

## Reaction of Phenylmercury Acetate with Lewis Bases

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### Abstract

Phenylmercury acetate reacts with tributylphosphine in benzene solution to form a 3-coordinate 1:1 adduct of high stability with a large negative enthalpy of formation ( $K > 10^4 \text{ l mol}^{-1}$ ,  $\Delta H = -66 \text{ kJ mol}^{-1}$ ). Similar adducts of lower stability ( $K < 50$ ) are formed by triphenylphosphine, unidentate aliphatic amines and heterocyclic bases and pyridine-*N*-oxide. The bidentate bases tetramethyl-1,2-diaminoethane and 1,10-phenanthroline form chelate, 4-coordinate 1:1 adducts of greater stability than the unidentate *N*-bases, but no reaction is evident with 2,2'-bipyridine. The results show the 'soft' character of the mercury atom and its reluctance to adopt a coordination number greater than three.

### Introduction

Thermodynamic data have been reported for the reactions in non-aqueous solution of Lewis bases with a variety of mercury(II) compounds, including halides [1], pseudohalides [2], organo-halides [3], bis(pentafluorophenyl)mercury [4] and butylmercury nitrate [5]. The Lewis acid behaviour of mercury compounds has been recently reviewed [6].

While quantitative data have not been reported, it has been shown that mercury(II) acetate forms both 1:1 and 1:2 adducts with tertiary phosphines; the 1:1 adducts are monomeric in solution in 1,2-dichloroethane but the 1:2 adducts are extensively dissociated in solution [7]. A crystal structure of diacetato{tris(*t*-butyl)phosphine}mercury(II) confirms that the mercury atom is strongly bonded only to one oxygen of each acetate and a phosphorus atom [8] and a recent crystal structure of phenylmercury acetate shows that the coordination number of the mercury atom is two with a nearly linear C–Hg–O group [9]; there appears to be no evidence in the literature for Lewis acidity of phenylmercury acetate.

This paper reports calorimetric studies in benzene solution of the formation of addition compounds of

phenylmercury acetate with tertiary phosphines, pyridine, 4-methyl-pyridine, piperidine, aliphatic amines, 1,10-phenanthroline (phen), *N,N,N',N'*-tetramethyl-1,2-diaminoethane (tmed) and pyridine-*N*-oxide.

### Experimental

#### Materials

Phenylmercury acetate was obtained from Merck and recrystallised from benzene. Liquid bases were purified by distillation and stored over anhydrous potassium carbonate. Solid bases were purified by crystallisation from ethanol; benzene solutions of phenanthroline were dehydrated by azeotropic distillation of part 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 were carried out in a LKB 8700 calorimeter using the previously described technique [10]. Successive increments of a benzene solution of the base, or in some instances where *K* is very small of the pure liquid base, were added to 100 ml of a benzene solution of phenylmercury acetate and the heat change measured after each addition. The enthalpy of reaction was calculated from the extrapolated, integrated heat of reaction and the equilibrium constant, *K*, calculated at each experimental point; the enthalpy was then refined iteratively to give consistent values of *K* throughout the titration. All reactions gave results consistent with the formation of addition compounds of 1:1 stoichiometry. Data in Table I are the average of at least three titrations over the range of concentrations of mercury compound quoted. Uncertainties in  $\Delta H^\circ$  are mean deviations; uncertainties in *K* are the sum of the mean deviation and the average standard deviation in individual titrations. Uncertainties in  $\Delta G^\circ$  and  $\Delta S^\circ$  are derived.

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

Base	[Hg] (mmol l <sup>-1</sup> )	K (l mol <sup>-1</sup> )	-ΔH° (kJ mol <sup>-1</sup> )	-ΔG° (kJ mol <sup>-1</sup> )	-ΔS° (J K <sup>-1</sup> mol <sup>-1</sup> )
PBu <sub>3</sub>	3.0–12.0	>10 <sup>4</sup>	65.6 ± 1.4	23.2	140
PPh <sub>3</sub>	3.0–11.0	44.4 ± 0.8	28.7 ± 0.3	9.6 ± 0.1	63 ± 1
BuNH <sub>2</sub>	8.6–15.2	15.8 ± 1.4	52.2 ± 1.6	6.9 ± 0.2	150 ± 6
Bu <sub>2</sub> NH	5.9–17.5	5.6 ± 0.1	15.8 ± 0.3	4.3 ± 0.1	38 ± 2
pip	7.1–15.1	10.3 ± 0.4	36.5 ± 1.5	5.9 ± 0.1	101 ± 5
Et <sub>3</sub> N	11.9	<1	~10	~0	~35
tmed	2.4–8.9	45.6 ± 2.9	41.6 ± 1.9	9.6 ± 0.2	105 ± 3
py	3.1–11.4	1.3 ± 0.1	24.3 ± 0.4	0.7 ± 0.2	77 ± 2
4-mepy	5.5–13.5	1.7 ± 0.1	22.0 ± 0.2	1.3 ± 0.2	69 ± 1
phen	3.4–11.1	484 ± 10	31.1 ± 0.1	15.6 ± 0.1	51 ± 2
py-NO	7.8–16.8	13.9 ± 0.5	11.3 ± 1.3	6.6 ± 0.1	16 ± 5

## Results and Discussion

Complete thermodynamic data are given in Table I for the formation of 1:1 addition compounds with all the bases studied.

Tributylphosphine forms an adduct of very high stability with a large enthalpy of formation, close to that previously reported for the addition of this base to arylmercury halides [3]; there was no evidence for the addition of a second base molecule, nor for dimerization of the adduct nor for symmetrization and the mercury atom must be considered as achieving a coordination number of three. Triphenylphosphine also forms a 3-coordinate 1:1 adduct, but of a much lower stability and with a much smaller enthalpy change, as has been previously observed in the reactions of phosphines with mercury halides [1].

The results for aliphatic amines are similar to those for triphenylphosphine: 1:1 adducts are formed of low stability with moderate enthalpy changes, both of which decrease from primary to tertiary amines, though some additional stability of the adduct is provided by the incorporation of the nitrogen atom in the ring in piperidine. The tertiary amines are particularly weak bases towards phenylmercury acetate, the heat produced being too small to be useful with tributylamine and so small with triethylamine that the data in Table I are only approximate; in contrast to this tetramethyl-1,2-diaminoethane forms a moderately stable adduct with a much larger enthalpy change and this base must be regarded as forming a chelate, 4-coordinate 1:1 adduct.

Pyridine forms an adduct of even lower stability than piperidine and with a less negative enthalpy of formation; the usual small increase in adduct stability is observed when methyl substitution occurs in the 4-position, but the reactivity of 2-methylpyridine

was so low that measurements could not be made. 2,2'-Bipyridine, a potentially bidentate base, was also unreactive but phenanthroline formed an adduct of fairly high stability, which like that of tmed must be considered as chelate and 4-coordinate; as has often been observed the enthalpy of formation of this phenanthroline adduct is only a little greater than that of the pyridine adduct despite its much higher stability, suggesting a mismatch between the steric requirements of the phenanthroline and the linear C–Hg–O unit. Pyridine-*N*-oxide formed an adduct comparable in stability to those of the aliphatic amines.

These results confirm the 'B' or 'soft' character of the mercury atom in phenylmercury acetate, the only highly stable adduct with a unidentate base being that with tributylphosphine. They also confirm the reluctance of the mercury atom to extend its coordination number beyond three, except when it is bound to highly electronegative groups and is also reacting with highly polarisable ligands.

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