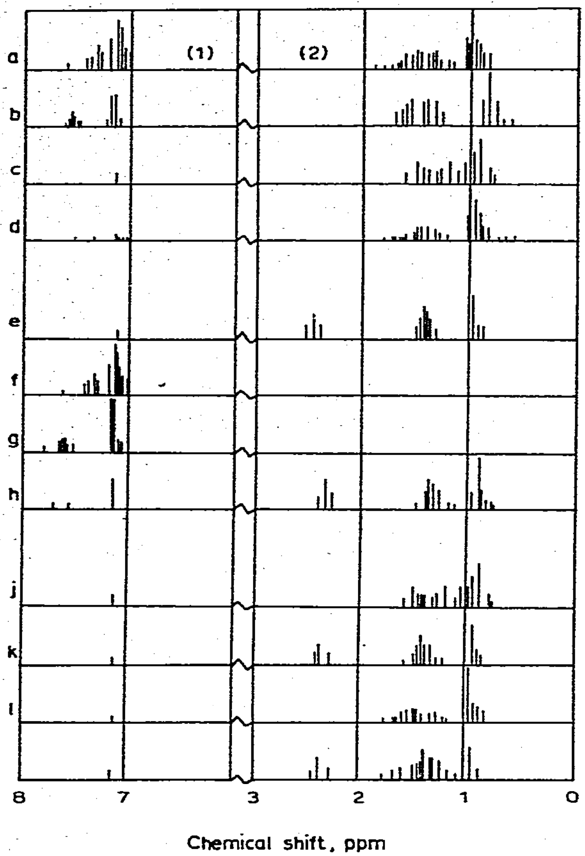
suggesting equilibria of the type 4 or 5:

$$2\ Ph_3SnNCS + Bu_3N \rightleftharpoons Ph_4Sn + Ph_2Sn(NCS)_2Bu_3N \qquad (4)$$

$$4\ Ph_3SnNCS + 2\ Bu_3N \rightleftharpoons 3\ Ph_4Sn + Sn(NCS)_2(Bu_3N)_2 \qquad (5)$$

for which ΔH^0 —46 kJ g-at Sn^{-1} and K 12.4 l g-at Sn^{-1}(Fig. 5). PMR spectra of the solutions are consistent with the disappearance of Ph_3SnNCS and formation of Ph_4Sn (Fig. 4).

It has been observed previously [1] that tributylamine can bring about disproportionation of compounds of the types R_2SnX_2 and $RSnCl_3$ and it is clear that the thiocyanates, R_3SnNCS, are affected similarly; in this case how-



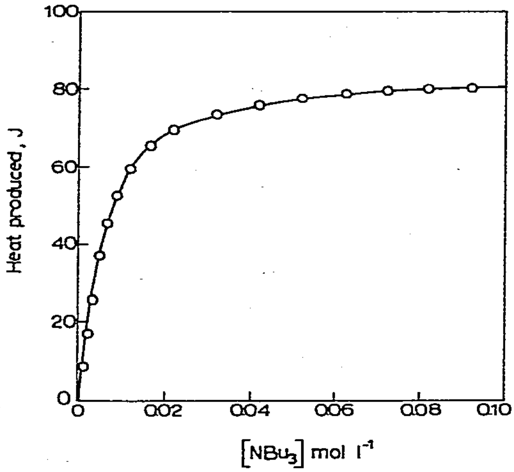


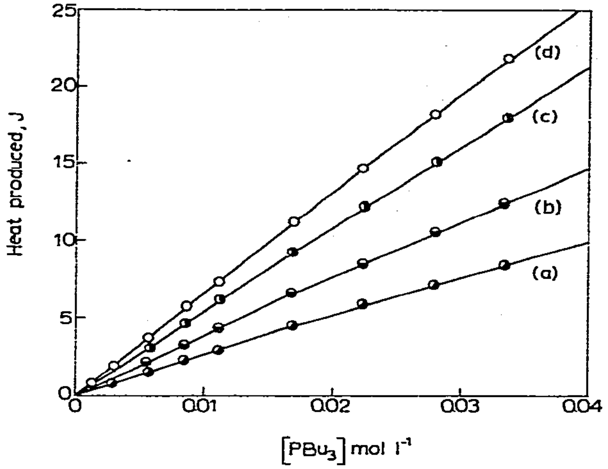
Fig. 4. 100 MHz PMR spectra of approximately 0.1 M solutions in C_6D_6: Ph_3SnNCS (a1), PBu_3 (a2), $PhPBu_2$ (b), Bu_3SnNCS (c), $Ph_3SnNCS + PBu_3$ (d); NBu_3 (e), Ph_3SnNCS (f), Ph_4Sn (g), $Ph_3SnNCS + NBu_3$ (h); Bu_3SnNCS (j), NBu_3 (k), Bu_4Sn (l) and $Bu_3SnNCS + NBu_3$ (m).

Fig. 5. Experimental points for calorimetric titration of 0.02 M Ph_3SnNCS with NBu_3. Curve computed for $K = [\text{product}]/([Ph_3SnNCS][NBu_3]^{1/2}) = 12.4$, ΔH^0 —46 kJ g-at Sn^{-1}.

ever the adducts are more stable and consequently exist in equilibrium at very low tin concentrations, which favour monomeric species. As the tin concentration rises so the disproportionation reactions become dominant. When the base is tmen disproportionation is apparently suppressed, probably because the weakly bidentate base forms a 1/1 adduct in which access to the tin atoms is restricted sterically.

Tributylphosphine. Titration of this base into solutions of R_3SnNCS also liberated heat, but the reactions taking place appeared to be more complex, probably involving disproportionation. With Bu_3SnNCS the calorimetric titration curves obtained fitted the equilibrium expression:

$$K = \frac{[\text{Product}]}{[Bu_3P][Bu_3SnNCS]^{1/2}}$$



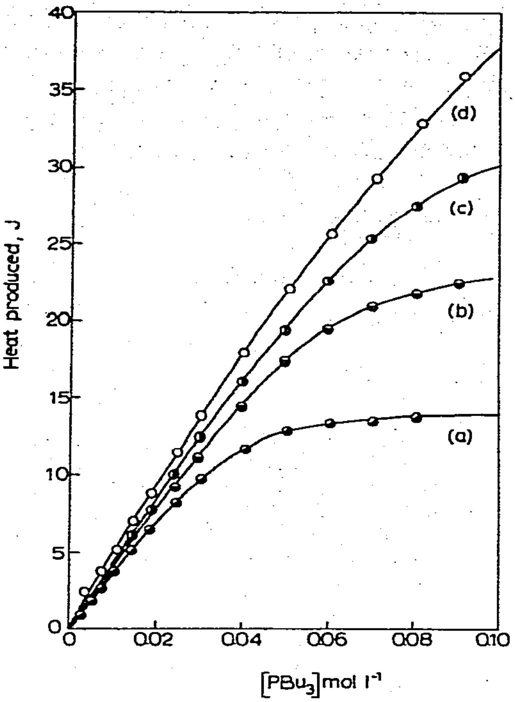


Fig. 6. Calorimetric titration of Bu_3SnNCS with PBu_3. Experimental points for $[Bu_3SnNCS]$ 0.005 *M* (a), 0.010 *M* (b), 0.020 *M* (c) and 0.030 *M* (d). Curves computed for $K = [\text{product}]/([Bu_3SnNCS]^{1/2}[PBu_3]) = 0.55$, ΔH^0 —78 kJ g-at Sn^{-1}.

Fig. 7. Calorimetric titration of Ph_3SnNCS with PBu_3. Experimental points for $[Ph_3SnNCS]$ 0.003 *M* (a), 0.005 *M* (b), 0.007 *M* (c) and 0.010 *M* (d). Curves computed for $K = [PhPBu_2]^3[Bu_3SnNCS \cdot PBu_3]/([Ph_3SnNCS][PBu_3]^4) = 2.0\ \text{l mol}^{-1}$, ΔH^0 —48 kJ g-at Sn^{-1}.

over a wide range of concentrations (Fig. 6). The simplest type of reaction from which this form of equilibrium constant can be derived is:

$$Bu_3SnNCS + 2\ Bu_3P \rightleftharpoons 2\ \text{products} \qquad (6)$$

but it has not been found possible to identify the products of this reaction.

With Ph_3SnNCS the calorimetric titration results required an even more complex equilibrium constant of the form:

$$K = \frac{[\text{Product}]}{[Bu_3P][Ph_3SnNCS]^{1/n}}$$

where the best fit of computed curves to the experimental points was obtained with n 6, but reasonably good fit could be obtained with n 4 (Fig. 7), which could be interpreted as a possible reaction:

$$Ph_3SnNCS + 4\ Bu_3P \rightleftharpoons Bu_3SnNCS \cdot PBu_3 + 3\ PhPBu_2 \qquad (7)$$

Some support for such a reaction was obtained from PMR spectra of the solutions, which show clearly the disappearance of Ph_3SnNCS and the appearance of butyl groups with splitting patterns characteristic of Sn—Bu compounds (Fig. 4). It is however likely that the reaction actually occurring, though similar in type to 7, is even more complex.

Attempts were also made to study the reactions of R_3SnNCS with triphenylphosphine and tetrahydrothiophene, but no reaction could be detected.

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