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THERMODYNAMICS OF METAL–LIGAND BOND FORMATION

XXXIV *. LEWIS ACIDITY OF ORGANOTIN IODIDES

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Summary

Thermodynamic data have been obtained by calorimetric titration in benzene solution at 30°C for reactions of *N*-donor Lewis bases with tin tetraiodide, dimethyl-, diphenyl- and dibenzyl-tin iodides, triphenyl- and tribenzyl-tin iodides, and di- and tri-benzyltin chlorides.

The triorganotin iodides form 1 : 1 adducts of low stability with pyridine or 4-methylpyridine, but do not react with 2,2′-bipyridine or 1,10-phenanthroline. The other compounds form 1 : 1 adducts with the bidentate bases and both 1 : 1 and 1 : 2 adducts with unidentate bases, always of lower stability than adducts with corresponding chlorides. Where addition of successive molecules of base occurs it is found that: $K_1 < K_2$ and $K_1 \Delta H_1 < K_2 \Delta H_2$.

Introduction

The Lewis acid behaviour of organotin chlorides has been studied in a variety of solvents [1–7] but there have been few studies of the iodides. Distorted tetrahedral structures for the organotin iodides in the solid state have been confirmed by Mössbauer spectroscopy [10] and a crystal structure of the bis(diphenylsulphoxide) adduct of tin tetraiodide reveals a *cis*-octahedral arrangement [8].

This paper reports thermodynamic data, obtained by calorimetric titration, for the formation in benzene solution of addition compounds of nitrogenous bases with a variety of organotin iodides and tin tetraiodide. To facilitate comparisions between the behaviour of the iodides and corresponding chlorides, data are also

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* For part XXXIII see Ref. 11.

reported for the formation of adducts with di- and tri-benzyltin chlorides, which were not included in previously reported data for organotin chlorides [1,4].

Experimental

Materials

Organotin iodides were prepared by adding the stoichiometric amount of sodium iodide to the corresponding chlorides in solution in dry methanol or ethanol. After standing overnight the precipitated sodium chloride was filtered, the organotin iodide recovered by evaporation and purified by repeated crystallisation from ethanol. Pyridine was purified by heating under reflux with potassium permanganate before distillation; 4-methylpyridine was purified by fractional distillation; both bases were dried by storing over anhydrous potassium carbonate. 2,2′-Bipyridine and 1,10-phenanthroline hydrate were purified by crystallisation from ethanol; solutions of phenanthroline were dehydrated by azeotropic distillation of some of the solvent before making up to volume. Benzene for use as solvent was purified by freezing and distillation and dried over calcium hydride.

Calorimetry

Calorimetric titrations in benzene solution were carried out on a LKB 8700 calorimeter using the previously described technique [9]. Briefly, a benzene solution of the base (or if adduct stability was very low, the pure liquid base) was titrated into 100 ml of a benzene solution of the tin compound and the heat produced 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 in the titration; the enthalpy was then refined iteratively by computer to give constant values of K throughout the titration. Data in Tables 1–3 are the average of at least three determinations for each system; the uncertainties quoted for ΔH are mean deviations from the average and for K are the sum of average standard deviations in individual titrations and the mean deviation from the average of several titrations.

In cases where 1 : 1 and 1 : 2 adducts were both formed the final refinement of the best-fit values of the four parameters K_1, K_2, ΔH_1, ΔH_2 was made using a computer programme which allowed visual matching of the experimental points to an enthalpogram calculated with variable values of the four parameters.

Results and discussion

Tin compounds R_3SnI

Thermodynamic data obtained for triorganotin iodides are given in Table 1, which also includes data for tribenzyltin chloride and previously reported data [1] for triphenyltin chloride.

The results show that the triorganotin iodides form 1 : 1 adducts with heterocyclic bases of even lower stabilities than those formed by the chlorides; since the enthalpies of adduct formation are also less negative this is probably due to the smaller inductive effect of the iodine atom. As in the case of the chlorides, there is no evidence for addition of a second molecule of base and bidentate bases do not react.

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1:1 ADDUCTS OF COMPOUNDS R_3SnX WITH PYRIDINE AND 4-METHYLPYRIDINE IN BENZENE SOLUTION AT 30 °C (K in l mol^{-1}, $\Delta H°$, $\Delta G°$ in kJ mol^{-1}, $\Delta S°$ in J K^{-1} mol^{-1})

R	X	Base	K	$-\Delta H°$	$-\Delta G°$	$+\Delta S°$
Ph	I	py	0.4±0.1	21.4±0.8	−2.2±0.4	78±3
Ph	I	4-mepy	0.5±0.0	32.5±0.2	−1.8±0.1	80±3
Ph	Cl [a]	4-mepy	2.3	44.8	2.1	141
Bz	I	py	0.5±0.1	30.8±1.0	−2.0±0.4	111±2

[a] Ref. 4.

Tin compounds R_2SnI_2

Calorimetric titration of these compounds with bidentate bases showed the formation of 1 : 1 adducts of high stability with 1,10-phenanthroline. Dibenzyltin iodide also formed a moderately stable adduct with 2,2′-bipyridine, but dimethyl- and diphenyl-tin iodides did not react with this base. This is in contrast to the behaviour of corresponding chlorides which formed highly stable adducts with both bases [1], though formation constants of those with 2,2′-bipyridine were lower by an order of magnitude. Data are summarised in Table 2.

As was previously observed with the corresponding chlorides [1] enthalpograms obtained by titration of the diiodides with unidentate bases could not be explained by the formation of only 1 : 1 adducts, but fitted very well when the formation of both 1 : 1 and 1 : 2 adducts was assumed, according to the equations:

$$R_2SnI_2 + B \rightleftharpoons R_2SnI_2B \qquad (1)$$

$$R_2SnI_2B + B \rightleftharpoons R_2SnI_2B_2 \qquad (2)$$

Thermodynamic data obtained for adduct formation according to these equations are summarised in Table 3, which also contains data for dibenzyltin chloride and previously published data for other corresponding chlorides [1].

TABLE 2

THERMODYNAMIC DATA FOR FORMATION OF 1:1 ADDUCTS OF COMPOUNDS R_2SnX_2 WITH BIDENTATE BASES IN BENZENE AT 30 °C (K in l mol^{-1}, $\Delta H°$, $\Delta G°$ in kJ mol^{-1}, $\Delta S°$ in J K^{-1} mol^{-1})

R	X	Base	K	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
Ph	I	phen	1.5×10^4	71.8±3.8	24.2	157
Ph	Cl [a]	phen	2×10^5	107.0	31	250
Me	I	phen	4.5×10^5	62.0±2.9	32.8	97
Me	Cl [a]	phen	5×10^4	86.0	27	195
Bz	I	phen	$>10^4$	73.1±1.5	> 23	< 165
Bz	I	bipy	660±11	58.1±1.6	16.3	138
Bz	Cl	phen	$>10^5$	74.4±4.7	> 29	< 150
Bz	Cl	bipy	5×10^4	62.8±4.1	27.2	117

[a] Ref. 1.

TABLE 3

THERMODYNAMIC DATA FOR SUCCESSIVE FORMATION OF 1:1 AND 1:2 ADDUCTS OF COMPOUNDS R_2SnX_2 WITH 4-METHYLPYRIDINE AND PYRIDINE IN BENZENE SOLUTION AT 30°C (K in l mol^{-1}, $\Delta H°$ in kJ mol^{-1})

R	X	Base	K_1	K_2	$-\Delta H_1°$	$-\Delta H_2°$	$-\Delta H_{1+2}°$
Ph	I	py	0.6	6	45	35	80
Ph	I	4-mepy	2.8	10	46	50	96
Ph	Cl [a]	4-mepy	200	150	50	56	106
Me	I	4-mepy	4	13	38	36	74
Me	Cl [a]	4-mepy	40	30	60	18	78
Bz	I	4-mepy	5	19	50	40	90
Bz	Cl	4-mepy	300	270	43	37	80
Bz	Cl	py	40	130	59	27	86

[a] Ref. 1.

Though the data for individual steps are less accurate than those for the overall reaction, the pattern of the results is quite clear and the following generalisations can be made:

(1) In all systems the enthalpy changes are roughly similar for the two steps. This could be expected if the major contribution to the enthalpy comes from the formation of a new Sn–N bond.

(2) The adduct formation constants are significantly different in the two steps: in the chloride systems the first is larger, but in the iodide systems the second is larger. This is observed in almost all systems and can hardly be an experimental artifact.

In aqueous solution where complex formation involves the replacement of coordinated solvent molecules by ligands it is usual to observe a decrease of about one or two orders of magnitude in successive formation constants due to statistical effects. In non-aqueous solution where complex formation involves increasing coordination number rather than solvent replacement successive adduct formation constants can be expected to be more nearly equal. This is what has been observed with organotin chlorides. In the organotin iodides, however, the relatively lower values of K reveal an unusually low stability of the 1 : 1 adducts, which never form more than a minor component of the equilibrium mixture. This unusually low stability of the five-coordinate species is of entropic origin, suggesting that it might arise from the large iodine atom restricting the fluxional behaviour of the species.

SnI_4

Tin tetraiodide, like other tin tetrahalides, reacts almost quantitatively with *N*-bases, but the enthalpy changes cannot usually be measured because the adducts crystallise from solution. The 1 : 1 adducts of tin tetraiodide with 2,2′-bipyridine and 1,10-phenanthroline however are sufficiently soluble in benzene for such measurements to be made. The formation of these adducts in solution is very exothermic:

$$SnI_4 + \text{bipy} = SnI_4 \cdot \text{bipy} \qquad \Delta H° \; -97 \text{ kJ mol}^{-1}$$

$$SnI_4 + \text{phen} = SnI_4 \cdot \text{phen} \qquad \Delta H° \; -110 \text{ kJ mol}^{-1}$$

confirming the usual increase in heat of adduct formation as alkyl or aryl groups on the tin atom are replaced by halogens.

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