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THERMODYNAMICS OF METAL—LIGAND BOND FORMATION

XXVI *. ADDUCTS OF TERTIARY PHOSPHINES WITH ORGANOTIN HALIDES

M.J. GALLAGHER, D.P. GRADDON * and A.R. SHEIKH
School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033 (Australia)

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Summary

Thermodynamic data, obtained by calorimetric titration in benzene solution at 30°C, are reported for formation of 1 : 1 adducts of Ph_2SnCl_2, Me_2SnCl_2 and Bu_2SnCl_2 with the tertiary phosphines PBu_3, $PhPBu_2$, $PhPPr_2$, $PhPMe_2$, Ph_2PPr and Ph_2PMe. Enthalpies of formation and stabilities of adducts decrease in the order $Ph_2SnCl_2 > Me_2SnCl_2 > Bu_2SnCl_2$. There is no systematic relationship between the enthalpies of adduct formation and phosphine structure, but adduct stabilities decrease in the order $PBu_3 > PhPAlk_2 \sim Ph_2PAlk > PPh_3$.

Introduction

Phosphines are usually regarded as typical "B-class" or "soft" donors, forming their most stable complexes with "soft" Lewis acids, such as compounds of mercury, gold or the platinum metals. They do, however, form addition compounds even with such typically "hard" Lewis acids as boron trifluoride [1]. The basic properties of the phosphines, PR_3, depend upon the substituents R and it has been found that their proton association constants are related to the Taft constants, $\Sigma\sigma^*$, of the substituents [2]. It has also been found that a similar relationship holds with the enthalpies of formation of 1 : 1 adducts of PR_3 with mercury(II) halides [3], which can be regarded as typical "soft" acids.

We have previously reported thermodynamic data for the reaction of various N-bases and PBu_3 with a range of organotin compounds [4,5]; since tin is regarded as a typical "A-class" metal [6] and its compounds as "hard" acids, it appeared to be interesting to determine the effect of substituents on the basicity of phosphines towards organotin compounds. We report now thermodynamic data, obtained calorimetrically in benzene solution, for the reaction of a series

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* Part XXV see ref. 8.

of tertiary phosphines with three reference organotin acids: Ph_2SnCl_2, Me_2SnCl_2 and Bu_2SnCl_2.

Experimental

Preparation and purification of phosphines has been described previously [3]. Organotin halides were obtained from ROC/RIC Chemical Corporation, Sun Valley, California and purified by crystallisation from absolute ethanol. Benzene for use as solvent was purified by freezing followed by distillation and dried over calcium hydride.

Calorimetric measurements were made by previously described techniques: briefly, a solution of the phosphine in benzene was titrated into a benzene solution of the tin compound; the heat change was measured after each incremental addition and the enthalpy determined from the extrapolated, integrated heat of reaction after correction for dilution effects. The adduct formation constant was calculated at each point in the titration and the enthalpy refined iteratively until constant values of *K* were obtained throughout the titration. All the calorimetric measurements were made on a LKB 8700 titration calorimeter.

In the table of results (Table 1) enthalpies are the average of at least three determinations over the range of concentrations of organotin compound shown and uncertainties are mean deviations; adduct formation constants for each titration were recalculated using the average value of the enthalpy and uncertainties in *K* are the sum of the mean deviation from different titrations and the average standard deviation for individual titrations.

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1 : 1 ADDUCTS OF TERTIARY PHOSPHINES WITH R_2SnCl_2 IN BENZENE SOLUTION AT 30°C (K in l mol^{-1}, ΔG°, ΔH° in kJ mol^{-1}, ΔS° in J K^{-1} mol^{-1})

Phosphine	R	$10^4[Sn]$	K	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$
PBu_3 [4]	Ph	22—110	1.9×10^4	73.7 ± 1.2	24.8 ± 2.0	161 ± 10
	Me	24—69	1002 ± 60	54.0 ± 1.6	17.4 ± 0.3	121 ± 7
	Bu	17—103	322 ± 17	54.8 ± 0.8	14.5 ± 0.2	133 ± 4
$PhPBu_2$	Ph	10—13	245 ± 19	42.2 ± 0.6	13.8 ± 0.3	94 ± 3
	Me[a]	10—15	51 ± 4	25.9 ± 2.3	9.9 ± 0.3	53 ± 9
	Bu[a]	10—20	15 ± 3	24.0 ± 2.8	6.8 ± 0.6	57 ± 11
$PhPPr_2$	Ph	8—15	120 ± 9	46.2 ± 3.1	12.1 ± 0.3	112 ± 11
	Me	10—17	53 ± 13	26.0 ± 1.9	10.0 ± 0.8	53 ± 9
	Bu[a]	15—30	16 ± 4	25	7.0 ± 0.6	60 ± 15
$PhPMe_2$	Ph	8—20	123 ± 10	59.7 ± 2.4	12.1 ± 0.3	157 ± 9
	Me	10—15	24 ± 4	31.4 ± 1.4	8.0 ± 0.4	77 ± 6
	Bu[a]	8—10	21 ± 2	42.2 ± 1.9	7.7 ± 0.3	114 ± 7
Ph_2PBu	Ph[a]	6—10	52 ± 9	46.4 ± 0.4	9.9 ± 0.6	117 ± 6
	Me[a]	6—10	53 ± 9	25	10.0 ± 0.6	50 ± 15
	Bu[a]	10—20	14 ± 6	25	6.7 ± 1.4	60 ± 15
Ph_2PPr	Ph	12—15	84 ± 5	61.5 ± 2.7	11.1 ± 0.2	166 ± 9
	Me	10—15	96 ± 6	39.0 ± 1.4	11.5 ± 0.2	91 ± 6
Ph_2PMe	Ph	8—12	130 ± 12	47.0 ± 3.0	12.3 ± 0.3	115 ± 11
	Me	8—12	62 ± 12	59.0 ± 3.0	10.4 ± 0.2	160 ± 11

[a] Confirmed by ampoule technique.

Accurate determination of the enthalpy by this method depends upon the reaction going close to completion at the end of the titration but in some of these systems it was not possible to achieve more than 50% conversion to adduct. In these cases the titration data were supplemented by experiments in which ampoules containing suitable amounts of the tin compound were broken into a solution of the phosphine. The results of the ampoule experiments were then included in the calculations of the enthalpy of reaction. These systems are indicated in the table of results as confirmed by ampoule breaking methods. In three systems the titration method gave very incomplete reaction and the enthalpies then depend wholly on the ampoule technique, but the enthalpies so obtained are of lower accuracy as the value of K is correspondingly uncertain; for these systems the value of the enthalpy used in calculating K is shown without uncertainties. The complete results obtained are given in Table 1.

Discussion

As previously observed when organotin compounds were treated with tributylphosphine [4], the calorimetric titration data could only be interpreted by assuming the formation of 1 : 1 addition compounds, in which the coordination number of the tin atom is presumably five. There is no evidence for the formation of addition compounds of any other stoichiometry.

In most cases it was not practicable to add large excesses of phosphine and, even with additional information from ampoule breaking experiments, many of these systems never achieved more than about 70% conversion to adduct. The results are therefore less accurate than in some similar systems. In spite of these uncertainties, some general relationships can be discerned:

1. Successive replacement of alkyl groups by phenyl in PR_3 produced only small changes in the enthalpies of reaction. There is no systematic variation of enthalpy with phosphine structure; this is in marked contrast to the data obtained for the reaction of phosphines with mercury(II) halides [3].

2. Although having little effect on the enthalpy of reaction, replacement of one alkyl group in PR_3 by phenyl greatly decreased the stabilities of the adducts; replacement of a second alkyl group, however had only a small further effect. A parallel but small variation in enthalpies: $PBu_3 > PhPAlk_2 \sim Ph_2PAlk$ suggests that this is an inductive effect, arising from withdrawal of the non-bonding electrons on the phosphorus atom in PR_3 into the aromatic system. When all alkyl groups were replaced by phenyl, adducts with PPh_3 were so much less stable that it was not possible to determine either the enthalpy or adduct formation constant, but enough heat was liberated to show that adduct formation does take place.

3. Adduct stabilities generally decrease in the order: $Ph_2SnCl_2 > Me_2SnCl_2 > Bu_2SnCl_2$. Since the enthalpies of formation are considerably larger with Ph_2SnCl_2 the difference between this and the dialkyltin chlorides is evidently an inductive effect. The differences between Me_2SnCl_2 and Bu_2SnCl_2 are, however, due to the entropy terms and may arise from a difference in steric effect of the two alkyl groups; support for this is provided by the high isoequilibrium temperatures for most of the reactions which involve Me_2SnCl_2; a similar effect was observed in the reaction of these tin compounds with N-bases [4].

Tin (IV) compounds like these adducts, which are 5-coordinate, frequently have fluxional structures [7] and some contribution to the entropy of adduct formation can be expected from minor steric effects, which may change the possibilities of fluxional behaviour. Such effects would be very difficult to predict and would possibly account for the rather random variations in adduct stability observed in these systems. Another possible source of irregularities is that variable contributions may be made by π- and σ-bonding between the P and Sn atoms; however as tin is regarded as an "A-class" metal [6], the contributions due to π-bonding should be relatively small. In keeping with this conclusion, the enthalpies of adduct formation are all considerably less than those of adduct formation with mercury(II) halides, in spite of the higher formal charge on the tin atom.

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